# Geochemical Origins of Travertine limestones in the Lake Edward Basin, Albertine Rift, DRC – UGANDA.

Master of Science (Research) Thesis of University of Dublin Trinity College

# 2020

# Sylvain Mangoni Kezir

DECLARATION

*I, Sylvain Mangoni Kezir, declare that this thesis is entirely my own work, except where duly acknowledged in the text. It has never been submitted as an exercise for any degree at this or any other University and henceforth owns the copyrights.*

*I agree to deposit this thesis in the University's open access institutional repository or allow the library to do so on my behalf, subject to the Irish Copyright Legislation and Trinity College Library conditions of use and acknowledgement.*

*Signed:  Sylvain Mangoni Kezir*                                   *Date:*


------------------------------                              ------------------------------------
-

# ABSTRACT

From 2007 to 2014, geological field surveys have been undertaken within the East African Rift System where hot spring Travertine and limestones have been discovered, precipitated at active, or palaeo-spring sites around the margins of the Lake Edward, Lake George and Lake Albert basins.

These Travertines are often outcroping over deep-seated rift-bounding faults, linking their origin to meso- and hydro-thermal groundwater flux along fault planes. For this groundwater to attain the necessary high concentration of bicarbonate to potentially precipitate the calcite found in spring pools at the surface, the requirement is that this ground water must have percolated through a substantial carbonate bedrock unit at depth, typically a regional sedimentary limestone. However, the Lake Albert and Lake Edward - Lake George rift basins are infilled by fluvial, deltaic and lacustrine siliciclastic sediments, such as sandstones, claystones and conglomerates. No limestone beds have been documented so far in Albertine rift-fill sediments, either at the surface in outcrop, or at subsurface level in well penetration.

Thin caliche paleosols are probably present in rift-fill sediments exposed around the margins of the lake, but these are only poorly developed carbonate concretionary horizons and have not developed into full, laterally continuous calcretes. Thus the presence of these Travertine outcrops, and more specifically, the origin of their bicarbonate, remains enigmatic. Considering the groundwater carbonate chemistry required to precipitate these Travertines, and the complete absence of any fluvial or lacustrine limestone beds in the Lake Albert and Lakes Edward – George rift-fill stratigraphy, the big question remains about how and why these unexpected Travertine limestones have been formed?

The present Master of Science degree by research titled "Geochemical Origins of Travertines in the Lake Edward Basin, Albertine Graben, DRC/ Uganda", succed to understand through the reversible reaction $Ca^{2+} + 2HCO_3^{--} = CaCO_3 + CO_2 + H_2O$, the source of the Bicarbonate by which carbonates, and therefore Travertine, are precipitated respectively in cold and hot springs very localized in lines along many Eastern Africa rifts bounding faults.

This geochemical origin inquiry has actually found evident answers by running from 2013 to 2018 three series of ICP-MS analyses on Rare Earth Element (& Yttrium) concentrations in a suite of 50 Travertines samples collected within the EARS.

Carbon $\delta^{13}$/Oxygen $\delta^{18}$ stables isotopes analyses on selected Travertine samples revealed the surface fractionation processes within the hot spring pools at the surface, because they are mostly affected from $CO_2$ outgassing as the water bubbles to the surface. Strontium isotope ratios low values (~0.703) suggested hydrothermal carbonatite origin while the marine sediment and the continental weathering origin has been easily recorded by their intermediate and high values (~0.708 and ~0.711).(Wierzbowski, 2013)

The Travertine respective REE concentrations MUQ normalized values gave the evidence to have derived their bicarbonate from one of three carbonate sources at depth:

- Igneous Carbonatites, either present at depth as buried carbonatite lavas, or as intrusives
- Marine Limestone, which suggests that it is part of a pre-Tertiary rift unit; likely to be either a failed Karoo-Mesozoic rift package, or part of the 'basement' Proterozoic (possibly Neoproterozoic 'Schisto-Calcaire')
- 'half-way house' mixture between these two end-members.

# SUMMARY

This thesis presents the possible geochemical origins of unpredicted Travertine recently discovered in outcrops in a series of lined localized cold springs in the Lake Edward Basin, DRC-Uganda.

The study area forms a part of the East African Rift System with a classical rift valley successions mainly fluvial and lacustrine deposits.

The East African Rift System (EARS) can be considered as a unique succession of graben basins linked by intracontinental transforms and segmented by transfer zones and accommodation zones. This could also be described like a lithospheric scale structure, characterized by uplift of hot asthenospheric elongate diapirs across the upper mantle, responsible for shoulder uplifts. This forms a kind of intracontinental ridge system of several hundreds of kilometres wide and several thousands of kilometres long, which is quite equivalent to the oceanic ridge system.

It clearly appears that the inscribed continental graben valleys and basins are organized over a major failure, related in the crust to a main border fault and low angle detachment fault, inducing asymmetric roll-over structure, eventually accompanied by smaller normal faulting and tilted blocks.

It seems to appear like external tensional stresses have caused the continent to split along lines of pre-existing lithospheric weaknesses marked by old tectonic patterns that focus the extensional strain.

Considering its size, structure and occurrence of oceanic lithosphere, the EARS could easily be taken as a model of the beginning of oceanic opening inside a continent.

This opening propagates normally on the whole from north to south— including local nucleation's of lithospheric faults—due to SE-ward relative divergent drifting of a not yet well individualized plate.

The EARS history is strongly linked by the role of plume impacts. This plume phenomenon which had occurred approximately at around 30 Ma, was in Lake Tana region (Ethiopia). His main action was weakening the lithosphere and preparing the first rifting along a Pan-African suture zone bordering the future Afar region. This rift propagated afterward along the suture zone, activation of low angle detachment fault reworking former opposing faults belonging to the double verging ancient belt associated to structure.

When supposing the plume has migrated southward, or other plumes emplaced, preparing other nucleations of failure along former suture or transform zones, the actual rift system propagated and is still developing southwards towards the Lake Edward basin.

Much about the geological history of the Lake Edward basin remains unknown. There is a lack of any useable age dates, either absolute or from biostratigraphy so other methods must be created to attempt to constrain unit deposition, including linking litho- and chrono-facies with glacial/interglacial episodes. Rapid lateral facies changes present in onshore sediments and the fact that all sediments are either lacustrine of fluvial mean that chrono-stratigraphic units must be used instead of more traditional 'formations' and at much higher resolution. Poor exposures across much of the vast area, and only one exploration well in the entire

basin make for a sparse data set which must be overcome to be able to explore successfully for hydrocarbons.

The Lake Edward basin geologic informations recorded so far by this thesis can be summarized as below:

- The presence of the numerous oil seeps observed in the Edward basin surface may indicate that organic rich Carbonate source rocks are present in subsurface;
- The organic rich clays observed outcropping in surface are suggesting that they were generated from source rocks deposited in a lacustrine environment and dominated by Type 1 algal Kerogen; (Nicholas, 2009)
- The organic rich black shales observed outcropping in surface are suggesting that they were generated from source rocks deposited in a more saline lacustrine environment;
- The weathering of basement rocks along the escarpment and rift flanks of the Albertine Graben , their subsequent transportation and deposition of their weathered products into the Graben could yield good reservoir quality sediments identifiable from their outcrop in the field;
- Sandstones in Edward basin outcrops help to define prior to the drilling the porosity trend of the potential reservoir which exact porosity % will be measured in the shallow cores;
- The aerial observation of modern rivers meanderings may be resulting from the palaeo depositional environment of sediments fill in the basin;(Nicholas, 2017)
- Many field observations of faults scarps, unconformities and difference of successive elevations in the surface are supposed to be correlate with Dip reversals against faults and fault and fault-on-fault traps structures which could be confirmed by seismic datas acquired throughout the whole basin;
- Clay's samples collected in the field, once analysed for mineral contents, may help to understand the protective skills of a potential regional seal covering sands reservoirs in place.
- Mysterious Travertine with great oolithes cavities found in outcrop with live Oil stains in Ugandan side and without proven live Oil stains in DR Congo side, may suggest a Cenozoic carbonate reservoir with a wonderful porosity network, if these Travertine could be confirmed in a potential exploration well; (SOCO, 2010)

This present thesis is focussed only on the research of the geochemical origins of these mysterious Travertine inside the classical siliclastic sediment fill of the EARS.

After its abstract, summary, dedication and acknowledgement, this thesis will present the whole work in the first Chapter: Introduction, hypothesis, aims and objectives.
The summary of all the books, articles, journal and previous published thesis consulted and referenced has been put together in the second Chapter: Literature Review.
The third Chapter is treating about the methodology and techniques used to achieve this thesis objectives
The fourth Chapter is detailing the three series of field trips from 2007 to 2009 in Uganda side, in 2010 and in 2014 in the DRC side of the Lake Edward basin, while the Chapter Five illustrates the Travertine petrography work. Chapter Six presents all results which argued the scientific discussions and geologic venues noted in Chapter Seven. This thesis is ending by some conclusions and petroleum implications in Chapter Eight.

# DEDICATION

*My daughter, Alliancia!*
*My beloved MingoDias!*


*Vital, Esther, Patrick, Lydia, Guyguy, Junior and Gloria!*
*Joëlle, Ariel, Christelle, Gaëlle, Gracia, Ethan, Splendeur and  Estelle,…..!*
*Miguel lanzaroti, Dr Susan, Andy, Trish, Eddy, Louis Fitzgerald,*
*All Dundalk Community Center,*

*All my Africa fellows,*

*Wherever you are, whatever you are doing, whenever you may (or not) read this page,*
*May you find here my sincere gratitude for all your encouragements and trust on me.*

*May this scientific work make each of and all around you more proud of  your son, brother,*
*uncle, father, love, friend, best friend,…I am and will always be for you.*

*I will never ever forgot anyone of all your support and trust on me.*

*Thank you again,*


Sylvain.

# ACKNOWLEDGEMENT

# TABLE OF CONTENTS

**LIST OF TABLES**

**LIST OF ENCLOSURES IN MEMORY STICK**

1. Literature review (Chapter 2): articles, revues, books…pdf versions.
2. 2013 ICP-MS results of Travertine samples collected from 2007 to 2010.
3. 2016 ICP-MS results of 2007 to 2010 and PCK samples for method confirmation.
4. 2018 ICP-MS results of Travertine samples collected in 2014 and Mandawa Samples.

**LIST OF APPENDICES**

1. Samples preparation lab notes
2. ICP-MS Results REE tables
3. Field notes

# TABLE OF FIGURES

## Chapter One

## Chapter Two

## Chapter Three

### Chapter Four

### Chapter Five

### Chapter Six

## LIST OF ABREVIATIONS

1. ICP-MS: Inducted coupled Plasma Mass Spectrometry

2. REE: Rare Earth Element

3. FP: Fort Portal

4. EARS: Eastern Africa Rift System

5. SSTs: Sandstones

6. LBF:  Lubero Border Fault

7. KF: Kichwamba Fault

8. KKK-FZ: Kazinga-Kiruruma-Kikarara Fault Zone

9. PEPD: Petroleum Exploration production Department ( Uganda)

10. MIS : Marine Isotope Stage

11. GC: Gas Chromatography

12. GCMS: Gas Chromatography Mass Spectrometry

13. IRMS : Isotope Ratio Mass Spectrometry

14. CMA: Centre for Microscopy Analysis

15. MUQ: Mud of Queensland

16. ZOI: Zone of Interest

# CHAPTER ONE: INTRODUCTION, AIMS AND OBJECTIVES

## I.1- INTRODUCTION

The multi-million dollar Oil exploration industry in the Albertine Rift Valley of East Africa is currently based entirely on the premise that there is only one rifting process happened in the region, this is the active East African Rift System (EARS). The basic assumptions being that the source rock for the oil and the reservoir sands that hold it in their traps, are all within this rift, which is no older than Miocene, approximately 10 million years.(Nicholas et al., 2016)

During series of geological field surveys conducted in the EARS from 2007 to present, live Oil have been discovered in Travertine limestones cavities at Lyemumbuza (Uganda) hot springs, precipitated as well as many others similar springs at active, or palaeo-, spring sites around the margins of the Lake Edward, Lake George and Lake Albert basins (Figure I.1).
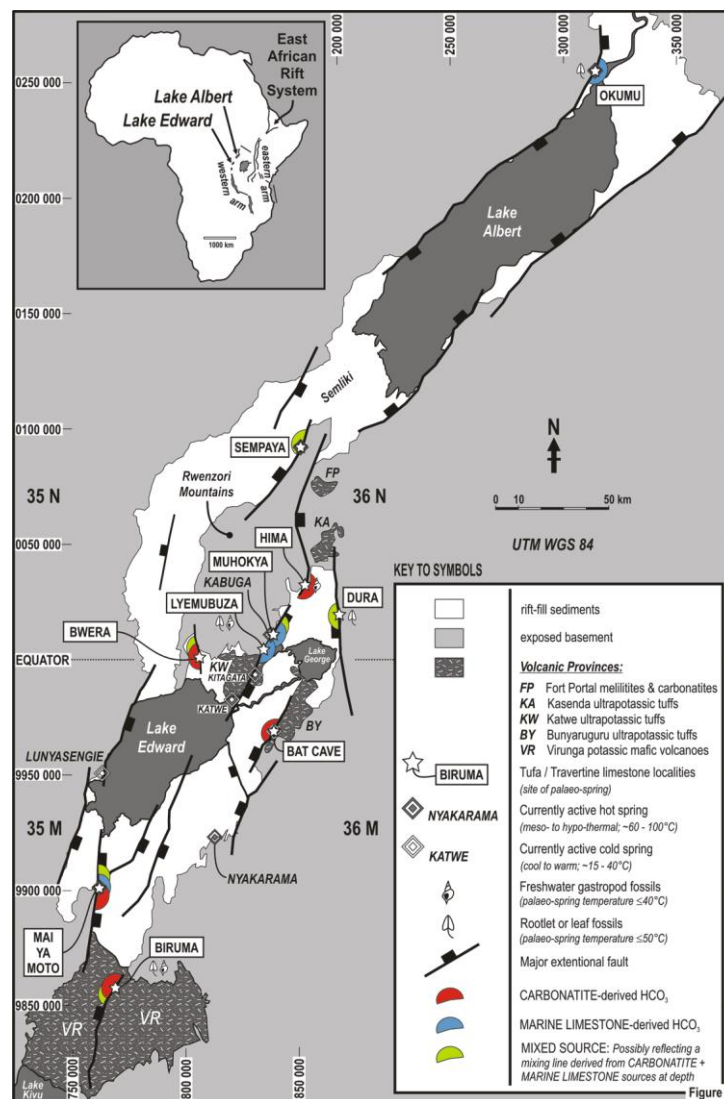


*Figure I.1: Travertine locations in the Eastern Africa Rift basins (Nicholas, 2016)*

These Travertine limestones are much localised and they are always situated over deep-seated rift-bounding faults, linking their origin to meso- and hydro-thermal groundwater flux along fault planes. For the groundwater to attain the high concentration of bicarbonate necessary to potentially precipitate calcite in a spring pool at the surface, the requirement is that it must have percolated through a substantial carbonate bedrock unit at depth, typically a regional sedimentary limestone. However, as shown in the Figures I.2 and I.3 below (Karp et al., 2012) and (Nicholas, 2009) both Lake Albert and Lake Edward rift basins are infilled by fluvial, deltaic and lacustrine siliciclastic sediments, such as sandstones, claystones and conglomerates.



Detailed lithology log of the Waki-B1 well (modified from Harris et al., 1956). Depth increments are given in meters. Relative grain size is expressed by the length of horizontal beds (ranging from oil shale to conglomerate). The well is shown with sequence-stratigraphic interpretations. Small triangles mark the locations of interpreted parasequences boundaries or flooding surfaces. Ribbons mark the locations of interpreted sequences. The overall coarsening-upward trend in the well reflects major changes in lake hydrology since the Miocene, likely responding to changes in regional precipitation patterns. See text for explanation.

*Figure I.2: Lithology log of the Waki-B1 in the Albert Basin (Karp et al., 2012)*
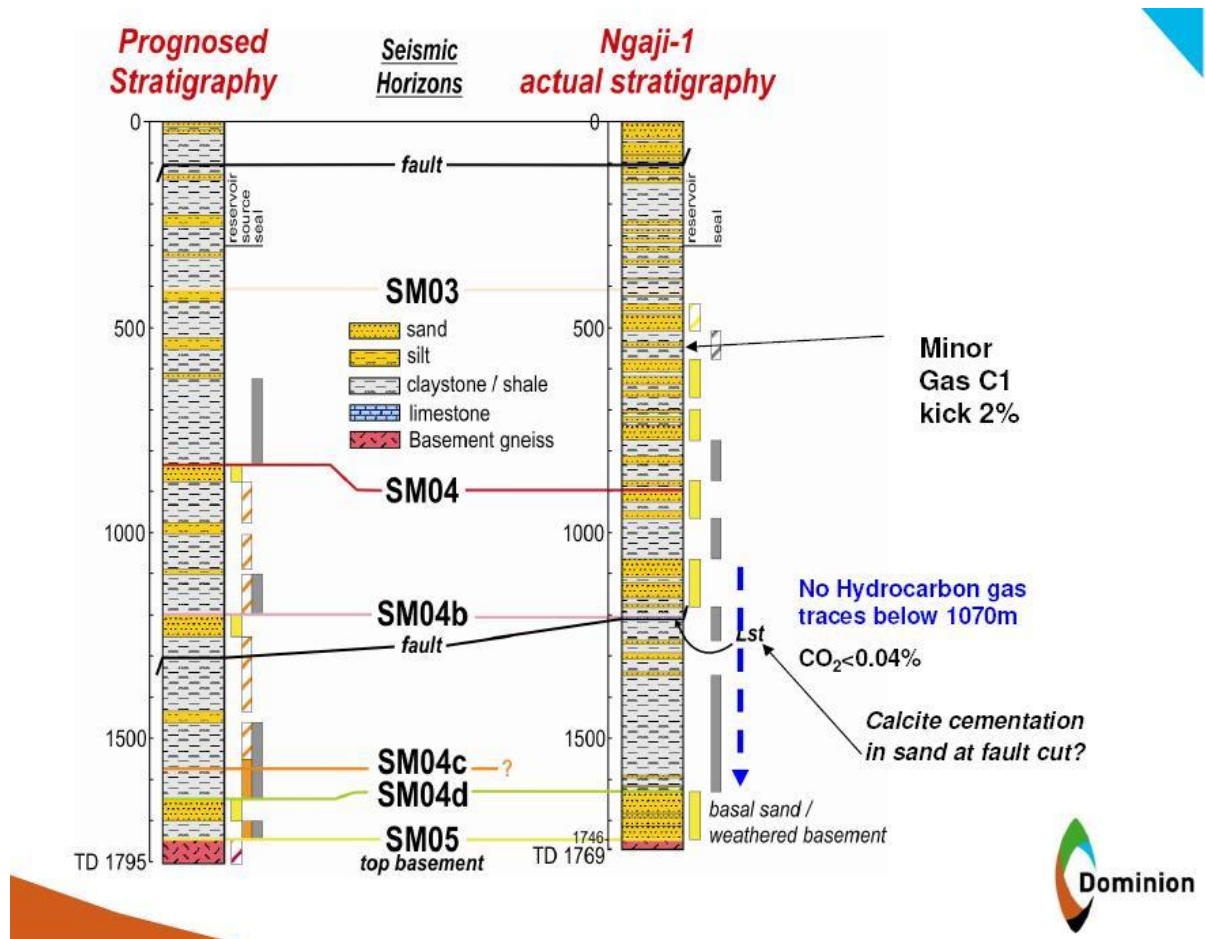
*Figure I.3: Lithology log of the Ngaji-1 well in the Edward Basin (courtesy of Dominion ltd)*

No limestone beds are known in Albertine rift-fill sediments, either at the surface in outcrop, or subsurface in well penetration. In Lake Albert, thin caliche paleosols are present in rift-fill sediments exposed around the margins of the lake, but these are only poorly developed carbonate concretionary horizons and have not developed into full, laterally continuous calcretes. Thus the presence of these Travertine limestones, and more specifically, the origin of their bicarbonate, remains enigmatic. Given the groundwater chemistry required to precipitate Travertine limestones, and the complete absence of any fluvial or lacustrine limestone beds in the Lake Albert and Lakes Edward rift-fill stratigraphy, it begs the question as to how and why the more or less relatively common Travertine occurrences have been formed.

I.2- HYPOTHESIS (problem to solve or questions to answer)

Rift fill sediments in the Albertine Graben are all siliclastics except for much localised patches of Travertine limestones precipitates which are very common in the Lake Edward and Lake Albert basins of the East African Rift System. Rift-fill sediments are usually entirely composed of siliciclastics and so, precipitation of the limestones is something of a mystery and could be linked to hydrothermal fluids passing up the major faults which bound the rift graben.

All this poses some questions which has a direct consequence for both the Geology understanding and Oil Exploration industry in the region:

**How and why did these Travertine limestones form?**
**What is the source of their originating carbonate?**
There would seem to be only 2 possible sources to be scientifically confirmed or not for the bicarbonate needed to precipitate the limestones:

- If the bicarbonate comes from Carbonatites, then igneous intrusive sills must be common at depth throughout the rift.

- If the bicarbonate comes from a marine limestone at depth there may be a pre-tertiary rift beneath the Cenozoic rift.

Extremely rare carbonatite lavas are exposed nearby and this raises the possibility that carbonatite magmas at depth might be the source of bicarbonate. Conversely, it has been hypothesised that older, pre-rift Cretaceous sediments may underlie the current Tertiary rift. **Could marine limestones in these have yielded carbonate to the hot fluids passing up faults?**

I.3- AIM AND OBJECTIVES:

The principal aim of the present MSc study is to give the scientific answer to the three (3) above geochemistry questions which will play a major role in understanding the geologic evolution of the Albertine sedimentary basin.

The main objective of this study is to understand through the reversible reaction $Ca^{2+} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O$, the geochemical source of the Bicarbonate by which carbonates in Travertine, are precipitated in hot springs very localized in straight lines along many Eastern Africa rifts bounding faults.

As specific objectives, this work will:

1. Undertake detailed field trips in the Albertine Rift and use the maximum of the field informations collected to understand and describe the geologic environment of these Travertine outcrops;

2. Describe and Collect properly the maximum Travertine samples from their originate field environment in order to make petrographic observations and geochemical analysis;

3. Make petrographic observations and describe the slabs and/or thin section using the latest Nikon microscope benefits;

4. Compare previous geochemistry results obtained from Carbon and Oxygen stable isotopes end Strontium isotope ratio run on selected Travertine samples;

5. Run ICP-MS on selected Travertine samples to determine the REE elemental concentrations in order to scientifically well discriminate the both end members: igneous Carbonatites intrusions/ volcanics and sedimentary marine Carbonates.

6. Discuss about all field trips, petrography and geochemistry results and publish any new scientific contribution to the best knowledge of the EARS geology.

*Chapter 1 Conclusion:*

*The present Msc. Research study aims to solve the geologic question about:*

- *the possible presence of a pre-tertiary rift marine limestone beneath the Cenozoic classical Eastern Africa Rift System by using the geochemistry to investigate the undocumented Travertines field evidences.*
- *the source of Carbonate found in these localized Travertines deposits mainly outcropping along both East and West Rift bounding faults through which the carbonated groundwaters are emerging in surface (hot and cold springs).*

*The next Chapter, named the Literature review:*

- *has been sourced from either the existing publications available in the public domain or Oil exploration reports obtained by the courtesy of SOCO Exploration Production DRC and its Partner Dominion Ltd.*
- *summarizes the revised Eastern Africa Rift System publications in regards to the geologic knowledge about the Travertines and other limestones found in outcrops within the Albert-Edward basins.*
- *allows the reader of the present Msc research to be aware of the actual level of geological knowledge of the Eastern Africa Rift System in order to better assess its scientific contribution to the Albert-Edward Basins geological knowledge.*
- *updates the reader with some of the previous, documented and successful uses of ICP-MS to detect the marine limestones REE signatures patterns and their respective correlation coefficients with published carbonates REE (Fort Portal, Devonian Reef, Sea Waters...)*

# CHAPTER TWO: LITTERATURE REVIEW

The Eastern Africa Rift System is an active continental rift zone in East Africa which consists of two main branches, the Eastern and Western Rift valleys. The Western branch of the EARS extends southwards from Sudan through Lakes Albert, George, Edward, Kivu, Tanganyika, Rukwa and Nyasa to the Urema Graben of Mozambique. Three sectors are recognised within the Western branch; northern, central and southern. The northern sector or Albertine Rift Valley comprises the three lakes of Albert, George, and Edward with the national border between Uganda and DRC passing along the centre of the valley. The Albertine Rift is structurally segmented into a series of asymmetric graben depocentres, or domains, each separated by NW-SE or W-E trending Accommodation Zones (Rubondo, 2005). For the purposes of petroleum exploration, each of the rift basins has been subdivided into blocks, like for instance Block V on the DRC side of Lake Edward, or 'Exploration Areas' (EA), and EA4A and EA4B on the Ugandan side. The Ruwenzori Mountains also separate Lake Albert from Lakes Edward and Georges.

Mandawa Basin located in coastal Tanzania, is geologically considered as a result of tensional forces related to the Gondwana break-up and the opening of the Indian Ocean. This Basin seems to have been created by transgressive and regressive phases which have led to deposition of various sedimentary sequences from Late Triassic to recent age. These sedimentary sequences have been deposited in different depositional environments, from alluvial fans proximal to source area to deep marine, distal environments. The sedimentary sequences display various mineralogical and textural compositions and heavy mineral contents. (Nerbråten, 2014). Samples from Mandawa basin have been used in this Msc to be referred as Marine limestone origin proxy.

Lake Edward basin, the case study of this MSc research project, consists of an asymmetric half-graben structure with major controlling faults bounding the western edge of the lake, filled with inter-bedded sands and clays, as is typical of continental rift basins. Both climate and tectonics have affected the sedimentation in the Lake Edward basin, periods of active or quiet tectonics have occurred in the past, as have glacial and/or interglacial periods of significant climate change, these have all caused fluctuations in the lake level and in the sedimentation style and its architecture over time.

Field mapping of the onshore part of the basin in Exploration Area 4B (EA4B) has shown that several sedimentary fan systems extend from the basin flanks NW towards the lake (Nicholas, 2009). More recently, a detailed map and working stratigraphic framework of EA4B has been established (Nicholas et al., 2016). Security issues in Block V on the DRC side of the basin prevented any field work from being undertaken until 2010 when a brief field reconnaissance was carried out by SOCO International plc. followed by a thorough field survey of Block V in July and August of 2014. This MSc. project had incorporated all these field works into it to form the basis of the first complete appraisal of the sedimentology, stratigraphy and structure, and petroleum geology of the entire Lake Edward basin.

## II.1- MODERN LIMNOLOGY

Lake Edward is the smallest one of the Great Rift Lakes of the East African Rift System and has a maximum depth of 117m (Beuning and Russell, 2004),(Russell and Johnson, 2005),(Russell et al., 2003) to 120m (Lærdal et al., 2002). Lake Edward drains to Lake Albert northwards via the Semliki channel (Russell and Johnson, 2005; (Lærdal et al., 2002) and Lake George to the northeast drains into Lake Edward via the Kazinga channel. The water level in Lake Edward, like most of the great rift lakes, is highly sensitive to rainfall due to the highly variable monsoonal rainfall pattern in the region of East Africa (Beuning and Russell, 2004). The lake is permanently anoxic below 80m depth and periodically anoxic below 40m depth, and it is considered a eutrophic system (Russell et al., 2003).

Palynological and sedimentary proxies indicate sub-millennial-scale events related to changes in riverine discharge and runoff in the Edward basin. These variability in runoff, and hence precipitation, could be attributed to Holocene variability in Indian or Atlantic Ocean SSTs or to shifts in the relative contribution of Indian and Atlantic moisture sources to the western Rift of equatorial Africa. (Beuning and Russell, 2004).

Sediments of the Edward Lake contain like the most of EARS lakes, a unique and sensitive record of past climate change. This unique and sensitive record is in part a consequence of hydrological balance that are dominated by evaporation rather than outflow that in turn influences the biological, geological, and chemical processes in the lake basins. (Beuning and Russell, 2004).


## II.2- BASIN STRUCTURE

The East African rift system comprises a unique succession of graben basins linked and segmented by intracontinental transform, transfer and accommodation zones. (Chorowicz, 2005).
The most characteristic features in the EARS are mainly narrow elongate zones of thinned continental lithosphere related to asthenospheric intrusions in the upper mantle. A part of the EARS structure could be observed on the surface by thermal uplift of the rift shoulders.
The Albertine graben valleys and basins have been in place over a major failure in the lithospheric mantle, and in the crust comprise a major border fault, linked in depth to a low angle detachment fault, inducing asymmetric roll-over pattern, eventually accompanied by smaller normal faulting and tilted blocks. (Chorowicz, 2005).
The Lake Edward basin is an extensional asymmetric half-graben basin (Fig.II.1: (Lærdal et al., 2002), with the major controlling fault bounding the western edge of the lake in the DRC (Nicholas et al., 2016) and an estimated sediment fill of up to 4 km (Upcott et al., 1996); (Byakagaba, 1997).
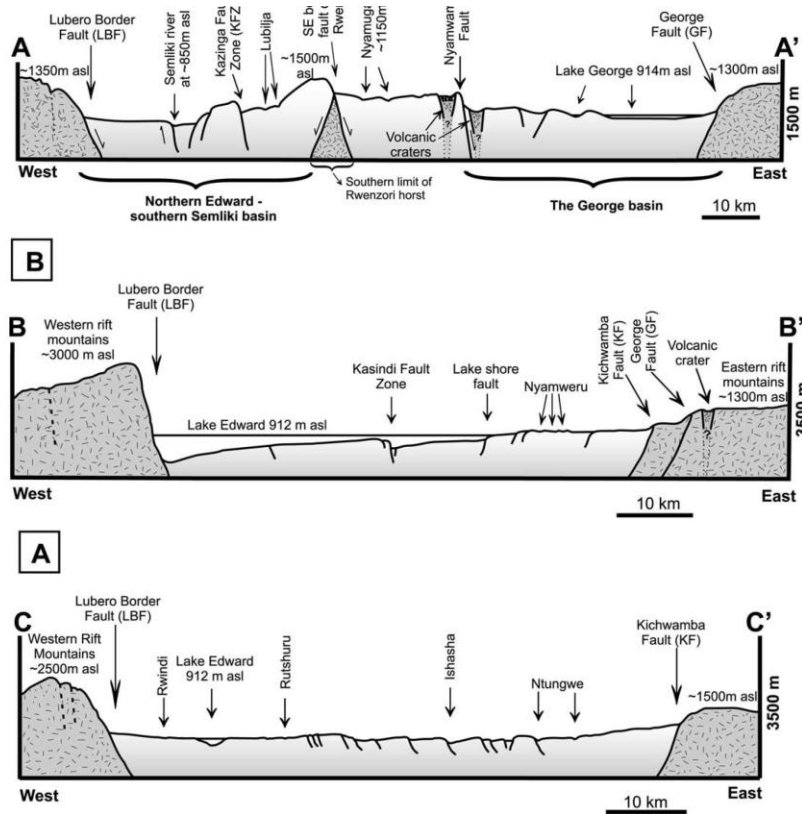
Fig.     Cross-section through the southern Edward basin. (B) Cross-section through the central Edward basin. (C) Cross-section through the northern Edward–George basin. See Fig. 5 for location of the transect lines. (Throw on the KFZ (B) is exaggerated relative to the vertical scale of the figures. Fault scarp is ∼12 m on the lake floor.)

*Figure II.1 :Southern Eduard Basin Cross section  (Lærdal et al., 2002)*

This asymmetric graben or asymmetric half-graben structure has been confirmed by Seismic sections combined with Airmag and magnetic data showing clearly that the Lake Edward basin has a  major controlling fault bounding the western edge of the lake in the DRC.　　　　　(Nicholas et al., 2016).

These successions of half-graben basins structures are generally bordered on the two sides by high relief, comprising almost continuous parallel mountain lines and plateaus, and sometimes volcanic massifs. Other uplifted areas in the region are due to belts, which may be recent (Atlas, Zagros belts) or ancient (Karroo belt), or to intracontinental hotspots (Hoggar, Tibesti plateaus).(Chorowicz, 2005).

The asymmetric nature of the basin can be seen in gravity survey images with the axis located close to the western bounding fault in Figure II.2: (SOCO, 2010).
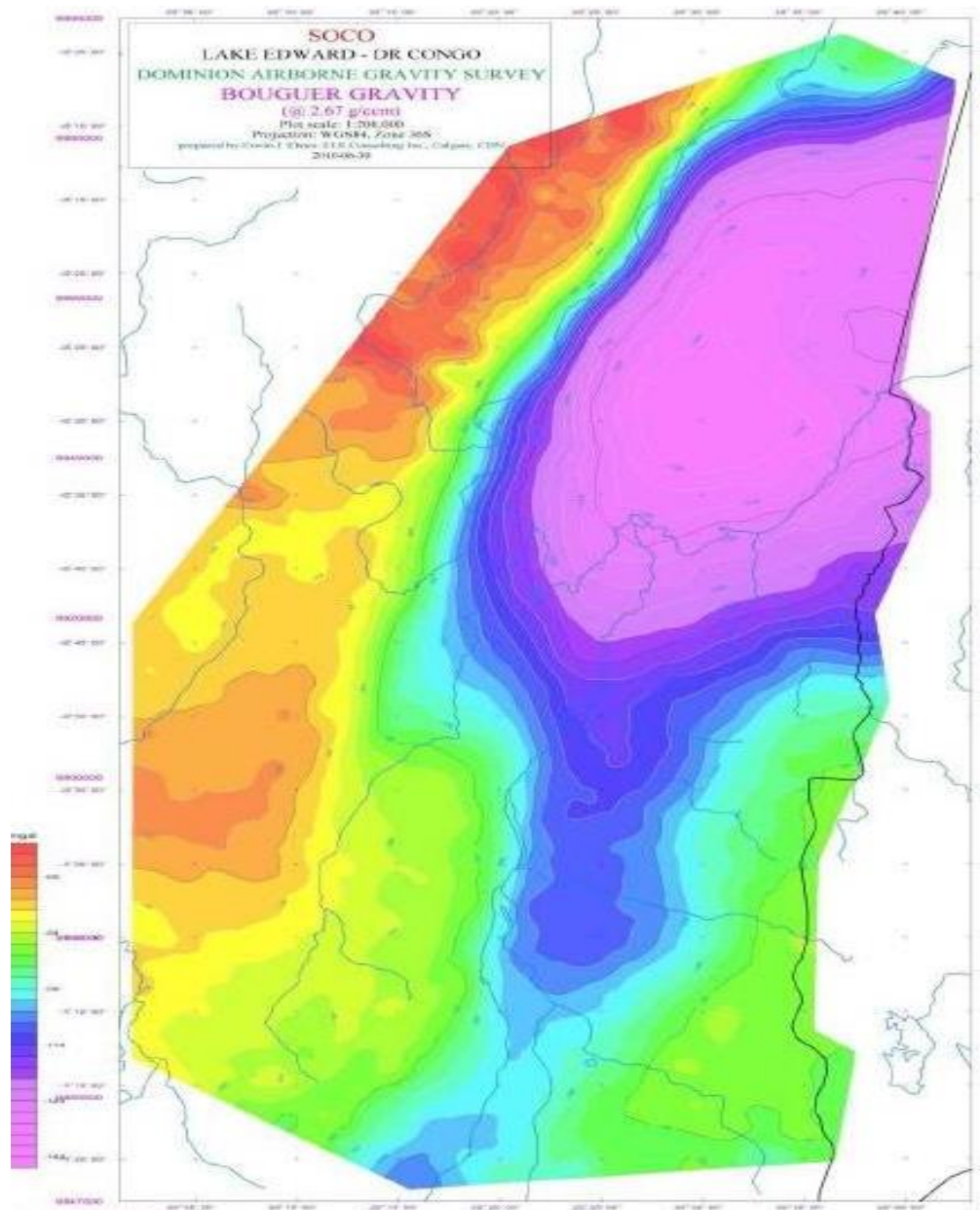


*Figure II.2 : Gravimetric Map of the Bloc V, DRC.(SOCO, 2010)*

The main boundary fault to the West of the basin is the Lubero Border Fault (LBF), and the main boundary fault to the East is the Kichwamba Fault (KF) (Figure II.3 :(Lærdal et al., 2002). The throw on the LBF estimated to be a maximum of 7km decreasing in a southerly direction. The Figure II.3: (Laerdal et al., 2002) below shows the decrease in

the difference between the cross sections from North to South (Upcott et al., 1996; Laerdal et al,. 2002).

Nicholas (2009, 2016) outlines the structure of exploration area EA4B to the SE of Lake Edward. A 15km wide NE-SW trending Kazinga-Kiruruma-Kikarara Fault Zone (KKK-FZ) is exposed across the centre of EA4B, the Kiruruma and Kikarara faults trend towards each other and are thought to have a relay ramp between them which is exploited by rivers for drainage and so are thought to be the same fault (Nicholas, 2009; Nicholas et al,. 2016).

When cross sections and seismic traces are correlated, it can be seen that a network of ESE dipping normal faults compartmentalise the basin. Extensional movement along the KKK-FZ has created a sub-basin known as the Bwambara Trough which trends NE-SW along the SE rift margin.

The oldest unit in the Bwambara Trough sediment fill (Kisenyi Formation) contains a bed of reworked tuffs at the top of the section, interpreted as originating from the nearby Bunyaraguru tuffs. This would date the beginning of subsidence of the Bwambara Trough to before the eruption of the Bunyaraguru tuffs estimated to within the last 84,000 yrs (Boven et al., 1998); Nicholas et al,. 2016). More recent raised 'pod' structures formed on the footwall crest where curved antithetic faults are seen to join up with the main fault scarp suggest that the neotectonic phase in onshore EA4B is compressional or transpressional.
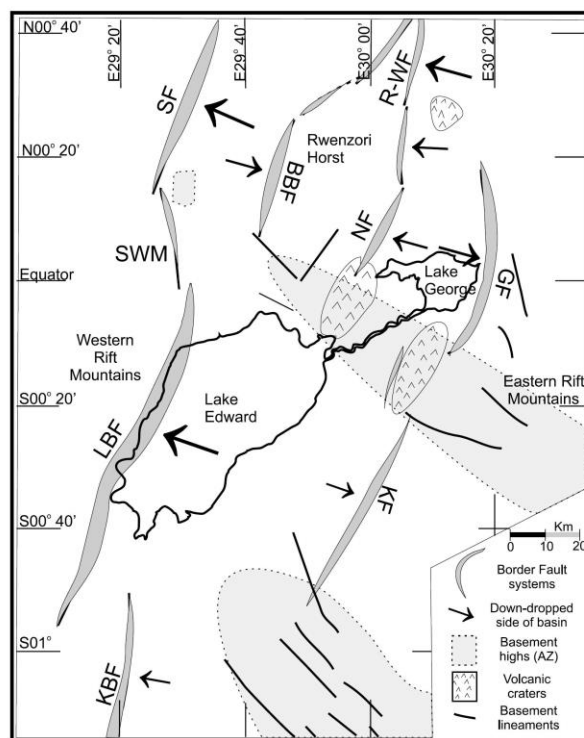


Map showing the location of the main boundary faults in the area. Arrows point towards down-thrown side of the basin. Shaded areas, with a roughly NW–SE orientation, correspond to basement highs (high relief AZs). Vocanis areas and basement lineaments show some correlation to these areas. Modified from McConnell (1972); Reynolds (1984); Ebinger (1989a) and Upcott et al. (1996).

*Figure II.3: Main boundary faults in the Eduard basin (Lærdal et al., 2002)*

The accommodation zone separating the Lake Edward basin and the Lake Albert basin consists of two small extensional basins; the Semliki basin and the Lake George basin, which are separated by the Ruwenzori Mountains (Ring, 2008). A general view of the area is shown in Figure II.4 : (Ring, 2008).
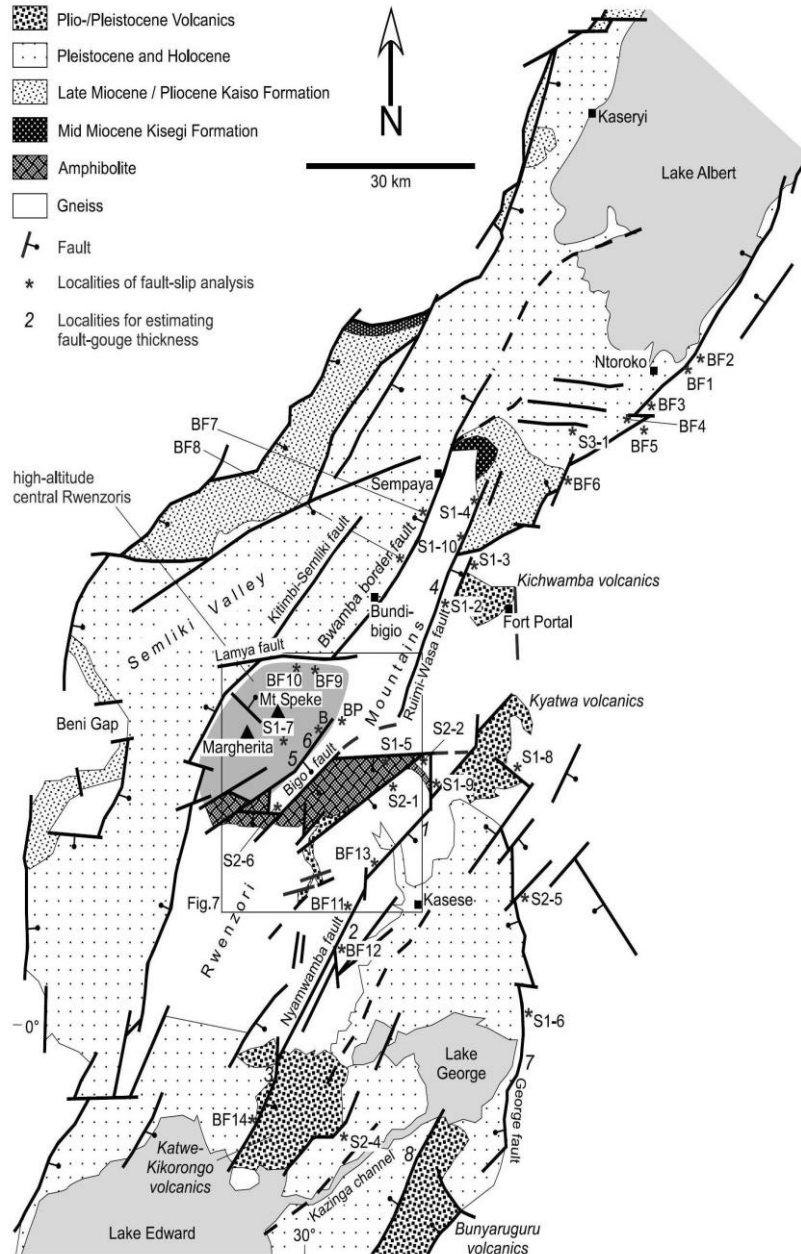


**Figure 5.** Detailed tectonic map of the Rwenzori region with locations of stations where fault-slip data have been obtained. The youngest volcanic rocks occur between Lake Edward and Fort Portal and are associated with young faulting (i.e. Nyamwamba fault); these volcanics in part obscure major rift faults. NNW of Fort Portal a NNE-striking fault cuts through young alluvial fan deposits. Box marks area of map shown in Figure 7; gray-shaded area marks region of high elevation in central Rwenzoris.

*Figure II.4 :Tectonic map of the Ruwenzori region (Ring, 2008)*

## II-3 RUWENZORI MOUNTAINS

The Ruwenzori Mountains are a 5 km high block of Precambrian metamorphic basement with peaks of amphibolite (Bauer et al., 2010) bounded by two major faults (Ring, 2008; Bauer et al., 2010). It is the only uplifted basement block in Africa which is glaciated and has deeply incised glacial valleys (Figure II.4: Ring, 2008) and so is an extreme expression of rift mountain-uplift (Ring, 2008).
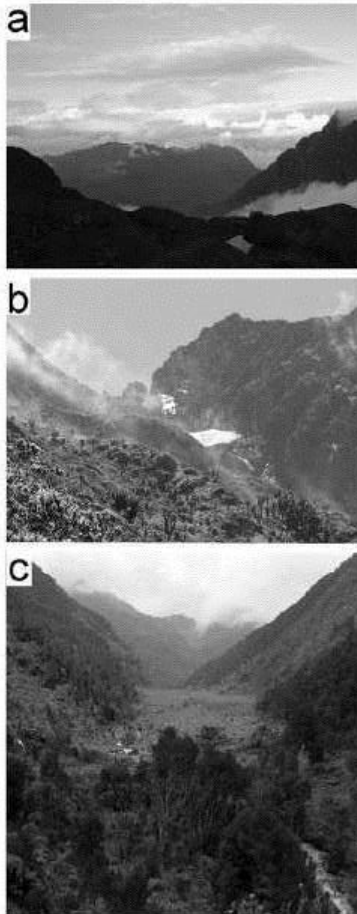


Photographs illustrating the pronounced topography in the central Rwenzori Mountains. The name Rwenzori comes from "rwe nzururu" meaning place of snow in Swahili. (a) The Portal Peaks are 3911 m high; note that the Portal Peaks are surrounded by deeply incised valleys. (b) The rugged topography of the Mt. Speke massif. (c) The Bigo valley; the floor of the deeply incised valley is about 3,800 m high and infilled with raised bog, to the left (N) is Mt. Speke (4,890 m) and to the right (S) is Mt. Edward (4,843 m); the image gives a qualitative impression that glaciers are very efficient erosive agents and that glacial (and fluviatile) erosion produced considerable relief.

*Figure II.5 :(Lærdal et al., 2002)*

It is the most seismically active area in Uganda with most earthquakes concentrated around border faults and volcanic zones (Lærdal et al., 2002) indicating that these faults are still active. The faults in the mountain range consist of both N-NNE striking normal faults, almost parallel to border faults (Ring, 2008) and local reverse faults and strike slip faults which traverse the range trending broadly E-W ((Lærdal et al., 2002); Ring, 2008; (Koehn et al., 2008)) such as the Buganda Toro Fault (Lærdal et al., 2002). These E-W trending faults appear to reactivate the foliation and shear zones in the basement rock (Ring, 2008). The onset of uplift of the Ruwenzori's ranges from 2.3Ma (Ring, 2008) to 10Ma (Bauer et al., 2010) and is thought to have been caused by Rift Induced delamination of the lithosphere and subsequent isostatic rebound of the mantle between the two rift segments (Wallner and Schmeling, 2010). The Semliki valley (or Semliki basin) (Figure II.5) borders the Rwenzori Mountains to the West, its Eastern border fault is the Bwamba Border Fault (BBF) and it is bordered to the West by the Semliki Fault (SF) (Figure II.3 : (Lærdal et al., 2002).

The Lake George basin sits directly to the East of the Rwenzori Mountains bounded to the West by the Nyamwamba Fault (NF), the Ruimi-Wasi Fault (R-WF) further to the North and to the East by the George Fault (GF) (Figure II.3 : (Lærdal et al., 2002)) which forms a 400m high fault scarp (Upcott et al., 1996). Lake George has an average depth of 2.4m but this varies due to wet/dry seasonal changes (Viner & Smith, 1973) to a maximum of around 3m, the lake is around 25km wide (E-W) and 20km long (N-S). Most of the water flow comes from the run off from the Ruwenzori Mountains (Viner and Smith, 1973) forming large alluvial fans prograding away from the mountains to the East (Lærdal et al., 2002).

Sedimentary strata are thought to be around 1.5km thick within the basin (Upcott et al., 1996) consisting of lacustrine, alluvial and fluvial sediments thought to be Pliocene-Pleistocene in age and tilted in a Westerly direction ((Ebinger, 1989);(Lærdal et al., 2002)). The area between the Lake Edward basin and the Lake George basin is thought to be a high relief accommodation zone associated with the Toro Ankole volcanic province.

II.4  ASSOCIATED VOLCANICS

The volcanic province closest to the Lake Edward basin is the Toro-Ankole volcanic field, located to the East of the Ruwenzori Mountains (Figure II.6 : (Rosenthal et al., 2009)) related to the accommodation zone separating the Lake Edward and Lake George basins (Lærdal et al., 2002).
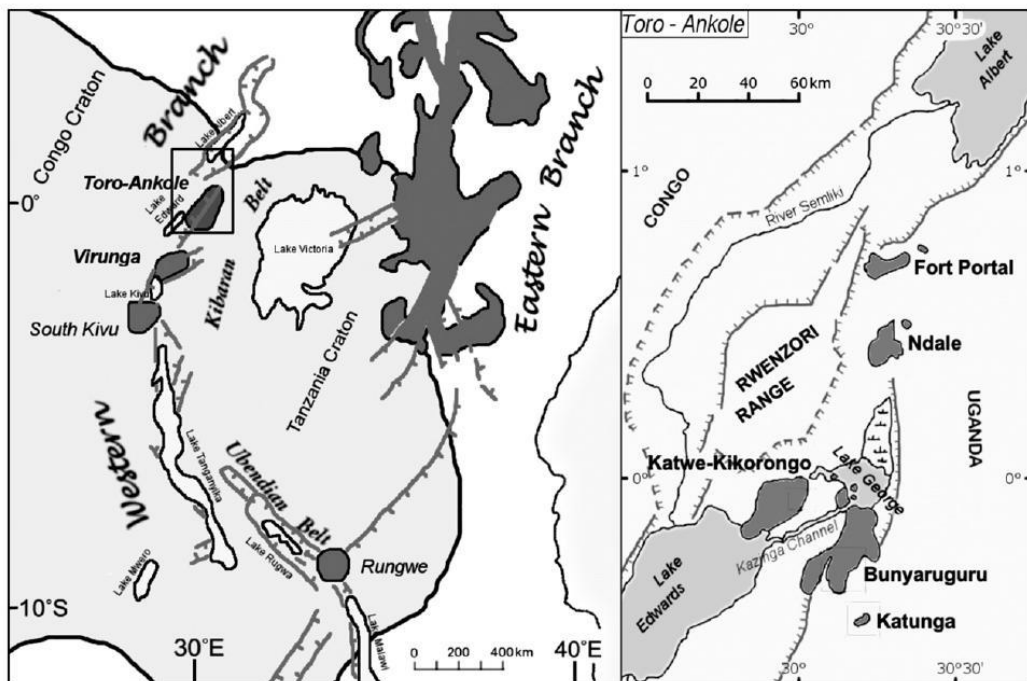


Simplified map of the equatorial part of the East African Rift (left; modified after Tappe et al., 2003) and the distribution of the volcanic fields within the Toro-Ankole province of the western branch, lying E and SE of the Rwenzori Mountains (right; modified after Holmes, 1950). Dark shading indicates extent of volcanic rocks, light shading indicates lakes. The shaded region (left) is the continuous Congo–Tanzanian craton.

*Figure II.6: Map of equatorial part of the EARS (Rosenthal et al., 2009)*

It consists predominantly of kamafugites (strongly silica-undersaturated potassic lavas), often in the form of tuffs, lapilli tuffs or tuff breccias (Musisi, 1991) of varying compositions (Kampunzu et al., 1998) and carbonatite (over 50% carbonate minerals) tuffs. Carbonatites in the Toro-Ankole field occur in Fort Portal (and Kasakere). The Fort Portal carbonatites are dated to 6,000 to 4,000 yr BP by $C^{14}$ dating (Eby et al., 2009). These volcanics are the youngest and most northerly situated volcanics on the western arm of the East African Rift System (Rosenthal et al., 2009). They are dated to have erupted no earlier than 50 ka BP (Boven et al., 1998), and this 50 ka period coincides with renewed Quaternary volcanism in the Virunga and South Kivu volcanic provinces and a tectonically active period in the region (Lærdal et al., 2002).

The Virunga volcanoes trend approximately W-E and occur on the high relief accommodation zone between the Edward and Kivu basins (Ebinger, 1989); (Lærdal et al., 2002). The province has been subjected to two major eruption periods; the first occurred during the Miocene, ca.11 Ma, and consisted of basaltic lavas, the second consists of potassic lavas, began in the Pliocene and is ongoing today ((Bellon and Pouclet, 1980); Ebinger, 1989; Kampunzu et al., 1998). The Virunga fault separates the field into two segments (Figure II.7 : Eby et al., 2009) with only the Western segment exhibiting active volcanism (Platz et al., 2004).
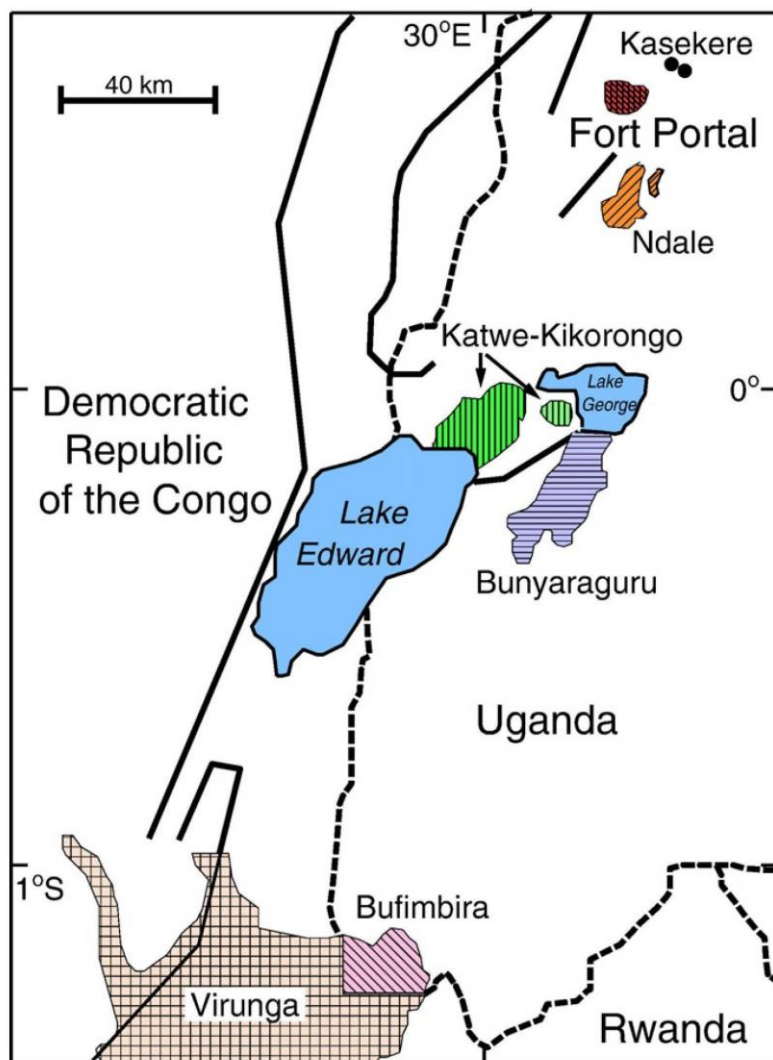


**Fig.** ations of the major volcanic fields in the southwest Uganda portion of the western branch of the East African rift system. Fort Portal and Kasekere – calciocarbona-tites; Ndale, Katwe–Kikorongo, and Bunyaraguru – kamafugites; Bufimbira (part of the larger Virunga field) – potassic mafic–felsic flows and pyroclastics.

*Figure II.7: Location of the major volcanic fields in the SW Uganda (Eby et al., 2009)*

<u>II.5- SEDIMENT FILL</u>

The sedimentation patterns in the EAR system are controlled by structures, with strong influence of climatic environments and occurrence of great lakes ((Crossley, 1984); (Le Fournier et al., 1985); (Tiercelin et al., 1992); (Frostick and Reid, 1990); (Lambiase and Bosworth, 1995).

Detritic sediments accumulate at piedmont of Lake Edward basin major border faults, forming alluvial cones, alluvial and delta systems, down slope fan deltas and deep fan deltas.
There is sometimes development of littoral platforms with fan deltas, prograding deltas, underflows from canyons, carbonate deposits, stromatolites. (Chorowicz, 2005).
Organic sediments are preserved in deep and sometimes shallow basins. Evaporitic sediments are under semi-arid climate, in shallow basins. Metallogenic deposits are related to hydrothermalism along major border faults ((Tiercelin et al., 1992);(Chorowicz, 1990).

Sedimentation in EARS could be considered like a combination of organic and detrital deposits in shallow lakes. The first sediments resting on the basement are sand-dominated fluviatile deposits (F in Figure II.8). They are followed by clay and silt deposits with high organic content corresponding to swamp environment (S in Figure II.8). In late stage of rifting, sedimentation changes and is characterized by thick deposits of deep lacustrine detrital sequences forming turbidites. (Chorowicz, 2005).



T : turbidites
S : swamp deposits
F : fluviatile deposits
B : basement
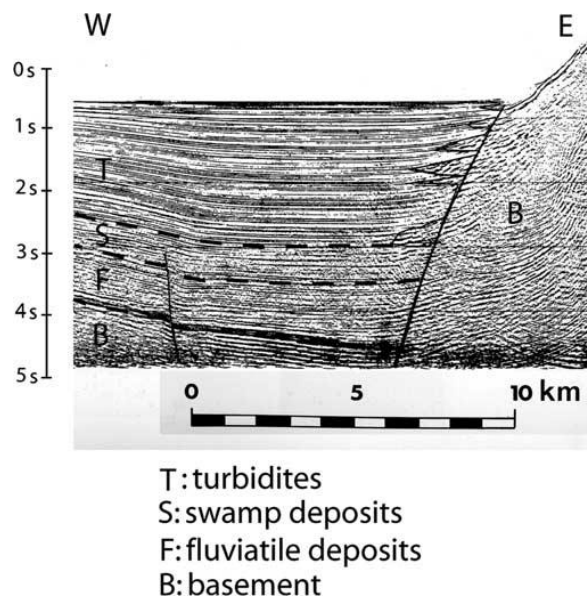
B: basement; F: sand-dominated fluviatile deposits; S: clay and silt deposits with high organic content, corresponding to swamp environment; T: turbidites

*Figure II.8: Typical sedimentation sequence in Rift Lake as seen from seismic Profile (Project PROBE)(Versfelt and Rosendahl, 1989)*

The oldest rift-fill sediments of the Albert – Edward basin are considered to be of Late Miocene age and contemporaneous with the onset of volcanic activity. Age dates of between 8 Ma to 12 Ma are proposed for the earliest lacustrine sediments (Hopwood and Lepersonne, 1953 cited by (Doornkamp and Temple, 1966); Ebinger, 1989a; (Pickford et al., 1993).

Thin, Neogene and younger formations have been recognised by Ugandan PEPD in the Ugandan side of Lake Edward basin and they include: Kazinga Formation, Kankoko Formation, Channel Formation, Ishasha Formation, Kiruruma Formation, Mweya Formation, Kikorongo Formation, Nchwera Formation and Rwenshama Formation. (Tumushabe, 2012).

Many studies before the year 2000 have identified stratigraphic units that were very difficult to correlate and lacked formal boundaries and defining facies characteristics. The mapped units; clays, sands and conglomerates were thought to date from the mid-Miocene onwards when they were dated by Pickford et al (1993). The Mid-Miocene date comes from bivalve and mollusc species found in association with mammalian species which are dated to Miocene in age in other East African locations. Other areas along the Albertine rift in Uganda also yielded Miocene ages, such as Karugamania, Nyamavi, and Sinda-Mohari, as a result of these fossil assemblage analysis (Pickford et al., 1993).

The problem is that these biostratigraphical constraints relied on the correlation between gastropod and mammalian fossil assemblages in Lake Edward with those found amongst dated tuffs in Ethiopia, and there is no way of proving that these fauna arose simultaneously in both locations. More recent Palynological analysis of onshore samples from EA4B produced a younger age of Pleistocene to Holocene (~20,000 yrs B.P. to the present day) and subsequent analysis of palynomorphs from the entire Ngaji-1 well, a 4.5km deep exploration well drilled by Dominion in EA4B and the only one in the basin, only extended this estimate to the Pliocene to present day (SOCO, 2010). The well showed interbedded sands and clays consistent with a fluvial-lacustrine depositional environment as seen onshore. The nature of large scale fluvial dominated deposits of this type means that facies are likely to vary significantly both laterally and distally down dip from the sediment source and this is proven when they are mapped (Nicholas et al, 2016).

Onshore EA4B has been mapped and a working stratigraphy established with five rift fill sediment formations (Nicholas et al, 2016).

The oldest *Kisenyi Formation* consists of low energy, distal fluvial flood basin plain and marginal lacustrine deposits and an abrupt change to a coarse, immature sedimentary fill to the south-east suggests that extensional movement has created a sub-basin known as the *Bwambara formation* trough which has been infilled with sediment shed directly from the exposed basement to the south-east. The Bwambara trough contains three recognisable units. The *Kayonza Formation* is a fluvial unit with ell developed channel conglomerates and thick clay intervals which were deposited drainage ponded during the initial subsidence of the trough. The *Kihihi formation* is characterised by low energy

fluvial sediments and occasional swamp hardground horizons with freshwater gastropods. To the NE of the Nyamirama high, the main area of subsidence accumulated the Bwambara Formation which is composed of thick comparatively structureless, dominantly coarse sands grits and conglomerates representing the immature relatively rapid sub basin fill in the trough (Nicholas et al, 2015). The youngest unit is the *Kikyere Formation*. It can be recognised only in sporadic exposures and is composed of swamp clays which are formed or are currently forming typically along the hanging walls of faults scarps due to the present day interglacial wet phase which East Africa is experiencing, equivalent to Marine Isotope Stage (MIS) 1 (Nicholas et al, 2016).

No dateable tuff deposits in any exposed or drilled sediments, or further indication from palynology make age constraints on stratigraphic units extremely difficult. Recognising arid intervals, wet phases, and their correlation with an oscillating East African climate during glacial/interglacial episodes in the litho-facies and chrono-facies of onshore Lake Edward may be the key to establishing a working stratigraphy for the basin.

According to Chris J. Nicholas, the spatial distribution of depositional environments of each sediments fill in EA4B and/or Bloc V (Lake Edward basin) are described as shown in the conceptual cartoon of typical alluvial structure below in Figure II.9 :
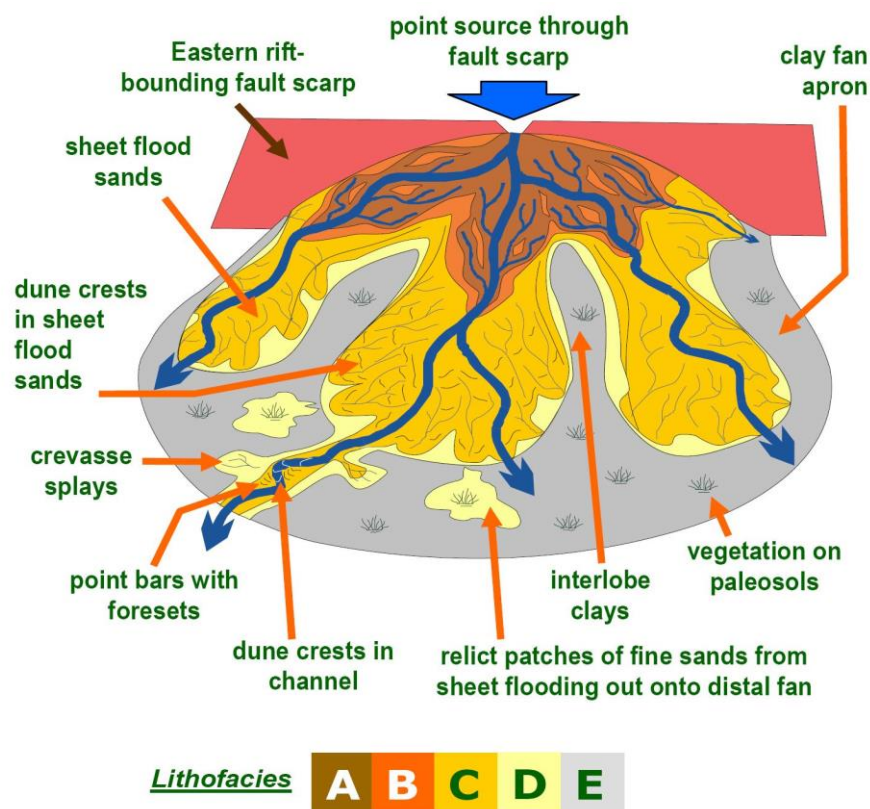


Fig      nceptual cartoon of typical alluvial fan structure and spatial distribution of depositional environments in EA4B.

*Figure II.9: Typical alluvial fan structure and spatial distribution of depositional environments in EA4B (Nicholas et al., 2016)*

Climate and tectonics both had major effects on the sedimentation with the Lake Edward basin so an attempt was made to reconcile these two effects over the history of the basin by creating a Coupled Climate-Tectonic Model to determine the effect both climate and tectonic mechanisms could have on lake water volume and accommodation space over sub-millennial timescales (Tumushabe, 2012). There are several processes that effect the climate on both short and long term timescales such as rainfall controlled by the two wet/dry seasons each year, Milankovitch cycles from which processional minima cause equatorial wet episodes, and longer term effects such as glacial episodes and processional cycles in the order of thousands of years. Tectonic effects would include the uplift of the Ruwenzori Mountains and the uplift of the East African Rift System as a whole which has contributed to the drying out of Africa (Tumushabe, 2012). Climate and tectonics are in operation separately but both affect sedimentation within the basin. Figure II.10 : (Nicholas et al., 2016) shows a model developed to analyse the effect both tectonics and climate have on sedimentation. At any one time the sedimentation in the Lake Edward basin would sit between the end members, the model can predict when source or reservoir for example would be deposited in the basin if the climatic and tectonic conditions for that time period were known.
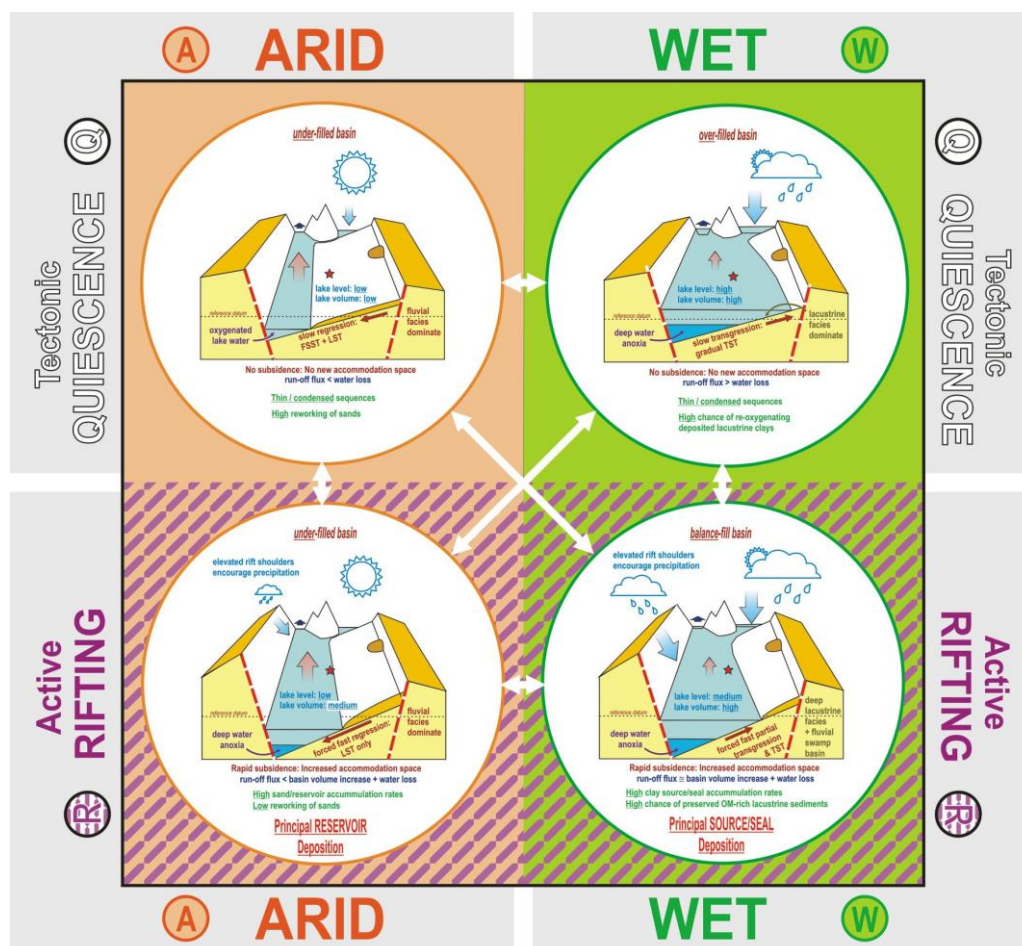


*Figure II.10: Effect of tectonics and climate have on sedimentation. (Nicholas et al., 2016)*

## II.6- PRE-RIFT BASEMENT

The Precambrian Basement in the area around Lakes Edward and George is composed of a variety of metasediments, mafic intrusives and acid gneisses. The Mbarara 1:250 000 sheet subdivides the Precambrian units of the region into Basement Complex, Toro System and Karagwe – Ankolean System (Geological Survey of Uganda, 1961) cited by (Hepworth and Macdonald, 1966).

PEPD reports do not use these divisions and instead subdivide on the basis of metamorphic facies (Byakagaba, 1997). Metasediments include irregularly-bedded silver white and reddish-brown phyllites and phyllitic shales, in some localities overlain by quartzites (Byakagaba, 1997). The quartzites are micaceous or at times schistose and ferruginous, ranging in colour from white to grey-brown. They are also found in association with metamorphosed cherts. Biotite-, quartz-, amphibole- and mica-schists are present in the region, indicative of a higher grade of metamorphism than the phyllites and quartzites. They apparently grade at times into gneisses or can be found interbedded with gneisses at some localities (Byakagaba, 1997). The gneisses themselves display a foliation parallel with the main regional structural trend. Although dominated by quartz and feldspar, they (gneisses) also contain accessory minerals of hornblende, biotite, tourmaline and muscovite. There are occasional pods of schists enclosed within the gneisses (Byakagaba, 1997). Mafic intrusions are also present in the Lake Edward – George basins. These consist of massive, little altered, dark green, porphyritic diorites and dolerites – gabbros (composed of plagioclase, augite, amphiboles, olivine, siderite,quartz and magnetite) which can be seen intruding the gneisses, quartzites and schists. However, they have not so far been observed to cross-cut the Neogene and younger rift fill sediments (Byakagaba, 1997). Thus, both their precise age and subgroup extent remain unclear at present.

## II.7- PETROLEUM POTENTIAL OF THE ALBERTINE GRABEN

According to Rubondo (2005) the Albertine Graben has good source and reservoir rocks, traps and seals.

## II.7.1- SOURCE ROCKS AND OIL SEEPAGES

There are over five confirmed substantial oil seepages in the Albertine Graben and these include two live oil seeps on the Victoria Nile near Paraa, two seeps at Kibuku in the Semliki basin and the Kibiro seepages on the shores of Lake Albert. The presence of these oil seeps indicates that organic rich source rocks are present.
Rubondo, 2005 reports that geochemical analysis of oils from these seepages indicates that they were generated from source rocks deposited in a lacustrine environment and dominated by Type 1 algal kerogen. There are differences between oils from the Paraa and Kibiro seeps and that of Kibuku in that the later depicts origins from source rocks deposited in a more saline lacustrine environment and with more contribution of higher land plants to the source rocks. This variation is important because it points the presence of at least two origins for oil in the graben (Rubondo, 2005).

## II.7.2- RESERVOIR ROCKS

Basement rocks along the escarpment and rift flanks of the Albertine Graben comprise mostly gneisses, granitic gneisses and quartzites. The weathering of these rocks, the subsequent transportation and deposition of their weathered products into the Graben could yield good reservoir quality sediments. Coarse clastics constitute much of the sedimentary formations outcropping in the Graben especially in the Kisegi and Kaisotonya river valleys of the Semliki basin (Rubondo, 2005).

Sandstones with good reservoir quality are present as porosities of over 30% have been measured in the shallow cores recovered from the Kibiro area. Porosities of up to 22% have also been measured in aeolian and fluvial channel deposits outcropping at Kibuku in the Semliki Basin (Rubondo, 2005).

Live Oil have been found and confirmed in cavities of Travertine in Lyemumbuza quarry in Uganda, suggesting a potential carbonate reservoir in the Edward lake basin. (Nicholas, 2009)

## II.7.3- TRAPS AND SEALS

Structural styles in the Graben are dominated by down-to–the basement block faulting which plays a major role in the formation of hydrocarbon traps. Dip reversals against faults and fault and fault-on-fault traps are present. A large number of small tilted fault blocks, apparent rollovers as well as anticlinal features associated with a fault block rotation were identified from the seismic data acquired in the Semliki Basin (Rubondo, 2005).

Relatively rapid facies changes common in terrestrial alluvial fan, deltaic and lacustrine sediments provide the potential for stratigraphic traps with or without structural components. Unconformities in the sedimentary section also provide for stratigraphic, combined stratigraphic and structural traps.

The more than 30m thick clay bed mapped on top of the good reservoir quality sandstone in the Kisegi area of the Semliki Basin is a potential regional seal (Rubondo, 2005).

## II.8- PREVIOUS PUBLISHED USE OF ICP-MS FOR CARBONATE DISCRIMINATION

Absolute geochemistry sourcing methods such as the ICP-MS uses isotope dilution techniques to provide the full suite of the REE range as well as other trace elements in very low detection limits, yielding precise and accurate data to present REE at ppb concentration levels. The geochemical sourcing of the EARS travertines, which is the primary objective of this MSc research, is focussed on any possible discrimination evidence between different carbonates structures, textures and/or fabrics visible in each analysed sample.

The REE are extremely advantageous geochemical proxies because the changes in their atomic structure across any carbonate sample vary predictably and in much smaller increments than any other group of elements (Lawrence and Kamber, 2006).

The analysis of REE in hydrogenous sediments (such those observed in EARS) has significantly increased in scope with the application of Inductively Coupled Plasma

Mass Spectrometry (ICP-MS), as exemplified by the landmark publications of Bau and others (Bau and Dulski, 1996; Möller and Bau, 1993; Bau and Möller, 1993).

The geochemical study of REE distribution spans decades and results obtained have answered many crucial biogeochemical questions such the carbonates' origin in travertines (Goldberg et al., 1963; Elderfield, 1988; Piepgras and Jacobsen, 1992; Sholkovitz, 1992, 1995; Sholkovitz et al., 1992; Zhang and Nozaki, 1996; Lerche and Nozaki, 1998; Runnalls and Coleman, 2003; Wyndham et al., 2004).

Byrne and Sholkovitz (1996; p. 529) suggest that the dependence of concentration and slope of REE pattern is chiefly controlled by surface reactions where pH is a variable parameter in establishing the absolute and relative lanthanide abundance.

Undeniably, REE traces found in Carbonates samples can, as per Elderfield's (1982) suggestion, be employed as tracers of geochemical processes in sea waters (Elderfield and Greaves, 1982; De Baar et al., 1985). More recently, the REE concentrations of terrestrial waters such as groundwaters and lakes have been examined as potential tracers of processes affecting their geochemical evolution (Banner et al., 1989; Smedley, 1991; Fee et al., 1992).

For this Msc correlations purposes, the following published use of ICP-MS for tracing back the carbonate sourcing have been considered:

- The Quaternary Fort Portal carbonates and Katwe Kikorongo carbonatitic lapilli-tuffs (4–6 m thick) samples have been analysed by Eby et al., 2009 and their geochemistry results provided referenced ppm values of La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu, and Y. (Eby et al., 2009)

- A. Bellanca has studied the REE distribution through the Albian-Cenomanian interval of a stratigraphic succession (Cismon section, Scaglia Variegata Formation, Venetian Prealps) consisting of rhythmically alternating carbonate-rich and carbonate-poor strata which are the sedimentary expression of systematic variations of surface fertility and bottom-water redox conditions in the depositional basin. (Bellanca et al., 1997)

- Rare earth element and yttrium (REE+Y) concentrations were determined in 49 Late Devonian reefal carbonates from the Lennard Shelf, Canning Basin, Western Australia. REE+Y normalized patterns of the Late Devonian samples display features consistent with the geochemistry of well-oxygenated, shallow seawater. (Balz et al., 2004)

- The purpose of the Corkeron et al., 2012 research was to test if trace element (primarily REE+Y) geochemistry could be used to determine if the sampled Neoproterozoic fine-grained stromatolites were the products of:(1) trapping and binding of ambient particulate sediment, or, (2)in situ precipitation of carbonate minerals. (Corkeron et al., 2012)

This MSc research study followed step-by-step the same procedures used by Balz Kamber (2004) who basically used ICP-MS and MUQ datas normalization to understand the carbonates' origin and involvement in the REE signal in the Achaean microbial carbonate and to document information on ocean redox and biogenicity. Balz Kamber (2004)

The carbonates samples have been entirely dissolved into 2% $HNO_3$ solution and the results obtained from the ICP-MS experiments on them revealed a scaled look at the carbonate chemistry in both major and trace REE. Field and laboratory blanks were prepared for each batch of samples and reference material were treated as unknown.

Two separate digestions of U.S.G.S. dolerite W-2 were used as calibration standards and two other U.S.G.S. basalt reference materials BIR-1 and BHVO-2 were analysed as unknowns. Comprehensive illustration of REE spectral signature patterns opens a discussion of the EARS travertine samples' overall shape with quantitative expression of anomalies. REE anomalies are calculated as REEn/REEn * where REEn * is the expected normalised concentration when interpolated from an appropriate combination of near neighbours (Lawrence and Kamber, 2006).

Values > 1 indicate a positive anomaly and values < 1 indicate a negative anomaly. We use the Prn/Ybn ratio as a general descriptor of the slope of the pattern, with values > 1 indicating light enrichment and values < 1 indicating heavy enrichment (neither Pr nor Yb behave anomalously thus are suitable representative elements) (Lawrence and Kamber, 2006).

Middle REE enrichments, similar to those described by Shiller (submitted), can be evaluated with Prn/Tbn and Tbn/Ybn. Anomaly calculations in aquatic REE are complex than in solid geological materials such as in our EARS travertine samples.

The principal satisfying requirement for calculating anomalies recorded in this Msc research was that the near neighbours used in the calculation do not show any anomalous behaviour themselves (Lawrence and Kamber, 2006). For instance, for the calculation of La* anomalies, we cannot use Ce as the oxidation from $Ce_3+$ to $Ce_4+$ as it often leads to an under abundance of Ce.

La anomalies were calculated using the nearest available non-anomalous REE Prn and Ndn. Similarly, Ce* was also calculated from Prn and Nd due to the possible overabundance of lanthanides (Lawrence and Kamber, 2006). The extent of La, Gd and Lu anomalies is expected to be small but well beyond analytical uncertainty.

Calculating anomalies with the Lawrence and Kamber (2006) method is assuming that the difference in concentration between neighbouring pairs is constant. Thereafter, graphically, the REE+Y spectral signature pattern will behave linearly in the region of the near neighbours on a linear-linear plot (Lawrence and Kamber, 2006). The majority of the REE speciation studies supporting this assumption have been conducted using seawater or other natural waters of moderate to high pH and less work has been focused on acidic waters.

The ICP-MS analysis run on freshwater samples reveal that lanthanide anomalies are relatively small compared to that of seawater in which it averages 2.62 (an average of MUQ-normalised values calculated from data published by Zhang and Nozaki (1996; 1998) (Zhang and Nozaki, 1998; Alibo and Nozaki, 1999; Nozaki and Alibo 2003; Nozaki et al., 1999).

Referring to Gadnium anomalies, previous studies have documented an anthropogenic origin for Gadnium anomalies (Bau and Dulski, 1996; Nozaki et al., 2000b), but there is no reason to suspect and no evidence to support an artificial Gd source in the EARS travertine samples.

Thermodynamic calculations performed by Akagi and Masuda (1998) indicate that Cerium oxidation is favoured under normal aquatic conditions, but comprehensive understanding of the weathering reactions of carbonate source bedrock and the subsequent transport of REEs appears critical to resolving the nature of freshwater carbonatites or marine limestone Cerium behaviour.

Lawrence and Kamber (2006) calculated Ce anomaly as a linear extrapolation between La and Nd (the closest available elements from isotope dilution methods), an approach that is naturally biased towards a substantially negative Ce anomaly due to the possible overabundance of La. The previously reported pH dependence of the negative Ce anomaly is in fact due to a pH dependence of the undetected La anomaly.
This requires further investigation with complete REE datasets (Lawrence and Kamber, 2006).
Negative Cerium anomalies represent a marine REE feature, but they are also commonly observed in river waters (Sholkovitz, 1995; Byrne and Sholkovitz, 1996).

According to Lawrence (2006) a negative cerium anomaly is developed in limestones due to differing mobility of Ce compared to other REE (Pinares-Patiño et al., 2003). This implies that this negative Ce anomaly is also a geochemical source with enough potential for providing the carbonate provenance information. Lawrence (2006) also suggested that the Ce anomaly is related to weathering, inorganic aquatic processes or biological mediation (Lawrence and Kamber, 2006). Cerium oxidation and precipitation is widely accepted as the mechanism for generating a negative Ce anomaly (Moffett, 1990; Alibo and Nozaki, 1999; Bau, 1999). Therefore, it is expected that the Ce anomaly should deepen with distance downstream, but this is clearly not the case in the EARS travertine samples analysed in our MSc research study.

One of the main features characterising the marine REE spectral signature patterns is the strong positive lanthanide anomaly (Bau and Dulski, 1996; Zhang and Nozaki, 1996; Shields and Webb, 2004). The explanation of this above-mentioned relative lanthanide abundance as presented by Lawrence and Kamber (2006) is that the removal of LREE expresses a positive lanthanide anomaly even before reaching the estuarine trap or when reaching the surface cooling depth. Lawrence and Kamber (2006) also indicate that this behaviour might be related to the electronic structure of the $La_{3+}$ ion which has a noble gas configuration.

Additionally, Kamber published in 2004 the following key criterias for recognizing a REE+Y marine limestone signature :

- Prn / Ybn <<1    Praseodymium / Ytterbium ratio
- Y/Ho > 40        Yttrium / Holmium ratio
- La/La* > 1.1     Lanthanum anomaly
- Gd/Gd* > 1.1   Gadolinium anomaly
- Ce/Ce* < 0.8   Cerium anomaly

Where:
- La/La* = La/ ((Pr*((Pr/Nd) 2)))
- Gd/Gd* = Gd/((Tb*(Tb/Dy)))
- Ce/Ce* = Ce/ ((Pr*(Pr/Nd)))

*Chapter 2 Conclusion:*

- *The starting point of this Msc. Research Study was the detailled review of all the Eastern Africa Rift System existing publications available in the public domain in terms of Modern limnology, Basin structure, associated metamorphic (Ruwenzori Mountains), associated volcanics (Fort Portal), Sediment fill, Pre-rift basement and the petroleum potential of the Albertine Graben.*
- *None of those previous studies mentioned the Travertines outcropping in hot springs or the possible pre-tertiary marine limestone under beneath the classical siliclastic Eastern Africa Rift System*
- *Details of previous published uses of geochemical data to discriminate and trace back the bicarbonate sources of Travertines have been reviewed and updated.*
- *The geochemistry analysis procedure to reach the objectives of the present Msc Research follows the published Balz Kamber (2014) ICP-MS experiment where Rare Earth Element + Y signals, particularly in combination with radiogenic isotopes (e.g. Pb and Sr; Kamber & Webb 2001; Bolhar et al. 2002), have been useful to discriminate the Archaean microbial carbonates depositional environments between stromatolites that formed in lacustrine, restricted marine and open marine depositional settings.*
- *Furthermore, the cited literature review helped us to use the initial set of geologic data package and the geochemistry analysis methods for planning and adjusting good samples field description and collection, and good petrography to select the ideal textures, structures or fabrics to drill through and carefully prepare input solutions.*

*The next Chapter, entitled Methodology:*

- *Describes the details of the methods and analytical procedures chosen to reach out the aims and objectives of this research paper.*
- *Allows the reader of this Msc Research to acknowledge the high confidence level in the efficiency of the opted methods and analytical procedures in terms of reducing risks of errors and samples contaminations in the lab.*

# CHAPTER THREE: METHODOLOGY

The aims and objectives of this MSc. Research will be achieved by following the below methodology:

1. Undertake series of field trips in the Lake Edward basin to describe the geologic environment , to log the reference cliffs , to record Spectral gamma ray responses and finally to collect Travertine samples for Petrography and geochemical analysis;

2. Undertake the Petrography analysis of Travertine samples in slabs and/or thin section stained in alizarin and /or observed in Cathodoluminescence if required. This just means to execute a serie of Carbonate microscopic observations through the most recent version of   Nikon optical microscope (available in TCD) on a suite of selected Travertine limestones slabs and alizarin stained thin section and Cathodoluminescence petrography of microstructural fabrics in deformed limestones to point out the fossils shoreline units, their petrographic composition (Ooids, Peloids, bioclasts), and structure / texture ( fibrous, grained cement, porous, crystalline phases) may reflect times  of partial, or modest platform flooding

3. Discuss in detail the Carbon and Oxygen stables isotopes analysis run in 2013 on the Block V 2010 field work Travertine collected samples ;

4. Discuss in detail the Strontium isotope ratio analysis run in 2013 on the Block V 2010 field work Travertine collected samples;

5. Run a serie of ICP-MS analysis on a suite of samples from Travertine limestones collected from around the margins of Lake Albert and Lake Edward for their whole rock and rare earth element (REE) concentrations, Carbon and Oxygen stable isotope and Sr isotope ratios, in an attempt to discern how limestones lie at depth within the rift, and their geochemical origin.

6. Interpret the final output results to provide key evidence about the interaction between deep structure, groundwater flux, geochemistry, and ultimately the geologic evolution and timing of rifting within these two Lake Albert and Edward basins.

III.1- FIELD TRIPS:

As an investigation method, field trips are a key aspect for the best understanding of the geologic environment where Travertine samples have been collected. They provided to this MSc research project the required back-up for any of the further analysis in laboratory.

The main benefit of these field trips was that they allowed a better visual understanding of: (1) the architecture of units; (2) multi-stage deformation during subduction/exhumation; (3) the geodynamic significance of continental basement juxtaposition with syn- to post-rift sediments.

The main objectives and steps of these field trips in each locality visited were:

- Identification of key stratigraphic units and their subsequent geological mapping across the region,
- Structural mapping across the region with a synthesis of structural style,
- Field observations,
- Rocks and mineral macroscopic descriptions,
- Limestone field tests,
- Spectral gamma ray acquisition,
- Field discussion,
- Sampling and packing for the shipment to laboratory.

The field trip logistic and equipments here below listed and shortly described have been provided by Oil companies and/or government (Uganda/DRC) for the best technical organization. They are here just for illustration to give an idea of how the field trips as a method of this MSc research project have been organized and how they did help to achieve their objectives efficiently.

1. <u>The base camp</u> : (SOCO,2014)

The ideal Base camp of these field trips we need to illustrate in this work is the Nyakakoma Base camp (DRC) provide by SOCO International Plc in 2014. (Figure III.1 to III.9). It was put in place originally in order to support the accommodation of the crew of seismic operations in the Edward Lake but its duration stay was extended to welcome the geologist's team. It was made of easily dismantled several tents (respecting the environment) around an oil generator for power supply. Water supply and waste management were perfectly organized.



*Figure III.1: Nyakakoma Base camp, SOCO 2014*

*Figure III.2: Geologist accommodation unit, SOCO 2014*



*Figure III.3: Ablution facilities and water tanks, SOCO 2014*



*Figure III.4: Kitchen, mess facilities and radio room, SOCO 2014*

The Nyakakoma Base Camp had got a special tent which was used as the Geologist office where A0 geologic and operations Maps were displayed, shelves have been put in place for the storage of samples daily collected before their final packing for shipment, samples bags and samples big boxes were available for the same purpose.

The Geologist's office in the Nyakakoma Base camp was fully provided with Wi-Fi laptop connected, printers, scanners, and all required extension cables.

*Figure III.5: Geologist's tent and office, SOCO 2014*



*Figure III.6: Shelves and Samples boxes, SOCO 2014*

2. <u>The Helicopter :</u> (SOCO, 2014)



*Figure III.7: Helicopter in its landing zone, SOCO 2014*

To facilitate the daily movement of geologists, their equipments, and their security teams in the field, and helicopter has been provided.  The different helicopter landing zones were chosen accordingly to the geologic objective in the area. The helicopter landed to the cleared zone the closest possible to the outcrop or cliff interesting the field trip geologist team.

<u>The field equipments</u>

1. **Structural map,**

2. **GPS,**

3. **Hand auger,**

4. **Hand held spectral gamma ray**

5. **Hammers**

6. **Topographic sheets**

7. **Sample bags**

8. **Compass**

9. **Cameras**

10. **Hand lens**

11. **Binoculars**

12. **Bags, Field notes, rain coats….**



*Figure III.8: Field equipments, SOCO 2014*
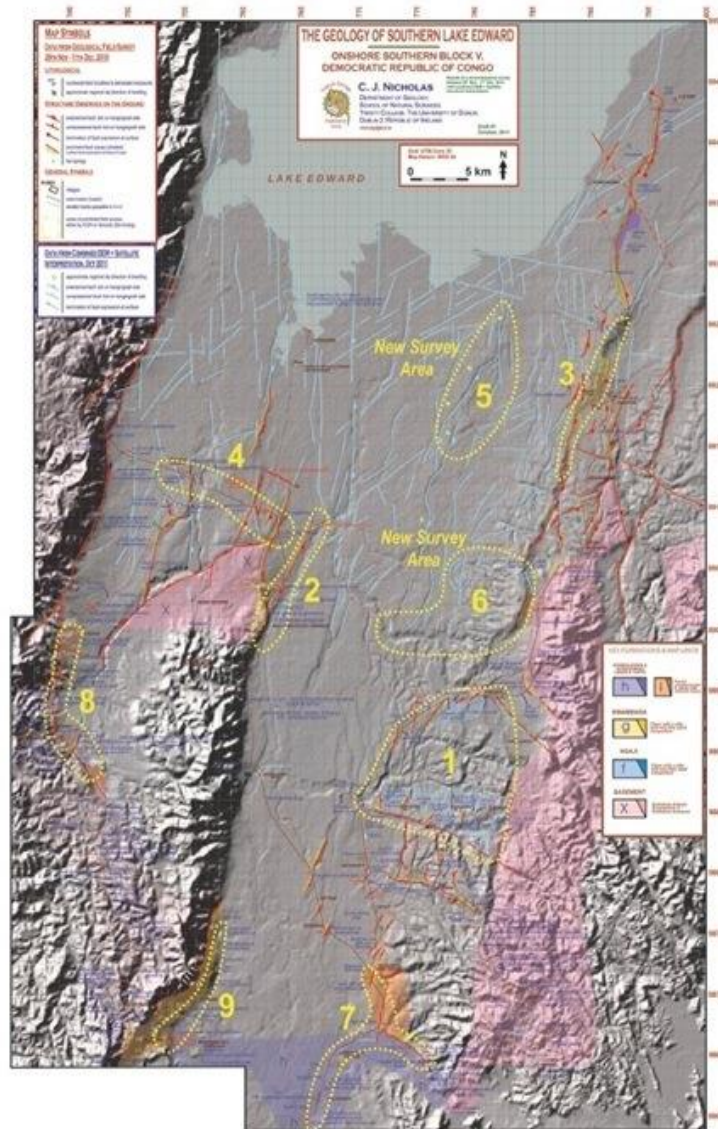
*Figure III.9: Field Maps (SOCO, 2014)*
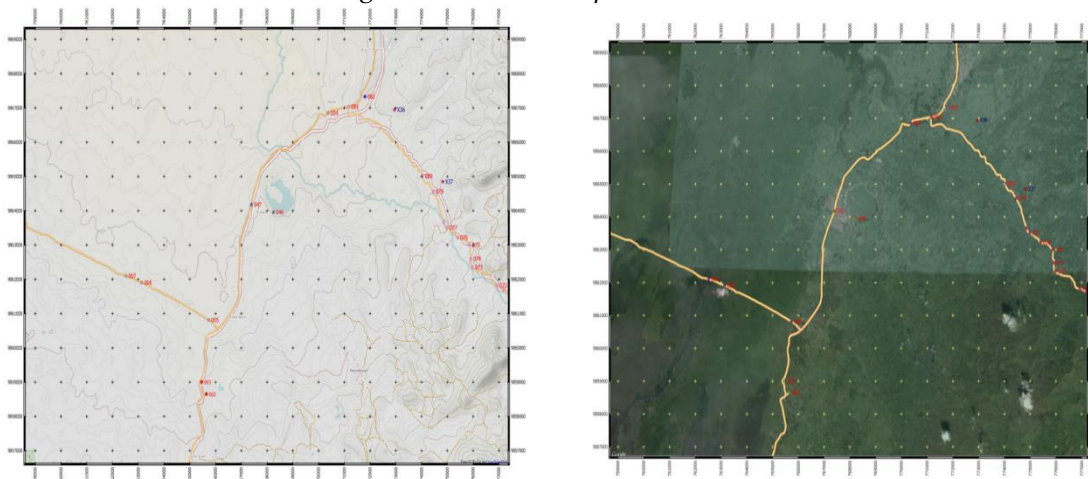


SRTM (Shuttle Radar Topographic Mission) and Landsat Satellite images of the region of interest at 1:50,000 have been provided to each geologist to fill his observations with coloured pencils.

3.  <u>Geologists activities in front of an outcrop</u>

A.  Observation from far firstly and from closer view



*Figure III. 10 a, b, c, d, e Field Observations (SOCO, 2014)*

B.  Field Macroscopic description ( human eyes)



C.  Field Microscopic observation ( Hand lens)
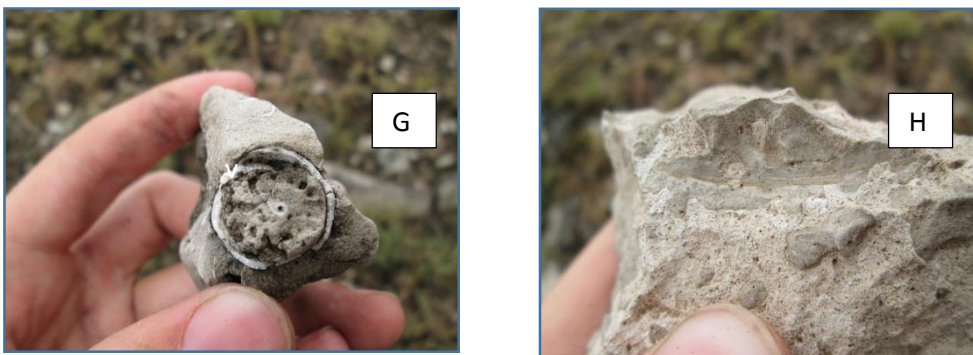


*Figure III.10 e, f, g, h: Field Observations (SOCO, 2014)*

## D. Spectral Gamma Ray recording and logging sheet filling
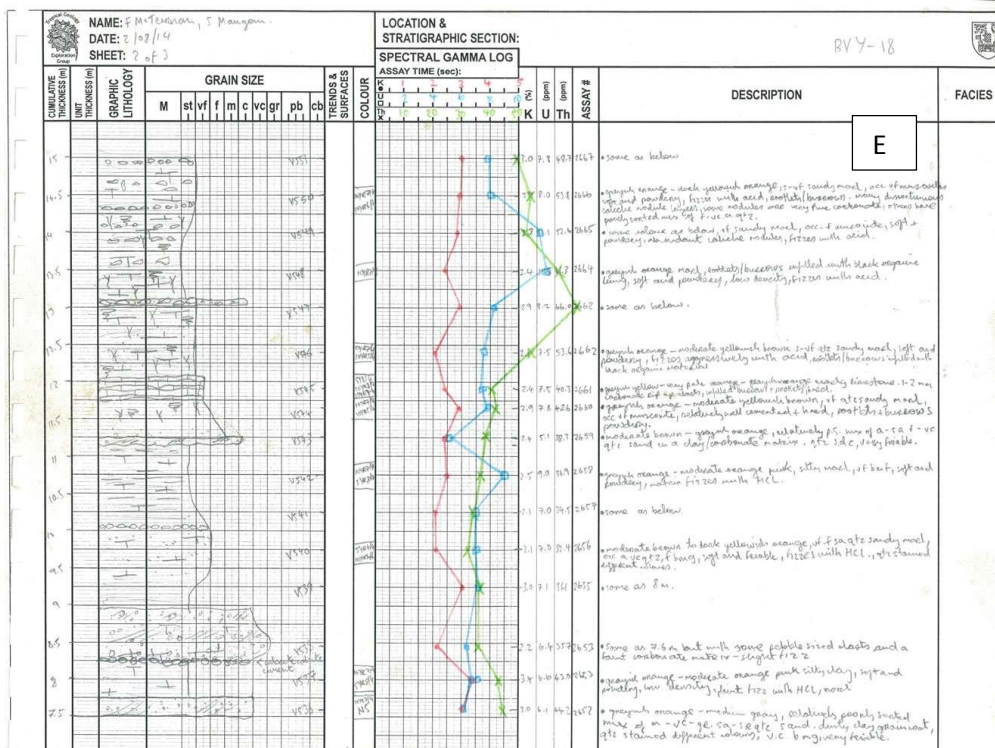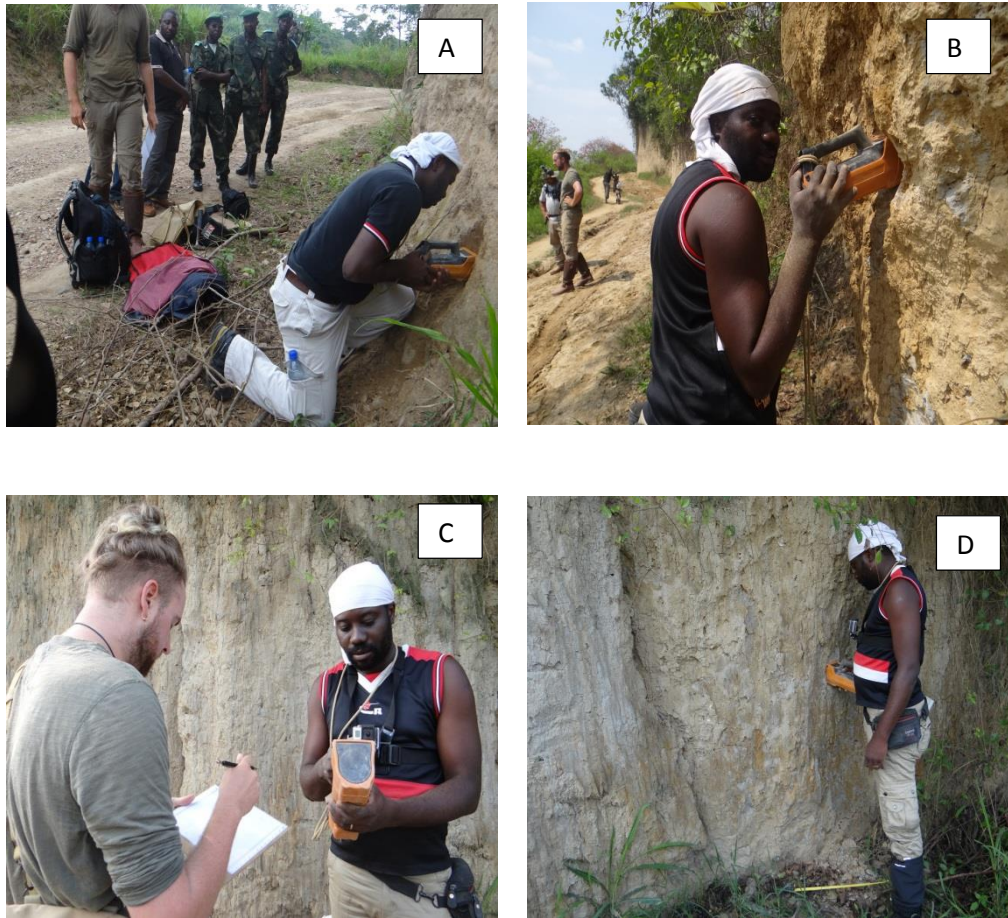


*Figure III.11 a, b, c, d, and e: Spectral Gamma Ray field recording and record sheet (Avalonia, 2014)*

E. Sample collection and packing



*Figure III.12 a, b : Samples collection (SOCO, 2014)*

III.2- TRAVERTINE PETROGRAPHY:

In order to achieve the objectives of this MSc. Research, the Travertine samples collected in the field should be prepared for laboratories analysis among them the Inducted Coupled Plasma Mass Spectrometry (ICP-MS) to detect Rare Earth Elements (REE) in any of each visible textures, structures and /or fabrics.

The Carbonates Petrography have been the perfect method to think about after theses series of field trips to get closer with these mysterious Travertine collected in the Eastern Africa Rift basins. Techniques for Examining Carbonate Rocks in Sawing and Polishing (slabs) have been used as well as the necessary basic procedure for limestones observation and description.

This method has been done entirely in the museum Building technician's lab and in the ICRAG facilities in the Trinity College, the University of Dublin.

The successive steps for the Travertine observation and description could be described as below:

- Cut a slab (3-5 cm square and a few mm thick) across or through any visible bedding, structure, texture and/or fabrics.
- Polish one side.
- Etch with weak acid.
- If required, use light mineral oil for fine observation.
- Study the slap under binocular scope with reflected light.

III.2.1- THIN SECTION PREPARATION

Samples have been cutted in the technician's lab using a small bench mounted cutter machine perfectly used for cutting small specimens, trimming, larger slabs, small slices, This tool have also been used to remove any kind of bulk in samples already mounted for thins section preparation.

The cutting discs size used for each Travertine sample varied between 120 mm to 250 mm according to the need of sample microscope observation. They were provisions of grinding wheel discs made available for replacing any broken cutting disc during operation, but this case never happened.

Thin Sections preparation process which mainly aimed to grind slightly thicker than 30 microns (for deeper colour contrast under plane light), was done following the basic principles of geological thin section preparation.

This very important process has been done according to the minimum standard requirements of carbonate study as below described (Allman, 1972):
- Cut or break the original specimen to produce a slice or chip.
- Grind one surface for the slice or chip on successively finer grades of abrasive to produce a flat, satin polished surface;
- Mount the chip, prepared surface downwards, on to a microscope glass slide;
- Grind the exposed surface of the chip so that it is parallel to the first face using, as before, successively finer grades of abrasive;
- When the chip is reduced to a thickness of 30 microns, as determined by observation through a microscope. Clean the section and cement a cover glass over it for protection;
- Clean again to remove surplus mounting medium and finally label.
- The section is then ready for study.

Each of this above stages is in fact made up several operations and every operation has associated dangers which if neglected may cause the destruction of the section.

Staining techniques for geological purposes is one of the methods based on selectivity of certain dyes. The term selectivity describes the ability of a dye or staining reagent to colour only a specific material, mineral or fossil, even in the presence of other similar materials. (Allman, 1972).

The selective property of this staining method on carbonates minerals is not only aiming to the simple differentiation of Calcite and Dolomite, but also the sophisticated methods devised by Friedman and later modified and extended by Warne, which allow the identification of some carbonates different types of  minerals. (Allman, 1972).

The staining of Travertine samples collected during series of field trips in the EARS basins has been done following the Rodgers method of Calcite discrimination on the surface of limestones blocks.

Many staining solutions, once made up, oxidise very quickly regardless of how many specimens have been processed. Provisions of solutions have been made available for the case of quick oxidisation during the process, however this case never happened during the staining process of this MSc research.

The staining of Travertine specimens of this MSc Research have been done according to the Friedman's method (1959) who devised the staining procedure suitable only for hand specimens, polished surfaces and chips of ce rocks which allow a very positive identification for Calcite, aragonite, dolomite, magnesite, high magnesium calcite, gypsum and anhydrite. (Allman, 1972)

According to Friedman (1959), the following satins should be made up as stock solution:
- Pre-stain etching bath.
- General solution Alizarin red S. + 30% sodium hydroxide.
- Alizarin red S. + 5% sodium hydroxide.
- Titan yellow (dolomite staining solution)
- Trypan blue (magnesite staining solution)
- Harris's haematoxylin (specific for calcite)
- Feigl's solution (specific for aragonite)

Only the following solutions have been made for the case of this present study:

1. <u>Solution A</u> : Pre-stain etching bath

10% Hydrochloric acid solution:

Add 100ml. HCl (36% fuming) to circa 500ml water and top up the solution with water to give a final volume of 1000ml.

2. <u>Solution B</u>: General solution Alizarin red S. + 30% sodium hydroxide

| Alizarin red S. | 1g |
|---|---|
| 0.2% hydrochloric acid (cold) | 1000 ml |
| Add 2ml. HCl (36% fuming) to circa | 500 ml water and top up the solution |

with water to give a final volume of 1000ml.

The steps and procedure below described have been followed (Allman, 1972):

1. Prepare the limestone sample by cutting and grinding flat one face;
2. Polish the surface using first 3F, then F600 and finally F800 grade Carborundum;
3. Ensure the surface is washed clean with soft brush and a Teepol solution and then dry it.
4. Immerse the specimen in the Alizarin red S. + 30% sodium hydroxide solution. (Do not allow the polished surface to contact with the bottom of the tank. This tank should have a close fitting lid to minimise evaporation. Before the next step, it is advisable to dip the specimen in distilled water once or twice although the pale green stain is very delicate at this stage.

5. Without washing and drying the specimen, immerse it in the ammonium hydroxide solution for about 30 seconds.

6. Wash the specimen and gently polish the surface with a soft cloth to remove any extra precipitate. The alizarin red S. Stain will be fixed and should not be damaged.

The colour formed on the calcite mineral varies from a pale (as in Figure III.13 below) to deep pink to Brown. This satin is very selective even in fine grained specimens. If calcite fossils are present in the specimen, this method will render them clearly visible more specifically if the reflected light is used.

The peel technique which can reveal a great deal of information or petrographic details not visible by the examination of the specimen itself, has been used as a thin section complementary method. All the 2014's Travertine samples have been peeled before their microscopic observations.

This old used technique consists in applying to a prepared surface on a specimen a thin coating or layer of suitable material in a solvent. The layer is allowed to harden and is then peeled from the specimen. So, the peel can have either a thin layer of the actual specimen which has been removed from the surface of the specimen adhering to the peel, or there will be impressed on one surface of the peel a very low relief pattern corresponding to the texture, structure of fabric of the specimen.

Very useful for the microscopic study of carbonaceous, calcareous, and siliceous fossils as coal balls and corals, this technique is specifically used to record the non-porous replicas structures.

Cellulose acetate sheets or films like Clarifoil or Kodatrace produce excellence peels of specimens which are non-porous and without holes in their surface and where it is possible to obtain only flat surface on the specimen.

The acetate sheet technique is very fast and cheap method to produce peels of very high quality with acetone as solvent. The others advantages of this peeling method are:

- Peels are excellent for high magnification work where crystals of a few microns need to be distinguished;
- Peels make good photographs;
- Peels can be used with transmitted light through any type of microscope ;
- No colour contrast;
- Few mineral identification
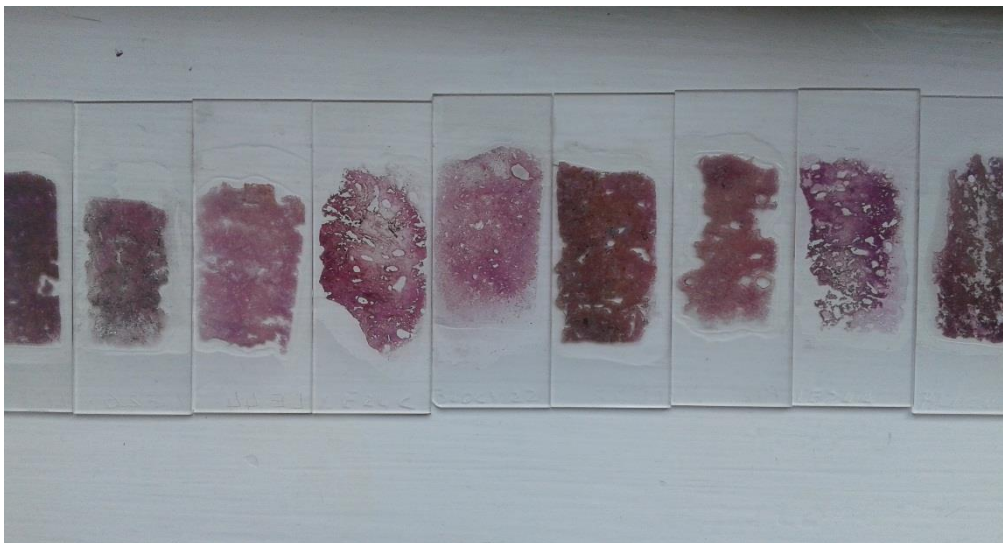


*Figure III.13 : Travertine thin sections (Sylvain ,TCD,2018)(Hill,*

III.2.2- <u>MICROSCOPY</u>

Microscopic observation is the most effective way of knowing the mineralogical, the structures, textures, fabrics and other constituents (like fossils) of the carbonate rocks.

For the Travertine study of the present MSc Research project , thin sections were prepared and studied under microscope, following the procedure of Folk (1959).

The volumetric analysis of different constituents had done with the help of manual counting technique, for the petrographical classification of Travertine limestone. The textural study had carried out for Dunham's classification (Dunham 1962).

The petrographic study from thin sections was prepared to identify and decipher the nature of different constituents, textures, structures and fabrics of the Travertine specimens exactly at the location where the samples have been drilled for ICP-MS analyses purposes.

Thin sections made from Travertine samples were observed with parallel and crossed Nicol prisms of the Nikon LV100 optical microscope offers 2.5, 10, 20, 50, and 100x magnification.  Integrated image capture software provides many options for processing as shown in the Figure III.14 below:



*Figure III.14:  Nikon LV 100 optical Microscope (CMA, 2018)*

## III.3- OXYGENE AND CARBONE STABLE ISOTOPES ANALYSIS:

In 2013, the Isotope ratio mass spectrometry (IRMS) was used by Sylvain and Jean to measure the isotopic ratios of carbon and oxygen. The IRMS equipment scheme illustrated in the Figure III.15 below, have been available in TCD to perform O and C stable isotope analysis as the ICP-MS complementary tool. Actually under repair works, this IRMS equipment was not available during the present MSc Research short time. So, only the first EARS field trips season Travertine samples have been run, and their results presented and discussed further down this thesis.
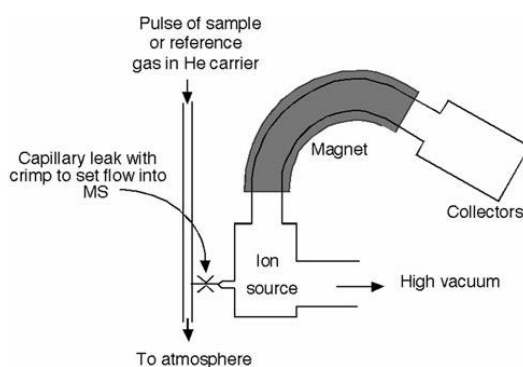


*Figure III.15: Typical diagram of an IRMS (lab notes sketch)*

## III.3.1- CARBONE STABLE ISOTOPE ANALYSIS:

Knowledge of the variations in the relative abundance of the stable (non-radioactive) isotopes of Carbon and Oxygen in any geologic material may furnish a powerful tool for the evaluation of the various geochemical and biochemical cycles through which this material has passed during very long time because of its geochemical and biochemical importance and also because of the relative ease of the laboratory technique required.(Craig, 1953)

$^{12}C$ and $^{13}C$ are the stable isotope ratio (noted $\delta^{13}C$) which were measured in the standard established Pee Dee Belemnite (PDB) based on a Cretaceous marine fossil, *Belemnitella Americana*, which was from the Pee Dee Formation in South Carolina. This material had an anomalously high $^{13}C{:}^{12}C$ ratio of 0.0112372 (Lynch-Stieglitz et al., 1995).

The variations in $^{13}C/^{12}C$ ratio $\delta^{13}C$ in limestones may be attributed to the following factors:
  (1) *variations in the calcium carbonate parts of organic debris incorporated in the rock, probably due in part to a vital effect of the organism,*
  (2) *variations in precipitated carbonate due to photosynthesis of marine plants,*
  (3) *possible equilibration with organically derived carbon dioxide, and*
  (4) *Degree of attainment of isotopic equilibrium during precipitation.*

The rate of precipitation of carbonate can affect the isotopic composition, and the oolitic character of these formations would indicate that both represent rapid precipitation. However, the fossiliferous character of the geologic formation appears to be a quite reasonable explanation of the isotopic difference.

The carbonates show a range of isotopic composition greater than that of any other group but the graphites, the range of δ being about 24 $^0/_{00}$,. However the marine limestones shows a range of only 5.7 $^0/_{00}$.  (Lynch-Stieglitz et al., 1995)

In the case of the present study:

- Magmatic carbon in a carbonate would be expected to have a $\delta^{13}C$ between -7 and -10 $^0/_{00}$ relative to PDB belemnite.

- Marine carbon in a carbonate would be expected to have a δ 13 C between -2 and +2 $^0/_{00}$ relative to PDB belemnite.

Therefore, higher $\delta^{13}C$ in marine fossils is indicative of an increase in the abundance of vegetation.(Craig, 1953).

The Carbone stable isotope ratio analysis $\delta^{13}C$ has been done on the EARS samples in 2013 using  TCD facilities and equipments by Sylvain K. Mangoni and Jean Dyer and the results are shown and discussed further in this thesis.

III.3.2- OXYGEN STABLE ISOTOPE ANALYSIS:

The presence of preserved physical characteristics of the past that stand in in a Travertine sample for direct meteorological measurements purposes are enabling scientists to reconstruct the climatic conditions over a longer fraction of the Earth's history. (Hays and Grossman, 1991)

Measurements of the ratio of oxygen-18 to oxygen-16 have been done by Sylvain K.M and Jean Dwyer in 2013 using TCD facilities to analyse some EARS Travertine samples and interpret their palaeoclimate changes. The calculated ratio of the masses of each Oxygen stable isotope present in the Travertine sample is then compared to a standard, which can yield information about the temperature at which the sample was formed. The microorganism most frequently referenced as standard is *foraminifera* from Standard Mean Ocean Water (SMOW).

A higher abundance of $^{18}O$ in calcite is indicative of colder water temperatures, since the lighter isotopes are all stored in the glacial ice and the lower abundance of $^{18}O$ in the calcite (Travertine samples) indicates the warmer temperatures.(Hays and Grossman, 1991)

The Figure III.16 below shows the long-term evolution of oxygen isotope ratios during the Phanerozoic eon as measured in fossils, reported by Veizer et al. (2000). Such ratios reflect both the local temperature at the site of deposition and global climate changes associated with the extent of permanent continental glaciation. As such, relative changes in oxygen isotope ratios can be interpreted as rough changes in climate. Quantitative conversion between these data and direct temperature changes is a complicated process subject to many systematic uncertainties, however it is estimated that each 1 part per thousand change in $\delta^{18}O$ represents roughly a 1.5-2 °C change in tropical sea surface temperatures (Veizer et al., 2000).
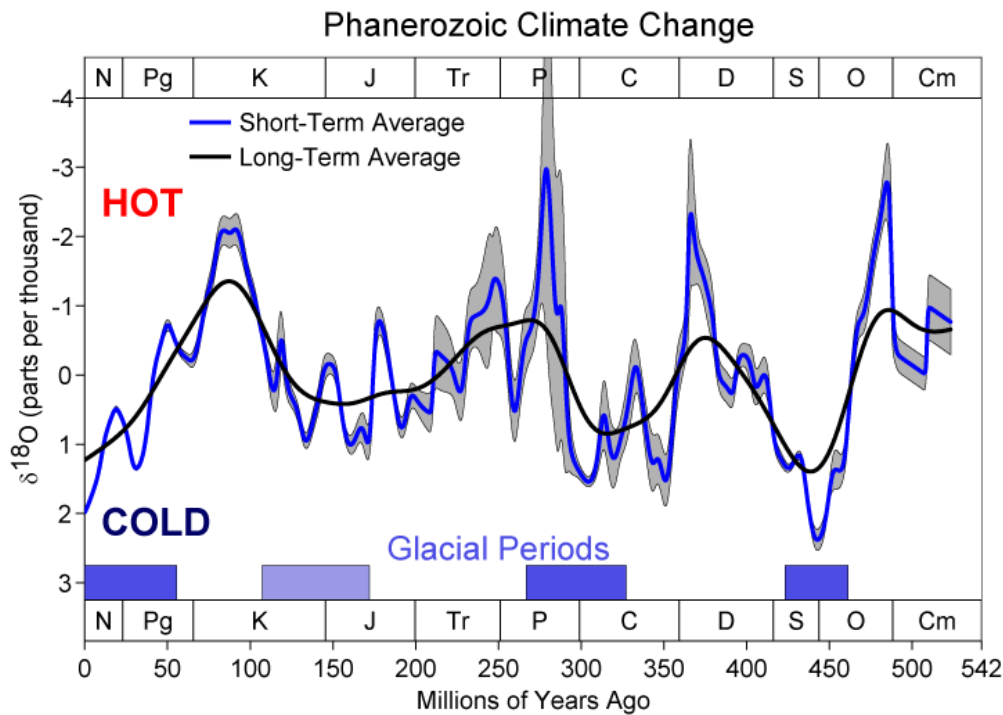
*Figure III.16:  Phanerozoic Climate change graph. (Veizer et al., 2000)*

III.4- STRONTIUM ISOTOPES RATIO ANALYSIS

Strontium isotope ratio of ancient sea waters may be reconstructed from well-preserved authigenic carbonate minerals and used for dating marine sediments.(Wierzbowski, 2013)

Because of a change in the Strontium isotope ratio between sea- and freshwaters it can also employed for the determination of the paleosalinities or the reconstruction of diagenetic processes of marine limestones.

Measurements of the $^{87}Sr/^{86}Sr$ have been done in 2013 by Sylvain and Jean Dwyer using TCD facilities to analyse and interpret some EARS Travertine samples palaeo origins.

The modern sea water $^{87}Sr/^{86}Sr$ ratio is 0.709175. The sea water Strontium isotope composition has changed through the geologic history of the Earth owing to changing inputs of Strontium.

Three major input sources influence the Strontium isotope composition of the sea water (Wierzbowski, 2013) :

- Strontium of low $^{87}Sr/^{86}Sr$ ratio  around 0.703 is derived from hydrothermal circulation at mid-ocean rides;

- Strontium of intermediate $87Sr/^{86}Sr$ ratio around 0.708 originates from submarine dissolution and recrystallization of carbonates sediments;

- Strontium of high $^{87}Sr/^{86}Sr$ ratio  around 0.711 is derived from continental weathering.

The temporal sea water Strontium isotope curve here below in Figure III.17 is characterized by several maxima and minima which shows the change in Strontium inputs. This Figure suggests that two deepest minima occurred in the Late Permian and at the Middle-Late Jurassic transition and an almost continuous increase of the sea water $^{87}Sr/^{86}Sr$ ratio has occurred since the Late cretaceous.
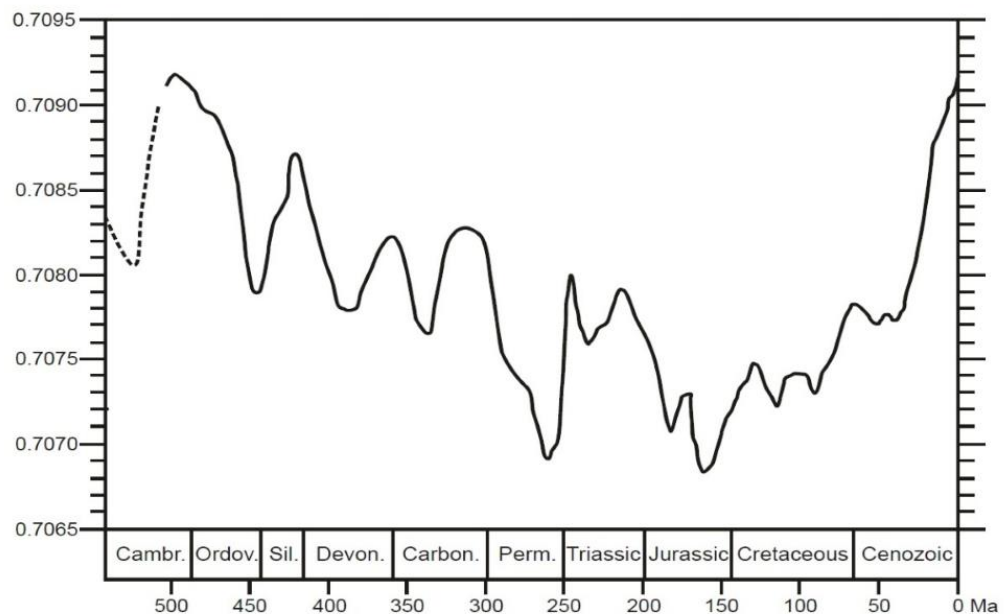


*Figure III.17 : Variation of 87Sr/86Sr ratio of the Phanerozoic sea waters.(Wierzbowski, 2013)*

III.5- GAS CHROMATOGRAPHY MASS SPECTROMETRY (GC-MS)

GC–MS has been carried out in 2008 at the LGC laboratory in London (www.lgcstandards.com) by means of an HP 5890-II series GC connected to a mass selective detector (MSD) 5970 (Hewlett-Packard, Palo Alto, CA). The system control and the data acquisition have been executed by an HP 59970 ChemStation (Hewlett-Packard). The GC-MS was operated in selected ion monitoring (SIM) mode, which allowed for the study of the ions that were selective for the previously mentioned compounds with respect to the identification goals. A quartz capillary column (25-m × 0.32-mm × 0.52-μm film Ultra-2) was used. The GC operation conditions were as follow: carrier gas, helium (1.4 mL/min); and injector and detector temperature, 300°C. The temperature program was 0 min at 90°C, then ramped to 270°C at 6°C/min, and held for 30 min at 270°C. The injected quantity was 1 μL of 2% volume solution in tetra chloromethane of the Oil slick sample.(Pavlova and Papazova, 2003)

The GC-MS method which may be able to separate the hydrocarbons molecule types according to their weight, therefore size, and their petrochemical affinity to the column used, has been used for performing qualitative and quantitative analysis on two (2)

Lyemubuza oolithes samples found in outcrop with evident black staining resembling to crude oil in them.

Broad range of petrochemicals, fuels and hydrocarbon mixtures, including gasoline, kerosene, naphthenic acids, diesel fuel various oil types, transformer oil, biodiesel, wax and broad range of geochemical samples (including waxes up to $C_{74}H_{150}$) can be analysed by this GC- GCMS method of analysis that measures the peaks in relation to one another.

In this method, the tallest peak is assigned 100% of the value, and the other peaks being assigned proportionate values.

The unique aim of the GC-GCMS analysis in this present MSc Research, is to determine the chemical composition and properties of these evident black staining.

In other terms, this method will suggest the natural (live oil) origin or artificial (Oil distilled products) of these black staining compound discovered in outcrop in Lyemubuza quarry in Uganda.

III-6. INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS) ANALYSIS

Rare earth elements (REE) in geological materials provide important information about the formation and the geochemical processes that rocks undergo. Therefore, there is a constant necessity for accurate data and reliable and fast analytical methods. However, the low concentrations of these elements typically found in rocks require quantification by sufficiently sensitive techniques, such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS).(Mastandrea et al., 2010)

In order to trace the geochemical origin of Travertine limestones samples collected during the long field season (from 2007 to 2010, in 2014 and 2017) in the Albertine Graben of the East African Rift, the main and unique method we used was the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) which behave in the same time as a method, a technique and as well as also an instrument.
The present MSc. Research project is trying to use the previously demonstrated power of ICP-MS as a tool in petrogenetic studies, mineral tracing, and geologic story by showing that ICP-MS is able to perform a quantitative trace metal analysis with the lowest detection limits (part per trillion ‰) for the greatest level of productivity by measuring the isotopic composition of any sample except these containing the Mendeleev periodic table elements which don't have isotopes and also H, C, N, O, F, He, and Ne. The Figure III.18 below shows the range of chemical elements detected only by ICP-MS, ICP-OES only and both ICP methods.

*Figure III.18: Periodic table of the elements highlighting those obtained by ICP- OES and MS analysis. (McCabe, 2015)*

The main reasons ICP-MS technique has been chosen for the geochemical tracing origin of Travertine samples from the Albertine Graben in the East African Rift is because (Wolf, 2005):

- ICP-MS has many chemical elements detection advantages over other elemental analysis techniques such as atomic absorption, optical emission spectrometry (ICP-OES)and ICP Atomic Emission Spectroscopy (ICP-AES)
- ICP-MS is so far the mostly appropriate pre concentration methods used for his low detection limits on Rare Earth Elements (REEs) in the limestones or any Carbonate rock samples.
- ICP-MS seems to be likely the most appropriate or the only possible method so far, which can provide the analysis of all REEs with high sensitivity and acceptable precision with the lowest limit of detection.
- ICP-MS superior detection capabilities, particularly for the rare-earth elements (REE).

This method has been used three times for this MSc research purposes:
- In 2013 for the Travertine samples collected in EARS from 2007 to 2010;
- In 2016 on the same previous Travertine samples to check the result reproducing ability of the ICP-MS Method;
- In 2018 on the 2014 Travertine samples collected in Block V.

During this initial experiment in 2013, the ICP-MS analysis has been done according to the following steps:

- 1st step: Sample initial preparation from solid rock stage to powder stage;
- 2nd step: Sample special preparation from powder to solution stage before ICP-MS analysis;
- 3rd step: ICP-MS analysis on samples in solution;
- 4rd step: Results interpretation.

III.6.1- SAMPLE INITIAL PREPARATION FROM SOLID TO POWDER STAGE

During the field sample collection, only fresh and non-weathered samples have been chosen. These samples have been collected from the most massive portion of the outcrop after chipping out the top weathered layers. (At least) 0.5-1 kg of the rock sample was collected for the ICP-MS analysis purpose from each location. To avoid any cross contamination, the samples were reduced to centimetre size (2-5 cm) on the outcrop itself by sledge hammer and packed in cloth bags.

For the best result to obtain through geochemistry, the representative Travertine samples from each location have been checked through hand specimen and thin section observation.

The initial sample preparation for ICP-MS analysis consisted in breaking Travertine rock samples collected in the field in small pieces then cutted in slabs representing in each of them, the maximum amount of their characterized fabrics, textures and/or structures.

Each Slab of Travertine samples has been observed in the macroscopic size and any of their eyes level visible texture or structure has been correctly outlined and described. Any confusing texture or structure in the slab suggested a deeper observation in the microscopic level to well outline them for drilling purposes.

The Figure III.19 below is showing an example of microscopic observation and description in the lab notebook of the confusing structure and texture in the Travertine slab.



*Figure III.19: Microscopic observation and texture/structure description, Drilling of Travertine rock samples by Sylvain K.M. & J. Dwyer in 2013*

Each piece of Travertine slab has been cutted according to their visible textures /structures or fabrics in slices of 0.5 cm thick each then, washed with deionized water for cleaning of any extra material which may have adhered to the samples and finally dried in the ambient air. The Figure III.20 below is showing the Travertine 0.5 cm thick slices cutted as they've been washed and dried in 2013.



*Figure III.20: Travertine Slices sample preparation, cutted, washed and dried by Sylvain K. M and Jean Dwyer in 2013*

After their washing and drying, all the cutted slabs have been drilled in their two sides according to any visible textures, structures or fabrics.

The drilling process have been done accordingly to the thickness size of the visible textures, structures or fabrics outlined in the sample which has also determined the size of the drill bit used for the drilling.

The small drill bit (Bosh Silver concrete drill bit 5x35 mm) was used to drill through the small thickness size of textures, structures and/or fabrics seen in the sample while the bigger one (Bosh Silver concrete drill bit 25x85 mm) was used for greater thickness sizes. The Figures III.21, III.22 and III.23 below show respectively the drilling process through visible textures, structures and/or fabrics present in the sample, the drilling tool and all different sizes of the drill bit.
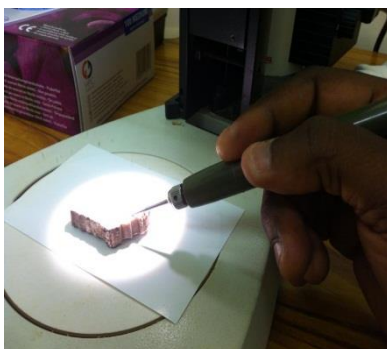


*Figure III.21: Drilling process trough visible textures, structures and/or fabrics present in the sample.*



*Figure III.22: Drilling tool used in 2013*
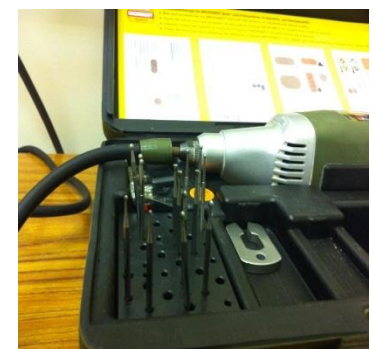


*Figure III.23: Different sizes of the drill bits used for different thickness size of textures, structures and/or fabrics present in the sample.*

Each visible textures, structures and /or fabrics found in each rock sample has been drilled through and their respective residual powders shown in Figure III.24 below have been described in the lab notebook and stored in small tubes illustrated in Figure III.25 below.



*Figure III.24: Example of the drilling residual powder of a visible textures, structures and/or fabrics present in the sample.*

*Figure III.25: Small tubes for textures, structures and/or fabrics powder storage*

8 to 13 milligrams of the residual powders (grain size around between 45 μm and 53 μm) from drilled Travertine textures, structures and or fabrics have been diluted and put in $HNO_3$ solution before they become ready for ICP-MS analysis.

The details of the next following steps: sample dilution, solution, ICP-analysis and results interpretation are available in both Jean Dwyer and Mike Babechuk lab notebook and ICP-MS analysis report TCD, 2013.

III.6.2- SAMPLE SPECIAL PREPARATION FROM POWDER TO SOLUTION STAGE

Before running the ICP-MS, routine lab procedures for this trace element analysis were performed in a clean lab environment. Nitric acid used for cleaning and digestion was prepared from in-house triply distilled stock diluted with Milli-Q (18Ω) water. Aliquots of sample powder were weighed (1 ± 0.01 mg) and transferred into acid-leached, polypropylene micro-centrifuge tubes. The sample powders were digested by adding 2 mL of 5% $HNO_3$.

For analysis, an aliquot of the 5% $HNO_3$ was diluted gravimetrically to a 2% $HNO_3$ solution containing an internal standard mixture ($^6$Li, Rh, Re, Bi, $^{235}$U). Solutions were analysed with an iCAP-Q ICP-MS equipment which was tuned for optimal sensitivity across the full analyte range (Li to U). This experiment was done at Unit 7 in the Expertise lab center of Trinity College Dublin.

Samples were injected into the nebuliser from a 1.5 mL Teflon loop at a stable rate of 250μ Lmin-1 over an interval of 6 minutes using an ESI microFAST system.

Experiment design followed a method adapted from (Eggins et al., 1997) where batches of 20-25 unknowns were bracketed with repeated measurement of a monitor sample for external drift correction and preceded by blanks and calibration and quality control standards.

Calibration of sample unknowns was performed using multiple digestions of USGS standard W-2 diluted between 20,000 and 80,000 with the preferred values reported elsewhere (Babechuk et al., 2010).

This technique, appropriate for minerals easily dissolved in diluted $HNO_3$ (e.g., carbonate, apatite) is advantageous in permitting detection of very low-level concentrations with negligible blank contribution by avoiding the use of large quantities of concentrated acids.

This is evident by the total procedural rare earth element blanks: Y (0.2 ppt), La (2 ppt), Ce (4 ppt), Pr (0.4 ppt), Nd (1.5 ppt), Sm (0.2 ppt), Eu to Lu (<0.1 ppt). Error in the accuracy of the final concentration is generated primarily by the available precision of the balances used for weighing the ultra-low masses of sample powder, yet robust normalised REE+Y patterns and element ratios were generated from samples even at the lowest signal intensity.

### III.6.2.1- LAB EQUIPMENT CLEANING

The cleaning of the lab equipments is an obligatory process before the beginning in of any type of analysis. Depending on the chemicals that are on the equipment and how the equipment is going to be used, cleaning protocols differ drastically. A good rule of thumb followed was to overclean instead of underclean, but always we did ensure that any cleaning chemicals would not interfere with future experiments using the equipment.

This cleaning process has been done twice during each of our ICP-MS analysis. Firstly, when the lab is being set up for the experiment and during the last task to do before to conclude the experiment.

It's never been done in between every batch of Travertine samples as the contamination risk has been reduced the more possible and more precautions has been taken during each Travertine sample manipulation.

The lab internal environment, the tools, the equipments and all others lab items involved in the Travertine samples ICP-MS experiment have been carefully and totally cleaned in acid by Michael Babechuk in 2013 and Cora in 2016 and 2018, enough to avoid any kind of contamination before, during and after the samples preparation for and during each of our ICP-MS analysis.

The first task done before this present MSc Research ICP-MS experiment was only the cleaning of the lab work station and all items involved in our analysis, not the whole lab. This washing work took 14 days approx. and consisted in successive and repeated operations aiming to wash and rinse 3 times with Milli-Q ultra-pure water, then dry all the lab items to be used in the fume hood and wrap them with a transparent plastic sheet (parafilm paper) in order to avoid any dust to come down in and contaminate them.

All the items used for the samples preparation and ICP-MS analysis have been taken out from the Unit 7 Expertise Center lab warehouse, clearly identified by labels as well inventoried in a register book and get ready for their cleaning process before their use.

The required items for the samples preparation and ICP-MS analysis which have been ordered and got delivered from the TCD usual provider of geochemical analysis items, were cleaned again three times, even if they've never been used and they're new delivery from the geochemical items provider.

The cleaning steps followed were:

- Clean the involved items (glass items like beachers, tubes...) thoroughly with soap and water for basic cleaning. We may needed to use sometimes a wire brush to remove some residue.
- Rinse with purified Milli-Q ultra-pure water to ensure that all soap residue is removed.
- Rinse in the case, the lab Polypropylene items, with boiled purified water to remove any evident caked-on material like solidified agar or other gelatine-like products.
- Rinse in the case, with acetone to remove traces of organic materials including soap residue.
- Rinse in the case, with ethanol to sterilize any lab equipment that must have all bacteria and other microorganisms removed before use.
- Dry in the fume hood the necessary time to get the lab equipment completely dried and ready for use.
- Wrap the items grouped in a parafilm paper and store them for the next use.

All the lab items used for samples preparation and ICP-MS analysis were in Polypropylene which is the best plastic material used so far because it produces the lowest amount of blanks and the native properties of polypropylene make the compound strong and resistant against many chemical solvents, acids and bases.
Here down are some others advantages of the Polypropylene which made us think of it a suitable choice for our ICP-MS analysis:
1. Polypropylene is readily available and relatively inexpensive.
2. Polypropylene has high flexural strength due to its semi-crystalline nature.
3. Polypropylene has a relatively slippery surface.
4. Polypropylene is very resistant to absorbing moisture.
5. Polypropylene has good chemical resistance over a wide range of bases and acids.
6. Polypropylene possesses good fatigue resistance.
7. Polypropylene has good impact strength.
8. Polypropylene is a good electrical insulator.

For each of batch containing 20 Travertine samples (plus standards and blanks included) to be prepared and analysed, the lab items were:

- +/- 50 test tubes (13 ml) with their cap seals (lid);
- +/- 150 microtubes (2ml) with incorporated lids;
- +/- 250 pipettes (up to 1 ml)

III.6.2.2 – ACID DIGESTION

A- Weighing the stock tubes:

Before their weighing, all the test tubes (13ml) have been firstly labelled. A new ID (lab ID) was necessary to make the difference between the field ID and the lab ID of the samples analysed.

The label SMK followed by 3 digits (SMK=Sylvain Mangoni Kezir) was chosen. The first batch of 20 samples have been labelled from SMK 001 to SMK 020.

The blank procedural which was used has been labelled as SMK blank 1 and the limestone standard prepared has been labelled as SMK LTD 1.

B- Weighing the sample powder :

The samples powders were stored in their initial microtubes from the drilling operation of the field samples slices cutted according to their original textures and fabrics. Before to weight them, they have been transferred with many cares from their microtubes (which were their drilling storage during the previous operation on samples) to their test tubes (which will be their lab storage for the next operations on samples).

The electronic weight scale illustrated in the Figure III.26 a&b here below, was used and set up to minimise the error to +/- 0.01.
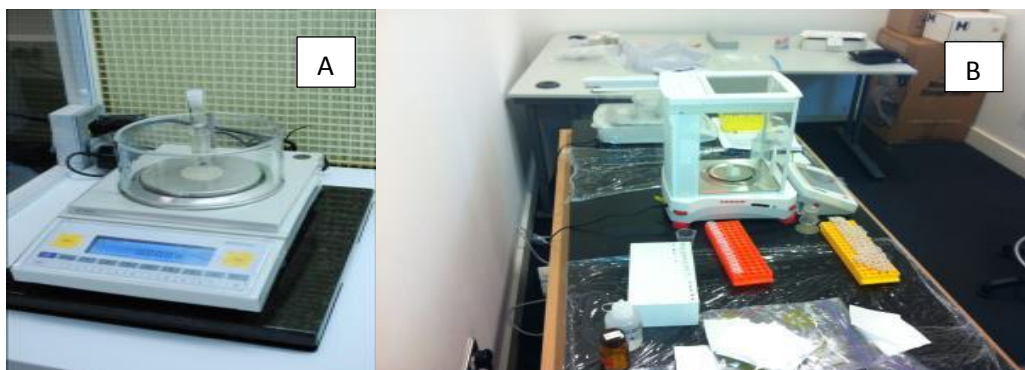


*Figure III.26: Electronic scale used to weight the Travertine samples powder analysed by ICP-MS.*

0.6 to 0.9 mg of sample powder have required for the ICP-MS analysis but the better was to have more available sample than to lack. If any powder were spilt away during the transfer operation, then the action to take was to clean properly the lab environment with a tissue and purified Milli-Q water with a piece of lab absorbent paper then change the glove before processing next.

We note that two scales have been used to weight the required amount of sample powder.

The steps here below have been carefully followed to weight the Travertine samples powder drilled from each fabric, textures and /or structures (Figure III.27 below):

- Place an empty stock tube in the first scale and note its initial weight;
- Tare the first scale;
- By using tweezers cleaned in ethanol Fold in half and Put a 5cm x5cm coated paper in the second scale; then note the weight
- Tare the second scale;
- Open the drilled sample microtube lid and carefully tipping its bottom and reverse around 0.6 mg of the sample powder onto the coated paper;
- Tap gently the bottom of the microtube and stop when the sufficed quantity of powder value is reached in the scale screen;
- Note the weight of the coated paper + sample powder;
- Roll up the coated paper and carefully tipping the sufficed weighted powder into new stock tube; close the lid and note the weight of Stock tube+sample powder.
- Place the stock tubes containing around 0.6 to 0.9 mg of sample powder in a rack Tupperware box for acid digestion which is the next step.



*Figure III.27: weighting of the Travertine samples powder analysed by ICP-MS*
*by Sylvain KM. and jean D., 2013*

C- <u>Acid digestion</u>:

The next step for the ICP-MS sample preparation is the "Acid digestion". This step is best to be done close to the time of running the samples in the ICP-MS machine. So, less risk of contamination leech out of the plastic tubes.

As per rule, acid digestion procedures are employed for the determination of chemical elements in solids subsequent to sampling and mechanical samples preparation in order to completely transfer the analytes into solutions so that can be introduced into the determination step of ICP-MS in a "liquid form".

The goal of every digestion process is therefore the complete solution of the analytes (samples powder) and the complete decomposition of the solids (matrix) while carefully avoiding loss or contamination of the analyte.

<u>Goals</u>:

• Make the samples powder (analytes) completely in acid solution for digest purposes;

- Get the complete decomposition of the matrix;
- Avoiding as possible analytes losses and/or contamination;
- Reduction of handling and process times.

In this context, wet chemical digestion can/will utilize various minerals acids (eg. HCl, $HNO_3$, HF, $H_2SO_4$, etc…)

During the samples preparation of this present ICP-MS experimentation, the $HNO_3$ acid was utilized.

Regarding the sensitivity of the actual stage of the process, firm instructions have been given by the Lab responsible who showed herself the right way to do things with the blanks, the standard and then samples SMK 001, SMK002, SMK003. Then the lab responsible supervises me doing the same for the samples SMK 004, SMK 005, SMK 006 before she felt confident of my work technique and let me go ahead with the all remaining samples.


D- <u>Adding 0.1 ml of $HNO_3$ @ 10%:</u>

All the $HNO_3$ acid couldn't be put in the samples tubes in one time for digestion because of their strong potential feezing reaction with Carbonates samples. If all the 10% $HNO_3$ stronger acid was initially put in Carbonates samples, the feezing reaction would be completely out of control.
The best way to operate was then suggested to add the acid gradually in different times with short break of time between successive acid adding.

Firstly, the sample digestion carefully started by the 5% less concentrated acid $HNO_3$ to allow that all the possible reaction to be done with safety then, the stronger $HNO_3$ 10 % acid concentration was used to complete the sample digestion with safer carbonates predictable reaction.

Leaving all the stock tubes overnight with lid loose allowed to any possible feezing HNO3 acid reaction to be slowly done. The next morning, all the stock tubes were found without any feezing.

After the passage of all the samples test tubes in the fume hood overnight, they have been totally degased and absolutely out of feezing reactions. 5% $HNO_3$ reacts with $CaCO_3$ release $CO_2$ with slow feezing reaction and deposit of residue.

The majority of Travertine samples have been found with "No obvious residue" but some of them have been found with either small or large amount of residue from impurities from surrounding rocks. The colour of these residues varies from dark brown-light brown- light grey-dark grey.

Due to the time restrictions, these residues weren't run for X-Rays Diffraction (XRD) even if a full training on radiological protection and some preliminary XRD theory and practical exercises have been done under the supervision of Dr. Robbie Goodhue.

### III.6.2.3 - <u>FINAL DILUTION</u>

Due to the small diameters of the orifices in the sampler and skimmer cones of the instrument, ICP-MS may have some limitations regarding the amount of total dissolved solids present in the solution samples.

Generally, it is recommended that solution samples have no more than 0.2% total dissolved solids (TDS) for best instrument performance and stability.

If samples with very high TDS levels were run, the orifices in the cones would eventually become blocked, causing decreased sensitivity and detection capability and requiring the system to be shut down for maintenance.

This is why many sample types, including digested soil and rock samples have been very well diluted before running on the ICP-MS.

The Travertine limestones samples have strictly respected all the technical requirements before to be analysed in the ICP-MS. Firstly, they have been diluted once again from the digested solution to a new solution with the right concentration for more trustable results obtained by ICP-MS.

### III.6.3- <u>ICP-MS ANALYSIS ON SAMPLES IN SOLUTION</u>

The technique described by Ruth E. Wolf recommend that the sample to be analysed is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebulizer or using a laser to directly convert solid samples into an aerosol (colloid of fine solid particles or liquid droplets, in air or another gas. Eg: fog, forest exudates and geyser steam which are natural or haze, dust, particulate air pollutants and smoke which are artificial). (Wolf, 2005)

Once the Travertine samples in aerosol form have been introduced into the ICP torch, they are completely desolvated and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma.

Once all the elements in the sample are converted into ions, they are then brought into the mass spectrometer via the interface cones.
The interface region in the ICP-MS transmits the ions traveling in the argon sample stream at atmospheric pressure (1-2 torr) into the low pressure region of the mass spectrometer ($<1 \times 10^{-5}$ torr). (Note that the 1 torr is an atmospheric unit which equals 0.00131579 atm.)
 This is done through the intermediate vacuum region created by the two interface cones, the sampler and the skimmer. The sampler and skimmer cones are metal disks with a small hole (~1mm diameter) in the center.

The purpose of these cones is to sample the center portion of the ion beam coming from the ICP torch. A shadow stop or similar device blocks the photons coming from the ICP torch, which is also an intense light source.

The ions coming from the ICP source are then focused by the electrostatic lenses in the system. Remember, the ions coming from the system are always positively charged, so the electrostatic lens, which also has a positive charge, serves to collimate the ion beam and focus it into the entrance aperture or slit of the mass spectrometer.

The ICP-MS equipment used on this MSc research Travertine samples was a Quadrupole Model ICAP-Q ICP-MS manufactured by Thermoscientific combined with a sample holder Model MVX 7200 manufactured by Teledynicetac. The Figure III.28 and III.29 illustrate the ICP-MS quadrupole geometry and equipment used.
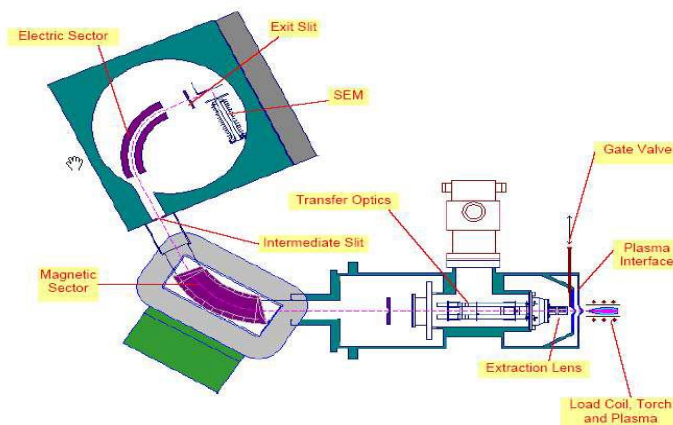


*Figure III.28: Geometry the ICP-MS quadrupole (Wolf, 2005) (Courtesy of Thermo Finnegan, San Jose, CA.)*



*Figure III.29: Quadrupole Model ICAP-Q ICP-MS, (TCD, unit 7)*

In any analytical chemistry process, the Instrumental Detection Limit (IDL) which is also called the lowest limit of detection (LOD), is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated confidence limit. The detection limit is estimated from the mean of the blank, the standard deviation of the blank and some confidence factor.

Another consideration that affects the detection limit is the accuracy of the model used to predict concentration from the raw analytical signal. (Wolf, 2005) .

For the case of this present study, IDL of each element to be detected have been calculated as 3 times the standard deviation of a blank measurement and represent the best possible detection capability of the instrument.

The Figure III.30 below, used by Ruth E. Wolf with the courtesy of PerkinElmer, Inc. shows the approximate detection capabilities of the ELAN 6000/6100 quadrupole ICP-MS which expresses the elements traditionally determined by ICP-MS and their approximate Instrumental Detection Limit (IDL).
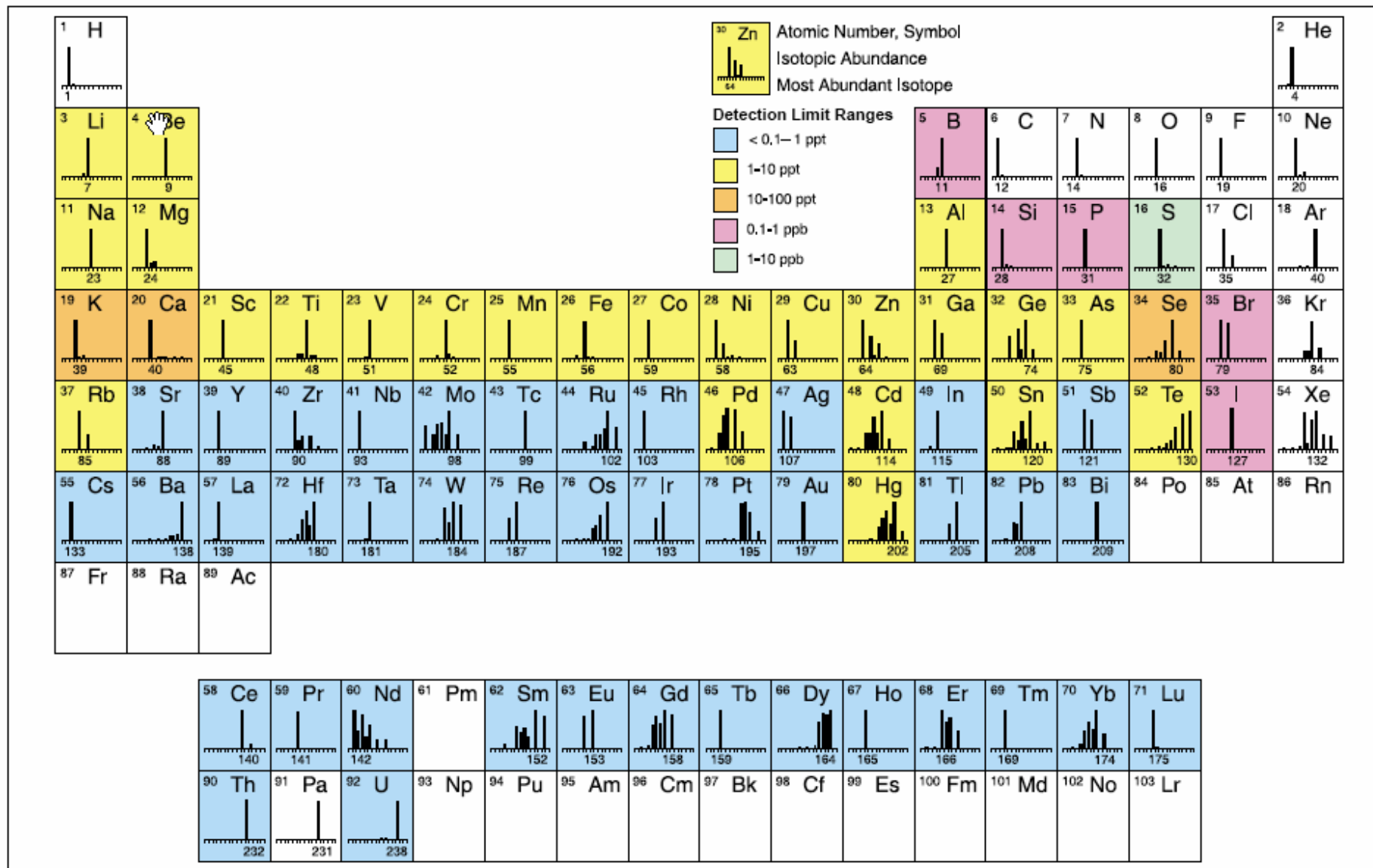
*Figure III.30 :  Approximate detection capabilities of the ELAN 6000/6100 quadrupole ICP-MS. (Wolf, 2005)(Courtesy of PerkinElmer, Inc.)*

Due to the fact that the ICP-MS analysis in 2013 didn't detected the Europium element in the Travertine samples from 2007 to 2010 field trips, the ICP-MS method needed to be fully checked and confirmed trustable by its ability to reproduce at anytime and anywhere else the same results on the same samples whoever would be the lab operator. Before to run the ICP-MS analysis of Travertine collected in 2014 and 2017 in the Graben Albertine of the Eastern African Graben, it was necessary to reproduce the same experiment on the main end member's samples in order to fully trust this method used the first time on our Travertine samples in 2013.

From July to September 2016, ICP-MS lab analysis were done on the same Travertine samples collected during the 2007-2010 field trips in the Albertine Graben which were already analysed at the TCD Enterprise Centre Unit 7 (in 2013 by Jean Dwyer and Mike Babechuk). This aimed to compare the obtained results in both 2013 and 2016 experiments and confirm or not the confidence with the ICP-MS method by its ability to reproduce the same results on the same samples whoever (Cora McKenna and Sylvain M.K in 2016-2018) would be the lab operator.

The Travertine samples proposed to double check the ICP-MS experiment in 2016 have been collected during 2007 to 2010 field's works in ten (10) palaeo-spring sites in the Albertine Graben, East African Rift system where no previous literatures have mentioned their presence so far. However, the ICP-MS experiment results obtained in 2013 revealed the both end members Carbonatites lavas (hot origin) signature and marine limestone (cold origin).

The Twenty (20) Travertine samples presented in the table 1 below were drilled exactly from the same drilling sites drilled in 2013 and run in 2016.
All these 20 samples re-drilled ( with a powder weight of around 8 to 10 mg each) for the second time in 2016 have been labelled with the same label used in 2013 added with slash two (/2) new label to make the difference and to show that they have been drilled for the second time.

| Carbonatites signature in 2013 | | Marine limestones signature in 2013 | |
|---|---|---|---|
| 1 | V2b/2 | 1 | P12b/2 |
| 2 | V20a/2 | 2 | LE24a/2 |
| 3 | V20b/2 | 3 | LE24b/2 |
| 4 | V22a/2 | 4 | LE26a/2 |
| 5 | LE44a/2 | 5 | LE26b/2 |
| 6 | LE44b/2 | 6 | LE28a/2 |
| 7 | LE41a/2 | 7 | LE28d/2 |
| 8 | LE41b/2 | 8 | V19a/2 |
| | | 9 | PCK a/1 |
| | | 10 | PCK b/1 |
| | | 11 | PCK c/1 |
| | | 12 | PCK d/1 |

*Table 1:  the 20 End members Samples from the 2013 experiment run again in 2016*

The Procokin PCK limestone sample has been collected in a quarry in the western side of DRCongo were literature universally recognized the presence of stromatolites fossils which suggest a fresh water depositional environment or origin. It represents actually the closest limestone outcrop found in DRC side.

The ICP-MS analysis of the four (4) PCK limestone samples during 2016 experiment aims to confirm by ICP-MS method and instrument the fresh waters origin of these stromatolites neighbouring samples which would later be used as matching correlation tool or comparator for / with any other previously known fresh water limestone REE signature or isotopic fingerprint sample to increase again our confidence in the ICP-MS methods ability to trace back the origin of carbonates

The sample forms and photos in Appendix I, are describing the details of the drilling operation highlighting the sample texture/fabric description, the weight of the empty tube, the weight of the tube with sample, the drill bit size, the powder colour after drilling, and remarks during the Travertine slabs drilling.

III.6.4- <u>ICP-MS RESULTS INTERPRETATION</u>

Considering the work done by Kamber in 2014, The REE + Y, particularly in combination with some of radiogenic isotopes (e.g. Pb and Sr) , are useful to discriminate between stromatolites that formed in lacustrine, restricted marine and open marine depositional settings, and in exceptional cases it is also possible to infer relative water depth or proximity to hydrothermal fluid sources in a sequence of microbial carbonates (Kamber et al., 2014).

However, in order to eliminate the Oddo-Harkins effect which is the presence of obsolete concentrations values in datas of some odd-even REE naturally occurring differently in cosmos, a normalization process of restructuring the Excel database REE results in accordance with a standard has been done prior to averaging in order to reduce data redundancy and improve data integrity.

Following exactly the Kamber method for carbonates depositional environment and their respective geochemical origin discrimination used in TCD in 2014, all the ICP-MS concentrations values obtained during this MSc work have been normalized to the standard of 'Mudstone of Queensland (MuQ)': i.e. 'typical' upper crustal siliciclastics. (Kamber et al., 2014)

The Tables in Appendix 2 show the original results (Trace elements datas in ppb and normalized in MuQ) of all the three above ICP-MS experiments which were run with a very low detection limits yielding to precise and accurate data for REE and Y elements present in the sample at ppb concentration levels.

Carbonatites limestones REE signatures or "hot" isotopic fingerprints are satisfying the following criteria:(Kamber et al., 2014)

- Light and heavy REE enriched
- High Li, Rb, Cs, and Ti concentration
- Perfect correlation matching with Fort Portal Carbonatites (universally recognized in the literature with Carbonatites fingerprint) with a correlation coefficient above or equal to 0.95 which express the measure that determined the degree to which these samples above are associated with the Fort Portal Carbonatites lavas origin.

This simply means that the correlation coefficient is a statistical measure of the strength of a linear relationship between paired data (eg in this case Fort Portal Carbonatite data with EAB and /or Block V carbonatite datas). This correlation coefficient can range from -1 to +1, with -1 indicating a perfect negative correlation, +1 indicating a perfect positive correlation, and 0 indicating no correlation at all.
The sample V20 ICP-MS result interpretation in the Figure III.31 below is taken as an example:
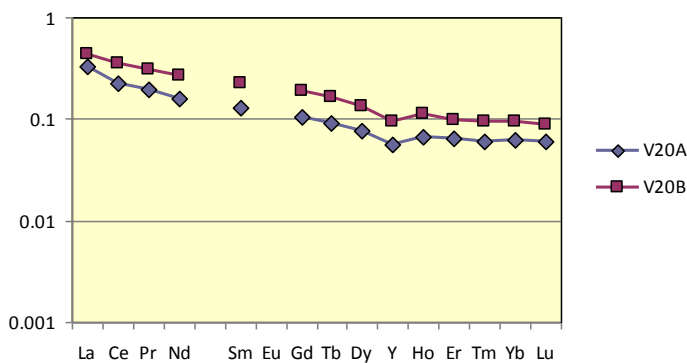


*MUQ values from the Original Excel file (enclosed in CD1) raw datas plotted in an exponential Excel chart, as per Kamber experiment results presentation.*

*V20A: Fabric: dark grey crystal*
*V20B: Replica from the other side of the slice*

*The REE normalized concentration chart shows signature curves almost matching between them with the published Carbonatites fingerprint curve of Fort Portal, Uganda.*
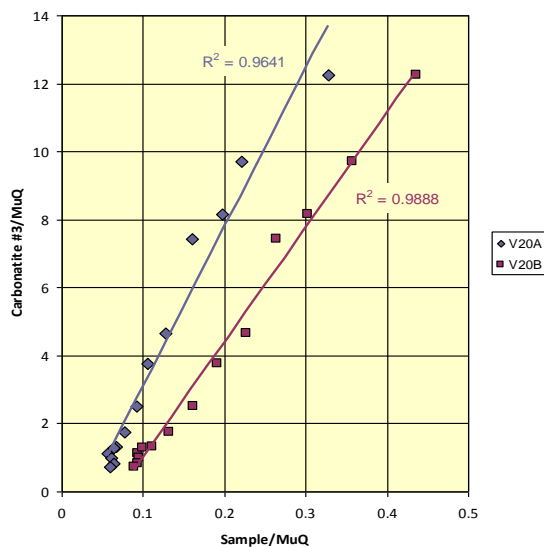
*Individual V20A and V20B samples from each slide did not matched with marine limestone criteria , then have been plotted in an Excel chart against Fort Portal Carbonatite #3: their Correlation Coefficient $R^2 = > 0.95023$*

*The Correlation Coefficient is never null and his graph can't be starting by the origin 0 because neither the large range (1 to +15) of published MUQ Fort Portal "lavas" Concentrations (Stoppa and Schiazza, 2013) nor the small range (0 to + 0.5) of MUQ Travertine deposited in Albertine Rift carbonate outcrop in hot springs by thermal less carbonated fluids, has null value.*

Marine limestones REE signatures or "cold" isotopic fingerprints had satisfied the following anomalies :(Kamber et al., 2014)

- Gd anomalies
- Ce anomalies
- La anomalies

Additionally, the following key criterias for recognizing a REE+Y marine limestone signature have been applied:(Kamber et al., 2014)

- $(Pr_n / Yb_n \ll 1$   Praseodymium / Ytterbium ratio
- Y/Ho > 40      Yttrium / Holmium ratio
- La/La* > 1.1   Lanthanum anomaly
- Gd/Gd* > 1.1   Gadolinium anomaly
- Ce/Ce* < 0.8   Cerium anomaly

Where:

- *La/La* = La/((Pr*((Pr/Nd) 2)))*
- *Gd/Gd* = Gd/((Tb*(Tb/Dy)))*
- *Ce/Ce* = Ce/((Pr*(Pr/Nd)))*

The reference graph below in Figure III.32 which show the characteristic REE+Y patterns in shallow seawater, freshwater sediments, marine limestones and rift Carbonatites, is used in this work as a comparison tool. Their MUQ values from the existing literatures extend in a large range from $10^{-3}$ and $10^{1}$ as per Kamber experiment graphs.
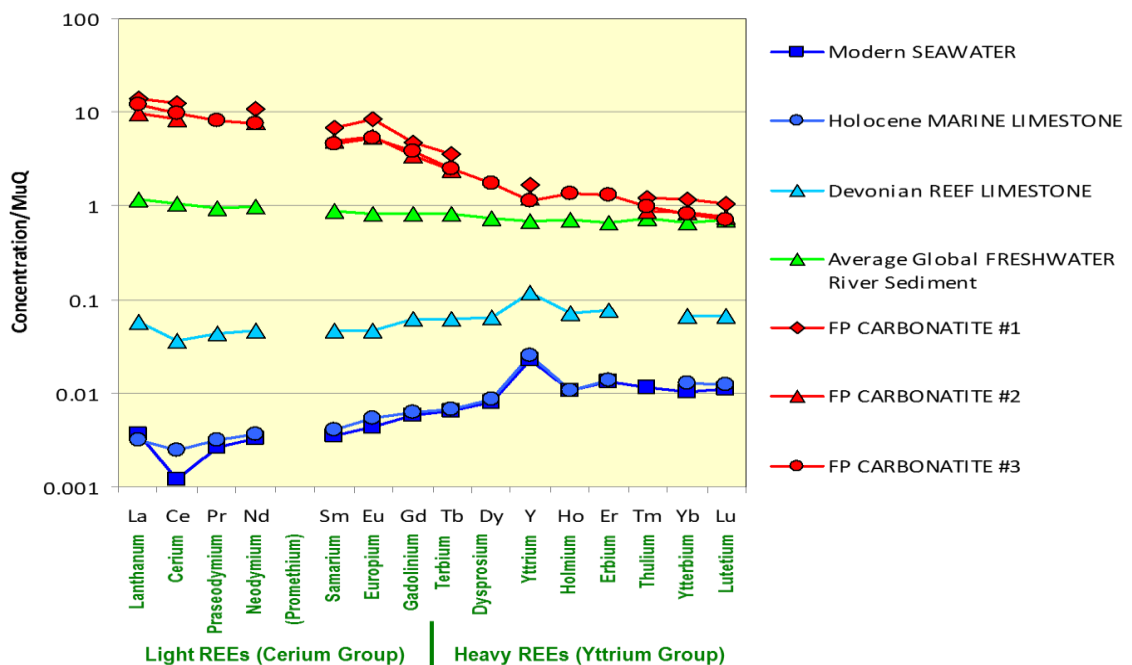


*Figure III.32 :  characteristic REE+Y patterns in shallow seawater, freshwater sediments, marine limestones and rift Carbonatites  (Stoppa and Schiazza, 2013) .(Nicholas, 2009)*

*Chapter 3 Conclusion:*

*To reach the objectives of this work, our methodology followed the following steps:*

1. *Travertines field investigation, description and sampling as above detailed in terms of logistic, equipments, field environment and geologist field activities.*

2. *Travertines petrography investigation: thin section preparation, microscopic observation using the latest technology to identify and describe the ideal structures, textures and/or fabrics containing carbonates mineral or cement for geochemistry analysis purposes.*

3. *Oxygen and Carbone stable isotope as well as Strontium isotopes analyses and Gas Chromatography Mass Spectrometry to evaluate the various geochemical and biochemical cycles they passed through during their geologic process of deposit.*

4. *Travertines palaeoclimate changes implications referring to SNOW and PDB values, and their depositional environments datation attempt referring to the Sr isotope ratio.*

5. *ICP-MS experiments on Carbonates diluted solutions for low detection of Rare Earth Element concentration in ppm, then normalized in MUQ as per Balz Kamber experiment in 2014.*

6. *REE spectral signatures correlation with the closest know signatures of Carbonatites (Fort portal, Uganda), marine limestones (Mandawa basin, Tanzania), mesooic karoo and Neoprotrozoic Schisto-calcaire (Stromatholites).*

*The next Chapter, titled Field Trips, highlights the different seasons of Travertines field investigations, description and sampling. The Travertines depositional environments have been documented by their field evidences using updated field data recording tools, methods and procedures all provided by Dr Chris Nicholas who participated personally in all the Travertines field investigations.*

# CHAPTER FOUR: FIELD TRIPS

This Chapter is treating essentially about all the field trips carried out around the region of the Travertine occurrences in the Albertine Rift. It describes both the Travertine samples collected and the geologic environment of the Hot springs generating these Travertine, coupled in some localities with the temperature records and the spectral gamma response.

Each of these field trips has been sponsored either by Government or Oil companies who provided all logistic and work plans needed for the well organization of the field work during these campaigns. The field trips treated in this present chapter have been supervised by Dr Chris Nicholas assisted by a mixed team made of geologists coming from either TCD postgrads students or respective Governments and Oil companies sponsoring. This Field trips Chapter presents the previous field trips history and then each of the most recent field trips summary highlighting their respective outputs in terms of field informations collected and incorporated to the general understanding of the Travertine presence in the Edward Lake basin.

## IV.1- HISTORY OF ALBERTINE RIFT FIELD WORKS

Initial mapping in the Edward Lake region was for the first time undertaken by the Geological Survey of Uganda in the late 1950's, mainly to identify mineral resources in the Proterozoic basement (Geological Survey of Uganda, 1961).(Rubondo, 2005)
Although the Late Pleistocene -Holocene Katwe and Bunyaruguru volcanics were identified, the remaining rift-fill sediments were left undifferentiated. However, some lineations on aerial photographs were recognised as potential faults trending NE-SW across the onshore area.(Rubondo, 2005)

Academic research in conjunction with some preliminary mapping and a prior gravity survey by the Petroleum Exploration and Production Department PEPD) of the Ministry of Energy and Minerals Development, Uganda between 1960 and 2000 in the Lake Edward - Lake George region identified up to approximately thirteen informal formations in various litho- and chrono-stratigraphic schemes.(Rubondo, 2005)

These were typically assigned an approximately age range of Late Miocene to Holocene. However, without clear field identification and definition of formational bounding surfaces, lateral geologic correlation of these units were still difficult.
Field mapping of the onshore part of the basin in Exploration Area 4 (EA4A) carried out in 2007 has shown that several sedimentary fan systems extend from the basin flanks NW towards the lake (Nicholas, 2009) and more recently from 2009 to 2011 a detailed field map and working stratigraphic framework of EA4B has been established (Nicholas et al, 2015).

Security issues in Block V on the DRC side of the Lake Edward basin prevented any field work from being undertaken until 2010 when a brief field recognisance and later a proper field campaign in 2014 were carried out by SOCO International plc.

IV.2- EA1, EA4A & EA4B (UGANDA) FIELD WORK


The geological survey of the Oil Blocks EA1, EA4A and EA4B in the Ugandan side of the Albertine Basin was undertaken by Chris Nicholas, PEPD and Dominion Petroleum Ltd as below:
- *Chris Nicholas (Chief Geologist, Dominion Petroleum),*
- *Dozith Abeinomugisha (Senior Geologist, PEPD),*
- *Catherine Amusugut (Geologist, PEPD),*
- *Tonny Sserubiri (Geologist, PEPD),*
- *Lauben Twinomujuni (Postgraduate Student, Makerere Univeristy, Kampala).*
- *Wilson Tumisabe (Geologist, PEPD and Postgraduate student TCD).*

Travertine samples have been found in outcrops whilst the team was trying to drive towards Kasese locality to look for evidences of exposed Ruwenzori border fault across Ugandan oil blocks EA1 and EA4A. Many lime works and quarries were visited along the road and gave enough interesting Travertine samples which have been firstly described in the field then collected and shipped to TCD for the petrography and geochemical analysis treated in this present study. Many active and not active hot springs surrounding the Travertine outcrops have been documented as possible generating factor.

The Table 2 below presents the Travertine samples described and collected, their respective origin localities as well as their related Oil exploration block geographic coordinates      (UTM 36S).

| Exploration Block | Locality | X | Y | Z | Travertine Samples |
|---|---|---|---|---|---|
| EA1 | Okumu, | 313104 | 252027 | 670 m | P12, |
| EA4A | Dura | 325823 | 0025483 | 767 m | LE 32 |
| EA1 | Hima | 185823 | 0031483 | 967 m | LE 37, 38 |
| EA1 | Bwera, | 806239 | 0001981 | 647 m | LE 41, and 42 |
| EA4A | Lyemubuza | 833417 | 0000617 | 974 m | LES 18, LE 19, and LE 20, LE26, LE 24, |
| EA4A | Muhokiya | 171989 | 0011737 | 949 m | LE 27 and LE 28 |
| EA4B | Bat Cave | 177790 | 9966892 | 683 m | LE 44 |

*Table 2: Travertine Samples collected in Uganda, 2007 -2009.*

The Figure IV.1 below gives the location of the above limestones quarries and lime works in the Ugandan Oil block EA4A.
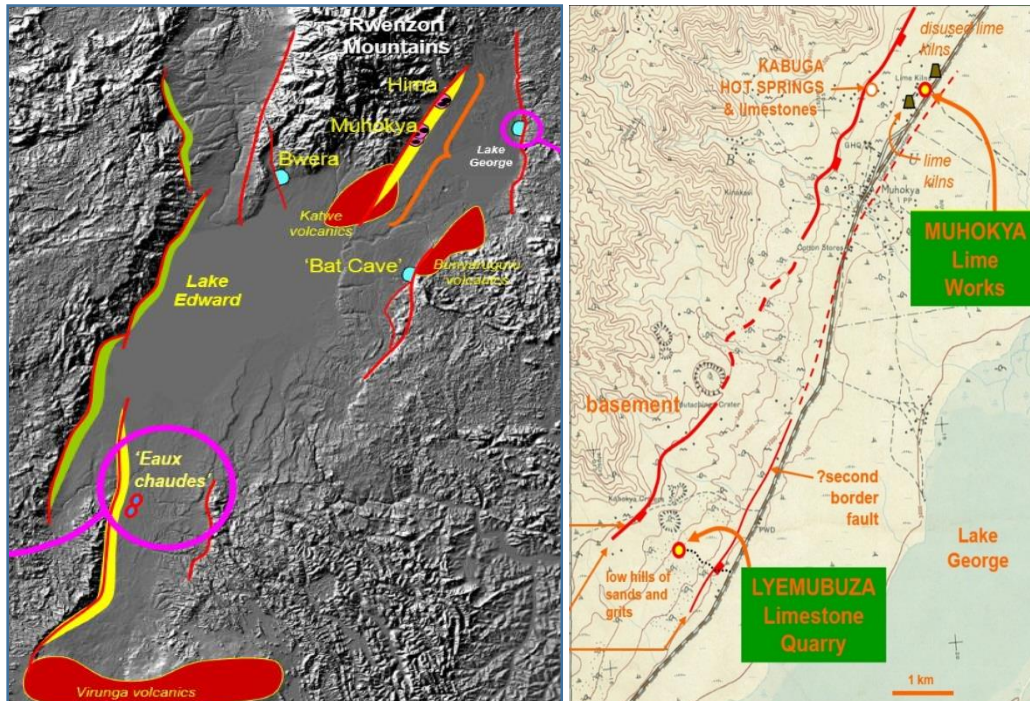


*Figure IV.1: Travertine location Field Maps (Nicholas, 2009)*

Travertine samples collected in Lyemubuza quarry have been found with Oil stain in cavities and two grabs of samples (LE 19 and LE 20) have been collected one of which (LE 20) appeared to have bitumen(?) Oil residue lighting into its cavities (?) at Lyemubuza quarry

The samples LES 15, 18, 20, 25 and LE 27 have been carefully collected, shipped in LGC Standards laboratory in London and analysed by GC-GCMS in 2008 and their results are presented with the courtesy of Dominion Petroleum Ltd in the Results chapter further in the present thesis.

The remaining samples have also been carefully collected, shipped in Ireland observed with the Nikon latest microscope available in the Centre of Microscopy Analyses (CMA) and analysed by ICP-MS in the Unit 7 Expertise Center of the Trinity College, the University of Dublin in 2013 and their results are also treated in the Results further in the present thesis.

# GEOLOGICAL ENVIRONMENT AND FIELD DESCRIPTIONS OF UGANDAN TRAVERTINE SAMPLES
*(Chris Nicholas field notes)*

1. **Sample P12**

- Geological environment: Okumu and Avoca Hot Springs.

  Moderately warm to hot but not too hot to touch located in a NE rift fault intersection with a younger NW active trending fault. No major stream flowing through gorge and the spring appears to be genuinely along the main rift fault.

  No obvious strong $H_2S$ smell. Dispersed Carbonatites caliche throughout.

- Field description: P12

  - Travertine with fossil tubes and visible rootlets;

  - Small blocks of basement caught up in these fossil tubes;

  - Few fossil leafs;

  - Apparent black relicts in cavities.

  - Feezing with HCl acid.


2. **Samples LE 32, 37 and LE 38**

- Geological environment: Hima cement works mine.

  Located just downstream north of a river bank flowing through the Ruwenzori border fault.

- Field description: LE 32, 37, and LE 38

  - Very porous light brown limestones;

  -  Vugs visible presence dispersed in all sample;

  - Feezing with HCl acid.

3. **Samples LE 41 and LE 42**

- Geological environment: Bwera Hot springs.

  Travertine exposed the East bank of a bounding and NW-SW trending fault against which the Hot springs have developed.

  Difficult to see how far they go deep into the hill or whether they are superficial covering. Excellent outcrop of paleostalactites.

- Field description:  LE 41 & LE 42

    - Light brown limestones;

    - Visible different layers spreaded in the whole sample;

    - Feezing with HCl acid.

4. **Oil slicks LES 15 and LES 18**

- Geological environment:

    Oil scum floating round Lake Margin at the SW side where "hot springs" are marked onshore Lyemubuza. Seems like an Oil seep underground conduit.

- Field description: LES 15 and LES 18

    - Black algal scum floating on the lake shore;

5. **Sample LE 20**

- Geological environment: Kasese towards Ruwenzori border fault.

    Travertine exposed around 92 m above the current level of Lake George which is not far away suggesting an uplift of limestones along the Ruwenzori border fault.

    Difficult to see how far they go deep into the hill or whether they are superficial covering.

- Field description: LE 20

    - Travertine with big cavities seeming to have bitumen residue lining the cavities and/or some black ore mineral growth.

    - Feezing with HCl acid.

### 6. Samples LE 24, LE 26, LE 27 and LE 28

- Geological environment:

  Calcite formed in an inverted fairly impressive cliff appearing like a rotational uplift on top of a normal fault block. No evidence of continuous limestone bands.

- Field description: LE 26, LE 27 and LE 28

  - Travertine with primary porosity seeming to have black organic rich fill to their primary porosity.

  - Feezing with HCl acid.

### 7. Sample LE 44

- Geological environment:  Bat cave

  Low tuffs roofed cave apparently with Travertine in its walls. The underground river system with potholes has produced the cave through the thin tuffs. Many pools flowing down west on uphill seeming to be springs bubbling along a geological junction looking like a border fault where thermal waters come up along the junction between impermeable basement and whatever sediments on top.

- Field description: LE 44

  - Stalagmites? Composed of several columnar fabrics layers where the crystals with intercrystalline voids elongated perpendicular to the substrate.

  - Moderately porous fine-medium crystalline Carbonate.

  - Feezing with HCl acid.

The Figures IV.2 *a,b* and IV.3*a,b* below show the geologic environment of LE 20 and LE24, 26, 27,28 samples collected from Lyemubuza quarry while the Figure IV.4 *a,b* and IV.5 *a,b* are showing the geologic environment of LE 41 and LE 42 samples collections respectively from Bwera and Hima localities.
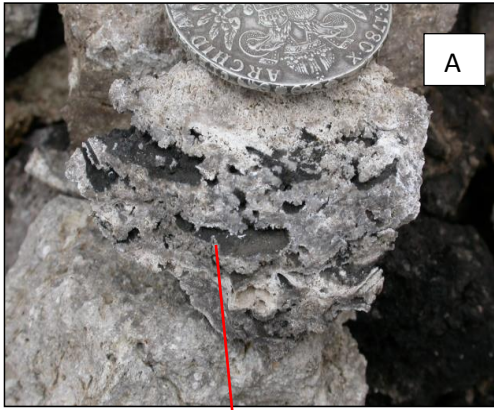
*Figure IV.2a: LE 20 (Nicholas, 2009)    Figure IV.3a:  LE 27 and 28 (Nicholas, 2009)*



*Figure IV.2b: Lyemubuza Quarry (Nicholas, 2009) Figure IV. 3b: Muhokiya Quarry*
*(Nicholas, 2009)*
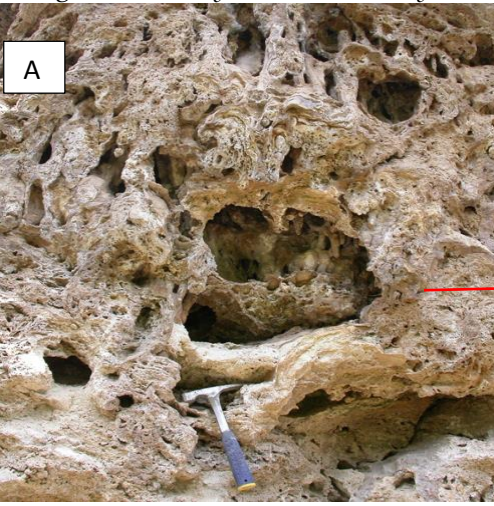


*Figure IV.4 a: LE 41 (Nicholas, 2009)    Figure IV.4 b: Bwera locality (Nicholas, 2009)*
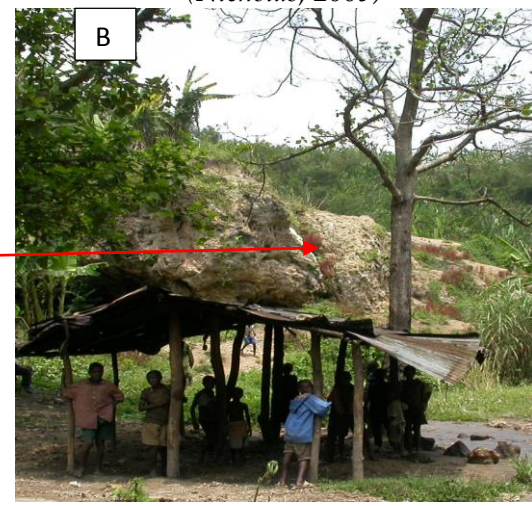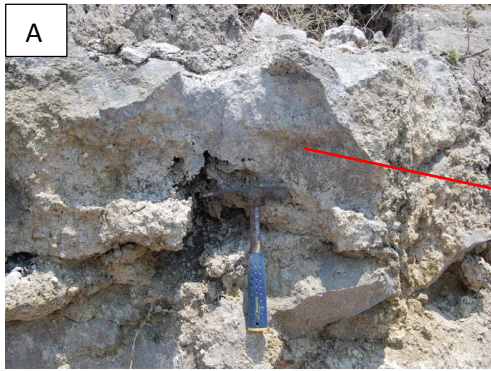
*Figure IV.5a: LE 42 (Nicholas, 2009)*        *Figure IV.5 b: Hima Quarry (Nicholas, 2009)*

IV.3- BLOCK FIVE (DR CONGO) 2010 FIELD WORK

The first geological field survey of Bloc V, the Congolese side of the Edward Lake Basin was undertaken by SOCO International Plc between November and December 2010.

The field team comprised the following people:

- Chris Nicholas (Trinity College, University of Dublin),
- **Sylvain K. Mangoni** (Geologist, SOCO DRC),
- Bichou Ndanze ( Driver, SOCO DRC),
- Jumbo Binji ( Security Officer, DRC army)
- Military escort.

This geological field survey was timed in part to coincide with the safe periods of the volatile security situation of the onshore of the Congolese side of the Edward Lake basin, the block V owned and operated by SOCO International Plc. This enabled the field team to use temporarily cleared itinerary to enter in safer areas. The Block V contains more than 70% of the area of the Virunga National Park itself a much protected world heritage owning. This much protected area status restricted the geologic work as the access to the National Park was subject of many authorizations and long administrative processes. No authorization have been granted.

An initial set of Travertine samples were collected in the field, correctly packed and shipped to Trinity College Dublin (TCD) for microscopy and geochemical analyses (ICP-MS) to augment field datas in order to identify if there were any mineralogical or geochemical differences between these samples structures/textures/ fabrics that might indicate the geochemical origin of the carbonates generating these Travertine.

The following Travertine samples have been collected for the purpose of geochemical analysis treated in this present study: V2 in Biruma (Southern East), V19, V20, V21, V22 in Mayi Ya Moto (West).

The field photos illustrated in figure IV.6,IV.7, IV.8 and IV.9 below shows the field environment of V2 and V19, V20, V21, V22 samples collected respectively from Biruma and Mayi ya Moto.

GEOLOGICAL ENVIRONMENT AND FIELD DESCRIPTIONS OF DR CONGO TRAVERTINE SAMPLES

V2: Light Brown very crumble limestone with vugs porosity and visible rootlets branches and plant tubes;

V19, V20, V21, and V22:  Black stained lining in white vugs spreaded Travertine.

Note:

Due to security issues, the number of localities to visit and field time restrictions per locality, we didn't have time to describe the geological environment and collected samples. No gamma ray has been recorded, the tool was not available. Mayi ya Moto locality has been targeted as main visit for the next field trip under better security conditions.



*Figure IV.6:  Sample V2 Biruma (SOCO, 2010)*



*Figure IV.7:  Sample V20 Mayi ya Moto (SOCO, 2010)*
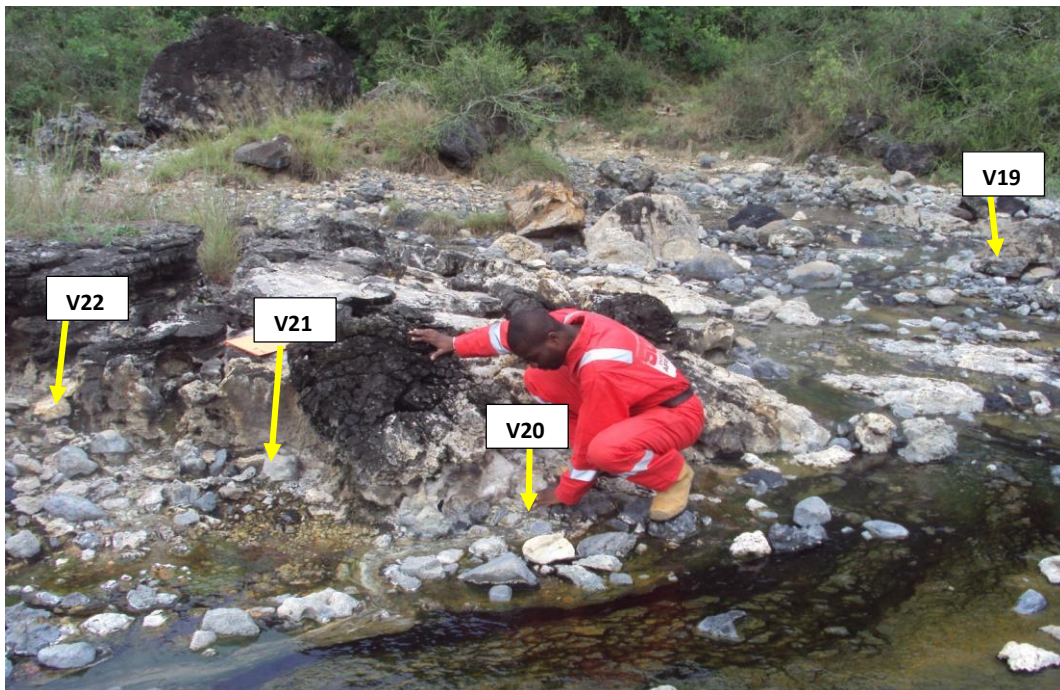


*Figure IV.8:  Sample V19, 20, 21 &22 @ Mayi ya Moto (SOCO, 2010)*

*Figure IV.9: V2 collection at Biruma Quarry (SOCO, 2010)*

## IV.4- BLOCK FIVE (DR CONGO) 2014 FIELD WORK

The second geological field survey of Bloc V, the Congolese side of the Edward Lake Basin was undertaken by SOCO International Plc. between May and August 2014. Figure IV.10 shows in red line the limits of Block V in the Lake Edward basin.
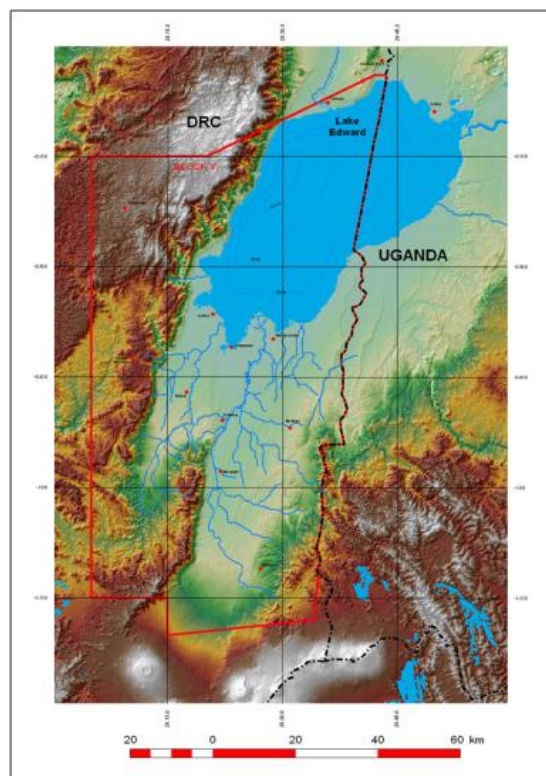


*Figure IV.10: Block V Field Map (SOCO, 2010)*

The field team assigned to this field trip comprised the following people:

- Chris Nicholas (Trinity College, University of Dublin),
- **Sylvain K. Mangoni** (Geologist, SOCO DRC),
- Finbaar Mc Teirran (Postgraduate student, Trinity College, University of Dublin)
- Peter Kock (Field Security Officer)
- Steve (Helicopter pilot)
- Bichou (driver)
- Military escort.

This geological field survey which was a bit longer than the previous, was timed in part to coincide with the access grant to the Virunga national park, the improvement of security situation of the whole Block V and the seismic acquisition operations in the offshore of the Congolese side of the Edward Lake basin as part of the block V owned and operated by SOCO International Plc. This enabled the field team to use temporarily cleared itinerary to enter in safer areas, SOCO base camp in Nyakakoma village and efficient field logistic support including the use of a Helicopter for survey flights with possibility of landing anywhere, the base camp of seismic operations, vehicles 4x4 wheels, radio tracking devices, etc .

In order to better understand the Travertine occurrences in the region, an investigation of others surrounding Carbonates outcrops have been done in the purpose of overview their spatial extend correlation in the regional level.

The main targets of this new field trip in Block V were:

- Revisit the 2010 Travertine localities ( Mayi ya Moto and Biruma) and visit new other limestones localities (Katanda Terraces and Vitshumbi unit),
- Detailed geological description of Travertine exposures (numbered as field localities), and recognition of a set of lithofacies associations,
- Sedimentology logs of reference cliffs along main hot springs faults.
- Spectral Gamma Ray recording at specific intervals from the base to the top of these cliffs,
- Travertine samples collections at each location of the Spectral Gamma ray recording,

## IV.4.1- GEOLOGIC ENVIRONMENT AND FIELD DESCRIPTIONS OF TRAVERTINE SAMPLES COLLECTED IN BLOC V IN 2014

(Sylvain's field notes)

The two sites (Mayi ya Moto and Biruma) visited in 2010 have been revisited in 2014 and two new sites (Katanda terrace with black shinning stuffs and Vitshumbi carbonate unit) have been added to the itinerary during this field trip.

The Table 3 below presents the Travertine samples described and collected, their respective origin localities as well as their related Oil exploration block geographic coordinates          (UTM 35M).

| Exploration Block | Locality | X | Y | Z | Travertine Samples |
|---|---|---|---|---|---|
| Block V | Mayi Ya Moto | 313104 | 252027 | 670 m | V149, V150, V153 |
| Block V | Katanda | 185823 | 0031483 | 967 m | V159, V161b, V162a, V163b, V164 |
| Block V | Vitshumbi | 806239 | 0001981 | 647 m | V338, V344, V352, V356 |
| Block V | Biruma | 833417 | 0000617 | 974 m | V363, V364, V385 |

*Table 3: Travertine samples collected in DR Congo, 2014*

Their geologic environment and samples field descriptions and their photos can be see here below:

The Travertine in and around Mai ya Moto (Figures IV.11 to IV.13) had very high TOTAL GR values, whereas the deposits in Biruma have very depleted KUTh values. It is mainly composed of clean white limestones with dense reed and rootlet beds where the carbonate has encrusted vegetation which probably grew in an extensive shallow pool fed by carbonate rich hot springs.
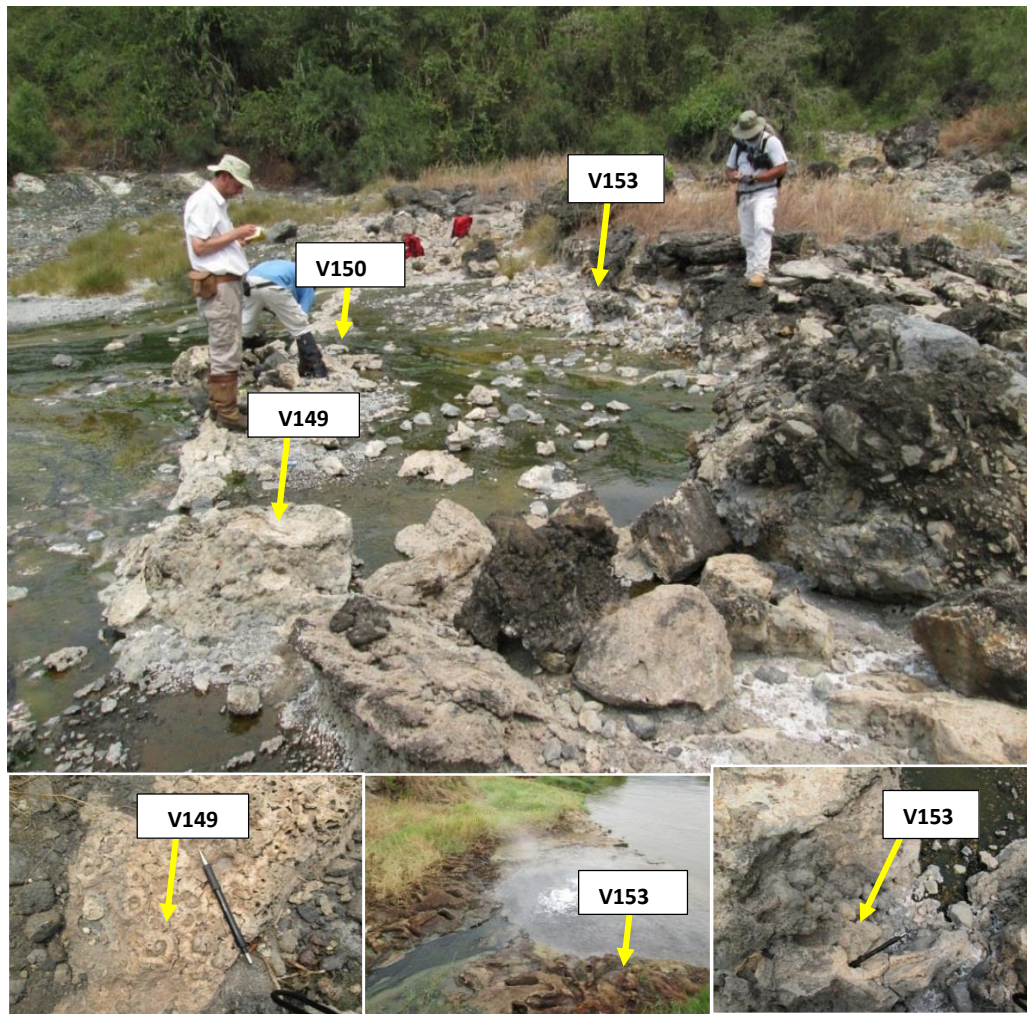


*Figure IV.11: Sample V149, V150 and V153 @ Mayi ya Moto (2014)*
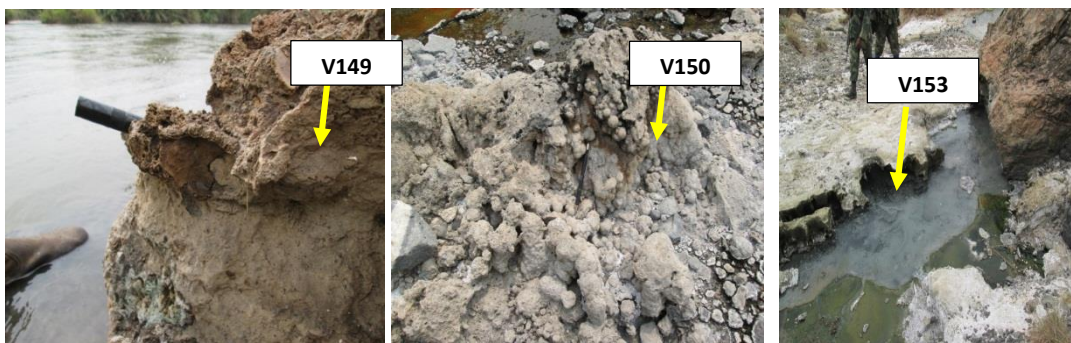
*Figure IV.12: Sample V149, V150 and V153 @ Mayi ya Moto (2014)*

At Katanda, a large active hot spring was located at the main western bounding fault's surface expression, with several palaeo-springs forming 'terraces' at intervals up the fault scarp.
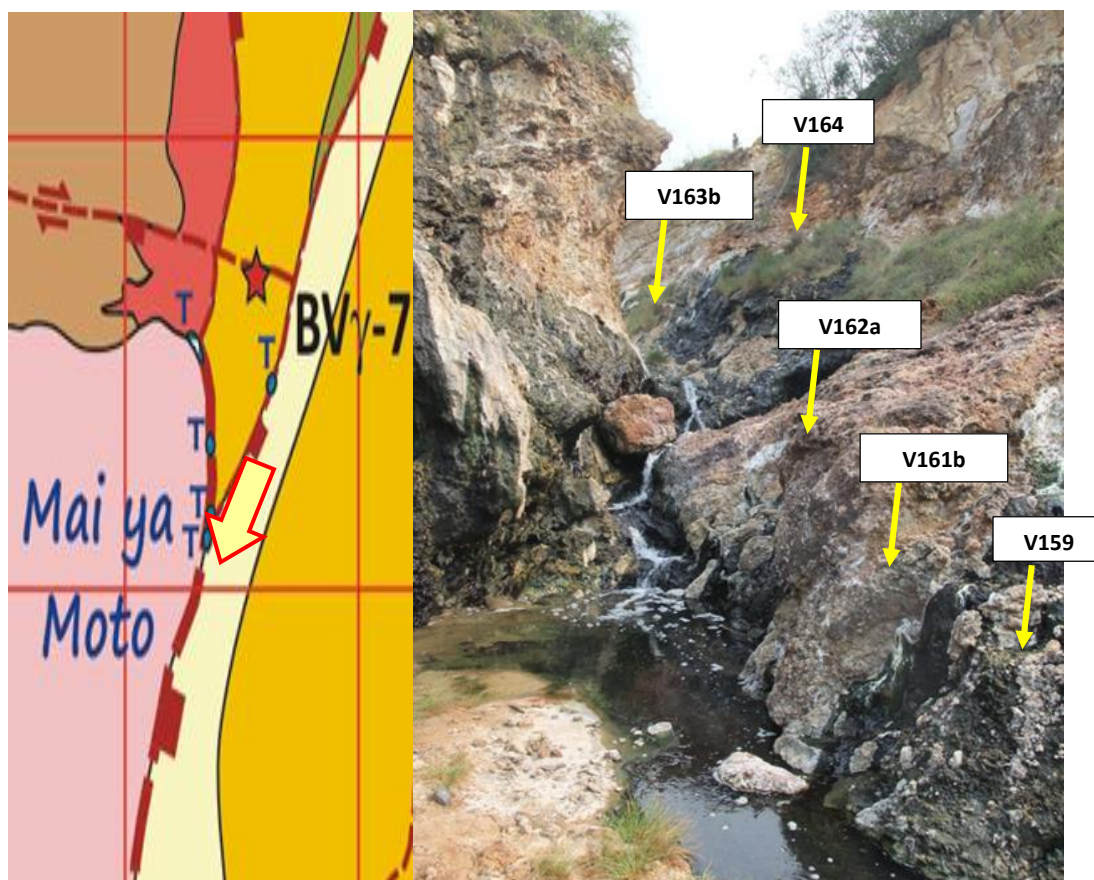


*Figure IV.13: Gorge (Katanda) with extensive Travertine limestones covering and hot spring pools linked by streams. Samples collected for ICP-MS*

These palaeo-springs may have been abandoned as movement on the fault shunted them upwards, away from the fault plane up which the fluids are fluxing. Samples V159, V161b, V162a, V163b and V164 have been collected for ICP-MS analyses.

Active hot springs were also found further north-east away from the main fault up a north-north-east – south-south-west fault on the banks of the Rutshuru River. This along with structural mapping suggests that the springs are situated around the triangular intersection of 3 major rift faults, and not solely associated with the main western bounding fault.

Another 1-2km$^2$ Travertine limestone outlier in Biruma was revisited on this trip. Here the limestones are apparently underlain by older basaltic volcanics and are at least 50m thick and are quarried by the locals to form lime for construction.

The Travertine in and around Mai ya Moto had very high TOTAL GR values, whereas the deposits in Biruma have very depleted KUTh values. It is mainly composed of clean white limestones with dense reed and rootlet beds where the carbonate has encrusted vegetation (Figure IV.14) which probably grew in an extensive shallow pool fed by carbonate rich hot springs.

Samples V338, V 344, V 352, V 356, V363, V 364, and V 385 have been collected for ICP-MS analyses.
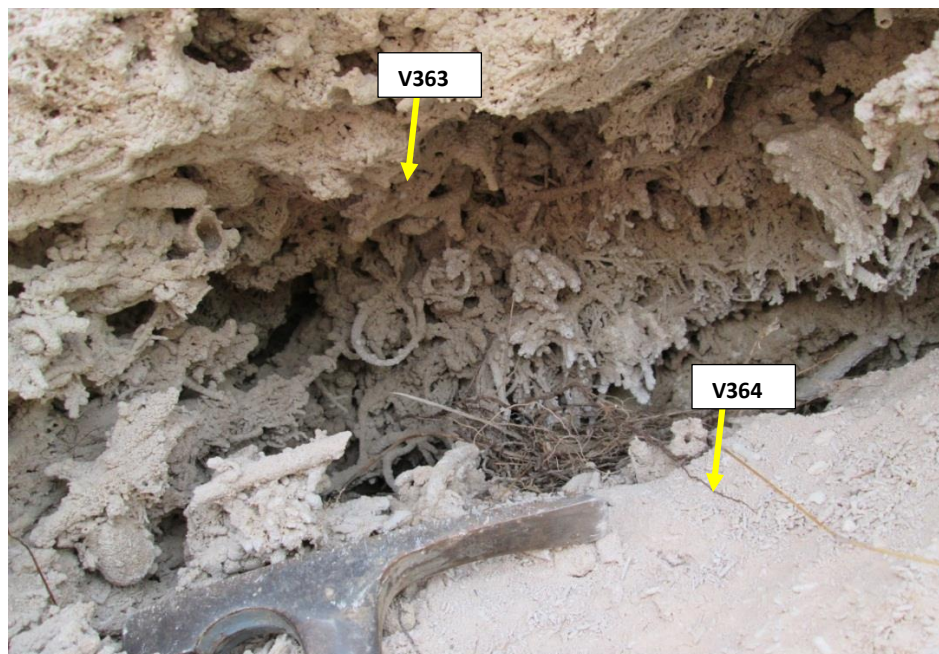


*Figure IV.14: White carbonate encrusts reeds and rootlets at Biruma.*
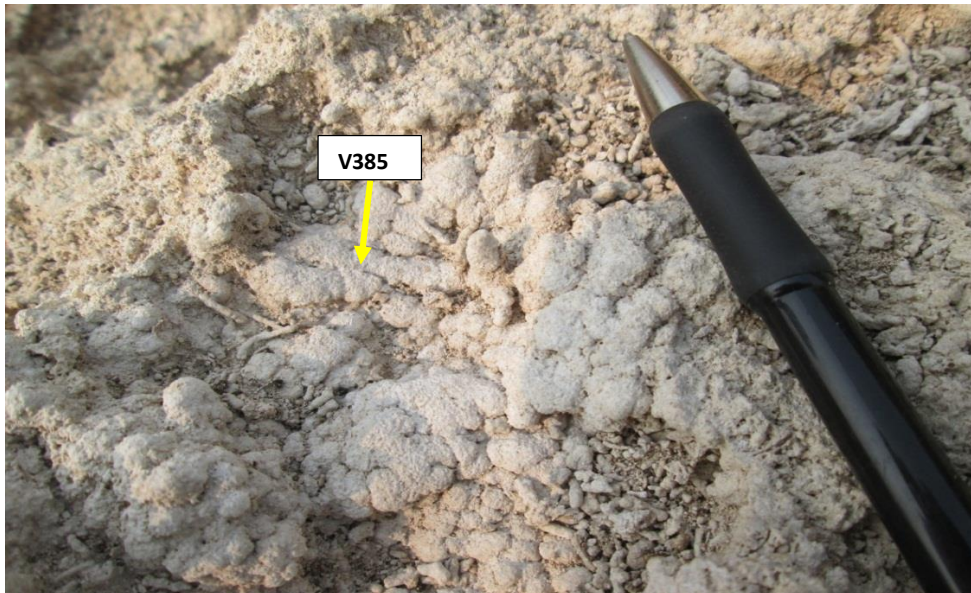
*Figure IV.15: Pustulous texture, similar to that seen at the mouth of active springs, precipitated close to where the spring would have emerged.*

GEOLOGICAL ENVIRONMENT AND FIELD DESCRIPTIONS OF DR CONGO TRAVERTINE SAMPLES 2014

## I. **Mayi ya Moto hot springs** (Revisited)

**Coordinates:**

761398
9900789
@ 605 m

## Geologic environment

Bubbling Hot springs lined just below an active fault evidence in the Eastern flank of the Eduard basin. Algal hot waters are flowing in small streams.
3 Patches of Travertine outcrops have been observed:

- Patch dipping 80/036 where the closest Hot spring temperature = 93°C
- Patch dipping 63/028 where the closest Hot spring temperature = 96°C
- Patch dipping 42014 where the closest Hot spring temperature = 93° C

## Gamma ray values:

K= 0.9 % U= 66.8 ppm Th = 12.7 ppm (assay 2265)

## Samples description

**V149**: single block. Light brown fibrous Travertine with Breccia gap and cavities.

**V150**: Microbially laminated white Travertine with fibrous layers.

**V153**: Travertine with chimney structure that provides ventilation for hot flue gases or smoke from underground processes, then cooled at surface in ambient temperature.

II. **Katanda gorge** (New locality)

**Coordinates:**

761494
9902714
@ 685 m

**Geologic environment**

Incised valley trending 320° NW at first glance from the helicopter (aerial view below in Figure IV.17) appeared to have relict Oil seep. In the ground, it is a linear Hot springs locality with algae growing up the steep sides.
A network of hematite veins sheets through the rift-fill sediment here and there. The Travertine are dragging the steep valley sides.
The hot water stream turn back on itself further to the NW and it is following the steeply dipping and curving basement edge, rather than linear rift-fault.

**Gamma ray values:**

K= 3.6 % U= 410.8 ppm Th = 11.8 ppm (assay # 2266) upstream
K= 1.4 % U= 309.2 ppm Th = 57.5 ppm (assay 2267) downstream
The GR values in general, Th and U values in particular appears to decrease downstream away from main stream full of cyanobacteria evidence suggesting increasing oxygenation downstream.

**Samples description:** (Upstream towards downstream)

| Travertine | Elevation | Sample | Field description |
|------------|-----------|--------|-------------------|
| Terrace #4 | 995 m | V162 a and b | Hematite stained Travertine crumbled |
| Terrace #3 | 985 m | V163 a and b | Hematite stained Travertine crumbled |
| Terrace #2 | 976  m | V159 ,V161 | Hematite stained Travertine crumbled |
| Terrace #1 | 962 m | V164 | Hematite stained Travertine crumbled |

III. **Mabenga hot springs** ( New locality)

**Coordinates:**

761774
9900764
@ 687m

**Geologic environment**

Small pool of 4 bubbling springs at eastern river bank.
Temperatures  84.7°C , 75.2 °C, 82.2 °C, 75.7°C . Presence of white salt crusts and small chimneys with maximal temperatures of 90 °C.

**Gamma ray values:**

K= 1.0 % U= 200.9 ppm Th = 25.1 ppm (assay # 2268) upstream

**Samples description:**

| Sample | Field description |
|--------|-------------------|
| V 344 | Travertine with inputs of plants and tree rootlets |
| V352&356 | Travertine with inputs of plants and tree rootlets |
| V363&364 | Vertical zoned Travertine including gas holes around large cavities |
| V385 | Vertical zoned Travertine including gas holes around large cavities |

**IV. Vitshumbi fault scarp** ( New locality)

**Coordinates:**

763580
9903605
@ 689 m

**Geologic environment**

Boiling springs on west side bank of Rutshuru River bubbling along a length of around 40 m in a series of pools as the main river.

AERIAL VIEW (BLING SATELLITE IMAGE) AND GROUND
CONSIDERATIONS OF EXPLORED SITES IN BLOC V.
(Figures IV.16 to IV.20)
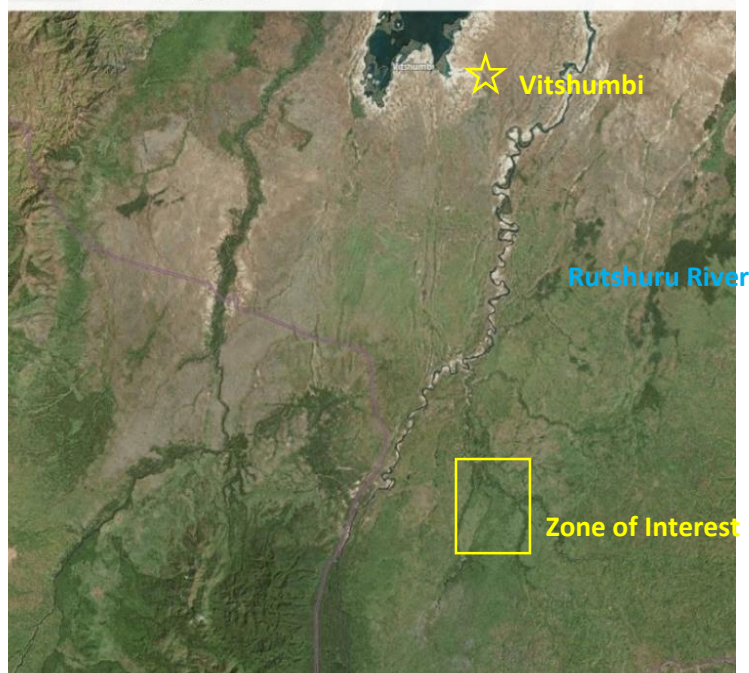


*Figure IV.16: ©Bing 2018 Aerial view of the Eduard basin Travertine occurrences. Zone*

*of interest. 1cm = 5 Km*
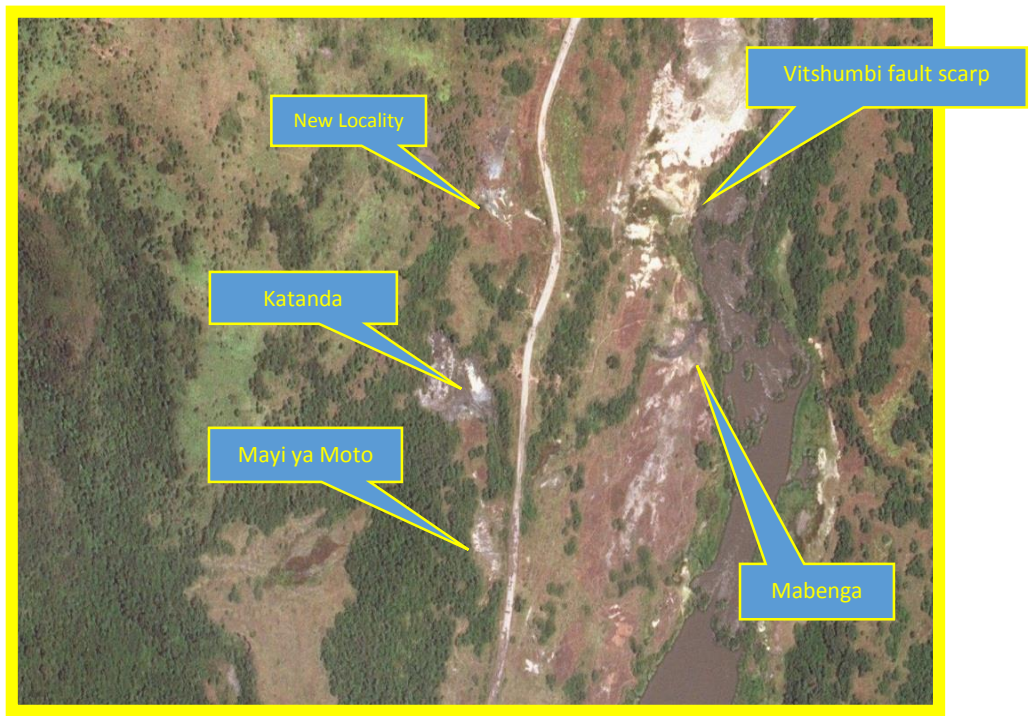
*Figure IV.17: ©Bing 2018 Aerial view of the ZOI ~5 Km2. Visited Sites*
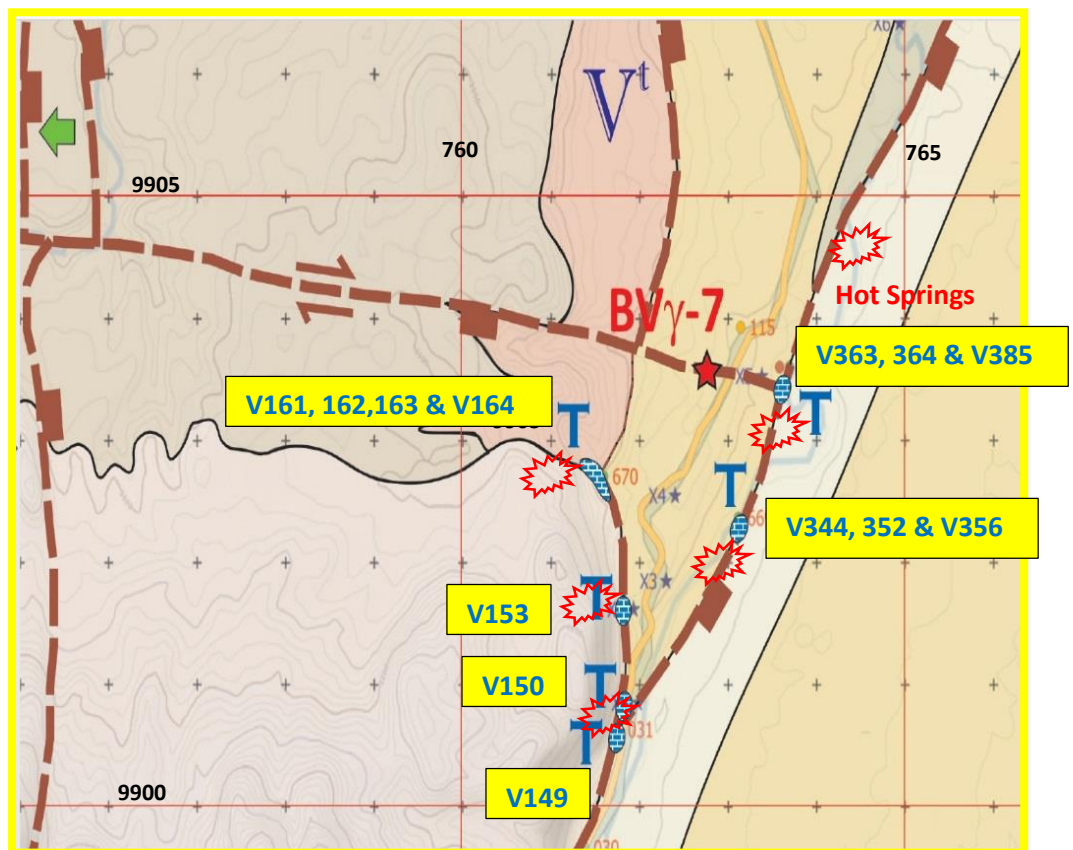


*Figure IV.18: Geologic considerations of the ZOI. Travertine samples collected. Hot Springs observed.*

*Figure IV.19: ©Bing 2018 Aerial view of the Biruma Quarry*
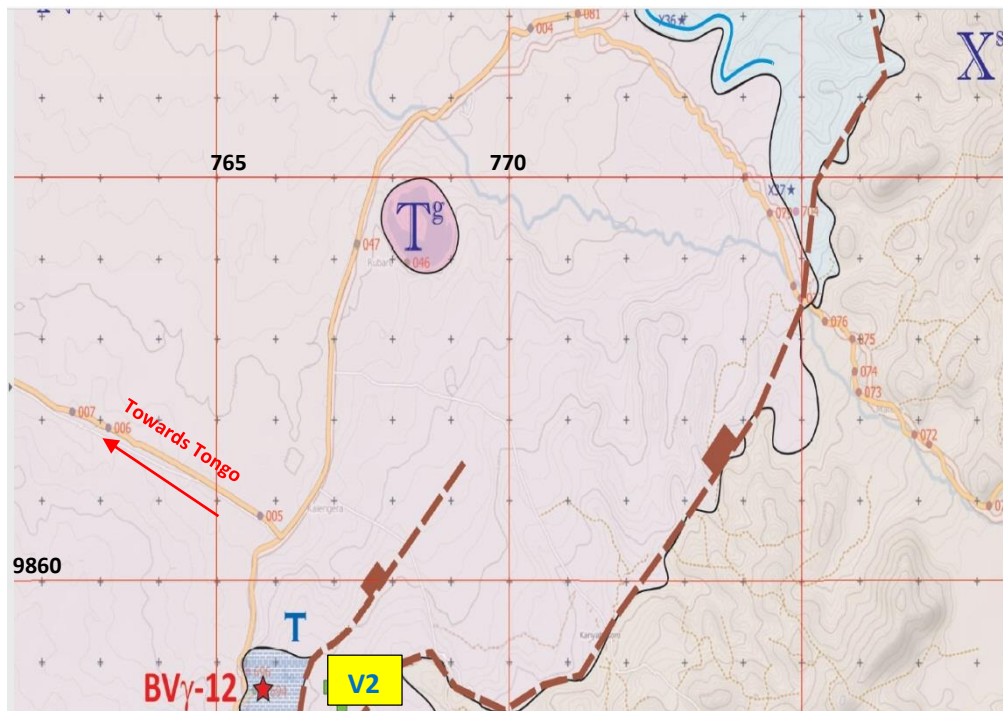


*Figure IV.20: Geologic considerations of the Biruma Quarry. Travertine samples collected*

The only others carbonates outcrops encountered during the field trip in the Block V were located in the Vitshumbi Unit. This unit is described and its spectral Gamma response are presented below:

### A.1 _Lithofacies and Stratigraphic Definition_

South of Lake Edward inland from its marshy margins are the mostly flat, sparsely vegetated grasslands. Exposures can be seen in the scarps of north-south and northeast-southwest trending faults South-south-west of the Village of Vitshumbi (Figure IV.21) which lies on the southern-most tip of the lake a well exposed scarp with prominent bedding stood out from the helicopter. The fault was followed north and south where its surface expression could be seen dying out in either direction so, the thickest and most well exposed point along the scarp was chosen for logging as time constraints related to permissions to work in the area meant the fault could not be explored further on foot.

The lack of vegetation made landing on the footwall dip-slope easy, and the lowest most in-situ exposure at the base of the scarp was found on foot. Standing on the top of the scarp looking east a smaller west-facing antithetic fault could be seen in the distance creating a miniature graben. This small valley runs north-south up to the western side of Vitshumbi village, and so its name was used to refer to the characteristic stratigraphic unit exposed here [UTM 761080 9915289; Locality CJN 263].



*Figure IV.21: Vitshumbi fault scarp looking north at log section BVγ-10.*

Further exploration later in the field trip added more informations to the Vitshumbi unit knowledge. A further exposure of this formation was scouted out east of the village of Kirima in the southern and highest part of the Ruindi sub-basin in a deeply incised river valley through which the Ruindi River flows.

The helicopter was landed in the village football field, much to the excitement of the locals, and then military vehicles were then taken to the river valley.

A dirty road handily shown below in Figure IV.22 cut into the sediments in the tall banks of the river runs from a bridge across the river to the top of the valley exposing, and allowing easy access to, approximately 20m of rift-fill sediments [UTM 745239 9890867; Locality CJN 095]. (Figure IV.22 below)

Security in the area allowed for only one days logging of this locality, but the ease of access to the exposure meant it was completed.

Both sections were defined as part of the Vitshumbi Formation due to having very similar lithofacies, the presence of abundant carbonate which fizzed readily in the presence of dilute HCL, their high Total GR (from 160-500 API) and very high U and Th concentrations earning them the name 'hot limestones'.

The fact that the better developed hard limestones of this unit weather proud and are easily visible even in small fault scarps, and that anything similar to this unit has not been seen elsewhere in the basin, suggests that the rest of this unit must lie deeper, buried under youger rift-fill sediments.

*Figure IV.22: Road cutting along the side of the Ruindi river valley to the east of Kirima village at log BVγ-18.*

These two sections were logged in detail and consist of marls and marly limestones with 5 main lithofacies: (Figures IV.23 to IV.26)

a) Light brown marly limestone with fine to medium sub-angular quartz, well rounded coarse quartz grains, abundant fine to medium sub-angular black mineral grains, hard crumbly calcitised plant material at small and large scale, rootlet/burrow systems and occasional shell fragments.

b) Pale reddish brown marl, poorly sorted mix of very fine, fine and medium sub-angular quartz stained different colours, fine to medium sub-angular black mineral grains.

b') As for b) but with a coarser quartz grain size making it more crumbly.

c) Light brown dominantly fine sandy limestone, quartz grains stained different colours, admixture of fine to medium sub-angular quartz, fine black mineral grains, hard calcretes layers with desiccation cracks and pustulous microbial mat texture.

d) Greyish orange to moderate orange pink silt to very fine quartz sandy marl, very fine black mineral flecks, powdery and friable, rootlet/burrow system sometimes still with black organic carbon lining cavities, discontinuous caliche nodule layers.

e) Greyish orange to medium grey relatively poorly sorted mix of medium to very coarse sized sub-angular to sub-rounded quartz grains, powdery clay grain coat, cross-bedding on 40cm scale, very coarse black mineral grains, quartz stained different colours, very friable, layers of marl rip-up clasts.
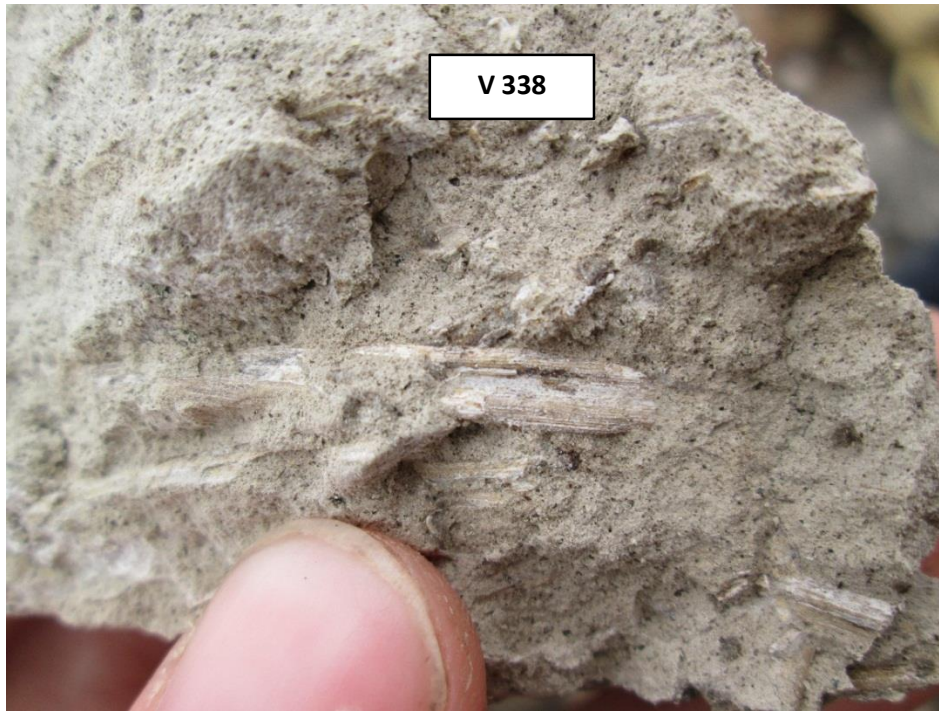
*Figure IV.23: Calcitised reed impression in Lithofacies 'a' at log section BVγ-10. (V338)*
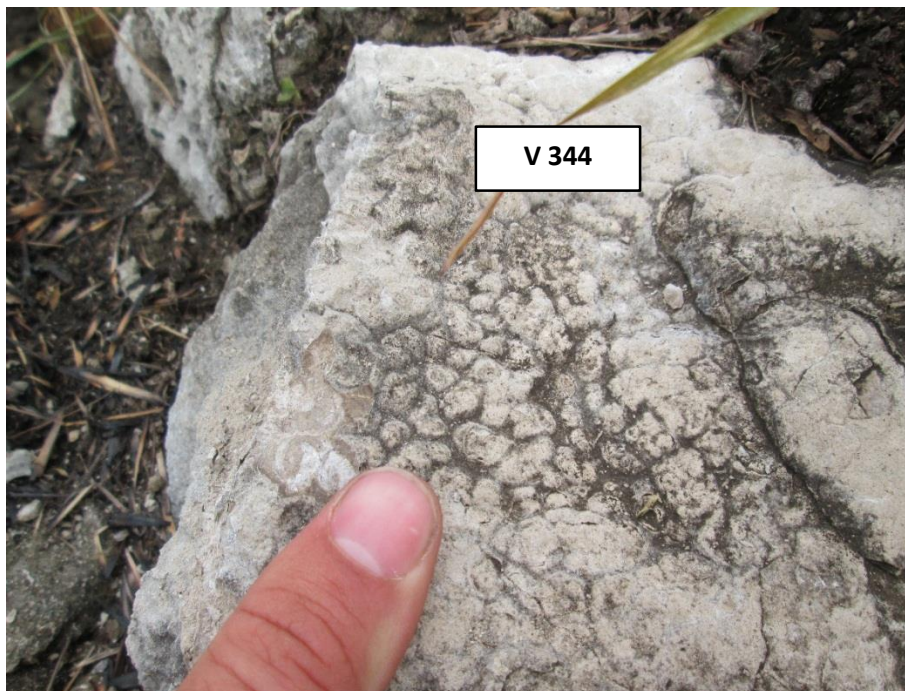


*Figure IV.24:  Pustulous textured microbial mat in Lithofacies 'b' at log BVγ-10. (V344)*
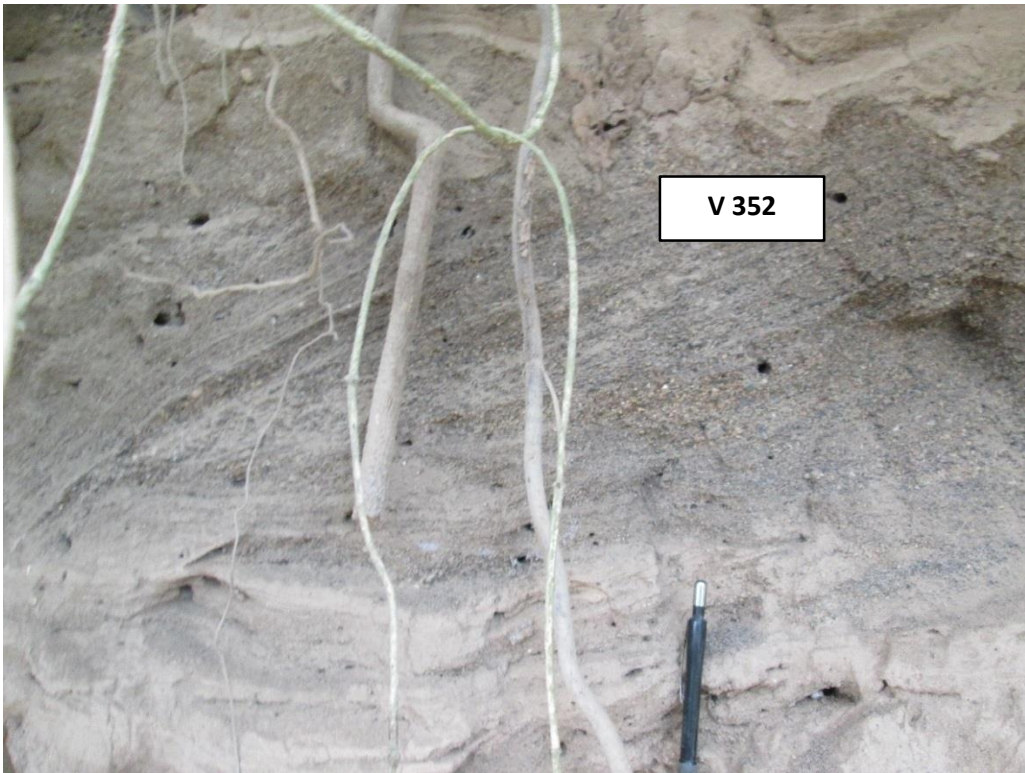
*Figure IV.25   Cross-bedding in Lithofacies 'e' at log BVγ-18 in Ruindi river valley.*
*(V352)*



*Figure IV.26:  Marl rip-up clasts in Lithofacies 'e' at log BVγ-18 in Ruindi river valley.*
*(V356)*

## A.2 *Spectral Gamma Response*
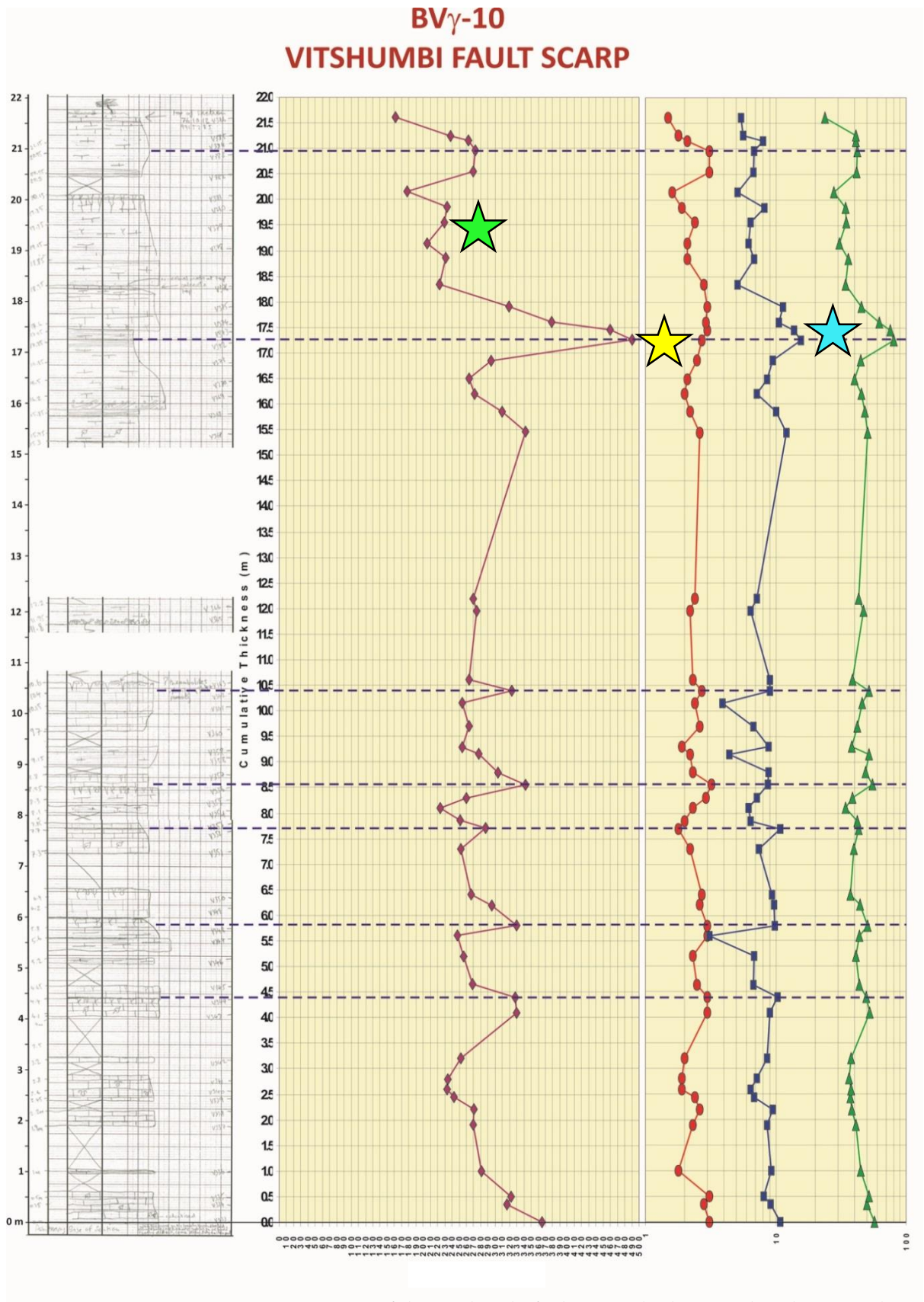


*Figure IV.27:  Gamma Ray response of the Vitshumbi fault scarp. (Sylvain and Finbaar 2014)*

BVγ-10: Vitshumbi Unit

- o Total Gamma from 160-500 API, higher than any other unit so far discovered in the basin.
- o Blue Star: K, U, Th all peak together in 1.5m-2m cycles.
- o Peaks are usually associated with hard calcretes tops with associated desiccation cracks and microbial mats.
- o Yellow Star: Marked spike in Total GR, U and Th in finer laminated silty marl.
- o Green Star: Total GR clearly falls towards top of the section.

The high gamma response (Figure IV.27 above) suggests that these carbonates are being precipitated from reducing, U and Th rich waters, possibly related to water perculateing up the main rift-bounding fault which still feed active hot springs today.

IV.4.3- <u>STRUCTURE, HEAT & FLUID FLOW</u>

As the hot springs and Travertine outcrops are located along margin faults, a structural study and heat flow research was necessary to understand in the field.

IV.4.3.1- <u>REGIONAL STRUCTURE</u>

A series of aerial surveys were flown systematically across Block V. By hovering directly above the fault's surface expression, an accurate GPS coordinate could be obtained allowing faults to be mapped onto topographic base maps during the flight. This produced a structural map showing all major rift faults in the region.

Some faults were easily recognised by the presence of major fault scarps with beds rotated to dip into the cliff, however, in areas with little or no exposure faults were identified using a number of observations, for instance:

- Markedly asymmetric hills with raised, angular or rounded footwall crests immediately above a scarp slope,
- The presence of marked scarps which are not obviously due to river incision,
- Low-angled, uniform dip slopes forming obvious benches in the topography,
- Clear elevation differences between hills separated by scarps and across valleys (lowering the helicopter down into valleys until level with the ridges at the top and looking side to side with the long axis parallel to the long axis of the valley made any difference in height extremely apparent.)
- Hanging wall lakes or swamp areas at the base of fault scarps.
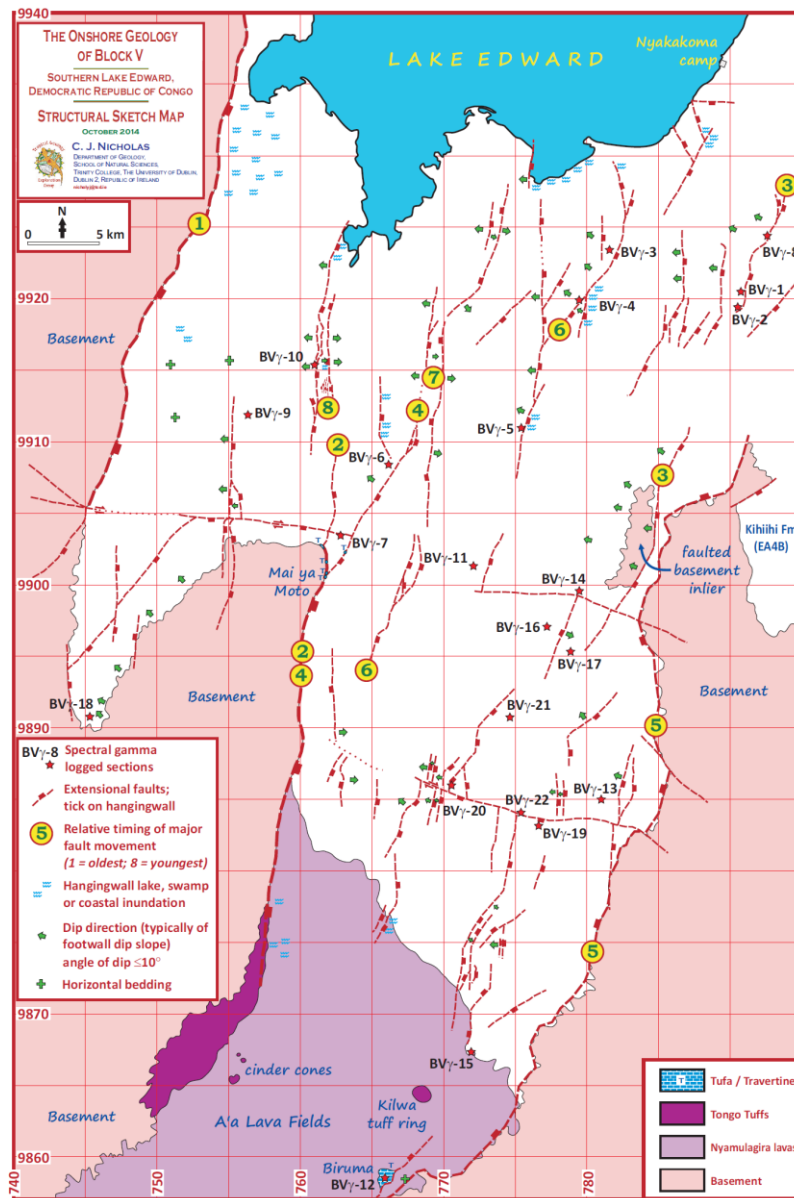
*Figure IV.28: Structural map of onshore Block V showing all major rift faults.*

The serie of field sketch below in figure IV.29 a, b, c, d (SOCO, 2010) illustrates the cross section (not in scale) of the Block V structural configuration evidences from field observations.
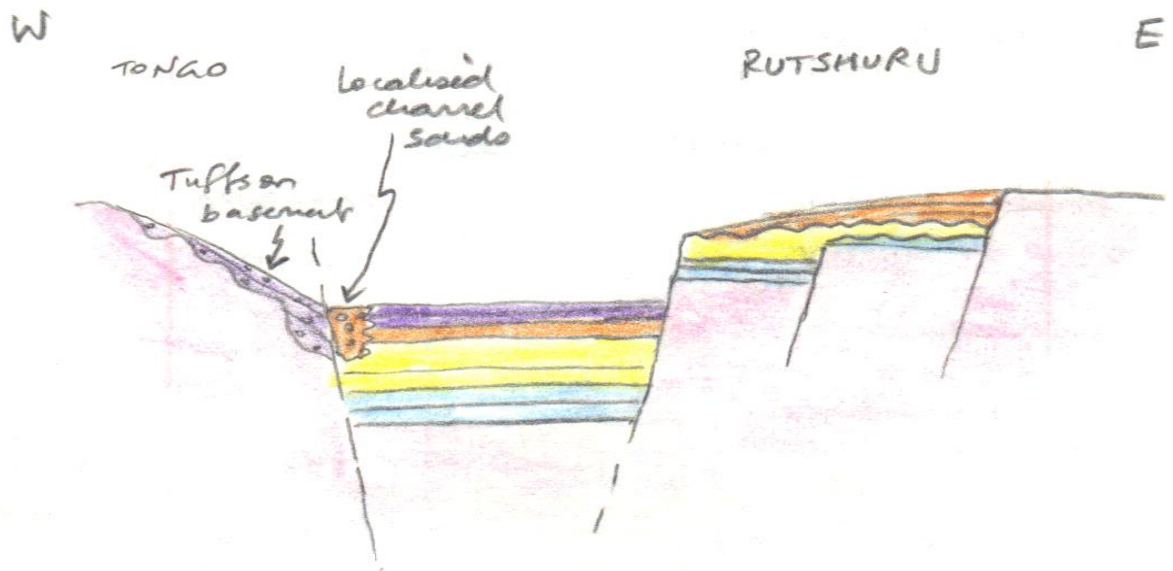
*Figure IV.29 a: not to scale Bloc V sketch cross section  (Nicholas, 2009)*

The Block V 2010 field trip observations helped to understand the generalized explanation of the propagation Rift and development of sequences on the flanks. The figures 52 b, c and d below from field sketch suggest that the propagation of active faults seems to be confined to the central axis and as extension product, the older faults tend to move away from the axis and become less active or inactive.
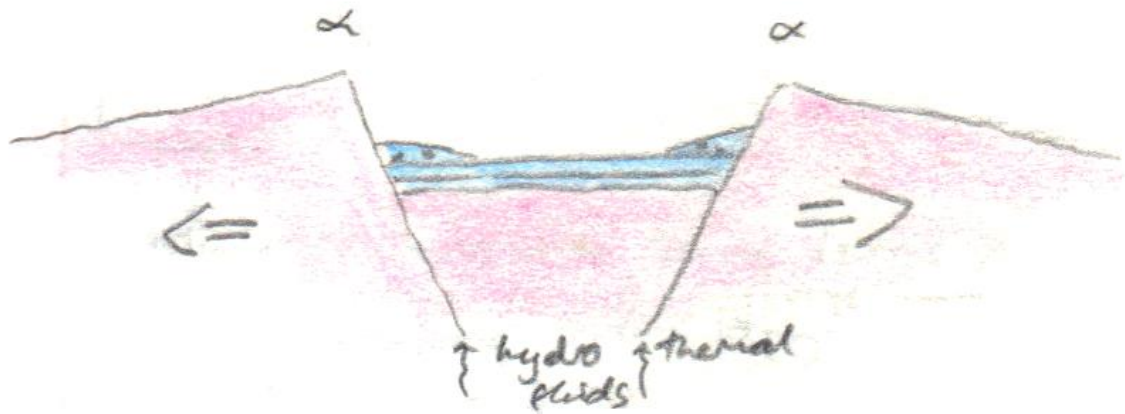


*Figure IV.29 b: not to scale Bloc V sketch cross section  (Nicholas, 2009)*
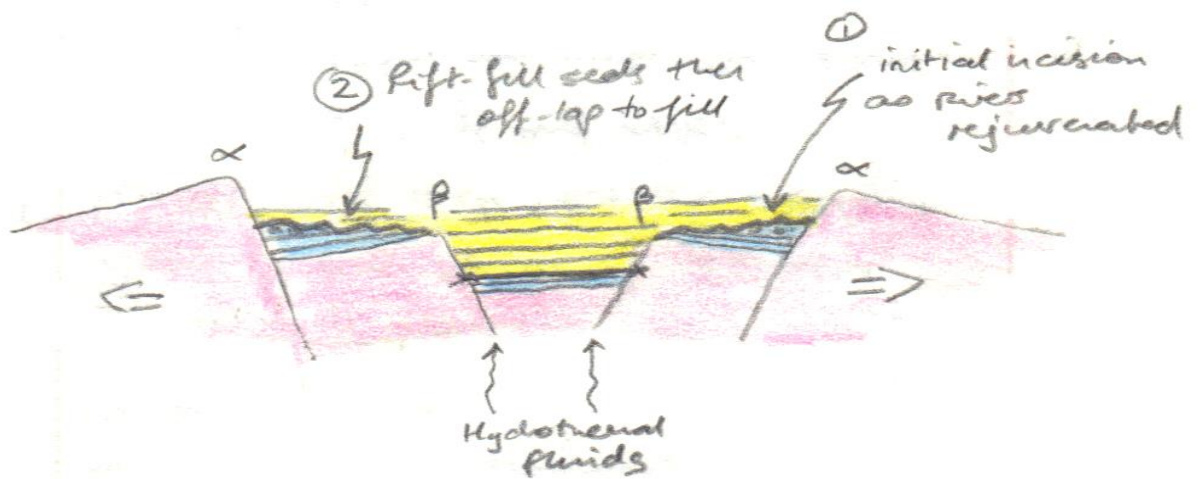
*Figure IV.29 c: not to scale Bloc V sketch cross section  (Nicholas, 2009)*

The structural configuration evidences from field observations reveal that Carbonates Hot water or "hydrothermal fluids" pass through a nearby fractures rocks (active, less active or inactive faults) and possible porous spaces within the rock, altering its own originate chemical composition This chemical alteration can be the result of "adding, removing, or the redistribution of the chemical components as for instance the Calcite content".

Many locations along margin faults field evidences show hot water bubbles up through the surface of the earth.  The related field observations suggest and confirm that each of their resulting Hot springs is produced by the emergence of geothermal heated groundwater that rises carbonates minerals from the Earth's crust.
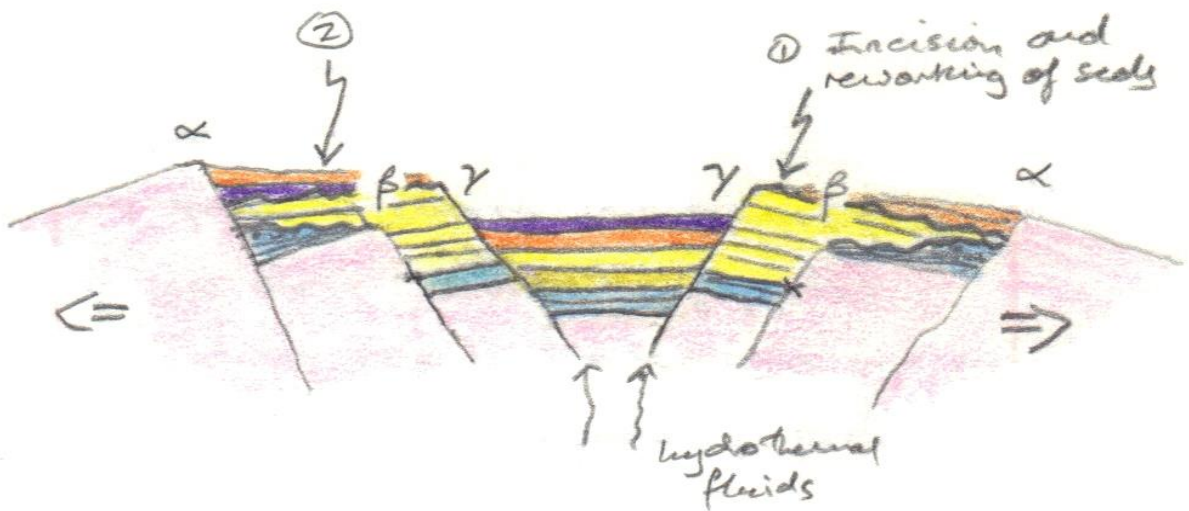


*Figure IV.29 d: not to scale Bloc V sketch cross section  (Nicholas, 2009)*

IV.4.3.2- <u>HEAT AND FLUID FLOW</u>

Hot springs are known at Mai ya Moto, and in 2010 associated palaeo-spring Travertine limestones were documented at Mai ya Moto and further to the south at Biruma.

On this trip several more hot springs and limestones at a further 5 localities were documented, all within 2-5km of Mai ya Moto.

Mai ya Moto itself is a small rocky opening in the bush across which several streams of steaming, foul smelling water slide, spewed from small bubbling springs dotted around the perimeter. Heat loving slimes of yellow, green and black thrive in the flows close to the boiling springs and form long gloopy trails that wiggle in the fast moving water.

These cyanobacteria and/or algae growing at hot spring mouths appear to actively scavenge uranium and thorium, giving them very high TOTAL GR values, with U & Th concentrations falling away over a few metres distance from the spring mouth.

Large black patches of algae were spotted from the air on a rock face just north or Mai ya Moto. Investigation on foot discovered extensive Travertine limestones precipitated along either side of an incised gorge which appeared to follow the basement margin around the nose of the basement spur. Several hot spring sites were present in a series of terraced pools connected by streams.

The Figure IV. 30 and IV.31 below illustrate one of the Hot springs temperature recording in the west bank of the Rutshuru River and the graph of the all temperatures recorded around the zone of interest.



*Figure IV.30:  Measuring the temperature of a hot spring on the east bank of the Rutshuru River.*
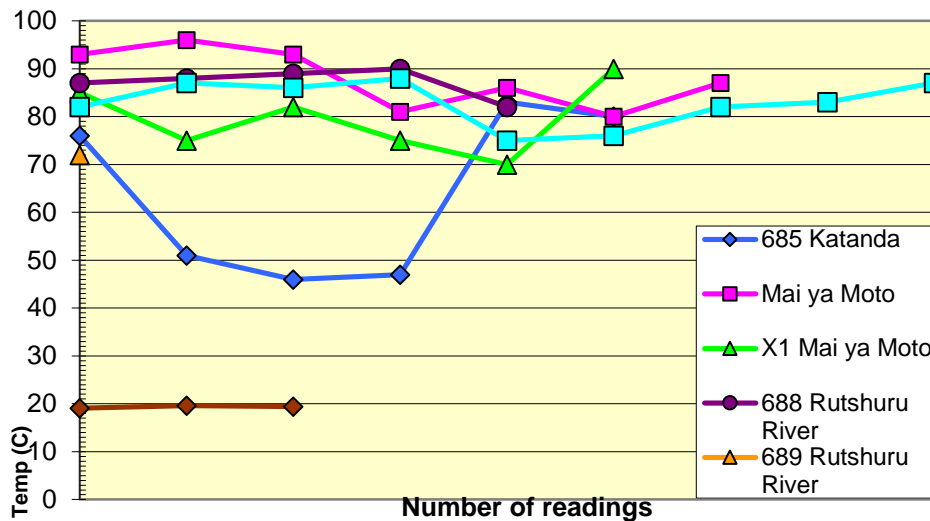
*Figure IV.31: Graph showing spring temperatures at each locality. Temperatures were often above 80 degrees where it hasn't been lowered by passing through a pool of water at the surface. Spring water temperatures were recorded with a digital infrared thermometer.*

<u>*Chapter 4 Conclusion*</u>

*Further to the samples collection for laboratory analysis, the outputs of the 2007 to 2014 series of Travertines field investigation are:*

- *Perfect geologic correlations made between outcrops from both sides of the Albertine Rift basin: for instance, the Bwambara formation in EA4B block in Uganda shows many petrographic similarities with Rutshuru formation in Block V in DRC; the same is for the Kihihi and Kayonza formations in EA4B in Uganda which show many field evidences of common deposit timing with Fuko and Ruindi formations in Block V in DRC. The Kisenyi and Ngaji formations in EA4B suggest approximately some petrographic similarities and common geologic timing of deposit with Kasoso and Kigunda units in Bloc V. The half graben structures from where hydrothermal fluids flow up to the surface along bounding faults are still producing mainly the same Travertine facies on both sides of the DRC and Uganda borders.*

- *The most updated geologic map across all the Lake Edward onshore basin. The figure IV.32 below is showing the whole view of the completed geologic map of the Southern Lake Edward basin summarizing all the updated field informations collected from 2007 to 2014.*
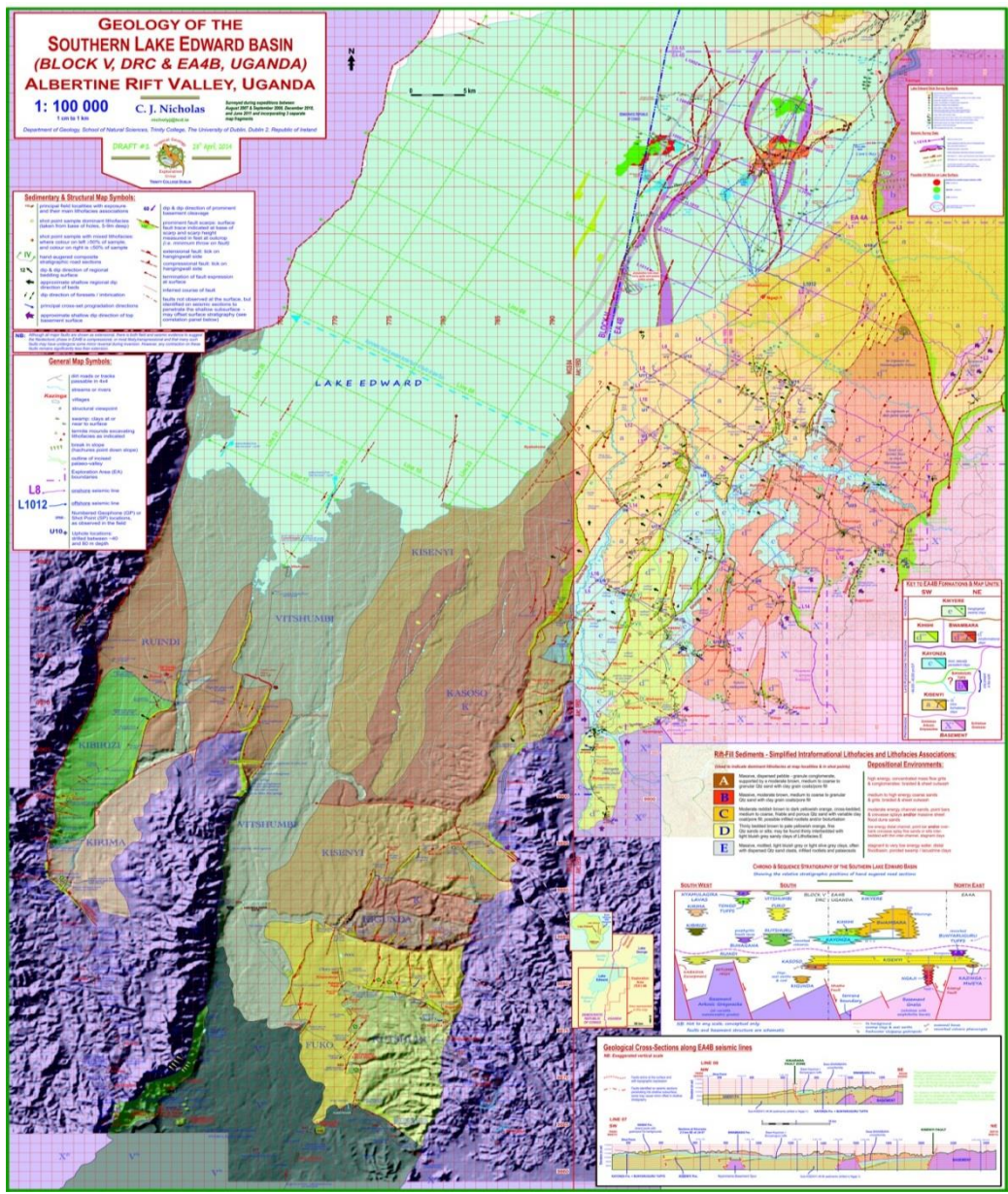
*Figure IV.32:   Completed Geologic Map of the Southern Lake Edward Basin*

- *The possible working chronostrastigraphic framework across southern the Lake Edward basin. As shown in the Figure IV.33 here below, the chrono and sequence stratigraphy of the southern Edward lake basin attempt from field trips informations made the geologic correlation between Block V (DRC) and EA4B ( Uganda).*
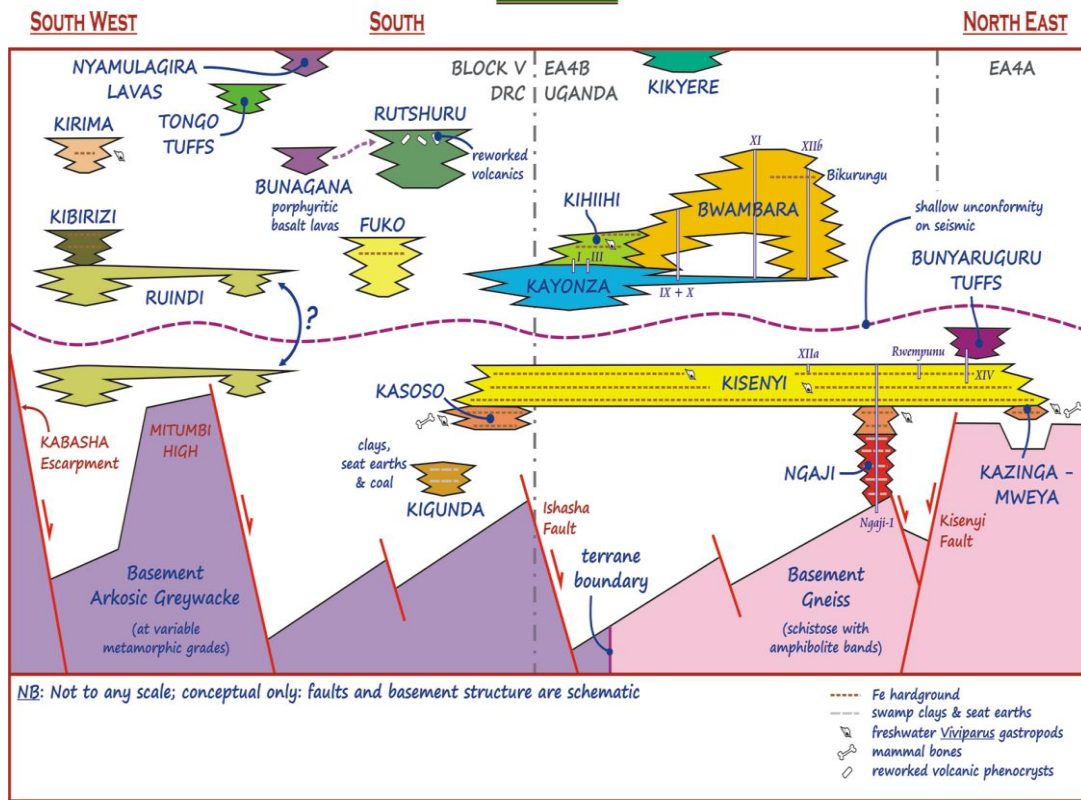
*Figure IV.33:   Completed chrono and sequence stratigraphy of the Southern Lake Edward Basin*

*The next Chapter, entitled Travertines Petrography, is essentially based on the collected Travertines field samples thin sections microscopic observation.*

*It gives the reader a good idea about the respective textures, structures and/or fabrics from each Travertines field samples ideally selected for REE detection by ICP-MS.*
*All the figures exposed in the Chapter below show the location drilling of each Travertine sample in classical thin section size and scale as observable in any microscope.*

# CHAPTER FIVE: EARS TRAVERTINE PETROGRAPHY

This Chapter presents the photographs of Travertine thin sections taken with the Nikon LV100 optical microscope in the Centre of Microscopy analysis (CMA). The Travertine slabs have been polished in thin sections through the fabrics, textures and structures drilled for ICP-MS. The respective microscopy descriptions and interpretations of each carbonate fabric, texture or structure are further discussed below in the discussion chapter.

V.1- TRAVERTINE SAMPLES FROM 2007 TO 2010 FIELD TRIPS

*(Figure V.1: 2007-2010 Travertine thin sections observations)*



P12 a

P12 b

P12 c

P12 d

**P12 e**



Primary porosity fossil tubes gaps lined by dark calcite deposit (7)

Primary porosity gaps filled by rich organic deposit (8)

**LE 24**



**LE 24 a**



**LE 26**



Vugs and Cavities Organic rich and Oil relict filled

**LE 27 a**



Same as LE 26

**LE 27 b**

Vugs and Cavities
Organic rich and Oil relict filled

**LE 27 c**

Same as LE 24

**LE 28 a**

Same as LE 24

**LE 28 b**

Vugs and Cavities
Organic rich and Oil relict filled

**LE 37**

(1)

Fibrous textures

**LE 38**

Vugs and Cavities
Organic rich and Oil relict filled

**LE 41**

Calcite lined Vugs and cavities
Organic rich filled

**LE 42**



Calcareous stalagmite texture with annual growing
layers? Speleothems? Microbial mats?

**LE 44**



Pellets

Vugs porosity calcite lined and visible
rootlets branches and plant
tubes;

**V2**



Black stained lining in white vugs spreaded brown
light carbonates matrix

**V19**



Black stained lining in white vugs spreaded in the
thin section.

**V20**



Black stained lining in white vugs spreaded in
visible carbonate big crystals and cement.

**V22**

## V.2- PCK LIMESTONES SAMPLES



*Figure V.2: PCK carbonate layered Slice.*

## V.3- TRAVERTINE SAMPLES FROM 2014 FIELD TRIP

*Same graphic scale as above thin sections*

◎ *Drilling location anyway into Calcite mineral and cement*
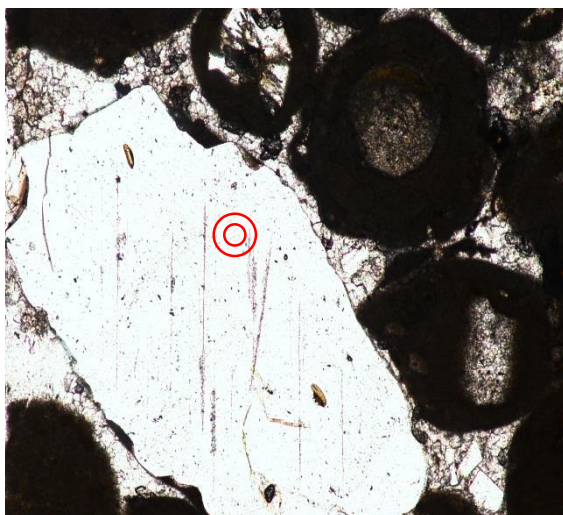


BV 125
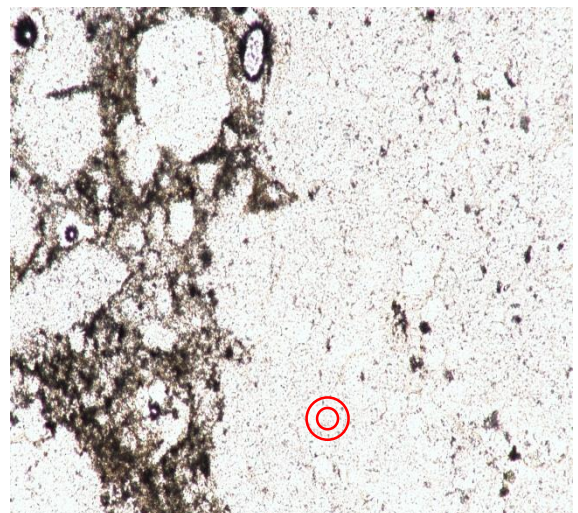


BV 149a
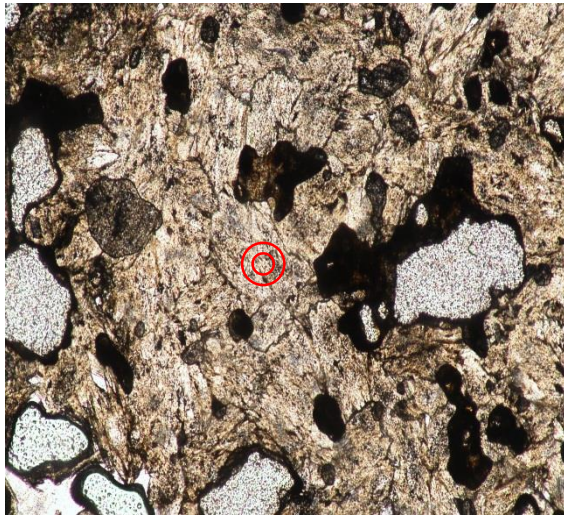
BV 150
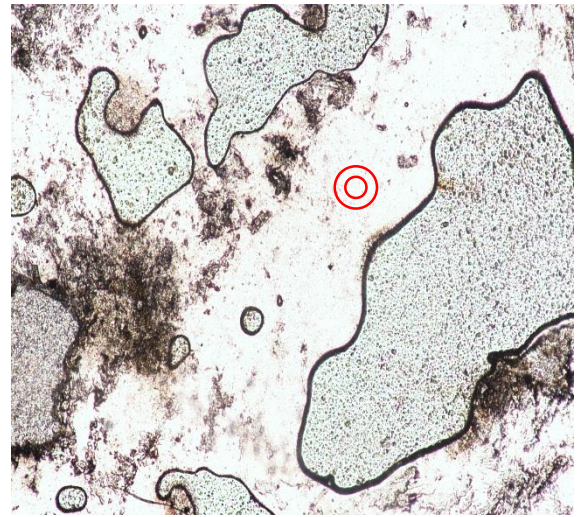

BV 153


BV 159
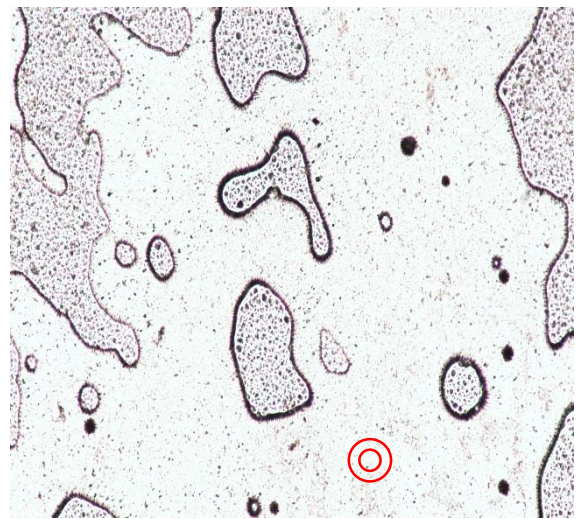

BV 161b
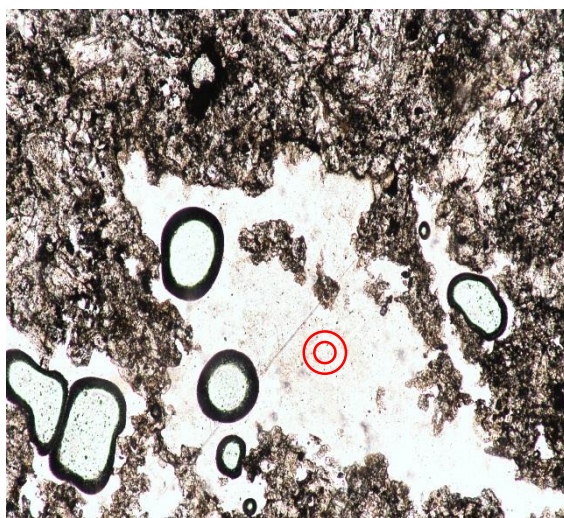

BV 162a
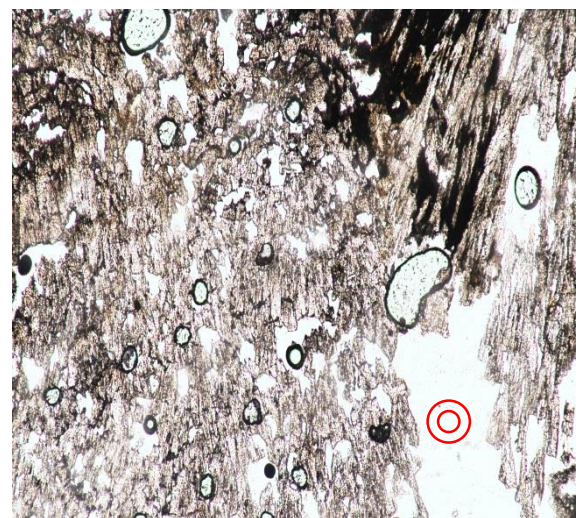

BV 163b
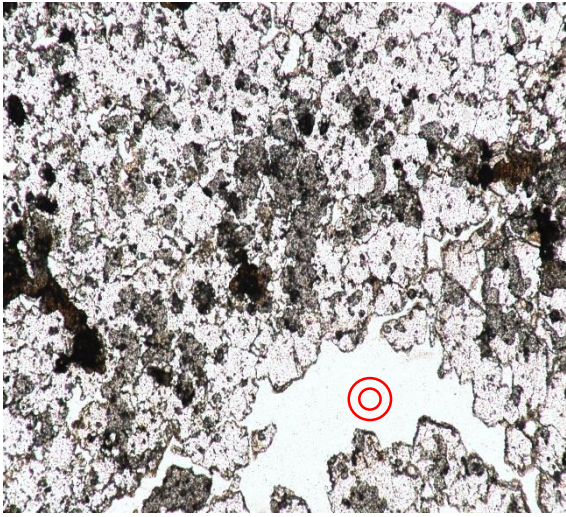
BV 164
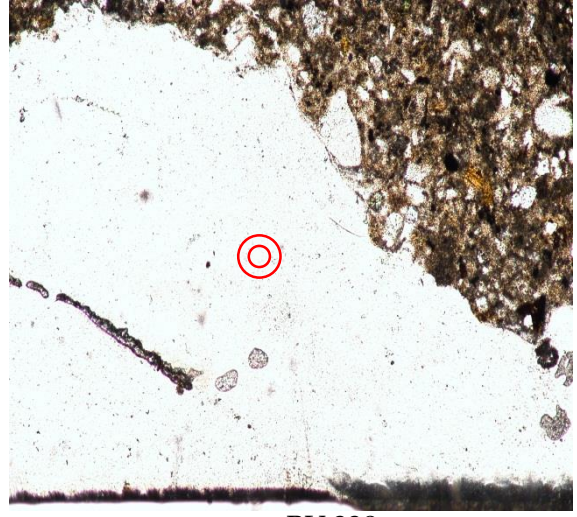

BV 338
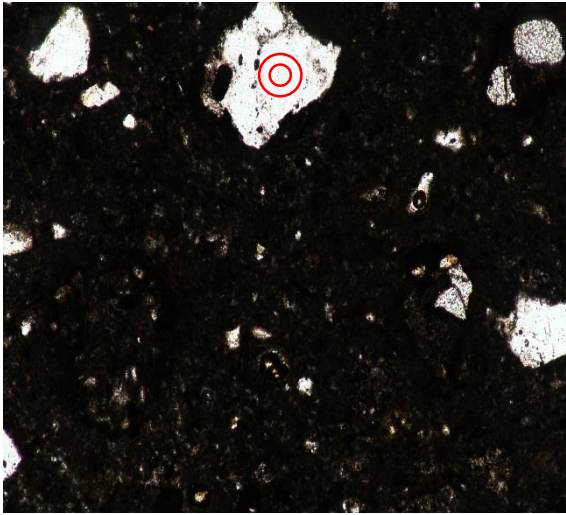

BV 352
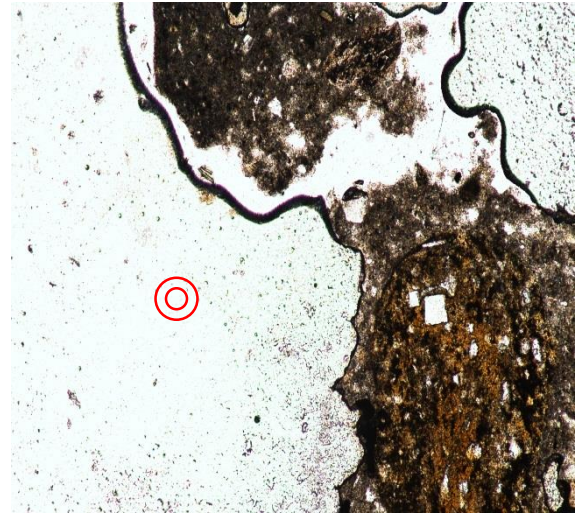

BV 356


BV 363
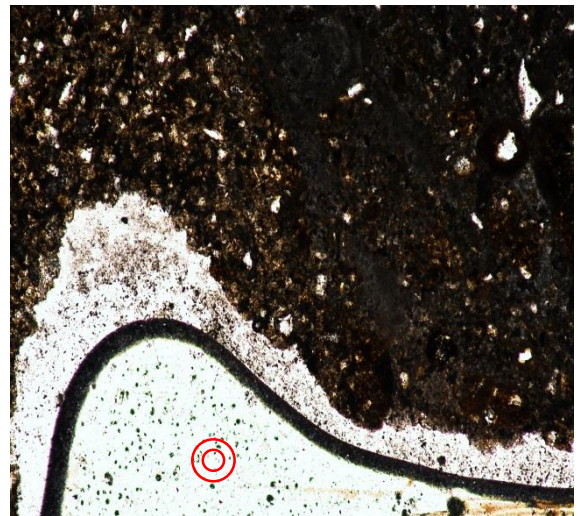

BV 385

## V.4- MANDAWA BASIN LIMESTONES SAMPLES



*MDW 42*



*MDW 43*
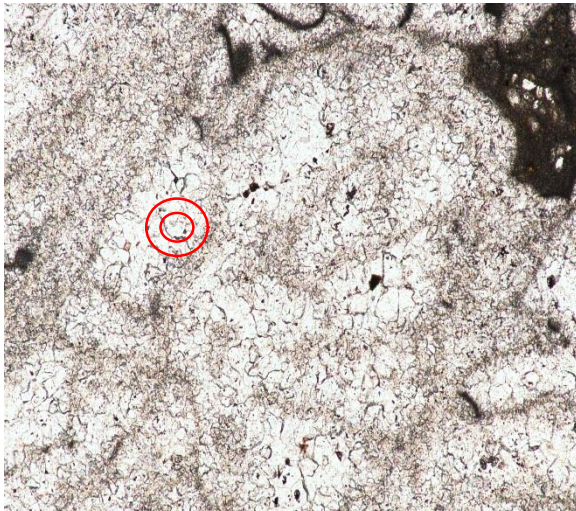


*MDW 74*
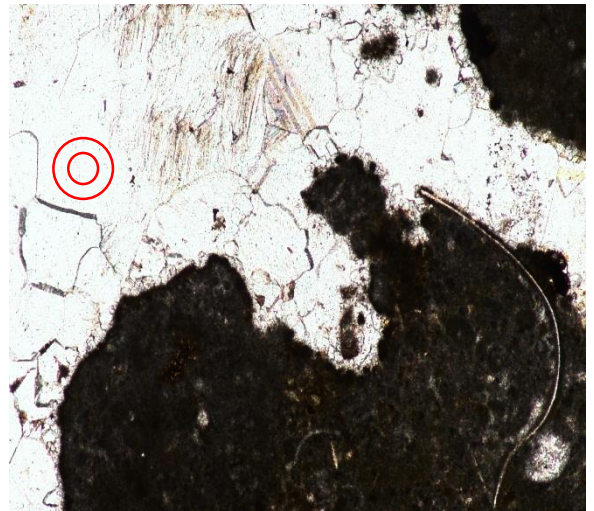


*MDW 162*



*MDW 276*
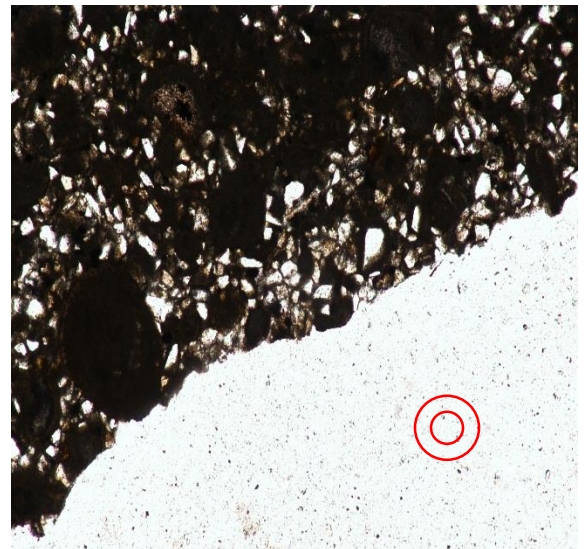


*MDW 277*

*Chapter 5 Conclusion*

*In order to reach out the answer of this present Msc research question about the geochemistry origin of the Bicarbonate found in the EARS Travertines samples, their petrography investigation contributed as below:*

- *The Carbonates textures, structures and/or fabrics observed in the microscope are matching with the Travertines field description and their geological environment location in the Eastern Africa Rift System.*

- *For ICP-MS analysis purposes, the ideal Travertines textures, structures and or fabrics have been identified and their drilling zone opted.*

- *Microscopic structures, textures and/or fabrics are showing the depositional story of successive carbonates layers which should be individually drilled for geochemistry analysis purposes.*

*The next Chapter, titled Geochemistry Results, exposes all the chemical outputs obtained from all samples analysed throughout the present Msc research work. The final results from analysed samples were presented according to their respective location and the timing of the geochemical analysis undertaken.*

# CHAPTER SIX: GEOCHEMISTRY RESULTS

VI.1- ISOTOPE RATIO MASS SPECTROMETRY (IRMS)

The Travertine samples run for IRMS analysis in 2013 were collected along the Edward Lake basin margin fault in Uganda (Lyemubuza, Muhokya, Dura, Hima, Bwera, Bat Cave, Okumu and Sempaya) and DRC (Biruma). The Mayi ya Moto Travertine were collected along the Western margin fault in DRC side. Figure VI.1 below:
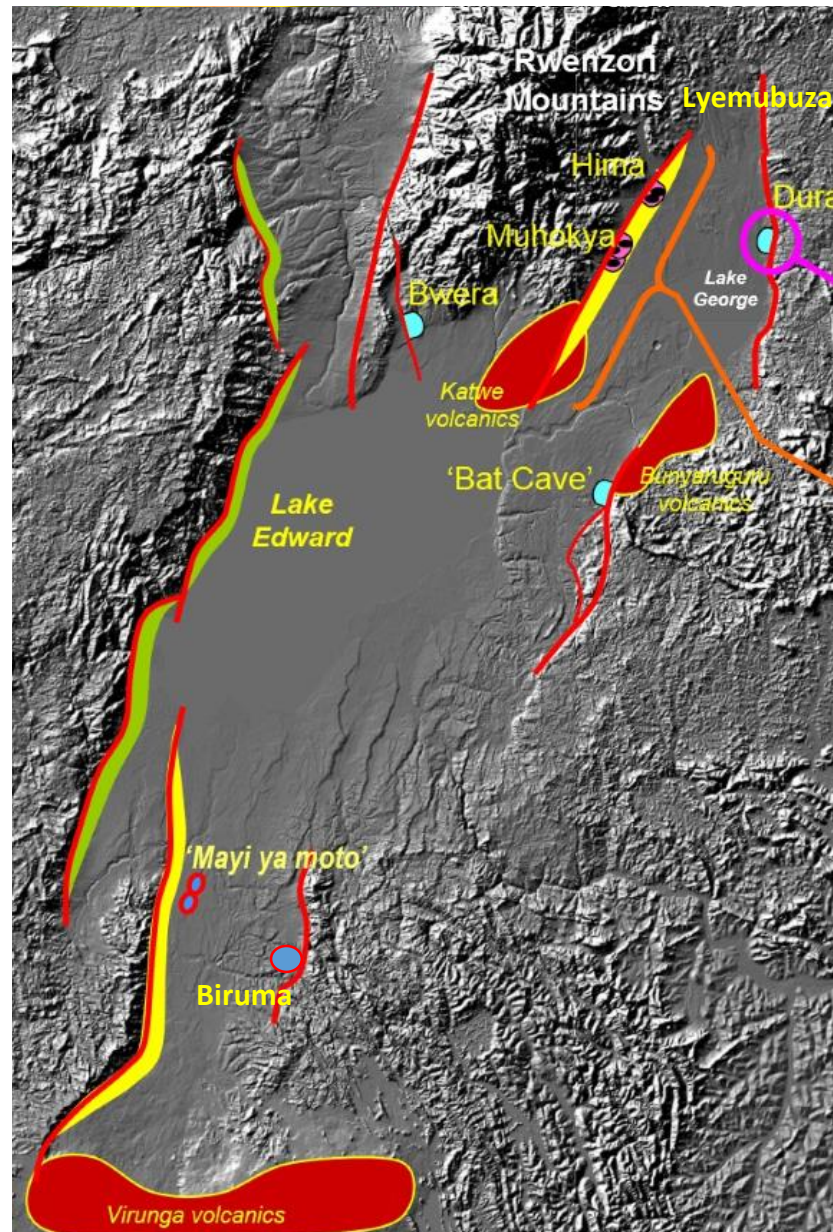


*Figure VI.1:  Travertine samples locations in the Lake Edward basin.(Nicholas et al., 2016)*

According to (Lynch-Stieglitz et al., 1995) :

- Magmatic carbon in a carbonate would be expected to have a $\delta^{13}C$ between -7 and -10 $^0/_{00}$ relative to PDB belemnite.

- Marine carbon in a carbonate would be expected to have a $\delta$ 13 C between -2 and +2 $^0/_{00}$ relative to PDB belemnite.

A higher abundance of $\delta^{18}O$ in calcite is indicative of colder water temperatures, since the lighter isotopes are all stored in the glacial ice and the lower abundance of $^{18}O$ in the calcite (Travertine samples) indicates the warmer temperatures.(Hays and Grossman, 1991)

The graph illustrated in the Figure VI.2 below, presents the C and O stable isotopes ratio of the Edward basin Travertine samples analysed by IRMS in 2013:
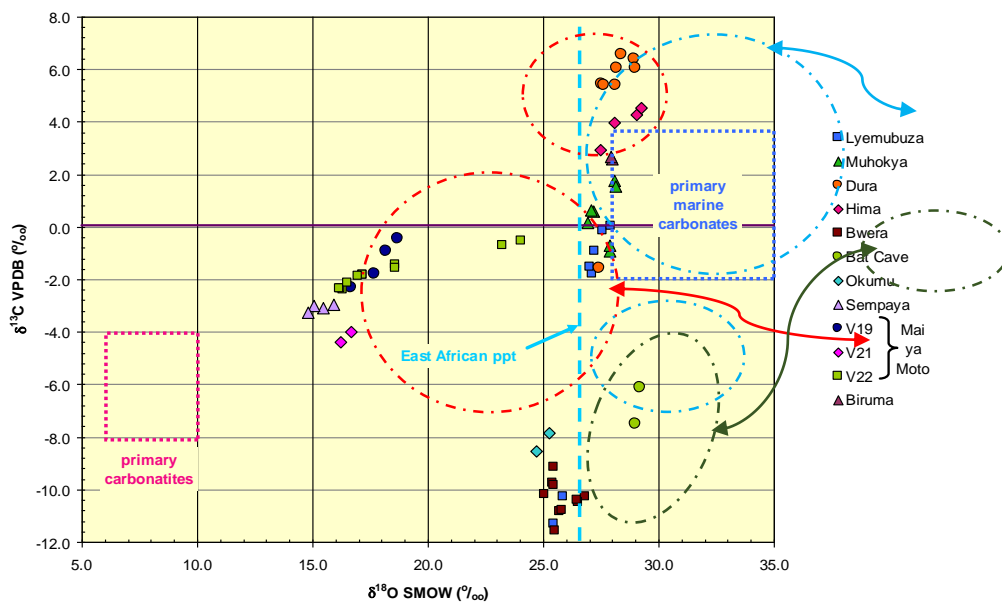


*Figure VI.2: Edward Lake basin carbon (PDB) versus oxygen (SMOW) stable isotopes*

VI.1.2- CARBON (PDB) VERSUS OXYGEN (PDB) STABLE ISOTOPES

According to (Lynch-Stieglitz et al., 1995) :

- Magmatic carbon in a carbonate would be expected to have a $\delta^{13}C$ between -7 and -10 $^0/_{00}$ relative to PDB belemnite.

- Marine carbon in a carbonate would be expected to have a $\delta$ $^{13}C$ between -2 and +2 $^0/_{00}$ relative to PDB belemnite.

A higher values of both $\delta^{13}C$ (PDB) and $\delta$ $^{18}O$ (PDB) in calcite is indicative of $CO_2$ outgassing evaporation, since the $^{16}O$ and $^{13}C$ isotopes are all removed and the lower values of both $\delta^{13}C$ and $\delta$ $^{18}O$ in calcite (Travertine samples) indicates a zone of $CO_2$ contribution.

The graph illustrated in the Figure VI.3 below, presents the C and O stable isotopes ratio of the Edward basin Travertine samples analysed by IRMS in 2013
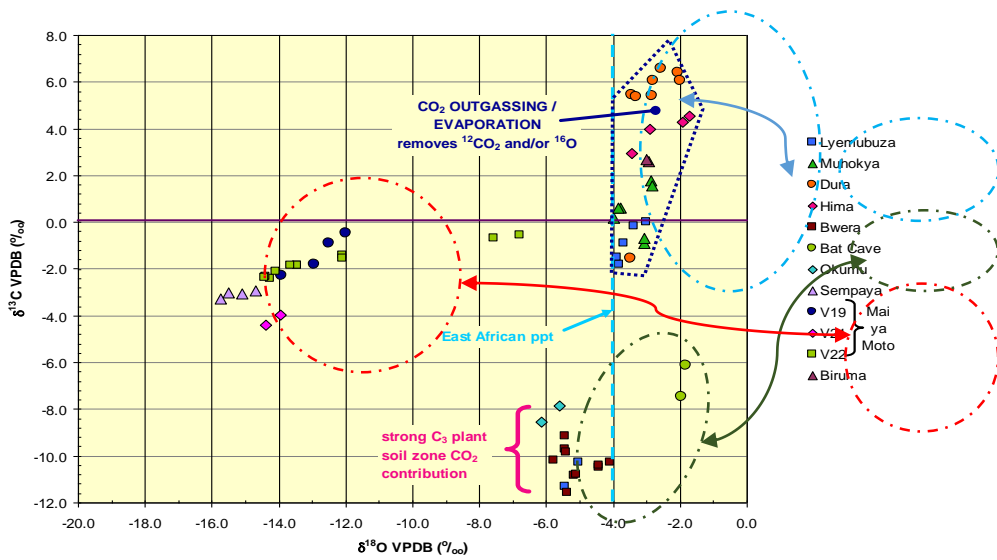


*Figure VI.3: Edward Lake basin carbon (PDB) versus oxygen (PDB) stable isotopes*

VI.1.3- CARBON (PDB) VERSUS TRAVERTINE PRECIPITATION TEMPERATURE

According to (Lynch-Stieglitz et al., 1995) :

- Magmatic carbon in a carbonate would be expected to have a $\delta^{13}C$ between -7 and -10 $^0/_{00}$ relative to PDB belemnite.
- Marine carbon in a carbonate would be expected to have a $\delta^{13}C$ between -2 and +2 $^0/_{00}$ relative to PDB belemnite.

The graph illustrated in the Figure VI.4 below, presents the C (PDB) stable isotopes ratio of the Edward basin Tufa/ Travertine samples analysed by IRMS in 2013.
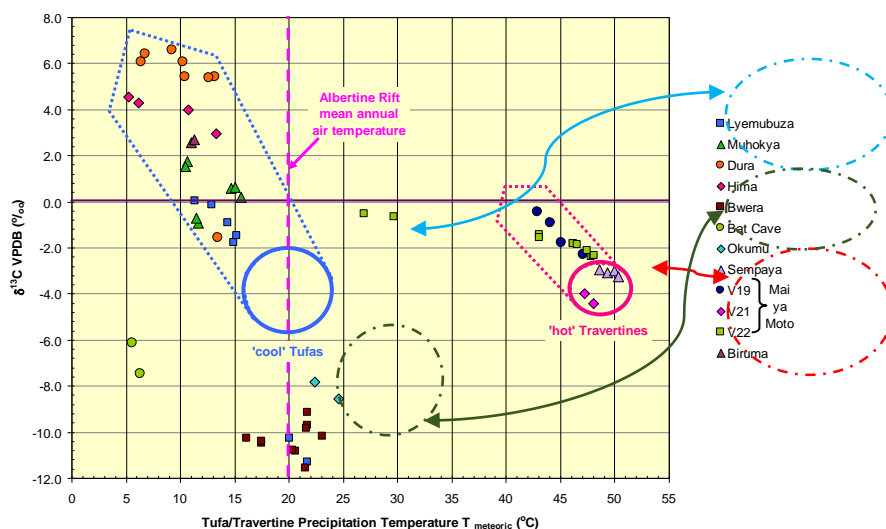


*Figure VI.4 Edward Lake basin carbon (PDB) stable isotopes versus site temperature*

## VI.2- STRONTIUM ISOTOPE RATIO ANALYSIS

Based on the following assumptions that three major input sources influence the Strontium isotope composition of the sea and ground water (Wierzbowski, 2013) :

- Strontium of low $^{87}Sr/^{86}Sr$ ratio around 0.703 is derived from hydrothermal circulation at mid-ocean rides and volcanic zones;
- Strontium of intermediate 87Sr/86Sr ratio between 0.707 and 0.709 originates from submarine dissolution and recrystallization of carbonates sediments.
- Strontium of high $^{87}Sr/^{86}Sr$ ratio around 0.711 is derived from continental weathering;

The analysis results of Travertine samples shown in the table below suggest a very high range of strontium isotope ratios from 0.7068069 to 0.7482648.

However, Only 2 values (LE 41 from Bwera and LE42 from Dura) are within the range expected for marine carbonates. These two values have been plotted in both the Burke and Wierzbowski Phanerozoic 87Sr/86Sr ratio variation graphs below: (Figure VI.5 and VI.6)

| Sample | LE24 A | LE26 A | LE27 A | LE28 A | LE41 A | LE42B A | LE37 A | LE38 A | V20B |
|---|---|---|---|---|---|---|---|---|---|
| $^{87}Sr/^{86}Sr$ | 0.7482 64 | 0.7487 56 | 0.7380 57 | 0.7388 00 | 0.7071 20 | 0.7068 06 | 0.7152 75 | 0.7153 47 | 0.7457 00 |
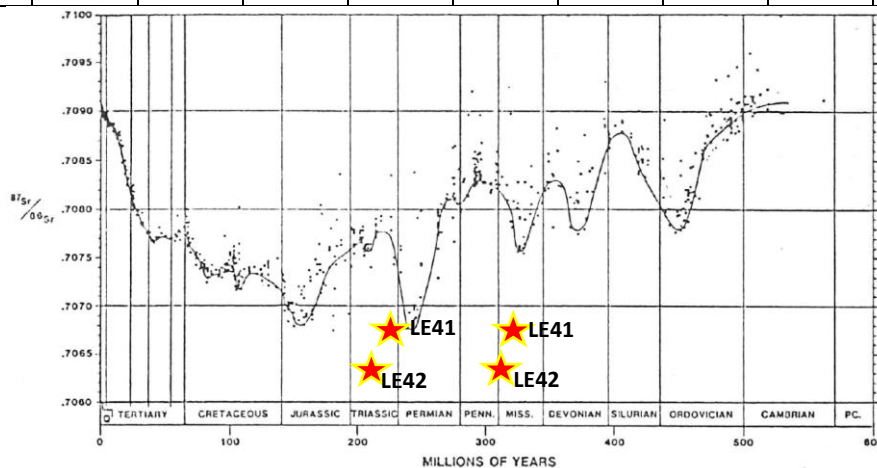


*Figure VI.5    87Sr/86Sr ratio variation of Phanerozoic seawater.(Burke et al., 1982)*
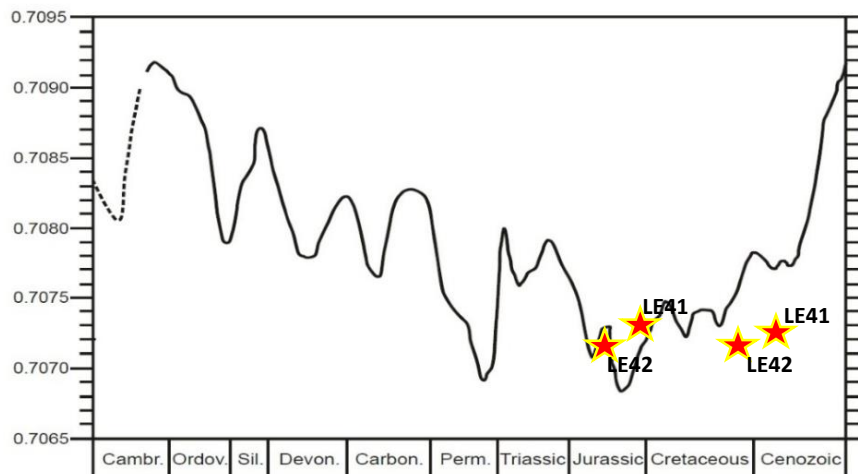


*Figure VI.6:    87Sr/86Sr ratio variation of Phanerozoic seawater. (Wierzbowski, 2013)*

The plotting of these 2 samples in the below Phanerozoic graphs suggest their possibly Late Jurassic or Late Permian age or possibly late Neoproterozoic as their plotting in the Sr seawater isotope curve here below in Figure VI.7 for the Late Neoproterozoic and Cambrian (Nicholas, 2009):
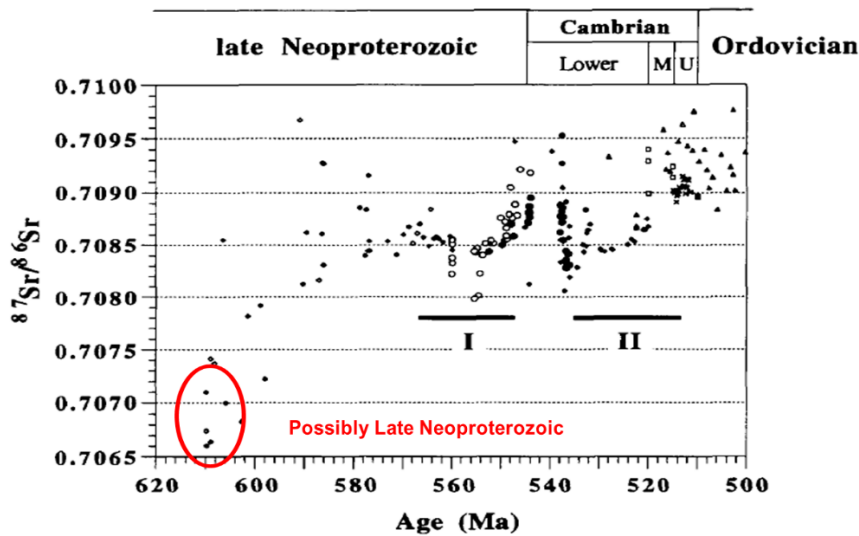


*Figure VI.7:    87Sr/86Sr ratio curve for the Proterozoic. (Nicholas, 2009)*

## VI.3- GC-GCMS ANALYSIS

The crude oil identification of the black staining in Lyemubuza (Uganda) Travertine is accomplished on the bases of a quantitative comparison between their respective ion chromatograms and biomarkers distribution with the famous Oil slick samples LES 15 and LES 18 collected from the Lake Edward during the slick survey conducted from 28th August to 1st September 2008.(Nicholas, 2009)

The slicks presenting the form of long trails of white 'foam' (Figure VI.8 below) were   investigated by GC-GCMS by the motivation of many various unconfirmed satellite and aerial reports of possible oil slicks out on the Lake Edward.



*Figure VI.8 :    Oil slicks collected  in the Lake Edward.(Nicholas, 2009)*

Sampling of these possible oil slicks was undertaken using special, sterile lyophilic cloths which absorb low concentrations of dispersed oil into the fabric.

As shown in the Figure VI.9 below, the sterile lyophilic cloths were attached to metal clips and secured on the end of a telescopic pole.



*Figure VI.9 :     Sterile lyophilic cloths for Oil slick collection.(Nicholas, 2009)*

GC / GCMS analyses which were then performed on the Lake Edward Oil slick samples have confirmed the mature hydrocarbons signature illustrated in the (X, Y) graph below (Figure VI.10) where:

- X axis indicates the retention times of the respective n-alkanes in the mass spectrograms;
- Y axis indicates the ions abundance number and % in the sample.
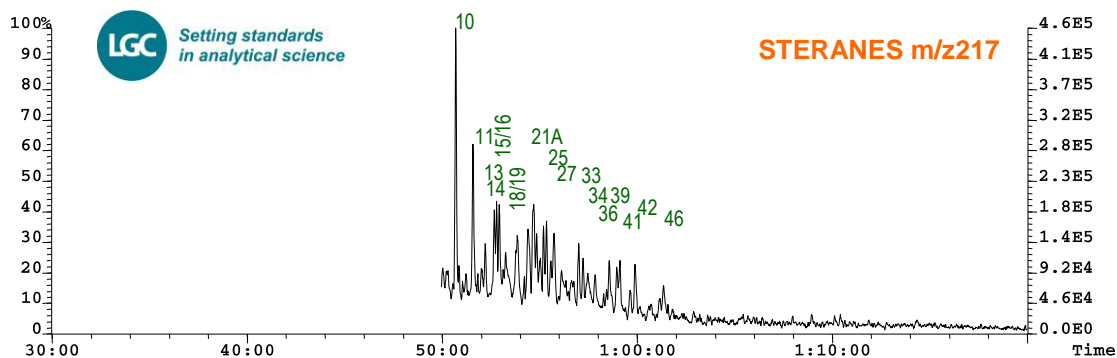


*Figure VI.10 :     GC–MS-extracted ion profiles of norhopanes, hopanes, methyl hopanes, steranes, and monoaromatic steranes in Lake Edward oil sample (LES 15).(Nicholas, 2009)*

The figure here above indicates the peaks distribution of n-alkanes, isoprenoids, polycyclic aromatic hydrocarbons and their alkyl-homologues, and biomarker compounds (hopanes and steranes) which were used as bench marks for certain $C_n$ interval fixation in the Oil slick collected in Lake Edward in 2008.

According to the results above illustrated, the Lake Edward slick is proven to be a live crude Oil and could be used for reference comparison with the Lyemubuza black staining in Travertine cavities.

## VI.3.1- GCMS RESULTS FOR (LES 18) SAMPLE

The GCMS results on the oil slick Sample LES 18 are presented in the graphs below:
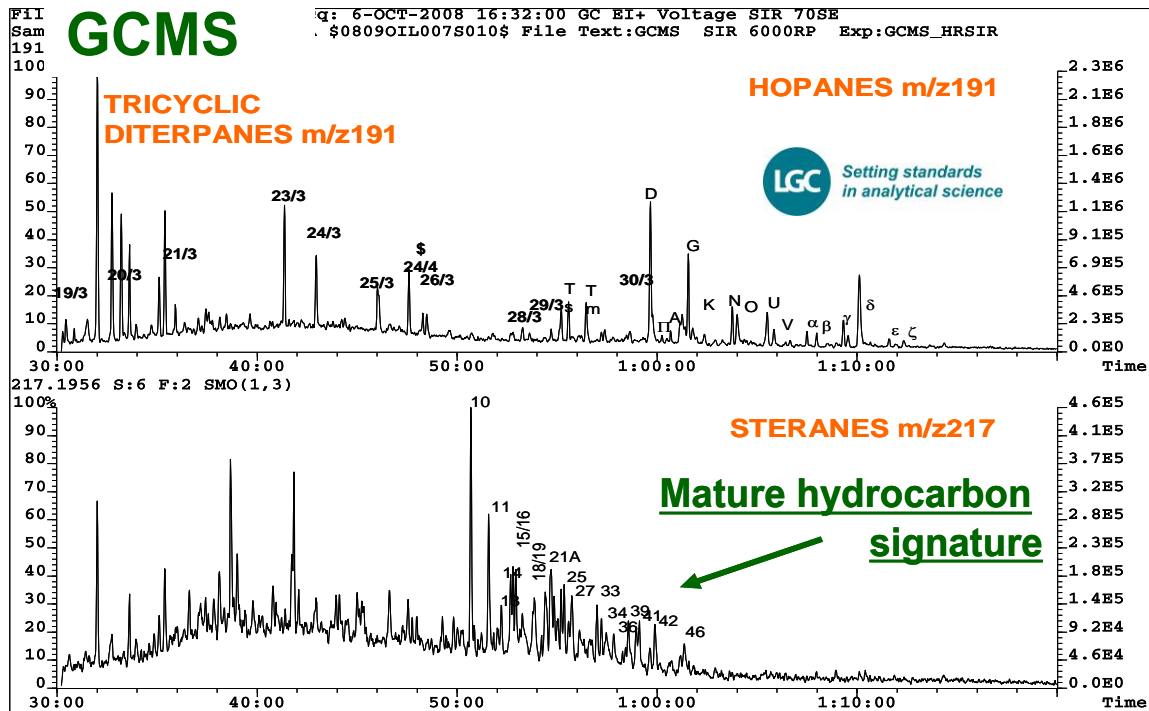


*Figure VI.11:    GC–MS-extracted biomarker distribution from sample LES 18.
(Nicholas, 2009)*

According to Chris Nicholas, The biomarker distribution from sample LES 18 indicates a marine shale source mixed with a waxier, lacustrine component.(Nicholas, 2009)

## VI.3.2 – GC-GCMS RESULTS FOR LYEMBUMUZA (LE25) SAMPLE

The GC results on the Sample LE 25 are presented in the graph below:
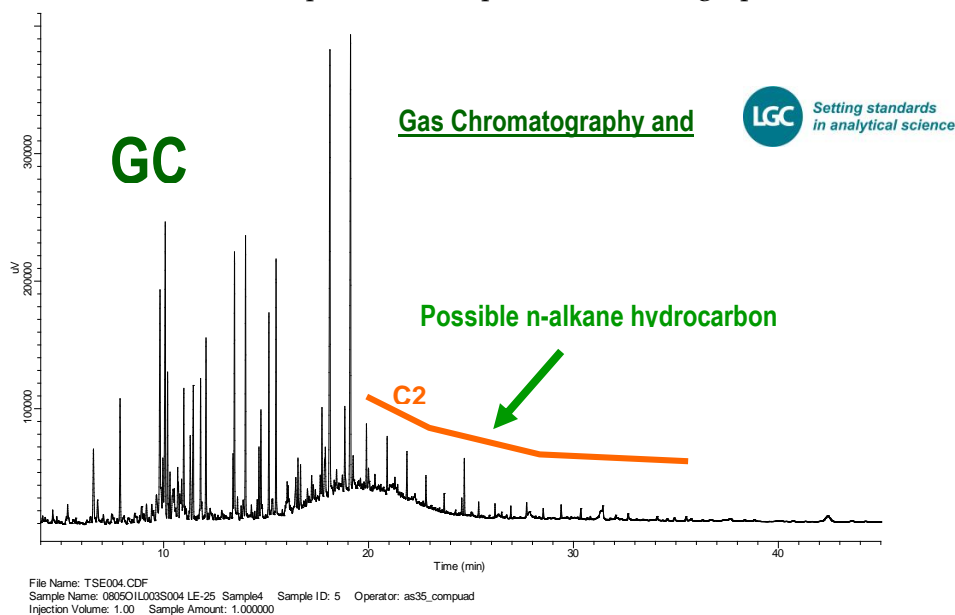


*Figure VI.12 :    GC results sample LE 25 from Lyemubuza quarry.(Nicholas, 2009)*

## VI.3.3 – GC-GCMS RESULTS FOR LYEMBUMUZA (LE25) SAMPLE

The GCMS results on the Sample LE 25 are presented in the graph below:
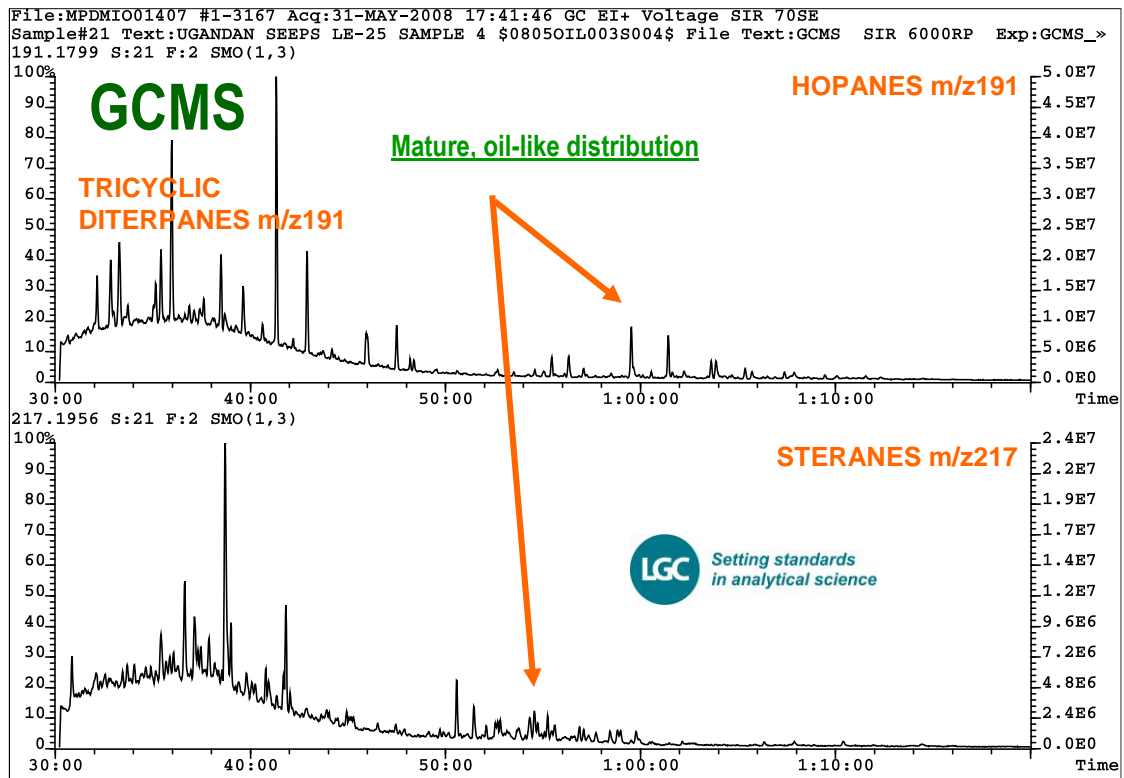


*Figure VI.13 :    GCMS results sample LE 25 from Lyemubuza quarry.(Nicholas, 2009)*

## VI.3.4- CG RESULTS FOR MUHOKIYA SAMPLE (LE 27)

The GC results on the Sample LE 27 are presented in the graph below:
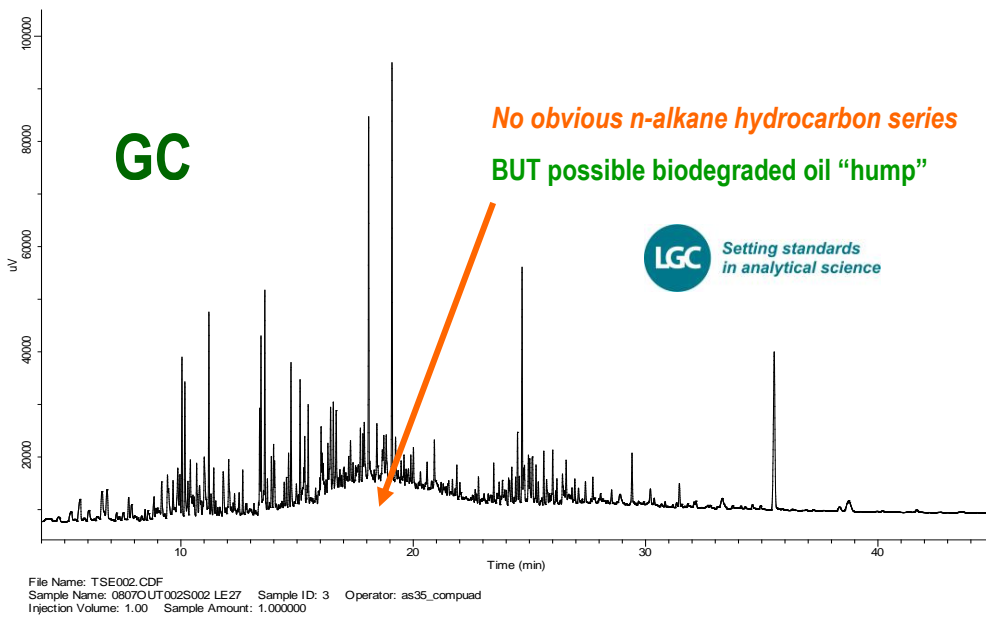


*Figure VI.14    GC results sample LE 27 from Muhokiya quarry.(Nicholas, 2009))*

## VI.3.5- CGMS RESULTS FOR MUHOKIYA SAMPLE (LE 27)

The GCMS results on the Sample LE 27 are presented in the graph below:
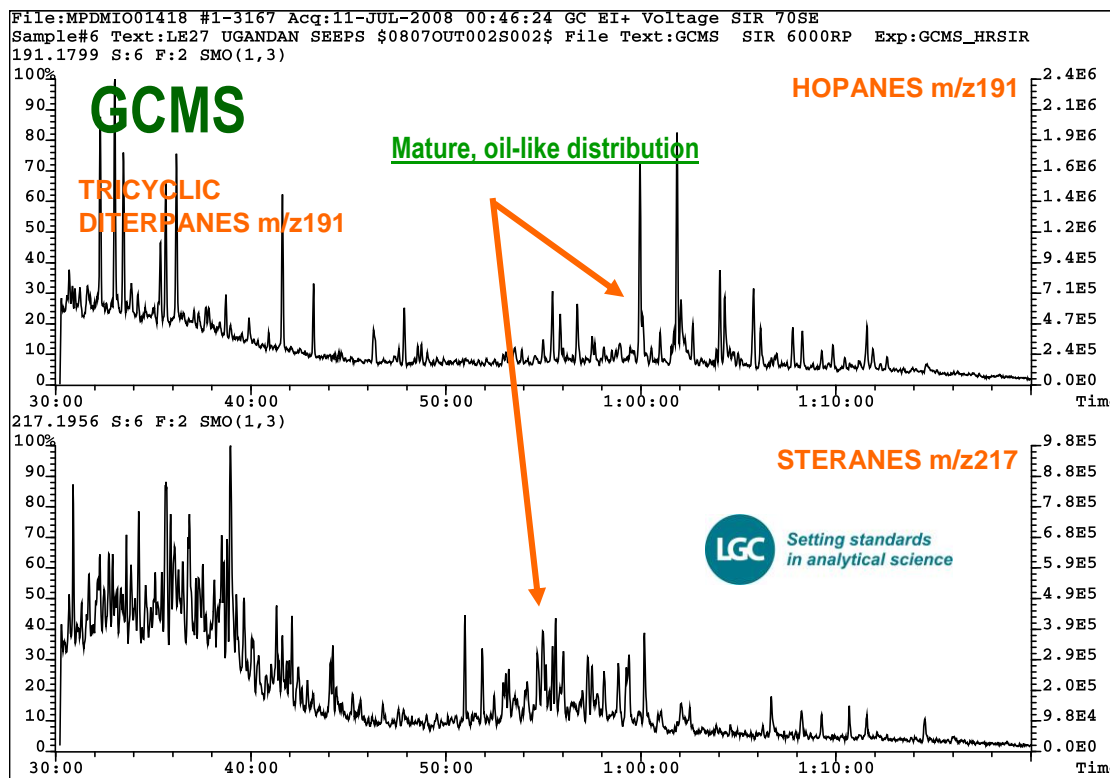


*Figure VI.15 :   GCMS results sample LE 27 from Muhokiya quarry.(Nicholas, 2009)*

## VI.3.6- SUMMARY OF THE GC-GMS RESULTS

The GC-GCMS results obtained in 2008 by LGC Standards from the EA4A onshore Oil stains found in oolithes of Tufa/Travertine samples have been compared to those of the Edward Lake slicks. Their summary has been plotted in the triangular graph below in Figure VI.16 illustrating the AAA Steranes Distribution of Ugandan seeps and slicks.
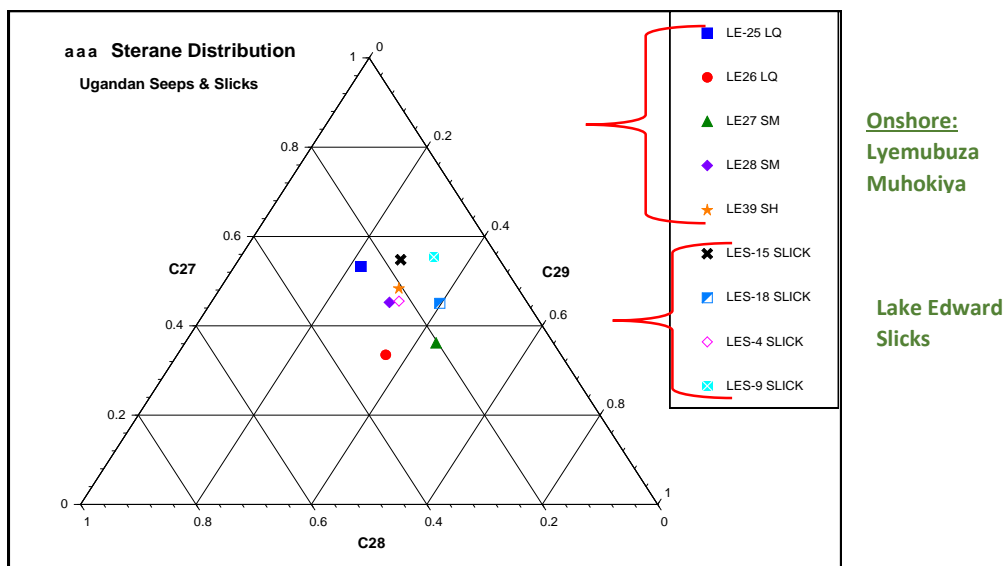


*Figure VI.16 :   Plots of C27 – C29, aaa and abb Steranes distributions from Lake Edward slicks and the Lyemubuza + Muhokya limestones.(Nicholas, 2009)*

## VI.4- INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)  results illustrate the measure of the low detection of  Rare earth elements (REE) concentrations including the lanthanide series elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) plus Sc and Y).

ICP-MS method which is the main experiment used to reach the objectives of this present MSc research, has been done three times for Carbonates geochemical origins purposes:

- *In **2013** by Jean Dwyer, Sylvain K. Mangoni and Michael Babechuk using the 2007 to 2010 Travertine samples collected in Albertine Rift basin;*
- *In **2016** by Sylvain K.M and Cora mc Kenna using the end members samples of the previous experiment and the PCK limestone sample to confirm the ICP-MS results reproducing ability regardless to the time and human resources (after 3 years and with different human resources team);*
- *In **2018,** after method confirmation by Sylvain and Cora using the 2014 Travertine samples collected in Block V;*

### VI.4.1 - ICP-MS RESULTS OF 2013 EXPERIMENT

The ICP-MS results of the 2013 experiment have produced the elements concentrations in ppb and normalized in MUQ as per Kamber experiment method. These values are presented in the tables in appendix 2 and their original excel files (ICP_MS2013.xls) enclosed to this thesis in memory stick.
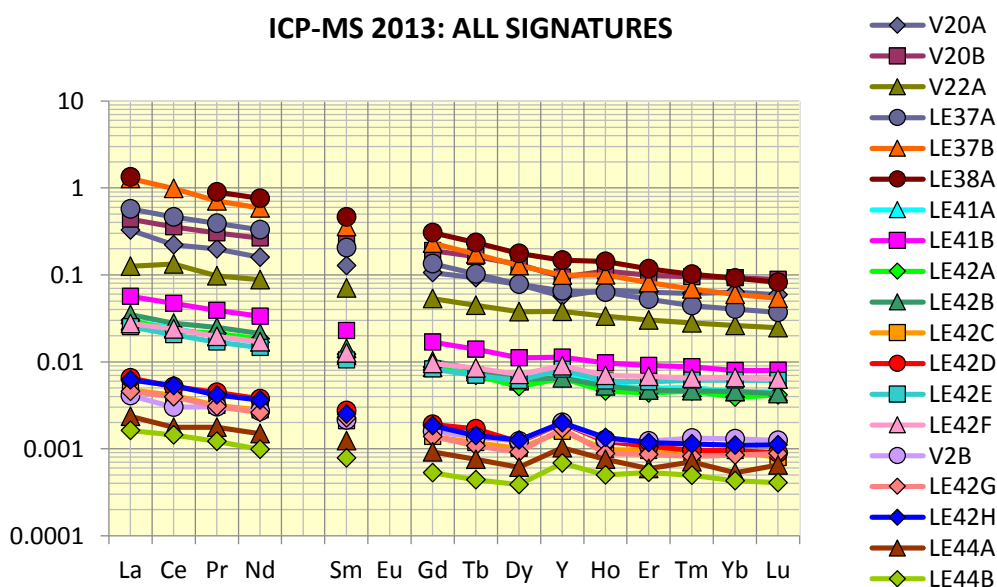


*Figure VI.17:    2007- 2010 Block V Travertine REE signatures by ICP-MS in 2013*

Samples (fabrics, textures, structure and/or their replica) correlating with Fort Portal Carbonatite #3 (Stoppa and Schiazza, 2013) with a Correlation Coefficient of R2 > 0.95, are shown plotted alongside all Fort Portal Carbonatites & Freshwater Sediments in the Figure VI.18 below:
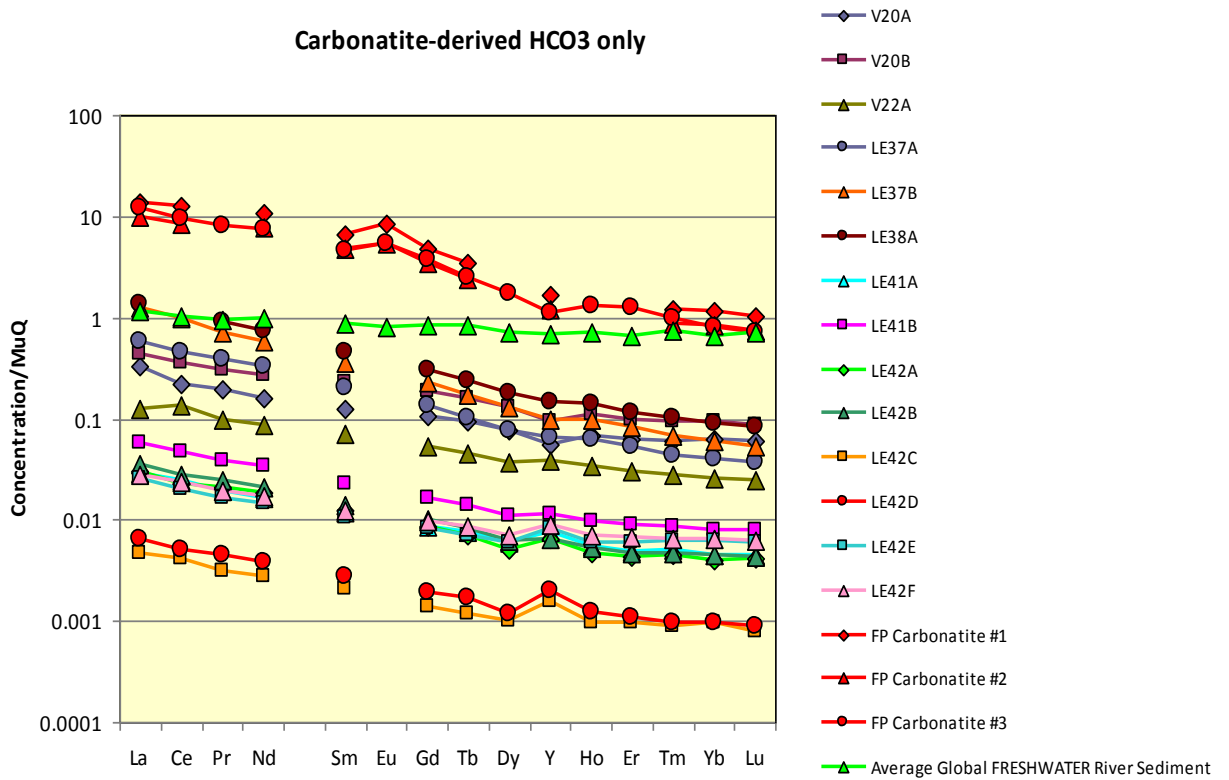


Figure VI.18:    ICP-MS Carbonatites Travertine signature shown plotted alongside all Fort Portal Carbonatites & Freshwater Sediments.

Samples (fabrics, textures, structure and/or their replica) correlating with Fort Portal Carbonatite #3 (Stoppa and Schiazza, 2013) with a Correlation Coefficient of R2 > 0.95, are shown plotted alongside all Fort Portal Carbonatites in the Figure VI.19 below:
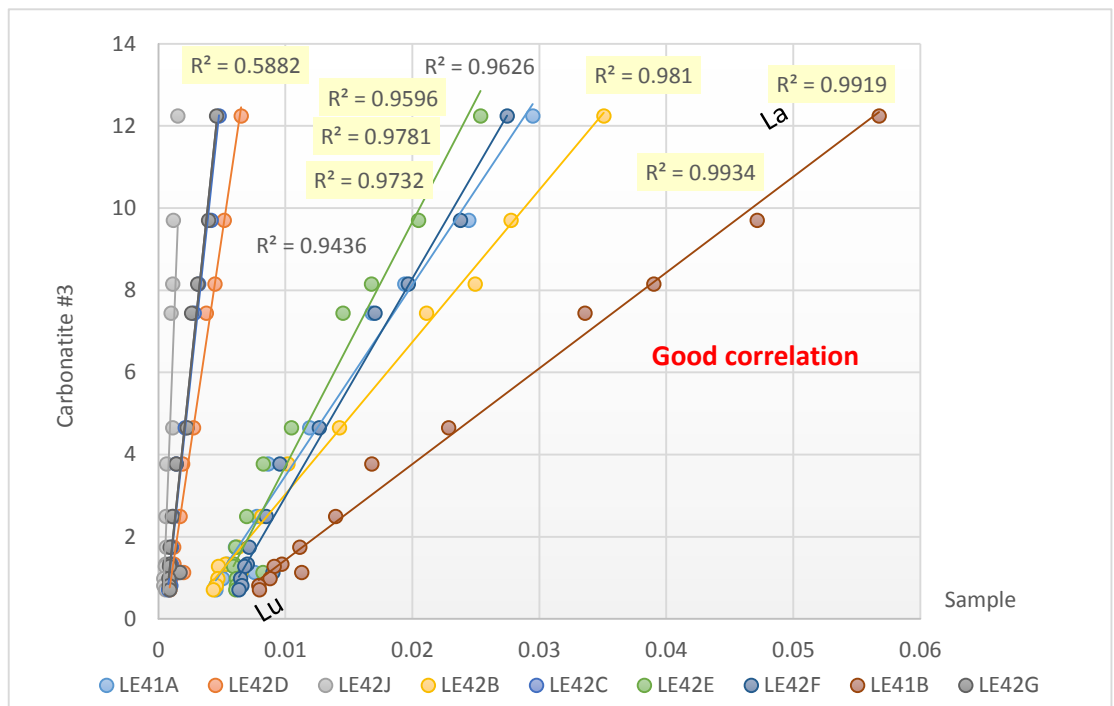
*Figure VI. 19:  Chart of Carbonatites Travertine correlation coefficient with Fort Portal Carbonatites.*

VI.4.1.2- <u>2013 TRAVERTINE WITH MARINE LIMESTONE SIGNATURES</u>

Samples (fabrics, textures, structure and/or their replica) satisfying all the 5 geochemical main criteria of Marine limestones involvement (Kamber et al., 2014), are shown plotted with modern Seawater, Holocene Marine Limestones and Devonian Reef Limestones in the Figure VI.20 below :
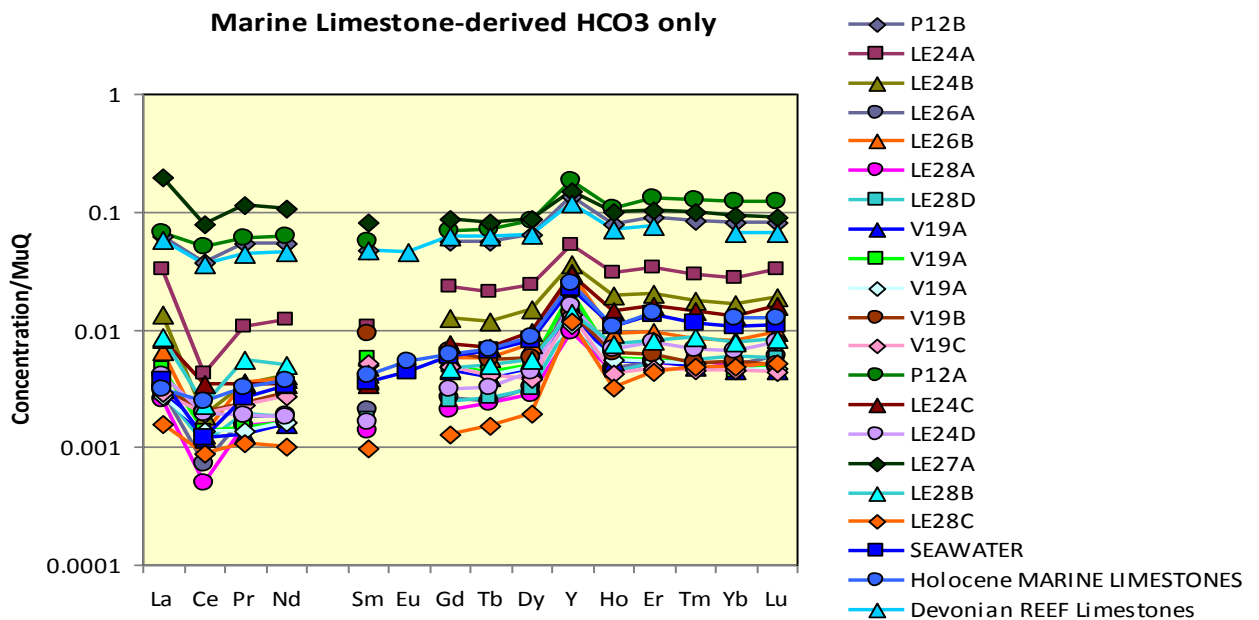


*Figure VI.20:    ICP-MS Marine limestones Travertine signature shown plotted alongside Holocene Marine Limestones and Devonian Reef Limestones & Seawater Sediments.*

Samples (fabrics, textures, structure and/or their replica) from Ugandan side correlating with Devonian Reef limestones (Stoppa and Schiazza, 2013) with a Correlation Coefficient of $R^2 > 0.80$, are shown plotted alongside modern Seawater, Holocene Marine Limestones and Devonian Reef Limestones in the Figure VI.21 below:
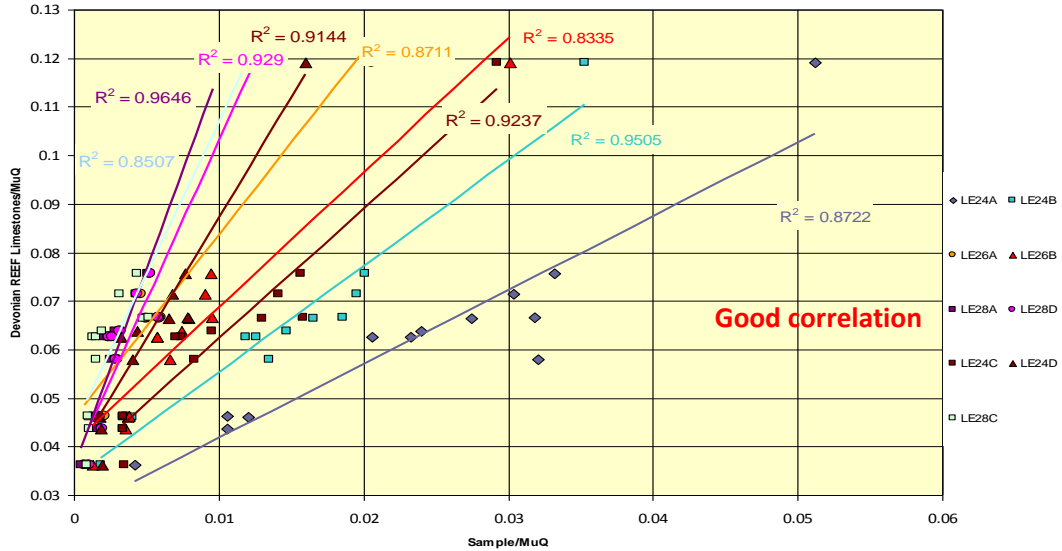


*Figure VI.21: Chart of Marine limestones Travertine correlation coefficient with Devonian Reef limestones.(Stoppa and Schiazza, 2013). Ugandan side of Albertine Rift basin*

Samples (fabrics, textures, structure and/or their replica) from DRC side correlating with Devonian Reef limestones (Stoppa and Schiazza, 2013) with a Correlation Coefficient of $R^2 > 0.80$, are shown plotted alongside modern Seawater, Holocene Marine Limestones and Devonian Reef Limestones in the Figure VI.22 below:
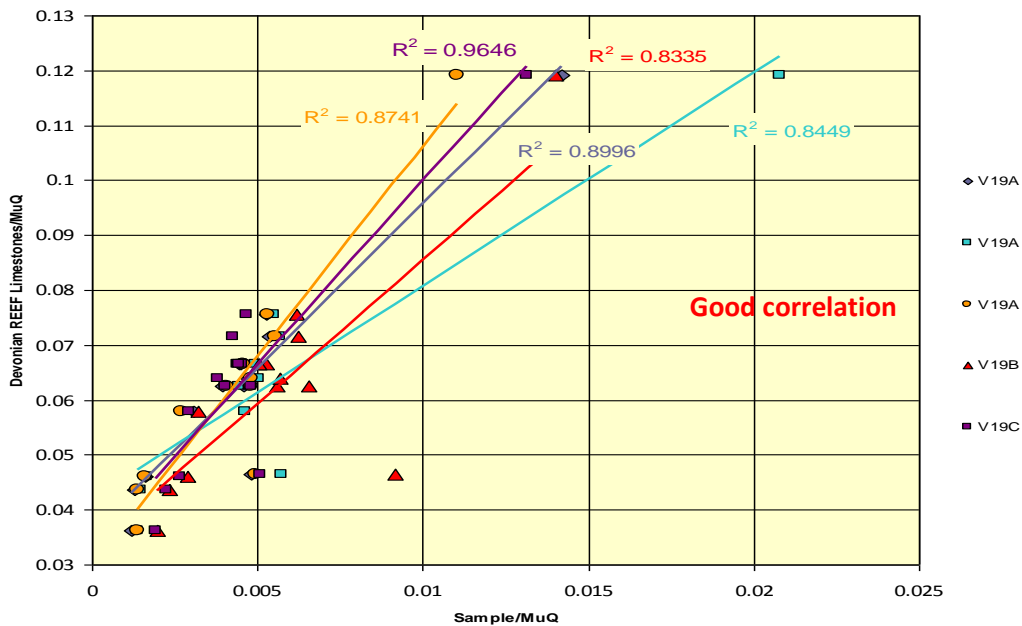


*Figure VI.22 : Chart of Marine limestones Travertine correlation coefficient with Devonian Reef limestones.(Stoppa and Schiazza, 2013). DRCongo side of Albertine Rift basin*

VI.4.1.3- <u>2013 TRAVERTINE WITH HYBRIDE SIGNATURES</u>

During the 2013 experiment, some samples like those LE 32 collected in Dura Uganda / EA4A have given different results from either Carbonatites or Marine limestones signatures.

The sample LE 32 was drilled through the visible textures, structures and fabrics and analysed gave  spectral signatures in Figure VI.23 below showing a decreasing the light rare earths

Lanthanum, cerium, praseodymium, neodymium, promethium, and samarium and an increasing the "heavy rare earths "Yttrium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.
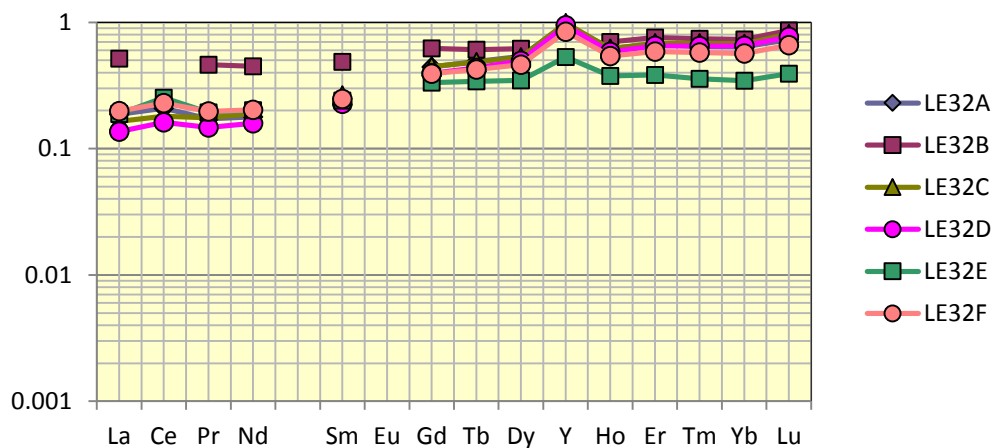


*Figure VI.23:    2013 Travertines Hybrid signature.*

REE values obtained for each structure, texture or fabric by ICP-MS and normalized in MUQ neither satisfy the Marine limestones criterias as per Balz Kamber approach nor the Correlation coefficient with Fort Portal Carbonatites. The Figures VI.24 and VI.25 below give respectively an overview of the LE 32 sample Correlation coefficient with Fort Portal and Marine limestone check box.
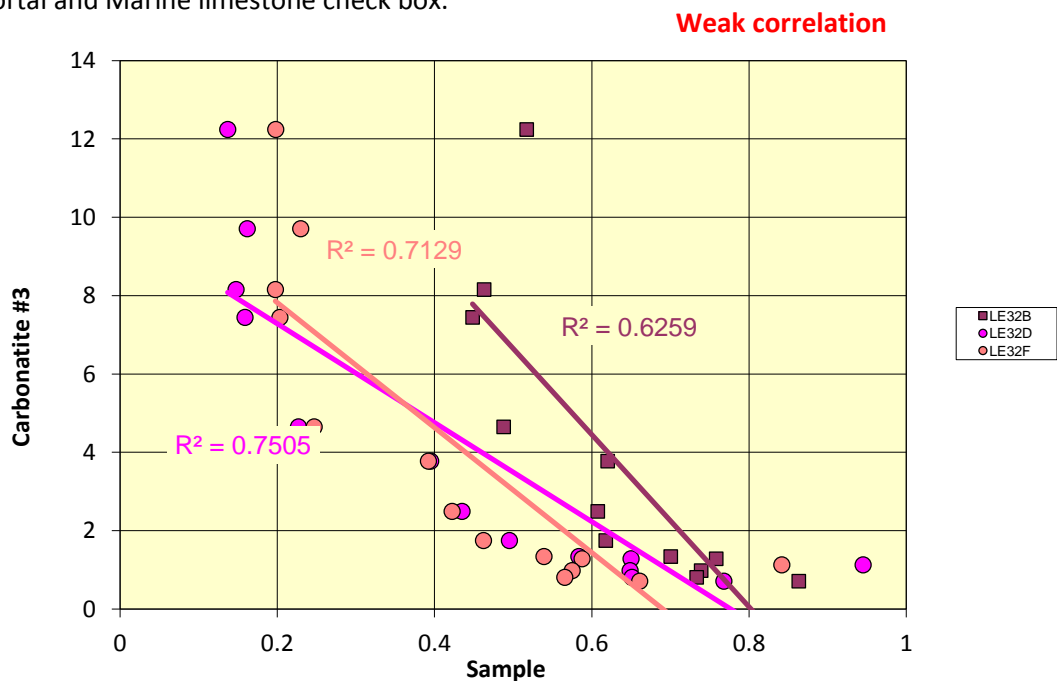


*Figure VI.24:    LE 32 Correlation coefficient with Fort Portal*

**Weak correlation**

| Key criteria for Marine Limestones | LE32A | LE32B | LE32C | LE32D | LE32E | LE32F |
|---|---|---|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Y/Ho > 40 | ✓ | ✗ | ✓ | ✓ | ✗ | ✓ |
| La/La* > 1.1 | ✓ | ✗ | ✓ | ✗ | ✗ | ✗ |
| Gd/Gd* > 1.1 | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ |
| Ce/Ce* < 0.8 | ✗ | ✓ | ✗ | ✗ | ✗ | ✗ |

*Figure VI.25:   LE 32 Marine limestones Criteria Check Box*

VI.4.2 - ICP-MS RESULTS OF 2016 EXPERIMENT

The 2016 ICP-MS experiment aimed to repeat exactly the 2013 experiment per Balz Kamber ideas, confirm the results reproducible ability and use the method on the last batch from 2014 samples with more confidence.

For unexpected spectral interferences on europium from may be $[BaO]^+$, the 2013 experiment didn't afford to detect it properly by the way of sensitive measurement of $Eu^{2+}$ ions. The europium has been properly detected during the 2016 experiment.

One of the main purpose of the 2016 ICP-MS experiment was to redo the 2013 experiment with both Carbonatites and Marine limestones end members Travertine samples, including Europium measurement in the final results.

All the signatures detected from 18 field samples during the 2016 ICP-MS experiment are represented in the logarithmic scale of 10 in the Figure VI.26 below:



## ICP-MS 2016: ALL SIGNATURES
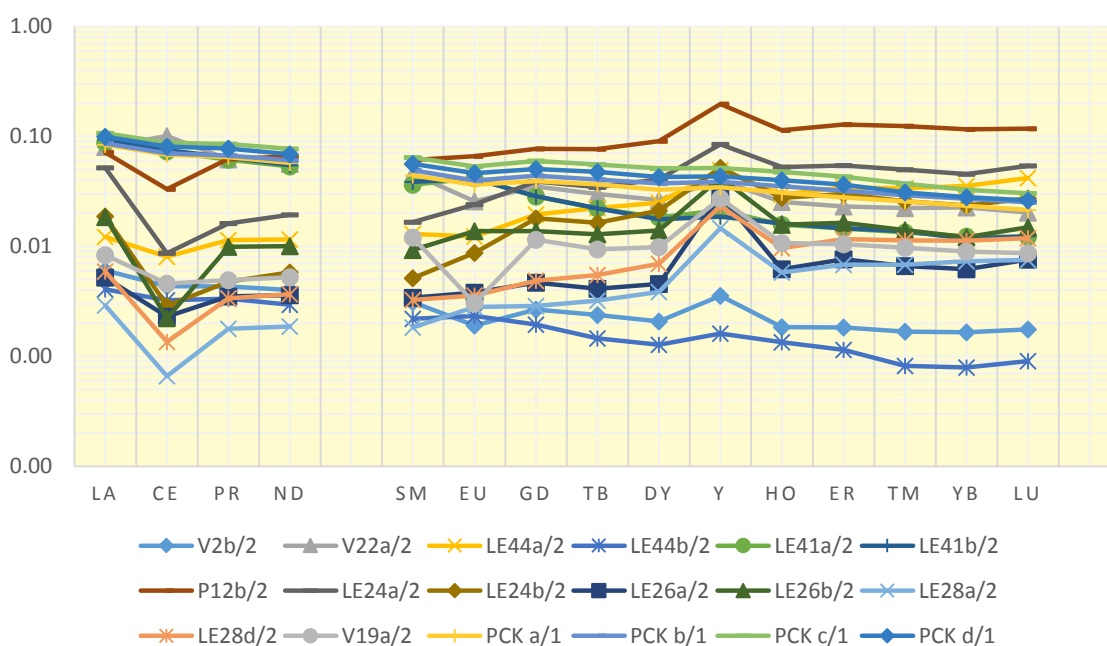
*Figure VI.26:   ICP-MS 2016: All spectral signatures*

The results from the 2007-2010 field samples of the rift end members found with Carbonatites signatures during the 2016 ICP-MS experiment are presented in Fig VI.27 below alongside with Fort Portal Carbonatites lavas.



*Figure VI.27:    ICP-MS 2016: Carbonatites  signatures alongside Fort portal Lava #1,#2 & #3*

Samples (fabrics, textures, structure and/or their replica) correlating with Fort Portal Carbonatite #3 (Stoppa and Schiazza, 2013) with a Correlation Coefficient of R2 > 0.75, are shown plotted alongside Fort Portal Carbonatites lavas in the Figure VI.28 below:



**ICP-MS 2O16: CARBONATITES CORRELATION COEFFICIENT**
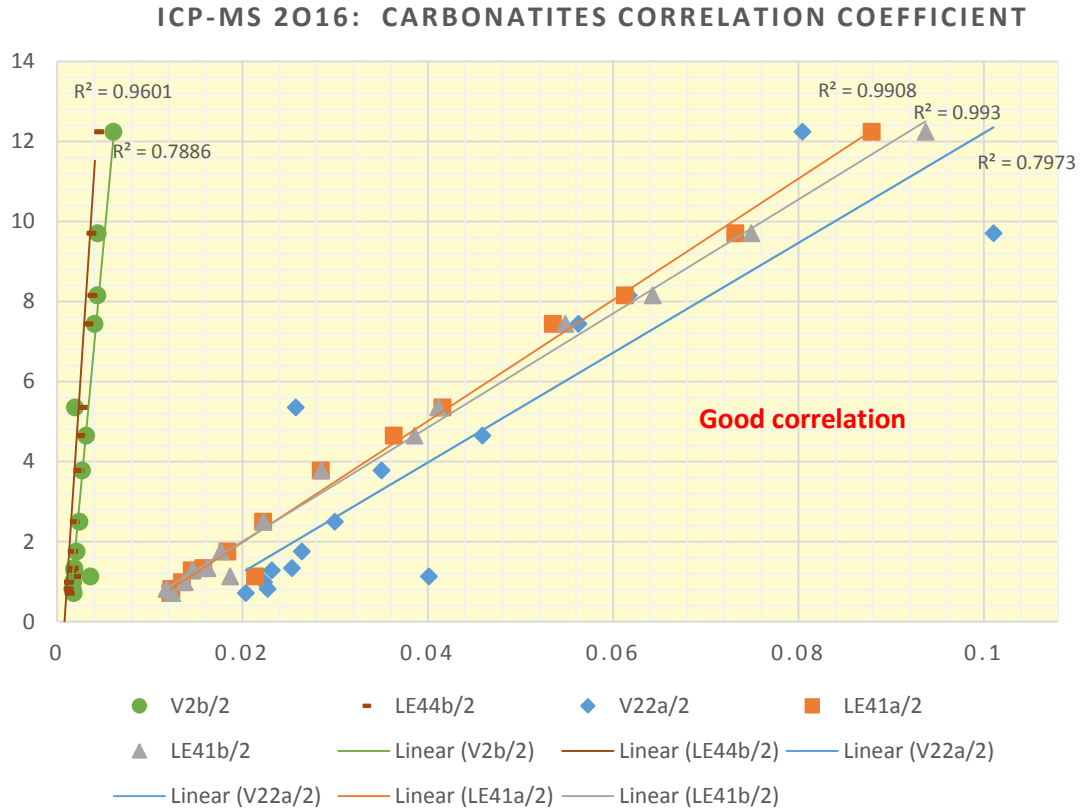
*Figure VI.28 :    2007- 2010 Block V Carbonatites correlation  coefficient with Fort Portal #3*

These results which have been made from the respective 2013 and 2016 MUQ raw datas in the table 2 of the appendix 2, are presented in form of comparative Charts. Each of these following Charts in Figure VI.29 below are showing comparisons of 2013 and 2016 REE concentrations spectral signatures and their respective positive correlation coefficient with the Fort Portal Carbonatite lava flow.

The 2016 Travertine Samples (fabrics, textures, structure and/or their replica) correlating with the 2013 Carbonatites rift end members samples with a Correlation Coefficient of R2 > 0.85, are shown plotted alongside in the graphs below which each of them, illustrates results comparisons of both above 2013 and 2016 experiments.

# Carbonatites Results Comparison of the 2013 – 2016 ICP-MS experiments
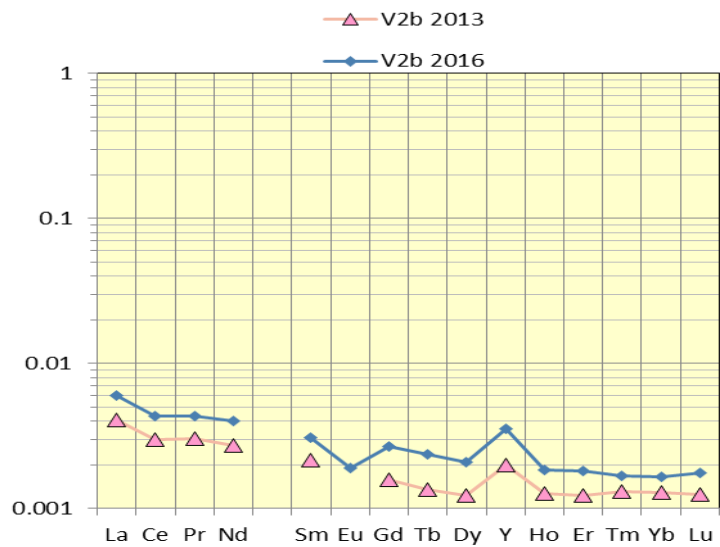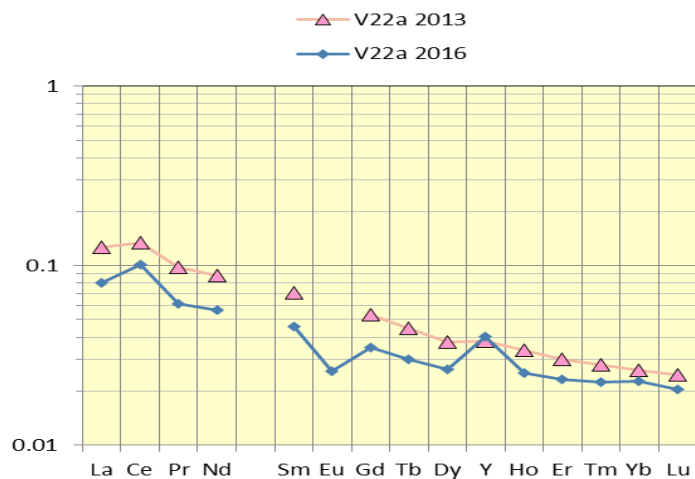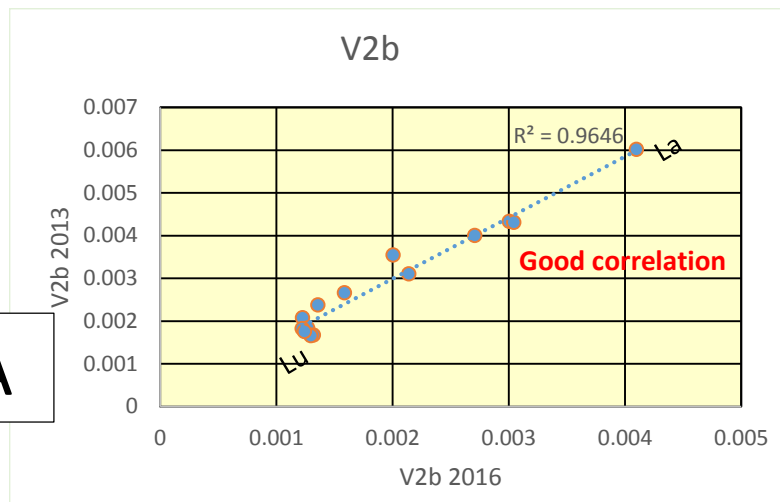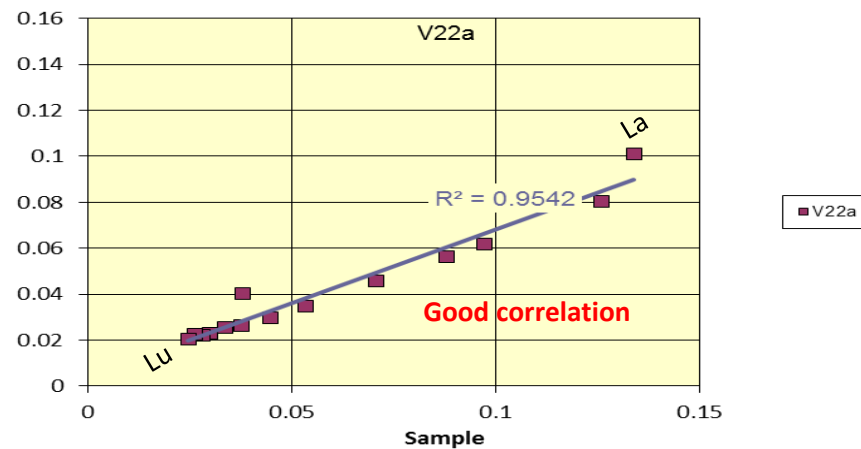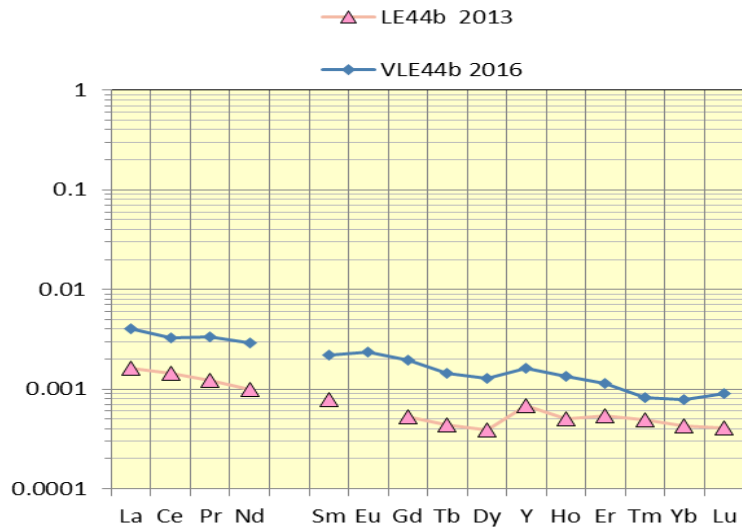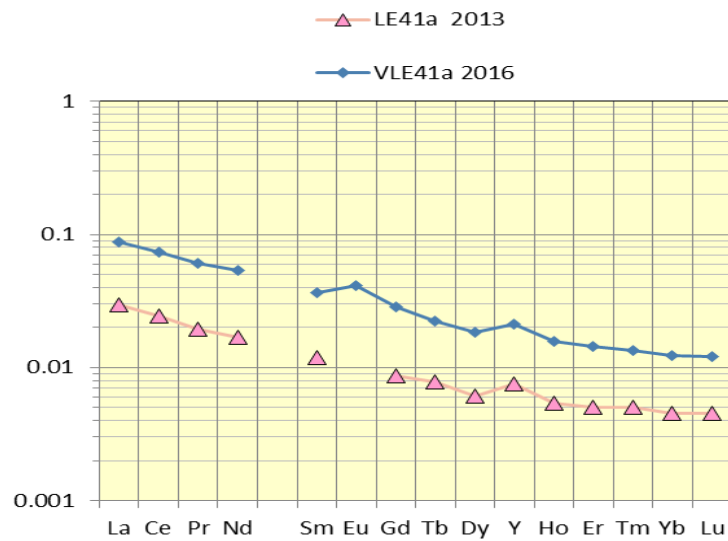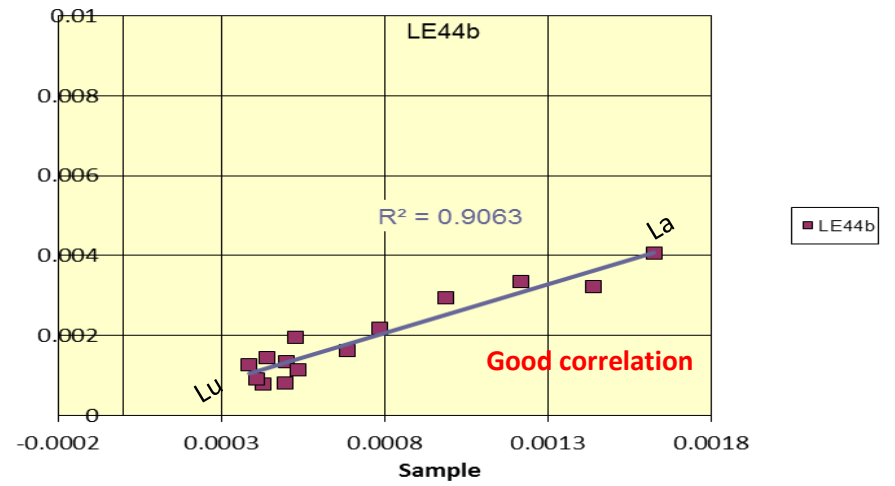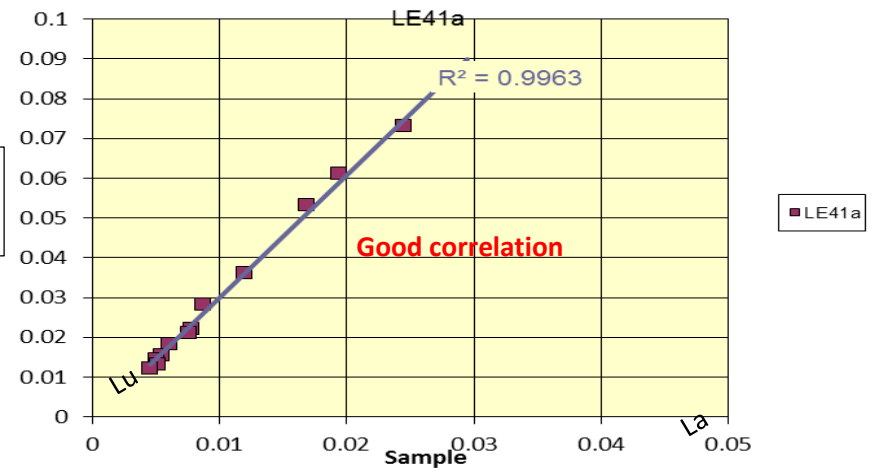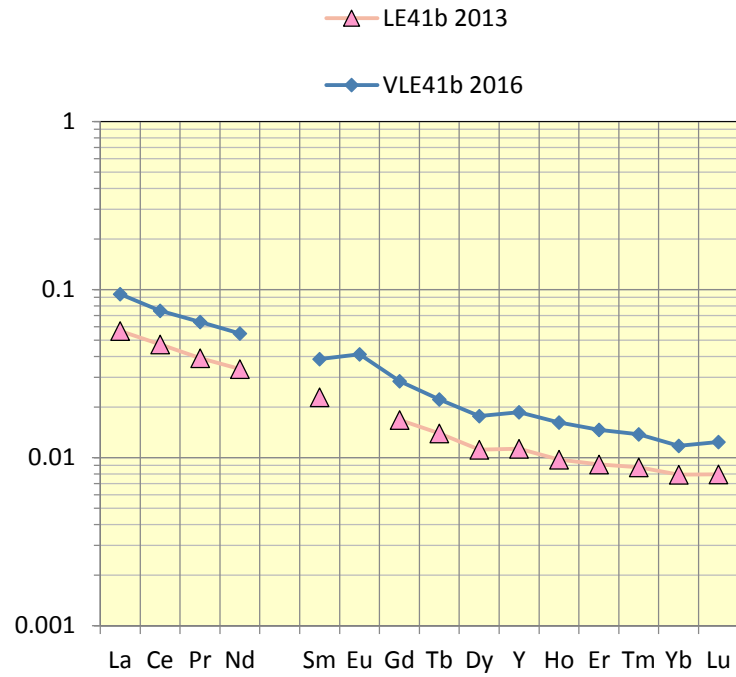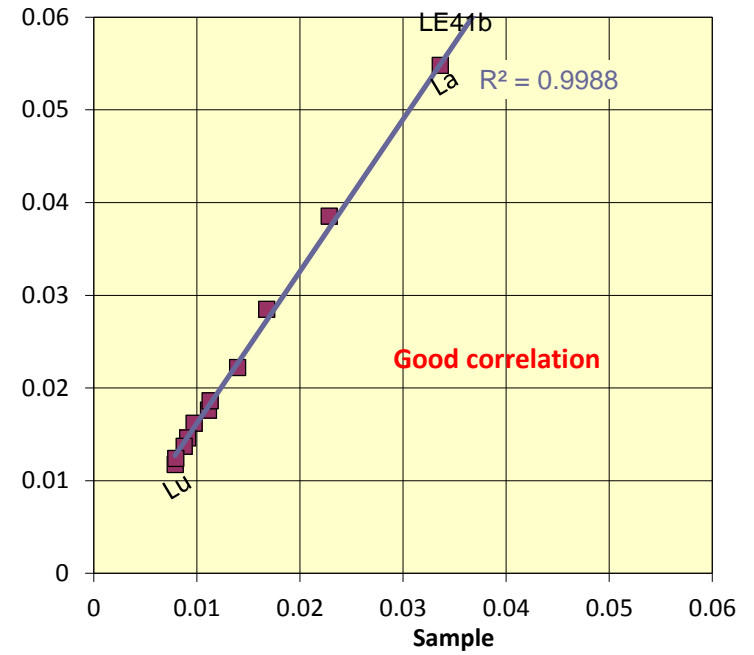
*Figure VI.29 a, b, c, d, and e:    Carbonatites signatures Comparison of the 2013 – 2016 ICP-MS experiments.*

From the analyzed sediment samples, it can be deduced that the Procokin samples have confirmed their known fresh waters origin as well as the 2013 marine limestones signatures have been close to the 2016 signatures with enough confidence. The Figures VI.27 and VI.28 below, show respectively the 2016 all marine limestones signatures alongside fresh waters, sea waters, Holocene marine, Devonian reef and their correlation coefficient

These results which have been made from the respective 2013 and 2016 MUQ raw datas in the table 3 of the appendix 2, are presented in form of comparative Charts. Each of these below Charts in Figure VI. 30 are showing together both 2013 and 2016 experiment REE concentrations spectral signatures and in Figure VI.31 their respective correlation coefficient R²> 0.80.



*Figure VI.30:    2007- 2010 Block V Travertine Marine limestone signatures by ICP-MS in 2016*

## ICP-MS 2016: MARINE LIMESTONE CORRELATION COEFFICIENT
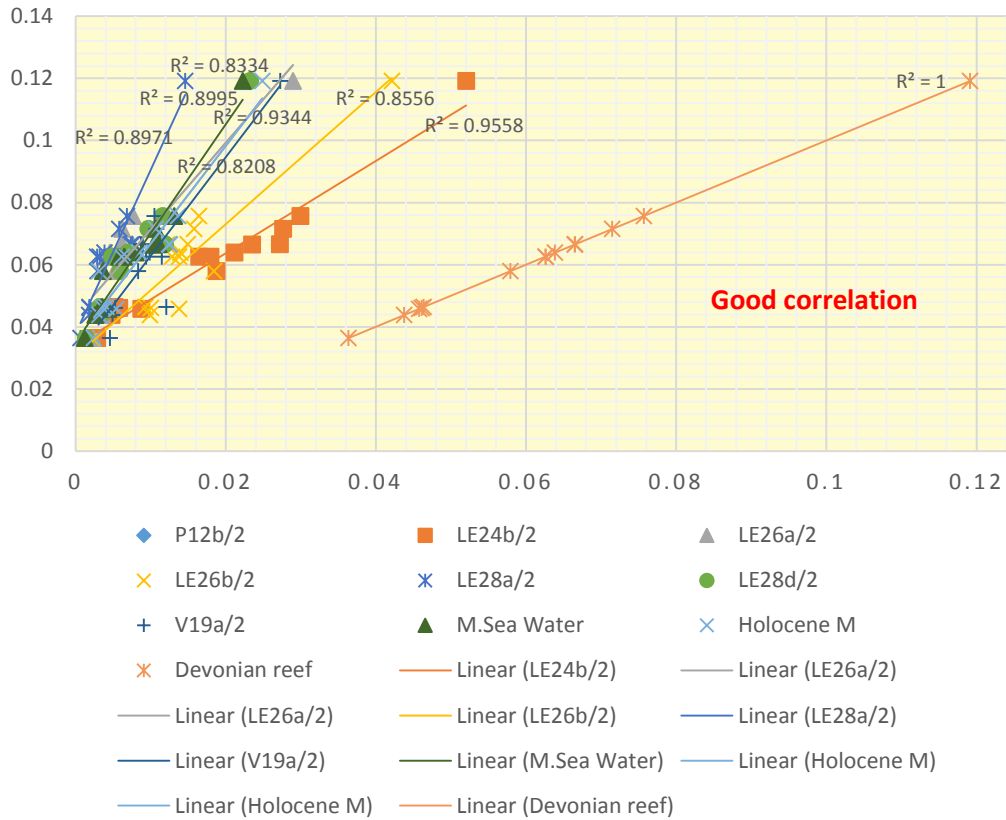
*Figure VI.31:    2007- 2010 Block V Marine limestone Correlation Coefficient*

The 2016 Travertine Samples (fabrics, textures, structure and/or their replica) correlating with the 2013  marine limestones end members samples  with a Correlation Coefficient of R2 > 0.85, are shown plotted alongside in the Figures below which illustrate results comparisons of both above experiments.

# Marine limestones Results Comparison of the 2013 – 2016 ICP-MS experiments



A
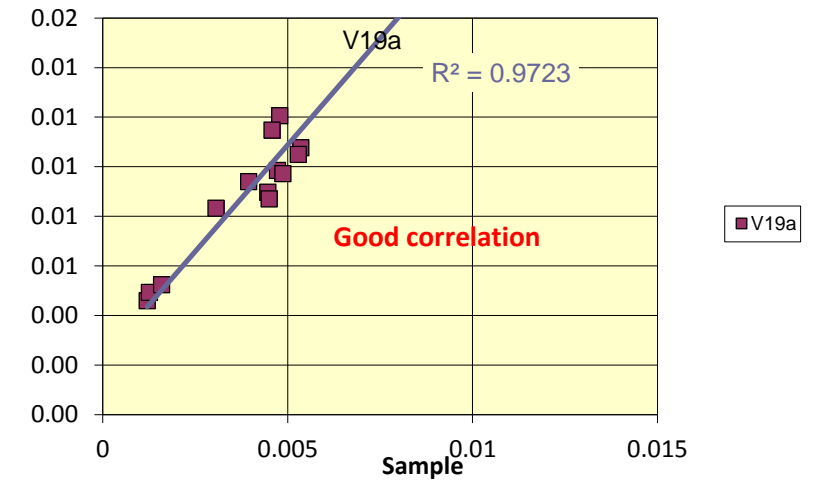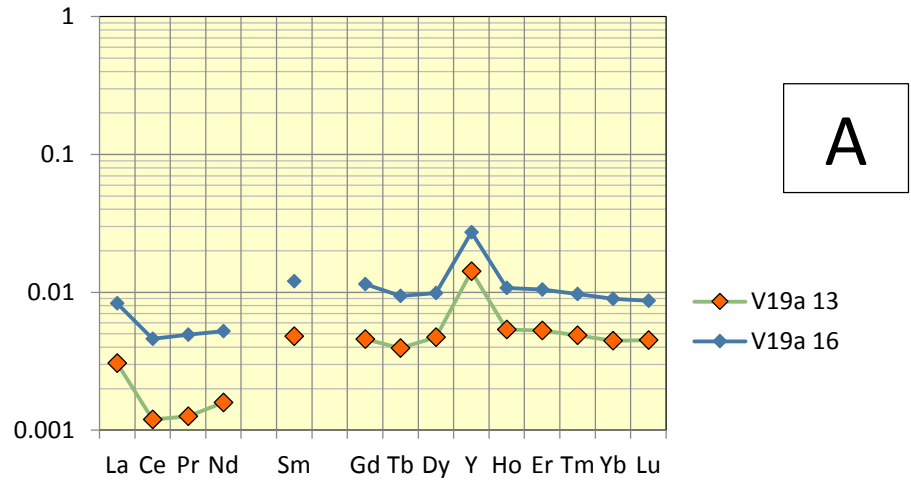


| | | V19_2013 | V19_2016 | CRITERIA |
|---|---|---|---|---|
| >>40 | Y/Ho | 2.647209 | 2.528275378 | No |
| >1.1 | La/La* | 3.862916 | 1.905987731 | Yes |
| <0.8 | Ce/Ce* | 1.196555 | 0.988580433 | No |
| >1.1 | Gd/Gd* | 1.390965 | 1.281446498 | Yes |
| <<1 | Prn/Ybn | 0.282225 | 0.549309056 | Yes |

B



R² = 0.9833

Good correlation
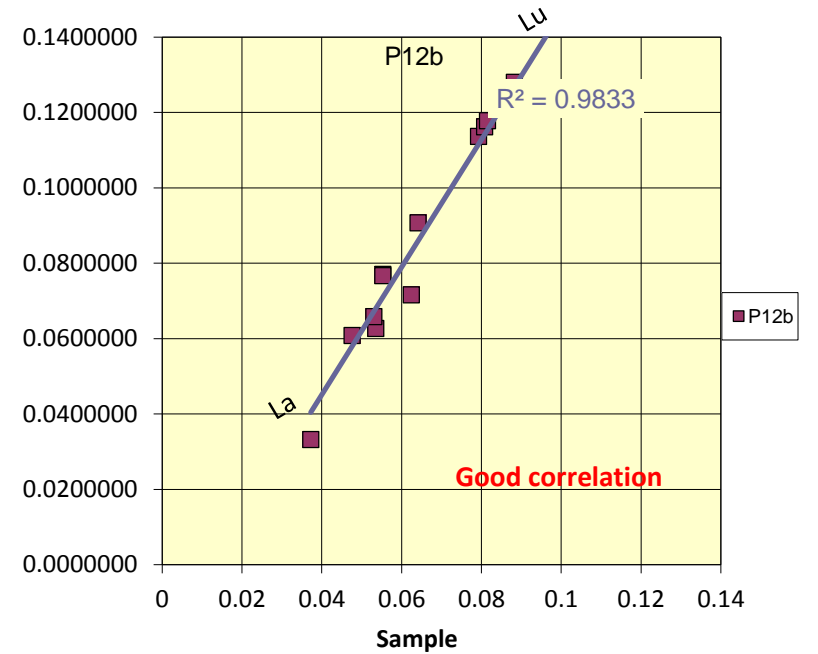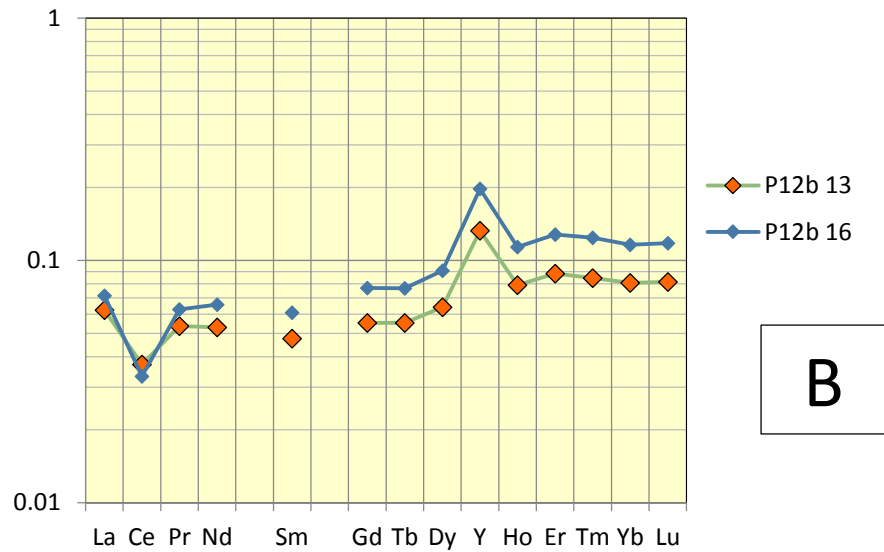
|  |  | P12b _2013 | P12b_2016 | CRITERIA |
|---|---|---|---|---|
| >>40 | Y/Ho | 1.676789 | 1.736822864 | No |
| >1.1 | La/La* | 1.144282 | 1.2565824 | Yes |
| <0.8 | Ce/Ce* | 0.688419 | 0.555940519 | Yes |
| >1.1 | Gd/Gd* | 1.159656 | 1.187210291 | Yes |
| <<1 | Prn/Ybn | 0.662329 | 0.539920851 | Yes |

C

Good correlation
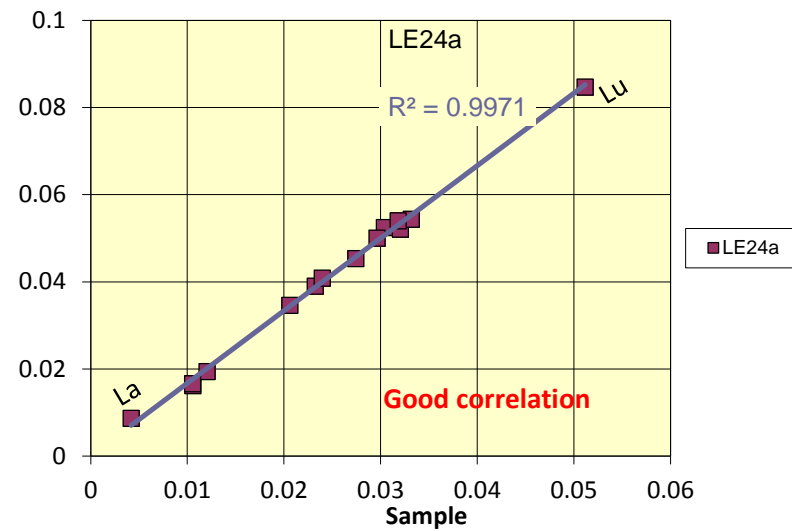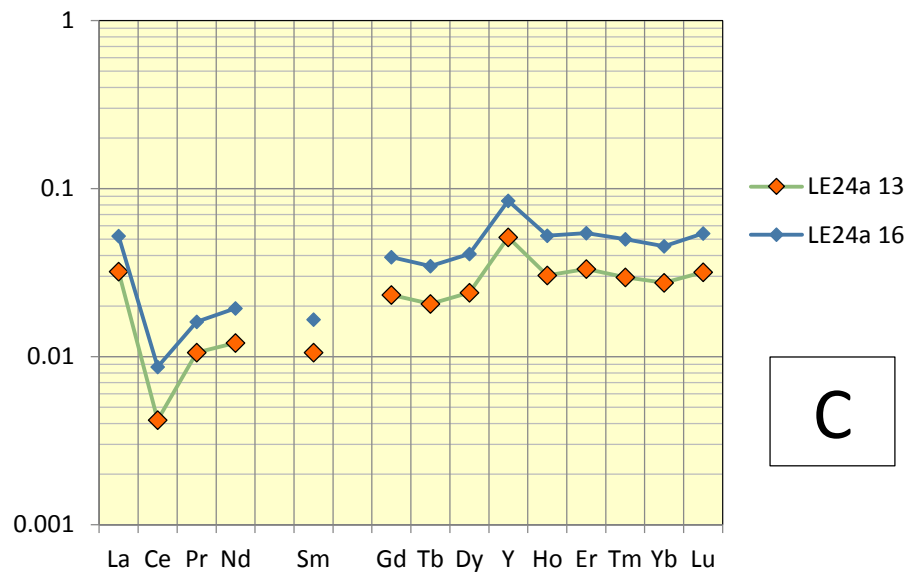
|  |  | LE24a_2013 | LE24a_2016 | CRITERIA |
|---|---|---|---|---|
| >>40 | Y/Ho | 1.684022 | 1.61376769 | No |
| >1.1 | La/La* | 3.930147 | 4.655112628 | Yes |
| <0.8 | Ce/Ce* | 0.450244 | 0.647059055 | Yes |
| >1.1 | Gd/Gd* | 1.312061 | 1.332444626 | Yes |
| <<1 | Prn/Ern | 0.318632 | 0.296964028 | Yes |
| >1.1 | Prn/Ybn | 0.385356 | 0.355994184 | Yes |
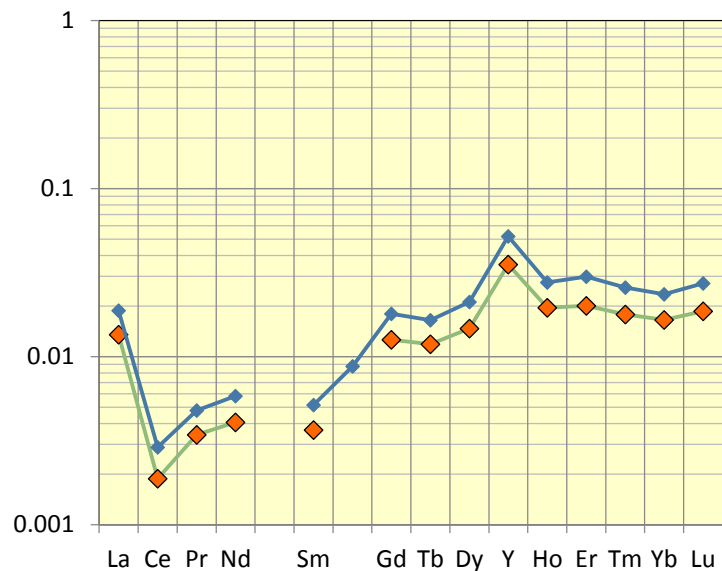
D
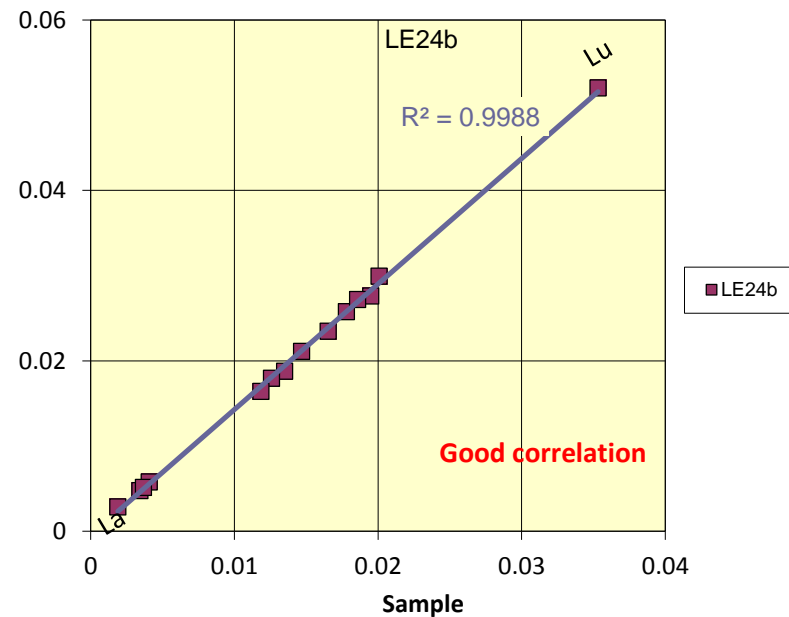
|  |  | LE24b_2013 | LE24b_2016 | CRITERIA |
|---|---|---|---|---|
| >>40 | Y/Ho | 1.810488 | 1.882843 | No |
| >1.1 | La/La* | 5.588996 | 5.850131 | Yes |
| <0.8 | Ce/Ce* | 0.653983 | 0.736502 | Yes |
| >1.1 | Gd/Gd* | 1.31779 | 1.403539 | Yes |
| <<1 | Prn/Ern | 0.170343 | 0.159299 | Yes |
| >1.1 | Prn/Ybn | 0.20682 | 0.202891 | Yes |

Chart legend: LE26a 13, LE26a 16

X-axis: La Ce Pr Nd Sm Gd Tb Dy Y Ho Er Tm Yb Lu

E

LE26a

R² = 0.9905

Good correlation

Lu

La

LE26a

**Sample**
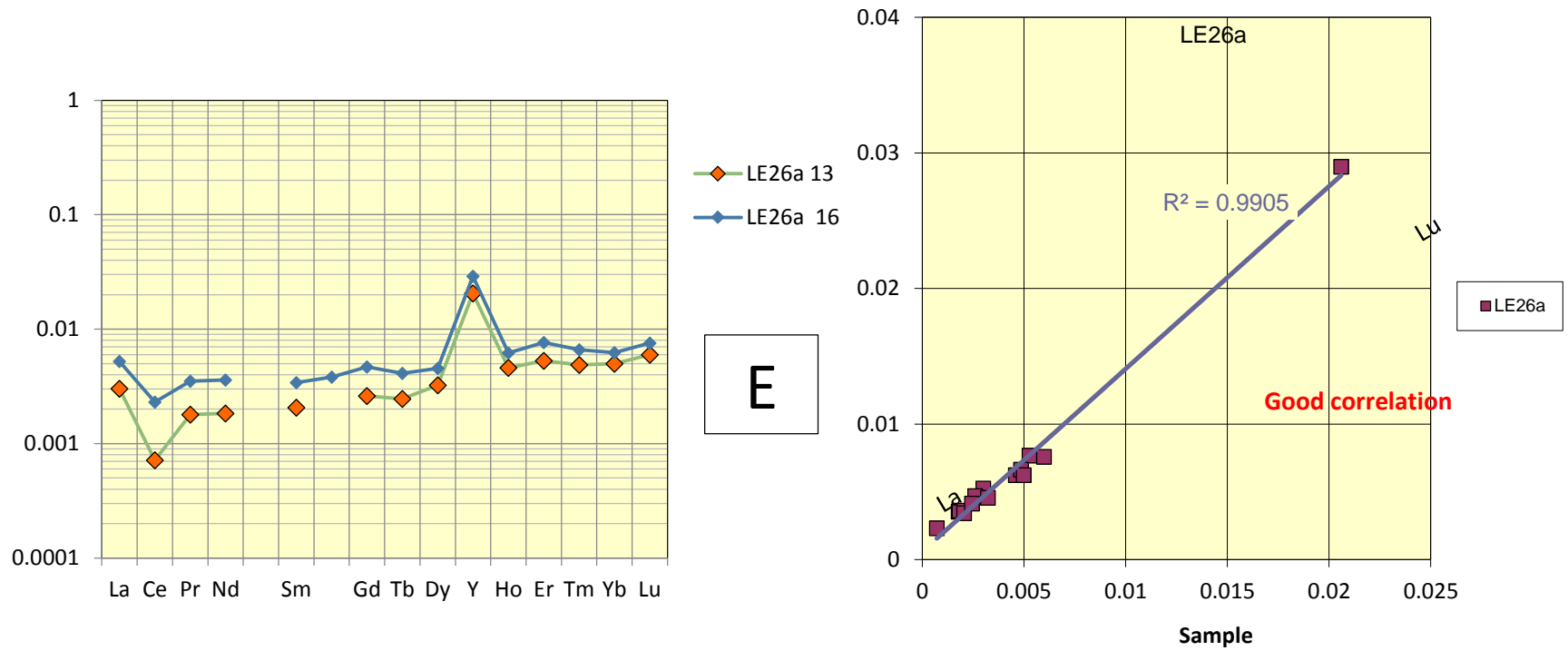
| | | LE26a_2013 | LE26a_2016 | CRITERIA |
|---|---|---|---|---|
| >>40 | Y/Ho | 4.466672 | 4.66481185 | No |
| >1.1 | La/La* | 1.754767 | 1.55708473 | yes |
| <0.8 | Ce/Ce* | 0.407432 | 0.66997316 | yes |
| >1.1 | Gd/Gd* | 1.405288 | 1.25855032 | yes |
| <<1 | Prn/Ern | 0.339981 | 0.45935575 | yes |
| >1.1 | Prn/Ybn | 0.359746 | 0.56559113 | yes |

F



LE26b

R² = 0.9385

Good correlation
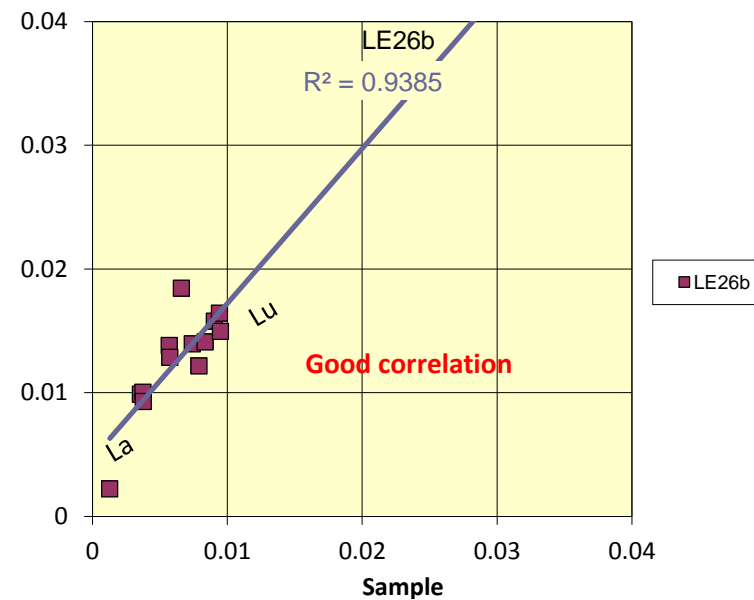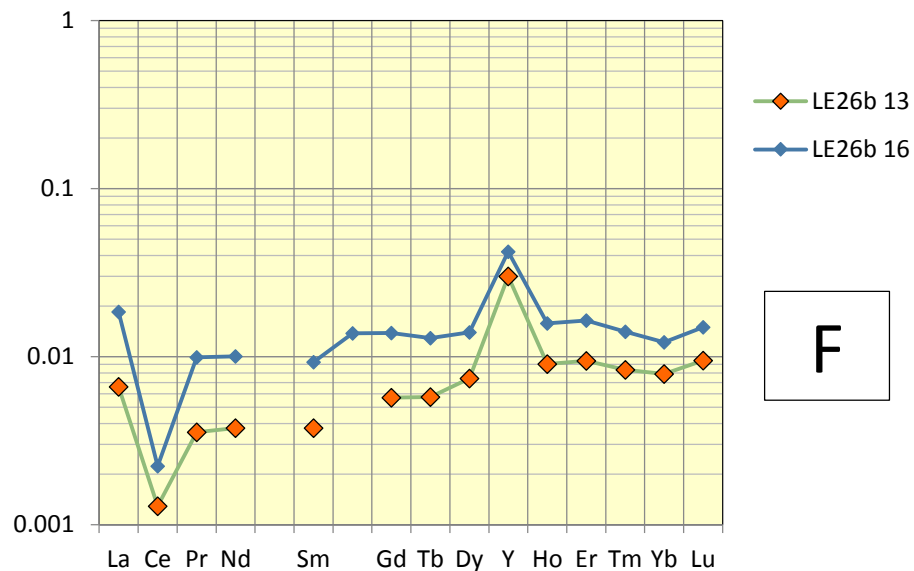
|  |  | LE26b_2013 | LE26b_2016 | CRITERIA |
|---|---|---|---|---|
| >>40 | Y/Ho | 3.3276 | 2.671762452 | No |
| >1.1 | La/La* | 2.069303 | 1.922907527 | Yes |
| <0.8 | Ce/Ce* | 0.382303 | 0.228412875 | Yes |
| >1.1 | Gd/Gd* | 1.277765 | 1.162146847 | yes |
| <<1 | Prn/Ern | 0.377323 | 0.602416007 | yes |
| >1.1 | Prn/Ybn | 0.450106 | 0.813763021 | Yes |

G
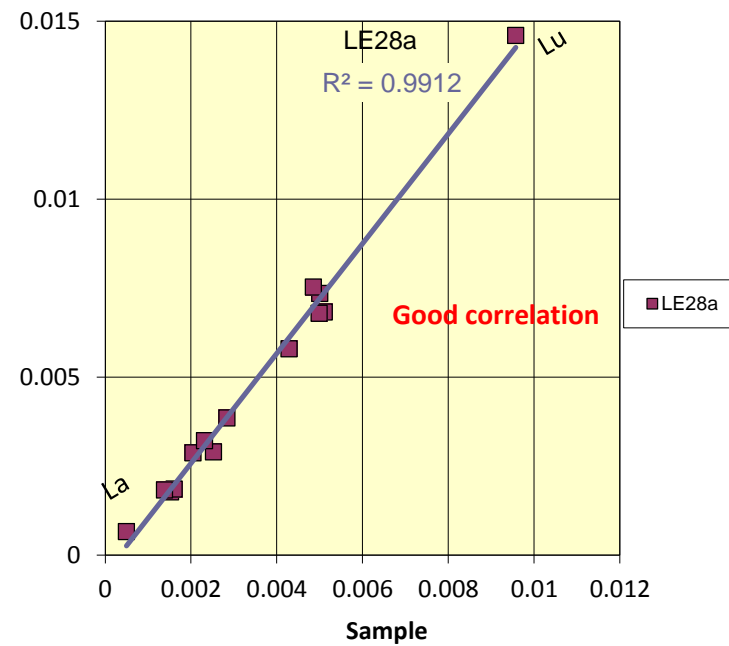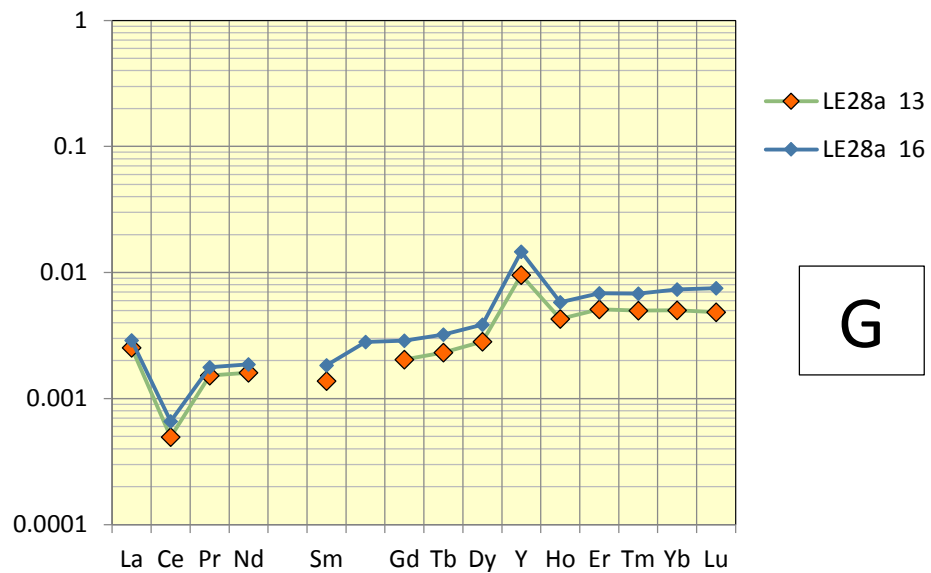
| | | LE28a_2013 | LE28a_2016 | CRITERIA |
|---|---|---|---|---|
| >>40 | Y/Ho | 2.233285 | 2.519508897 | No |
| >1.1 | La/La* | 1.834335 | 1.793265394 | yes |
| <0.8 | Ce/Ce* | 0.340781 | 0.389999676 | yes |
| >1.1 | Gd/Gd* | 1.077712 | 1.069167803 | No |
| <<1 | Prn/Ern | 0.298544 | 0.260256782 | yes |
| >1.1 | Prn/Ybn | 0.304755 | 0.241748024 | Yes |

H
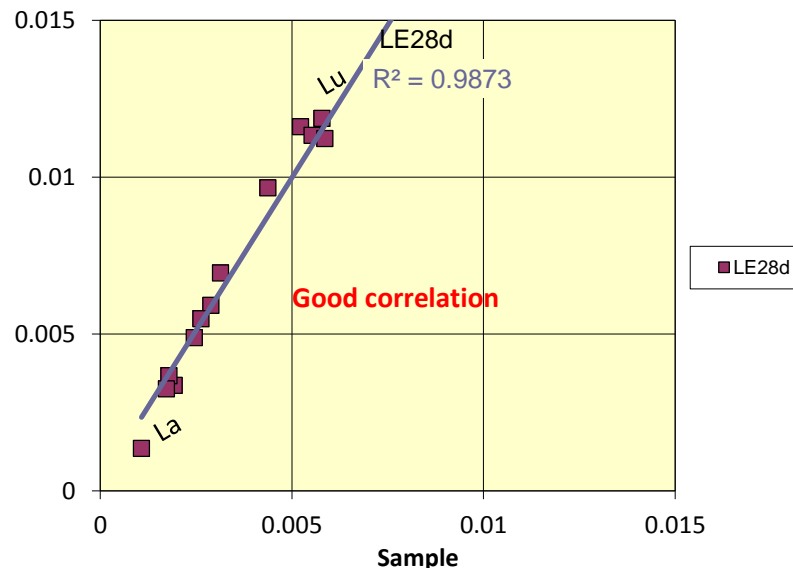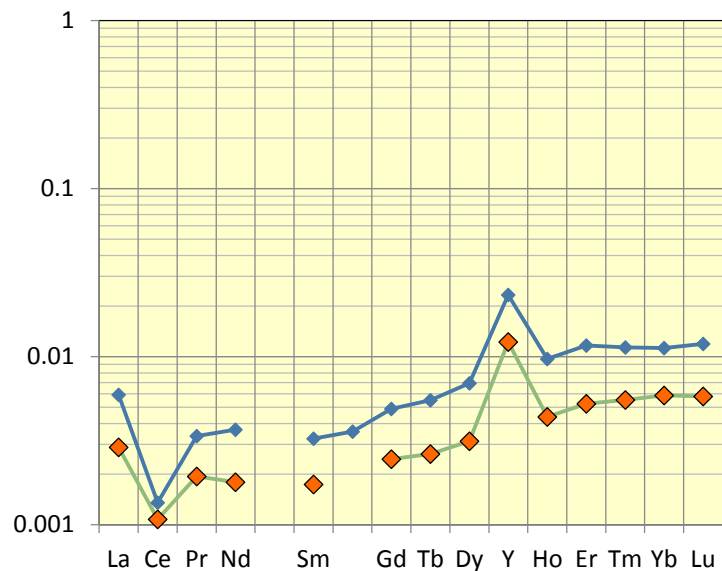
| | | LE28d_2013 | LE28d_2016 | CRITERIA |
|---|---|---|---|---|
| >>40 | Y/Ho | 2.799444 | 2.40548692 | No |
| >1.1 | La/La* | 1.284375 | 2.09905312 | Yes |
| <0.8 | Ce/Ce* | 0.515165 | 0.43903494 | Yes |
| >1.1 | Gd/Gd* | 1.11428 | 1.12480308 | Yes |
| <<1 | Prn/Ern | 0.369575 | 0.28947432 | Yes |
| >1.1 | Prn/Ybn | 0.329835 | 0.29935288 | Yes |

``

*Figure VI.32a, b, c, d,e,f,g,and h:   Marine Limestones signatures Comparison of the 2013 – 2016 ICP-MS experiments.*

VI.4.2.3- <u>PROCOKIN LIMESTONES</u>

The Procokin PCK limestone sample has been collected in a quarry in the western side of DRCongo were existing literature ( detailed in Chapter II) universally recognized the presence of stromatolites fossils which clearly suggest a fresh water depositional environment as origin.

The geochemical analysis of the four (4) PCK limestone samples in 2016 confirmed by ICP-MS method and available instrument the fresh water limestone origin of this stromatolites sample which was supposed to be used as matching correlation tool or geochemistry comparator factor with any other limestone REE signature from East African Rift System samples as the Fort Portal Carbonatites and Devonian Reef marine limestones are used through this whole study as geochemistry referring tool.

The table 4 below, shows the MUQ values of the PCK samples obtained in 2016 ICP-MS experiments :

|     | PCK 1    | PCK2     | PCK3     | PCK4     |
|-----|----------|----------|----------|----------|
| La  | 0.084436 | 0.086158 | 0.106982 | 0.099262 |
| Ce  | 0.068209 | 0.070235 | 0.087565 | 0.08063  |
| Pr  | 0.064645 | 0.067175 | 0.085331 | 0.077553 |
| Nd  | 0.05749  | 0.060468 | 0.07718  | 0.068976 |
| Sm  | 0.044346 | 0.049172 | 0.064215 | 0.05625  |
| Eu  | 0.036293 | 0.039803 | 0.053516 | 0.046363 |
| Gd  | 0.039151 | 0.043947 | 0.059906 | 0.050472 |
| Tb  | 0.036626 | 0.040586 | 0.055485 | 0.047495 |
| Dy  | 0.032784 | 0.037301 | 0.051138 | 0.042699 |
| Y   | 0.034505 | 0.038587 | 0.051523 | 0.043391 |
| Ho  | 0.030738 | 0.035303 | 0.047705 | 0.039852 |
| Er  | 0.027923 | 0.031958 | 0.042997 | 0.036439 |
| Tm  | 0.025765 | 0.029275 | 0.037255 | 0.030941 |
| Yb  | 0.023452 | 0.027068 | 0.032708 | 0.027966 |
| Lu  | 0.02149  | 0.025224 | 0.030388 | 0.026143 |

*Table 4: MUQ values of PCK samples obtained by ICP-MS in 2016*

The table 5 below which help to check the marine origin criterias, suggest that the PCK samples are effectively limestones, however, they are not from Marine origin.

|  |  | PCK 1 | PCK 2 | PCK 3 | PCK 4 | CRITERIA |
|---|---|---|---|---|---|---|
|  | Y/Ho | 1.122578755 | 1.093018229 | 1.080030426 | 1.088788393 | No |
| >>40 | La/La* | 1.032997327 | 1.039261044 | 1.025661941 | 1.012462442 | No |
| >1.1 | Ce/Ce* | 0.93834339 | 0.941160431 | 0.928161005 | 0.924690281 | No |
| <0.8 | Gd/Gd* | 0.956806242 | 0.99515329 | 0.995081664 | 0.955379132 | No |
| <<1 | Prn/Ern | 2.315143088 | 2.10194569 | 1.984578098 | 2.128291981 | No |
| >1.1 | Prn/Ybn | 2.756461791 | 2.481738751 | 2.60889605 | 2.773108949 | No |

*Table 5: Marine limestone criteria check box for the PCK samples*

The Figure VI.33 below, shows the fresh water limestones spectral signature obtain by ICP-MS for all the 4 layered structures drilled within the PCK sample.
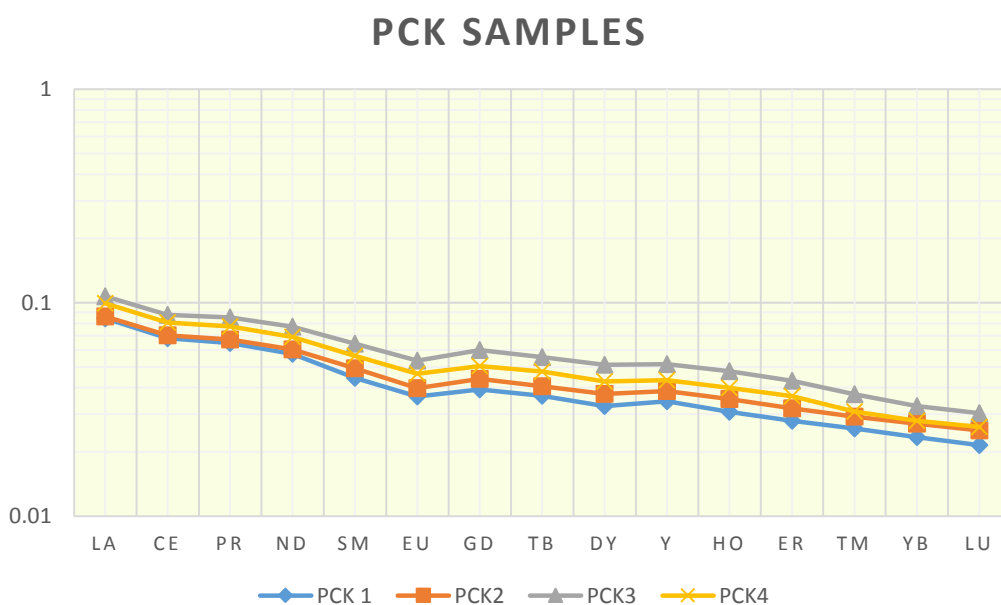
## PCK SAMPLES



*Figure VI.33: PCK Samples REE fresh water signature, ICP-MS, 2016*

The fresh waters PCK Samples are one of the first limestone DRC occurence documented so far. Comparing the Travertine limestones geochemistry found in Albertine Graben to these closest documented limestone found so far within DRC territory, would be ideal to guess their origin link. However, as shown in the figures VI.34 and VI.34 below, they are not good enough to be used for the case of this present study as a matching correlate or a comparator tool because they are not from Marine origin as those collected in East African Rift basin.

So, the need to find another comparator limestone rock sample which can be found in outcrop nearby the Albertine Graben pushed to run ICP-MS on Mandawa Basin limestones.
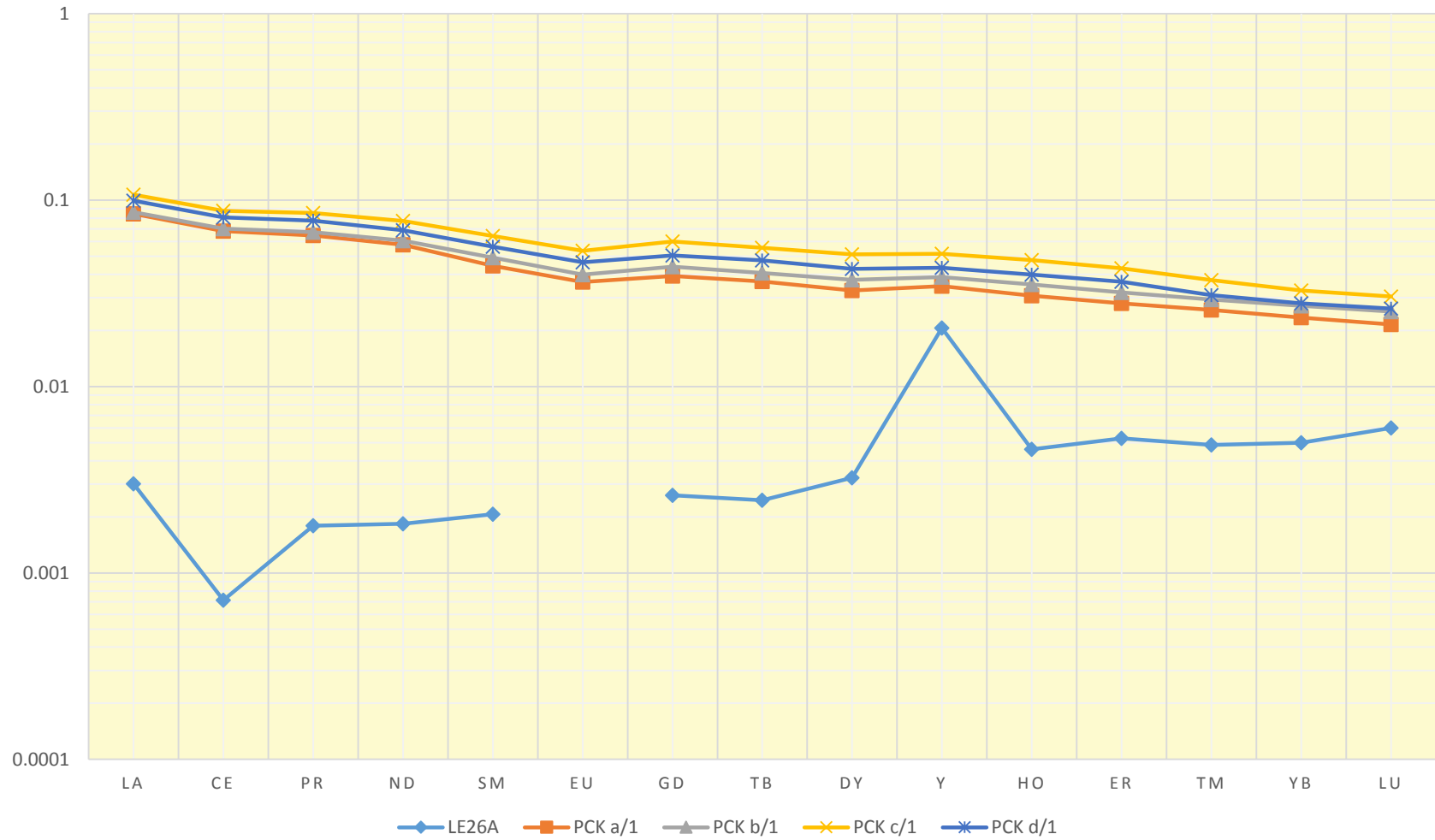
*Figure VI.34: PCK & LE 26  REE +Y  Patterns by ICP-MS*
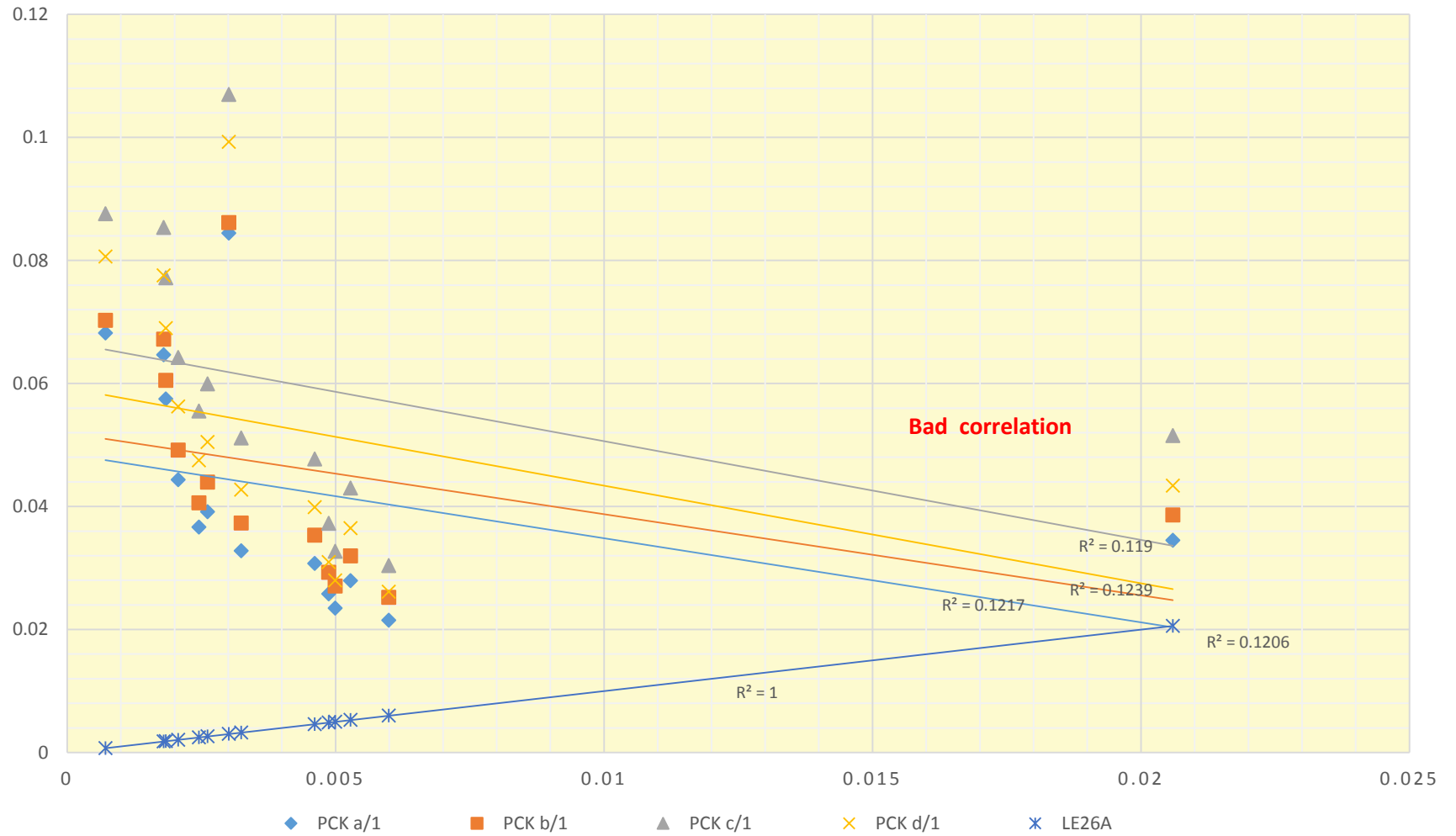
*Figure VI.35 : PCK & LE 26  Coefficient Correlation*
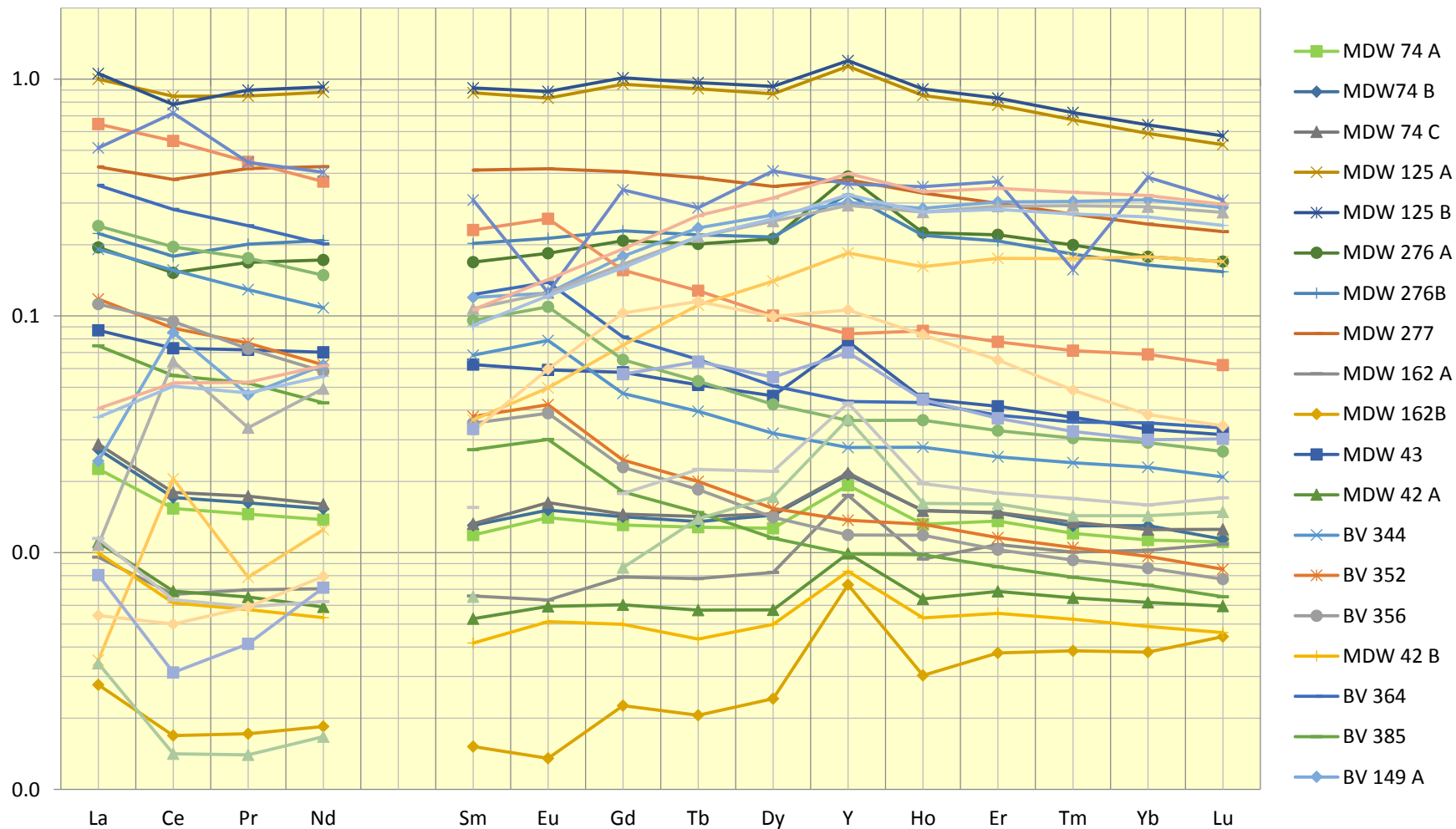
*Figure VI.36: ICP-MS, 2018: All spectral signatures*

## VI.4.3.1- <u>2018 TRAVERTINE WITH CARBONATITES SIGNATURES</u>

The results from the 2014 field samples found with Carbonatites signatures during the 2018 ICP-MS experiment are presented in Fig VI.35 below alongside with Fort Portal Carbonatites lavas as well as are lower illustrated in Fig. VI.36 their correlation coefficient $R^2 > 0.95$ to the Fort Portal Carbonatites samples.
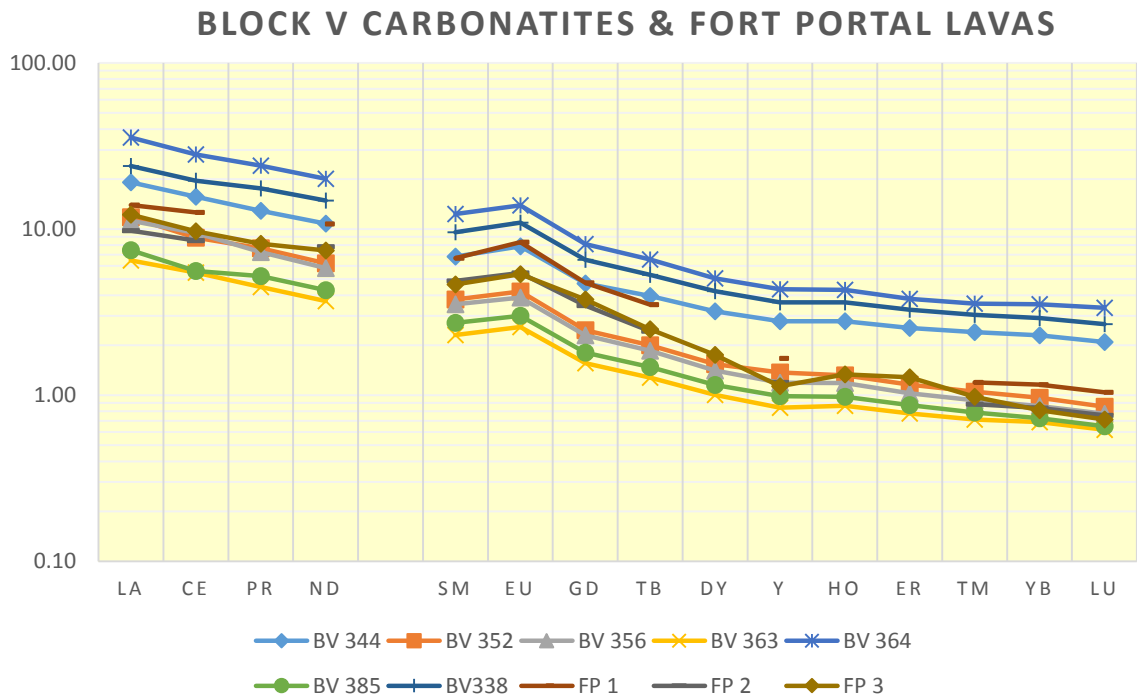


*Figure VI.37: ICP-MS, 2018: Carbonatites signatures*
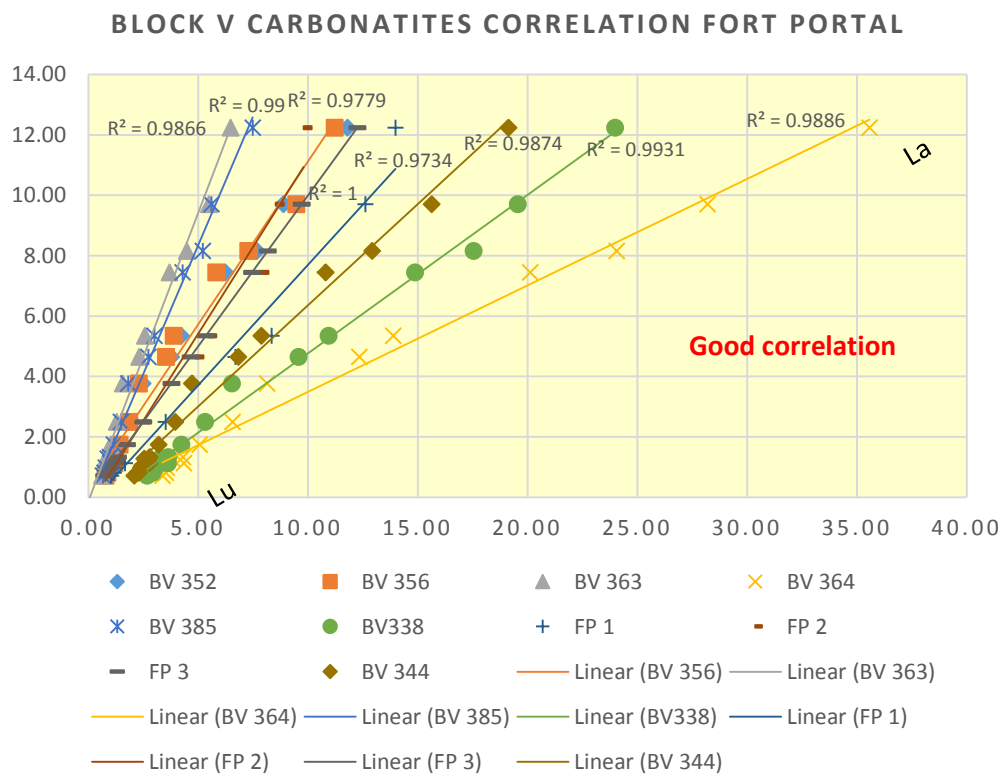


*Figure VI.38: Bloc V Carbonatites signatures correlation coefficient with Fort Portal #3*

The 2018 Travertine Samples (fabrics, textures, structure and/or their replica) correlating with the known marine limestones (Mandawa Basin Tanzania, Holocene Marine, Modern Sea water, Devonian reef)  with a Correlation Coefficient of R2 > 075, are shown plotted alongside in the Figures below which illustrate comparisons of results experiments.

Additionally, a check box table of the Kamber's paper Marine limestones key criteria has been set up for each Travertine with marine limestones spectral signature.

The table 7 below which help to check the marine origin criterias, suggest that some ones 2014 Bloc V field samples drilled regarding their textures, structures or fabrics have more Marine signatures involvement origin and some others don't.

|  |  | BV 161 B |  | BV 162 A |  | BV 163 A |  | BV 164 |  |
|---|---|---|---|---|---|---|---|---|---|
| >1.1 | La/La* | 2.154878 | YES | 1.660919 | YES | 5.823986 | YES | 3.464977 | YES |
| <0.8 | Ce/Ce* | 1.185219 | NO | 1.529005 | NO | 2.257441 | NO | 1.438689 | NO |
| >1.1 | Gd/Gd* | 0.778326 | NO | 0.771417 | NO | 0.761166 | NO | 0.765242 | NO |
| << 1 | Prn/Ybn | 0.371749 | YES | 0.154034 | YES | 0.137344 | YES | 0.097544 | YES |
| >40 | Y/Ho | 2.191354 | NO | 1.274174 | NO | 1.57862 | NO | 2.275306 | NO |

*Table 6:   Marine limestone criteria check box for the 2014 Bloc V field samples*

All these samples have satisfied only two (2)) of the marine limestones criteria). These results which have been made from the 2018 MUQ raw, are presented in the
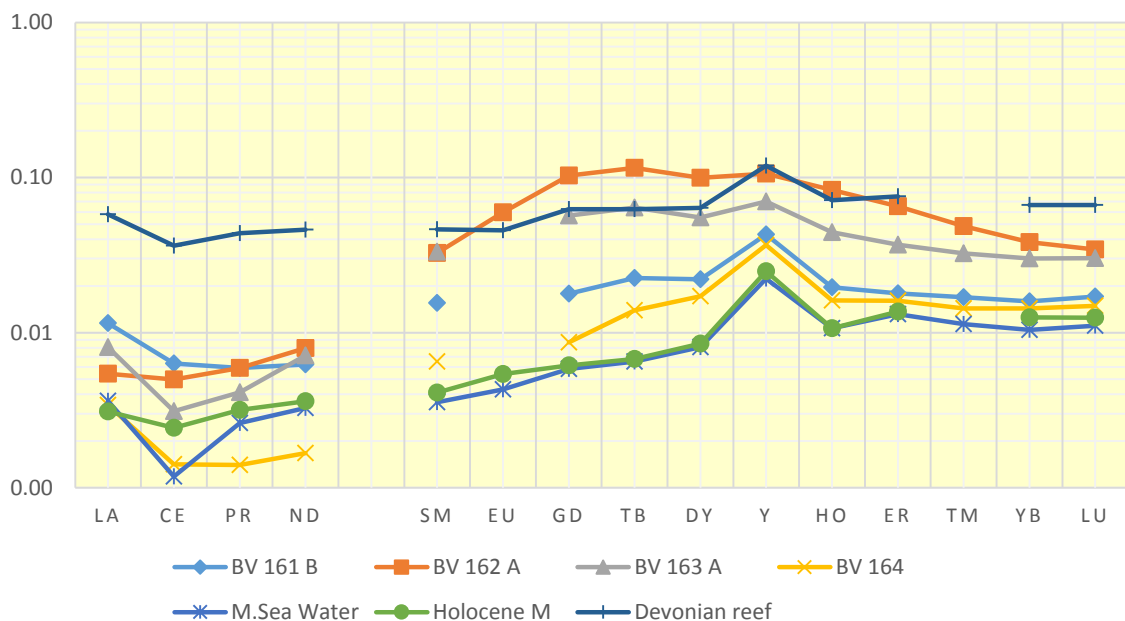


*Figure VI.39: Bloc V 2014 Marine Limestones signatures by ICP-MS 2018*

The Bloc V 2014 Travertine field Samples (fabrics, textures, structure and/or their replica) correlating with the known marine limestones (Mandawa Basin Tanzania, Holocene Marine, Modern Sea water, Devonian reef) with a Correlation Coefficient of R2 > 0.85, are shown plotted alongside in the Figure VI.38 below:

### ICP-MS 2018 : CORRELATION WITH KNOWN MARINE LIMESTONES
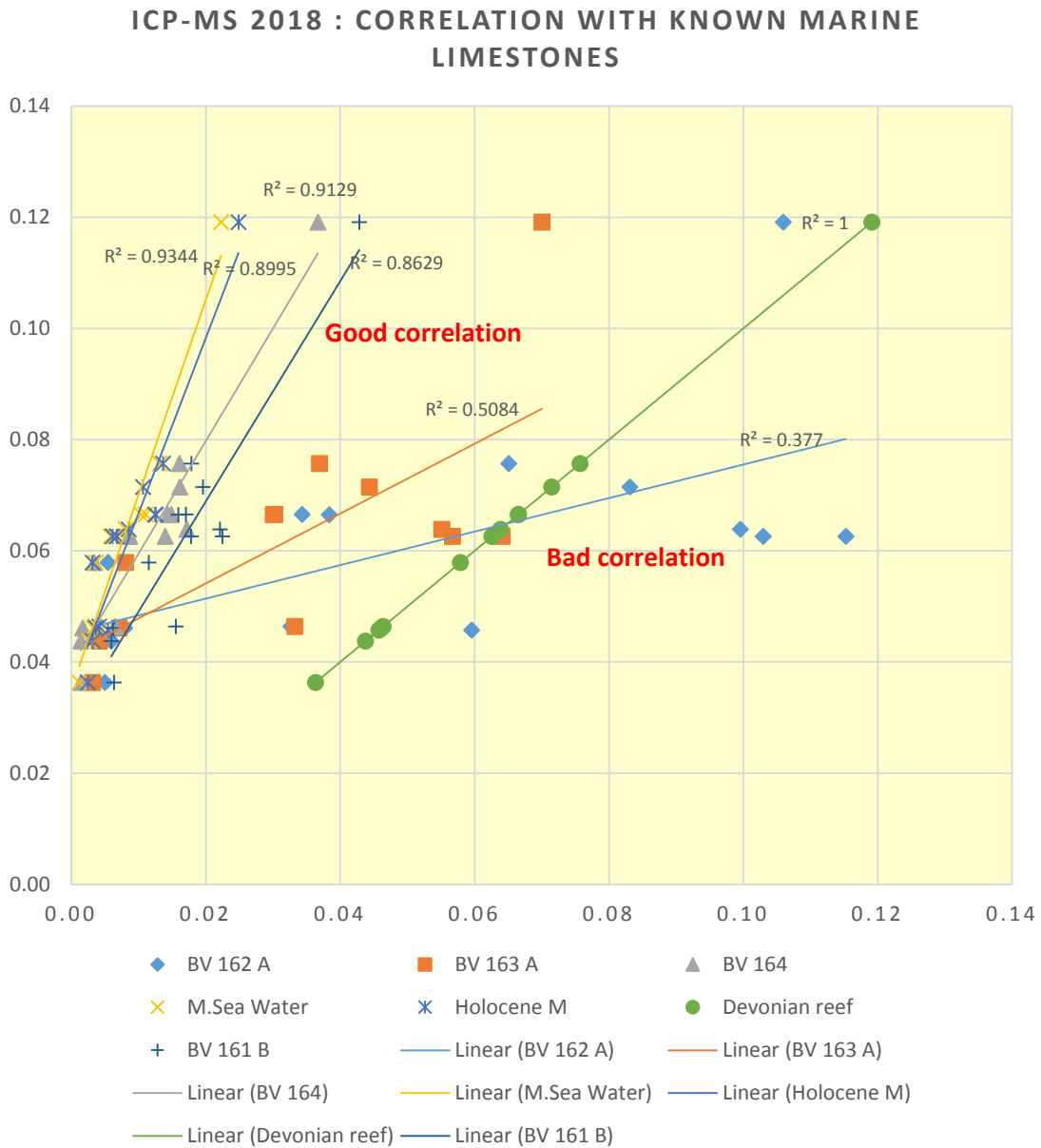


*Figure VI.40: Bloc V 2014 Marine Limestones Correlation coefficient with Devonian Reef*

This above graph shows clearly that samples BV 161 and 164 have marine limestones signatures correlating with Devonian Reef while clearly it's discriminating the samples BV 162 and BV 163 collected in the field few meters around in the same gorge (Katanda)

The ICP-MS results of the 2018 experiment have produced the elements concentrations in ppb and normalized in MUQ as per Kamber experiment method. These values are presented in the tables in appendix 2 and their original excel files enclosed to this thesis in a memory stick.

The Figures VI.39 to VI.44 below show the REE pattern graph of all Msc. ICP-MS marine limestones signatures and their respective correlation coefficient $R^2 > 0.80$ with Devonian reef.
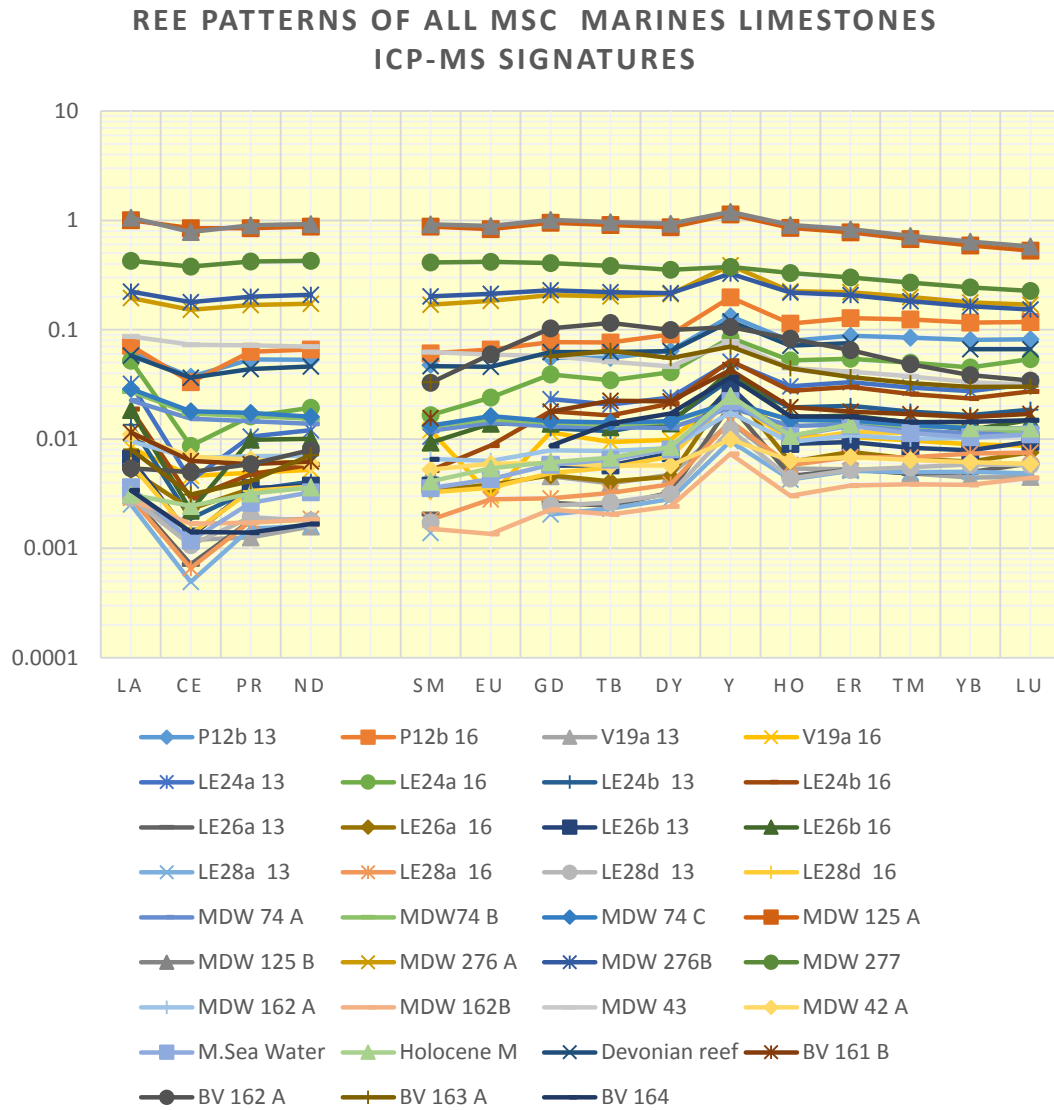


*Figure VI.41: REE patterns of all Marine Limestones signatures detected by ICP-MS from 2013 to 2018*
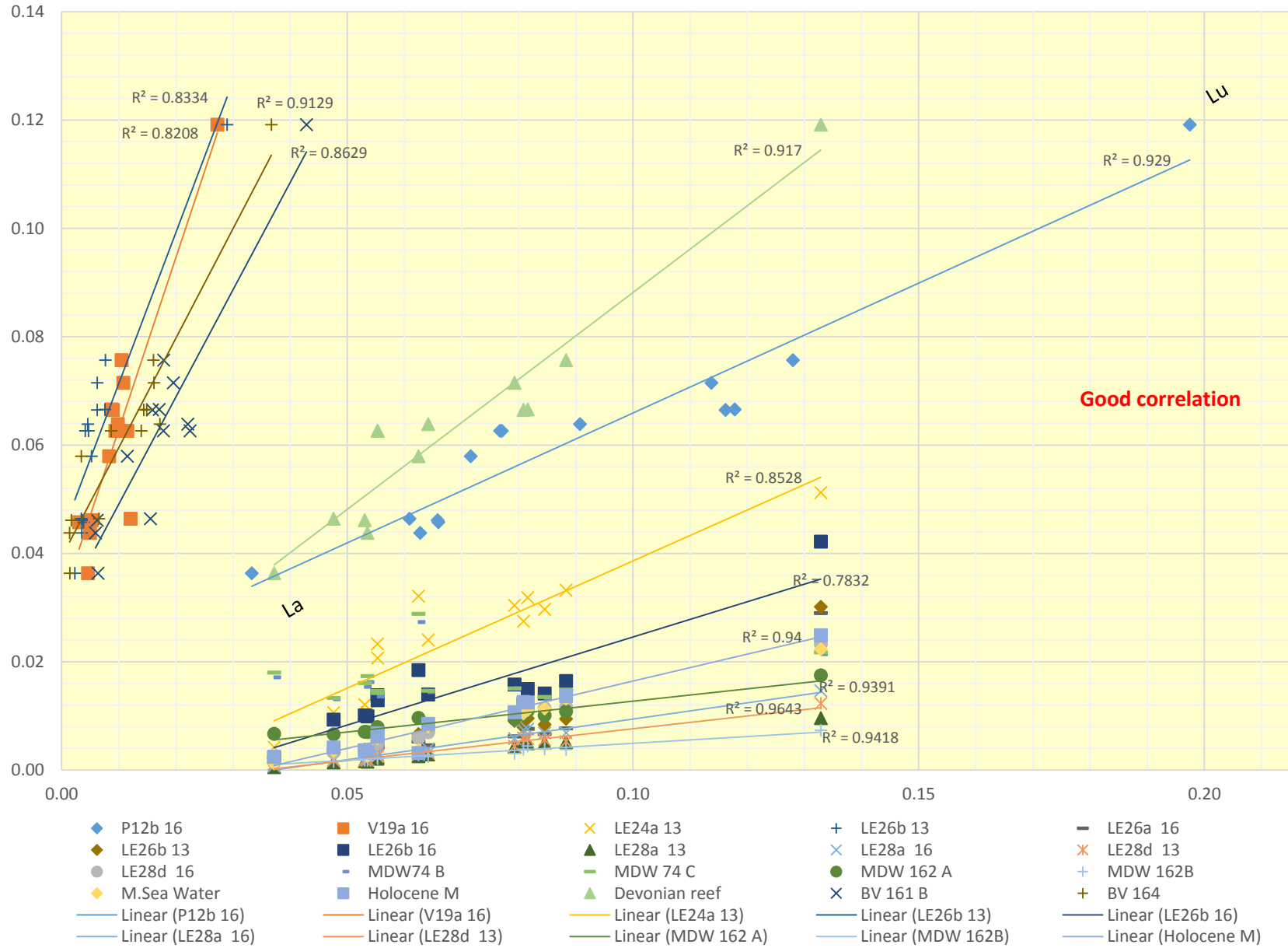
*Figure VI.42: All Marine Limestones Correlation coefficient with Devonian Reef*
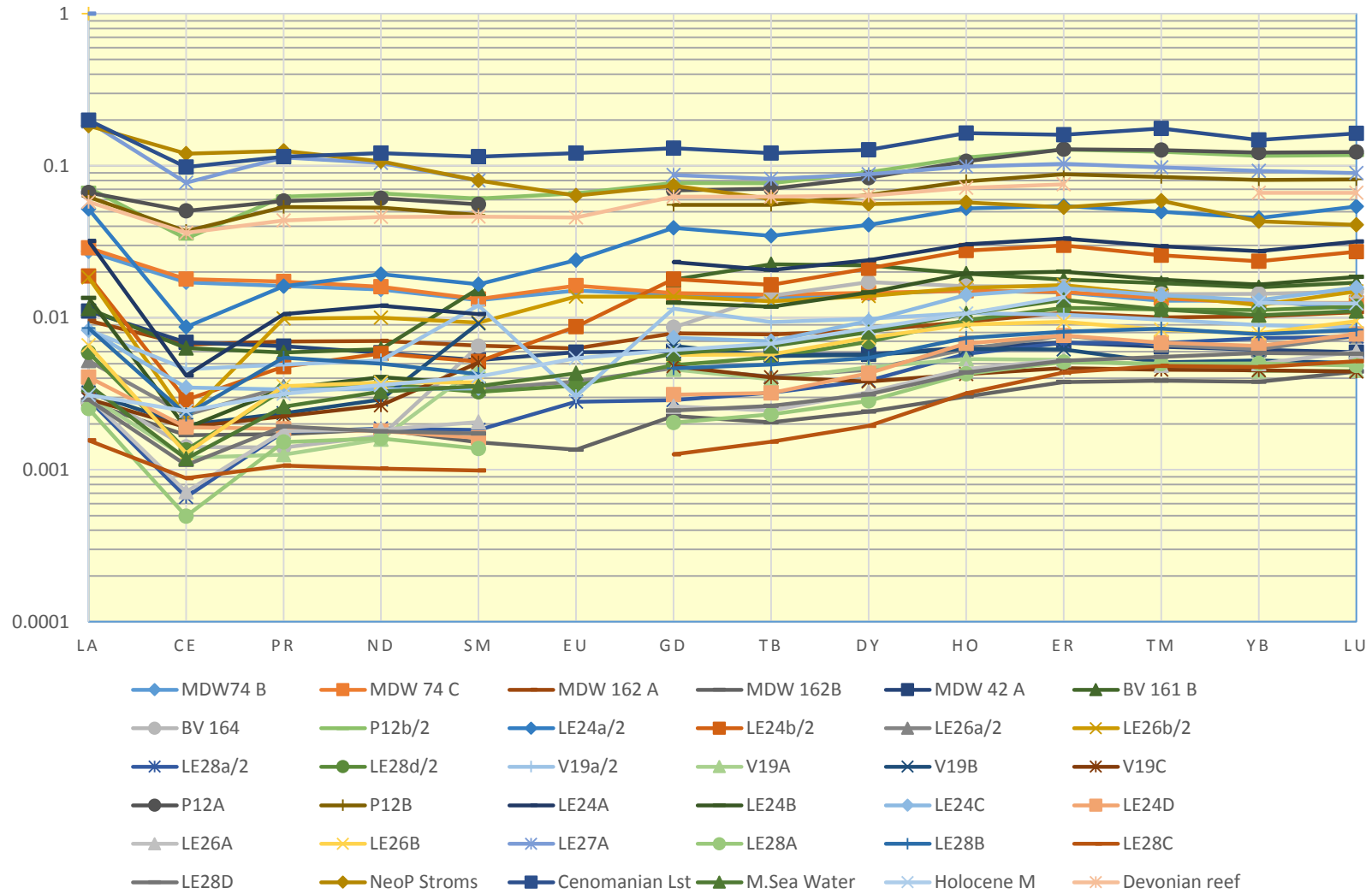
*Figure VI.43: REE patterns of all Marine Limestones signatures detected by ICP-MS from 2013 to 2018 & published marine limestones*

*Figure VI.44: Correlation coefficient of 2013 marine's limestones experiments, Cenomanian limestones and Neoproterozoic stromatolites with Devonian reef.*
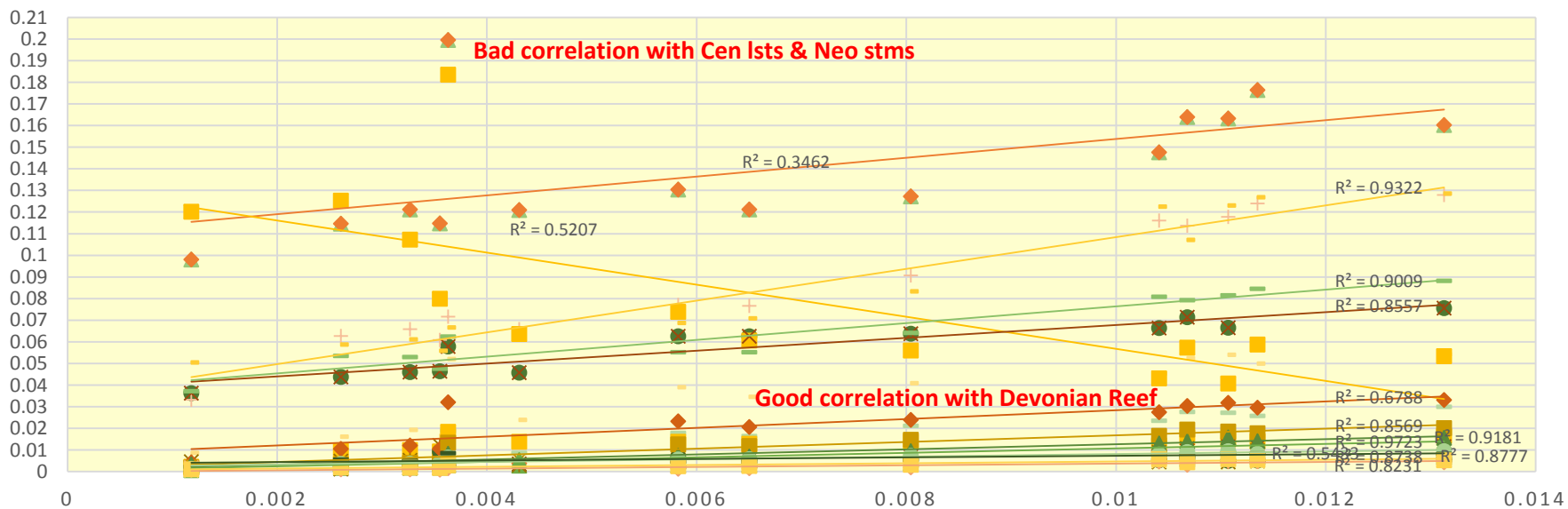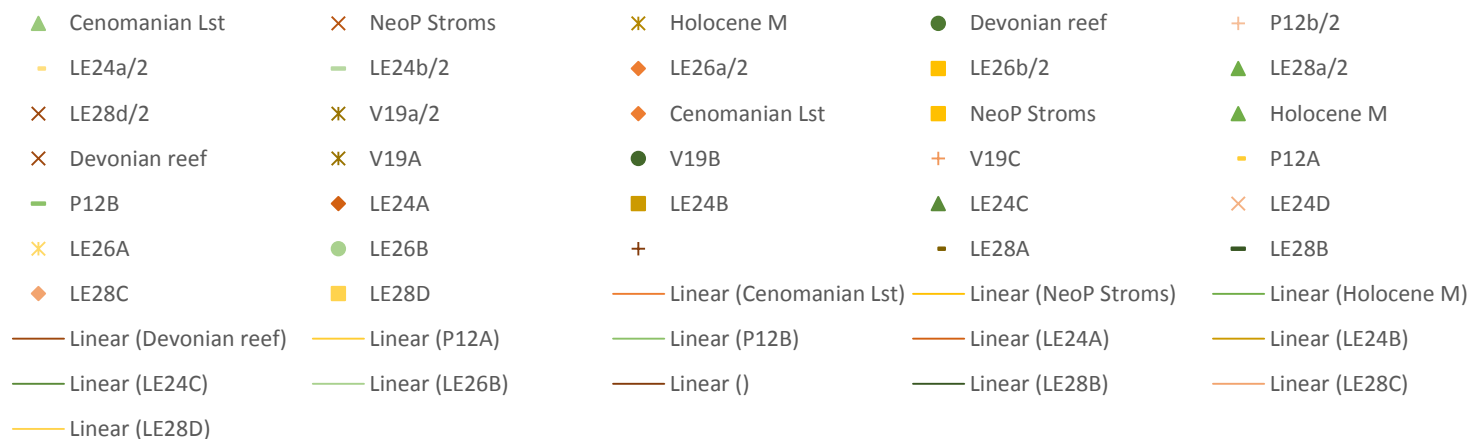
*Figure VI.45 Correlation coefficient of 2016 marine's limestones experiments, Cenomanian limestones and Neoproterozoic stromatolites with Devonian reef.*
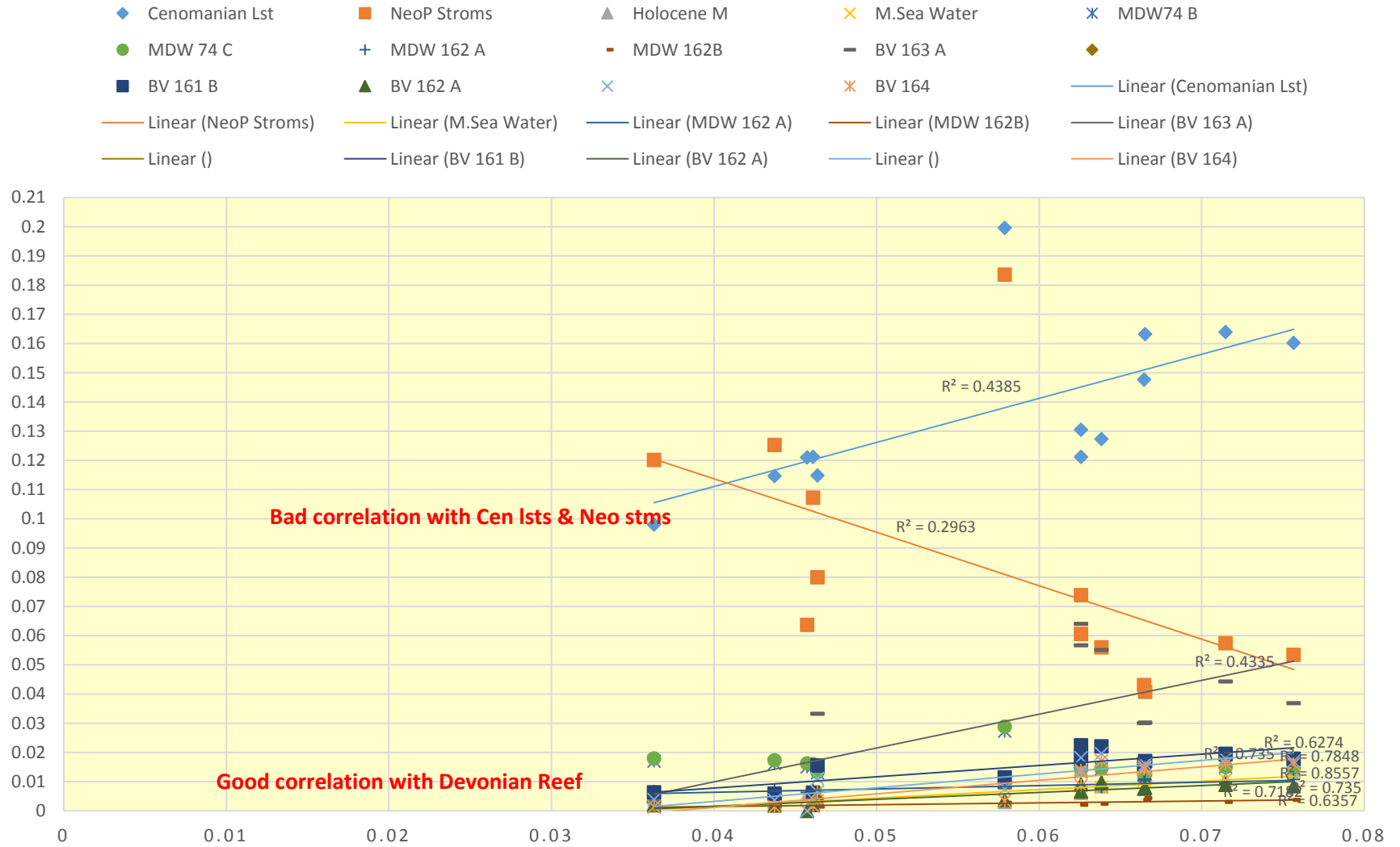
*Figure VI.46: Correlation coefficient of 2016 marine's limestones experiments, Cenomanian limestones and Neoproterozoic stromatolites with Devonian reef.*

12 Samples collected from the Mandawa basin have been drilled anyway regardless any structures textures / fabrics. Their resulted MUQ values are presented in the enclosed ICP_MS 2018 Excel file.

The table 6 below which help to check the marine origin criterias, suggest that some ones Mandawa samples drilled anywhere regardless their textures, structures or fabrics have more Marine signatures involvement origin and some others don't.

| | | MDW 74 A | MDW74 B | MDW 74 C | MDW 125 A | |
|---|---|---|---|---|---|---|
| Y/Ho | >40 | 1.464249325 | 1.417060269 | 1.44541142 | 1.328873324 | NO |
| La/La* | >1.1 | 1.390040154 | 1.502736134 | 1.426742804 | 1.262298878 | YES |
| Ce/Ce* | <0.8 | 1.185218824 | 0.940697888 | 0.889180228 | 1.067263955 | NO |
| Gd/Gd* | >1.1 | 1.007091911 | 1.11449575 | 1.05275512 | 0.997297002 | YES |
| Prn/Ern | << 1 | 1.068561526 | 1.10490484 | 1.171038765 | 1.09286449 | NO |

| | | MDW 162B | MDW 43 | MDW 42 A | MDW 125 B | |
|---|---|---|---|---|---|---|
| Y/Ho | >40 | 2.41541563 | 1.74105218 | 1.556907429 | 1.317345028 | NO |
| La/La* | >1.1 | 1.858908106 | 1.151967364 | 1.401107236 | 1.251236675 | YES |
| Ce/Ce* | <0.8 | 1.136103665 | 0.968169275 | 0.870740649 | 0.924284767 | YES |
| Gd/Gd* | >1.1 | 1.295522052 | 1.013696268 | 1.053472317 | 1.009120174 | YES |
| Prn/Ern | << 1 | 0.455385923 | 1.732430997 | 0.94878573 | 1.081120978 | YES |

| | | MDW 276 A | MDW 276B | MDW 277 | MDW 162 A | |
|---|---|---|---|---|---|---|
| Y/Ho | >40 | 1.725870939 | 1.49369084 | 1.13811642 | 1.856451681 | NO |
| La/La* | >1.1 | 1.213272103 | 1.19539257 | 1.05197194 | 1.401416525 | YES |
| Ce/Ce* | <0.8 | 0.94734948 | 0.95618783 | 0.93056389 | 0.975616616 | NO |
| Gd/Gd* | >1.1 | 1.085927382 | 1.01730623 | 0.97258153 | 1.078965793 | YES |

*Table 7:   Marine limestone criteria check box for the Mandawa samples*

Seven (7) in blue from 12 samples have satisfied at least three (3) of the marine limestones criteria) while five (5) in red haven't. These results which have been made from the 2018 MUQ raw, are presented in form of comparative Charts enclosed to this Msc in an Excel file. The Mandawa samples shows a clearly marine limestone origin as confirmed in the existing literature.

Both Lyemubuza and  Bloc V Travertine Samples (fabrics, textures, structure and/or their replica) REE values correlating with the known marine limestones Mandawa Basin Tanzania with a Correlation Coefficient of R2 > 075 are shown plotted alongside in the Figures VI. 45, VI.46, VI.47  and VI.48  below:
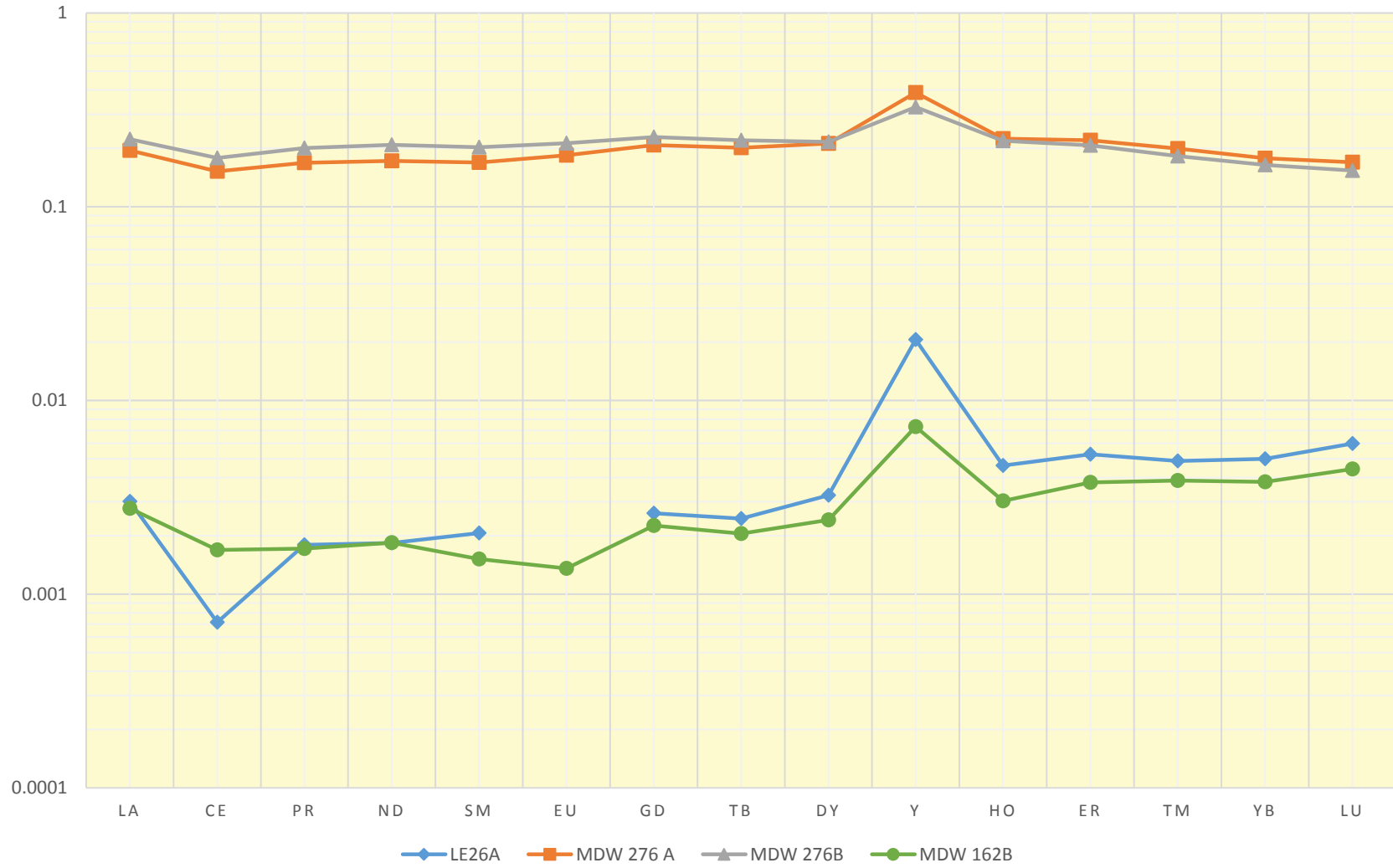
*Figure VI.47: Mandawa Basin & LE 26 REE+Y Patterns*
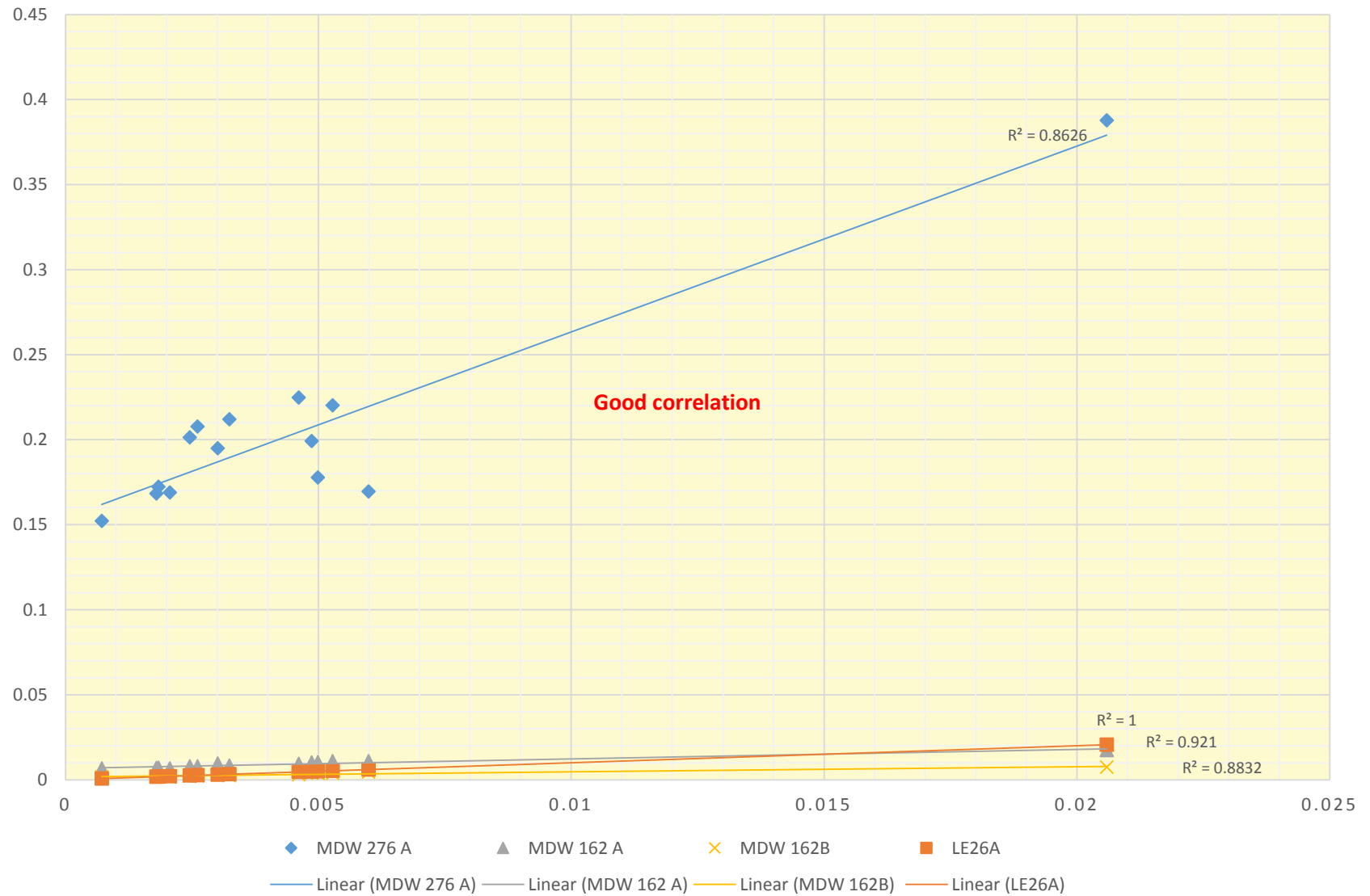
*Figure VI.48: Mandawa Basin & LE 26 correlation coefficient*

MANDAWA BASIN AND BLOC V REE + Y PATTERNS
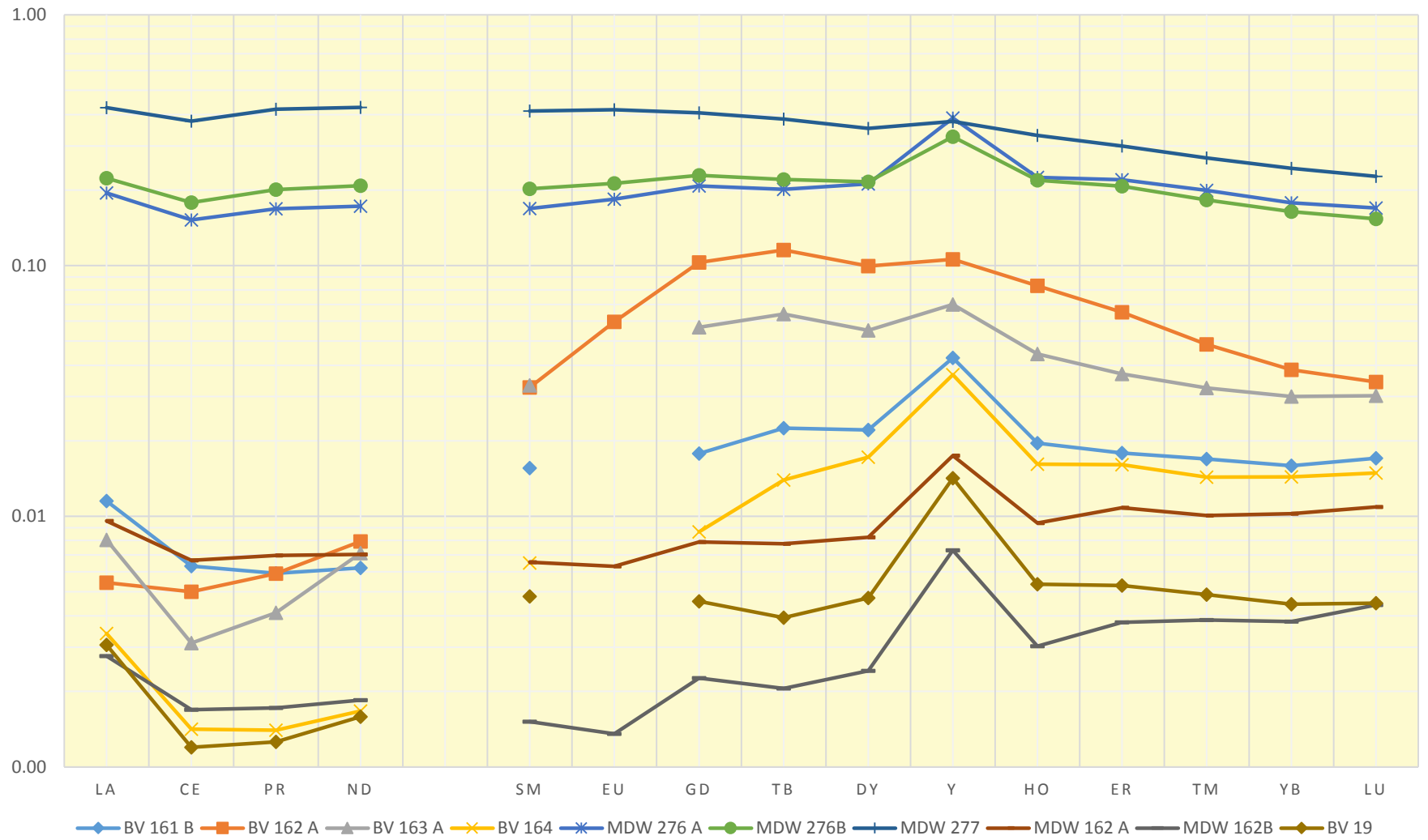
*Figure VI.49 :  Mandawa Basin & Bloc V  REE+Y Patterns*
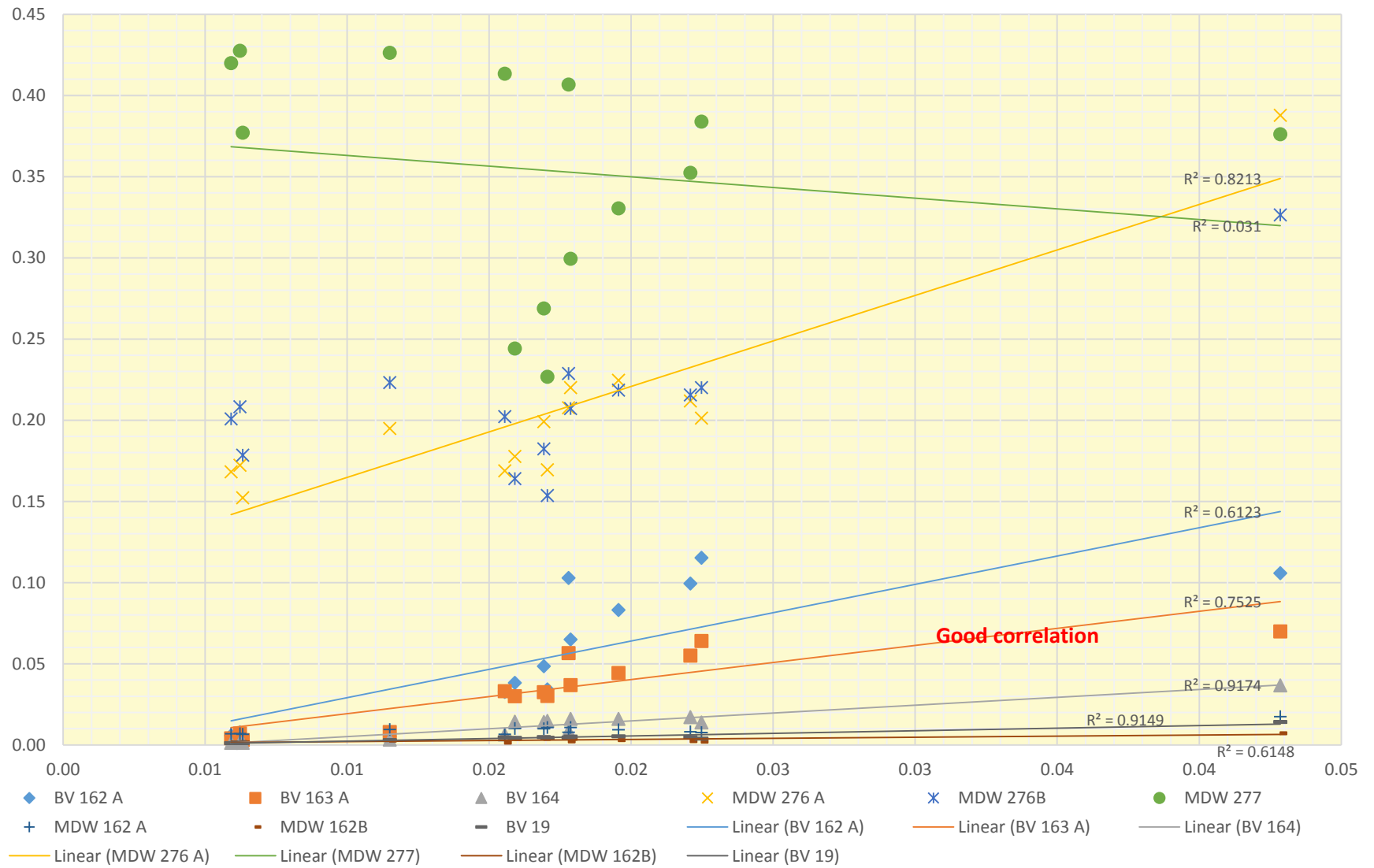
*Figure VI.50 : Mandawa Basin & Bloc V Correlation Coefficient*

Samples BV 149,150 and 159 have given different results far  from either Carbonatites or Marine limestones signatures. They gave spectral signatures in Figure VI.43 below showing a decreasing the light rare earths Lanthanum, cerium, praseodymium, neodymium, promethium, and samarium and an increasing the "heavy rare earths "Yttrium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Respective correlation with Marine limestones and Fort Portal are presented in Figures VI.47, 48, 49 and VI.50 below
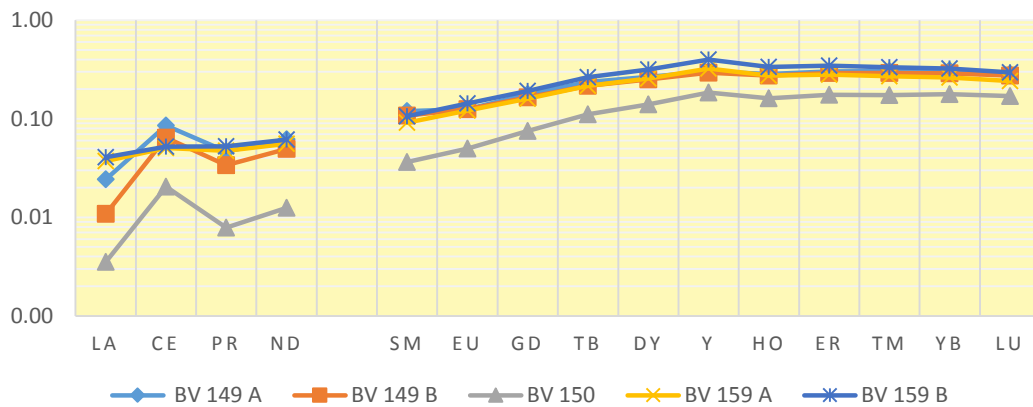


*Figure VI.51 : Bloc V 2014 Travertine Hybrid signatures by ICP-MS 2018*
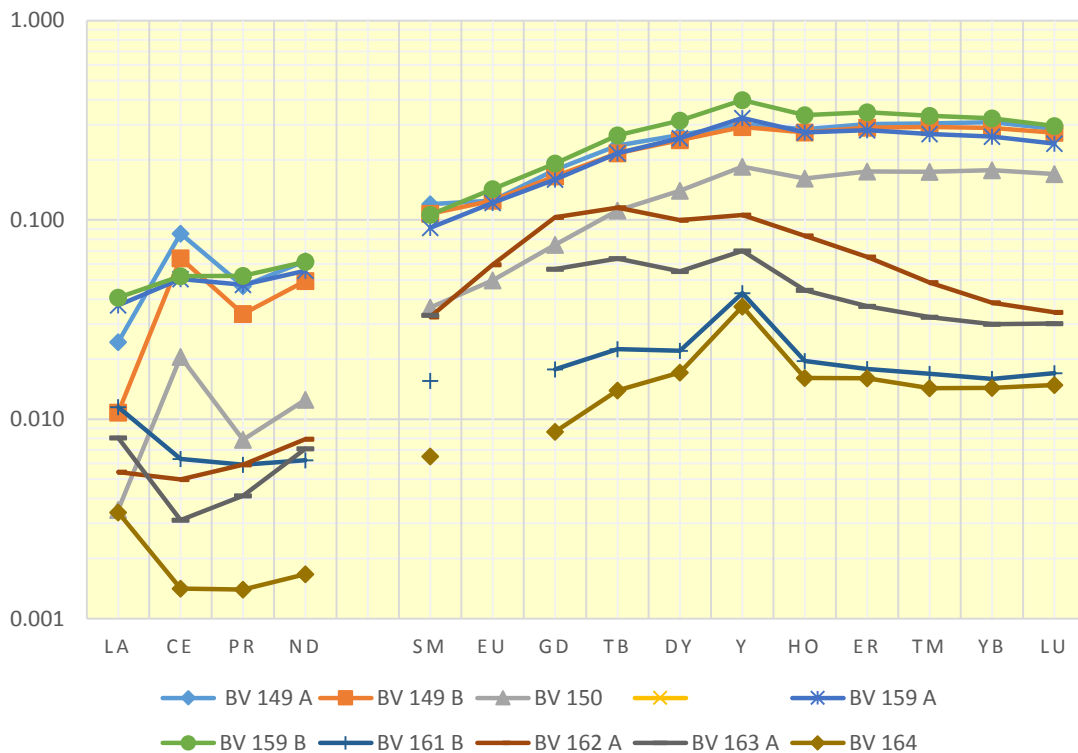


*Figure VI.52 : Bloc V 2014 Hybrid and Marine Limestones signatures by ICP-MS 2018*

## HYBRID SAMPLES CORRELATION WITH DEVONIAN REEF
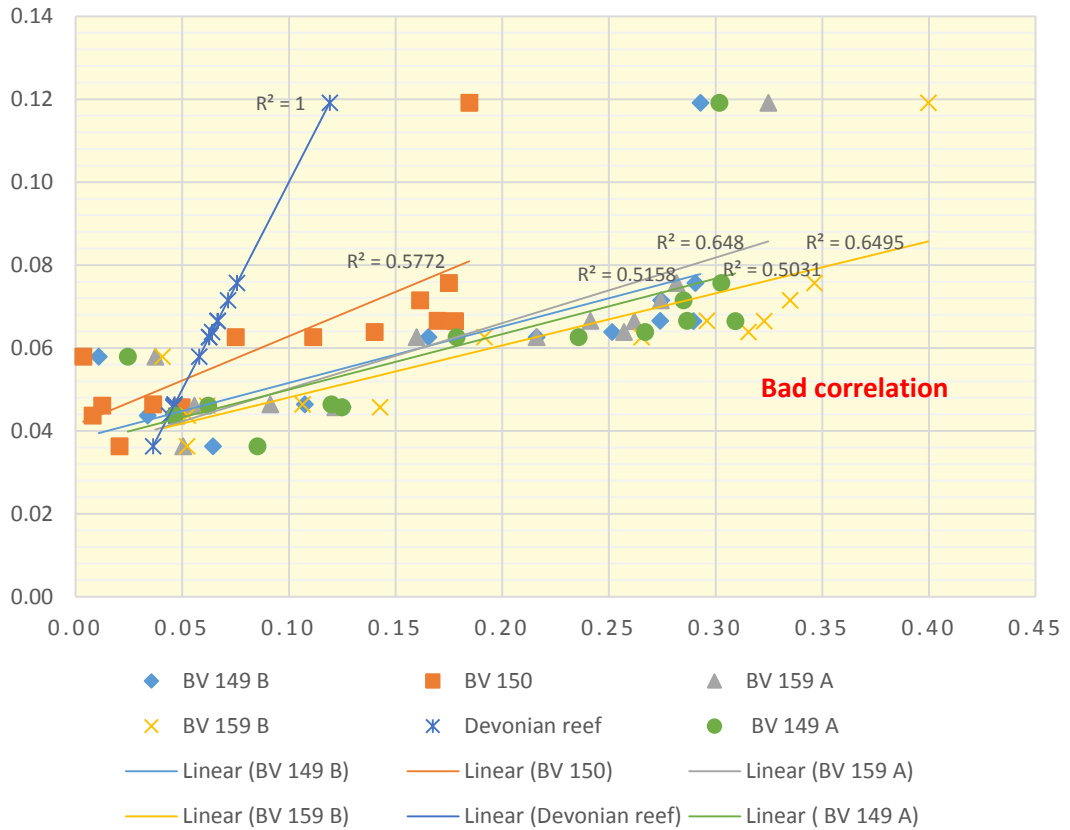
*Figure VI.53  Bloc V 2014 Hybrid Correlation coefficient with Devonian Reef*



## HYBRID SAMPLES CORRELATION WITH FORT PORTAL
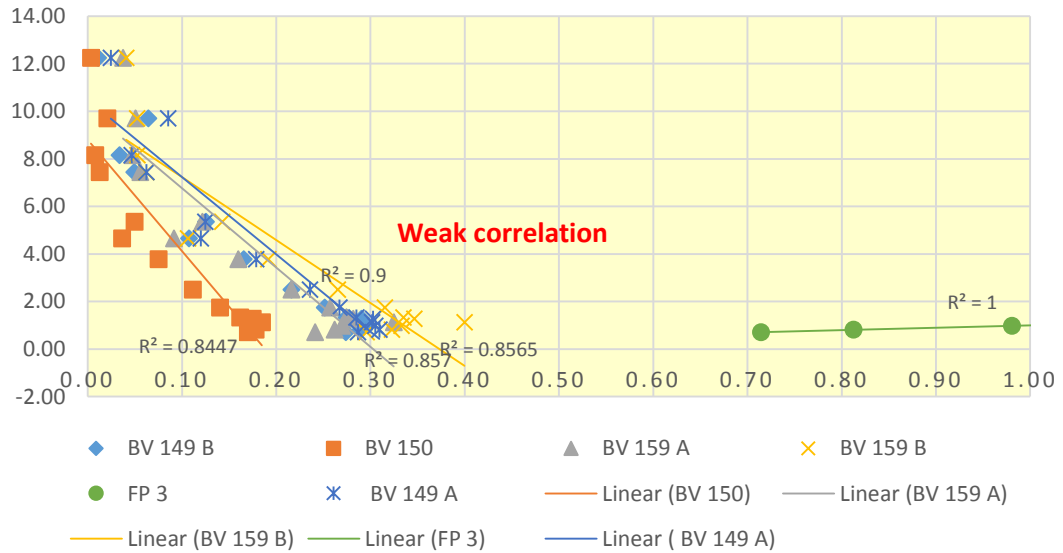
*Figure VI.54 : Bloc V 2014 Hybrid Correlation coefficient with Fort Portal Carbonatites #3*

*Chapter 6 Conclusion*

*The geochemistry analysis results obtained by the research methodology have been presented in tables, graphs and figures as below:*

- *The stable Carbon (PDB) and Oxygen (SNOW) signatures and Strontium isotopic ratio in order to define respectively the level of isomerism and aromatisation of their carbonates biomarkers and their palaeoclimate.*

- *Edward Lake offshore Oil slicks samples analysed by Gas Chromatography Mass Spectrometry and which results have been compared with the onshore Oil stains found in Travertines cavities described and collected in Lyemubuza and Muhokiya quarries located in Edward Lake onshore in Uganda. These results comparison suggested these offshore Oil slicks and onshore Oil stains origin as from a marine shale source with a waxier, lacustrine component.*

- *Around 50 Travertines samples described and collected throughout the Eastern Africa Rift System went through the ICP-MS experiments which processed well for all samples.*

- *The ICP-MS process gave in output the REE+Y concentrations in ppb normalised in MUQ as per Balz Kamber similar experiments in 2014.*

- *The EARS ICP-MS results presented REE spectral signatures graphs per their respective geochemical origin and correlation coefficient charts with Fort Portal lavas for Carbonatites signature and with Devonian reef limestones for marine signature.*

- *EARS Travertines marines' limestones correlations with Cenomanian limestones referring to the Mesozoic Karoo and Neoproterozoic stromatolites associated to the west Congo schisto-Calcaire have been done in order to discriminate definitively the marine source of their bicarbonate.*

*The next Chapter, named Results discussion, shows how our Msc research study used these above geochemistry results to solve the geologic answer of the possible carbonate origin of these Travertines samples in the siliclastic classical Eastern Africa Rift System.*

*This Chapter relates to the reader our personal thoughts and interpretations on the obtained geochemistry results based on scientific facts that we noted all along the previous sections of this present Msc research study.*

# CHAPTER 7: RESULTS DISCUSSIONS

VII.1 – FIELD TRIP RESULTS

The field trip outputs are the starting point of this MSc research study's discussions and interpretations. Different travertine lithofacies and/or lithofacies associations have been observed in the field and documented in Chapter IV. Each of these field observations have opened the way to many venues for further discussions and interpretations with respect to the Eastern African Rift System (EARS), our MSc research study's zone of interest.

The classical depositional framework of the Eastern African Rift System is generally dominated by clastic sediments among which fluvial and lacustrine environments have been the most commonly observed, documented and collected in the field during the recent geologic campaigns undertaken in the Eastern African Rift basin.

The above described (fluvial/lacustrine) deposit field evidences have confirmed their respective lithologies known from the existing literature, varying from conglomerates through sandstones to mudstones, cherts, oil shales and coals (Selley, 1982).

The distribution, orientation and internal geometry of these fluvial/deltaic deposits are controlled by many factors including climate, water discharge, sediment load, river mouth processes, waves, tides, currents, winds and the tectonics and geometry of the receiving basin (Selley, 1978).

Fluvial sediments are randomly located in the entire Eastern African Rift System. They are mostly dominated by sandstones, conglomerates, siltstones and interbedded sandstones. Lacustrine package outcrops were also clearly identified in many locations in the field. They are composed of siltstones, clay stones and thin clay layers in interbedded sandstones.

Moreover, many travertines occurrences have been found outcropping in the field, often associated with a biotype of flowing waters with high calcium content. The development of such carbonates might result from low-Mg calcite precipitation by cyanophytes, prokaryotes, eukaryotes, diatoms, bryophytes, tracheophytes and other bacteria (Pentecost, 2005).

During exceptionally rainy seasons, floodplain inundation promoted the seasonal growth of diverse environments ranging from fluvio-lacustrine basins to hydrothermal settings in which the above-mentioned travertine carbonates have been found biologically precipitated. They represent a particular continental carbonate facies providing an important source of geological data through their natural gamma radiations (GR) which were used in this MSc research field trip's discussion to provide evidence for carbonates' hydrological and physico-chemical deposit conditions.

The natural gamma radiations in sedimentary rocks are almost entirely attributable to Potassium and isotopes from the Uranium and Thorium families. Some carbonate rocks outcropping in the **Vitshumbi** formation (see point IV.4.2 in Field trip Chapter) showed high concentration of U, Th, and K visible in Figure IV.27 on page 99.

According to Adams and Weaver (1958), the Th/U ratio has proven to be useful in the recognition of geochemical facies.
This ratio can be used as a good indicator of sedimentary processes specifically in the determination of their geochemical facies.

The Th/U ratios in most sedimentary rocks range from less than 0.02 to more than 21. Ratios in many oxidised continental deposits are above 7, whereas most marine deposits have ratios much below 7. Therefore, the Th/U ratio varies with sedimentary processing and depositional environment. A cyclothem and several other sedimentary sequences illustrate the use of this ratio to distinguish environments and processes (Adams and Weaver, 1958).

The radiations recorded in the Vitshumbi unit (BV$\gamma$-10 page 99) reveal that the total GR varies from 160–500 API, which is higher than in any other carbonate unit discovered so far in the EARS basin. The Vitshumbi unit's recorded values suggest calcrete tops with associated desiccation cracks and microbial mats. A marked spike in the total GR, U and Th amounts are noticed in finer laminated silty marl. However, the total GR seems clearly depleted towards top of the section composed of sandy limestones with calcitised fragments. The high gamma response (Figure IV.27 page 99) suggests that these Vitshumbi carbonates with high U, K, Th pics are being precipitated from reducing U and Th rich waters. These U and Th reductions are due to the groundwater percolating up the main rift-bounding faults which are still feeding active cyanobacteria in hot springs today. These cyanobacteria and algae growing at hot spring mouths appear to actively scavenge U and Th by giving to them very high total GR values, and the U and Th concentrations fall away over a few metres' distance from the spring mouth.

From the gamma rays recorded in-depth during the drilling in Kansas, USA, Macfarlane (1989) suggests that the Th/K log defines the Cretaceous/Permian sharp boundary and, along with the Th/U log, they emphasise the contrast between marine Upper Cretaceous rocks of the Greenhorn depositional cycle and nonmarine to transitional rocks of the Lower Cretaceous. The long-term cyclic pattern of the Th/U log is an excellent indicator of a broad transgression/regression observed during the Greenhorn cycle on an open marine shelf. However, extreme fluctuations of Th/U in the Lower Cretaceous rocks suggest a high degree of short-term environmental variability (Macfarlane et al., 1989).

This short-term environmental variability has been shown to be applicable in areas with speleothem uraniferous groundwaters and low levels of natural lead (Richards et al., 1998). Indeed, during speleothem deposition, Uranium in solution in the percolating drip waters is co-precipitated into the calcite crystal lattice. Moreover, Thorium concentrations in the drip water and the deposited calcite are negligible, resulting in extreme fractionation between the parent and intermediate nuclides. Their Calcite deposition time is determined by U–Th dating from the ingrowth or decay of intermediate nuclides.

The U, Th, K gamma Ray values recorded in either the carbonates on the EARS travertines, calcitised reeds or pustulous textured microbial mat outcrops are all documented in detail by this MSc study's Chapter Four. They have been used as available geological instrument based on the idea that the determination of the relative Thorium and Uranium distribution in the speleothems found in **Bat cave** carbonate sediments (Sample LE 44 page 80, page 111) might be treated as a function of the depositional environment.

This means that the Th/U ratio could serve as atmospheric oxygen indicator and thereby provide more knowledge of the oxygen content of the palaeo atmosphere during these carbonates' deposition.

Speleothems and spring-deposited travertines over the last 160000 years have been climatically controlled largely by a combination of temperature and aridity effects (Baker et al., 1993).Speleothems observed in LE 44 thin sections (page 111) could be used as major palaeoclimate and palaeoenvironmental data archives because of their oxygen and carbon isotopic variation records which are supposed to rely on a trustable chronological framework with U-series dating. These isotopic signals help to efficiently interpret the isotopic fractionation conditions during calcite precipitation. The context of speleothem formation is somehow linked to Th and U isotopes.

$_{230}$Th/$_{234}$U isotope analysis of the speleothems found in the Bat cave carbonates has not been conducted in this MSc research because the suitable speleothems' identification for dating by Th/U analytical methods required further assessment of the degree of detrital thorium contamination (Moseley et al., 2013). Financial restrictions for the lab analysis did not allow further laboratory assessment. However, some interpretations described below have been made only regarding the K, U, and Th values recorded during the DRC field trip in 2014.

The gamma ray recorded for the travertines found in **Mayi ya Moto** (Samples V149, V150, V153 pages 89 and 112–113) provided the following mean values for K = 0.9 % U = 66.8 ppm Th = 12.7 ppm and deduced a ratio Th/U = 0.190, confirming the presence of speleothems in these carbonates. Moseley et al. (2013) found the same Th/U ratio value for the speleothems discovered in limestone caves in the Gunung Mulu national Park, Sarawak, Malaysia.

In **Katanda** (Samples V159, V161, V162, V163 and V164 pages 90 and 113) the following values were recorded:
- K= 3.6 % U= 410.8 ppm Th = 11.8 ppm (assay #2266) upstream
- K= 1.4 % U= 309.2 ppm Th = 57.5 ppm (assay #2267) downstream

In this locality, the GR, Th and U values appear to decrease downstream away from main stream abundant with cyanobacteria evidence. These decreasing Th and U values suggest increasing oxygenation downstream.

In **Biruma** (Samples V338, V 344, V 352, V 356, V363, V 364, and V 385 pages 91 and 114), the GR values K = 1.0 % U = 200.9 ppm Th = 25.1 ppm suggest that the carbonate deposits present substantially depleted the K, U, Th values. These deposits are mainly composed of clean white limestones with dense reed and rootlet beds because the carbonate has encrusted vegetation (samples V363 and 364 Figure IV.14 page 88) which probably grew in an extensive shallow pool fed by carbonate rich palaeo hot springs.

To summarise, the EARS travertines analysed in this research study show typical morphology and chemistry reflecting both formation conditions and the effects of post-diagenesis weathering processes. Their geological investigation in the field outcrops have been convenient for understanding their palaeo environments. Their carbonates dissolve in acidic waters but do not dissolve at equal rates; the process is dependent on joints and fractures in the potential carbonate bedrock as well as on porosity (Trudgill, 1985).

According to Williams (2004) such limestones could be formed from back-reef lagoonal environments (Williams et al., 2004); (Vinson, 1962).

Other studies suggest these limestones to be composed of shallow water sediments from the Jurassic to the Tertiary periods (Hartshorne, 1989).

Pentecost (2005) indicates that some calcite content minerals entered into the travertines as erosion or weathering products derived from the carbonate bedrock.

Most of these weathering products are water borne and the carbonate minerals enter in their structure through animal activity (Pentecost, 2005). A suggestive example is bats living in caves in the visited Bat Cave locality in Uganda where numerous phosphate minerals originating from the bat guano and bone beds are known from their association with cave travertine (Hill et al., 1997).

All the EARS travertines have been investigated, described and properly collected at a specific localised number of active and palaeo-spring sites around the margins of the Eastern Africa Rift System. These EARS travertines' occurrence is linked to the presence of hot springs and these are linearly situated along both the Eastern and the Western major rift-bounding faults where there is significant fluid flux from depth. Their fluid temperature field records show a range of high temperature around the aligned, bounding fault hot springs although the collected travertines have been found outcropping in surrounding cold areas.

The bicarbonate source of these EARS travertines is strongly linked to the significant geothermal fluid flux from depth flowing to the surface in hot springs which as quaternary volcanoes, fumaroles, boiling pools, hot and steaming grounds, geysers and sulphur deposits are manifesting the occurrences of geothermal activity within the EARS. However, geochemistry results clearly indicate a marine limestone involvement in some of the analysed carbonates samples. Active hot springs or inactive palaeo hot springs as well as the geothermal activity in the East African Rift System seem intricately connected to the occurrence of palaeo volcanoes located within the axis of the rifts. Documented examples of these geologic configuration are found on either side of the rift valley in the Fort Portal region in the north east and in Nyragongo Nyamulagira region in the south west. The EARS travertines have been observed in the field situated along deep-seated, rift-bounding faults. The discussion was still open, linking their origin to groundwater flux along these faults. This MSc research study terminated the mentioned discussion and confirms the geological fact that the carbonatite lavas' spectral signature is relatively close to the Fort Portal lavas in Uganda's side and from both Nyragongo and Nyamulagira in the DRC side. However, the clear marine signature found in localised hot springs definitely suggests the presence of a pre-tertiary carbonate bedrock underneath the EARS Cenozoic basin. The field evidence of these identical travertine outcrops observed in both Eastern (Uganda) and Western (DRC Bloc V) major rift-bounding faults have actually proved the geothermal flux involvement in the EARS carbonate precipitation on surface. Moreover, the geochemistry results opened the discussion regarding these travertine layers' thickness variation, which are possibly laterally impersistent and of limited subaerial extent. The travertine samples with marine limestones' spectral signatures, found on both sides of the EARS aligned along the western and the eastern bounding faults, lead to presume to have geothermal waters pure Calcite contamination from a Devonian carbonate bedrock from depth. This supports the geologic considerations about the possible presence of a marine limestone bedrock unit beneath the classical known siliclastic deposit in the Eastern African Cenozoic rifting.

A fissure ridge can be defined as a Travertine fault trace fissure-ridge, adding a helpful example for studying the relationship between faulting and travertine deposition (Brogi and Capezzuoli, 2009). Based on Brogi and Capezzuoli's (2009) studies, the idea of the presence of travertine fissure-ridges within the EARS bounding fault is not negligible.

Some possible fissure-ridge developments along the trace of a normal fault with small displacement were found located in the margin of EARS basins.

Brogi and Capezzuoli (2009) point out that these fissure ridges are often formed from supersaturated hot waters (39.9°C) flowing from thermal springs aligned along the trace of the normal fault, dissecting limestones not older than Late Pleistocene (24 ± 3 ka). They indicate also that hot fluids flowing up from cones are located at the extremities of the ridge exactly where the travertine is deposited. More possible fissure-ridge evidences are still being researched and if found, they would entirely diversify the depositional morphology in the Eastern Africa Rift System because they will always appear in the field formed around the area in which hot spring waters emerge along a joint, extensional fracture or fault on an elevation.

The fissure-ridge sedimentation style described above suggests that it could have resulted from seasonal higher and lower water table levels that allow temporary pools to form with organic matter and low Ph, favouring the EARS travertines formation.

All these travertines field considerations are not sufficient to determine the origin of the bicarbonates which constitute the EARS travertines samples. They need to be sustained by the following microscopy inputs and furthermore by geochemical analysis to assist this MSc study in the EARS travertines' possible palaeoclimate reconstruction.

Combining the existing literature reviewed in Chapter Two and field results obtained in Chapter Four, it was advantageous to use microscopic observation prior to geochemistry analysis to document the petrography of each travertine texture, structures and/or fabrics followed by drilling through each of them and running the ICP-MS process. In other terms, the microscopic section below highlights the strong link between each petrographic observation of textures, structures and/or fabrics and their respective ICP-MS results. This means that each of the observed EARS travertine textures, structures and/or fabrics' respective REE+Y ppb values and spectral signatures would be correlated as per the Balz Kamber method (Kamber et al., 2014) with the universally recognised Fort Portal Carbonatite lavas or Devonian reef and Mandawa basin marine limestones.

## VII.2 – MICROSCOPY OBSERVATION RESULTS

The microfacies analysis of EARS travertines' thin sections was performed, where applicable, with Alizarin red stain to efficiently distinguish the calcite from the dolomite. The microscopic observations were complemented with field-documented data including determination of the HCl acid freezing reaction.

The EARS travertines' thin-section observations indicate a progressive development of successive carbonate layers which occurred during the deposit and culminated in parallel and subsequent layering. In a later stage of subaerial exposure, calcification occurred, overlapping the original facies. Around the beginning of the Tertiary, a marine transgression favoured this EARS calcification overlapping process involving a sea level rise. Due to this palaeo sea level changes and climatic factors, these carbonate sediments were seen superimposed lacustrine or in intertidal to subtidal horizons, diagenetically altered, thereby presenting a complicated REE+Y facies pattern.

Spring limestones precipitate at several temperatures and this can be observed under the microscope in different fabrics, textures and structures in association with plant rootlets, tubes and leaf prints. The main carbonate fabrics, structures and textures observed microscopically are fibrous, crystalline, speleothems and porous.

Therefore, fine structures of calcite crystal lattice were examined but the existence of fossils were not clearly observed in the EARS travertines.

The microscopic observations of the above structures, textures and/or fabrics suggest that these travertines are commonly formed in clear, warm, near-surface and shallow marine waters in environments such as deltas and/or estuaries. They appear similar to organic sedimentary filling formed by the precipitation of calcium carbonate from lake or ocean water accumulation of shell, coral, algal, and faecal debris. The chief mineral component of our EARS travertines is calcite which is mostly composed of a heterogeneous aggregation of fine, medium and coarse grains mixed with white and striped calcite veins. This particular structure is due to further carbonation of fine grains of limestone.

The observed constituents of Eastern Africa Rift travertines, as visible under a microscope, have been categorised as follows:

1. Terrigenous constituents

These are the materials derived from outside the basin of deposition, through the process of weathering, erosion and transportation, as sediments to the depositional site. They were also named detrital travertines by Casanova (1994) in his attempts to trace back the EARS palaeo drainage patterns. The observed terrigeneous materials in the P12 thin section (on page 105) are colourless, anhadral quartz grains from the basement and show wavy extinction under crossed nicols.

2. Allochemical constituents

The Allochemical constituents or 'Allochems' are the dominant constituents and are those materials which are formed within the basin of deposition by chemical and bio-chemical precipitation but are organised into discrete aggregated bodies and have mostly suffered some degree of transportation (Folk, 1959). The allochemical constituents observed in this study are categorised as follows:

i.   Intraclasts, including early carbonate sediment fragments, that have been eroded or by biochemical activity from the adjoining areas of the sea bottom and redeposited to form new sedimentary rock (Folk, 1959), leaving spaces between them and yielding the primary porosity of samples V 162 on page 113 and samples LE 24, LE26, LE27 and LE28 on page 109.

ii. <u>Ooids</u> are spherical or sub-spherical accretionary bodies, less than 2mm in diameter, and thin section oolites often show concentric structures. Its nucleus might be composed of a carbonate but different from carbonate in colour and texture. No ooids evidence was found in thin sections. However, the concentric layers observed in samples P12 on page 108 and samples LE 26 and LE 27 on page 109 are not confirmed as ooids but are merely root traces and plant tubes filled with sparry calcites.

iii. <u>Fossils</u> are the broken and unbroken skeleton and trace of carbonate secreting organisms as one of the major constituents of these three limestone members, no fossil evidence was found in the EARS travertines thin sections.

iv. <u>Pellets</u> are the homogeneous aggregate of microcrystalline calcites and small spherical-to elliptical-shaped bodies and are devoid of any internal structure. They are distinguished from oolites by their lack of radial or concentric structures, from fossils by their lack of internal structures and from intraclasts by their uniformity of size and shape. They have been observed in samples V2 on page 111 and the LE 24, 26, 27 and 28 thin sections on pages 109.

3. <u>Orthochemical constituents</u>

Orthochemical constituents are those precipitated in the basin of deposition or within the rock itself. They show little or no evidence of significant transportation. The following have been observed in most of the travertine thin sections observed:
- Microcrystalline calcite matrix (micrite): Sample V125 on page 112
- Sparry calcite (spar): Samples V161 on page and 113, V338, V356, V385 on page 114

4. <u>Fabric and micro-texture</u>

The study of Travertine fabrics and microstructures is applicable because it specifies the chemical activity and mode of occurrences within the EARS carbonate sediments. The main fabrics and microstructures found in the EARS Travertines are grouped as follows:

i. Strained calcite crystal lattices have been observed as turbid, showing undulose extinction. The strained calcite crystals in the EARS travertine thin section samples V149 on page 115 and V164 on page 116 seem to be formed by the diagenetic neomorphism of microcrystalline calcite matrix under stress, i.e. the product of tectonic effect on neomorphic sparry calcite grains.

ii. Veins observed in sample V2 on page 111 are usually composed of microspar and sparry calcite and vary in shape from straight to irregular with uniform thickness throughout the thin section. These calcitised veins are the rootlet traces and tube plant fingerprints, testifying delta or estuary vegetation presence during the depositional time.

iii. Microstylolites observed in samples V150 and V163 on page 113 are commonly intergranular and mark contacts between adjacent structures.

5. <u>Depositional structures:</u>

A sedimentary structure is deemed a primary depositional feature of sediment that is large enough to be seen by the naked eye (Selley, 2000) and is distinguished from the fabric which has microscopic structural features of sediment. The EARS travertine sedimentary structures observed are arbitrarily divided into the following:

i. Primary (physical) classes: Primary structures are those generated in sediment during or shortly after deposition. They result mainly from the physical processes e.g., cross bedding and slumps. They were observed in samples V352 on page 114, MDW 42, 43, 74,162, 276 and MDW 277 on page 115.

ii. Secondary (chemical) classes: Secondary sedimentary structures are those that are formed sometime after sedimentation i.e., they are post-depositional microstructures. They essentially result from chemical processes such as those which lead to the diagenetic formation of concretions, microbial mats and/or speleothems (Selley, 2000). They were observed in samples V 153 on page 113 and LE 44 on page 111.

The PCK limestone sample from West DR Congo (see page 109) categorised in the above-mentioned secondary class presents some alternately grey and white layered mounds, columns and sheet-like sedimentary rocks. Their original formation designates a progressive growth of overlapping layers of cyanobacteria activity photosynthesizing microbe in the shallow shelf such as lakes, fresh waters rivers, and even soils.

Stromatolites, known as one of the earliest fossil evidence of life on Earth, have been observed in the Procokin quarry in a visible layer containing calcium carbonate precipitated over the growing mat of bacterial filaments. Assuming that photosynthesis in the cyanobacteria depletes the carbon dioxide in the surrounding water, it is clear that the carbonate precipitation in PCK Samples was most abundant during the Late Proterozoic, about 3.8 billion years ago. The PCK limestone samples' petrography analysis suggests that they were formed in shallow fresh water because cyanobacteria use water, carbon dioxide and sunlight to create their food and expel oxygen.

However, the petrography analysis of Mandawa carbonate sediments reveals that they display enough similarities under the microscope with EARS Travertines samples P12, LE 24, LE 26, LE 28 and V 19 found with marine limestones' spectral signature. Microscopic analysis has been used as a tool for reconstructing the provenance of the marine limestone sedimentary sequence. The Mandawa samples' carbonate mineral assemblages in the Tanzanian Basin seem to be influenced by several different processes such as transport, weathering and digenesis, which can alter the original composition such that they might no longer reflect the true composition of their source area. More petrographic studies are required to identify these microscopic similarities.

## VII.3 – STABLE CARBON AND OXYGEN ISOTOPE RESULTS

The use of carbon and oxygen's stable isotopes on terrestrial carbonate deposits as recorders of climatic and environmental change through the present MSc research study was inspired by the fact that carbonates, including travertines, contain regional climatic and environmental signals (Andrews et al., 1994).

Numerous recent studies (Chafetz et al., 1991; Merz, 1992; Andrews et al., 1994) suggest that the interpretation of carbon and oxygen's stable isotopic compositions obtained from the Eastern African Rift travertines' isotope ratio mass spectrometry (IRMS) analysis are based on certain assumptions about the conditions of carbonate precipitation. These assumptions are summarised below.

The oxygen-stable IRMS assumptions specify that the possible relationship between $\delta_{18}O$ of meteoric water precipitation and temperature is developed by the condensation of water vapour as a direct consequence of cooling. Further condensation of a given air mass occurs at lower temperatures which is isotopically lighter than previously formed phases, proving the hidden link between temperature and rainout effects. Therefore, temperature changes might be responsible for much of the 1% variability of our results even if we are unable to obtain evident respective contributions from source and rainout effects. Oxygen isotope ratios in the calcites are close to equilibrium with mean $\delta_{18}O$ in rainfall at average annual water temperatures, while carbon isotope variations reflect carbon inputs from soil, aquifer rock dissolution and equilibration with atmospheric $CO_2$ (Andrews et al., 1994).

However, Atkinson et al. (1987) indicates that the dependence of $\delta_{18}O$ on temperature is not linear, and at some values around 8 to 10°C this dependence is suitable for most English Holocene sites; in this case, 1% change in $\delta w$ corresponds to about a 2°Cmax change in air temperature (Yurtsever, 1975).

Moreover, Pazdur similarly (1988) suggests that oxygen-derived isotopes might be efficiently used to determine the palaeotemperatures from Tufas and Travertines and constrain their palaeoenvironmental and palaeoclimatic reconstructions.

According to Lawler (1987), the observed changes in the oxygen isotopic composition of travertine-precipitating waters ($\delta w$) would be controlled by variation in rainfall composition which feed the groundwater and ultimately surface river water.

The results presented in section VI.1.1, Figure VI.2 page 118, indicate that travertine samples collected in Bwera (samples LE41 and LE42), Bat cave (Sample LE44) and OKUMU (Sample P12a and P12b) present values from -7 to -10‰ of PDB Belemnite and high abundance of $\delta_{18}O$ between 25 and 29.

The stable isotope results for the travertine samples collected in Lyemubuza (Samples L24 and LE26), Muhokiya (LE 28 and LE27), Dura (Sample LE32) and Hima (Samples LE37 and LE38) show values from -2 to +7 ‰ relative to PDB Belemnite and the same high abundance of $\delta_{18}O$ between 25 and 29. Interpreting the results shown in Figure VI.2 in page 118, it is noted that higher $\delta w$ values in carbonates correspond to lower temperatures (colder climate during Pleistocene glaciation) therefore the lower $\delta w$ values in carbonate samples refers to higher temperatures (warmer climate during Holocene interglacial) (Yurtsever, 1975; Siegenthaler, 1979; Rozanski et al., 1993).

The IRMS results plotted in Figure VI.3 on page 119 reveal that the travertine samples collected from the localities of Lyemubuza, Muhokiya, Dura and Hima (Uganda) have higher $\delta w$ values in carbonates between 27 and 30 corresponding to lower temperatures of marine carbonate deposition conditions. These results also indicate that the travertine samples collected from the localities of Sempaya (Uganda), Mayi ya Moto and Biruma (DRC) have lower $\delta w$ values in carbonates between 15 and 23 corresponding to higher temperatures of carbonatite deposition conditions. Figure VI.3 also confirms that the travertine samples collected from localities of Bwera, Bat cave and Okumu (Uganda) have medium $\delta w$ values in carbonates between 23 and 27 corresponding to a mixture of both the above deposition conditions. At a given latitude, a number of mechanisms are known to cause variations in $\delta w$, including variation in the source of an air mass (e.g., Heathcote and Lloyd, 1986; Lawler, 1987), temperature of the air mass (Yurtsever, 1975), successive precipitation ('rainout' or 'amount') effects (Dansgaard, 1964) and altitude effects (Gat, 1980).

This implies that, for a given geographic locality, some of these effects will be either constant (e.g., altitude effects) or will fluctuate on short term (<seasonal) timescales, e.g., rainout effects. Temperature effects have been seen to vary over seasonal (Siegenthaler, 1979) or longer timescales (Rozanski et al., 1993) and this is most clearly seen in polar continental regions (Lawrence and White, 1991).

In temperate regions, the temperature effect is more difficult to resolve from the rainout effects in historical proxy records (Lawrence and White, 1991). Airmass source effects might also vary over longer timescales (Mckenzie and Hollander, 1993) although there is relatively little evidence available to demonstrate the significance of this effect in equatorial regions at any EARS given site.

Regarding the carbon stable Isotope Ratio Mass Spectrometry assumptions, they indicate that the depositional environment of the EARS travertines could be well understood and documented using $^{14}C$ and biostratigraphy (Andrews et al., 1994).

However, it can be argued that smooth $^{18}O$ variations in the travertines as well in the Tufa calcite are caused by changes in the isotopic composition of regional rainfall which in turn were caused primarily by changes in air temperature (palaeoclimate).

Generally, lower $^{13}C$ values for calcite correspond to higher $^{18}O$ values, suggesting a stronger component of soil-derived carbon during warmer climatic phases.

This assumption implies that variations in carbon isotope geochemistry can be related to environmental changes which affected the carbonate precipitating waters.

Kinetic isotope effects are insignificant, except at spring heads (TURI, 1986), as observed in most of the EARS travertine sites discussed in this research study.

The stable carbon and oxygen isotopic signatures obtained from IRMS analysis on selected EARS travertine samples reflect surface fractionation processes within the hot or cold spring pools at the surface. They are affected mostly by the $CO_2$ outgassing as the water bubbles to the surface. This field evidence suggests that the $CaCO_3$ precipitation is differently distributed within the EARS travertine depositional environment. In some locations, this precipitation was not sufficiently effective to complete the calcification process at this end.

Therefore, it is interpreted that the EARS travertine calcites precipitate within a range of precipitation rates when dissolved $CO_2$ held under pressure underground outgasses upon reaching the surface at a spring, pushing the reversible reaction to the right ($CO_2$ is present in groundwaters by dissociation of biogenic methane at depth etc.).

Plotting the EARS travertine IRMS result data in C-O isotopic chart in Figure VI.2 on page 118 and VI.3 in page 119, it is evident that in general, lower $\delta_{13}C$ values correspond to higher $\delta_{18}O$ values. This implies that EARS warmer climatic phases were characterised by a stronger component of isotopically light, soil-derived carbon. This climate-soil relationship is plausible as warmer climatic phases might be related to more active plant growth, soil-activity and higher soil $CO_2$, (Buyanovsky and Wagner, 1983).

The IRMS analysis conducted in this MSc research study on EARS travertine samples reveals that the values of $_{13}C$ and $_{18}O$ respectively vary between -6.47 to -15.10 ‰ and 20 to 30 ‰. Regarding the $_{18}O$ ‰, SMOW and $_{13}C$ ‰ PDB values, intersect with each other. Therefore, it can be concluded that an isotopic clumping supports the venue that the travertines have precipitated in different depositional conditions and hybrid environments. The resultant $_{13}C$ were found unexpectedly low enough in the EARS travertine lithofacies to characterise either pools or stagnant water conditions.

According to Lynch-Stieglitz (1995), the 20 to 30 ‰ PDB value range found in these aforementioned travertines localities could be interpreted as evidence of marine carbon involvement (Lynch-Stieglitz et al., 1995); this is generally supposed to occur in colder temperatures due to the high abundance of $\delta_{18}O$ as the majority of the lighter oxygen isotopes are stored in the glacial ice as suggested by Hays and Grossman (1991). Andrews et al. (1994) indicate that climatic warming corresponding to wetter conditions caused more effective flushing of soil-carbon into groundwater and river systems. They are appropriate as independent palaeoclimate indicators for the EARS travertine samples.

Based on the aforementioned C/O isotope ratio considerations and IRMS results presented in Chapter Six, Figure VI.4 on page 119 reveals the three travertine palaeo environments according to the chart comparing $\delta_{13}C$ PDB with palaeo temperature:

i.    Closer to primary marine limestones in *Lyemubuza, Muhokiya, Duma* and *Hira* localities in Uganda where carbon dioxide outgassing evaporation removes C and O isotopes;

ii.   Approximately primary carbonatite lavas in *Mayi ya Moto* and *Biruma* localities in DRC;

iii.  Hybrid results mixing both the above palaeo environments in *Bat Cave, Okumu* and *Bwera* localities in Uganda where strong carbon plant soil zone a $CO_2$ contribution.

The same figure also suggests that the palaeo environment temperature of EARS carbonates is divided in two main groups of cold marine limestones (e.g. tufa, travertines) and hot carbonatite (e.g. travertines) and clearly a kind of intermediate mixed group considered like the hybrid one.

VII.4 – STRONTIUM ISOTOPE RATIO RESULTS

Discovered by Adair Crawford in 1790, strontium is beneficial for this MSc research study because carbonate minerals generally contain relative constant abundance of incorporated $^{87}Sr$ in many carbonate crystal lattices.

Strontium is also a mobile element during carbonate weathering and dissolution (Vaniman and Chipera, 1996). A positive correlation between Sr and REE reflects the epigenetic influence of meteoric waters moving over the bedrock (Tlig and M'Rabet, 1985).

Considering the fact that continental weathering and oceanic hydrothermal processes are potentially able to deliver $^{87}Sr/^{86}Sr$ to seawater, our perspective is that some global tectonic activity which would control the relative proportions of the wide variation of $^{87}Sr/^{86}Sr$ in seawater through geologic time. Seawater $^{87}Sr/^{86}Sr$ is related to a major erosion of ancient limestones which reflect earlier seawater O and C isotopic compositions (Dickson et al., 1990). Furthermore, the strontium isotopic ratio contained in marine limestones and dolomites, has its isotopic composition that depends on the age of the rocks, reflecting the temporal variations in oceanic $^{87}Sr/^{86}Sr$. Considering the actual equatorial climate in the EARS, a consideration could be made on early meteoric diagenesis where the $^{87}Sr/^{86}Sr$ signature of calcite precipitated during stabilisation of aragonite and magnesian calcite might generally be inherited from the previous phase of metastable carbonate phase.

This very high Sr content of marine carbonates is relative to the levels of Sr usually seen in dilute fresh meteoric waters (Banner et al., 1989).

The relative abundances of $^{87}Sr$ in the Eastern Africa Rift travertine samples are expressed as the ratio $^{87}Sr/^{86}Sr$ and are presented in Figures VI.5 on page 120, VI.6 on page 120 and VI.7 on page 121. The charts of $^{87}Sr/^{86}Sr$ secular variation for the Phanerozoic sea waters from Burke et al., (1982), Wierzbowski, (2013) and Nicholas, (2009) in Figures VI.5 on page 120 and VI.6 on page 120 are sufficiently detailed to permit the use of strontium isotope ratios in high-resolution stratigraphy and chronology. Strontium isotope ratios of selected EARS travertine samples with a strong marine limestone or carbonatite REE+Y signature showed a very high range of strontium isotope ratios from 0.7068069 to 0.7482648.

However, only 2 values LE 41 and LE 42 (a, b) are within the range expected for marine carbonate dating from Jurassic to Permian. These are from Bwera and Dura at the northern end of Lake Edward. Sr isotope ratios within the seawater carbonate range might be Late Neoproterozoic, Late Permian or Late Jurassic in age.

Most of the remaining travertine samples exhibit a very high radiogenic strontium value, suggesting crustal contamination from Rubidium, but there is no correlation between Rb concentration and Sr isotope ratios. This could explain how the $^{87}Sr/^{86}Sr$ of marine carbonate samples might differ from the value of seawater at the time of its deposition; thus, their difference value can be attributed to diagenetic alteration by either younger seawater or nonmarine fluids.

VII.5– GC-GCMS RESULTS

Both gas chromatography (GC) and mass spectrometry (MS) yield better detailed geochemistry results by their conjoint use. GC can effectively separate volatile and semi-volatile compounds with acceptable resolution but unfortunately cannot identify them. MS might be able to provide detailed structural information on most compounds such that they can be exactly identified but unfortunately it cannot separate them. Therefore, the combination of the two techniques is preferably suggested for the geochemistry results' efficiency, targeting the study of biomarkers (Strandberg et al., 2001).

This suggests that very sensitive methods of analysis employing gas chromatography-mass spectrometry (GC-MS) are absolutely necessary for the biomarkers' scientific recording.

Biomarkers consist of complex organic molecules from chemical structures which could stay largely unchanged during the diagenesis and oil generation processes. This chemical property allows these biomarkers to get traced back to their original molecules in living organisms.

This suggests that generally, biomarkers are proven to be able to retain the majority of the original carbon skeleton from the initial organisms. Biomarkers are also called molecular fossils because of their possible structural similarities to diagenetic alteration of natural products from living organisms. This is why these structural similarities have been called, in some previous works, "molecular fossils". Biomarkers are also considered a group of parcels, mainly hydrocarbons, often found in oils, rock extracts, recent sediment extracts and soil extracts. Biomarkers are considered minor components of a crude oil or rock extract. According to Wheaterford (2018), some biomarkers are prolific in many organisms while others are only found in specific types of organisms and hence these can be used as markers of source input. Additionally, some biomarkers do not appear until their parent organism has evolved, and therefore, the presence of these compounds are used as an age diagnostic marker. Similarly, some biomarker structures are more stable in certain depositional environments than others and hence their abundance can be used to infer depositional environments. Moreover, subtle chemical transformation from one chemical structure into another can occur due to thermal stress and, hence, the ratio of these biomarkers can be used as a maturity marker. When oil samples are available and their potential source rocks are known, biomarkers can be used to make oil source rock correlations.

However, if source rocks samples are neither available nor known, the biomarker distribution in oil can be used to infer characteristics of the source rock that generated the oil without examining the source rock itself.

Specifically, biomarkers obtained by GC-GCMS from an oily sample can reveal the relative amount of oil-prone vs. gas-prone organic matter in the source kerogen, the age of the source rock, the environment of deposition as marine, lacustrine, fluvio-deltaic or hyper saline, the lithology of the source rock (carbonate vs. shale) and the thermal maturity of the source rock during generation (Peters and Moldowan, 1993).

The main reason to use Dominion Ltd.'s GC-GCMS analysis results in this MSc research study is to explore the constituents of biomarkers from the Edward Lake oil slicks and compare them with the black-lined substance found in cavities in the EARS travertines collected and documented in the Lyemubuza quarry in EA4A in Uganda. There are significant parameters of biomarkers which makes them important to study in this MSc research work, for instance, the use of biomarkers in oil to assess source thermal maturity as a function of source rock maturity is indicative of source rock organic matter input and depositional conditions. Consequently, a variety of biomarker parameters have been identified that are applicable for characterising the source rock maturity simply from the analysis of the migrated oil (e.g., Peters and Moldowan, 1993).

These above-mentioned maturity parameters are appropriate to explain the processes that occur during source rock maturation such as cracking (large molecules break into smaller molecules), isomerisation (changes in the 3-dimentional arrangements of atoms in molecules.) and finally aromatisation (formation of aromatic rings by loss of hydrogen from naphthenes). In order to better access the EARS travertine source rocks by interpreting the biomarker results presented and described in section VI.3 page 121, the following aspects have been considered. The relationship between a biomarker and the source maturity is a function of heating rate, source lithofacies and source organic facies (kerogen type). From the GC-GCMS results obtained through this research study, we note that the maturity (i.e., vitrinite reflectance equivalent) is linked to specific values from biomarker parameters showing few (negligible) changes from offshore oil slicks in the Edward basin to onshore Lyemubuza carbonate outcrops. This reveals the non-linear relationship between a biomarker maturity indicator and source rock maturity. Observing the local increase of maturity indicators in some locations within the Edward Lake basin close to the Kigunda locality in the South West of Edward Lake where Black shales were found flaming smokes in the surface, it is proven that many biomarkers within the EARS might reach terminal values, in others words, the stage of "overmaturity". Moldowan et al. (1992) argue that the concentrations of biomarkers in petroleum decrease with thermal maturity. Despite these limitations, biomarkers as indicators of source maturity are extremely convenient. Moreover, biomarker maturity parameters are used to determine if the API gravity of biodegraded oil was or not prior to biodegradation. This is possible by collecting a suite of non-degraded oils from the same petroleum system as the degraded oils. Using the non-degraded oils, the geochemist develops a correlation or "transform" between a biomarker maturity parameter and API gravity. Moldowan et al. (1992) provide an excellent example of this approach in which they determine the original gravity of degraded Adriatic oils. The same biomarker parameter is then measured on degraded oil, and its original gravity is determined using the transform developed from the non-degraded oil suite. This MSc research study used the GC-GCMS analysis to correlate their respective biomarkers' behaviour in detail. The most effective biomarkers studied in this work are those based on GC-GCMS analysis (Hopanes m/z 191, Tricyclic Diteranes m/z 191 and Steranes m/z) of compounds that are highly resistant to biodegradation such as the n-alkane hydrocarbon series from sample LES 18 presented in figure VI.11 on page 123.

The Dominion Ltd. GC/GCMS analyses demonstrate that duplicate samples from Lyemubuza Quarry and Muhokya Lime Works, localities ~10km apart, contain the same mature oil biomarkers. This correlating fact suggests the lateral extension of a possible limestone extended cavity layer containing the same migrating pre-peak oil. The different levels of isomerism and aromatisation observed in the biomarker compounds of traces of a relict, biodegraded oil, lining the cavities of the travertine samples collected at Lyemubuza Quarry and Muhokya Lime Works along the Ruwenzori border fault, suggest early (pre-peak) oil generation. The obtained results of the GC/GCMS analyses indicate that this is pre-peak oil apparently generated from a marine shale source rock and migrated into these very porous EARS travertines. This is interpreted as the source rock type that would typically generate oils such that the relict biomarker distributions seen in these samples are from the marine shales source. Not only do the Lake Edward slick samples show a mature hydrocarbon signature but the polycyclic ring biomarkers are strikingly similar – particularly the 4-ring steranes – to the relict oil extracted from the travertines documented at Muhokya. Figure VI.16 on page 125 presents plots of C27 – C29, AAA and ABB sterane distributions from the Lake Edward slicks and the Muhokya limestones which reveals that the data are homogenous and cluster together. This is the scientific evidence that the GC/GCMS analysis run by Dominion Ltd. proved that the relict oil preserved in the travertine cavities at Lyemubuza and the one leaking to the surface on Lake Edward are from the same marine shale source rock.

## VII.6– <u>ICP-MS RESULTS INTERPRETATION</u>

The main reason to use rare earth element detection with ICP-MS analysis for the EARS travertine samples collected from each of the geological sites being investigated through the present MSc research study is linked to its great advantage to identify and distinguish at very low level all the inherited carbonate material from a potential local limestone rock at depth. On this basis Allwood et al., (2009) and Allwood and Goodacre, (2010) infer that the very low detection limits of modern ICP-MS instruments allows the analysis of full REE + Y patterns for samples smaller than 100 µg.

The REE concentrations found in EARS travertines samples which were selected because of their potential importance in carbonate minerals were obtained in the full suite of trace elements detected by the ICP-MS method which has proven a very low detection limit by providing precise and accurate output data for elements (Sc, Y, la, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) present in the sample at ppb concentration levels.

However, results for Be, K, Ti, As, and Sb are not reported because they were below the instrument's detection limits. As the REE are considered reliable indicators of the chemical evolution of waters flowing through carbonates (Vaniman and Chipera, 1996), their concentrations in each EARS travertine's respective textures, structures and/or fabrics were relevant to analyse in the purpose of understanding the geochemical origin of the bicarbonate contained in the EARS travertine samples and determine the geological environment for their time of deposition.

The objective of this present section (ICP-MS result discussion) is firstly to examine and interpret the geochemical footprints obtained from the EARS travertine samples to determine their intra-sample and inter-site variability.

Secondly, is to compare their spectral signature trends to those obtained either for Fort Portal carbonatite lava samples in Uganda or Devonian Reef fresh waters and Mandawa marine limestones in Tanzania which are both universally recognised and studies on them have been published in the actual literature like their respective spectral signatures references.

This section summarises the geochemical findings and scientific contributions obtained from the use of ICP-MS method on carbonates for the detection of lowest EARS travertine REE spectral signatures. The ICP-MS analyses conducted in our MSc research study performed well, yielding both significant positive and negative correlation results. The respective ICP-MS spectral signatures detected on each EARS travertine analysed sample purposed to correlate them with either Fort Portal or Devonian Reef reference spectral signatures. The acceptable threshold of the positive correlation coefficient used for this MSc experiment ranged from $1.00 \geq R_2 \geq 0.96$. Any correlation coefficient value under 0.90 was considered a negative correlation. The results of this MSc research study confirmed that ICP-MS is one of the most appropriate methods which helps to understand the geochemical origins of carbonates found in travertines and other limestones found in outcrop whenever can arrive in the laboratory after their field collection. As the EARS samples collected from 2007 to 2011 analysed in 2016 gave the same results with those obtained from the same samples after their 2013 analysis, this method proved its results reproducing whenever, whatever the lab operator, wherever the experiments were done.

The ICP-MS results presented in (the previous) Chapter 6 demonstrated the following geologic evidences:

The Procokin limestone samples drilled through their visible textures, structures or fabrics presented typical spectral signatures which confirmed their stromatolites and microbial mat structures and their geochemical fresh water origin as universally recognised in the existing literature (Casanova, 1994). Some of the Mandawa (Tanzania) limestones drilled regardless of their visible textures, structures or fabrics presented typical spectral signatures which confirmed their geochemical marine limestone origin also universally recognised in the existing publications (Nerbråten, 2014).

Both Procokin and Mandawa ICP-MS analysis performed well in this MSc laboratory work. The respective results confirmed the spectral signature evidence for Procokin fresh water and Mandawa marine limestones. The respective analysis allowed the discovery of the closer fresh water and marine limestones outcropping in and around the Albertine Graben Rift to compare their spectral signature patterns as well as their correlation coefficient.

The EARS travertine geochemistry results obtained using ICP-MS analysis varies according to deposition conditions and post-diagenesis processes affecting their chemistry.

Some selected EARS travertines samples analysed through this present MSc research study show negative Cerium anomalies with an average value of approximately 0.86.

This value means that there is no correlation between the extents of Cerium anomaly or between the concentrations of Mn and Ce (considering that variations in catchment geology would probably mask such kind of correlation).

Referring to Cerium anomaly (Ce/Ce*) and total REE abundance (ΣREE) preserved in our EARS travertines, three possible depositional environments could be suggested: spreading ridge proximal, ocean-basin floor and continental margin. These three (3) depositional environments which are based on Cerium anomalies provide a potential tool for tectonic and stratigraphic reconstructions which are subdivided as follows:

Extremely low Ce anomalies (Ce/Ce*=0.29) found in some EARS travertines with marine limestone spectral signature reveal that they were deposited near the spreading ridge under the influence of metalliferous activity. Less extreme Ce anomalies (Ce/Ce* ~0.55) correspond to an ocean-basin floor deposit, and the deposit from continental margin regimes corresponds to slight anomalies (Ce/Ce* ~0.90 to 1.30).

Calculation of the Gd anomaly (relative to MUQ) for the ultra-filtered depth profiles presented by Alibo and Nozaki (1999) yields the same range for EARS travertine samples from 1.02 in the surface waters to a maximum of 1.32 in the intermediate carbonate geothermal water with an average of 1.13. Some of the freshwater PCK samples have shown the same comparably Gadnium large anomalies.

The Y/Ho ratio found in the EARS travertine samples is variable. It ranges from 1.015 to 5.8025 (average of 3.0467) which is different from the average upper continental crust, and chondrite value of 26 to 39 indicates significant fractionation (Kamber et al., 2005a). This clearly indicates less fractionation. According to Kamber et al., (2005), the Y/Ho ratio of the marine limestone criteria is required to be more or less higher than 40. However, many marine limestones universally recognised in the existing literature do not fill this Y/Ho ≥ 40 criteria.

In a carbonate sample, the level of Y/Ho ratio is either an anthropogenic feature or a fractionation feature. This assumption suggests that the EARS travertine samples presenting low Y/Ho ratio (average 3.4) reflect a non-anthropogenic source while elevated Y/Ho is a feature of marine phosphate deposits, which are a major source of phosphate fertilisers (Hu et al., 1998).

There is a surprisingly high level of coherence in the EARS REE spectral signature obtained by ICP-MS analysis. This described coherence further enhanced the reliability of the results discussed in the following paragraphs.

Considering the comparisons of all the REE spectral signature patterns including La, Gd, Y and Ho, it is clearly evident that a strong linear correlation is noticed between respective EARS individual REE concentrations with either carbonatite spectral signatures or marine limestones ones, with high correlation coefficients ($R_2$)>0.96 (Lawrence and Kamber, 2006).

This strong correlation between the REEs spectral signature indicates that no significant fractionation occurs between the respective REE spectral signatures within the same EARS travertine sample structures, textures or fabrics despite the significant change they show in their respective concentrations (Lawrence and Kamber, 2006).

This is clearly visible where the REE+Y MUQ normalised data in combination with radiogenic isotopes e.g. Pb and Sr are applicable to discriminate between carbonates that formed in lacustrine, restricted marine and open marine depositional settings (Kamber and Webb, 2001; Bolhar et al., 2002). In exceptional cases, it is also possible to infer relative water depth or proximity to hydrothermal fluid sources in a sequence of microbial carbonates (Kamber et al., 2014).

REE concentrations are altered by dolomitization as well as other epigenetic weathering processes, but the exact relationship between them is still unclear (Bolhar et al., 2002; Nothdurft et al., 2004).

Ji and Gao, (2004) indicate that the weathering of dolomites causes the uneven transport of REE which is strongly dependent on the climatic weathering conditions and the stability of the REE-carrying rock. This is why microscopic observations were necessary prior to the geochemistry analysis to avoid these above-mentioned unclear dolomitization issues. This petrographically guided micro-sampling allowed the removal of micro-samples from each crystal lattice in a portion of limestone rock less affected by later overprint (Kamber et al., 2004).

This crystal lattice structure inside the calcite mineral is highly robust and can absorb a variety of divalent metal cations, in addition to Mg and Sr, without becoming disordered (Ford and Williams, 1989). According to Reeder (1996), this mode of sharing cations of varying sizes is favoured by the calcite lattice because its corner sharing structure can take in ions larger or smaller than calcium. Other metals commonly adsorb onto the calcite crystal surface rather than being incorporated into the calcite crystal lattice. However, the elements that substitute directly into the Ca site in the lattice are the most common minor components.

Moreover, Wolf et al. (1967) note that many epigenetic factors involved in such recrystallization processes causes the leaching and migration of trace and minor elements.

The behaviour of minor and trace REE found either in the calcite crystal lattice or as inclusions in the EARS travertines themselves are important for distinguishing the spectral signature between different travertine textures, structures and /or fabrics because their respective REE geochemistry results document different geologic formations and epigenetic conditions. This means that the spectral signature differences shown in the trace and minor elements' composition of carbonates at the EARS sites are effectively demonstrated by their respective REE concentrations. This demonstration is not only by characterising their spatial geochemical variations at their respective field sites but also by distinguishing spectral signature discrimination between their different textures, structures and /or fabrics.

Based on the visible structures, textures and or fabric result discriminations, the ICP-MS experiments conducted through this MSc research study suggest that the results within each single travertine sample seems very similar.
However, the experiments done in this MSc research reveal that the EARS travertine samples from the same field location do not have completely identical ICP-MS results. This implies that their respective spectral signature patterns are not identical irrespective of the fact that they have been collected around the same hot springs where degassing waters bubbles are visible. This could be explained by the fact that fractionation processes at the surface are continually changing the REE initial distribution in each EARS travertine structure, texture and fabric.

Additionally, some geochemical data obtained through statistical interpretations allowed to draw appropriate comparisons between both EARS travertine samples' internal sets and their respective site locations. Consequently, the ICP-MS results obtained from each of the travertine samples analysed suggest the geologic evidences of a questionable carbonate bedrock chemistry across the EARS.

Regarding geothermal waters-rock interactions, Hodder (1991) suggests that rainwater that percolates down major faults and fractures is retained in suitably porous and permeable rocks. This rainwater can be heated by molten rocks at great depths in the crust.
Rather dilute brines are formed as a result of fluids and gases from the molten rocks being mixed with the rainwater and also because of reactions that occur between the water and the rocks at these high temperatures (~250°C) and pressures (~12 bar) (Hodder et al., 1991).

Knowing that carbonate rocks generally dissolve slowly in water, most of their dissolution reactions occur more readily at higher temperatures, and if we assume that the water-rock interaction liberates ionic species which can produce a metal-saturated liquid as well as calcite-saturated water passing through carbonates rocks, it is understood that the rising water to the surface cools itself slowly.
Therefore, silica and other carbonate minerals are precipitated. Hodder et al. (1991) also contend that this might help "cap" the aquifer and prolong the geothermal system's existence. This implies that underground water that does reach the surface through faults and fractures will cool further and produce sinter mounds and terraces that are typical around geysers and hot springs.

Several chemical reactions occur within geothermal waters. These are mostly associated with interactions between the geothermal water and the rock of the chambers in which it is located (Hodder et al., 1991). The rock of the chambers in which the geothermal waters are located have clear carbonate characteristics as suggested by ICP-MS results obtained through geochemistry analysis. It is clearly noted that many other reactions occurred and these typically involved sulphur, calcium and/or metal cations.

EARS rock-water interactions involving calcium carbonates are more frequent because of the geothermal waters that have moved away from the aquifer are likely to have lower temperatures derived from silica concentrations than higher temperatures derived from concentrations of Na, K and Ca (Hodder et al., 1991).

Any hydrating layer of water containing trace metals, adsorbed onto the calcite surface, initially interacts with partially unsatisfied charges of the Ca and $CO_3$ ions which might result in a hydrolysed layer on the mineral surface that can become incorporated into the structure upon recrystallization (Lakshtanov and Stipp, 2007).

Geothermal waters in EARS are often associated with active (or recently active) areas of volcanic activity.
Moreover, several lined springs in the most significant EARS sites have been associated with tectonics activities rather than magmatism (e.g. rift bounding faulting process).

However, weathering and karstification processes caused due to the exposure of underlying carbonate strata are adding some variability in the composition, density and porosity of the carbonate bedrock (Trudgill, 1985).

As interpreted from the obtained ICP-MS spectral signatures of REE concentrations, each of the EARS travertine samples have been weathered by geothermal waters and have been washed in formations since their deposition time. This should more or less confirm Trudgill's (1985) assumption on weathering and karstification processes. Therefore, it is noted that groundwaters can obtain REE signatures from the rocks or aquifer material with which they interact (Lawrence and Kamber, 2006).

Consequently, Choppin et al. (1986), Wood (1990) and Lee and Byrne (1992) demonstrated with models, the importance of speciation and complexion of the REEs with various ligands in controlling their dissolved concentrations.

From the present MSc research study geochemical results and its key findings that emerge from the REE+Y data obtained by ICP-MS experiments the following three types of sample can be recognised:

- Samples which have derived their HCO3 from a carbonatite source are only as observed in samples V20, V22, LE37, LE38, LE41 and LE42 in Figure VI.18 on page 127 and Figure VI.19 on page 128 and samples BV 344, BV 352, BV356, BV 363, BV 364 and BV 385 in Figures VI.35 and VI.36 on page 150.

- Samples which have derived their HCO3 from a marine limestone source are only as observed in samples P12, LE 24, LE 26, LE 28 and V19 in Figure VI.20 on page 129 and Figure VI.21 on page 129 and samples BV 161, BV 162, BV 163, BV 164, MDW 42, MDW 43, MDW 74, MDW 125, MDW 276 and MDW 277 in Figure VI.37 on page 151 and Figure VI.38 on page 152.

- Samples which have a mixed source, possibly mixture of carbonatite-marine limestone are as observed in samples LE32 in Figures VI.23 and VI.24 on page 130 and samples BV 149, BV 150 and BV 159 in Figures VI.47-VI.48 on page 161 and VI.49-VI.50 on page 162.

The source of bicarbonates is more of predictable, expected geochemical origin because the EARS region is very closely surrounded by active and inactive volcanoes such as Nyragongo, Nyamulagira and Ruwenzori. The mixed source of bicarbonates is more confusing but explicable by the surface CO2 degassing where carbonates minerals from different origins are mixed in a kind if messy bubbling visible activity.

However, the marine limestone source clearly discriminated by the ICP-MS results is the most important finding of the present MSc research study because this unexpected geochemical origin represents a significant discovery for the best understanding of the geologic wonder about the potential presence of a pre-tertiary (Cenozoic) carbonate basin underneath the Albertine Rift. This MSc research has discovered that there is definitely a Devonian marine limestone beneath the Cenozoic EARS although not all Balz K marines' limestone criteria were met. Indeed, Mandawa (Tanzania) limestones did not meet all these criteria, however, they are recognised from the literature to belong to the marine limestone family.

Figure VI.37 on page 151 and here below reproduced shows the graph of all EARS travertine samples analysed using ICP-MS the results of which confirmed the marine limestone signature patterns. This logarithmic graph of REE concentrations in their carbonates mineral reveal that all the EARS travertine samples analysed in this MSc research, presenting marine limestones' spectral signatures patterns, corresponds to the Devonian Reef's spectral signatures referencing the marine limestones. This means that there is clearly a marine limestone source of bicarbonate found in some of the EARS travertines.



REE PATTERNS ALL MSC MARINES LIMESTONES ICP-MS SIGNATURES
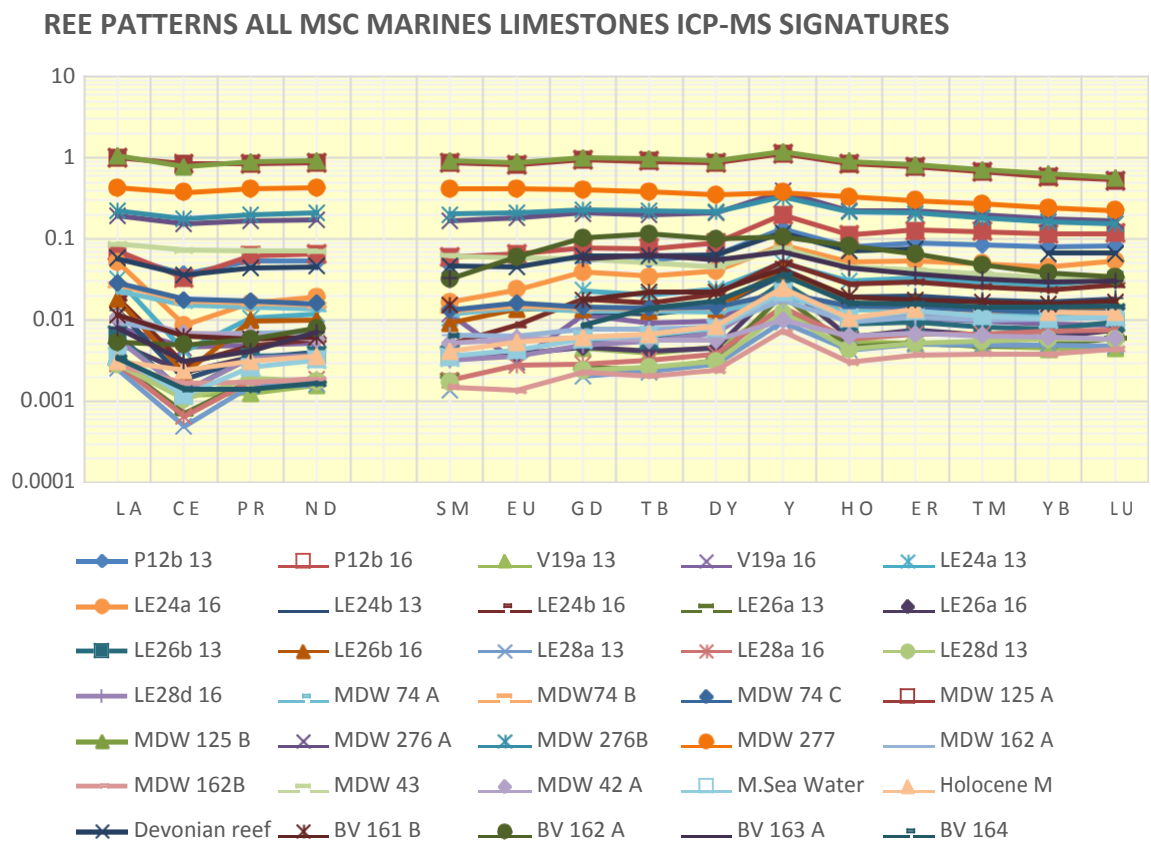
Indeed, from the general overview of the graph, it is evident that Cerium anomalies are marked by a depletion in the spectral signature pattern and Y/Ho ratios are marked by an uplift in the referenced spectral signatures of Devonian Reef, Holocene Marine and marine sea water. This graph also suggests that the selected EARS travertine spectral signatures correspond to the marine limestones in different levels of alteration and field location. This is visible in this graph by the logarithmic different value of Y-axis. Some of these selected EARS travertine samples have satisfied, 80% that is four of the five Balz (2004) criteria. This definitely confirms the presence of marine limestones in the EARS.

Figure VI.38 on page 152 and here below reproduced shows the chart of all EARS travertine samples analysed by ICP-MS the results of which confirmed their respective correlation coefficient $R^2 > 0.80$ with Devonian reef.

This logarithmic graph of REE concentrations in their carbonates mineral reveal that all the EARS travertine samples analysed in this MSc research, presenting marines limestones REE MUQ values by ICP-MS, corresponds to the Devonian Reef's correlation coefficient referencing the marine limestones.



ICP-MS 2018 : CORRELATION WITH KNOWN MARINE LIMESTONES
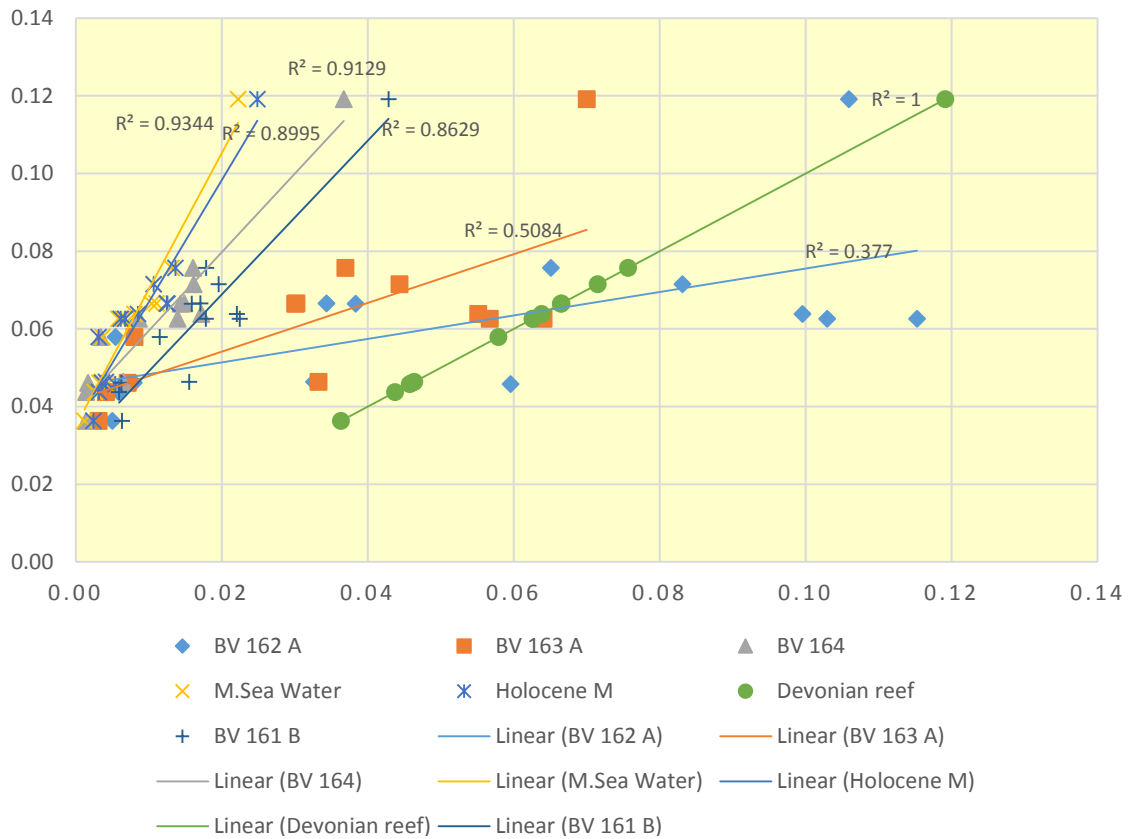
Indeed, from the general overview of this graph, it is evident that the EARS travertines found with marine limestone spectral signature have a positive correlation coefficient $R_2 \geq 0.80$ with the referenced Devonian Reef. This graph also suggests that the selected EARS travertine spectral signatures correspond to the marine limestones in different levels of alteration and field location with a correlation coefficient variation of $R_2$ values in the range $1 \geq R2 \geq 0.80$. Some of these selected EARS travertine samples have satisfied with 80% that is four of the five Balz (2004) criteria. This definitely confirms the presence of marine limestones in the EARS.

The 3 charts in Figure VI.42 in page 156, Figure VI.43 in page 157 and Figure VI.44 in page 158 reveal respectively the correlation coefficient of 2013, 2016 and 2018 ICP-MS experiments Marine limestones with published Cenomanian limestones, Neoproterozoic stromatolites with Devonian reef.

All the EARS Travertines samples found with marine limestones REE signatures correlate to:

- Devonian Reef REE signatures (Balz et al., 2004) with a correlation coefficient $R^2 \geq 0.80$
- Cenomanian Limestones (Bellanca et al. 1997) with a correlation coefficient $R^2 = 0.3462$
- Neoproterozoic Stromatolites (Corkeron et al. 2012) with a correlation coefficient $R^2 = 0.5207$

This definitively provide the geologic sourcing of the bicarbonate marine limestones found in the EARS Travertines samples as regrouped in the tables below.

II.6.1- BLOC EA41 AND EA4 UGANDA FIELD TRIP, 2007-2009 / ICP-MS 2013

Eleven travertine samples collected in Uganda from 2007 to 2009 show their 2013 ICP-MS results grouped as follows:

| CARBONATITES | MIXTURE | MARINE LIMESTONE |
|---|---|---|
| LE 44 | LE 27 | LE 24, LE 26 |
| LE 41 | LE 32 | LE 28 |
| LE 42 | LE 37, LE 38 | P12 |
|  |  |  |

VII.6.2- BLOC V, DRCONGO FIELD TRIP, 2010 / ICP-MS 2013

5 Travertines samples collected in DRC in 2010 show their 2013 ICP-MS results grouped as below:

| CARBONATITES | MIXTURE | MARINE LIMESTONE |
|---|---|---|
| V2 | V 21 | V 19 |
| V 20 | V 22 |  |
|  |  |  |

VII.6.3- METHOD CONFIRMATION / ICP-MS 2016

16 Travertines samples analysed in 2013 and run again in 2016 show their ICP-MS results grouped as below:

| CARBONATITES | MIXTURE | MARINE LIMESTONE |
|---|---|---|
| V2b, V20a, V20b | - | P12b, |
| V22a | - | V19a |
| LE44a, LE44b | - | LE24a,LE24b, LE26a,LE26b |
| LE41a, LE41b | - | LE28a,LE28b |

VII.6.4- BLOC V, DRCONGO, FIELD TRIP 2014 / ICP-MS 2018

13 Travertines samples collected in DRC in 2014 show their 2018 ICP-MS results grouped as below:

| CARBONATITES | MIXTURE | MARINE LIMESTONE |
|:---:|:---:|:---:|
| BV 338 | BV 149 | BV 161 |
| BV 352 | BV 150 | BV 164 |
| BV 356 | BV 153 | |
| BV 363 | BV 159 | |
| BV 364 | BV162 | |
| BV 385 | BV 163 | |

The 46 EARS Travertines samples analysed by this research study using ICP-MS, as above grouped in tables by their geochemistry results from their respective geochemical origin spectral signature, their respective field location, field trip period and their respective ICP-MS analysis calendar, are summarized below with a general view on each Travertine field location and a combination of geologic and geochemistry informations collected by this Msc Research study.

Each of the posters below which group the 46 above Travertines samples regarding their respective field localities, is composed of the Field location of the sample collection in the top left, the sample ID and locality in the top center, the geologic sample and environment description in the top right.
These below posters contain also the thin section microscopic image of each sample and the summary of the geochemistry results obtained in laboratory.

The geochemistry obtained in laboratory by ICP-MS as per our methodology steps, are presented in the below posters in forms of comparative charts showing the spectral signatures of their respective REE obtained values in logarithmic scale from 0 to 10, their respective correlation coefficient charts with Fort Portal for Carbonatites REE and Devonian Reef and Mandawa Basin for Marines limestones as well for hybrid signature. Additionally to the Marine limestones typical signature spectral recognized by the Cerium depletion and Y high pic, the Balz Kamber (2014) Marine limestones criteria check table is associated to each EARS Travertines samples found with Marine limestones and these Key criterias matching are then evaluated and defined as well as are done all the correlation coefficient.

The geological and geochemistry informations gathered together in the below posters are so useful for the better understanding of the palaeo environment of each of the EARS Travertines analysed through this present research study.

For the best overview of the geochemical origin of EARS travertines, all the samples analysed by ICP-MS in the present MSc research study have been grouped in the following posters according to their exploration basins' field trip period and their respective ICP-MS analysis year. These posters summarise the EARS travertines' geochemical origin field configuration, each sample's petrography and respective ICP-MS results. They also show their respective field samples photos, field environment photo and thin section microscopic photo graphically scaled 1cm to 500 µm.

## BAT CAVE
## Eastern Lake Edward,
## EA4A, Uganda
## Sample LE44

### Sample LE 44

<u>Geological environment</u>: Bat cave

Low tuffs roofed cave apparently with Travertine in its walls. The underground river system with potholes has produced the cave through the thin tuffs. Many pools flowing down west on uphill seeming to be springs bubbling along a geological junction looking like a border fault where thermal waters come up along the junction between impermeable basement and whatever sediments on top.

<u>Field description:</u> LE 44

Stalagmites? Microbial mats? Composed of several columnar fabrics layers where the crystals with intercrystalline voids elongated perpendicular to the substrate. Moderately porous fine-medium crystalline Carbonate. Feezing with HCl acid.

**Key criteria for Marine Limestones**

| | LE44A | LE44B |
|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✗ | ✗ |
| $Y/Ho > 40$ | ✗ | ✗ |
| $La/La^* > 1.1$ | ✗ | ✗ |
| $Gd/Gd^* > 1.1$ | ✗ | ✗ |
| $Ce/Ce^* < 0.8$ | ✗ | ✗ |

**No matching**



$R^2 = 0.923$

$R^2 = 0.9388$

**Good correlation**

# BWERA
## Northern Lake Edward, EA4A, Uganda
## Samples LE41 & LE42
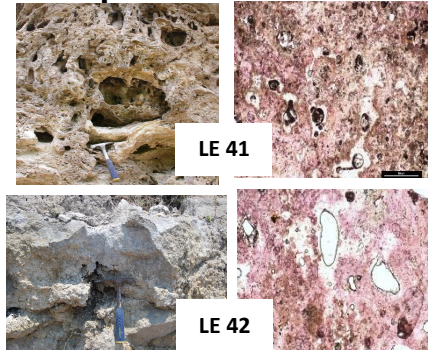


LE 41

LE 42

### Samples LE 41 and LE 42

Geological environment: Bwera Hot springs.

Travertine exposed the East bank of a bounding and NW-SW trending fault against which the Hot springs have developed.

Difficult to see how far they go deep into the hill or whether they are superficial covering. Excellent outcrop of paleostalactites.

Field description:

LE 41: Light brown limestones; visible vacuoles. High porosity. Possible Veins Network; Feezing with HCl acid.

LE 42: Feezing with HCl acid. Carbonate grains and cement. Visible different layers spreaded in the whole sample



| | LE41A | LE41B | LE42A&B LE42C | LE42D&G | LE42H | LE42I | LE42J |
|---|---|---|---|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ |
| Y/Ho > 40 | ✗ | ✗ | ✗ | ✓ | ✓ | ✗ | ✓ | ✓ |
| La/La* > 1.1 | ✓ | ✗ | ✗ | ✓ | ✗ | ✓ | ✓ | ✗ |
| Gd/Gd* > 1.1 | ✗ | ✗ | ✗ | ✗ | ✗ | ✓ | ✗ | ✓ |
| Ce/Ce* < 0.8 | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ |

**No matching**

*Key criteria for Marine Limestones*



Good correlation
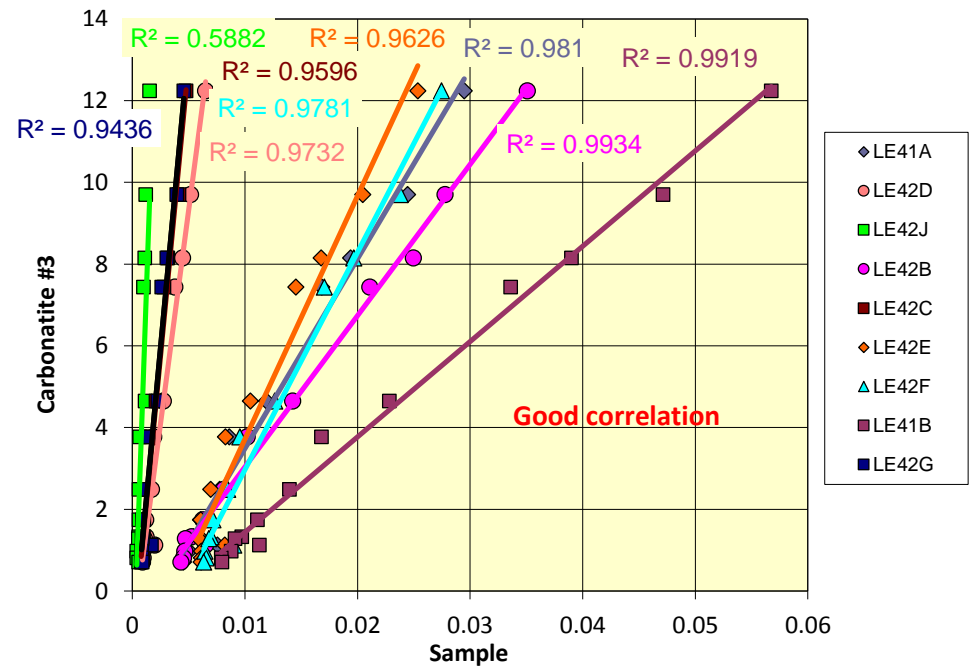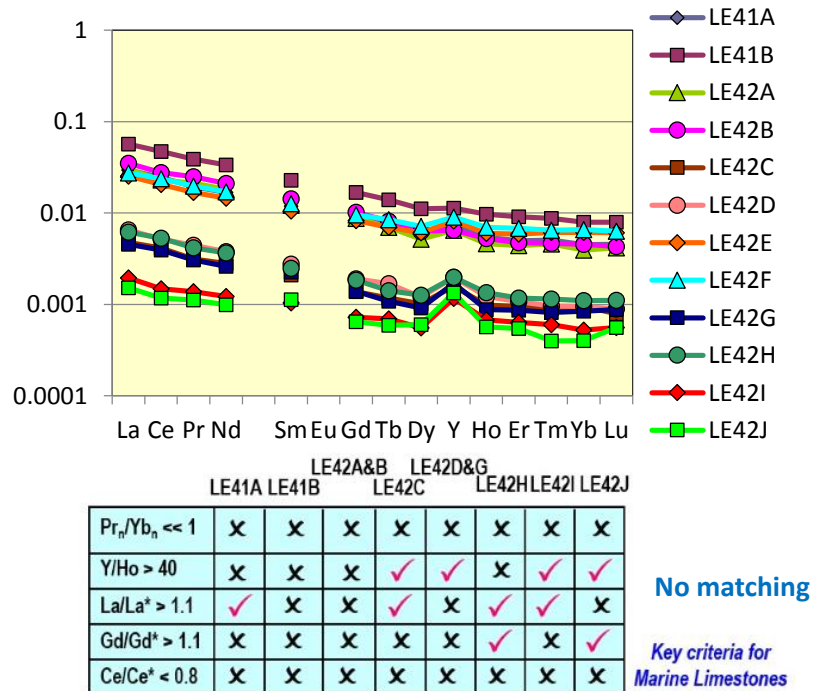
## OKUMU (HOT SPRINGS) North-western Lake Albert, EA1, Uganda Sample P12



### Sample P12

Geological environment: Okumu and Avoca Hot Springs. Moderately warm to hot but not too hot to touch located in a NE rift fault intersection with a younger NW active trending fault. No major stream flowing through gorge and the spring appears to be genuinely along the main rift fault. No obvious strong H2S smell. Dispersed Carbonatites caliche throughout.

Field description: P12

Travertine with fossil tubes and visible rootlets;
Small blocks of basement caught up in these fossil tubes;
Few fossil leafs;
Apparent black relicts in cavities.
Feezing with HCl acid.



$R^2 = 0.3669$

**No correlation**

$R^2 = 0.5029$
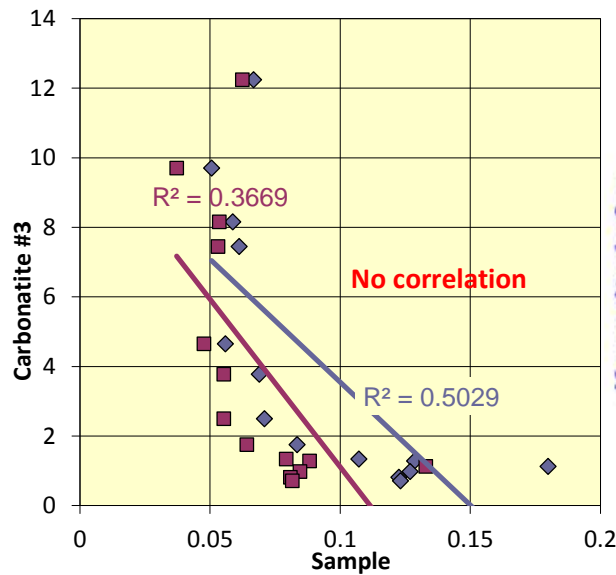
| Matching | P12A | P12B |
|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✓ | ✓ |
| Y/Ho > 40 | ✓ | ✓ |
| La/La* > 1.1 | ✓ | ✓ |
| Gd/Gd* > 1.1 | ✓ | ✓ |
| Ce/Ce* < 0.8 | ✗ | ✓ |

*Key criteria for Marine Limestones*
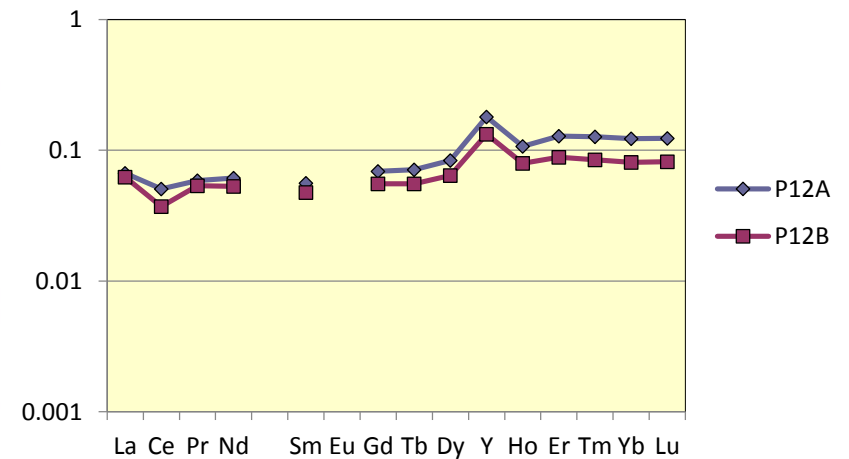
## LYEMUBUZA
## Western Lake George,
## EA4A, Uganda
## Samples LE24 & LE26
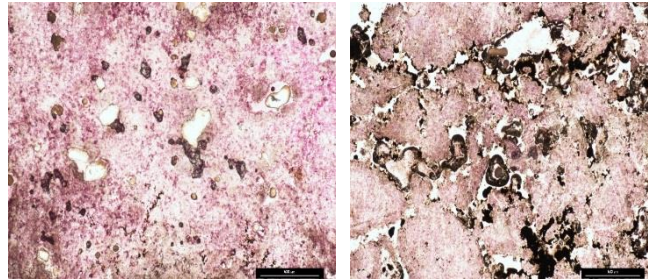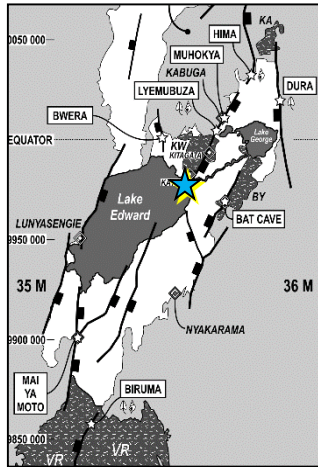
**Samples LE 24, and LE 26,**

Geological environment:

Calcite formed in an inverted fairly impressive cliff appearing like a rotational uplift on top of a normal fault block. No evidence of continuous limestone bands.

Field description: LE 24 and LE 26

Travertine with primary porosity seeming to have black organic rich fill to their primary porosity.
Feezing with HCl acid.

$R^2 = 0.1906$

No correlation

$R^2 = 0.279$

$R^2 = 0.391$

- ◆ LE24A
- ▲ LE24C
- ■ LE26A

Carbonatite #3 (y-axis) vs Sample (x-axis)



REE plot legend:
- LE24A
- LE24B
- LE24C
- LE24D
- LE26A
- LE26B
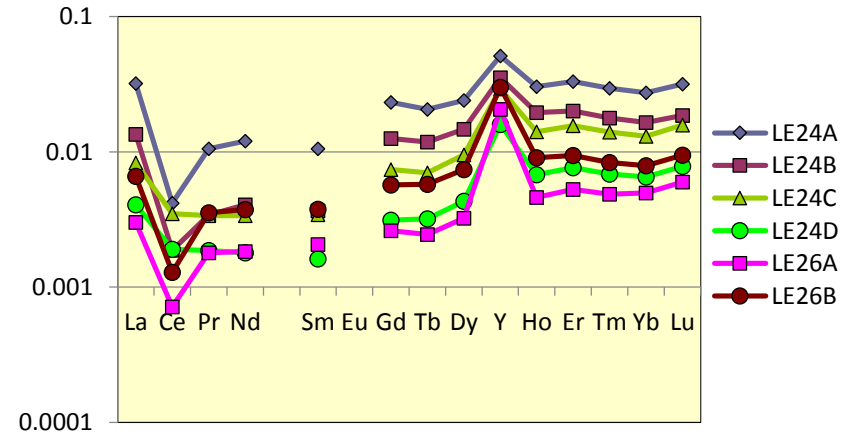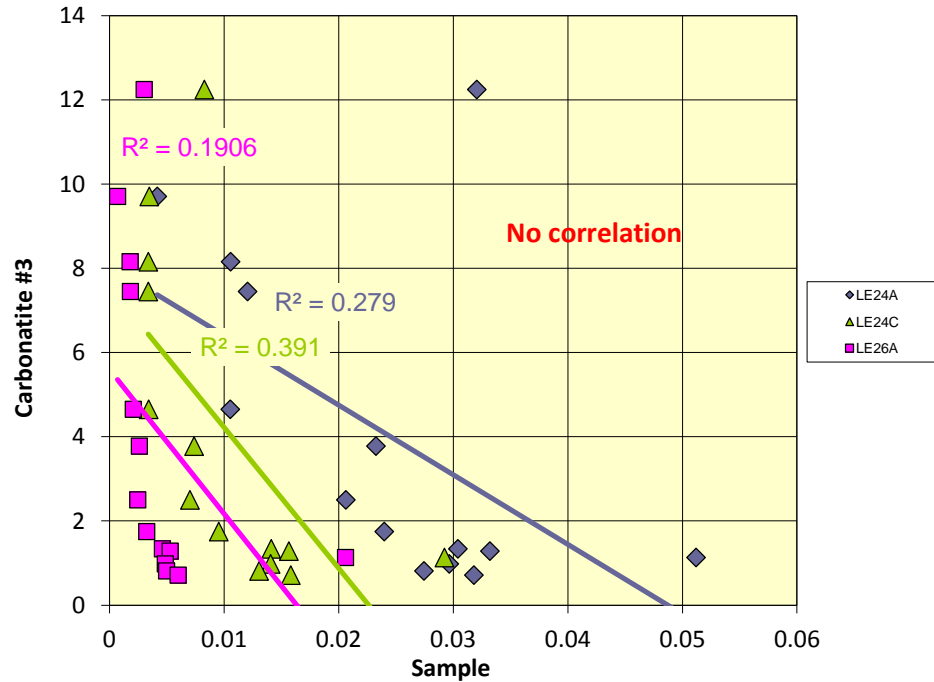
| Matching | LE24A | LE24B | LE24C | LE24D | LE26A | LE26B |
|---|---|---|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| $Y/Ho > 40$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| $La/La^* > 1.1$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| $Gd/Gd^* > 1.1$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| $Ce/Ce^* < 0.8$ | ✓ | ✓ | ✗ | ✗ | ✓ | ✓ |

Marine Limestones
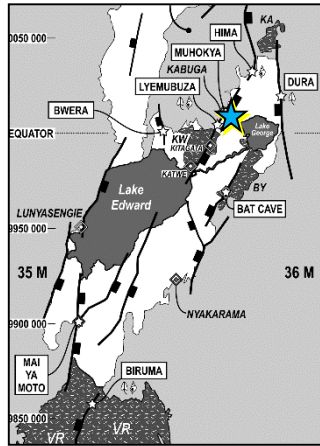
## MUHOKYA
## Western Lake George,
## EA4A, Uganda
## Sample LE28
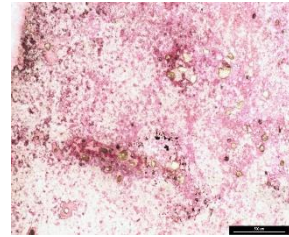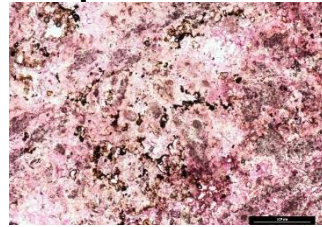


**Samples LE 28**

Geological environment:

Calcite formed in an inverted fairly impressive cliff appearing like a rotational uplift on top of a normal fault block. No evidence of continuous limestone bands.

Field description:, LE 28

Travertine with primary porosity seeming to have black organic rich fill to their primary porosity.
Feezing with HCl acid.



Carbonatite #3 vs Sample

R² = 0.3414

No correlation

R² = 0.1655

R² = 0.3194

- ■ LE28B
- ▲ LE28C
- ● LE28D



REE plot: La Ce Pr Nd Sm Eu Gd Tb Dy Y Ho Er Tm Yb Lu

- ◆ LE28A
- ■ LE28B
- ▲ LE28C
- ● LE28D
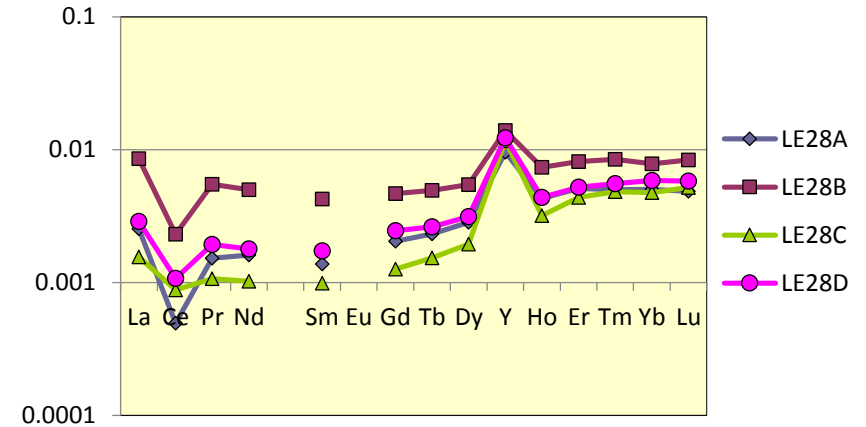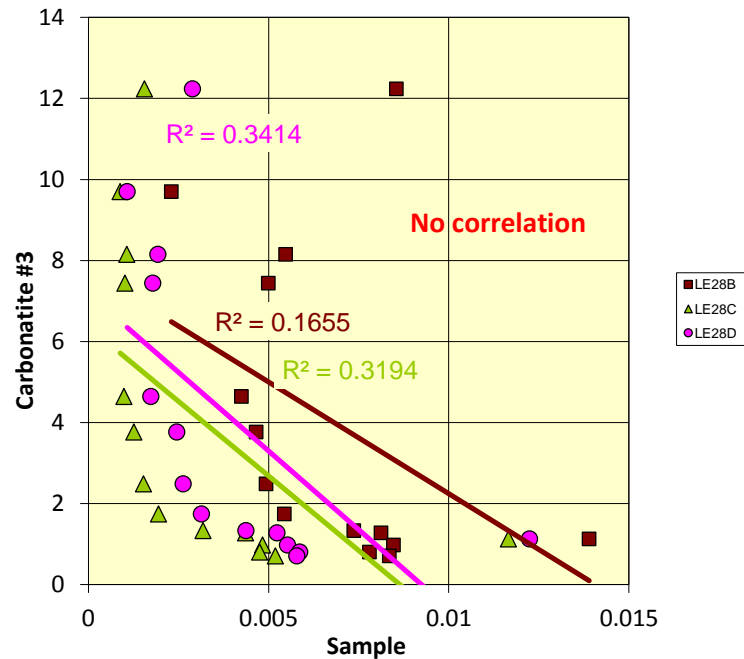
| Matching | LE28A | LE28B | LE28C | LE28D |
|---|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✓ | ✓ | ✓ | ✓ |
| $Y/Ho > 40$ | ✓ | ✓ | ✓ | ✓ |
| $La/La^* > 1.1$ | ✓ | ✓ | ✓ | ✓ |
| $Gd/Gd^* > 1.1$ | ✓ | ✓ | ✓ | ✓ |
| $Ce/Ce^* < 0.8$ | ✓ | ✗ | ✗ | ✓ |

Key criteria for Marine Limestones
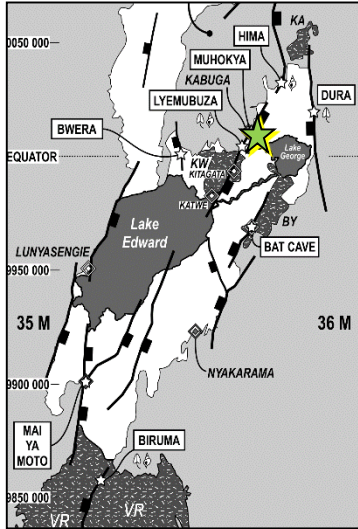
# MUHOKYA
## Western Lake George, EA4A, Uganda
## Sample LE27
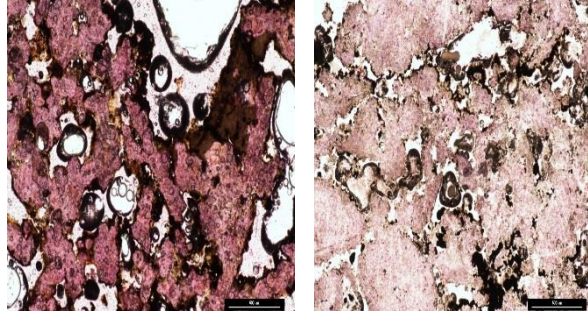


**Samples LE 27**

Geological environment:

Calcite formed in an inverted fairly impressive cliff appearing like a rotational uplift on top of a normal fault block. No evidence of continuous limestone bands.

Field description:, LE 27

Travertine with primary porosity seeming to have black organic rich fill to their primary porosity.
Feezing with HCl acid.



$R^2 = 0.1844$

$R^2 = 0.8402$

**Moderate correlation**
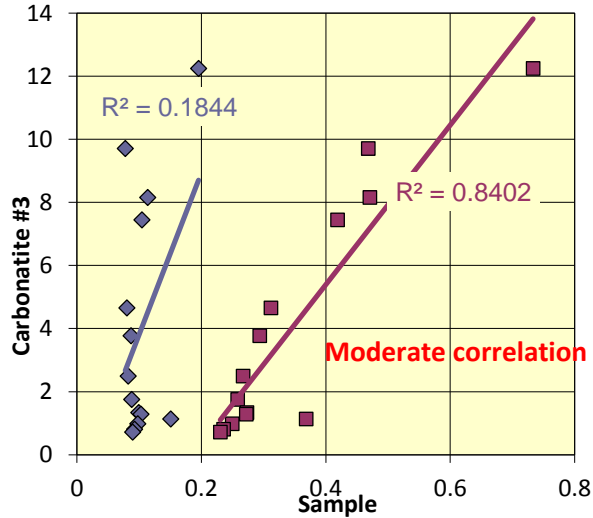
LE27A
LE27B

| | LE27A | LE27B |
|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✗ | ✗ |
| Y/Ho > 40 | ✓ | ✗ |
| La/La* > 1.1 | ✓ | ✓ |
| Gd/Gd* > 1.1 | ✓ | ✗ |
| Ce/Ce* < 0.8 | ✓ | ✗ |

*Key criteria for Marine Limestones*

**Moderately Matching**

# HIMA CEMENT QUARRIES
## Western Lake George,
## EA4A, Uganda
## Samples LE37 & LE38

Legend:
- LE37A
- LE37B
- LE38A
- LE38B

**No matching**



$R^2 = 0.9938$   $R^2 = 0.9769$

$R^2 = 0.9922$   $R^2 = 0.8838$

**Moderate correlation**

Carbonatite #3

Legend:
- LE37A
- LE37B
- LE38B
- LE38A
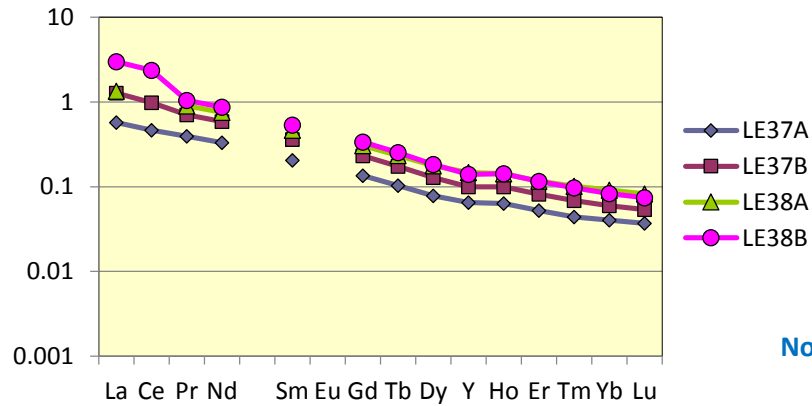
| Key criteria for Marine Limestones | LE37A | LE37B | LE38A | LE38B |
|---|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✗ | ✗ | ✗ | ✗ |
| $Y/Ho > 40$ | ✗ | ✗ | ✗ | ✗ |
| $La/La^* > 1.1$ | ✗ | ✓ | ✗ | ✓ |
| $Gd/Gd^* > 1.1$ | ✗ | ✗ | ✗ | ✗ |
| $Ce/Ce^* < 0.8$ | ✗ | ✗ | ✓ | ✗ |
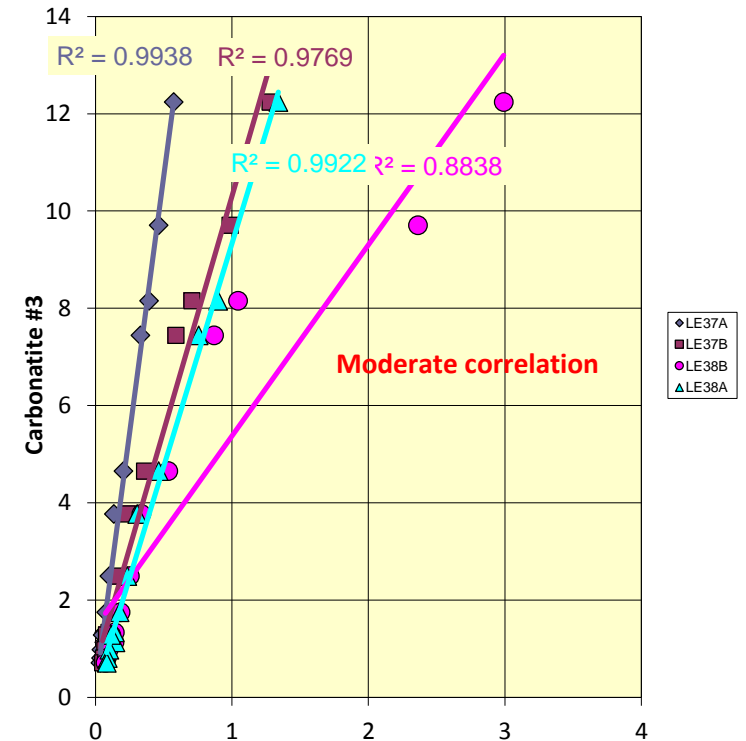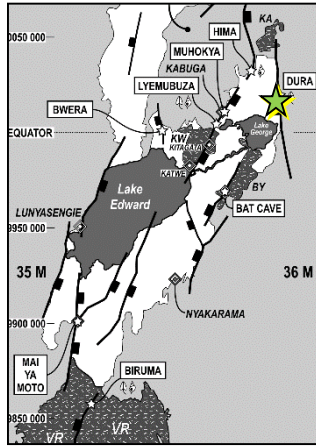
**DURA**
**Eastern Lake George,**
**EA4A, Uganda**
**Sample LE32**
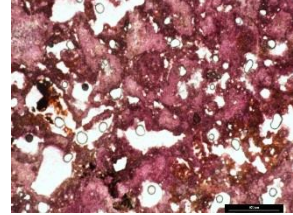
**Samples LE 32**

Geological environment: Dura cement Works mine.

Located just downstream north of a river bank flowing through the Ruwenzori border fault.

Field description: LE 32, 37, and LE 38

Very porous light brown limestones;

Vugs visible presence dispersed in all sample;

Feezing with HCl acid.

**Moderate correlation**

R² = 0.7129

R² = 0.6259

R² = 0.7505

- LE32B
- LE32D
- LE32F



- LE32A
- LE32B
- LE32C
- LE32D
- LE32E
- LE32F

**Moderately matching**

| Key criteria for Marine Limestones | LE32A | LE32B | LE32C | LE32D | LE32E | LE32F |
|---|---|---|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Y/Ho > 40 | ✓ | ✗ | ✓ | ✓ | ✗ | ✓ |
| La/La* > 1.1 | ✓ | ✗ | ✓ | ✗ | ✗ | ✗ |
| Gd/Gd* > 1.1 | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ |
| Ce/Ce* < 0.8 | ✗ | ✓ | ✗ | ✗ | ✗ | ✗ |

The result here above provides some evidence of geochemistry origin for different Carbonates outcropping in the Ugandan side of Albert Graben, EARS. They have demonstrated that:

- Samples LE 44A & B, drilled respectively through its white and dark layers, gave a typical Carbonatites signature with high pics of light REE (lanthanide) and Yttrium concentrations which are characterizing apatite's Carbonatites associations with very good correlation coefficient $R^2 > 0.90$ with Fort Portal sample #3. No Marine limestones criteria matching. These basic findings are consistent with this research objectives showing that there is involvement of Carbonatites emerging from depth to the subsurface through groundwaters;

- LE 41 & LE 42, drilled through vacuoles, grains or cement, gave also a typical Carbonatites signature with also high pics of light REE (lanthanide) and Yttrium concentrations which are characterizing apatite's Carbonatites associations with a very good correlation coefficient $R^2 > 0.94$ with FP #3. Very few marine (negligible) limestones criteria matching not enough to conclude a marine limestone involvement. This fact clearly implies the involvement of Carbonatites groundwaters deposing Carbonatites in around an evident hot spring;

- P12, drilled through carbonates fill tubes avoiding rootlets, fossil leaves, small basement blocs caught up in these fossil tubes and black relics in the cavities, the P12 ICP-MS results revealed a Marine limestones spectral signatures interesting facts. Negative correlation coefficient $R^2 = 0.36$ with FP#3 has been scientifically established while a matching has been found with the Marine Limestones Balz procedure criteria with Ce anomalies ($Ce/Ce^* \sim 0.55$) suggesting palaeo ocean-basin floor setting. This result demonstrates the first clear evidence of underneath Marine limestone deposit involvement for the origin of the carbonates in this Travertine outcrop;

- LE 24, LE 26 and LE 28, have been drilled as above through visible carbonates textures, structures or fabrics avoiding any black organic rich fill to their primary porosity, these samples ICP-MS results revealed a Marine limestones spectral signatures interesting facts. No correlation with FP#3 has been scientifically established while a matching has been found with the Marine Limestones Balz paper procedure criteria with Ce anomalies ($Ce/Ce^* \sim 0.55$) suggesting palaeo ocean-basin floor setting. This result demonstrates further evidence of underneath Marine limestone deposit involvement for the origin of these carbonates;

- LE 27, 32, 37 and 38 , have been drilled as above through visible carbonates textures, structures or fabrics avoiding any black organic rich fill to their primary porosity, these samples ICP-MS results revealed a kind of weird

spectral signatures different from typical Carbonatites or Marine limestones. Negative to Moderate correlation with FP#3 and No to moderately matching with Balz paper criteria. These results demonstrate that a kind of hybrid (intermediate) source of carbonates does exist within the Rift basin. This hybrid source seems to be a mixture of Carbonatites and Marine limestones sources.
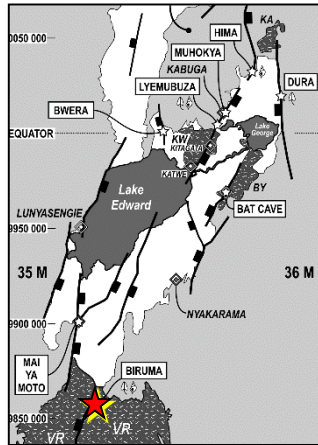
**BIRUMA**
**Southern Lake Edward,**
**Block V, DRC**
**Sample V2**
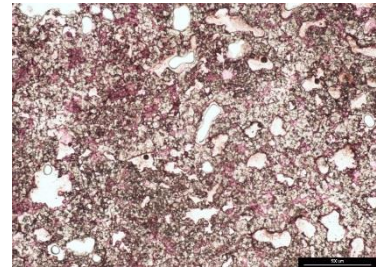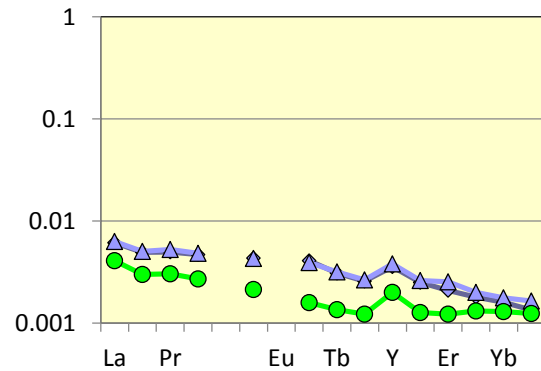
| No matching | V2A | V2A | V2B |
|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✗ | ✗ | ✗ |
| $Y/Ho > 40$ | ✗ | ✗ | ✓ |
| $La/La^* > 1.1$ | ✓ | ✗ | ✗ |
| $Gd/Gd^* > 1.1$ | ✓ | ✗ | ✗ |
| $Ce/Ce^* < 0.8$ | ✗ | ✗ | ✗ |
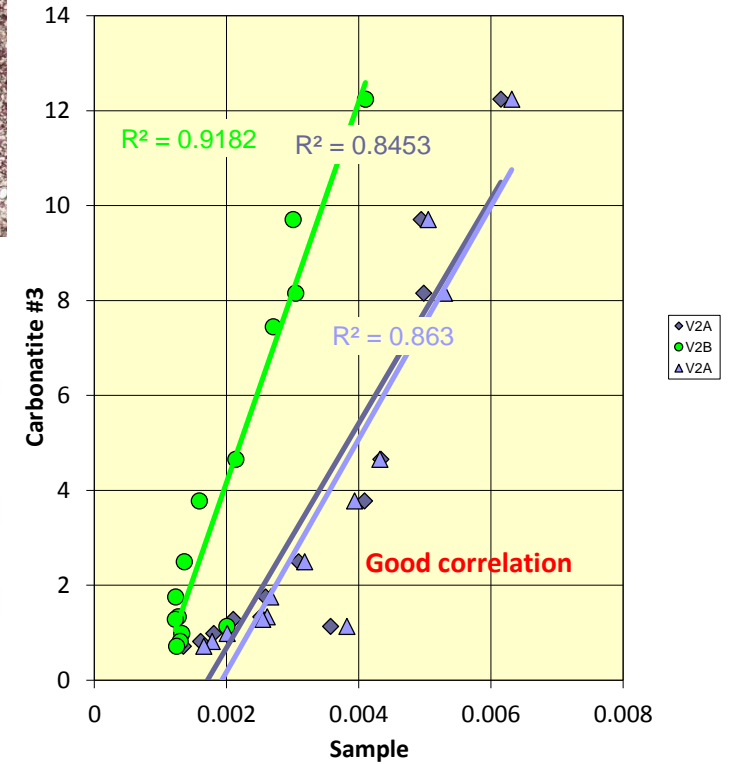
Key criteria for Marine Limestones



$R^2 = 0.9182$   $R^2 = 0.8453$

$R^2 = 0.863$

**Good correlation**

# MAI YA MOTO (HOT SPRINGS)
## Southern Lake Edward, Block V, DRC
## Sample V20

**No matching**

| Key criteria for Marine Limestones | V20A | V20B |
|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✗ | ✗ |
| $Y/Ho > 40$ | ✗ | ✗ |
| $La/La^* > 1.1$ | ✗ | ✓ |
| $Gd/Gd^* > 1.1$ | ✗ | ✗ |
| $Ce/Ce^* < 0.8$ | ✗ | ✗ |



$R^2 = 0.9641$

$R^2 = 0.9888$

**Good correlation**
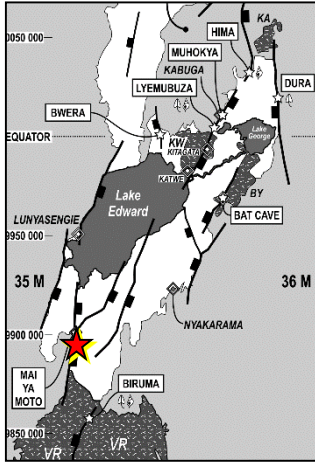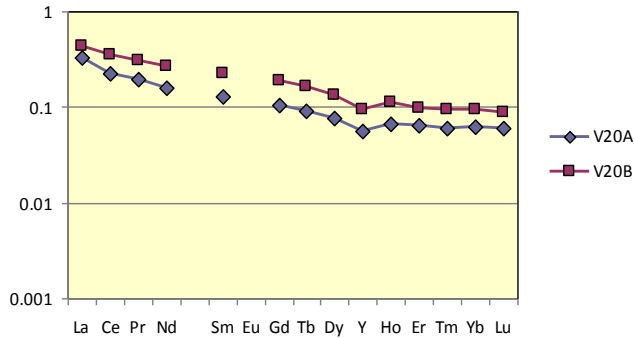
# MAI YA MOTO (HOT SPRINGS) Southern Lake Edward, Block V, DRC
## Sample V19





**Samples V19:**

Black stained lining in white vugs spreaded Travertine.

For security reasons and safety, field time was restricted for more field detailed description.



REE diagram legend:
- V19A (diamond)
- V19A (square)
- V19A (triangle)
- V19B
- V19C
- V19D

Scatter plot: Carbonatite #3 vs Sample

**No correlation**

R² = 0.3112
R² = 0.1866
R² = 0.2418
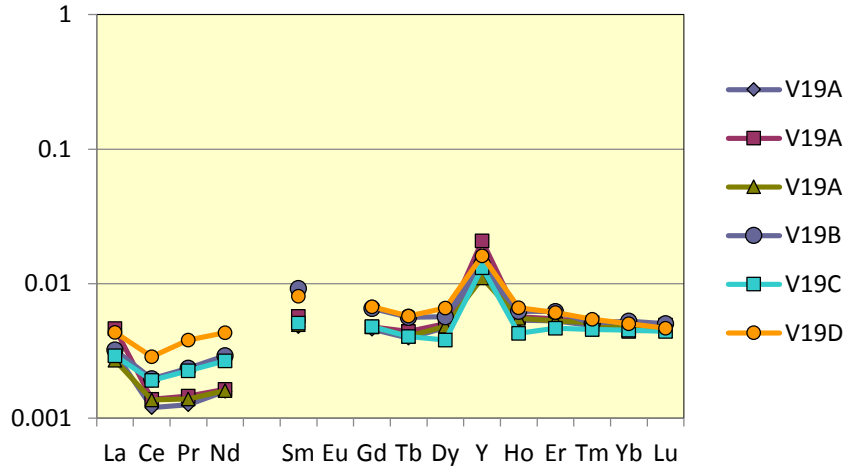
Legend: V19A, V19C, V19D

| Key criteria for Marine Limestones | V19A | V19A | V19A | V19B | V19C | V19D |
|---|---|---|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✗ |
| $Y/Ho > 40$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| $La/La^* > 1.1$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| $Gd/Gd^* > 1.1$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| $Ce/Ce^* < 0.8$ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ |
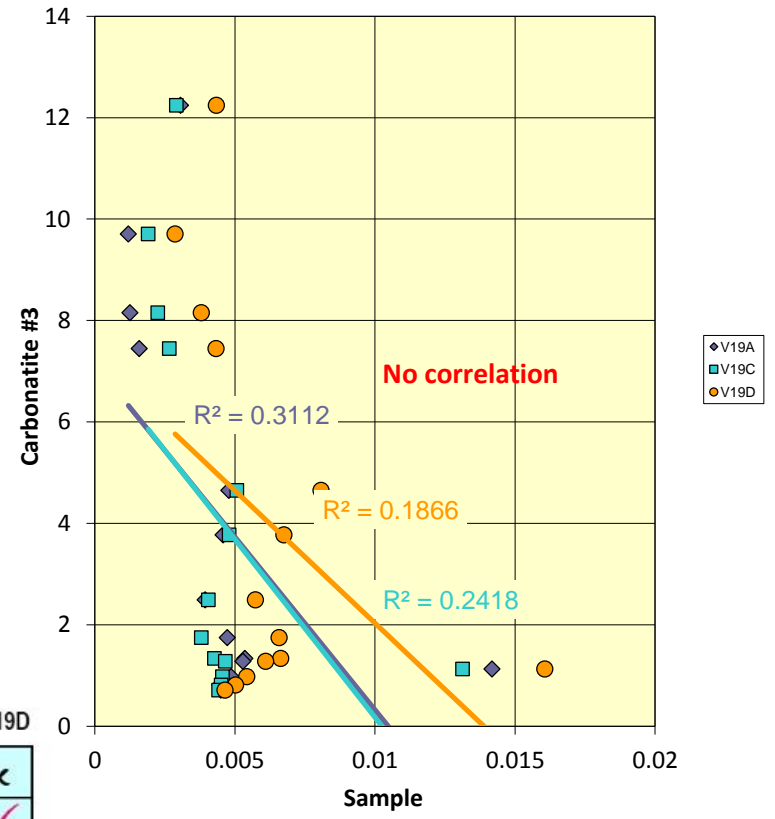
**Matching**

# MAI YA MOTO (HOT SPRINGS)
## Southern Lake Edward, Block V, DRC
## Sample V21



**Samples V21:**

Black stained lining in white vugs spreaded Travertine.

For security reasons and safety, field time was restricted for more field detailed description.



Carbonatite #3 vs Sample

R² = 0.6643
R² = 0.6618
**No correlation**
◆V21A
▲V21B

REE plot: V21A, V21A, V21B
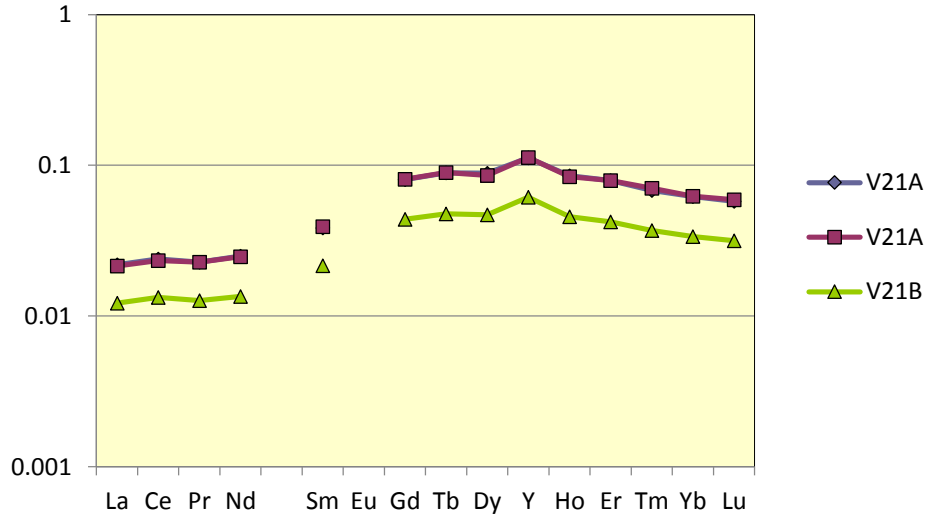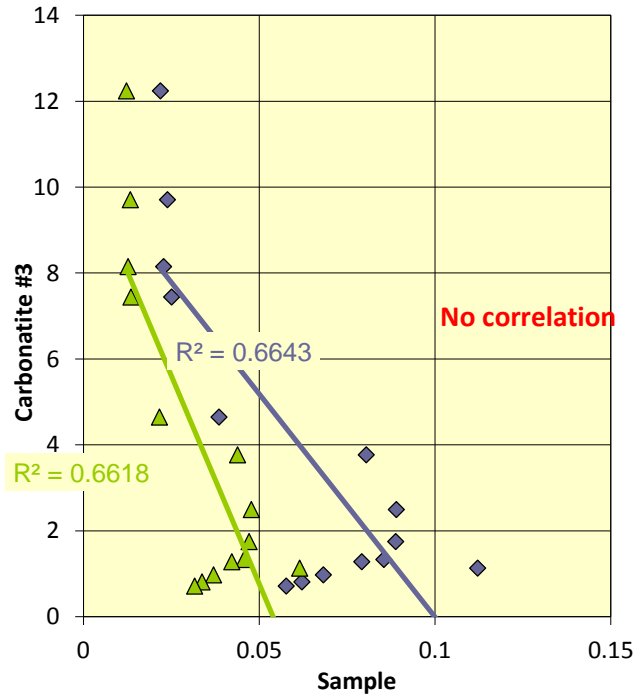
**No matching**

| Key criteria for Marine Limestones | V21A | V21A | V21B |
|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✓ | ✓ | ✓ |
| $Y/Ho > 40$ | ✗ | ✗ | ✗ |
| $La/La^* > 1.1$ | ✓ | ✓ | ✓ |
| $Gd/Gd^* > 1.1$ | ✗ | ✗ | ✗ |
| $Ce/Ce^* < 0.8$ | ✗ | ✗ | ✗ |

## MAI YA MOTO (HOT SPRINGS) Southern Lake Edward, Block V, DRC
## Sample V22

**Samples V22:**

Black stained lining in white vugs spreaded Travertine.

For security reasons and safety, field time was restricted for more field detailed description.
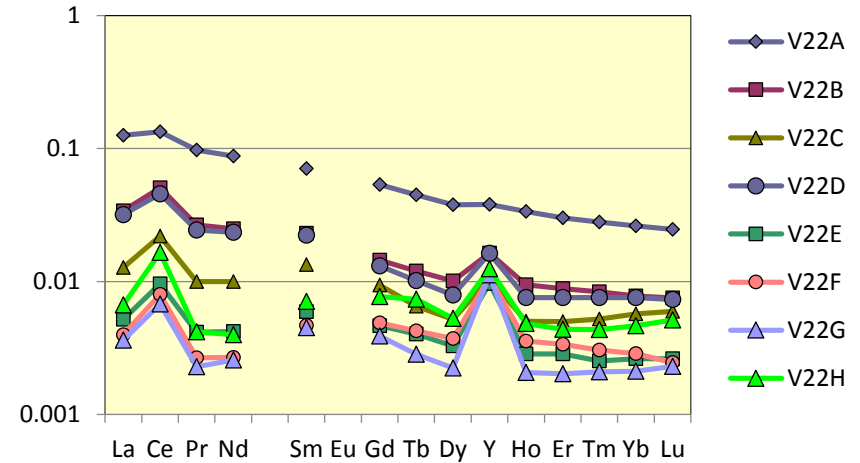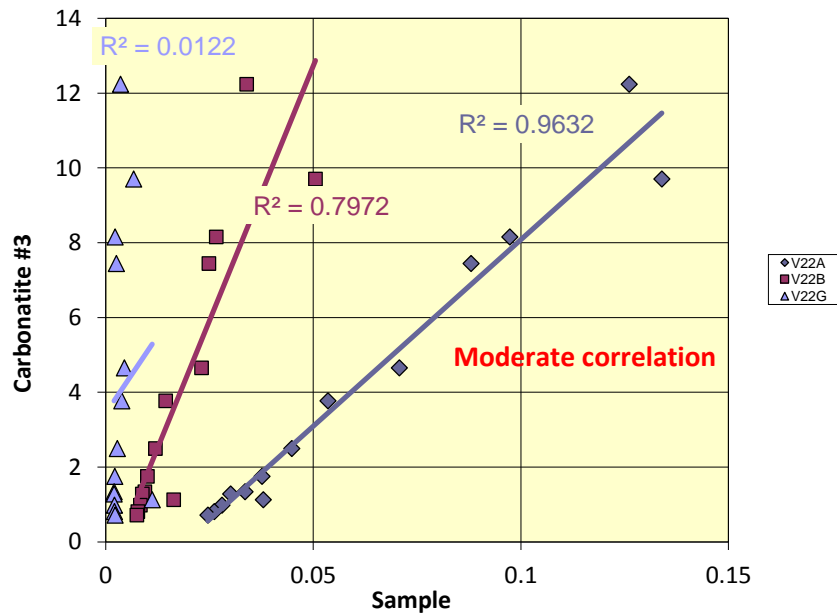


**Moderately matching**

|  | V22A | V22B | V22C | V22D | V22E | V22F | V22G | V22H |
|---|---|---|---|---|---|---|---|---|
| $Pr_n/Yb_n \ll 1$ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ |
| Y/Ho > 40 | ✗ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| La/La* > 1.1 | ✗ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Gd/Gd* > 1.1 | ✗ | ✗ | ✓ | ✗ | ✗ | ✗ | ✗ | ✗ |
| Ce/Ce* < 0.8 | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ |

The result here above provides some evidence of geochemistry origin for different Carbonates outcropping in the DR Congo side of Albert Graben, EARS. They have demonstrated that:

- V2, drilled respectively through its light brown very crumble and carbonates in vugs porosity layers avoiding the visible rootlets, branches or plant tubes, gave a typical Carbonatites signature with very good correlation coefficient $R^2 > 0.90$ with FP#3. No Marine limestones criteria matching. These basic findings are consistent with this research objectives showing that there is involvement of Carbonatites emerging from depth to the subsurface through groundwaters;

- V20, drilled through the carbonates porosity filled textures avoiding the black stained lining in white vugs, gave a typical Carbonatites signature with very good correlation coefficient $R^2 > 0.90$ with FP#3. No Marine limestones criteria matching. These basic findings are consistent with this research objectives showing that there is involvement of Carbonatites emerging from depth to the subsurface through groundwaters;

- V19, drilled through the carbonates porosity filled textures avoiding the black stained lining in white vugs, the V19 ICP-MS results revealed a Marine limestones spectral signatures interesting facts. No correlation with FP#3 has been scientifically established while a matching has been found with the Marine Limestones Balz paper criteria. This result demonstrates the first evidence of underneath Marine limestone deposit involvement for the origin of the carbonates in this Travertine outcrop;

- V21 and V22, have been drilled as above through the carbonates porosity filled textures avoiding the black stained lining in white vugs, these samples ICP-MS results revealed a kind of weird spectral signatures different from typical Carbonatites or Marine limestones. No to Moderate correlation with FP#3 and No to moderately matching with Balz paper criteria. These results demonstrate that a kind of hybrid source of carbonates does exist within the Rift basin. This hybrid source seems to be a mixture of Carbonatites and Marine limestones sources.

The figures below show all the 2014 field samples analysed by ICP-MS in 2018. These Figures highlight for each sample analysed that little is known about:

- Sample location in the map region
- Sample field photo and description
- Sample geologic environment
- Sample thin section and petrography comments
- The results of ICP-MS, which show planned correlation comparisons revealing either the Carbonatites, marine limestones or mixture involvement in their respective spectral signatures.

Labels on map and figures:

V 159, V161, 162, 163 & V164

V363, 364 & V385

Hot Springs

BVγ-7

V344, 352 & V356

9905

V153

V150

V149

## Mai Ya Moto
## Southern Lake Edward,
## Block V, DRC
## Sample V 149

**Samples V149:**
Light Brown very crumble limestone with vugs porosity and visible rootlets branches and plant tubes;   Single block. Light brown fibrous Travertine with Breccia gap and cavities.





### HYBRID SAMPLES CORRELATION WITH DEVONIAN REEF



R² = 1

R² = 0.5158  R² = 0.5031

### ICP-MS 2018: HYBRID SIGNATURES



LA  CE  PR  ND    SM  EU  GD  TB  DY  Y  HO  ER  TM  YB  LU

◆ BV 149 A  ■ BV 149 B  ▲ BV 150  ✕ BV 159 A  ✳ BV 159 B

◆ BV 149 B        ✕ Devonian reef
● BV 149 A        — Linear (BV 149 B)
— Linear (Devonian reef)  — Linear ( BV 149 A)

## Mai Ya Moto
## Southern Lake Edward,
## Block V, DRC
## Sample V 149

**Samples V149:**

Light Brown very crumble limestone with vugs porosity and visible rootlets branches and plant tubes; Single block. Light brown fibrous Travertine with Breccia gap and cavities.

### HYBRID SAMPLES CORRELATION WITH FORT PORTAL



### ICP-MS 2018: HYBRID SIGNATURES

## Mai Ya Moto
## Southern Lake Edward,
## Block V, DRC
## Sample V 150



**Samples V150:**
Light Brown very crumble limestone with vugs porosity and visible rootlets branches and plant tubes. Microbially laminated white Travertine with fibrous layers.





### HYBRID SAMPLES CORRELATION WITH DEVONIAN REEF



### ICP-MS 2018: HYBRID SIGNATURES

## Mai Ya Moto
## Southern Lake Edward,
## Block V, DRC
## Sample V 150

**Samples V150:**
Light Brown very crumble limestone with vugs porosity and visible rootlets branches and plant tubes. Microbially laminated white Travertine with fibrous layers.





### HYBRID SAMPLES CORRELATION WITH FORT PORTAL



$R^2 = 1$

$R^2 = 0.8447$

### ICP-MS 2018: HYBRID SIGNATURES



BV 149 A    BV 149 B    BV 150    BV 159 A    BV 159 B

BV 150    FP 3    Linear (BV 150)    Linear (FP 3)

# Mai Ya Moto
# Southern Lake Edward,
# Block V, DRC
# Sample V 153

**Samples V153:**

Light Brown very crumble limestone with vugs porosity and visible rootlets branches and plant tubes; Travertine with chimney structure that provides ventilation for hot flue gases or smoke from underground processes, then cooled at surface in ambient temperature.



## HYBRID BV 153 SAMPLE CORRELATION WITH DEVONIAN REEF
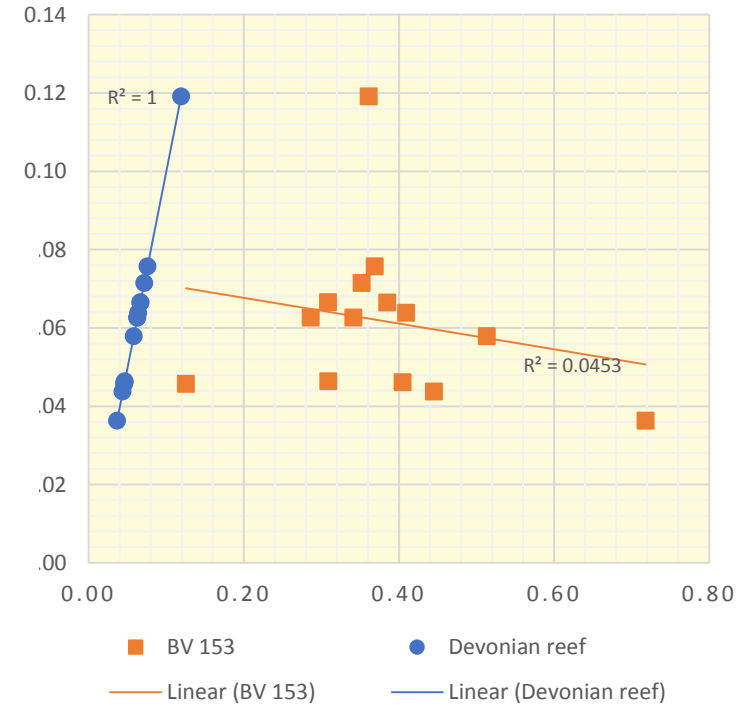


## REE  BV 153 HYBRID SIGNATURE
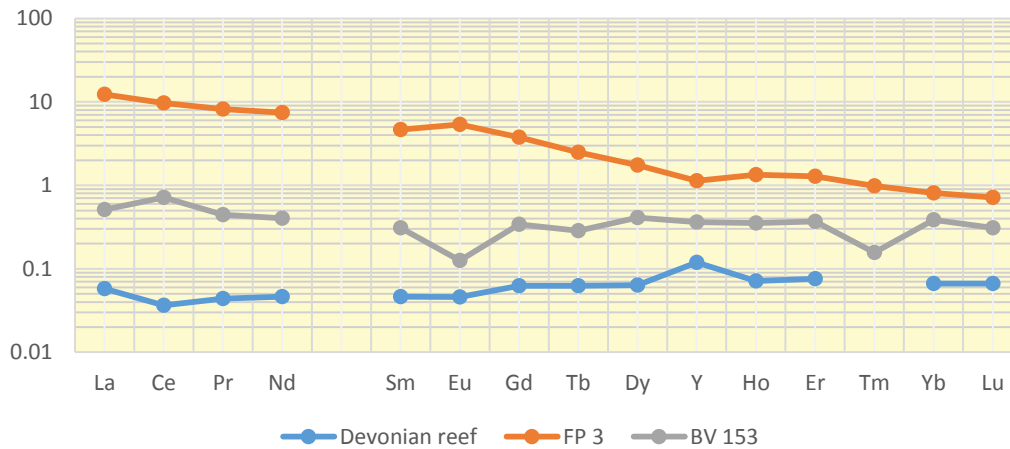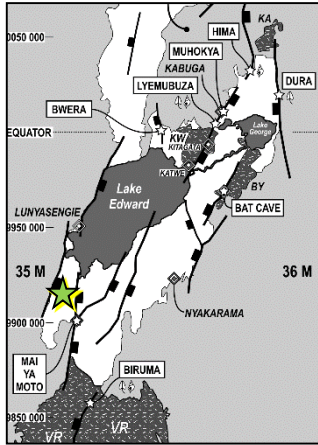
## Mai Ya Moto
## Southern Lake Edward, Block V, DRC
## Sample V 153

**Samples V153:**

Light Brown very crumble limestone with vugs porosity and visible rootlets branches and plant tubes; Travertine with chimney structure that provides ventilation for hot flue gases or smoke from underground processes, then cooled at surface in ambient temperature.





### HYBRID SAMPLES CORRELATION WITH FORT PORTAL



$R^2 = 0.3318$

$R^2 = 1$

Legend: ■ BV 153   ✳ FP 3   — Linear (BV 153)   — Linear (FP 3)

### REE  BV 153 HYBRID SIGNATURE



Legend: Devonian reef   FP 3   BV 153
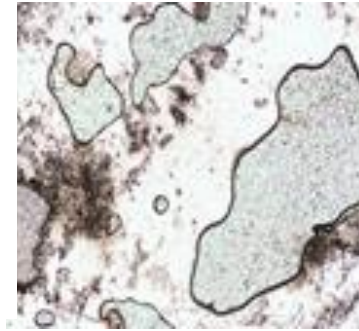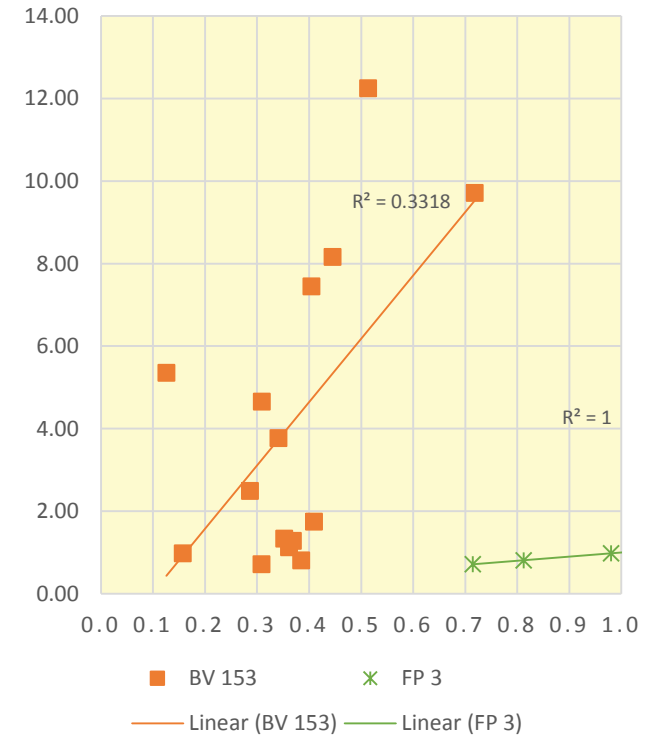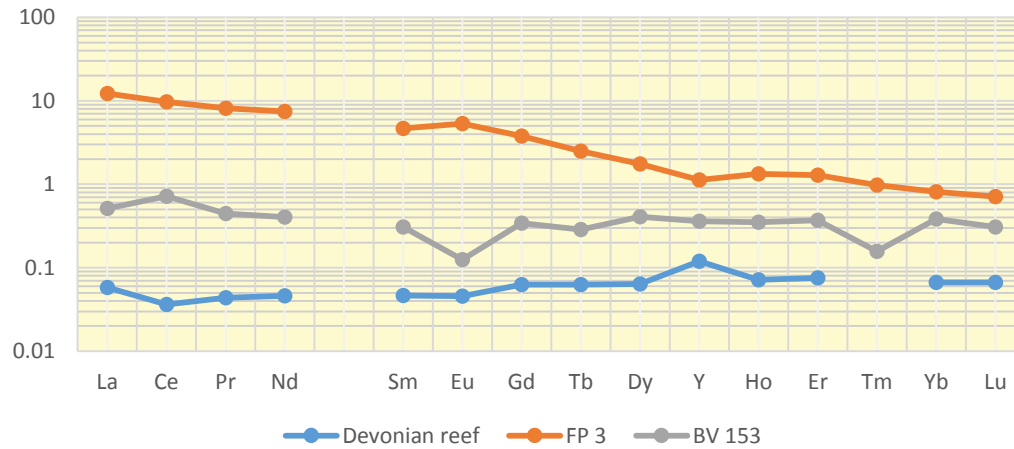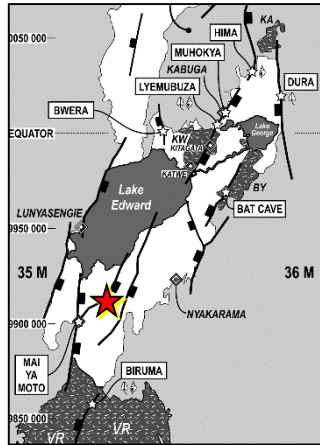
## Mabenga
## Southern Lake Edward, Block V, DRC
## Sample V 344

**Samples V344:**

Travertine with inputs of plants and tree rootlets. Presence of white salt crusts and small chimneys with maximal temperatures of 90 °C.

**Gamma ray values:**

K= 1.0 % U= 200.9 ppm Th = 25.1 ppm (assay # 2268)
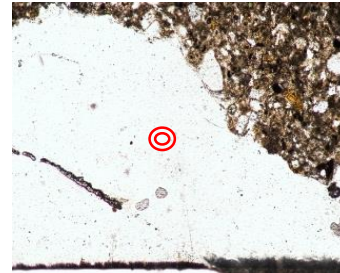


### BLOCK V CARBONATITES CORRELATION FORT PORTAL
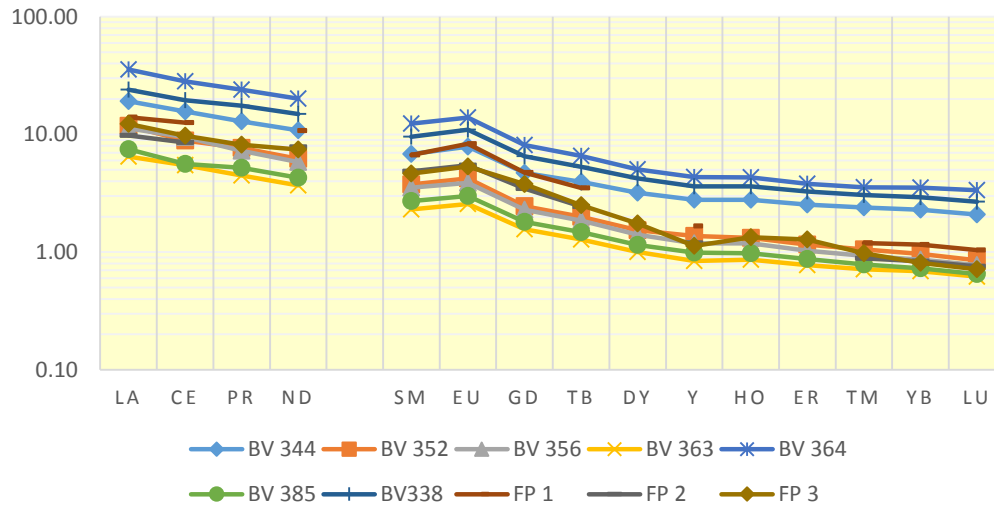


### BLOCK V CARBONATITES & FORT PORTAL LAVAS
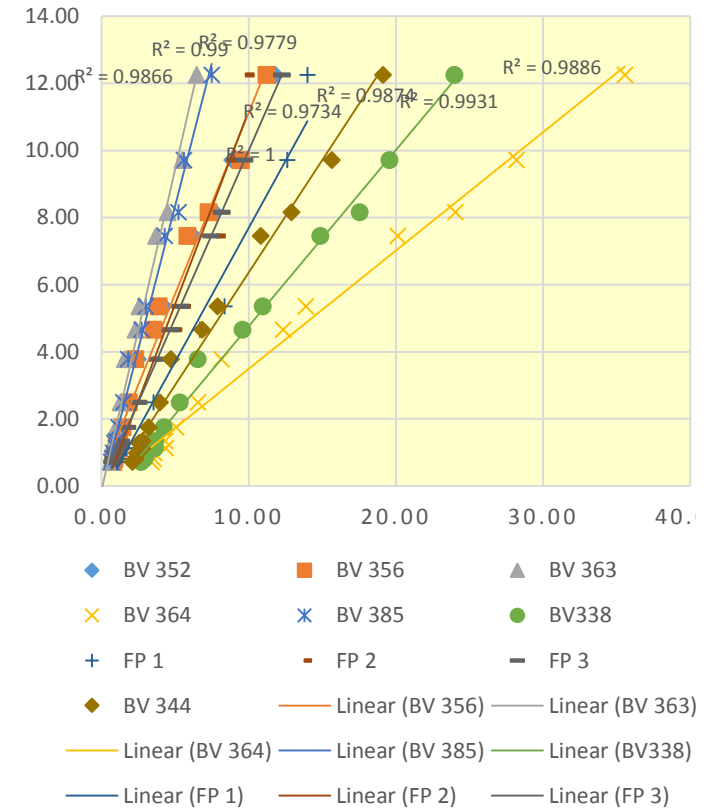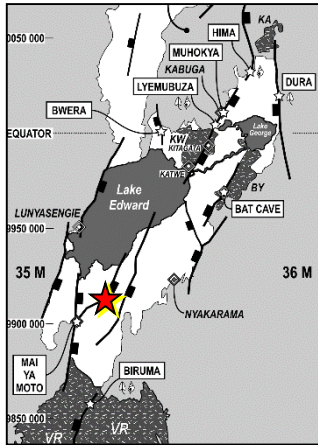
## Mabenga
## Southern Lake Edward,
## Block V, DRC
## Sample V 352 & V356

**Samples V352 & 356:**

Travertine with inputs of plants and tree rootlets. Presence of white salt crusts and small chimneys with maximal temperatures of 90 °C.

**Gamma ray values:**

K= 1.0 % U= 200.9 ppm Th = 25.1 ppm (assay # 2268)
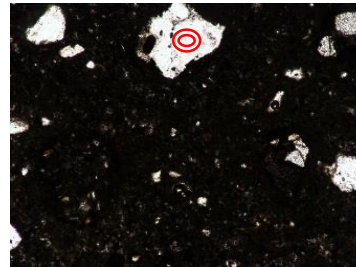


### BLOCK V CARBONATITES CORRELATION FORT PORTAL
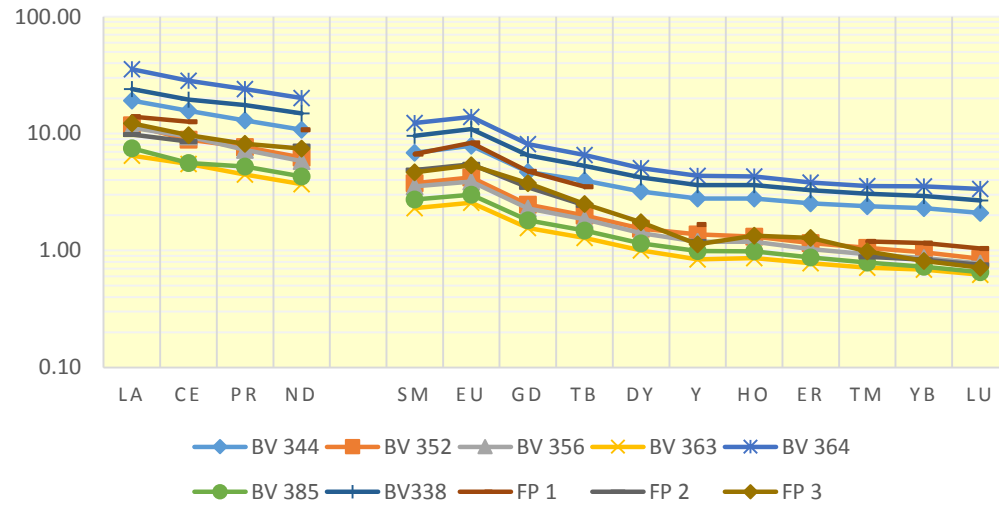


### BLOCK V CARBONATITES & FORT PORTAL LAVAS
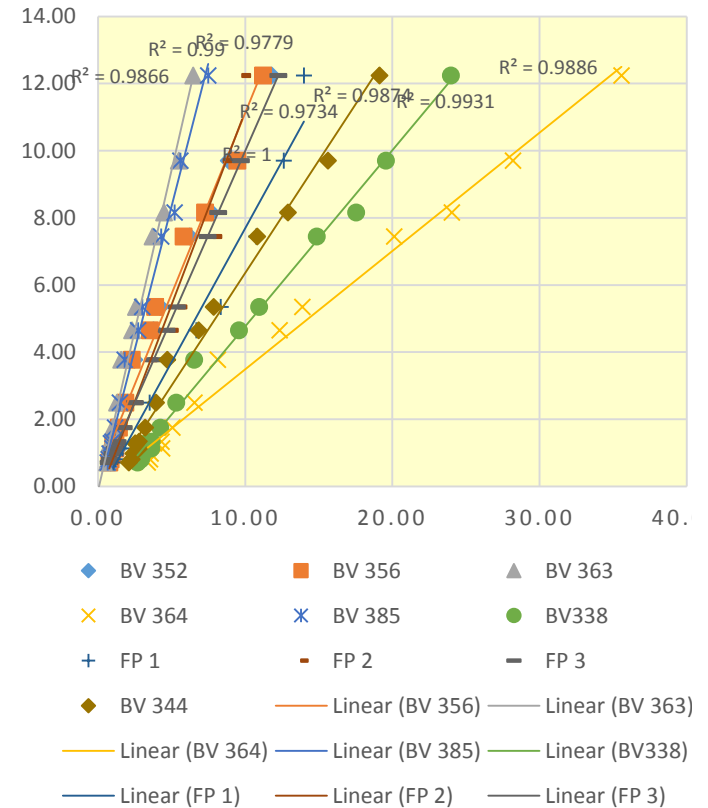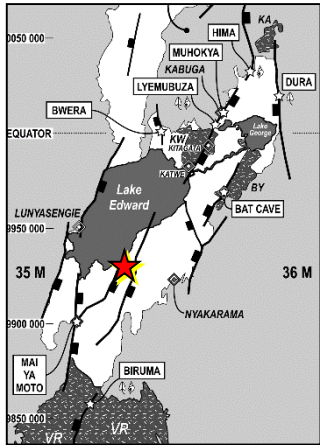
## Vitshumbi fault scarp South Eastern Lake Edward, Block V, DRC Sample V 363 & 364

**Samples V363 & 364:**
Vertical zoned Travertine including gas holes around rootlets cavities.
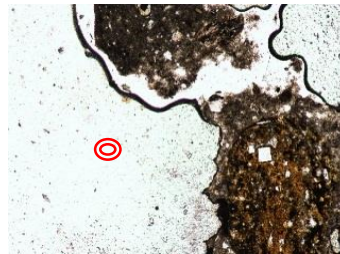




### BLOCK V CARBONATITES CORRELATION FORT PORTAL
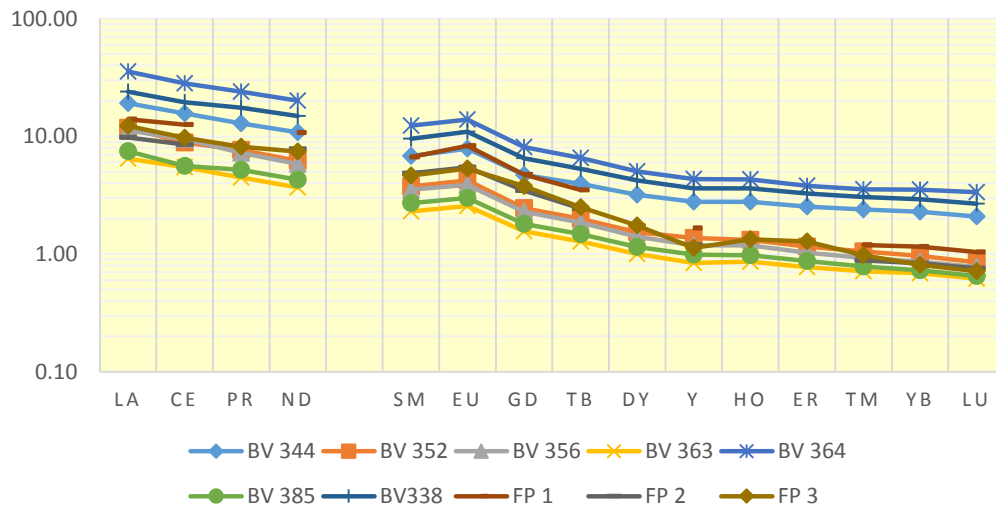


### BLOCK V CARBONATITES & FORT PORTAL LAVAS
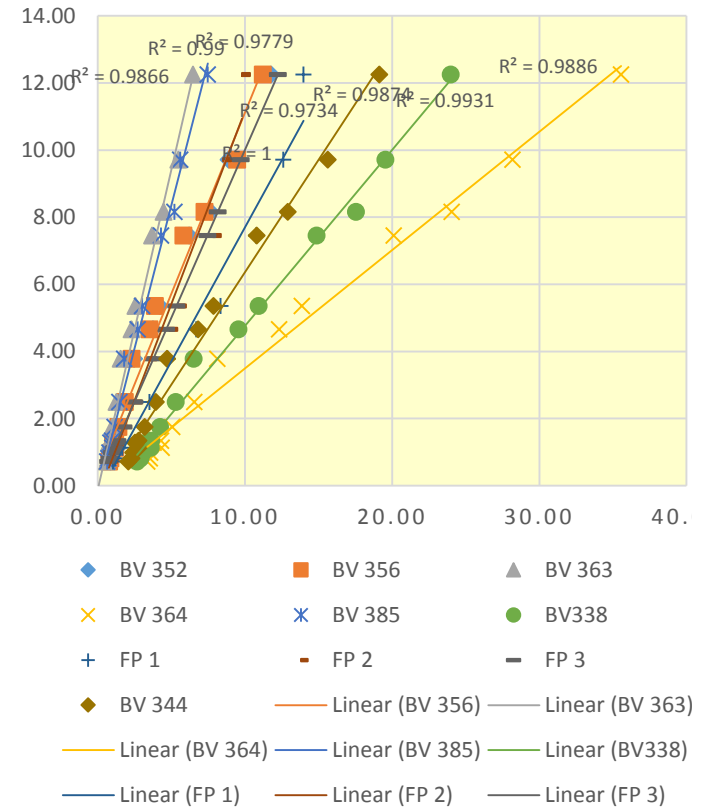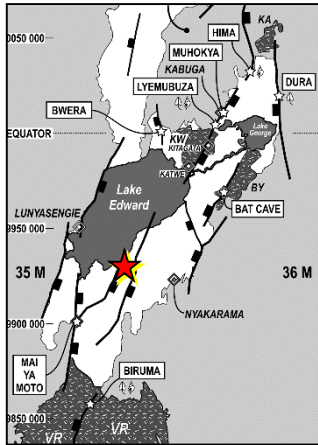
# Vitshumbi fault scarp South Eastern Lake Edward, Block V, DRC Sample V 385



**Samples V385:**
Vertical zoned Travertine including gas holes around rootlets cavities.
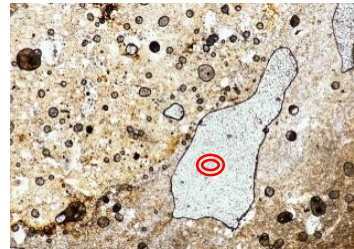




## BLOCK V CARBONATITES CORRELATION FORT PORTAL
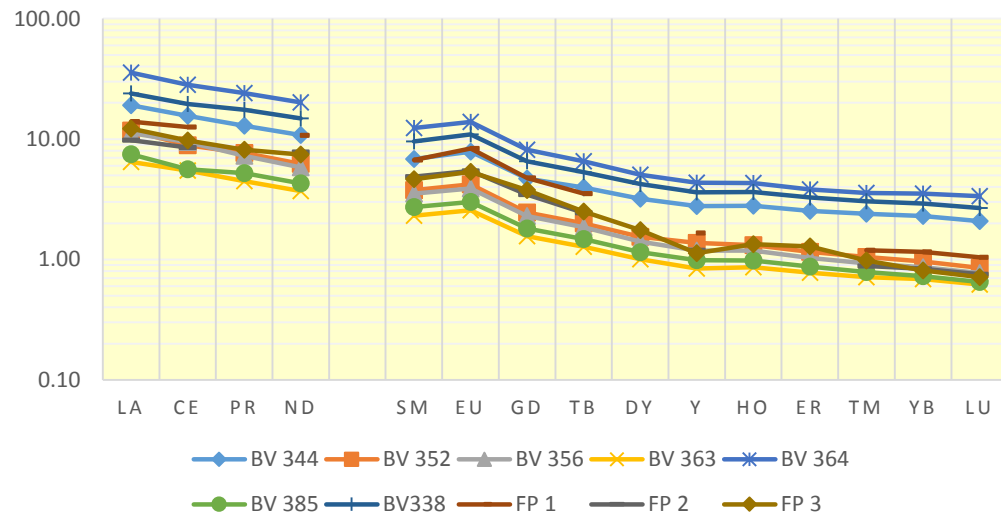


## BLOCK V CARBONATITES & FORT PORTAL LAVAS
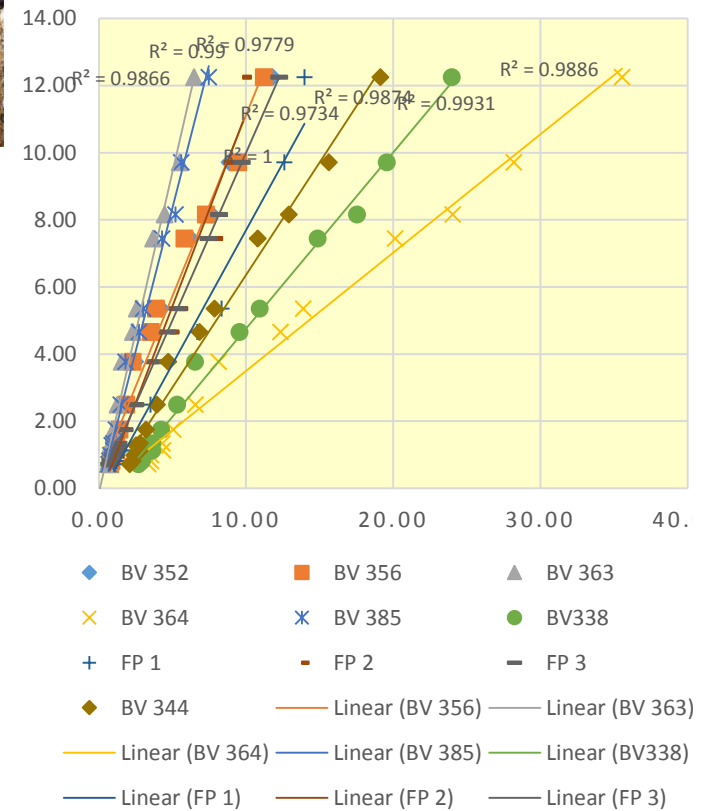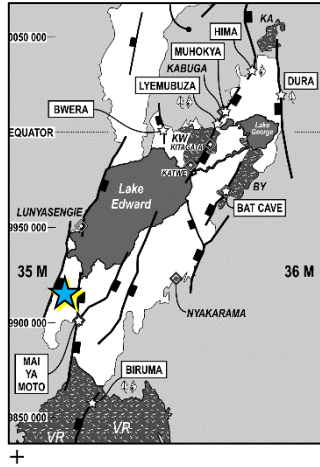
## Katanda Gorge
## Southern Lake Edward,
## Block V, DRC
## Sample V 161



**Samples V161:**

Hematite stained Travertine crumbled.
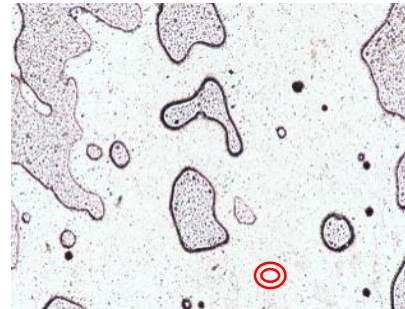




### BV 161 B

| | | | |
|------|--------|----------|-----|
| >1.1 | La/La* | 2.154878 | YES |
| <0.8 | Ce/Ce* | 1.185219 | NO |
| >1.1 | Gd/Gd* | 0.778326 | NO |
| << 1 | Prn/Ybn | 0.371749 | YES |
| >40  | Y/Ho   | 2.191354 | NO |

### BLOCK V (2018) & KNOWN MARINE LIMESTONE



### ICP-MS 2018 : CORELATION WITH KNOWN MARINE LIMESTONES



Good corelation
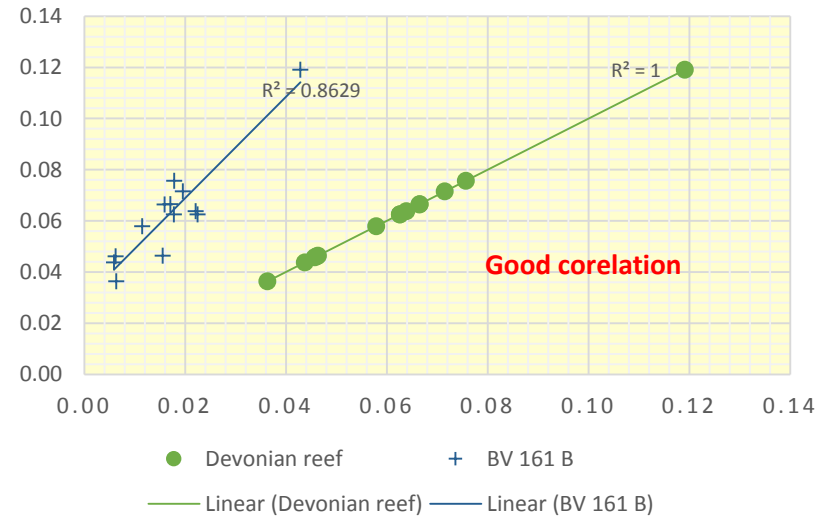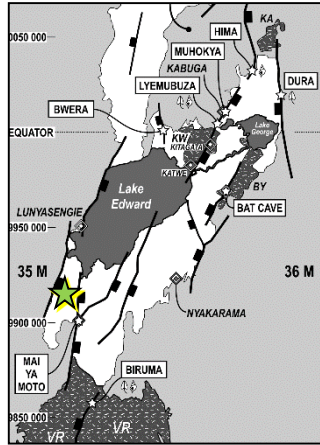
## Katanda Gorge
## Southern Lake Edward,
## Block V, DRC
## Sample V 162



**Samples V162:**
Hematite stained Travertine crumbled interbedded with some clastic facies.
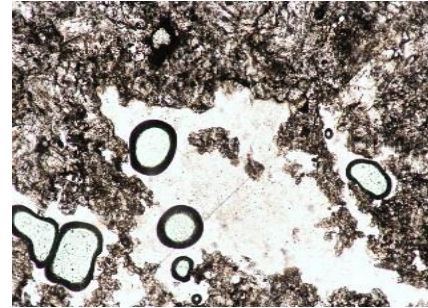




| | | BV 162 | |
|---|---|---|---|
| >1.1 | La/La* | 1.660919 | YES |
| <0.8 | Ce/Ce* | 1.529005 | NO |
| >1.1 | Gd/Gd* | 0.771417 | NO |
| << 1 | Prn/Ybn | 0.154034 | YES |
| >40 | Y/Ho | 1.274174 | NO |

### BLOCK V (2018) & KNOWN MARINE LIMESTONE



### ICP-MS 2018 : CORELATION WITH KNOWN MARINE LIMESTONES



No corelation
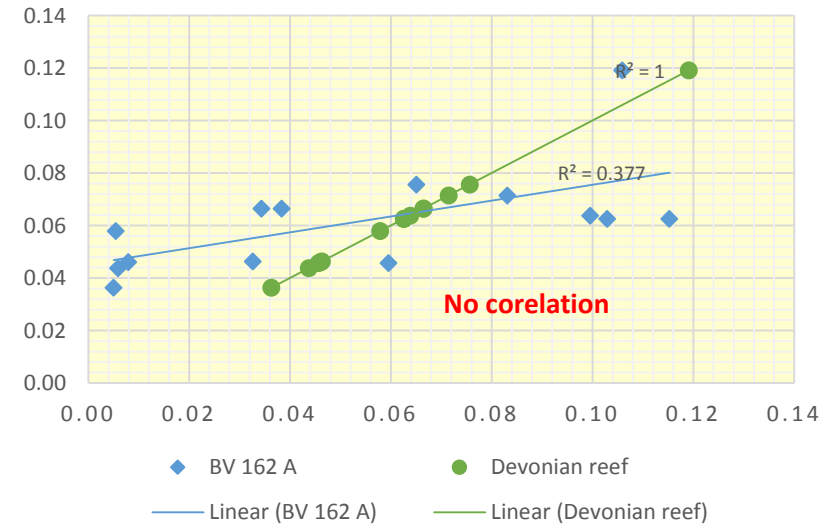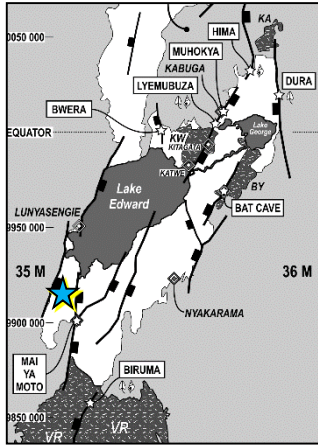
## Katanda Gorge
## Southern Lake Edward,
## Block V, DRC
## Sample V 163

**Samples V163:**

Hematite stained Travertine crumbled.
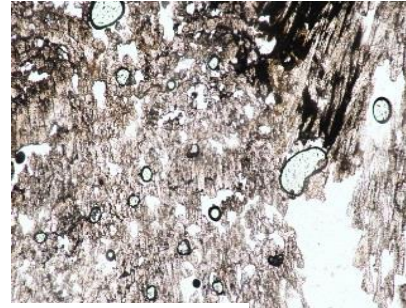


|  |  | BV 163 |  |
|---|---|---|---|
| >1.1 | La/La* | 5.823986 | YES |
| <0.8 | Ce/Ce* | 2.257441 | NO |
| >1.1 | Gd/Gd* | 0.761166 | NO |
| << 1 | Prn/Ybn | 0.137344 | YES |
| >40 | Y/Ho | 1.57862 | NO |

### BLOCK V (2018) & KNOWN MARINE LIMESTONE
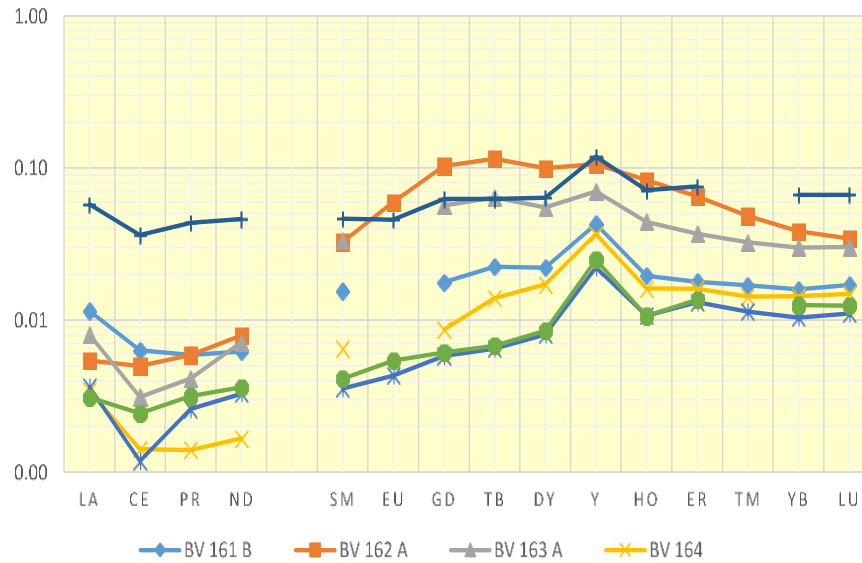


### ICP-MS 2018 : CORELATION WITH KNOWN MARINE LIMESTONES
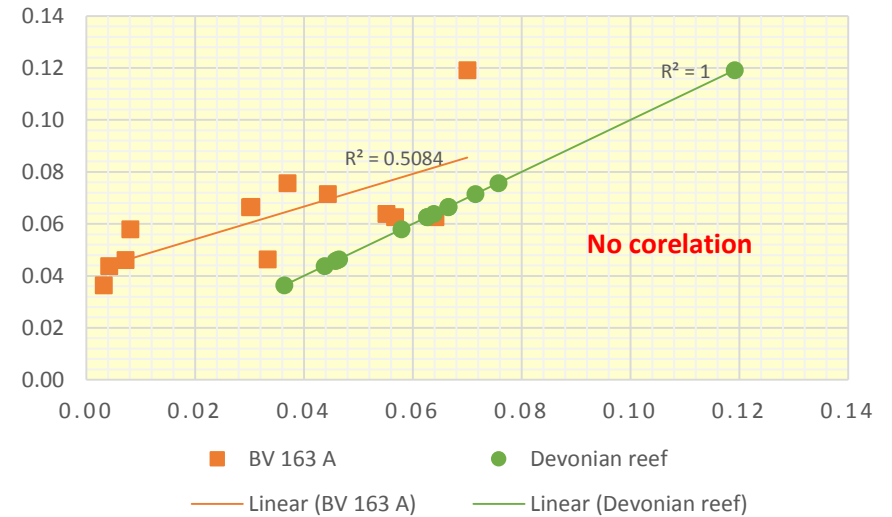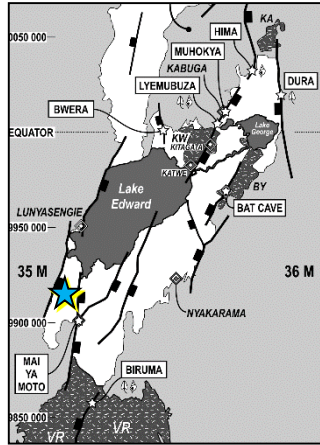
## Katanda Gorge
## Southern Lake Edward,
## Block V, DRC
## Sample V 164

**Samples V164:**

Hematite stained Travertine crumbled.

*( due to security and logistic conditions, the restricted time on the field didn't allow more field description)*
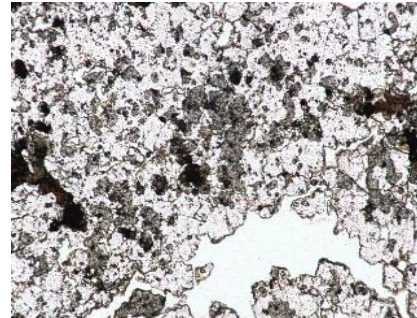




|  |  | BV 164 |  |
|---|---|---|---|
| >1.1 | La/La* | 3.464977 | YES |
| <0.8 | Ce/Ce* | 1.438689 | NO |
| >1.1 | Gd/Gd* | 0.765242 | NO |
| << 1 | Prn/Ybn | 0.097544 | YES |
| >40 | Y/Ho | 2.275306 | NO |

### BLOCK V (2018) & KNOWN MARINE LIMESTONE



Legend: BV 161 B, BV 162 A, BV 163 A, BV 164, M.Sea Water, Holocene M, Devonian reef

### ICP-MS 2018 : CORELATION WITH KNOWN MARINE LIMESTONES



R² = 0.9129  R² = 1

**Good correlation**

Legend: BV 164, Devonian reef, Linear (BV 164), Linear (Devonian reef)
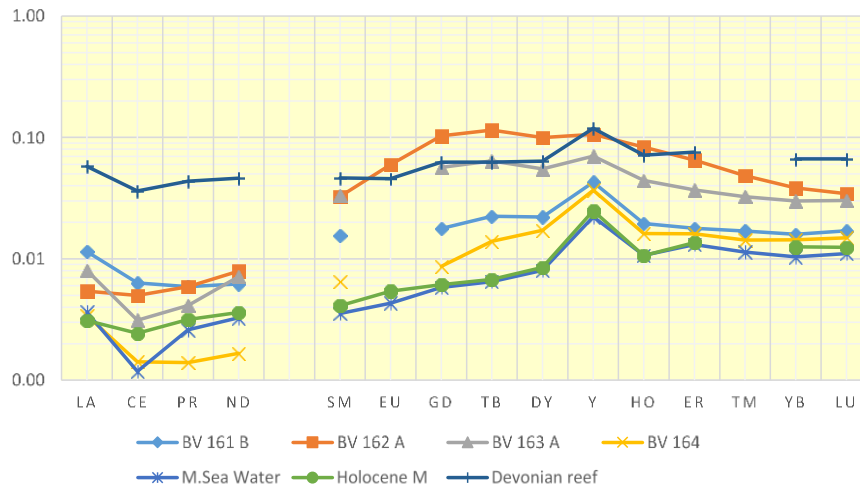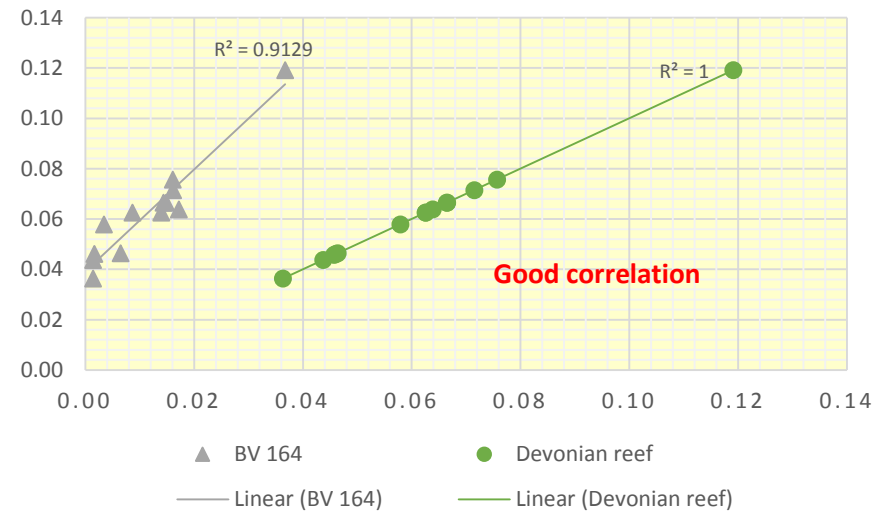
From these results here above it is clear that the 2018 ICP-MS provides some more evidence of geochemistry origin for different Carbonates outcropping in the DR Congo side of Albert Graben, EARS. They have demonstrated that:

- BV344, BV 352,BV 356, BV 363, BV 364, BV 385, drilled respectively through their light carbonates minerals avoiding the visible rootlets, branches or plant tubes, gave a typical Carbonatites signature with very good correlation coefficient R²> 0.90 with FP#3. ( Figures VII.35 and VII.36) No Marine limestones criteria matching. These basic findings are consistent with this research objectives showing that there is involvement of Carbonatites emerging from depth to the subsurface through groundwaters;

- BV150, BV 161, and BV 164, drilled through the carbonates porosity filled textures avoiding the black stained lining in white vugs, these samples ICP-MS results revealed a Marine limestones spectral signatures interesting facts. (Figures VII.44 and VII.45) No correlation with FP#3 has been scientifically established while a matching has been found with the Marine Limestones Balz paper criteria. This result demonstrates another further evidence of underneath Marine limestone deposit involvement for the origin of the carbonates in this Travertine outcrop;

- BV 149, BV 153, BV 162, and BV 163, have been drilled as above through the carbonates porosity filled textures avoiding the black stained lining in white vugs, these samples ICP-MS results revealed a kind of weird spectral signatures different from typical Carbonatites or Marine limestones. No to Moderate correlation with FP#3 and No to moderately matching with Balz paper criteria. (Figures VI. 44 and VI.45)These results demonstrate that a kind of hybrid source of carbonates does exist within the Rift basin. This hybrid source seems to be a mixture of Carbonatites and Marine limestones sources.

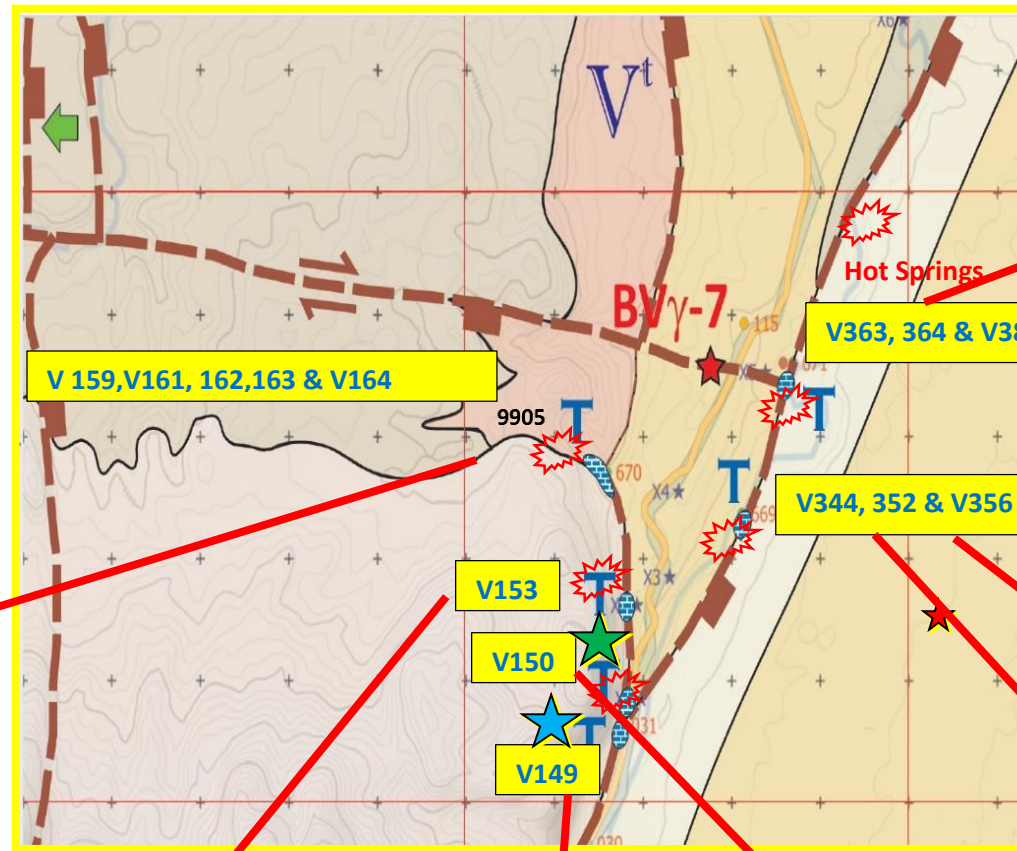The ICP-MS results obtained for each sample analysed in the present Msc research study revealed 3 sources of Bicarbonates in the EARS Travertines which have been grouped per field locations as below:

| *Definite presence of Marine Limestones at depth at:* | | *Definite presence of Carbonatites at depth at:* | |
|---|---|---|---|
| Mai ya Moto hot springs | (Bloc V, DRC) | Biruma quarry | (Bloc V, DRC) |
| Katanda gorge | (Bloc V, DRC) | Mai ya Moto springs | (Bloc V, DRC) |
| Lyemubuza quarry | (EA4A, Uganda) | Mabenga springs | (Bloc V, DRC) |
| Muhokya | (EA4A, Uganda) | Vitshumbi fault scarp | (Bloc V, DRC) |
| Okumu | (EA1, Uganda) | Bat cave | (EA4B, Uganda) |
| | | Bwera | (EA4A, Uganda) |
| | | Hima | (EA4A, Uganda) |

**Definite presence of hybrid signature**
**At depth at:**
**Bwera, Dura and Muhokiya (Uganda)**
**Mai ya Moto, Katanda and Biruma (DR CONGO)**

Consequently to this above field location sorting, all of this allowed to update the Travertines occurrence map in the Albertine Graben as illustrated in the Figure VII.1 below:
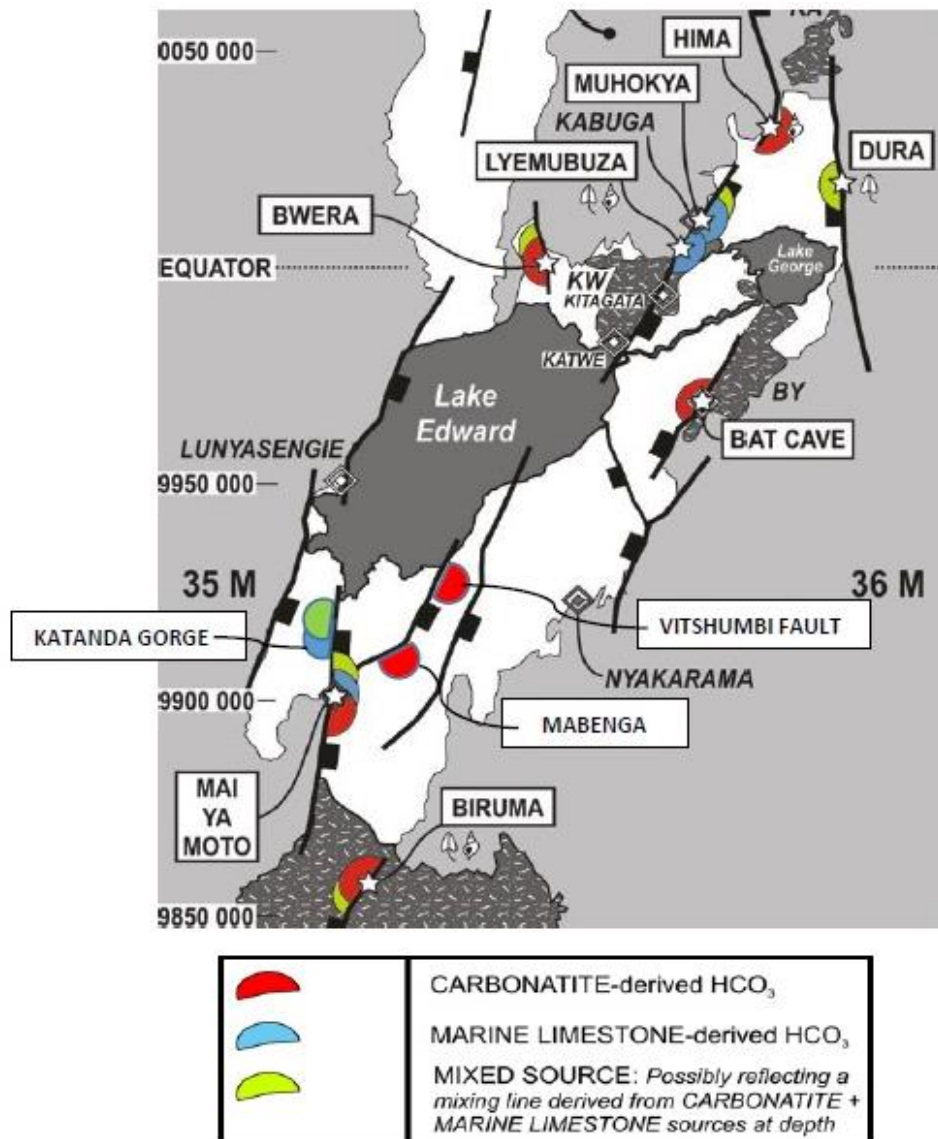


*Figure VII. 1: Travertine ICP-MS results Map of Albertine Rift basin*

Combining all the results discussions and interpretations with some geologic correlations and considerations allow to the assay of overlapping different analysis results and obtain the helpful general framework of the geologic theory, field evidences, microscopy facts, and geochemical laboratory results for answering the query about the geochemical origins of Travertines in the Eastern Africa Rift System and confirm this Msc Research study hypothesis.

The Figure VII.2 below illustrate a correlation chart assay trying to compare the Travertine ICP-MS results with the Carbon and Oxygen stable isotopes results. It allow to have a general view of the ratio between Travertines from Carbonatites sources marked in red and those from Marine limestones marked in blue.

Travertines in the center of the graph represent the intermediate geochemistry source.
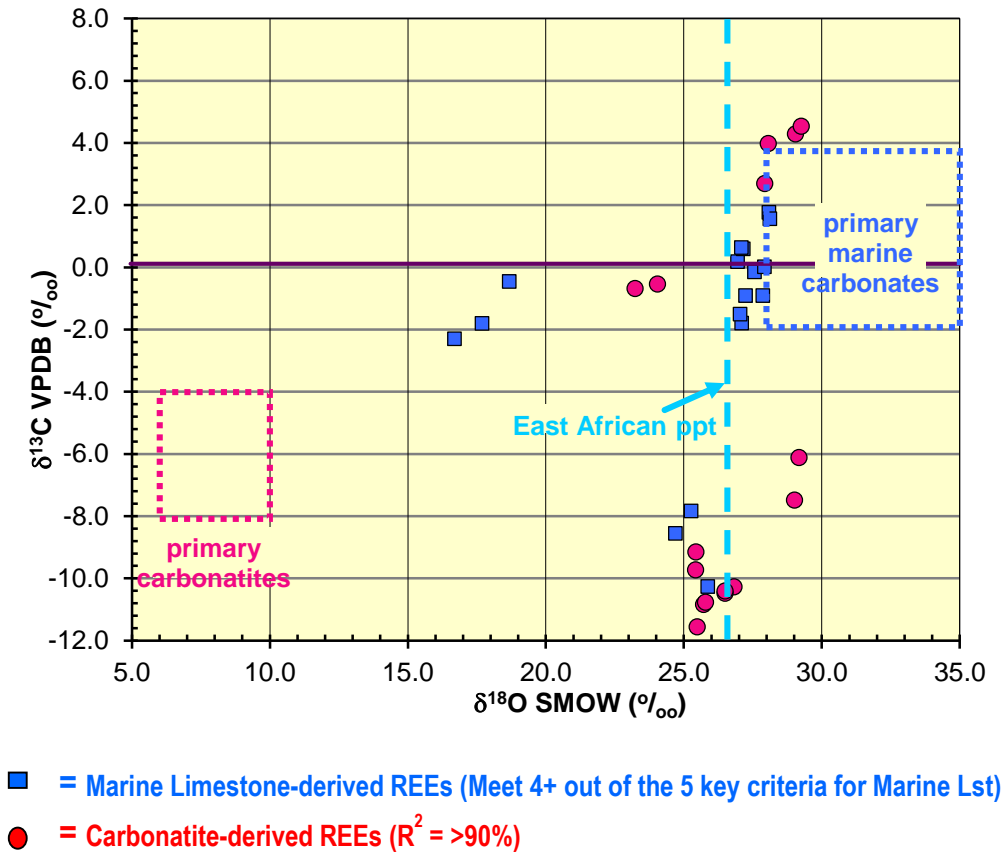


Figure VII. 2:    Travertine ICP-MS results Vs Carbon and Oxygen stable isotopes results.

The figure VII.2 above, show the relative abundance discrimination of Carbonatites and Marines limestones based on their respective values of Oxygen (SNOW) in x axis, and Carbon (PDB) in y axis.

We can interpret from this above Chart that no apparent correlation seems to be between REE carbonatite signature and Marine limestone isotopic composition. This make them enough far away results to be considered like the two end-members of the EARS Travertines geochemical origin.  This figure suggests also that no apparent correlation seems to be between REE marine limestones signature and Carbonatites isotopic composition.

Most of REE signature seems to be derived from carbonate at depth, but the typical Travertine isotopic signature is acquired during surface fractionation processes in the hot spring pool.

Most of the REE signature derived from marine limestones at depth, but the Travertines isotopic signature is progressively reduced during geothermal waters fractionation processes upraising them at the surface.

The chart in the above figure allow also the hybrid isotopic signature to be considered like intermediate source between the two Carbonatites and marines limestones end-members of the geochemical origins of EARS Travertines.

*Chapter 7 Conclusion*

*The field investigations and descriptions for Travertines samples collection, their microscopy observations and petrographic descriptions merged with all geochemistry results provided the scientific facts and geological evidences used to interpret and document this chapter.*

*All the above Travertines results have been respectively discussed in detail regarding their:*

- *Location map in the field;*
- *Sample photo in the field;*
- *Field description (sample and outcrop environment);*
- *Sample thin section photo in microscopic sizes;*
- *ICP-MS spectral signatures charts and marine limestones Balz's criteria check boxes;*

*The conclusive thoughts and venues summarized in the next Chapter titled Conclusion, are based on geologic evidences and scientific facts discussed in details throughout all the previous Chapters.*

*They provided a high level of confidence to give the geologic answer of the geochemical origin of the Travertines samples found in outcrops throughout the Eastern Africa Rift System, then help to write down this Msc research study conclusion and give a range of strong recommendations for further improvements in the actual knowledge of the entire rift and its implications for the Oil exploration industry.*

# CHAPTER 8: CONCLUSIONS

This MSc research study has demonstrated the success of the methodology in achieving its objectives. The methodology began with a literature review to document a proper field campaign for sample collections and documentation. After field considerations and macroscopic observations, a detailed microscopy was necessary to determine the appropriate carbonate textures, structures and/or fabrics to run the geochemical analysis using carbon, oxygen and strontium isotopes ratios. The use of GC-GCMS, both Ce and La anomalies ICP-MS combined with Y/Ho ratios helped to find out the most plausible origin of the bicarbonates contained in the EARS travertines samples found in outcrops around faulting lined hot springs in the basin boundaries.

The detailed review of previous literature revealed that there are no Travertines outcrops signalled in the whole classical siliclastic rift fill sediment deposited in the EARS. These old studies indicate most of the oldest geologic units lying within sediments are close to the rift shoulders while the youngest are comprised of sediments laying in the middle basin fill closer to the present-day sediment filling. Moreover, these publications document that all the EARS geologic units have no clear bounding surfaces defined to be correlated laterally with enough degree of certainty and confidence. According to earlier literature, the EARS is mostly dominated by both fluvial-alluvial distributary fan packages and lacustrine depositional environment. The described lacustrine deposits are selectively located within the centre basin fill sediments while the observed alluvial-fluvial fan packages are mainly encountered and located closer to the rift shoulders. However, no literature has mentioned the existence and field location of any Travertines outcrops in the EARS.

The evidence of Travertines spring outcrops discovered in the EARS siliclastic basin, was the main reason for undertaking detailed field trips in the region. The above-mentioned literature review provided a good tool for planning several site visits to find, describe and collect the famous Travertines outcrops in the EARS. The gamma ray values recorded in some of the EARS cliffs in DRC recommended using the Th/U ratios as both good indicators of sedimentary processes and a tool for the recognition of their geochemical facies. They suggested also separately using the Th/K log sharpness to define the Cretaceous/Permian boundary and the Th/U log sharpness as an excellent indicator of transgression/regression contrasting the marine upper cretaceous rocks and the non-marine to transitional rocks of the lower cretaceous. The macroscopic field observations demonstrated the famous EARS Travertines observed in hot spring outcrops have been formed in clear, warm, near surface, shallow marine waters in palaeo environments such as deltas and/or estuaries where organic filling is caused by the precipitation of calcium carbonate from lake or ocean water accumulation of shell, coral, algal, and faecal debris within their visible structures, textures and/or fabrics.

The microscopic observations of the EARS Travertines structures, textures and or fabrics have revealed their originate calcium carbonate from various precipitation processes in a variety of temperatures, palaeo environments, deposit conditions and palaeo climates.

The petrography work done in this Msc research study has compared the EARS travertines thin section microscopic observations with the main petrographic specifications of referenced Fort Portal, Mandawa Basin and Devonian Reef. It is observed in the microscopic size that the Mandawa carbonates sediments displayed in the microscope with enough petrographic similarities to EARS Travertines samples P12, LE 24, LE 26, LE 28, V 19 found with marine limestones spectral signature within their related structures, textures and/or fabrics.

The C/O isotopes ratio experiments run through this study were convenient to define the palaeo temperatures at the time of deposition. Once combined with IRMS results on EARS Travertines samples, they suggest the three Travertines follow palaeo environments:

- Primary marine limestones in Lyemubuza, Muhokiya, Duma, Hira localities in Uganda where carbon dioxide outgassing evaporation removes C and O isotopes;
- Primary carbonatite lavas in Mayi ya Moto and Biruma localities in DRC;
- Hybrid results mixing both above palaeo environments in Bat Cave, Okumu and Bwera localities in Uganda where strong carbon plants soil zone a CO2 contribution.

In others terms, these above palaeo environment temperature of EARS carbonates C/O ratios reveal three (3) main groups made of cold marine limestones (eg. Tufa, Travertines), hot Carbonatites (eg. Travertines) and clearly a kind of intermediate mixed group considered like the hybrid one.

The strontium isotope ratios of selected EARS Travertines samples showed a very high range of strontium isotope ratios from 0.7068069 to 0.7482648. Sr Isotope Ratios within the seawater carbonate range may be Late Neoproterozoic, Late Permian or Late Jurassic in age.

However, only two values LE 41 and LE 42 (a, b) correspond with marine limestones dating from Jurassic to Permian. These samples are from Bwera and Dura, at the northern end of Lake Edward.

The GC / GCMS analysis results indicate that the pre-peak oil apparently generated from a marine shale source rock has migrated into the very porous EARS Travertines Lyemubuza outcrops. This is interpreted as the source rock type that would typically generate oils with the relict biomarker distributions seen in the EARS Travertines samples being from MARINE SHALES source. This is the scientific evidence the GC/GCMS analysis run by Dominion Ltd in 2011 proved the relict oil preserved in the Travertines cavities at Lyemubuza and the same one leaking to the surface on Lake Edward are from the same originate marine shale source rock.

The specific study of hydrothermal chemistry in the EARS helped to better understand the potential impact hydrothermal emissions have on the chemistry of the crossing geologic formations, and how this chemistry differs between the varied geologic units crossed through, during the uprising process to flush the geothermal waters out to the surface at hot springs pools. Hydrothermal fluid formed as circulating groundwaters are modified through interactions with heat and the earth's crust. These kinds of fluids may emanate back into underground water affected by geothermal gradient from the volcanic region of Nyragongo and Nyamulagira, the closest volcanoes to Biruma Travertines outcrops in the south east of the Albertine Graben.

The hydrothermal fluids encountered in the EARS are subdivided into two categories: the high-temperature or focused flow, and the low-temperature or diffuse flow.

The high-temperature fluids, generally > 100–150°C, have been described in the field as focused jets of water that have precipitated from the hydrothermal fluids themselves due to the mixing of hydrothermal fluids with carbonatite lavas. The low-temperature fluids, generally < 75°C have been observed in the field as the flows of water that have precipitated from the hydrothermal fluids themselves when they encountered some possible cold marine limestones.

The use of ICP-MS as per Balz Kamber's (2004) procedures for successful quantification of REE concentrations in EARS Travertines samples by ICP-MS. Balz Kamber (2004) suggested the best procedures to reliably determine REE abundances in carbonate waters with REE high concentrations with more or less accurate result confidence.

The MUQ (Queensland alluvial sediment average representing a compilation of the sedimentary composition of 25 Queensland rivers (Kamber et al., 2005b)) normalized results obtained from experiments done on diluted natural rock standard correlate favourably with previously published results on fresh water and Devonian reefs spectral signatures. (Lawrence and Kamber, 2006)

The differences in the REE pattern of the respective carbonates textures, structures and /or fabrics as analysed by ICP-MS, are explained by differences in soil-type, lithology or different weather patterns and are likely the result of differing deposit conditions (resulting in a lowering of pH).

The REE concentrations in EARS palaeo deposits from geothermal water flux have been discussed in terms of their carbonate sourcing and the major solute chemistry employed to model the REE speciation according to Balz Kamber procedures.

These procedures tested also the robustness of the relative REE anomalies calculated to MUQ by normalising with data interpretation provided by Kamber et al (2004).

The choice of normalising REE concentrations to MUQ has a greater improvement in the final interpretation of the obtained results. The most important calculated anomalies are more specifically the Ce anomaly (0.727) which is normally (~0.93) if calculated from Pr and Nd.

Whilst the magnitude of the La, Ce and Gd anomalies vary according to the choice of the normaliser, the other REE concentrations themselves keep the same pattern. The biggest deviations are found when comparing MUQ-normalised anomalies with those calculated using PAAS normalisation, probably due to slightly inaccurate PAAS Pr values, see (Kamber et al., 2005a) for a full discussion.

The key point to retain from the EARS Travertines ICP-MS results is that the anomalies are real, and not the result of inappropriate normalisation. However, we still observe variability in REE anomalies when PAAS normalising. Therefore, if the ICP-MS experiment consistently uses the same normalising MUQ-normalised anomalies values for all samples, the relative differences in the REE anomalies indicate that these anomalies have the potential to serve as provenance tracers.

In order to assess the geochemical origin of the carbonate REE fingerprint in the EARS Travertines, an extensive REE dataset of concentration values from Fort Portal Carbonatites lavas, Devonian reef marine limestones normalized from South East Queensland Carbonates were developed using an ICP-MS technique capable of directly quantifying all 15 naturally occurring heavy and light detectable REE.

This study demonstrates a remarkable variability in REE abundance within the EARS Travertines samples from a relatively huge region. This suggests that REE have the potential to be used as a source of geochemical fingerprint.

Furthermore, the results have proven that certain typical 'marine' REE features appear to develop in essentially carbonate layers beneath the Cenozoic basin, prior to entering the surface outlet boiling springs. According to (Kamber and Webb, 2001; (Van Kranendonk et al., 2003), 2004; Nothdurft et al., 2004) the geochemical origin of the marine dissolved REE abundance has attracted renewed attention as hydrogenous sediments (e.g. cherts, iron oxide, carbonate) appear to preserve marine REE features as far back as 3.71 Ga.

Combining all the above literature review, field geology, microscopy observations and geochemical analysis (Stables C and O isotopes, Sr isotopic ratios, CG/CGMS, ICP-MS) from the EARS study area, the following conclusions can be deduced:

This project succeeds at answering the geologic question to determine the origin of the Travertine limestones in the Albertine Graben in EARS by mainly analysing their respective stable isotopic and elemental geochemistry. This answer is that there is enough scientific evidence of three (3) geochemical sources of bicarbonate precipitating in the EARS Travertines.

The first of these geochemical sources is the igneous Carbonatites lavas or intrusions, either present at depth as buried carbonatite lavas, or as intrusives within the rift. Rare carbonatite lavas are indeed present at the surface at a single locality in the Albertine rift to the east of the Ruwenzori Mountains, between Lakes Albert and Edward. However, this result greatly increases the geographical extent of carbonatite within the rift than previously thought.

The second geochemical source is a marine limestone, which suggests that it is part of a pre-Tertiary rift unit; likely to be either a failed Karoo-Mesozoic rift package, or part of the 'basement' Proterozoic (possibly Neoproterozoic 'Schisto-Calcaire'). This is more intriguing, as the current EARS contains no marine sediments and it is still essentially a rift in progress. If any limestones were to occur, they would eventually be freshwater lacustrine units because there is no sea story in the region.

However, no fresh water lacustrine spectral signature has been found in the EARS REE plots which rather indicate the presence of a marine limestone source for bicarbonate at depth.

The third geochemical source does exist and seems to be a 'half-way house' mixture between these two previous geochemical sources.

Figure VIII.1 below illustrates the predictive cross-section (not to scale) describing the hypothetical configuration of the Bloc V DRC with the potential hydrothermal fluids up movement through both Eastern and Western bounding faults:
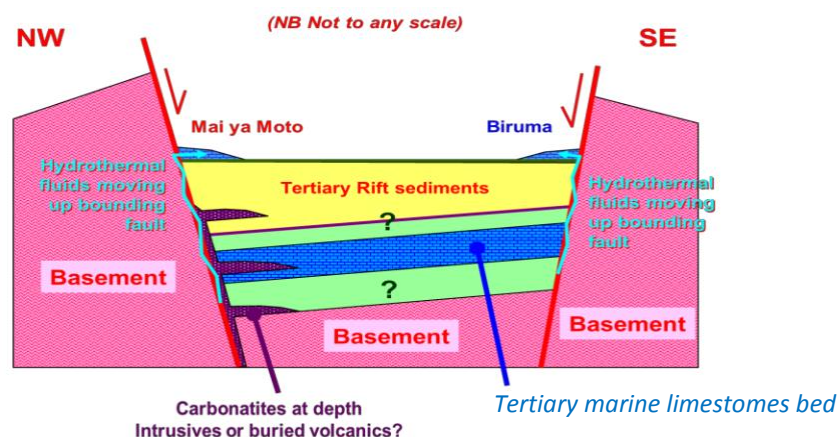


*Figure VIII.1: Schematical hypothetical cross section of Bloc V, DRC. (Nicholas, 2013)*

In summary, the curiosity created by the unexpected Travertine's occurrences found within the classical siliclastic EARS sediment fill type, has pushed this present research study to successfully trace back their geological and geochemistry origins according to their spatial extension in the regional level. In order to reach each of this study objectives (detailed in the Introduction Chapter one), the literature review (presented in the Literature Review Chapter two) allowed reviewing the existing documentation related to any Travertine's previous publications. The appropriate methodologies for field sample collection, petrography and geochemical analysis to undertake have been detailed step by step (in the methodology Chapter three). The EARS field investigation details (summarized in Field Trips Chapter four) allowed to macroscopically describe document and collect the Travertines samples for geochemistry analysis purposes.

In order to follow the intra- and inter- sites geochemistry variability REE+Y results, a detailed microscopic samples observation have been undertaken on all the collected Travertine's petrography. These sample's respective micro textures, structures and /or fabrics have been detailed (in Geochemical analysis Chapter five) prior to drill through them. These residual powders obtained for each sample drilling, have been fully dissolved and digested in $HNO_3$ then run through the ICP-MS geochemical process. All the results obtained have been presented (in Results Chapter Six) and their related discussions mainly based on various additional contributions varying from recent publications to our own interpretation have been placed in evidence (in Discussion Chapter Seven).

In conclusion from all above sets of recorded information, and consequently to the fruitful discussion here above, it is absolutely evident that there is no more doubt about the definite presence of marine limestone REE clear signatures + increase of Yttrium (within the Bloc V) as the figure below points the same pattern it:



BLOCK V 2014 SAMPLES & KNOWN MARINE LIMESTONE REE PATTERNS
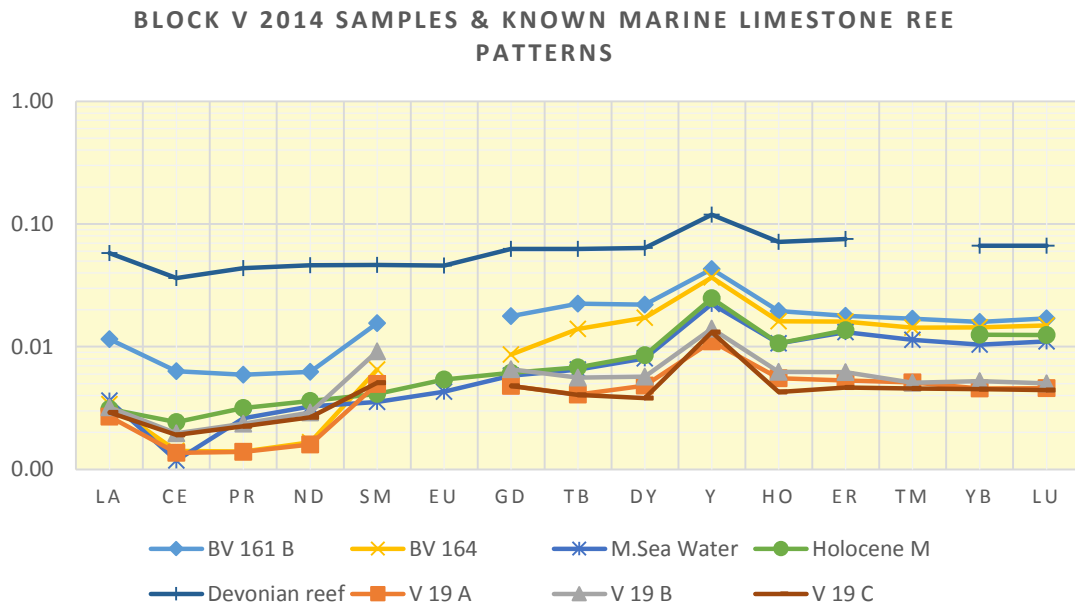
This evident presence is also pointed out in the following graph below indicating that these Bloc V Travertine's samples found with Marine limestone REE signatures are greatly correlating with the Devonian reef with a correlation coefficient above $R^2 \geq 75\%$.



BLOC V 2014 SAMPLES: CORELATION WITH KNOWN MARINE LIMESTONES
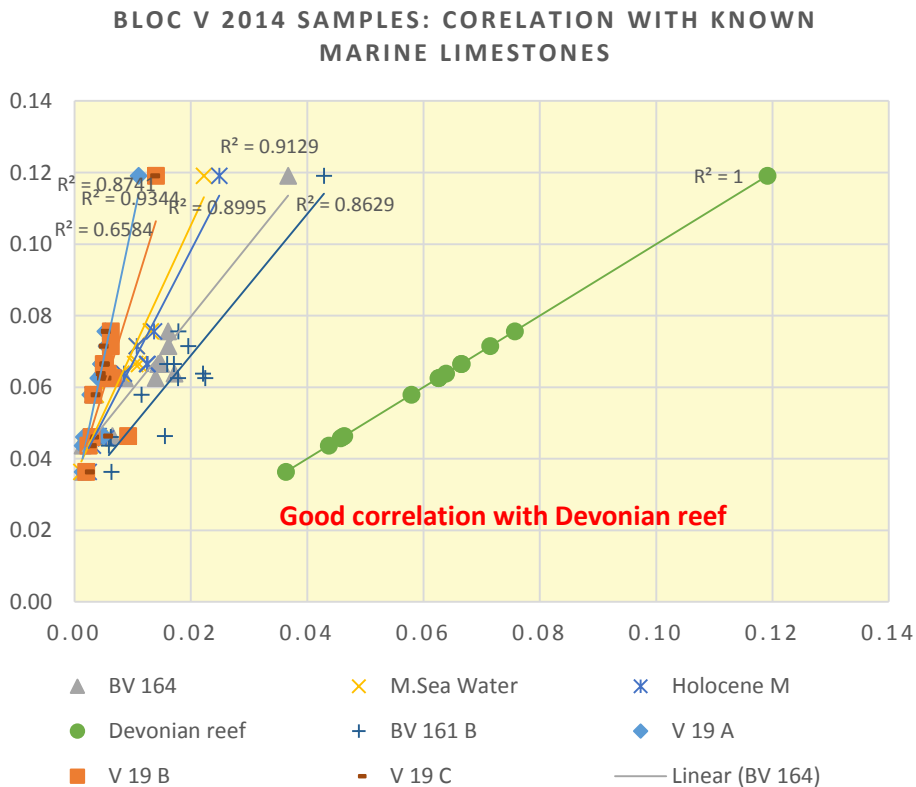
The presence of these carbonates sourcing the deposit of Marine Travertines in Mayi ya Moto hot springs and Katanda gorge (DRC) and Lyemubuza Quarry (Uganda) with matching REE+Y patterns with low Cerium and high Yttrium concentrations confirms the   geological hypothesis that a potential pre-tertiary marine limestone bedrock could exist beneath the Cenozoic EARS basins through which, geothermal waters are passing and obtaining their spectral signature observed and interpreted from the ICP-MS results here compared in the figures below:

### BLOC V 2014 MARINE LIMESTONES & LYEMUBUZA REE SIGNATURES
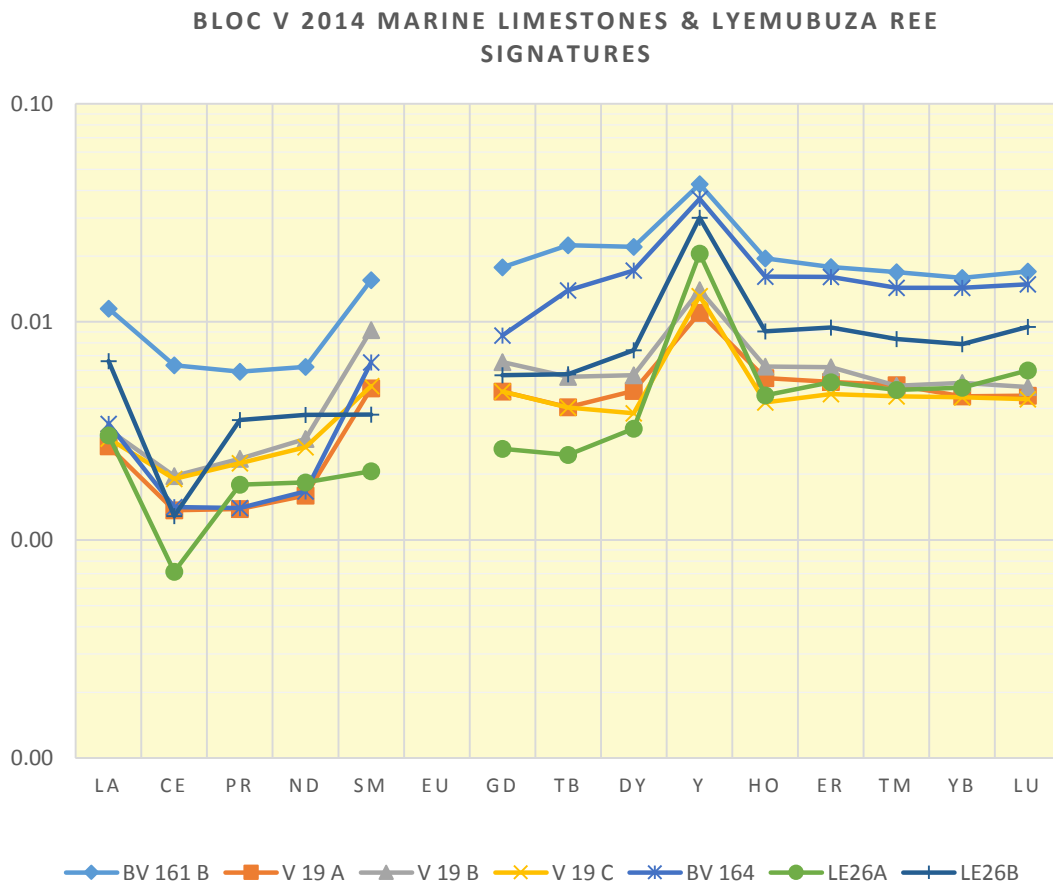


This potential pre-tertiary marine bedrock evidence has been possible through geochemistry results on carbonates structures, textures or fabrics from EARS Travertines samples V 19, BV 161 and BV 164 respectively in Mayi ya Moto hot Springs and Katanda Gorge along the western bounding fault (DRC side of the basin) and sample LE 26 found with living oil relics in Lyemubuza quarry along the eastern bounding fault (Ugandan side of the basin).

However, further field investigations are recommended to deepen these marine limestones' involvement. More samples should be collected in the basin margins and more geochemical analysis are needed not only to confirm these findings but also to define their spatial extension within the EARS basin. Exploration drillings in the linear axis (SW-NE) between Mayi ya Moto and Lyemubuza (where Oil relic have been found in cavities) would be better to confirm more evidences of pre-tertiary carbonate bedrock in cuttings.

The correlation coefficients of all MUQ normalized values have clearly discriminated the Marine limestone source of bicarbonate and excluded the possible correlation with either the Permian Karoo ( Cenomian limestones) or the west Congo   Schisto-Calcaire (Neoproterozoic stromatolites). The figures Vi.42,VI.43 and VI.44 in pages 156,157 and 158 detail more about this no correlation discrimination with a coefficient $R^2 \ll 75\%$..

Evidently, the correlation coefficient between Bloc V (V19, BV 161 and BV 164) and Lyemubuza Travertines (LE 26) as shown in the figure below, reveals a good correlation above $R^2 \geq 75\%$.but also to define their spatial extension within the EARS basin.



BLOC V 2914 MARINE LIMESTONES CORELATION WITH LYEMUBUZA  SAMPLE
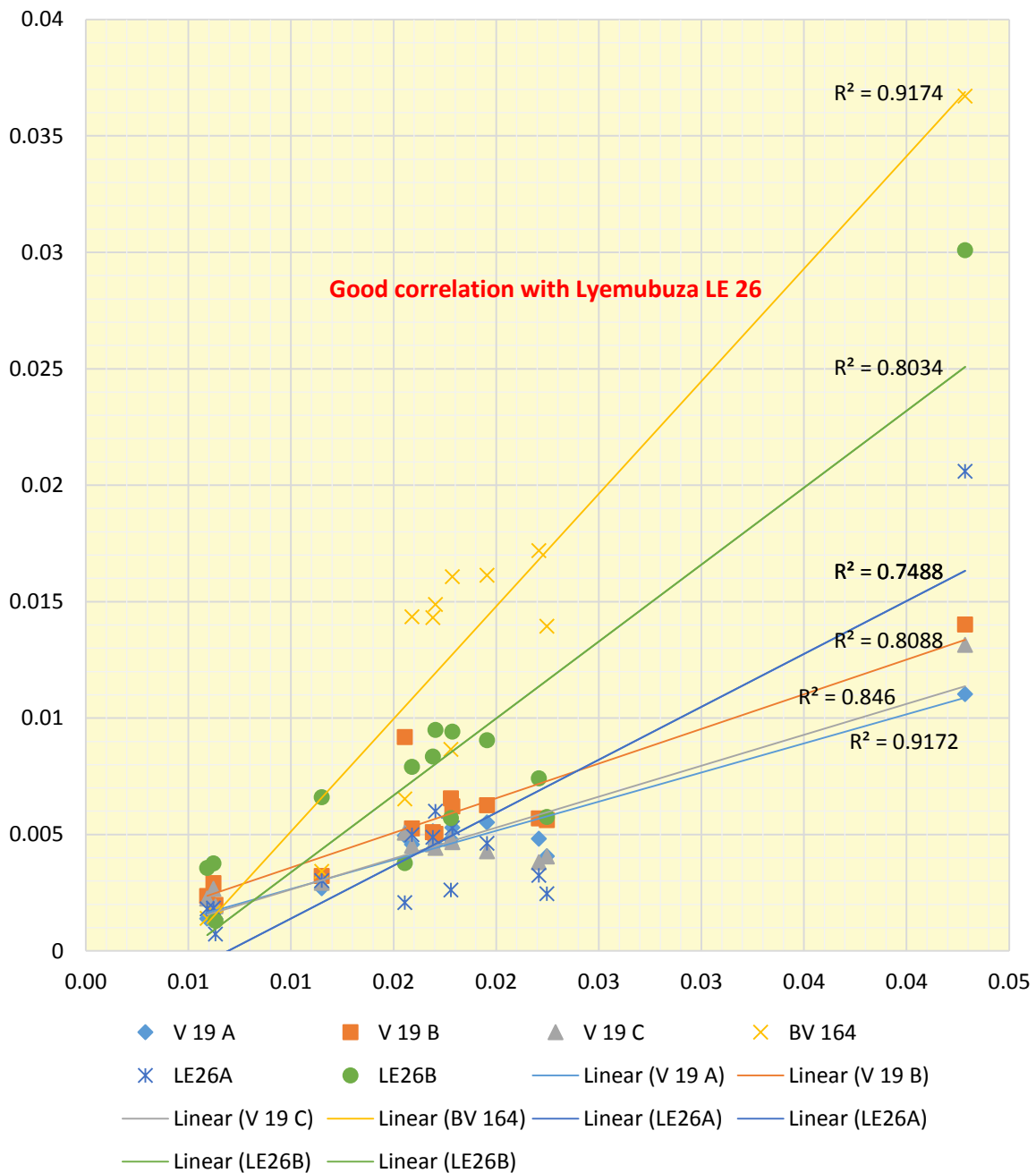
The map in Figure VIII.2 below, which illustrates the actual locations of the EARS Travertine samples in the Albertine Graben according to their respective geochemical origin, has updated the Introduction Map in Figure I.1 in page15, published in 2013 by Dr Chris Nicholas. (Nicholas, 2013). The Marine limestones considered of cold geochemical origin are marked from the Map legend in blue, while the Carbonatites considered of hot geochemical origin are in red and the hybrid geochemical origin or mixed geochemistry in green light.
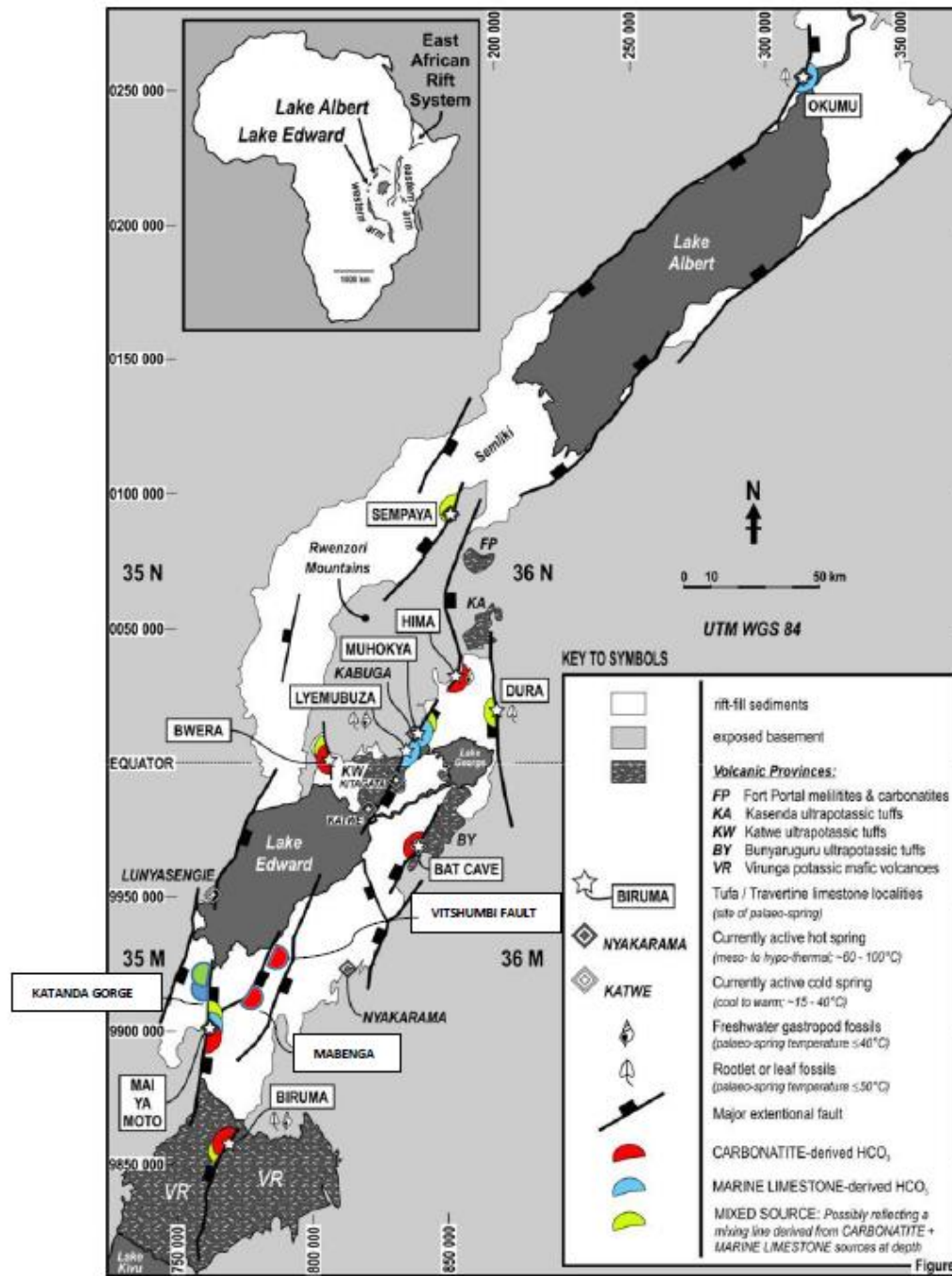


*Figure VIII.2 Updated Map of Travertine geochemical origin localisation in the Albertine Graben (Kezir, Nicholas, 2020)*

# RECOMMENDATIONS FOR PETROLEUM EXPLORATION IN THE LAKE EDWARD BASIN

Thus, the marine limestones must have been deposited in an older sedimentary basin that lies buried beneath the present Albertine Rift. The presence of such an older basin greatly multiplies the petroleum exploration opportunities in this region, with the possibility of potential oil source rocks, reservoirs and traps below the Albertine Rift. It also raises the possibility that marine shale source rocks are present beneath EARS basins, generating oil to migrate into it, thus delivering a higher quality light sweet crude than waxier, lacustrine sources.

This part of the rift is currently undergoing active petroleum exploration and the presence of either extensive igneous intrusives (Carbonatites "hot" origin), or Cretaceous pre-rift sediments (marine limestones "cold" origin) would have a huge impact on exploration (for very different reasons).

The "hot" origin of Travertine Carbonatites is helping the Oil exploration industry to derisk technically and financially their exploration operations by avoiding the surroundings of Carbonatites signatures locations in the basin because of the risk of high thermal gradient level supposed to have burned all the Oil prone out of the Oil window to the gas prone side.

The only previously known example of carbonatite at the surface is at Fort Portal, east of the Ruwenzori Mountains; the presence of several examples of Carbonatites at depth clearly has important implications for petroleum exploration:
   a. Avoid these 'hot spots' as any pre- carbonatite emplacement petroleum will be over-matured;
   b. Alert that they may be encountered on seismic surveys both onshore and offshore along major rift faults.

However, the "cold" origin of Travertine marine limestones is helping the Oil exploration to focus on a new opportunity to think and explore for the Oil potential of a probable Cenozoic basin under the siliclastic rift sediments in the Eastern Africa Rift System. This is something which will be very enthusiastic topic needing to be dug deeply beyond this present MSc. Research project from which the obtained results may be a good scientific article to publish.

As no known Marine Limestones are supposed to be present in the Tertiary Rift, the carbonate REE+Y signature must probably come from a limestone unit in the pre-rift section considering the following new knowledges:

- The REE normalized values correlates neither with Karoo-Mesozoic nor with Late Neoproterozoic 'Schisto-Calcaire'. The fact is clearly that it is definitively a marine limestone evident source of bicarbonate which raises the possibility of a deeper, 'pre-tertiary rift' petroleum play system.
- Given the asymmetry of the Lake Edward basin, this marine limestone unit may have a greater relict thickness on the western side of the basin – note on the maps that the presence of a marine limestone was always recorded in samples lying on a western bounding fault in the sub-basins.

# REFERENCES

BABECHUK, M. G., KAMBER, B. S., GREIG, A., CANIL, D. & KODOLÁNYI, J. 2010. The behaviour of tungsten during mantle melting revisited with implications for planetary differentiation time scales. *Geochimica et Cosmochimica Acta,* 74**,** 1448-1470.

BAUER, F., GLASMACHER, U., RING, U., SCHUMANN, A. & NAGUDI, B. 2010. Thermal and exhumation history of the central Rwenzori Mountains, Western Rift of the East African Rift system, Uganda. *International Journal of Earth Sciences,* 99**,** 1575-1597.

BELLANCA, A., MASETTI, D. & NERI, R. 1997. Rare earth elements in limestone/marlstone couplets from the Albian-Cenomanian Cismon section (Venetian region, northern Italy): assessing REE sensitivity to environmental changes. *Chemical geology,* 141**,** 141-152.

BELLON, H. & POUCLET, A. 1980. Datations K-Ar de quelques laves du Rift-Ouest de l'Afrique Centrale; implications sur l'évolution magmatique et structurale. *Geologische Rundschau,* 69**,** 49-62.

BEUNING, K. R. & RUSSELL, J. M. 2004. Vegetation and sedimentation in the Lake Edward Basin, Uganda–Congo during the late Pleistocene and early Holocene. *Journal of Paleolimnology,* 32**,** 1-18.

BOVEN, A., PASTEELS, P., PUNZALAN, L., YAMBA, T. & MUSISI, J. 1998. Quaternary perpotassic magmatism in Uganda (Toro-Ankole Volcanic Province): age assessment and significance for magmatic evolution along the East African Rift. *Journal of African Earth Sciences,* 26**,** 463-476.

BURKE, W., DENISON, R., HETHERINGTON, E., KOEPNICK, R., NELSON, H. & OTTO, J. 1982. Variation of seawater 87Sr/86Sr throughout Phanerozoic time. *Geology,* 10**,** 516-519.

BYAKAGABA, A. 1997. Report on the Geological mapping of the Lakes Edward-George Basin. *Report of the Department of Petroleum Exploration and Production***,** 1-55.

CHOROWICZ, J. 1990. Dynamics of the different basin-types in the East African Rift. *Journal of African Earth Sciences (and the Middle East),* 10**,** 271-282.

CHOROWICZ, J. 2005. The east African rift system. *Journal of African Earth Sciences,* 43**,** 379-410.

CORKERON, M., WEBB, G. E., MOULDS, J. & GREY, K. 2012. Discriminating stromatolite formation modes using rare earth element geochemistry: Trapping and binding versus in situ precipitation of stromatolites from the Neoproterozoic Bitter Springs Formation, Northern Territory, Australia. *Precambrian Research,* 212**,** 194-206.

CRAIG, H. 1953. The geochemistry of the stable carbon isotopes. *Geochimica et Cosmochimica Acta,* 3**,** 53-92.

CROSSLEY, R. 1984. Controls of sedimentation in the Malawi rift valley, central Africa. *Sedimentary Geology,* 40**,** 33-50.

DOORNKAMP, J. & TEMPLE, P. 1966. Surface, drainage and tectonic instability in part of southern Uganda. *The Geographical Journal,* 132**,** 238-252.

EBINGER, C. 1989. Tectonic development of the western branch of the East African rift system. *Geological Society of America Bulletin,* 101**,** 885-903.

EBY, G. N., LLOYD, F. E. & WOOLLEY, A. R. 2009. Geochemistry and petrogenesis of the Fort Portal, Uganda, extrusive carbonatite. *Lithos,* 113**,** 785-800.

EGGINS, S., WOODHEAD, J., KINSLEY, L., MORTIMER, G., SYLVESTER, P., MCCULLOCH, M., HERGT, J. & HANDLER, M. 1997. A simple method for the precise determination of≥ 40 trace elements in geological samples by ICPMS using enriched isotope internal standardisation. *Chemical Geology,* 134**,** 311-326.

FROSTICK, L. & REID, I. 1990. Structural control of sedimentation patterns and implication for the economic potential of the East African Rift basins. *Journal of African Earth Sciences (and the Middle East),* 10**,** 307-318.

HAYS, P. D. & GROSSMAN, E. L. 1991. Oxygen isotopes in meteoric calcite cements as indicators of continental paleoclimate. *Geology,* 19**,** 441-444.

HEPWORTH, J. & MACDONALD, R. 1966. Orogenic belts of the northern Uganda basement. *Nature,* 210**,** 726.

HILL, R. 2007. MAKING THIN SECTIONS BY HAND.

KAMBER, B. S., WEBB, G. E. & GALLAGHER, M. 2014. The rare earth element signal in Archaean microbial carbonate: information on ocean redox and biogenicity. *Journal of the Geological Society,* 171**,** 745-763.

KAMPUNZU, A., BONHOMME, M. & KANIKA, M. 1998. Geochronology of volcanic rocks and evolution of the Cenozoic Western Branch of the East African Rift System. *Journal of African Earth Sciences,* 26**,** 441-461.

KARP, T., SCHOLZ, C. A. & MCGLUE, M. M. 2012. Structure and stratigraphy of the Lake Albert Rift, East Africa: Observations from seismic reflection and gravity data.

KOEHN, D., AANYU, K., HAINES, S. & SACHAU, T. 2008. Rift nucleation, rift propagation and the creation of basement micro-plates within active rifts. *Tectonophysics,* 458**,** 105-116.

LÆRDAL, T., TALBOT, M. R. & RUSSELL, J. M. 2002. Late Quaternary Sedimentation and Climate in the Lakes Edward and George Area, Uganda—Congo. *The East African Great Lakes: Limnology, Palaeolimnology and Biodiversity.* Springer.

LAMBIASE, J. & BOSWORTH, W. 1995. Structural controls on sedimentation in continental rifts. *Geological Society, London, Special Publications,* 80**,** 117-144.

LE FOURNIER, J., CHOROWICZ, J., THOUIN, C., BALZER, F., CHENET, P.-Y., HENRIET, J.-P., MASSON, D., MONDEGUER, A., ROSENDAHL, B. & SPY-ANDERSON, F.-L. 1985. Le bassin du lac Tanganyika: évolution tectonique et sédimentaire. *Comptes rendus de l'Académie des sciences. Série 2, Mécanique, Physique, Chimie, Sciences de l'univers, Sciences de la Terre,* 301**,** 1053-1058.

LYNCH-STIEGLITZ, J., STOCKER, T. F., BROECKER, W. S. & FAIRBANKS, R. G. 1995. The influence of air-sea exchange on the isotopic composition of oceanic carbon: Observations and modeling. *Global Biogeochemical Cycles,* 9**,** 653-665.

MASTANDREA, A., BARCA, D., GUIDO, A., TOSTI, F. & RUSSO, F. 2010. Rare earth element signatures in the Messinian pre-evaporitic Calcare di Base formation (Northern Calabria, Italy): evidence of normal seawater deposition. *Carbonates and Evaporites,* 25**,** 133-143.

MCCABE, R. 2015. Inorganic Geochemistry of the South Eastern Tanzanian Sedimentary Basins.

MUSISI, J. 1991. *The neogene geology of the Lake George–Edward basin, Uganda.* PhD thesis.

NERBRÅTEN, K. B. 2014. *Petrology and sedimentary provenance of Mesozoic and Cenozoic sequences in the Mandawa basin.*

NICHOLAS, C. J. 2009. Summary technical evaluation of Exploration Area 4B, Ugandan Lake Edward.

NICHOLAS, C. J. 2017. Atlas of Fluvial, Deltaic, and Marginal Lacustrine Depositional Environments in Continental Rift Settings of the equatorial Tropics. *Avalonia Geosciences***,** 190.

NICHOLAS, C. J., NEWTH, I. R., ABEINOMUGISHA, D., TUMUSHABE, W. M. & TWINOMUJUNI, L. 2016. Geology and stratigraphy of the south-eastern Lake Edward basin (Petroleum Exploration Area 4B), Albertine Rift Valley, Uganda. *Journal of Maps,* 12**,** 237-248.

PAVLOVA, A. & PAPAZOVA, D. 2003. Oil-spill identification by gas chromatography-mass spectrometry. *Journal of chromatographic science,* 41**,** 271-273.

PICKFORD, M., SENUT, B. & HADOTO, D. P. M. 1993. *Geology and Palaeobiology of the Albertine Rift Valley, Uganda-Zaire: Geology*, Cifeg.

PLATZ, T., FOLEY, S. F. & ANDRÉ, L. 2004. Low-pressure fractionation of the Nyiragongo volcanic rocks, Virunga Province, DR Congo. *Journal of Volcanology and Geothermal research,* 136**,** 269-295.

RING, U. 2008. Extreme uplift of the Rwenzori Mountains in the East African Rift, Uganda: Structural framework and possible role of glaciations. *Tectonics,* 27.

ROSENTHAL, A., FOLEY, S., PEARSON, D. G., NOWELL, G. M. & TAPPE, S. 2009. Petrogenesis of strongly alkaline primitive volcanic rocks at the propagating tip of the western branch of the East African Rift. *Earth and Planetary Science Letters,* 284**,** 236-248.

RUBONDO, E. 2005. The hydrocarbon potential of the Albertine Graben, Uganda.**,** 22.

RUSSELL, J. M. & JOHNSON, T. C. 2005. A high-resolution geochemical record from Lake Edward, Uganda Congo and the timing and causes of tropical African drought during the late Holocene. *Quaternary Science Reviews,* 24**,** 1375-1389.

RUSSELL, J. M., JOHNSON, T. C., KELTS, K. R., LÆRDAL, T. & TALBOT, M. R. 2003. An 11 000-year lithostratigraphic and paleohydrologic record from equatorial Africa: Lake Edward, Uganda–Congo. *Palaeogeography, Palaeoclimatology, Palaeoecology,* 193**,** 25-49.

SOCO 2010. Partner Technical Meeting Report. 69.

STOPPA, F. & SCHIAZZA, M. 2013. An overview of monogenetic carbonatitic magmatism from Uganda, Italy, China and Spain: volcanologic and geochemical features. *Journal of South American Earth Sciences,* 41**,** 140-159.

TIERCELIN, J.-J., SOREGHAN, M., COHEN, A. S., LEZZAR, K.-E. & BOUROULLEC, J.-L. 1992. Sedimentation in large rift lakes: example from the Middle Pleistocene—Modern deposits of the Tanganyika Trough, East African Rift System. *Bulletin des Centres de Recherches Exploration-Production Elf-Aquitaine,* 16**,** 83-111.

TUMUSHABE, W. M. 2012. *Sedimentary Response to Coupled East Africa Climate Change and Active Rifting in the Lake Edward Basin, Albertine Rift, Uganda.* Trinity College Dublin.

UPCOTT, N., MUKASA, R., EBINGER, C. & KARNER, G. 1996. Along-axis segmentation and isostasy in the Western rift, East Africa. *Journal of Geophysical Research: Solid Earth,* 101**,** 3247-3268.

VEIZER, J., GODDERIS, Y. & FRANÇOIS, L. M. 2000. Evidence for decoupling of atmospheric CO 2 and global climate during the Phanerozoic eon. *Nature,* 408**,** 698.

VERSFELT, J. & ROSENDAHL, B. 1989. Relationships between pre-rift structure and rift architecture in Lakes Tanganyika and Malawi, East Africa. *Nature,* 337**,** 354.

VINER, A. & SMITH, I. 1973. Geographical, historical and physical aspects of Lake George. *Proceedings of the Royal Society of London B: Biological Sciences,* 184**,** 235-270.

WALLNER, H. & SCHMELING, H. 2010. Rift induced delamination of mantle lithosphere and crustal uplift: a new mechanism for explaining Rwenzori Mountains' extreme elevation? *International Journal of Earth Sciences,* 99**,** 1511-1524.

WIERZBOWSKI, H. Strontium isotope composition of sedimentary rocks and its application to chemostratigraphy and palaeoenvironmental reconstructions. Annales Universitatis Mariae Curie-Sklodowska, 2013. De Gruyter Open Sp. z oo, 23.

WOLF, R. E. 2005. What is ICP-MS? and more importantly, what can it do. *US Geological Survey,* 7.

**Appendix 1: Samples preparation lab notes**

Museum Building, TCD
9th July 2016
**SAMPLES PROPOSED FOR THE FIRST BATCH OF 2016 ICP-MS ANALYSIS.**

The Tufa / Travertines samples shipped to TCD for lab analysis have been collected during fields works in ten (10) palaeo-spring sites in the Albertine Graben, East African Rift system were no previous literatures have mentioned their presence so far. However, successive field works and some of exploration drillings have reported their presence in the Albertine Basin.

The ICP-MS method and instrument which rapidly become established as a preferred way for the analysis of trace elements in geological samples aims to find out the detailed geochemical origin of these "weird" limestones which are not theorically supposed to outcrop or to meet a drilling there. The hypothetic origins could be Carbonatites lavas (hot origin) lacustrine (palaeo-lake) or fluvial (palaeo river) (cold) origin.

***Sixteen (16) Tufas / Travertines samples*** drilled exactly from the same drilling sites in 2013 and prepared for their re-analysis now in 2016, have already been analyzed in 2013 by the ICP-MS by Mike Babechuk with the help of Jean Dwyer.

➕ Samples found with Marine limestones REE signatures or isotopic fingerprints had satisfied the following 5 key criteria:
- *High ratio of Y/Ho*
- *Light REE depletion*
- *High Sr*
- *High ratio U/Th*
- *Ce anomalies*
- *La anomalies*

➕ Samples found with Carbonatites limestones REE signatures or isotopic fingerprints had satisfied the following criteria:
- *Light and heavy REE enriched*
- *High Li, Rb, Cs, and Ti concentration*
- *Perfect matching correlation with Fort Portal Carbonatites (universally recognized in the literature with Carbonatites fingerprint) with a correlation coefficient above or equal to 0.95.*

The Procokin PCK limestone sample has been collected in a quarry in the western side of DRCongo were literature universally recognized the presence of stromatolites fossils which suggest a shallow water depositional environment or origin.

The laboratory analysis of the ***four (4) PCK limestone samples*** in 2016 aims to confirm by ICP-MS method and instrument the marine limestone origin of this stromatolites neighboring sample which will later be used as matching correlation tool or comparator for or with any other marine limestone REE signature or isotopic fingerprint sample from East

African Rift System exactly as it was done in 2013 for the Fort Portal Carbonatites.
All the samples re-drilled for the second time in 2016 has been labelled with the same label of 2013 and added with slash two **/2** to make the difference and to show that they have been drilled for the second time in 2016.

The ICP-MS analysis which will be run by Cora Mc Kenna and Sylvain M.Kezir in September 2016 will double-check the 2013 results reproducing ability using different way and different people involved in.

So, a total of 20 powder samples (weight about 8 to 10 mg each) has been prepared for the first batch of 2016 lab analysis as below:

| Carbonatites | | Correlation coefficient with Fort Portal lavas | Marine limestones | | Comments On Kamber (2014) Criterias |
|---|---|---|---|---|---|
| 1 | V2b/2 | $R^2 = 0.9$ | 1 | P12b/2 | Satisfy all 5 criteria |
| 2 | V20a/2 | $R^2 = 0.95$ | 2 | LE24a/2 | Satisfy all 5 criteria |
| 3 | V20b/2 | $R^2 = 0.95$ | 3 | LE24b/2 | Satisfy all 5 criteria |
| 4 | V22a/2 | $R^2 = 0.95$ | 4 | LE26a/2 | Satisfy all 5 criteria |
| 5 | LE44a/2 | $R^2 = 0.95$ | 5 | LE26b/2 | Satisfy all 5 criteria |
| 6 | LE44b/2 | $R^2 = 0.95$ | 6 | LE28a/2 | Satisfy all 5 criteria |
| 7 | LE41a/2 | $R^2 = 0.9$ | 7 | LE28d/2 | Satisfy all 5 criteria |
| 8 | LE41b/2 | $R^2 = 0.9$ | 8 | V19a/2 | Satisfy 4 of 5 criteria |
| | | | 9 | PCK a/1 | Grey texture |
| | | | 10 | PCK b/1 | Replica of Grey texture |
| | | | 11 | PCK c/1 | Light texture |
| | | | 12 | PCK d/1 | Replica of Light texture |

**SAMPLES DESCRIPTIONS AND DRILLING OPERATIONS SUMMARY.**

| Sample ID 01/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| V2b/2 | - No visible fabrics or crystal phases; <br> - Very crumbly texture | 0.906 g | 8.514 mg | Small | Dark brown | |

| Sample ID 01/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| V20a/2 | - Dark grey crystal surrounded by a lighter matrix containing orange /rusty flecks<br>- The matrix is in lands and too friable to drill | 0.909 g | 9.518 mg | medium | Dark grey | One sample and one replica of the dark grey crystal avoiding as possible the matrix have been drilled |
| V20b/2 | Replica of V20a/2 | 0.912 g | 8.520 mg | Medium | Grey | Replica drilled from different site of the same slice face |

| Sample ID 30/08/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| V22a/2 | - 4 crystals fabrics were identified, a portion of the sample contained large pores (up to 5mm in diameter) and the large pore appeared lined with a light coloured calcite; <br> - Some portions of the sample near the edges had smaller more uniform pores in a darker coloured calcite with very few pores; <br> - These areas were concentrated in the centre of the sample. | 0.910 g | 10.521 mg | Small | white | 15 samples were drilled with replicas for the purpose of having enough material to run ICP-MS. |

| Sample ID 01/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| LE44a/2 | - No visible fabrics/textures differences; <br> - Moderately porous fine-medium crystalline carbonate. | 0.911 g | 7.518 mg | medium | White | Some black flecks in the white powder may have come from weathered surface of the sample while tapping out the powder from the sample. |
| LE44b/2 | Replica of LE44a/2 | 0.910 g | 9.523 mg | Medium | White | Replica drilled from different site of the same slice face. Black flecks still present. |

| Sample ID 01/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| LE41a/2 | - 2 (two) colours of carbonates crystals were visible: A milky cream colour and light brown colour.<br>- Although the two are too finely interspersed for separate sampling. | 0.909 g | 9.518 mg | medium | Milky cream | One sample and one replica were drilled from an area enough representative of the whole sample. |
| LE41b/2 | Replica of LE41a/2 | 0.913 g | 10.522 mg | Medium | Milky cream to Light brown | Replica drilled from different site of the same slice face. Black flecks still present. |

| Sample ID 02/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| P12b/2 | - Crumbly, porous light brown carbonate;<br>- Deposits around the pores look more crystalline than surrounding carbonates. However, they are smaller than the drill bit tip. | 0.905 g | 8.515 mg | Small, then well cleaned medium | Light brown | The sample was much harder than expected, it was crystalline and not crumbly (as previously described) beneath the surface.<br>Presence of some small black flecks. |



P12 b/2

| Sample ID 02/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| LE24a/2 | - Porous sample with a black lining in the cavities;<br>- Two distinct colours of Carbonates: Grey and Creamy.<br>- Although, individual crystals are not regularly visible and are very fine when they are.<br>- The two Carbonates can be drilled separately.<br>However the boundaries between the two are<br>quite gradational/diffuse | 0.910 g | 8.319 mg | medium | Creamy | Care was taken to avoid the cavities lined in black. However, they cannot be accurately avoided in 3 dimensions.<br><br>Black flecks visible in the powder appear to confirm this contamination. |
| LE24b/2 | Replica of LE24a/2 | 0.911 g | 9.520 mg | Medium | Creamy without blacks flecks avoided while drilling | Replica drilled from different site of the same slice face |

| Sample ID 02/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| LE26a/2 | - No visible fabric or crystal phase apart from the dark cavity lining.<br>- Drilled samples on a large Patch | 0.996 g | 10.004 mg | medium | Dark brown | One sample and one replica were drilled. Exhaustion of tube stock. No time to wait new stock. Change in the tube size. |
| LE26b/2 | Replica of LE26a/2 | 0.997 g | 11.006 mg | Medium | Dark brown | Replica drilled from different site of the same slice face |

| Sample ID 02/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| LE28a/2 | - The sample is layered with creamy and pink brown layers and cavities lined in black which were avoided while drilling. | 0.911 g | 9.520 mg | medium | creamy | Drilled texture: *pink brown* layer. |
| LE28d/2 | Replica of LE28c/2 | 0.910 g | 7.918 mg | Medium | Creamy with black flecks | Drilled texture: *cream* layer. Replica drilled from different site of the same slice face |

| Sample ID 02/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder colour | Remarks |
|---|---|---|---|---|---|---|
| V19a/2 | Two textures are visible:<br>• *A more porous darker portion;*<br>• *A lighter coloured less porous portion.* | 0.920 g | 8.752 mg | medium | white | Drilled texture: lighter less porous texture |
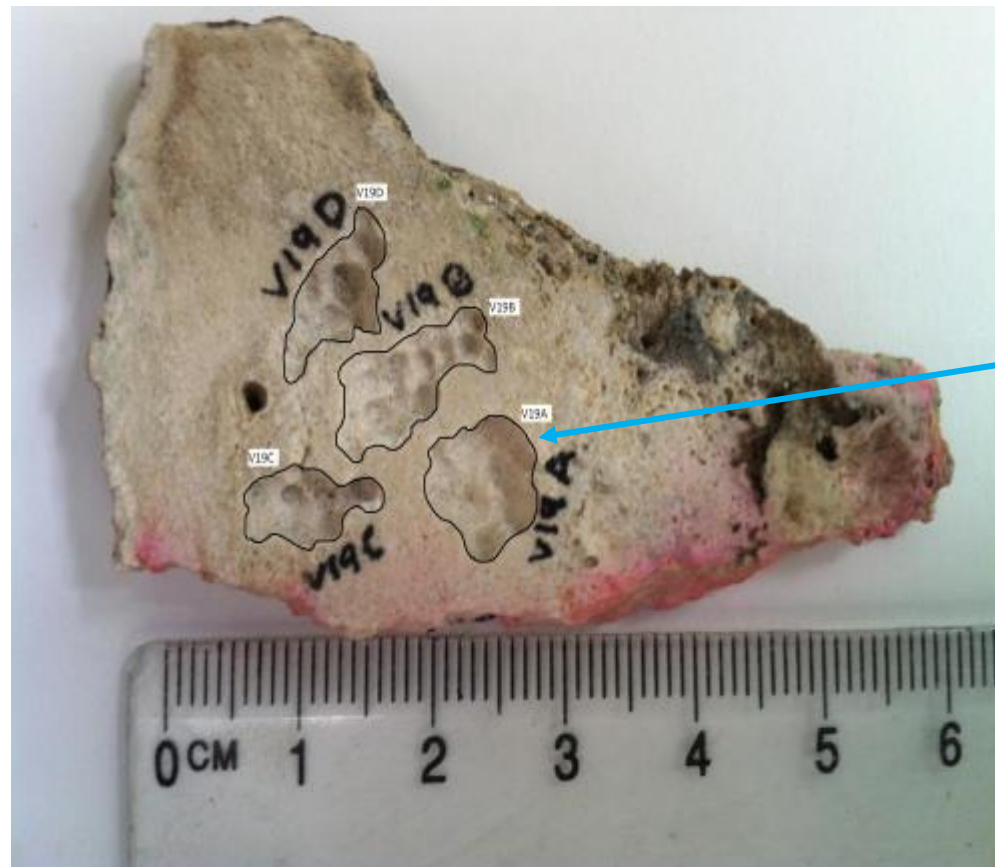


V19 a/2

| Sample ID 02/09/2016 | Sample description | Weight tube | Weight Sample | Drilling bit size | Powder color | Remarks |
|---|---|---|---|---|---|---|
| PCK a/1 | 2 crystal phases are visible:<br>- **Grey crystal phase**, the most common;<br>- Light /white phase with most euhedral and irregular crystals. | 0.913 g | 9.458 mg | medium | white | Drilled samples will be probably containing all the 2 phases; however will be mostly one kind and will hopefully maintain "geochemical difference". Hard to drill, very small Black flecks. |
| PCK b/1 | Replica of PCK a/1 | 0.912 g | 10.345 mg | Medium | White | Replica drilled from different site of the same slice face |
| PCK c/1 | **Light /white phase** with most euhedral and irregular crystals | 0.913 g | 13.246 mg | Medium | White | Hard to drill, very small black flecks. |
| PCK d/1 | Replica of PCK c/1 | 0.914 g | 12.653 mg | Medium | White | Replica drilled from different site of the same slice face |



PCK a/1
PCK b/1
PCK c/1
PCK d/1

<div style="border:1px solid">
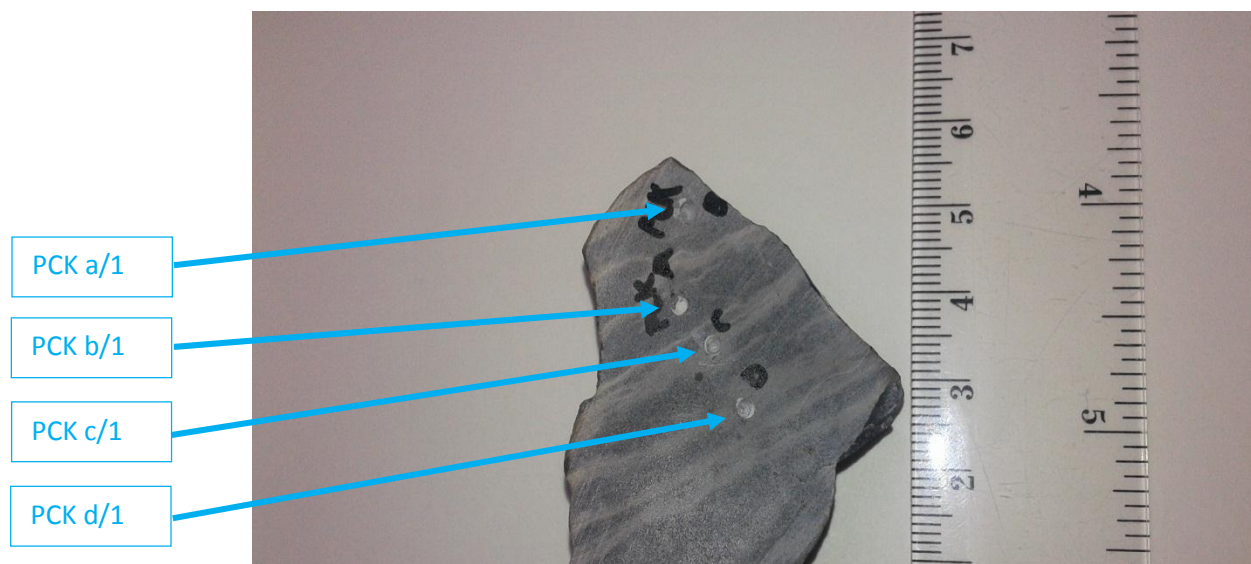
2nd batch of Limestones samples for REE ICP-MS

</div>

Objective:

Being more confident during the analyse of the 1st batch of limestones samples (collected during the Albertine Graben field trips from 2007 to 2010 and analysed in 2013) by the ICP-MS method ability to reproduce identical results whenever the time or whatever the team involved to run it, the next batch (2nd one) of limestones samples (collected during 2014's field trip) would be ideally analysed and interpreted in June 2017 before the next and last field trip planned in July 2017.

The main objective of this actual (2nd batch samples) 2017 REE- ICP/MS analyse is to give the best geochemical understanding of the bicarbonate double origin in the limestones outcropping in the western branch of the East African Rift System "before" to re-visit the field for more samples collection helping to fill any gap in the geochemical understanding of the historical way of bicarbonate dissolving in the outcropping limestones.

Method:

The results confidence got after the REE ICP-MS analyse of the 1st batch of limestones samples imposed to reduce the number of analyses per sample during the analysis of the 2nd batch.

Indeed, for the 1st batch of limestone samples, the necessity to drill through any visible texture/structure/fabric in each limestone sample collected from 2007 to 2014, was due to the geochemical need to see how the REE-Y trends are varying through all carbonate textures/structures/fabric present in one single sample in order to confirm the method results reproducing ability in the same sample.

However, as this reproducing ability is confirmed, there is no more need to drill any visible texture in a single sample. In order to get only the origin of the bicarbonate (Carbonatites lavas or marine limestone), each limestone sample will be drilled through any white/ lightest single texture/structure/fabric which represents the most carbonate fabric. Avoid to drill through any black or dark texture/structure/fabric.

Samples considered as references:

The Fort Portal Carbonatites lavas have got from the existing literature a known REE-Y Spectral signature which characterizes the "hot" origin of bicarbonates in the outcropping limestones. All the East African Rift Carbonatites lavas could be easily correlated with Fort portal as they are close located and have approximately the same age. So, the Fort Portal Carbonatites are the best reference so far to correlate all the East African possible Carbonatites spectral signatures in the future.

Unfortunately, no marine limestones so far could be considered as the best reference in term of close location and age dating for any East African Rift marine limestone characterizing the "cold" origin of their bicarbonate:

- The Procokin (PCK) limestone sample analysed in 2016 by REE-Y ICP-MS met the marine limestone criterias but gave a very different trend of Spectral signature from these collected in Albertine Graben from 2007 to 2010 and analysed twice in 2013 and 2016 during the results reproducing ability check experiment. This could be explained by the facts that the PCK sample doesn't

have the same location than the Albertine Rift limestones. Either they're all from a marine source, they didn't followed the same geochemical process to be precipitated. Also, the PCK sample doesn't have the same age with the Albertine Rift marine limestones. The different trend of the PCK spectral signature suggests different age while the criteria indicates marine limestone same origin.

- The <u>Mandawa</u> (MDW) basin in the Southern coastal Tanzania is closer to the Albertine Rift than the PCK quarry located in the western DRC. MDW limestones have been found in outcrop and samples properly collected and analysed by REE ICP-MS in October 2010 by Wellington Hudson (PhD, Trinity College). The results trend is likely marine limestone spectral signature with a suggested ages from Jurassic, Early to late Cretaceous.

## Samples analysed by ICP-MS in June 2018

| N° | Sample Field ID | Area | X | Y | Field descriptions |
|----|----------------|------|------|------|-------------------|
| 1 | V149 | Katanda | 761765 | 9900632 | Mai ya Moto hot springs and limestones |
| 2 | V150 | Katanda | 761980 | 9900850 | Tufa limestone on roadside |
| 3 | V153 | Katanda | 762300 | 9901850 | ?Hot springs |
| 4 | V159 | X3-L688 | | | Terrace with black shinning stuffs above Mai moto |
| 5 | V161b | X2-L690 | | | Terrace with black shinning stuffs above Mai moto |
| 6 | V162a | X2-L690 | | | Terrace with black shinning stuffs above Mai moto |
| 7 | V163b | X2-L690 | | | Terrace with black shinning stuffs above Mai moto |
| 8 | V164 | X2-L690 | | | Terrace with black shinning stuffs above Mai moto |
| 9 | V338 | Vitshumbi | 761012 | 9915285 | Samples collected from a cliff of 21.5m height @ 50cm interval.  BV- G 10 |
| 10 | V344 | Vitshumbi | 761012 | 9915285 | |
| 11 | V352 | Vitshumbi | 761012 | 9915285 | |
| 12 | V356 | Vitshumbi | 761012 | 9915285 | |
| 13 | V363 | Vitshumbi | 761012 | 9915285 | |
| 14 | V364 | Vitshumbi | 761012 | 9915285 | |
| 15 | V385 | Vitshumbi | 761012 | 9915285 | |
| 16 | MDW 42 | Kiturika fm | | | Early cretaceous Reef limestones |
| 17 | MDW 43 | Kiturika fm | | | Early cretaceous Peloids limestones |
| 18 | MDW 74 | Kiturika fm | | | Early cretaceous Coral |
| 19 | MDW 125 | Lower Mitole | | | Late Jurassic Oolithic limestones |
| 20 | MDW162 | Mtumbei fm | | | Middle Jurassic Reef limestones |
| 21 | MDW 276 | Mtumbei fm | | | Middle Jurassic light grey bioclast and ooids lst |
| 22 | MDW 277 | Mtumbei fm | | | Middle Jurassic light green ooids + Qtz lst. |

**Supervisor's instructions:**
- *Use petrographic observations of the above samples as background for drilling*
- *Drill trough the best Carbonates texture/structure/fabrics evidences in each sample*
- *Avoid any weathered layers, black stains, or confusing texture/structure/fabrics*
- *Respect the lab quality-quantity requirements for the results efficiency (see Cora)*

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements



Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

Sample drilled accordingly to Supervisor instruction

Powder well conserved accordingly to lab requirements

| name: | Sylvain Mangoni | project: | batch no 2 | date: | 02/05/2018 | | |
|---|---|---|---|---|---|---|---|

| Sample ID | Lab ID | Empty Tube (g) | Tube + 1.5ml 5% HNO3 (g) | Weigh Paper (mg) | Mass of sample (mg) | Mass Sample (g) | Weigh Paper (After Sample) (mg) | Tube + acid + sample (g) |
|---|---|---|---|---|---|---|---|---|
| SMK IS B | SMK IS B | | | | | | | |
| Procedural Blank 2 | SMK Blank 2 | 1.0251 | 2.5322 | 46.324 | 8.000 | 0.0080 | 46.26 | 2.5318 |
| Procedural Blank 3 | SMK Blank 3 | 1.0198 | 2.5567 | 50.478 | 8.000 | 0.0080 | 50.49 | 2.5567 |
| Limestone BCS 393 | SMK LSTD 2 | 0.9961 | 2.4045 | 49.925 | 7.965 | 0.0080 | 50.50 | 2.4079 |
| Limestone JLs-1 | SMK JLS 1 | 1.0079 | 2.5288 | 44.903 | 7.902 | 0.0079 | 45.34 | 2.5330 |
| Dolomite BCS 368 | SMK DMR 1 | 0.9962 | 2.5163 | 57.321 | 9.798 | 0.0098 | 57.34 | 2.5255 |
| MDW 74 A | SMK 021 | 1.0185 | 2.5433 | 50.579 | 6.997 | 0.0070 | 51.08 | 2.5452 |
| MDW74 B | SMK 022 | 1.008 | 2.5253 | 51.665 | 7.429 | 0.0074 | 52.69 | 2.5262 |
| MDW 74 C | SMK 023 | 1.0292 | 2.5404 | 38.847 | 6.282 | 0.0063 | 39.33 | 2.5421 |
| MDW 125 A | SMK 024 | 1.0373 | 2.5517 | 39.717 | 9.098 | 0.0091 | 39.71 | 2.5596 |
| MDW 125 B | SMK 025 | 1.0193 | 2.5344 | 39.827 | 7.581 | 0.0076 | 40.32 | 2.5391 |
| MDW 276 A | SMK 026 | 1.0192 | 2.5358 | 56.028 | 7.789 | 0.0078 | 56.58 | 2.5391 |
| MDW 276B | SMK 027 | 1.0293 | 2.5465 | 58.216 | 7.980 | 0.0080 | 58.22 | 2.5398 |
| MDW 277 | SMK 028 | 0.9966 | 2.2554 | 39.946 | 9.097 | 0.0091 | 39.98 | 2.5525 |
| MDW 162 A | SMK 029 | 1.0221 | 2.5191 | 39.681 | 8.619 | 0.0086 | 40.56 | 2.5320 |
| MDW 162B | SMK 030 | 1.0191 | 2.5492 | 39.462 | 11.456 | 0.0115 | 40.45 | 2.5227 |
| MDW 43 | SMK 031 | 1.0293 | 2.5583 | 43.083 | 9.294 | 0.0093 | 44.58 | 2.5532 |
| MDW 42 A | SMK 032 | 1.0373 | 2.5532 | 43.323 | 5.994 | 0.0060 | 44.02 | 2.5621 |
| BV 344 | SMK 033 | 1.0329 | 2.5523 | 42.128 | 10.767 | 0.0108 | 42.33 | 2.5560 |
| BV 352 | SMK 034 | 1.0289 | 2.5463 | 41.343 | 8.856 | 0.0089 | 41.94 | 2.5622 |
| BV 356 | SMK 035 | 1.0219 | 2.5502 | 42.268 | 10.750 | 0.0108 | 42.81 | 2.5520 |
| MDW 42 B | SMK 036 | 1.0371 | 2.5513 | 37.342 | 11.330 | 0.0113 | 37.48 | 2.5578 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| BV 364 | SMK 037 | 1.0322 | 2.5498 | 46.721 | 7.930 | 0.0079 | 46.78 | 2.5593 |
| BV 385 | SMK 038 | 1.0223 | 2.5405 | 47.656 | 10.096 | 0.0101 | 47.78 | 2.5571 |
| BV 149 A | SMK 039 | 1.0322 | 2.5476 | 54.667 | 7.039 | 0.0070 | 54.69 | 2.5493 |
| BV 363 | SMK 040 | 1.0247 | 2.5486 | 59.465 | 8.300 | 0.0083 | 59.46 | 2.5531 |
| BV 149 B | SMK 041 | 1.0374 | 2.5484 | 59.867 | 9.917 | 0.0099 | 59.97 | 2.5566 |
| BV 150 | SMK 042 | 1.0322 | 2.5613 | 58.743 | 8.507 | 0.0085 | 58.95 | 2.5664 |
| BV 153 | SMK 043 | 1.0289 | 2.5416 | 59.601 | 8.706 | 0.0087 | 59.74 | 2.5480 |
| BV 338 | SMK 044 | 0.9966 | 2.5253 | 60.366 | 8.617 | 0.0086 | 60.45 | 2.5334 |
| BV 159 A | SMK 045 | 1.0289 | 2.5544 | 44.259 | 10.479 | 0.0105 | 44.67 | 2.5613 |
| BV 159 B | SMK 046 | 1.0373 | 2.5502 | 46.320 | 10.791 | 0.0108 | 46.56 | 2.5576 |
| BV 161 B | SMK 047 | 1.0184 | 2.5483 | 57.081 | 11.125 | 0.0111 | 57.24 | 2.5560 |
| BV 162 A | SMK 048 | 1.0393 | 2.5635 | 44.662 | 10.298 | 0.0103 | 44.69 | 2.5713 |
| BV 163 A | SMK 049 | 1.0294 | 2.553 | 43.875 | 9.854 | 0.0099 | 43.96 | 2.5600 |
| BV 164 | SMK 050 | 1.0193 | 2.5005 | 45.800 | 8.530 | 0.0085 | 45.83 | 2.5069 |
| SMK IS C | SMK IS C | | | | | | | |

| |
|---|
| white - fill in |
| green - fixed calcs |

**Appendix 2 : ICP-MS  Results Tables**

## 2007-2010 Field works:  Travertines samples results obtained by the ICP-MS 2013 Experiment

| | ppb | V2A | V2A | V2B | V19A | V19A | V19A | V19B | V19C | V19D | V20A |
|---|---|---|---|---|---|---|---|---|---|---|---|
| La | | 199.9501 | 205.2632 | 133.3059 | 99.64422 | 150.6873 | 87.41905 | 104.3309 | 94.85417 | 140.9222 | 10643.84 |
| Ce | | 351.6072 | 359.0498 | 213.7606 | 85.02589 | 98.3204 | 97.12464 | 139.7895 | 135.5724 | 203.7521 | 15734.55 |
| Pr | | 42.16585 | 44.80458 | 25.75071 | 10.65297 | 12.37874 | 11.72978 | 19.91068 | 19.01688 | 32.17197 | 1675.517 |
| Nd | | 155.2363 | 158.8085 | 89.10466 | 52.20575 | 53.80405 | 52.61852 | 95.55807 | 87.56833 | 142.341 | 5253.763 |
| Sm | | 29.81596 | 29.70705 | 14.73693 | 32.94166 | 39.22575 | 34.0704 | 63.1377 | 34.92836 | 55.55133 | 877.0401 |
| Gd | | 26.00549 | 25.04321 | 10.0951 | 29.09465 | 30.37674 | 30.47925 | 41.63514 | 30.53021 | 42.92982 | 672.9751 |
| Tb | | 3.059212 | 3.149175 | 1.344655 | 3.902009 | 4.378444 | 4.025846 | 5.552049 | 4.009274 | 5.673344 | 91.36803 |
| Dy | | 15.24285 | 15.7029 | 7.22501 | 27.82158 | 29.61542 | 28.38052 | 33.50993 | 22.42983 | 38.7763 | 458.1363 |
| Y | | 113.8247 | 121.6527 | 63.85561 | 451.7733 | 661.417 | 350.9032 | 446.2395 | 418.2968 | 511.6283 | 1800.525 |
| Ho | | 3.071848 | 3.190915 | 1.549314 | 6.537065 | 6.935108 | 6.731718 | 7.620653 | 5.210771 | 8.090806 | 81.78915 |
| Er | | 7.081965 | 8.585806 | 4.125496 | 17.81907 | 18.46056 | 17.84956 | 20.89055 | 15.71339 | 20.55745 | 213.8294 |
| Tm | | 0.921339 | 1.023871 | 0.672814 | 2.484238 | 2.605084 | 2.617191 | 2.59899 | 2.326124 | 2.768509 | 31.17804 |
| Yb | | 5.221316 | 5.784631 | 4.217063 | 14.50067 | 14.33109 | 14.83114 | 17.08097 | 14.65864 | 16.32676 | 205.0678 |
| Lu | | 0.659482 | 0.811154 | 0.60934 | 2.206648 | 2.417504 | 2.245177 | 2.460903 | 2.165773 | 2.280742 | 29.07088 |
| | | | | | | | | | | | |
| | MUQ | V2A | V2A | V2B | V19A | V19A | V19A | V19B | V19C | V19D | V20A |
| La | 32510 | 0.00615 | 0.006314 | 0.0041 | 0.003065 | 0.004635 | 0.002689 | 0.003209 | 0.002918 | 0.004335 | 0.327402 |
| Ce | 71090 | 0.004946 | 0.005051 | 0.003007 | 0.001196 | 0.001383 | 0.001366 | 0.001966 | 0.001907 | 0.002866 | 0.221333 |
| Pr | 8460 | 0.004984 | 0.005296 | 0.003044 | 0.001259 | 0.001463 | 0.001386 | 0.002354 | 0.002248 | 0.003803 | 0.198052 |
| Nd | 32910 | 0.004717 | 0.004826 | 0.002708 | 0.001586 | 0.001635 | 0.001599 | 0.002904 | 0.002661 | 0.004325 | 0.15964 |
| Sm | 6880 | 0.004334 | 0.004318 | 0.002142 | 0.004788 | 0.005701 | 0.004952 | 0.009177 | 0.005077 | 0.008074 | 0.127477 |
| Gd | 6360 | 0.004089 | 0.003938 | 0.001587 | 0.004575 | 0.004776 | 0.004792 | 0.006546 | 0.0048 | 0.00675 | 0.105814 |
| Tb | 990 | 0.00309 | 0.003181 | 0.001358 | 0.003941 | 0.004423 | 0.004067 | 0.005608 | 0.00405 | 0.005731 | 0.092291 |
| Dy | 5890 | 0.002588 | 0.002666 | 0.001227 | 0.004724 | 0.005028 | 0.004818 | 0.005689 | 0.003808 | 0.006583 | 0.077782 |
| Y | 31850 | 0.003574 | 0.00382 | 0.002005 | 0.014184 | 0.020767 | 0.011017 | 0.014011 | 0.013133 | 0.016064 | 0.056531 |
| Ho | 1220 | 0.002518 | 0.002616 | 0.00127 | 0.005358 | 0.005685 | 0.005518 | 0.006246 | 0.004271 | 0.006632 | 0.06704 |
| Er | 3370 | 0.002101 | 0.002548 | 0.001224 | 0.005288 | 0.005478 | 0.005297 | 0.006199 | 0.004663 | 0.0061 | 0.063451 |
| Tm | 510 | 0.001807 | 0.002008 | 0.001319 | 0.004871 | 0.005108 | 0.005132 | 0.005096 | 0.004561 | 0.005428 | 0.061133 |
| Yb | 3250 | 0.001607 | 0.00178 | 0.001298 | 0.004462 | 0.00441 | 0.004563 | 0.005256 | 0.00451 | 0.005024 | 0.063098 |
| Lu | 490 | 0.001346 | 0.001655 | 0.001244 | 0.004503 | 0.004934 | 0.004582 | 0.005022 | 0.00442 | 0.004655 | 0.059328 |
| | ppb | V20B | V21A | V21A | V21B | V22A | V22B | V22C | V22D | V22E | V22F |
| La | | 14185.2 | 712.273 | 699.6443 | 396.6492 | 4099.455 | 1103.198 | 413.8515 | 1032.56 | 168.8862 | 129.0359 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ce | | 25421.05 | 1697.035 | 1662.928 | 943.8481 | 9519.382 | 3594.647 | 1556.216 | 3236.047 | 683.2962 | 568.8726 |
| Pr | | 2560.361 | 193.0548 | 192.7117 | 107.0222 | 823.4895 | 225.394 | 84.34469 | 206.4269 | 35.20515 | 22.51037 |
| Nd | | 8709.86 | 823.9725 | 813.4504 | 443.7006 | 2895.007 | 818.3797 | 328.3413 | 770.2204 | 138.3396 | 88.32151 |
| Sm | | 1563.174 | 265.064 | 269.6611 | 148.8356 | 486.4496 | 158.6087 | 91.95915 | 153.2306 | 40.8409 | 32.17411 |
| Gd | | 1214.438 | 511.5588 | 513.6503 | 278.7251 | 340.3917 | 91.77841 | 59.63234 | 83.45047 | 29.50919 | 31.0496 |
| Tb | | 160.4293 | 88.0588 | 88.5061 | 47.29053 | 44.347 | 11.83335 | 6.443131 | 10.0314 | 3.983675 | 4.198801 |
| Dy | | 780.1142 | 522.939 | 505.2738 | 277.248 | 221.8342 | 59.43712 | 30.4639 | 46.51887 | 19.21987 | 21.8377 |
| Y | | 2989.628 | 3569.666 | 3582.377 | 1957.937 | 1210.054 | 520.5079 | 334.7962 | 517.6278 | 307.1092 | 341.4442 |
| Ho | | 135.0681 | 104.1986 | 102.5893 | 55.70823 | 40.97336 | 11.50446 | 6.133336 | 9.223445 | 3.470626 | 4.335542 |
| Er | | 334.9313 | 266.763 | 266.6615 | 142.28 | 101.5155 | 29.76953 | 16.7924 | 25.47915 | 9.573451 | 11.35229 |
| Tm | | 48.26288 | 34.79452 | 35.95574 | 18.85502 | 14.29745 | 4.259307 | 2.660388 | 3.855092 | 1.286439 | 1.553524 |
| Yb | | 301.6627 | 201.8633 | 202.5283 | 109.5866 | 85.02826 | 25.28603 | 18.4739 | 24.55243 | 8.50056 | 9.299934 |
| Lu | | 43.32317 | 28.23824 | 28.94557 | 15.47436 | 12.08704 | 3.688308 | 2.917776 | 3.588966 | 1.282174 | 1.204398 |

| | MUQ | V20B | V21A | V21A | V21B | V22A | V22B | V22C | V22D | V22E | V22F |
|---|---|---|---|---|---|---|---|---|---|---|---|
| La | 32510 | 0.436333 | 0.021909 | 0.021521 | 0.012201 | 0.126098 | 0.033934 | 0.01273 | 0.031761 | 0.005195 | 0.003969 |
| Ce | 71090 | 0.35759 | 0.023872 | 0.023392 | 0.013277 | 0.133906 | 0.050565 | 0.021891 | 0.04552 | 0.009612 | 0.008002 |
| Pr | 8460 | 0.302643 | 0.02282 | 0.022779 | 0.01265 | 0.097339 | 0.026642 | 0.00997 | 0.0244 | 0.004161 | 0.002661 |
| Nd | 32910 | 0.264657 | 0.025037 | 0.024717 | 0.013482 | 0.087967 | 0.024867 | 0.009977 | 0.023404 | 0.004204 | 0.002684 |
| Sm | 6880 | 0.227205 | 0.038527 | 0.039195 | 0.021633 | 0.070705 | 0.023054 | 0.013366 | 0.022272 | 0.005936 | 0.004676 |
| Gd | 6360 | 0.190949 | 0.080434 | 0.080763 | 0.043825 | 0.053521 | 0.014431 | 0.009376 | 0.013121 | 0.00464 | 0.004882 |
| Tb | 990 | 0.16205 | 0.088948 | 0.0894 | 0.047768 | 0.044795 | 0.011953 | 0.006508 | 0.010133 | 0.004024 | 0.004241 |
| Dy | 5890 | 0.132447 | 0.088784 | 0.085785 | 0.047071 | 0.037663 | 0.010091 | 0.005172 | 0.007898 | 0.003263 | 0.003708 |
| Y | 31850 | 0.093866 | 0.112077 | 0.112477 | 0.061474 | 0.037992 | 0.016342 | 0.010512 | 0.016252 | 0.009642 | 0.01072 |
| Ho | 1220 | 0.110712 | 0.085409 | 0.08409 | 0.045662 | 0.033585 | 0.00943 | 0.005027 | 0.00756 | 0.002845 | 0.003554 |
| Er | 3370 | 0.099386 | 0.079158 | 0.079128 | 0.04222 | 0.030123 | 0.008834 | 0.004983 | 0.007561 | 0.002841 | 0.003369 |
| Tm | 510 | 0.094633 | 0.068225 | 0.070501 | 0.036971 | 0.028034 | 0.008352 | 0.005216 | 0.007559 | 0.002522 | 0.003046 |
| Yb | 3250 | 0.092819 | 0.062112 | 0.062316 | 0.033719 | 0.026163 | 0.00778 | 0.005684 | 0.007555 | 0.002616 | 0.002862 |
| Lu | 490 | 0.088415 | 0.057629 | 0.059073 | 0.03158 | 0.024667 | 0.007527 | 0.005955 | 0.007324 | 0.002617 | 0.002458 |

| | ppb | V22G | V22H | P12A | P12B | LE24A | LE24B | LE24C | LE24D | LE26A | LE26B |
|---|---|---|---|---|---|---|---|---|---|---|---|
| La | | 117.392 | 216.0105 | 2167.09 | 2029.377 | 1042.287 | 438.514 | 269.4935 | 132.1388 | 97.88369 | 214.6054 |
| Ce | | 481.5143 | 1175.271 | 3594.861 | 2644.704 | 297.3215 | 133.553 | 247.648 | 135.4144 | 50.82687 | 91.50231 |
| Pr | | 19.31949 | 35.30733 | 496.8179 | 452.8864 | 89.48443 | 28.92648 | 28.545 | 15.75259 | 15.18296 | 30.06095 |

| | MUQ | V22G | V22H | P12A | P12B | LE24A | LE24B | LE24C | LE24D | LE26A | LE26B |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Nd | | 84.38802 | 130.6892 | 2013.917 | 1745.219 | 396.381 | 133.9366 | 111.5104 | 59.06835 | 60.40458 | 123.4174 |
| Sm | | 30.85784 | 48.59279 | 384.3884 | 327.2836 | 72.60106 | 25.20869 | 23.58911 | 11.15856 | 14.20824 | 25.88511 |
| Gd | | 24.71482 | 48.89867 | 437.8467 | 351.444 | 147.897 | 80.00905 | 47.03425 | 19.8956 | 16.61448 | 36.25812 |
| Tb | | 2.804386 | 7.276705 | 70.13979 | 54.73034 | 20.41159 | 11.72009 | 6.938539 | 3.16882 | 2.429906 | 5.692518 |
| Dy | | 13.10911 | 31.13047 | 491.0079 | 377.7735 | 141.2702 | 86.47117 | 56.14521 | 25.46508 | 19.08796 | 43.64721 |
| Y | | 357.2993 | 395.9129 | 5728.19 | 4231.744 | 1630.249 | 1124.699 | 931.3594 | 509.3773 | 655.8235 | 958.3634 |
| Ho | | 2.51633 | 5.875525 | 130.6869 | 96.66989 | 37.08142 | 23.7953 | 17.23531 | 8.269785 | 5.624103 | 11.03188 |
| Er | | 6.802767 | 14.74952 | 433.4099 | 297.4275 | 111.8711 | 67.64439 | 52.77571 | 25.76731 | 17.78938 | 31.73575 |
| Tm | | 1.064532 | 2.215279 | 64.70834 | 43.10357 | 15.11544 | 9.077764 | 7.165181 | 3.505534 | 2.482704 | 4.256531 |
| Yb | | 6.875204 | 15.04475 | 398.1464 | 262.681 | 89.20682 | 53.72979 | 42.38417 | 21.25619 | 16.21336 | 25.65673 |
| Lu | | 1.121446 | 2.518959 | 60.33363 | 39.96341 | 15.58615 | 9.103461 | 7.757396 | 3.827187 | 2.935213 | 4.650298 |
| | **MUQ** | **V22G** | **V22H** | **P12A** | **P12B** | **LE24A** | **LE24B** | **LE24C** | **LE24D** | **LE26A** | **LE26B** |
| La | 32510 | 0.003611 | 0.006644 | 0.066659 | 0.062423 | 0.032061 | 0.013489 | 0.00829 | 0.004065 | 0.003011 | 0.006601 |
| Ce | 71090 | 0.006773 | 0.016532 | 0.050568 | 0.037202 | 0.004182 | 0.001879 | 0.003484 | 0.001905 | 0.000715 | 0.001287 |
| Pr | 8460 | 0.002284 | 0.004173 | 0.058726 | 0.053533 | 0.010577 | 0.003419 | 0.003374 | 0.001862 | 0.001795 | 0.003553 |
| Nd | 32910 | 0.002564 | 0.003971 | 0.061195 | 0.05303 | 0.012044 | 0.00407 | 0.003388 | 0.001795 | 0.001835 | 0.00375 |
| Sm | 6880 | 0.004485 | 0.007063 | 0.05587 | 0.04757 | 0.010552 | 0.003664 | 0.003429 | 0.001622 | 0.002065 | 0.003762 |
| Gd | 6360 | 0.003886 | 0.007688 | 0.068844 | 0.055258 | 0.023254 | 0.01258 | 0.007395 | 0.003128 | 0.002612 | 0.005701 |
| Tb | 990 | 0.002833 | 0.00735 | 0.070848 | 0.055283 | 0.020618 | 0.011838 | 0.007009 | 0.003201 | 0.002454 | 0.00575 |
| Dy | 5890 | 0.002226 | 0.005285 | 0.083363 | 0.064138 | 0.023985 | 0.014681 | 0.009532 | 0.004323 | 0.003241 | 0.00741 |
| Y | 31850 | 0.011218 | 0.012431 | 0.179849 | 0.132865 | 0.051185 | 0.035312 | 0.029242 | 0.015993 | 0.020591 | 0.03009 |
| Ho | 1220 | 0.002063 | 0.004816 | 0.10712 | 0.079238 | 0.030395 | 0.019504 | 0.014127 | 0.006779 | 0.00461 | 0.009043 |
| Er | 3370 | 0.002019 | 0.004377 | 0.128608 | 0.088257 | 0.033196 | 0.020073 | 0.01566 | 0.007646 | 0.005279 | 0.009417 |
| Tm | 510 | 0.002087 | 0.004344 | 0.126879 | 0.084517 | 0.029638 | 0.0178 | 0.014049 | 0.006874 | 0.004868 | 0.008346 |
| Yb | 3250 | 0.002115 | 0.004629 | 0.122507 | 0.080825 | 0.027448 | 0.016532 | 0.013041 | 0.00654 | 0.004989 | 0.007894 |
| Lu | 490 | 0.002289 | 0.005141 | 0.12313 | 0.081558 | 0.031808 | 0.018578 | 0.015831 | 0.007811 | 0.00599 | 0.00949 |

| | ppb | LE27A | LE27B | LE28A | LE28B | LE28C | LE28D | LE32A | LE32B | LE32C | LE32D |
|---|---|---|---|---|---|---|---|---|---|---|---|
| La | | 6351.464 | 23835.61 | 82.24817 | 278.0228 | 50.74439 | 93.9399 | 6076.536 | 16809.3 | 5356.619 | 4441.579 |
| Ce | | 5515.583 | 33287.38 | 35.14719 | 163.9083 | 62.55929 | 76.37994 | 14865.53 | * | 12816.63 | 11499.91 |
| Pr | | 959.4462 | 3984.488 | 12.91078 | 46.34273 | 9.013477 | 16.35604 | 1458.818 | 3916.117 | 1480.873 | 1246.02 |
| Nd | | 3437.245 | 13779.03 | 52.8306 | 164.4387 | 33.55761 | 58.98192 | 5865.9 | 14755.89 | 6259.755 | 5228.115 |
| Sm | | 550.7019 | 2144.552 | 9.50594 | 29.26509 | 6.796352 | 11.91887 | 1700.787 | 3357.133 | 1811.707 | 1559.607 |

| | MUQ | LE27A | LE27B | LE28A | LE28B | LE28C | LE28D | LE32A | LE32B | LE32C | LE32D |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Gd | | 553.9223 | 1866.873 | 13.00591 | 29.6337 | 8.033465 | 15.61177 | 2815.659 | 3943.266 | 2831.572 | 2510.649 |
| Tb | | 81.28811 | 264.5246 | 2.297671 | 4.885708 | 1.514085 | 2.603287 | 483.2861 | 601.5753 | 480.2789 | 430.5847 |
| Dy | | 518.4445 | 1520.685 | 16.72013 | 32.05666 | 11.46062 | 18.48793 | 3173.966 | 3638.042 | 3117.662 | 2915.834 |
| Y | | 4807.563 | 11737.04 | 304.8989 | 442.5796 | 371.1597 | 389.9112 | 30448.35 | * | 31452.73 | 30093.95 |
| Ho | | 120.7872 | 333.4857 | 5.229524 | 8.987425 | 3.883309 | 5.335123 | 759.1098 | 854.4365 | 755.3507 | 711.6104 |
| Er | | 347.1573 | 916.7331 | 17.22676 | 27.36456 | 14.71579 | 17.62931 | 2259.765 | 2555.082 | 2307.188 | 2189.441 |
| Tm | | 49.83461 | 127.1526 | 2.544856 | 4.320554 | 2.464802 | 2.820819 | 328.8425 | 376.7705 | 347.4808 | 330.813 |
| Yb | | 301.5185 | 765.2787 | 16.27476 | 25.34957 | 15.45057 | 19.04999 | 2082.714 | 2382.461 | 2190.511 | 2116.251 |
| Lu | | 43.82354 | 112.9508 | 2.379555 | 4.094086 | 2.542166 | 2.836512 | 357.3331 | 422.9293 | 395.1442 | 376.1889 |
| | MUQ | LE27A | LE27B | LE28A | LE28B | LE28C | LE28D | LE32A | LE32B | LE32C | LE32D |
| La | 32510 | 0.19537 | 0.733178 | 0.00253 | 0.008552 | 0.001561 | 0.00289 | 0.186913 | 0.51705 | 0.164768 | 0.136622 |
| Ce | 71090 | 0.077586 | 0.468243 | 0.000494 | 0.002306 | 0.00088 | 0.001074 | 0.209109 | * | 0.180287 | 0.161765 |
| Pr | 8460 | 0.11341 | 0.47098 | 0.001526 | 0.005478 | 0.001065 | 0.001933 | 0.172437 | 0.462898 | 0.175044 | 0.147284 |
| Nd | 32910 | 0.104444 | 0.418688 | 0.001605 | 0.004997 | 0.00102 | 0.001792 | 0.178241 | 0.448371 | 0.190208 | 0.158861 |
| Sm | 6880 | 0.080044 | 0.311708 | 0.001382 | 0.004254 | 0.000988 | 0.001732 | 0.247207 | 0.487955 | 0.26333 | 0.226687 |
| Gd | 6360 | 0.087095 | 0.293534 | 0.002045 | 0.004659 | 0.001263 | 0.002455 | 0.442714 | 0.62001 | 0.445216 | 0.394756 |
| Tb | 990 | 0.082109 | 0.267197 | 0.002321 | 0.004935 | 0.001529 | 0.00263 | 0.488168 | 0.607652 | 0.48513 | 0.434934 |
| Dy | 5890 | 0.088021 | 0.258181 | 0.002839 | 0.005443 | 0.001946 | 0.003139 | 0.538874 | 0.617664 | 0.529314 | 0.495048 |
| Y | 31850 | 0.150944 | 0.36851 | 0.009573 | 0.013896 | 0.011653 | 0.012242 | 0.955992 | * | 0.987527 | 0.944865 |
| Ho | 1220 | 0.099006 | 0.273349 | 0.004286 | 0.007367 | 0.003183 | 0.004373 | 0.622221 | 0.700358 | 0.61914 | 0.583287 |
| Er | 3370 | 0.103014 | 0.272028 | 0.005112 | 0.00812 | 0.004367 | 0.005231 | 0.670553 | 0.758185 | 0.684625 | 0.649686 |
| Tm | 510 | 0.097715 | 0.249319 | 0.00499 | 0.008472 | 0.004833 | 0.005531 | 0.644789 | 0.738766 | 0.681335 | 0.648653 |
| Yb | 3250 | 0.092775 | 0.23547 | 0.005008 | 0.0078 | 0.004754 | 0.005862 | 0.640835 | 0.733065 | 0.674003 | 0.651154 |
| Lu | 490 | 0.089436 | 0.230512 | 0.004856 | 0.008355 | 0.005188 | 0.005789 | 0.729251 | 0.863121 | 0.806417 | 0.767733 |

| | ppb | LE32E | LE32F | LE37A | LE37B | LE38A | LE38B | LE41A | LE41B | LE42A | LE42B |
|---|---|---|---|---|---|---|---|---|---|---|---|
| La | | 6116.652 | 6435.41 | 18636.77 | 41607.05 | 43548.97 | 97236.54 | 958.4531 | 1844.765 | 977.815 | 1140.12 |
| Ce | | 17950.37 | 16338.17 | 32971.29 | 70077.88 | * | 168041.9 | 1737.101 | 3351.368 | 1631.759 | 1973.748 |
| Pr | | 1632.923 | 1670.609 | 3322.877 | 5974.386 | 7619.252 | 8846.702 | 164.0832 | 329.9259 | 178.9129 | 211.0226 |
| Nd | | 6631.197 | 6690.313 | 10871.24 | 19410.58 | 24929.53 | 28614.15 | 553.4254 | 1105.671 | 601.1938 | 694.2109 |
| Sm | | 1652.766 | 1698.691 | 1408.216 | 2481.606 | 3189.255 | 3665.443 | 81.88093 | 157.1 | 83.89447 | 98.0512 |
| Gd | | 2117.884 | 2494.841 | 856.6686 | 1477.174 | 1949.033 | 2144.948 | 54.80583 | 106.7644 | 55.34537 | 64.80149 |
| Tb | | 337.5046 | 417.9429 | 101.8886 | 171.8369 | 232.1214 | 249.8993 | 7.672973 | 13.80094 | 6.893728 | 8.039725 |

| | MUQ | LE32E | LE32F | LE37A | LE37B | LE38A | LE38B | LE41A | LE41B | LE42A | LE42B |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dy | | 2041.187 | 2722.071 | 459.1262 | 754.3759 | 1043.1 | 1084.319 | 35.70604 | 65.4915 | 30.40134 | 36.82773 |
| Y | | 16925.44 | 26798.08 | 2081.298 | 3162.46 | 4692.575 | 4443.927 | 240.6644 | 359.1923 | 206.0185 | 206.8756 |
| Ho | | 458.8679 | 657.5855 | 77.25407 | 121.4204 | 174.2283 | 174.4784 | 6.601662 | 11.84898 | 5.629232 | 6.423365 |
| Er | | 1292.607 | 1979.867 | 177.0549 | 275.3026 | 394.4399 | 389.9945 | 16.80468 | 30.69669 | 14.77757 | 15.91692 |
| Tm | | 181.9866 | 293.254 | 22.50851 | 35.03818 | 51.77739 | 49.59052 | 2.575572 | 4.47076 | 2.344939 | 2.377014 |
| Yb | | 1119.075 | 1837.957 | 131.4095 | 194.3761 | 297.2072 | 270.9112 | 14.6663 | 25.69766 | 12.77215 | 14.77464 |
| Lu | | 192.0323 | 323.7433 | 18.1881 | 26.34753 | 40.37461 | 36.49252 | 2.219722 | 3.899193 | 2.042076 | 2.111293 |
| | MUQ | LE32E | LE32F | LE37A | LE37B | LE38A | LE38B | LE41A | LE41B | LE42A | LE42B |
| La | 32510 | 0.188147 | 0.197952 | 0.573263 | 1.279823 | 1.339556 | 2.990973 | 0.029482 | 0.056745 | 0.030077 | 0.03507 |
| Ce | 71090 | 0.252502 | 0.229824 | 0.463797 | 0.985763 | * | 2.363791 | 0.024435 | 0.047143 | 0.022953 | 0.027764 |
| Pr | 8460 | 0.193017 | 0.197471 | 0.392775 | 0.706192 | 0.900621 | 1.045709 | 0.019395 | 0.038998 | 0.021148 | 0.024944 |
| Nd | 32910 | 0.201495 | 0.203291 | 0.330332 | 0.589808 | 0.757506 | 0.869467 | 0.016816 | 0.033597 | 0.018268 | 0.021094 |
| Sm | 6880 | 0.240228 | 0.246903 | 0.204683 | 0.360699 | 0.463555 | 0.532768 | 0.011901 | 0.022834 | 0.012194 | 0.014252 |
| Gd | 6360 | 0.333001 | 0.392271 | 0.134696 | 0.23226 | 0.306452 | 0.337256 | 0.008617 | 0.016787 | 0.008702 | 0.010189 |
| Tb | 990 | 0.340914 | 0.422165 | 0.102918 | 0.173573 | 0.234466 | 0.252424 | 0.00775 | 0.01394 | 0.006963 | 0.008121 |
| Dy | 5890 | 0.346551 | 0.462151 | 0.07795 | 0.128077 | 0.177097 | 0.184095 | 0.006062 | 0.011119 | 0.005162 | 0.006253 |
| Y | 31850 | 0.531411 | 0.841384 | 0.065347 | 0.099292 | 0.147334 | 0.139527 | 0.007556 | 0.011278 | 0.006468 | 0.006495 |
| Ho | 1220 | 0.376121 | 0.539005 | 0.063323 | 0.099525 | 0.14281 | 0.143015 | 0.005411 | 0.009712 | 0.004614 | 0.005265 |
| Er | 3370 | 0.383563 | 0.587498 | 0.052539 | 0.081692 | 0.117044 | 0.115725 | 0.004987 | 0.009109 | 0.004385 | 0.004723 |
| Tm | 510 | 0.356836 | 0.575008 | 0.044134 | 0.068702 | 0.101524 | 0.097236 | 0.00505 | 0.008766 | 0.004598 | 0.004661 |
| Yb | 3250 | 0.344331 | 0.565525 | 0.040434 | 0.059808 | 0.091448 | 0.083357 | 0.004513 | 0.007907 | 0.00393 | 0.004546 |
| Lu | 490 | 0.391903 | 0.660701 | 0.037119 | 0.05377 | 0.082397 | 0.074475 | 0.00453 | 0.007958 | 0.004168 | 0.004309 |
| | ppb | LE42C | LE42D | LE42E | LE42F | LE42G | LE42H | LE42I | LE42J | LE44A | LE44B |
| La | | 155.3588 | 211.6713 | 824.4166 | 892.7311 | 148.3533 | 201.4321 | 63.55093 | 49.45939 | 76.7662 | 52.8725 |
| Ce | | 294.2449 | 367.9756 | 1455.84 | 1691.191 | 280.4893 | 377.8635 | 105.3039 | 83.40076 | 125.5427 | 102.4533 |
| Pr | | 26.61657 | 37.63918 | 141.9585 | 166.4948 | 25.96657 | 35.1339 | 11.6424 | 9.41596 | 14.96193 | 10.31803 |
| Nd | | 91.9328 | 123.7713 | 477.997 | 560.8917 | 85.85461 | 119.9662 | 40.23213 | 32.65993 | 48.96881 | 32.51104 |
| Sm | | 14.37981 | 18.89813 | 72.10125 | 87.03561 | 15.50659 | 17.14074 | 7.157597 | 7.750896 | 8.509481 | 5.404087 |
| Gd | | 8.780098 | 12.1206 | 52.5059 | 60.7801 | 8.80177 | 11.74228 | 4.596066 | 4.094044 | 5.856876 | 3.361825 |
| Tb | | 1.160466 | 1.673868 | 6.876559 | 8.395098 | 1.072411 | 1.402627 | 0.68622 | 0.584265 | 0.748726 | 0.435928 |
| Dy | | 5.966414 | 7.062149 | 35.8762 | 42.08304 | 5.357945 | 7.401093 | 3.271195 | 3.536209 | 3.599987 | 2.272966 |
| Y | | 50.21269 | 62.89558 | 261.61 | 286.5142 | 54.28185 | 63.29994 | 36.89933 | 42.36883 | 32.6667 | 21.81886 |

| | MUQ | LE42C | LE42D | LE42E | LE42F | LE42G | LE42H | LE42I | LE42J | LE44A | LE44B |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ho | | 1.196406 | 1.483016 | 7.275962 | 8.511413 | 1.073568 | 1.635458 | 0.82517 | 0.691325 | 0.926362 | 0.610373 |
| Er | | 3.195134 | 3.618218 | 19.8824 | 22.86938 | 2.898702 | 3.949154 | 2.142766 | 1.841253 | 1.991589 | 1.800528 |
| Tm | | 0.454106 | 0.489135 | 3.126772 | 3.294261 | 0.417021 | 0.581886 | 0.304877 | 0.202453 | 0.359437 | 0.252643 |
| Yb | | 3.099815 | 3.082795 | 19.95993 | 21.33987 | 2.739724 | 3.559133 | 1.694092 | 1.307025 | 1.723429 | 1.397868 |
| Lu | | 0.38724 | 0.438274 | 2.985499 | 3.09818 | 0.431301 | 0.543984 | 0.272908 | 0.272908 | 0.318625 | 0.20023 |
| | MUQ | LE42C | LE42D | LE42E | LE42F | LE42G | LE42H | LE42I | LE42J | LE44A | LE44B |
| La | 32510 | 0.004779 | 0.006511 | 0.025359 | 0.02746 | 0.004563 | 0.006196 | 0.001955 | 0.001521 | 0.002361 | 0.001626 |
| Ce | 71090 | 0.004139 | 0.005176 | 0.020479 | 0.023789 | 0.003946 | 0.005315 | 0.001481 | 0.001173 | 0.001766 | 0.001441 |
| Pr | 8460 | 0.003146 | 0.004449 | 0.01678 | 0.01968 | 0.003069 | 0.004153 | 0.001376 | 0.001113 | 0.001769 | 0.00122 |
| Nd | 32910 | 0.002793 | 0.003761 | 0.014524 | 0.017043 | 0.002609 | 0.003645 | 0.001222 | 0.000992 | 0.001488 | 0.000988 |
| Sm | 6880 | 0.00209 | 0.002747 | 0.01048 | 0.012651 | 0.002254 | 0.002491 | 0.00104 | 0.001127 | 0.001237 | 0.000785 |
| Gd | 6360 | 0.001381 | 0.001906 | 0.008256 | 0.009557 | 0.001384 | 0.001846 | 0.000723 | 0.000644 | 0.000921 | 0.000529 |
| Tb | 990 | 0.001172 | 0.001691 | 0.006946 | 0.00848 | 0.001083 | 0.001417 | 0.000693 | 0.00059 | 0.000756 | 0.00044 |
| Dy | 5890 | 0.001013 | 0.001199 | 0.006091 | 0.007145 | 0.00091 | 0.001257 | 0.000555 | 0.0006 | 0.000611 | 0.000386 |
| Y | 31850 | 0.001577 | 0.001975 | 0.008214 | 0.008996 | 0.001704 | 0.001987 | 0.001159 | 0.00133 | 0.001026 | 0.000685 |
| Ho | 1220 | 0.000981 | 0.001216 | 0.005964 | 0.006977 | 0.00088 | 0.001341 | 0.000676 | 0.000567 | 0.000759 | 0.0005 |
| Er | 3370 | 0.000948 | 0.001074 | 0.0059 | 0.006786 | 0.00086 | 0.001172 | 0.000636 | 0.000546 | 0.000591 | 0.000534 |
| Tm | 510 | 0.00089 | 0.000959 | 0.006131 | 0.006459 | 0.000818 | 0.001141 | 0.000598 | 0.000397 | 0.000705 | 0.000495 |
| Yb | 3250 | 0.000954 | 0.000949 | 0.006142 | 0.006566 | 0.000843 | 0.001095 | 0.000521 | 0.000402 | 0.00053 | 0.00043 |
| Lu | 490 | 0.00079 | 0.000894 | 0.006093 | 0.006323 | 0.00088 | 0.00111 | 0.000557 | 0.000557 | 0.00065 | 0.000409 |
| | ppb | SEMPA | SEMP B | SEMP C | SEMP D | FP #1 | FP #2 | FP #3 | ppb | Neo. Stroms | Cenom Lst |
| La | | 139.6259 | 287.3266 | 152.7857 | 312.8726 | 454500 | 318500 | 398000 | | 5970 | 6490 |
| Ce | | 308.4762 | 671.3686 | 364.3443 | 821.7321 | 896500 | 606100 | 690000 | | 8540 | 6970 |
| Pr | | 31.8839 | 67.03131 | 37.07521 | 107.5204 | | | 69000 | | 1060 | 970 |
| Nd | | 126.5569 | 267.1093 | 147.8366 | 472.6629 | 354000 | 257600 | 245000 | | 3530 | 3990 |
| Sm | | 28.96897 | 61.23731 | 34.61996 | 105.3005 | 46000 | 33500 | 32000 | | 550 | 790 |
| Gd | | 31.68512 | 65.55687 | 36.86235 | 101.8932 | 30200 | 22000 | 24000 | | 470 | 830 |
| Tb | | 5.150497 | 11.13068 | 6.382101 | 15.17451 | | | | | 60 | 120 |
| Dy | | 32.26325 | 69.27499 | 37.28253 | 85.38841 | | | 10300 | | 330 | 750 |
| Y | | 1244.018 | 872.1245 | 674.6628 | 859.0509 | 53000 | 38000 | 36000 | | 1770 | |
| Ho | | 7.467053 | 16.01281 | 8.722975 | 17.14336 | | | 1630 | | 70 | 200 |
| Er | | 23.71041 | 47.51117 | 26.39717 | 47.27499 | | | 4320 | | 180 | 540 |

| | MUQ | SEMPA | SEMP B | SEMP C | SEMP D | FP #1 | FP #2 | FP #3 | MUQ | Neo. Stroms | Cenom. Lst |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Tm | | 3.407051 | 7.532899 | 3.98353 | 7.23992 | 610 | 450 | 500 | | 30 | 90 |
| Yb | | 23.74783 | 47.84925 | 27.28967 | 45.22595 | 3760 | 2720 | 2640 | | 140 | 480 |
| Lu | | 3.573556 | 7.524985 | 4.101395 | 6.851154 | 510 | 370 | 350 | | 20 | 80 |
| La | 32510 | 0.004295 | 0.008838 | 0.0047 | 0.009624 | 13.980314 | 9.79699 | 12.2424 | | 0.183635804 | 0.199631 |
| Ce | 71090 | 0.004339 | 0.009444 | 0.005125 | 0.011559 | 12.610775 | 8.52581 | 9.70601 | | 0.120129413 | 0.098045 |
| Pr | 8460 | 0.003769 | 0.007923 | 0.004382 | 0.012709 | | | 8.15603 | | 0.125295508 | 0.114657 |
| Nd | 32910 | 0.003846 | 0.008116 | 0.004492 | 0.014362 | 10.756609 | 7.82741 | 7.44455 | | 0.10726223 | 0.12124 |
| Sm | 6880 | 0.004211 | 0.008901 | 0.005032 | 0.015305 | 6.6860465 | 4.86919 | 4.65116 | | 0.07994186 | 0.114826 |
| Gd | 6360 | 0.004982 | 0.010308 | 0.005796 | 0.016021 | 4.7484277 | 3.45912 | 3.77358 | | 0.073899371 | 0.130503 |
| Tb | 990 | 0.005203 | 0.011243 | 0.006447 | 0.015328 | 3.5151515 | 2.43434 | 2.49495 | | 0.060606061 | 0.121212 |
| Dy | 5890 | 0.005478 | 0.011761 | 0.00633 | 0.014497 | | | 1.74873 | | 0.056027165 | 0.127334 |
| Y | 31850 | 0.039059 | 0.027382 | 0.021183 | 0.026972 | 1.6640502 | 1.19309 | 1.1303 | | 0.055572998 | |
| Ho | 1220 | 0.006121 | 0.013125 | 0.00715 | 0.014052 | | | 1.33607 | | 0.057377049 | 0.163934 |
| Er | 3370 | 0.007036 | 0.014098 | 0.007833 | 0.014028 | | | 1.2819 | | 0.053412463 | 0.160237 |
| Tm | 510 | 0.00668 | 0.01477 | 0.007811 | 0.014196 | 1.1960784 | 0.88235 | 0.98039 | | 0.058823529 | 0.176471 |
| Yb | 3250 | 0.007307 | 0.014723 | 0.008397 | 0.013916 | 1.1569231 | 0.83692 | 0.81231 | | 0.043076923 | 0.147692 |
| Lu | 490 | 0.007293 | 0.015357 | 0.00837 | 0.013982 | 1.0408163 | 0.7551 | 0.71429 | | 0.040816327 | 0.163265 |

| | ppb | V2b/2 | V22a/2 | LE44a/2 | LE44b/2 | LE41a/2 | LE41b/2 | P12b/2 | LE24a/2 | LE24b/2 |
|---|---|---|---|---|---|---|---|---|---|---|
| La | | 195.7 | 2614 | 396.8 | 131.7 | 2857 | 3047 | 2328 | 1693 | 610.7 |
| Ce | | 308 | 7183 | 572.1 | 229.9 | 5201 | 5323 | 2363 | 618 | 204.9 |
| Pr | | 36.46 | 521.7 | 96.48 | 28.25 | 518.2 | 543.4 | 530.7 | 136.5 | 40.35 |
| Nd | | 131.7 | 1850 | 380 | 96.65 | 1760 | 1804 | 2166 | 637.7 | 191.3 |
| Sm | | 21.37 | 315.6 | 89.03 | 15.09 | 249.8 | 265.2 | 418.7 | 114.2 | 35.44 |
| Eu | | 2.982 | 40.39 | 19.29 | 3.669 | 65.21 | 64.52 | 103.5 | 37.59 | 13.74 |
| Tb | | 2.356 | 29.64 | 22.11 | 1.438 | 21.98 | 22 | 75.95 | 34.25 | 16.28 |
| Gd | | 16.96 | 222.5 | 124.2 | 12.37 | 180.7 | 181.3 | 489.8 | 248.3 | 114.2 |
| Dy | | 12.24 | 155.4 | 147.7 | 7.493 | 108 | 103.9 | 534.4 | 240.6 | 124.5 |
| Y | | 113.072 | 1276.754 | 1580.262 | 51.28363 | 679.6646 | 593.6026 | 6288.787 | 2698.247 | 1656.768 |
| Ho | | 2.241 | 30.88 | 36.01 | 1.637 | 19.19 | 19.77 | 138.7 | 64.04 | 33.71 |
| Er | | 6.16 | 78.01 | 115.2 | 3.855 | 48.82 | 49.24 | 431.4 | 183.1 | 100.9 |
| Tm | | 0.856 | 11.38 | 17.21 | 0.418 | 6.853 | 7.003 | 63.23 | 25.5 | 13.14 |

| | | 5.392 | 73.72 | 115 | 2.566 | 39.96 | 38.22 | 377.6 | 147.3 | 76.4 |
|---|---|---|---|---|---|---|---|---|---|---|
| Yb | | 5.392 | 73.72 | 115 | 2.566 | 39.96 | 38.22 | 377.6 | 147.3 | 76.4 |
| Lu | | 0.862 | 9.968 | 20.54 | 0.444 | 5.969 | 6.079 | 57.73 | 26.47 | 13.34 |
| | **MuQ** | **V2b/2** | **V22a/2** | **LE44a/2** | **LE44b/2** | **LE41a/2** | **LE41b/2** | **P12b/2** | **LE24a/2** | **LE24b/2** |
| La | 32510 | 0.00602 | 0.08041 | 0.01221 | 0.00405 | 0.08788 | 0.09373 | 0.07161 | 0.05208 | 0.01878 |
| Ce | 71090 | 0.00433 | 0.10104 | 0.00805 | 0.00323 | 0.07316 | 0.07488 | 0.03324 | 0.00869 | 0.00288 |
| Pr | 8460 | 0.00431 | 0.06167 | 0.01140 | 0.00334 | 0.06125 | 0.06423 | 0.06273 | 0.01613 | 0.00477 |
| Nd | 32910 | 0.00400 | 0.05621 | 0.01155 | 0.00294 | 0.05348 | 0.05482 | 0.06582 | 0.01938 | 0.00581 |
| Sm | 6880 | 0.00311 | 0.04587 | 0.01294 | 0.00219 | 0.03631 | 0.03855 | 0.06086 | 0.01660 | 0.00515 |
| Eu | 1570 | 0.00190 | 0.02573 | 0.01229 | 0.00234 | 0.04154 | 0.04110 | 0.06592 | 0.02394 | 0.00875 |
| Gd | 6360 | 0.00267 | 0.03498 | 0.01953 | 0.00194 | 0.02841 | 0.02851 | 0.07701 | 0.03904 | 0.01796 |
| Tb | 990 | 0.00238 | 0.02994 | 0.02233 | 0.00145 | 0.02220 | 0.02222 | 0.07672 | 0.03460 | 0.01644 |
| Dy | 5890 | 0.00208 | 0.02638 | 0.02508 | 0.00127 | 0.01834 | 0.01764 | 0.09073 | 0.04085 | 0.02114 |
| Y | 31850 | 0.00355 | 0.04009 | 0.04961 | 0.00161 | 0.02134 | 0.01864 | 0.19746 | 0.08471 | 0.05203 |
| Ho | 1220 | 0.00184 | 0.02531 | 0.02952 | 0.00134 | 0.01573 | 0.01620 | 0.11369 | 0.05249 | 0.02763 |
| Er | 3370 | 0.00183 | 0.02315 | 0.03418 | 0.00114 | 0.01449 | 0.01461 | 0.12801 | 0.05433 | 0.02994 |
| Tm | 510 | 0.00168 | 0.02231 | 0.03375 | 0.00082 | 0.01344 | 0.01373 | 0.12398 | 0.05000 | 0.02576 |
| Yb | 3250 | 0.00166 | 0.02268 | 0.03538 | 0.00079 | 0.01230 | 0.01176 | 0.11618 | 0.04532 | 0.02351 |
| Lu | 490 | 0.00176 | 0.02034 | 0.04192 | 0.00091 | 0.01218 | 0.01241 | 0.11782 | 0.05402 | 0.02722 |

# 2007-2010 Field works: Travertines samples results by ICP-MS 2016 Experiment (Results Reproducibility of the Method )

| | ppb | LE26a/2 | LE26b/2 | LE28a/2 | LE28d/2 | V19a/2 | PCK a/1 | PCK b/1 | PCK c/1 | PCK d/1 |
|----|----|---------|---------|---------|---------|--------|---------|---------|---------|---------|
| La | | 169.9 | 599.5 | 94.32 | 192.3 | 270.6 | 2745 | 2801 | 3478 | 3227 |
| Ce | | 163.6 | 158.1 | 47.02 | 96.08 | 326.1 | 4849 | 4993 | 6225 | 5732 |
| Pr | | 29.74 | 83.63 | 15.04 | 28.45 | 41.71 | 546.9 | 568.3 | 721.9 | 656.1 |
| Nd | | 118.4 | 330.3 | 61.33 | 120.9 | 172.4 | 1892 | 1990 | 2540 | 2270 |
| Sm | | 23.47 | 63.89 | 12.6 | 22.39 | 82.98 | 305.1 | 338.3 | 441.8 | 387 |
| Eu | | 5.985 | 21.61 | 4.409 | 5.613 | 4.781 | 56.98 | 62.49 | 84.02 | 72.79 |
| Tb | | 4.07 | 12.73 | 3.188 | 5.439 | 9.298 | 36.26 | 40.18 | 54.93 | 47.02 |
| Gd | | 29.71 | 87.75 | 18.28 | 31.08 | 72.98 | 249 | 279.5 | 381 | 321 |
| Dy | | 26.82 | 82.03 | 22.72 | 40.92 | 58.02 | 193.1 | 219.7 | 301.2 | 251.5 |
| Y | | 922.4897 | 1342.21 | 465.0734 | 740.3612 | 867.3339 | 1098.509 | 1228.574 | 1641.364 | 1382.347 |
| Ho | | 7.575 | 19.24 | 7.071 | 11.79 | 13.14 | 37.5 | 43.07 | 58.2 | 48.62 |
| Er | | 25.79 | 55.3 | 23.02 | 39.15 | 35.35 | 94.1 | 107.7 | 144.9 | 122.8 |
| Tm | | 3.378 | 7.184 | 3.468 | 5.785 | 4.96 | 13.14 | 14.93 | 19 | 15.78 |
| Yb | | 20.2 | 39.48 | 23.9 | 36.51 | 29.17 | 76.22 | 87.97 | 106.3 | 90.89 |
| Lu | | 3.711 | 7.321 | 3.693 | 5.822 | 4.261 | 10.53 | 12.36 | 14.89 | 12.81 |
| | MuQ | LE26a/2 | LE26b/2 | LE28a/2 | LE28d/2 | V19a/2 | PCK a/1 | PCK b/1 | PCK c/1 | PCK d/1 |
| La | 32510 | 0.00523 | 0.01844 | 0.00290 | 0.00592 | 0.00832 | 0.08444 | 0.08616 | 0.10698 | 0.09926 |
| Ce | 71090 | 0.00230 | 0.00222 | 0.00066 | 0.00135 | 0.00459 | 0.06821 | 0.07023 | 0.08757 | 0.08063 |
| Pr | 8460 | 0.00352 | 0.00989 | 0.00178 | 0.00336 | 0.00493 | 0.06465 | 0.06717 | 0.08533 | 0.07755 |
| Nd | 32910 | 0.00360 | 0.01004 | 0.00186 | 0.00367 | 0.00524 | 0.05749 | 0.06047 | 0.07718 | 0.06898 |
| Sm | 6880 | 0.00341 | 0.00929 | 0.00183 | 0.00325 | 0.01206 | 0.04435 | 0.04917 | 0.06422 | 0.05625 |
| Eu | 1570 | 0.00381 | 0.01376 | 0.00281 | 0.00358 | 0.00305 | 0.03629 | 0.03980 | 0.05352 | 0.04636 |
| Gd | 6360 | 0.00467 | 0.01380 | 0.00287 | 0.00489 | 0.01147 | 0.03915 | 0.04395 | 0.05991 | 0.05047 |
| Tb | 990 | 0.00411 | 0.01286 | 0.00322 | 0.00549 | 0.00939 | 0.03663 | 0.04059 | 0.05548 | 0.04749 |
| Dy | 5890 | 0.00455 | 0.01393 | 0.00386 | 0.00695 | 0.00985 | 0.03278 | 0.03730 | 0.05114 | 0.04270 |
| Y | 31850 | 0.02896 | 0.04214 | 0.01460 | 0.02325 | 0.02723 | 0.03451 | 0.03859 | 0.05152 | 0.04339 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ho | 1220 | 0.00621 | 0.01577 | 0.00580 | 0.00966 | 0.01077 | 0.03074 | 0.03530 | 0.04770 | 0.03985 |
| Er | 3370 | 0.00765 | 0.01641 | 0.00683 | 0.01162 | 0.01049 | 0.02792 | 0.03196 | 0.04300 | 0.03644 |
| Tm | 510 | 0.00662 | 0.01409 | 0.00680 | 0.01134 | 0.00973 | 0.02576 | 0.02927 | 0.03725 | 0.03094 |
| Yb | 3250 | 0.00622 | 0.01215 | 0.00735 | 0.01123 | 0.00898 | 0.02345 | 0.02707 | 0.03271 | 0.02797 |
| Lu | 490 | 0.00757 | 0.01494 | 0.00754 | 0.01188 | 0.00870 | 0.02149 | 0.02522 | 0.03039 | 0.02614 |

**2014 Field works: Travertines samples results obtained by the 2018 ICP-MS Experiment**

| | ppb | MDW 74 A | MDW74 B | MDW 74 C | MDW 125 A | MDW 125 B | MDW 276 A | MDW 276B | MDW 277 | MDW 162 A | MDW 162B |
|---|---|---|---|---|---|---|---|---|---|---|---|
| La | | 734 | 888 | 936 | 32550 | 34340 | 6337 | 7255 | 13860 | 312 | 90 |
| Ce | | 1092 | 1215 | 1276 | 60180 | 55470 | 10820 | 12690 | 26810 | 474 | 120 |
| Pr | | 123 | 137 | 146 | 7188 | 7602 | 1424 | 1699 | 3553 | 59 | 15 |
| Nd | | 453 | 505 | 527 | 28940 | 30510 | 5670 | 6855 | 14070 | 232 | 61 |
| Sm | | 82 | 90 | 91 | 6028 | 6318 | 1162 | 1392 | 2844 | 45 | 10 |
| Eu | | 22 | 24 | 26 | 1306 | 1393 | 289 | 334 | 657 | 10 | 2 |
| Tb | | 13 | 13 | 14 | 901 | 958 | 199 | 218 | 380 | 8 | 2 |
| Gd | | 83 | 90 | 93 | 6060 | 6448 | 1321 | 1455 | 2587 | 50 | 14 |
| Dy | | 75 | 85 | 86 | 5104 | 5484 | 1248 | 1270 | 2076 | 49 | 14 |
| Y | | 614 | 681 | 691 | 36080 | 38140 | 12350 | 10400 | 11980 | 556 | 233 |
| Ho | | 16 | 18 | 18 | 1040 | 1109 | 274 | 267 | 403 | 11 | 4 |
| Er | | 46 | 50 | 50 | 2620 | 2801 | 742 | 698 | 1009 | 36 | 13 |
| Tm | | 6 | 7 | 7 | 344 | 368 | 102 | 93 | 137 | 5 | 2 |
| Yb | | 37 | 42 | 41 | 1917 | 2082 | 578 | 534 | 794 | 33 | 12 |
| Lu | | 5 | 6 | 6 | 259 | 282 | 83 | 75 | 111 | 5 | 2 |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |

|     | MUQ   | MDW 74 A  | MDW74 B   | MDW 74 C | MDW 125 A  | MDW 125 B  | MDW 276 A  | MDW 276B   | MDW 277  | MDW 162 A  | MDW 162B |
|-----|-------|-----------|-----------|----------|------------|------------|------------|------------|----------|------------|----------|
| La  | 32510 | 0.0225623 | 0.0273024 | 0.0288   | 1.00123039 | 1.05629037 | 0.19492464 | 0.2231621  | 0.42633  | 0.00958167 | 0.002767 |
| Ce  | 71090 | 0.0153608 | 0.017091  | 0.017949 | 0.84653256 | 0.78027852 | 0.15220143 | 0.17850612 | 0.377128 | 0.00667042 | 0.001691 |
| Pr  | 8460  | 0.0145508 | 0.0162293 | 0.017305 | 0.84964539 | 0.89858156 | 0.16832151 | 0.20082742 | 0.419976 | 0.006974   | 0.001717 |
| Nd  | 32910 | 0.013777  | 0.0153388 | 0.016022 | 0.87936797 | 0.92707384 | 0.17228806 | 0.20829535 | 0.42753  | 0.00704345 | 0.001845 |
| Sm  | 6880  | 0.0118663 | 0.0130538 | 0.013266 | 0.87616279 | 0.91831395 | 0.16889535 | 0.20232558 | 0.413372 | 0.00655959 | 0.001516 |
| Eu  | 1570  | 0.0140573 | 0.0151338 | 0.016268 | 0.83184713 | 0.88726115 | 0.18401274 | 0.21261146 | 0.418535 | 0.00630828 | 0.001355 |
| Gd  | 6360  | 0.0130818 | 0.0141887 | 0.014557 | 0.95283019 | 1.01383648 | 0.2077044  | 0.22877358 | 0.406761 | 0.00790252 | 0.002263 |
| Tb  | 990   | 0.0128283 | 0.0135354 | 0.014212 | 0.90989899 | 0.96717172 | 0.20131313 | 0.22020202 | 0.383939 | 0.00777071 | 0.002056 |
| Dy  | 5890  | 0.0126689 | 0.0143905 | 0.014608 | 0.86655348 | 0.93106961 | 0.21188455 | 0.21561969 | 0.352462 | 0.00824448 | 0.002419 |
| Y   | 31850 | 0.0192873 | 0.0213721 | 0.021705 | 1.13281005 | 1.19748823 | 0.3877551  | 0.32653061 | 0.376138 | 0.01745369 | 0.007316 |
| Ho  | 1220  | 0.0131721 | 0.015082  | 0.015016 | 0.85245902 | 0.90901639 | 0.22467213 | 0.21860656 | 0.330492 | 0.00940164 | 0.003029 |
| Er  | 3370  | 0.0136172 | 0.0146884 | 0.014777 | 0.77744807 | 0.83115727 | 0.22008902 | 0.20718101 | 0.299407 | 0.01081009 | 0.003772 |
| Tm  | 510   | 0.0120765 | 0.0129824 | 0.013465 | 0.67352941 | 0.72215686 | 0.19921569 | 0.18245098 | 0.268824 | 0.01007059 | 0.003857 |
| Yb  | 3250  | 0.0113138 | 0.0130031 | 0.012529 | 0.58984615 | 0.64061538 | 0.17775385 | 0.16415385 | 0.244215 | 0.01024308 | 0.0038   |
| Lu  | 490   | 0.011098  | 0.0113878 | 0.012539 | 0.52918367 | 0.57571429 | 0.1695102  | 0.15361224 | 0.226735 | 0.0108898  | 0.004424 |

|     | ppb | MDW 43 | MDW 42 A | BV 344  | BV 352 | BV 356 | MDW 42 B | BV 364  | BV 385 | BV 149 A | BV 363  |
|-----|-----|--------|----------|---------|--------|--------|----------|---------|--------|----------|---------|
| La  |     | 2824   | 360      | 621800  | 383200 | 364400 | 324      | 1156000 | 243100 | 792      | 2102000 |
| Ce  |     | 5190   | 490      | 1111000 | 631200 | 672900 | 436      | 2004000 | 397800 | 6059     | 3898000 |
| Pr  |     | 608    | 55       | 109200  | 64900  | 61480  | 49       | 203400  | 44080  | 393      | 378600  |
| Nd  |     | 2309   | 194      | 355600  | 204700 | 191500 | 175      | 662100  | 141200 | 2042     | 1215000 |
| Sm  |     | 429    | 36       | 46980   | 25890  | 24240  | 29       | 84840   | 18720  | 825      | 158700  |
| Eu  |     | 93     | 9        | 12350   | 6626   | 6088   | 8        | 21790   | 4719   | 196      | 40330   |
| Tb  |     | 51     | 6        | 3910    | 1977   | 1832   | 4        | 6488    | 1463   | 233      | 12650   |
| Gd  |     | 367    | 38       | 29910   | 15660  | 14580  | 32       | 51750   | 11490  | 1135     | 99300   |
| Dy  |     | 271    | 34       | 18820   | 9057   | 8303   | 29       | 29800   | 6791   | 1572     | 59060   |

| | MUQ | MDW 43 | MDW 42 A | BV 344 | BV 352 | BV 356 | MDW 42 B | BV 364 | BV 385 | BV 149 A | BV 363 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Y | | 2479 | 316 | 88670 | 43630 | 37840 | 265 | 138600 | 31450 | 9607 | 267700 |
| Ho | | 55 | 8 | 3401 | 1607 | 1445 | 6 | 5255 | 1196 | 348 | 10540 |
| Er | | 140 | 23 | 8551 | 3897 | 3469 | 19 | 12830 | 2936 | 1020 | 26170 |
| Tm | | 19 | 3 | 1223 | 536 | 474 | 3 | 1817 | 402 | 156 | 3642 |
| Yb | | 108 | 20 | 7461 | 3134 | 2800 | 16 | 11480 | 2365 | 1005 | 22370 |
| Lu | | 15 | 3 | 1023 | 418 | 379 | 2 | 1649 | 319 | 140 | 3037 |
| La | 32510 | 0.086866 | 0.01108 | 19.12642 | 11.78714 | 11.20886 | 0.009969 | 35.55829 | 7.477699 | 0.024371 | 6.465703 |
| Ce | 71090 | 0.073006 | 0.006886 | 15.62808 | 8.878886 | 9.465466 | 0.006136 | 28.18962 | 5.595724 | 0.08523 | 5.48319 |
| Pr | 8460 | 0.071868 | 0.006504 | 12.9078 | 7.671395 | 7.267139 | 0.005752 | 24.04255 | 5.210402 | 0.046466 | 4.475177 |
| Nd | 32910 | 0.070161 | 0.005898 | 10.80523 | 6.219994 | 5.8189 | 0.005314 | 20.11851 | 4.290489 | 0.062048 | 3.691887 |
| Sm | 6880 | 0.062369 | 0.005263 | 6.828488 | 3.763081 | 3.523256 | 0.004158 | 12.3314 | 2.72093 | 0.119855 | 2.306686 |
| Eu | 1570 | 0.05914 | 0.005937 | 7.866242 | 4.220382 | 3.877707 | 0.00512 | 13.87898 | 3.005732 | 0.124777 | 2.56879 |
| Gd | 6360 | 0.057736 | 0.006019 | 4.70283 | 2.462264 | 2.292453 | 0.004987 | 8.136792 | 1.806604 | 0.178459 | 1.561321 |
| Tb | 990 | 0.051182 | 0.005724 | 3.949495 | 1.99697 | 1.850505 | 0.004317 | 6.553535 | 1.477778 | 0.235657 | 1.277778 |
| Dy | 5890 | 0.045993 | 0.005735 | 3.195246 | 1.537691 | 1.409677 | 0.004983 | 5.059423 | 1.152971 | 0.266893 | 1.002716 |
| Y | 31850 | 0.077834 | 0.009925 | 2.783987 | 1.369859 | 1.188069 | 0.008333 | 4.351648 | 0.987441 | 0.301633 | 0.840502 |
| Ho | 1220 | 0.044705 | 0.006375 | 2.787705 | 1.317213 | 1.184426 | 0.005308 | 4.307377 | 0.980328 | 0.284836 | 0.863934 |
| Er | 3370 | 0.041484 | 0.006855 | 2.537389 | 1.15638 | 1.029377 | 0.00554 | 3.807122 | 0.871217 | 0.302671 | 0.776558 |
| Tm | 510 | 0.037314 | 0.006445 | 2.398039 | 1.051765 | 0.930196 | 0.005233 | 3.562745 | 0.787255 | 0.304902 | 0.714118 |
| Yb | 3250 | 0.033231 | 0.006163 | 2.295692 | 0.964308 | 0.861538 | 0.004886 | 3.532308 | 0.727692 | 0.309231 | 0.688308 |
| Lu | 490 | 0.03151 | 0.005941 | 2.087755 | 0.852653 | 0.773673 | 0.004594 | 3.365306 | 0.650816 | 0.286531 | 0.619796 |

| | ppb | BV 149 B | BV 150 | BV 153 | BV 338 | BV 159 A | BV 159 B | BV 161 B | BV 162 A | BV 163 A | BV 164 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| La | | 351 | 114 | 16680 | 779500 | 1213 | 1323 | 374 | 176 | 262 | 111 |
| Ce | | 4573 | 1460 | 51040 | 1390000 | 3587 | 3706 | 450 | 355 | 222 | 101 |
| Pr | | 285 | 67 | 3764 | 148400 | 400 | 444 | 50 | 50 | 35 | 12 |
| Nd | | 1623 | 412 | 13310 | 489100 | 1831 | 2029 | 205 | 261 | 234 | 55 |
| Sm | | 739 | 250 | 2125 | 65800 | 628 | 732 | 107 | 225 | 229 | 45 |
| Eu | | 197 | 78 | 197 | 17170 | 191 | 224 | * | 94 | * | * |

| | MUQ | BV 149 B | BV 150 | BV 153 | BV 338 | BV 159 A | BV 159 B | BV 161 B | BV 162 A | BV 163 A | BV 164 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Tb | | 214 | 110 | 284 | 5251 | 214 | 263 | 22 | 114 | 63 | 14 |
| Gd | | 1051 | 477 | 2169 | 41500 | 1016 | 1218 | 113 | 655 | 361 | 55 |
| Dy | | 1481 | 825 | 2411 | 24890 | 1514 | 1857 | 130 | 586 | 325 | 101 |
| Y | | 9325 | 5879 | 11500 | 115100 | 10340 | 12730 | 1365 | 3373 | 2230 | 1169 |
| Ho | | 335 | 197 | 429 | 4427 | 335 | 409 | 24 | 101 | 54 | 20 |
| Er | | 979 | 589 | 1243 | 11030 | 949 | 1167 | 60 | 219 | 124 | 54 |
| Tm | | 149 | 89 | 80 | 1555 | 138 | 170 | 9 | 25 | 17 | 7 |
| Yb | | 941 | 578 | 1251 | 9482 | 851 | 1049 | 52 | 125 | 98 | 47 |
| Lu | | 134 | 83 | 151 | 1310 | 118 | 145 | 8 | 17 | 15 | 7 |
| | MUQ | BV 149 B | BV 150 | BV 153 | BV 338 | BV 159 A | BV 159 B | BV 161 B | BV 162 A | BV 163 A | BV 164 |
| La | 32510 | 0.0108 | 0.003516 | 0.513073 | 23.97724 | 0.037312 | 0.040695 | 0.011501 | 0.005426 | 0.008053 | 0.003408 |
| Ce | 71090 | 0.064327 | 0.020537 | 0.717963 | 19.55268 | 0.050457 | 0.052131 | 0.006326 | 0.004995 | 0.003121 | 0.001415 |
| Pr | 8460 | 0.0337 | 0.007882 | 0.444917 | 17.54137 | 0.047317 | 0.05247 | 0.005913 | 0.005905 | 0.004124 | 0.0014 |
| Nd | 32910 | 0.049316 | 0.012504 | 0.404436 | 14.86174 | 0.055637 | 0.061653 | 0.006223 | 0.00794 | 0.007122 | 0.001669 |
| Sm | 6880 | 0.10734 | 0.036366 | 0.308866 | 9.563953 | 0.091206 | 0.106323 | 0.015552 | 0.032645 | 0.033256 | 0.006516 |
| Eu | 1570 | 0.125159 | 0.049707 | 0.12535 | 10.93631 | 0.121656 | 0.142675 | * | 0.059573 | * | * |
| Gd | 6360 | 0.165252 | 0.075063 | 0.341038 | 6.525157 | 0.159748 | 0.191509 | 0.017799 | 0.10294 | 0.056698 | 0.008654 |
| Tb | 990 | 0.21596 | 0.111313 | 0.286364 | 5.30404 | 0.216061 | 0.265253 | 0.022475 | 0.115253 | 0.064081 | 0.013939 |
| Dy | 5890 | 0.251443 | 0.140119 | 0.409338 | 4.225806 | 0.257046 | 0.31528 | 0.022088 | 0.099542 | 0.055127 | 0.017182 |
| Y | 31850 | 0.292779 | 0.184584 | 0.361068 | 3.613815 | 0.324647 | 0.399686 | 0.042857 | 0.105903 | 0.070016 | 0.036703 |
| Ho | 1220 | 0.274344 | 0.161475 | 0.351721 | 3.628689 | 0.274262 | 0.334918 | 0.019557 | 0.083115 | 0.044352 | 0.016131 |
| Er | 3370 | 0.290386 | 0.174896 | 0.368843 | 3.272997 | 0.281632 | 0.346291 | 0.017864 | 0.065074 | 0.036914 | 0.016062 |
| Tm | 510 | 0.291961 | 0.174431 | 0.157059 | 3.04902 | 0.269608 | 0.332745 | 0.016924 | 0.04849 | 0.03249 | 0.014312 |
| Yb | 3250 | 0.289508 | 0.177785 | 0.384923 | 2.917538 | 0.261846 | 0.322769 | 0.015905 | 0.038338 | 0.030028 | 0.014348 |
| Lu | 490 | 0.273878 | 0.169633 | 0.308367 | 2.673469 | 0.241224 | 0.295918 | 0.017047 | 0.034327 | 0.030245 | 0.014871 |

**Note:**

*for diverse technical reasons, the ICP-MS equipment didn't detect some few elements signature in some samples.

# Appendix 3 : Travertines  investigation Field Notes

*Special acknowledgement :*

*The  field notes  from the  2007-2009 Travertines investigation campaigns  in Uganda and 2014 in DRC  are personal notes and scketchs drawn  by  Dr Christopher Nicholas.*

025 @
827 709
9994 238

Western wall of Kyemango crater (Baboon cliffs)
Another excellent viewpoint stop.
To the NNE of here you can see into the wall of the crater west of Kyanaturun hill.
Apparent extensional faults are present on both flanks, and possibly in back wall - tectonic? or more likely to be extensional collapse as floor of crater subsides post eruption.



View looking NNE at ~1km wide crater ~2.5km away.

026
830930
9992 854

(LE18)
bottle of black scum

Continued driving, and from eastern flank of Lake Kitagata saw 'oily' scum floating round lake margins on SW side where hot springs are marked.
Fought our way down and sampled a black algal scum floating on the lake shore. Translucent bubbles.
oil seep up spring conduit?

Drove on towards Kasese to look for exposed border fault.

027 @
167 867
0005 261
@
1007 ^
(MC 1950)

Tried getting a track west into the Ruwenzori border fault.
Failed once.
Second one here ended in a Lst Quarry.
Collected two grab samples, one of which appears to have ?bitumen residue lining the cavities.
Collected both as LE19 and LE20 (bitumen? or is it some sort of matt black ore mineral growth?)
Bucketing down with rain.

NB. the Lsts at 027 are 92m above the current level of Lake George. Which is not far away from here.
Uplift of Lsts along Ruwenzori border fault?

C. J. Nicholas

Tropical Geology
Exploration Group

TUES 14th    THE QUESTION OF THE BORDER LIMESTONES

028a
833417
0000617
@974m
The GPS
position
is at
entrance
to dry
stream
bed

028b
is ~200m
NW of
28a at
behind
of the
stream

Left cars at end of track just North
of Kasese / Congo border road junction.
A series of 3 valleys incise the low hills
along the Rwenzori Mtn front.
We have walked up the base of the middle
one to here.

Here there are dark yellowish orange
fine coarse Qtz sands, grits and pebbly
sands ~10m thick unconformably overlain
with extreme angularity by Kaiso tuffs
~2m thick.
No evidence of continuous lst bands
here, but top of the sands has formed
a calcite.                    (incision)
Fairly impressive cliffs here — uplift or
rotational uplift on top of normal fault
block?
Dry waterfall here testifies to incision of
channel.
Traced down about 2m from old river
floor too. — Recent base level fall?



Syn-depositional
normal
faulting

or
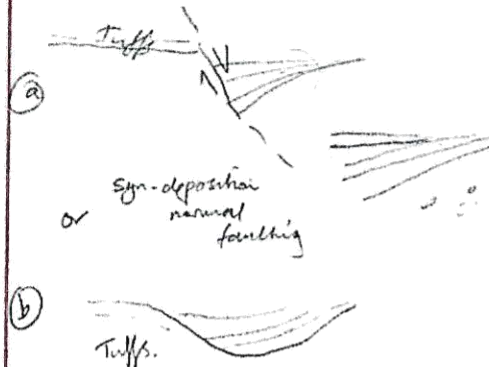
Tuffs.

Tuffs fill erosional gully?
View from road back at our valley.
The tuffs on the N side far or thicker
against a fault active during Kaiso
eruption?? or just an erosional valley?

029 @
995m
167934
0005144

Actually in the lst quarry we visited
yesterday in the rain — allowed access and
it is now clear that there is a black
organic-rich fill to the primary porosity in
the tufa limestone.
It crumbles with the finger nail but we
are undecided about the oily/bituminous
smell.
Samples for petrographic study: LE21,22,23
24,25
2x bags LE26 for geochemistry

C. J. Nicholas

This place is called LYGMUBUZA

The black organic-rich deposit appears to fill vuggy cavities in the tufa. In terms of the original depositional environment, were these algal organic-rich beds within the tst forming pools - ie farm district beds?

In the fresh cliff exposure the presence seems to be cavity fill only and there are no 'shale' beds or laminae. Also there are exposures where the 'black' vug fill cross-cuts the tufa in cross-section very irregularly ie it is a later migration not an original in situ feature conclusion - relict hydrocarbons.

030 @
1134m
831712
0002091
Kikoringo

Quarry in greissic basement close to Border fault

[sketch]
craters
Tuffs?
Thick trees
E Road
lst at surface
green grass (veg change)
Blocks of cuvias
looking S. from Quarry
Border fault must almost follow road
not fills
NW - SE fault along stream?
why are the lsts on the footwall of the border fault here should be hangs?

The lst at the surface that the locals have led us to is actually fine feature ash with calcite developed in it so that it fizzes.

031
171989
0011737
@ 949m

Drove back N. towards Kasese. Stopped just on N side of Muhokya.
Only ~100m NW of the tarmac road they are quarrying lst in a stream bed.
Here the lst is 'cleaner'. There is less porosity (and surely less effective porosity).
There is evidence of bitumen fill in the tufa cavities, but it is far less well developed and clearly in more porous patches.
Conclusion - Bitumen present, but less porosity in lst has blocked much of its migration.
LE27 for geochem: had bituminous smell when freshly broken
LE28 } for petrography.     raw tweaking
LE29 }

032 @
989m
171394
0011611

MUHOKYA village
KABUGA Hot springs - follow path up to S. of line hills at 031

Unit 2 has same effective porosity as there are same later calcite cement fringes in the cavities.
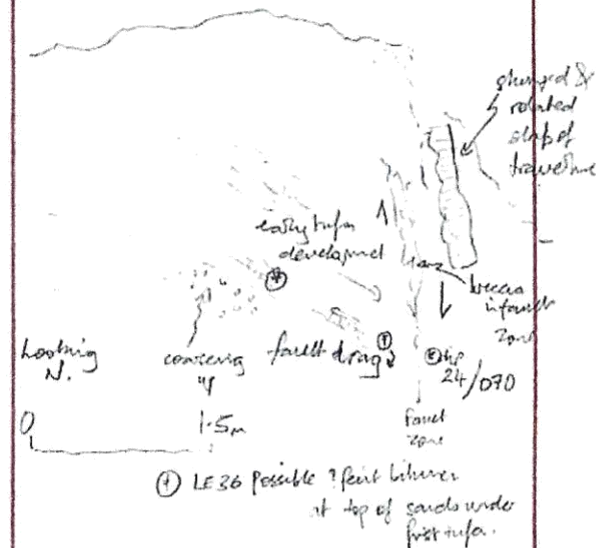
However the cavities (which are rarer) in the travertine unit ③ are 'clean' ie. no fluid has subsequently passed through these.

Overall, the presence of poorly sorted sands mixed in with the tufa here suggests more clastic debris was being influxed down the active border fault scarp during hot spring tufa deposition. The border fault this side seems to be sealing.

LE 32 – Unit 2
LE 33 – Unit 3
LE 34 – Unit 4
LE 35 – Unit 5

• Another 10m W. the scarp at the same level shows easterly dipping Ms. friable Qtz sands and grits, poorly sorted in a really soft matrix pale grey/buff, passing up into sands with early tufa tst development.



Looking N.

coarsening ↑    fault drag ①    ⑪ bhg 24/070

0          1·5m                fault zone

early tufa 1 development horizon

slumped & rotated slab of travertine

breccia in fault zone

① LE 36 Possible ? fault between at top of sands under first tufa.

035
185 823
0031483
@867m

Drove back to Thira, to the cement works mine on the N River bank, just downstream. Here they pulled several samples from the ore shute in the adit far no and poured hot water on them. Half stayed normal, but half heated up, went white (speckled with bitumen in vuggy cavities) and became extremely hot.
Sodium or potassium salts?
The porosity in the tst is much tighter

than the vugs previously on this
Ruwenzori border fault.
Sampled ?bituminous Na or K carb
and vuggy carb.

LE 37 - Lsts
LE 38 - Lsts
LE 39 - Na/K ? partly burnt?
LE 40 - Na/K ? prehnic

**THURS 13th**

## ROAD TO BWERA/CONGO BORDER

Drove round to junction between Kasese
and Bwera tarmac roads at kikorango
crater.
Took the road to Bwera at the Congo
border.

**THE 'EQUATOR ROAD SECTION'**

Almost immediately that the road starts
to climb, there is an excellent road
section exposed for about ~250m on the
SW cutting of the road, actually
crossing the equator walking through
the section!

Took a series of panoramic photos
of the section, but what follows are
key points along its length.



overall structure
looking SW
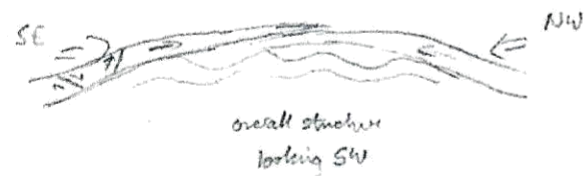
Hill they go or whether it is a
superficial covering only.
If into hill, must be a Lst thickness of
~50m
At the base there are angular pebbles
which suggests they are developed on
old fluvial seds.

Must be a bounding fault trending
NW-SE, against which the hot springs
have developed.



Looking NW

⑫ LE41 - tufa at base.
No bitumen present, but there are some
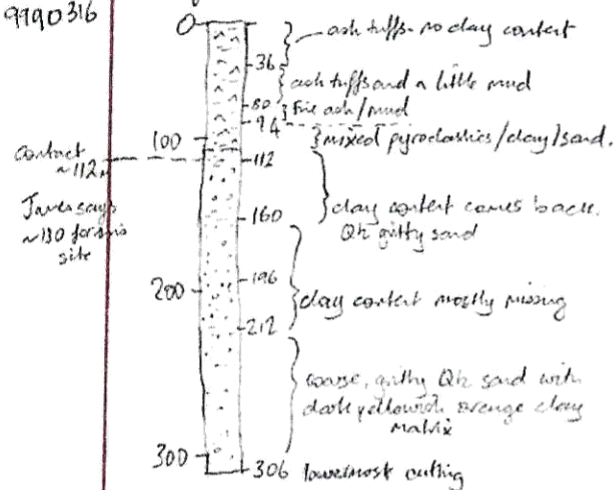excellent examples of palaeo stalactites
collected a couple as LE42.

044 @
823 097
9986612

[310m deep cased hole #1]
Drove back to meet the Geothermal
Drilling team from Ministry of Energy –
drilling shallow holes in and around native
volcanics

045 @
822 374
9790316

Next hole they have just finished
drilling. We were able to look at the cuttings



0 — ash tuffs - no clay content
36 — ash tuffs and a little mud
80 — fine ash / mud
94 — mixed pyroclastics / clay / sand.
Contact ~112m
James says ~130 for this site
112
100
160 — clay content comes back.
Qtz gritty sand
196
200
212 — clay content mostly missing
coarse, gritty Qtz sand with
dark yellowish orange clay
matrix
300 — 306 lowermost cutting

Still close to the mountain front – fluvial
fans delivering immature seds from S end
of Ruwenzori's.
So, no source rocks under here as likely
as not.

| | |
|---|---|
| 049 @ 176156 9971630 | Quickly stopped at a nice quarry in the wall of a crater. Total mess of boulders/blocks and some steeping normal faults |
| 050 @ 177790 9966892 | Narrowing wedge of volcanics – here there is an excellent view of folded basement to the SSW (see map). turned back. |

Turned down the track to JACANA LODGE, to head for the 'BAT CAVE'.
Parked and walked in through forest for ~15-20min
later led to box-roofed cave apparently with before in its walls, but a roof of tuffs.
Took a piece of the tuffs. LE64
Walked on up hill to see pools – these seen to be springs emanating here and

Spring @
051
171976
9969576

the river flows down and has produced the cave (which is more of an underground river system with potholes through the thin tuff roof.
spring river flows to 264° (almost due W).
spring must be along a geological junction – border fault? Water comes up along

---

junction between impermeable basement and structured seds on top?
Potholes through tuff just N of river ravine @ 171883, 9969620 (052)
Downstream entrance to bat cave (which slopes). @ 171930, 9969684 (053)

055 Car park at end of track @ 171607 9968758.
Lst hor.
fine wispy cavities, friable and no bitumen.

NB If the Buyanguru Volcanoes are older than the Kabwe, then the eastern lits are older than those at Muhalapa ie, because fault moved ?? eastern boundary fault

| | |
|---|---|
| 27/11/2010<br>locality 002<br>@<br>833417<br>0000 617<br>Elevation 974 (✳) ✓<br><br>Local name<br>Biruma | Biruma quarry<br>Limestone quarry operated by<br>artisanal diggers extracting<br>limestones block, crushed and<br>sold for construction purposes<br>2 : light brown, very crumble<br>lst + vugs porosity +<br>visible rootlets branches<br>and plant tubes |
| 03/12/2010<br>locality<br>006<br>@<br>313104<br>252027<br>Elevation:<br>670 m | Mayi ya Moto<br>Hot springs : boiling waters<br>Black stained lining liquid<br>flowing along the parallel<br>direction of the road<br>Goma - Vitshumbi<br>→ Black stain in white<br>vugs spreaded travertines |

Mayi ya Moto

(*) $V_{19}$ : Possible relict, degraded
on coating cavities in
a hot spring Travertines
limestone

Looks more "soily" but enough
worth at look

→ Due to safety issue, no
time to examine in details

(*) $V_{20}$ : Travertine samples identical
with $V_{19}$ but collected in
the same line downstream the
(*) $V_{21}$ : liquid flow

travertines samples collected
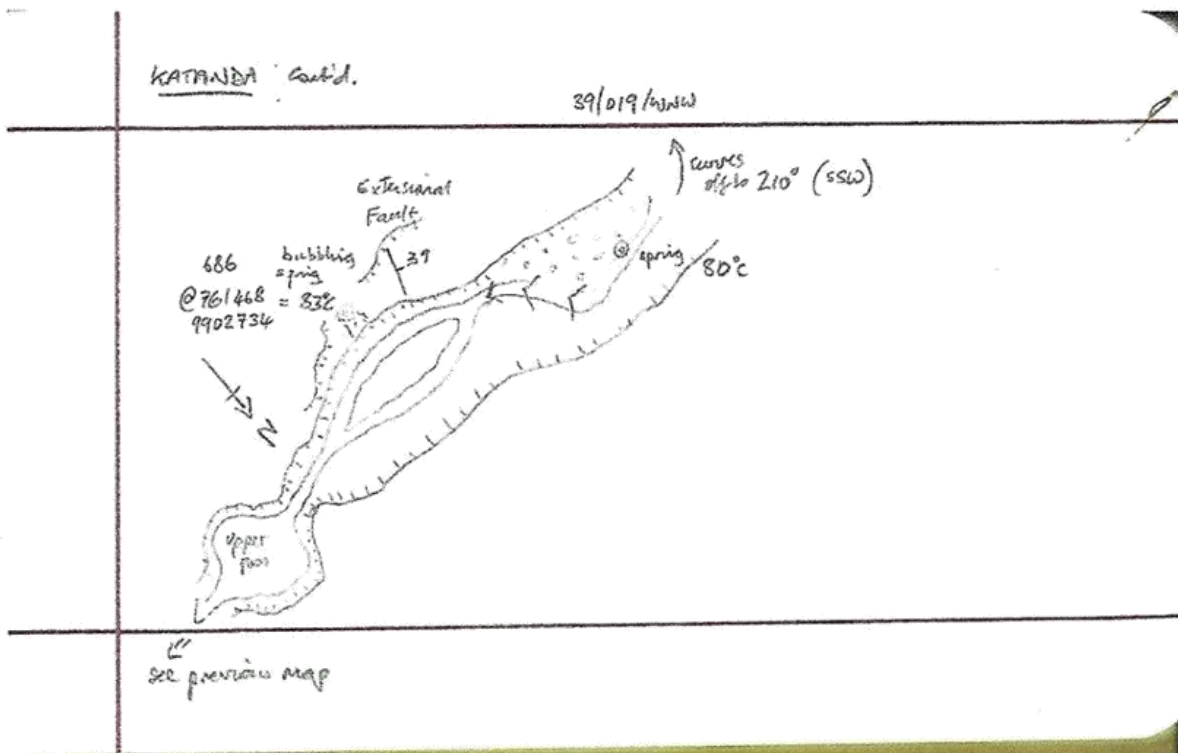further downstream of $V_{20}$

KATANDA.

see next map ↗

slope covered with black algae

Tufa 1st drape

spring with flowstone breaks

Dipping water @51°C

upper pool

76°C

V153 stalactite

Spring

Spring

Falls

47°C

lower pool

Tufa 1st couplet drape

Black slate V152

46°C

Strong H2S smell

Tufa 1st drape on cliffs.

"illustrated length" ~100m

↓N

(V149)
(V150)
(V151)

---

TUES 15th.

685 @
7014814
1902 9714

local name = KATANDA
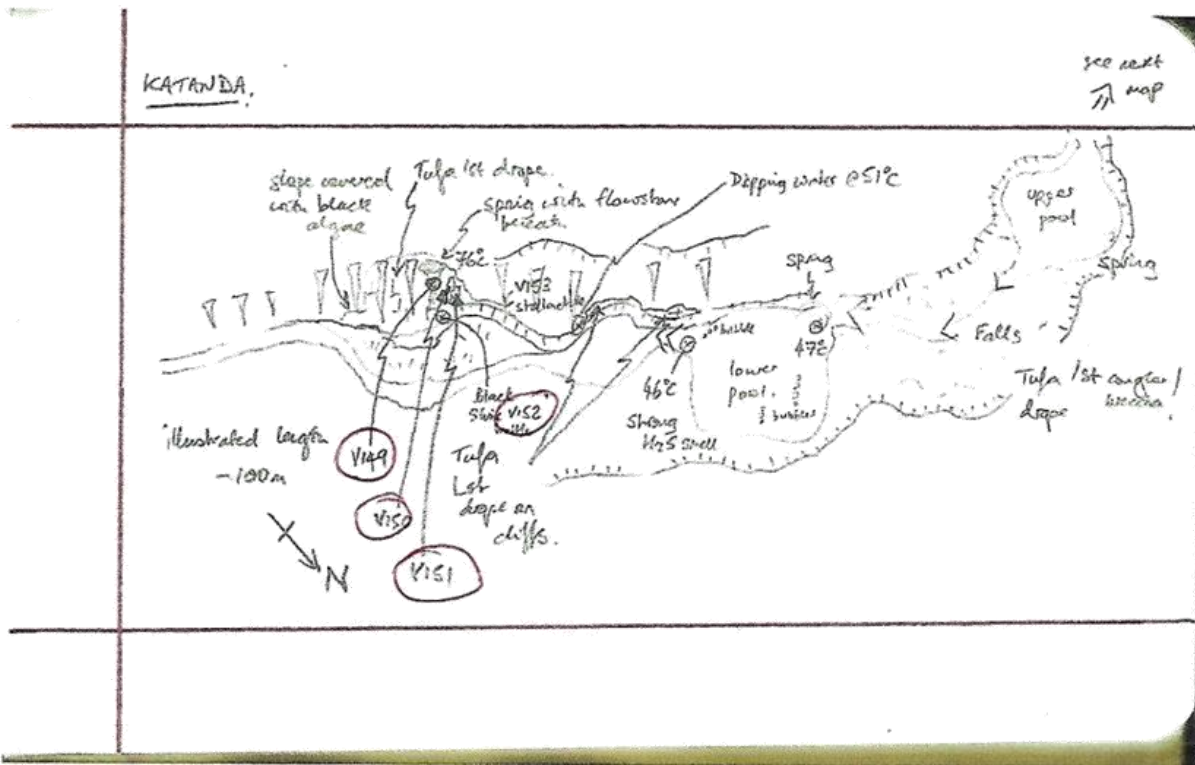
MAI YA MOTO : AREA 2

Here a incised valley trending 320° (NW) at first glance from the helicopter appeared to have a relict oil seep.

Now here on the ground it is a linear hot spring locality with algae growing up the steep sides.

A network of lesser-white veins shoots through the cliff. fall side here, and there is tufa 1st draping the steep valley sides.

The stream flows back on itself further to the NW and it suggests it is following the steeply dipping and curving basement edge, rather than a 'linear' rift fault.

• see over for map ..

NE

→ trending ? from faulting

SW
faults

031

Moved on to Mai ya Moto:

KUTh #2263

S.9.5043 282.1  3 Sept such?

Just below one of the main active
bubbling vents on southern margin

Vent temp = 93°C

Next vent to SSW, at 96°C
and the next is 93°C

• New patches of dripping tufa cut:
2 distinct beds

KUTh
0.9 66.8 12.7

39/036
and 63/028
42/014

cavity top
pendant stalactite
VISS scar block
filereno layers
breccia gap
VIS4on
primarily laminated fibrous layers
VIS4e
VIS4f
VIS5d

---

KATANDA cont'd.

39/019/WNW

curves off to 210° (SSW)

extensional Fault

666
@761468 = 83°
9902734

bubbling spring
37
@ spring 80°C

N

upper pool

see previous map

Moved north to west of roadside at x1.

Small pool of 4 bubbling vents:
- main one 84.7°c
- 2nd 75.2°c
- 3rd 82.2°c
- 75.0°c
- 69.8°c

No tufa tests as such, just white salt crusts.

Small chimney on its own @ 90°c

Flow on to Luc – no access to x2 from roadside.

Here a boiling spring is present on the eastern river bank – max temp 90°c

($67, 68, \to 90$)

Mostly white salt crusts, but here just found sand tufa 1st, with imprints of plant and tree profiles, by the 'piss-hole'; coming out at 82°c.

V158
V159
V160 — vertical zoned pipe.
— includes zoning around large cavity.

687 @
761774
9900764

688 @
763142
9902342
Strong $H_2S$
smell

---

Mai Ya Moto

sampling              →N

Botryoidal around chimney (abandoned)

Main Springs
93° 96° 93°

V154 V155
Pool #2
V156
81°c
V157   Tufa lss

58/274   botryoidal chimney.

strat:
157
156
155
154

Strong $H_2S$.

Pool #1
86°c
87°c   80°c

689
@763580
1903605

K    V    Th    #2265
1.0   200.9   25.1

Moved on to former X5.

Here, boiling springs on west bank of Rutshuru River — bubbling along a length of ~40m in a series of pools on the main river. Meas. at one of the main pools 71.5°C

---

NED 16th. Return to Mai ya Moto. Area 2.

After threading through thick bush, arrived here at '×2'.

Moderate-strong smell of H₂S. No clear oil.

Small cave on hillside seems to be main hot spring, at base of overhang. Above it, however, is a sloping drape of older tufa lobes.

670 @
761 634
9901849

As for sketch on last page – have just realised there are a series of notch dyke patches up-hill from the active one; A measure of (footwall uplift? (or ?subsidence rate on W border fault)

collect each: Highest @ 691 781804 9401639 @995m.

Tufa Terrace #4

Tufa Terrace @ 985m slightly south of active #3 spring

Tufa Terrace @ 976m, directly above overhang of #2 active spring;

Tufa Terrace currently forming #1 tufa.. @972m at spring mouth.

K U Th
3·6 410·8 111·8 #2266.
1·4 3042 57·2 #2267 A little further (~S-) downstream.

V162 a&b
V163 a+b
V161 (restricted sample in bag.)
V164

---

K U Th #2268 Another
2·5 210·3 44·1 ~Sn downstream.

The U and Th values appear to decrease downstream away from the main stream – scavenged by the cyanobacteria!!
(~ Increasing oxygenation downstream)

Did low aerial film over the hot spring and then moved on to XT. Ruindi is 17km away – ? Ruindi Biohief. Large river cliff here on west bank of Rutshuru River;
BVy - 6.

692
Base of section@
766111
9908410
@937m

LOCATION &
STRATIGRAPHIC SECTION:

SPECTRAL GAMMA LOG
ASSAY TIME (sec):

| CUMULATIVE THICKNESS (m) | UNIT THICKNESS (m) | GRAPHIC LITHOLOGY | GRAIN SIZE | | | | | | | | | | | TRENDS & SURFACES | COLOUR | K U Th | (%) | (ppm) | (ppm) | ASSAY # | DESCRIPTION | FACIES |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | M | st | vf | f | m | c | vc | gr | pb | cb | | | | K | U | Th | | | |

NAME:
DATE:
SHEET: 2 of 3

LOCATION &
STRATIGRAPHIC SECTION:

SPECTRAL GAMMA LOG
ASSAY TIME (sec):

| CUMULATIVE THICKNESS (m) | UNIT THICKNESS (m) | GRAPHIC LITHOLOGY | GRAIN SIZE | | | | | | | | | | | TRENDS & SURFACES | COLOUR | K U Th (Spectral Gamma) | K (%) | U (ppm) | Th (ppm) | ASSAY # | DESCRIPTION | FACIES |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | M | st | vf | f | m | c | vc | gr | pb | cb | | | | | | | | | |

Tropical Geology Exploration Group

**NAME:** F McTaggart, C Nicholson, S. Mangan
**DATE:** 21/07/14
**SHEET:** 2 of 3

**LOCATION & STRATIGRAPHIC SECTION:** Vitshuake fault scarp — face of section 761080 9915289 — CJN 263 — EVY-10

**SPECTRAL GAMMA LOG**
ASSAY TIME (sec):



CUMULATIVE THICKNESS (m)
UNIT THICKNESS (m)
GRAPHIC LITHOLOGY
GRAIN SIZE
M st vf f m c vc gr pb cb
TRENDS & SURFACES
COLOUR
K● U□ Th x
top of section
761012 4336
9915285
V385
V384
V383
V382
V381
V380
V379
V378
V377
21.15
20.9
20.55
20.5
20.15
19.95
19.55
19.15
18.95
18.80

| K (%) | U (ppm) | Th (ppm) | ASSAY # | DESCRIPTION | FACIES |
|---|---|---|---|---|---|
| 1.5 | 4 | 22.7 | 2493 | • same as below with increasing calcification to calcrete at top | |
| 1.8 | 5.6 | 41.0 | 2492 | • same colour, c-vf qtz sandy marl, vf & m f, qtz s dc, soft, some root cavities and onset of calcification calcrete | |
| 2.1 | 5.0 | 41.4 | 2491 | • same as below. | |
| 2.1 | 6.8 | 42.3 | 2490 | • same colour, vf-f ca qtz sandy marl, vf & m f, qtz s d c, occ. ca qtz, 2-3mm marl rip-up clasts, soft. | |
| 2.1 | 6.7 | 41.7 | 2489 | • same colour, c-vf qtz sandy marl, faintly laminated on 1-2mm scale, logs and clay rich. | |
| 1.6 | 7.1 | 27.9 | 2488 | • same as below with calcrete top 10cm. | |
| 1.9 | 8.2 | 34.3 | 2487 | • same colour, vf qtz sandy marl, f-m s & qtz, f-f b.n f, pedogenic root system | |
| 2.4 | 6.4 | 34.9 | 2486 | • same colour, f qtz sandy marl, occ. m-c a qtz, vf bmd, q s d c, occ. mottle cavities, soft | |
| 2.1 | 4.2 | 30.6 | 2485 | • pale [illegible] qtz sandy marl, predominance of f-m sa qtz, q s d c, [illegible] qtz, [illegible] soft | |
| [illegible] | [illegible] | [illegible] | 2484 | • previous page | |