

Deciphering geochemical signals across a Cambro-Ordovician carbonate platform

Ph.D Thesis

2020

Stephen Patrick Coakley



Trinity College Dublin
Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work.

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 Irish Copyright Legislation and Trinity College Library conditions of use and acknowledgement.

Stephen Patrick Coakley

Deciphering geochemical signals across a Cambro-Ordovician carbonate platform

Stephen Patrick Coakley

Summary

Sulfur isotopes ($\delta^{34}\text{S}$) preserve a geological record of seawater sulfate that permit insights into biogeochemical cycling, surface redox conditions and microbial activity over geological time. However, isotopic records from carbonate-associated sulfate, sulfate bound within the calcium carbonate mineral matrix (CAS and $\delta^{34}\text{S}_{\text{CAS}}$), frequently exhibit poorly understood stratigraphic and lateral variation that cannot be explained by evolution of the marine sulfate reservoir alone. As marine carbonate rocks are composed, in varying abundance, of cement, micrite, abiotic grains and fossils, it is important to identify both those components that can provide information about ancient marine conditions and the controls on their chemical composition. Existing bulk-rock $\delta^{34}\text{S}_{\text{CAS}}$ records from the Lower to Middle Ordovician San Juan Formation of the Argentine Precordillera are up to 20‰ lighter than coeval records. These observed differences with coeval carbonate records and observed rapid secular variability over short stratigraphic distances are too large a magnitude to be explained by changes to the marine sulfate reservoir alone, without implying a significantly reduced concentration in the marine sulfate reservoir and inferring deep water euxinia.

This study investigates one of the possible alternative causes of variation in the $\delta^{34}\text{S}_{\text{CAS}}$ record. Syn-depositional processes, including microbial fractionation and physical reworking, have been observed in modern depositional environments to result in sulfur isotope fractionation in shallow porewaters. Characteristics such as sedimentation rate, organic carbon loading, grain size and shape, and mineralogy potentially all influence the distribution, size and microecology of microbial redox zones and porewater exchange with the water column. We consider the scale of $\delta^{34}\text{S}_{\text{CAS}}$ variation in a number of different depositional facies at the Cerro La Silla stratigraphic section of the San Juan Formation by linking outcrop scale observations (lithofacies) with thin section petrology (microfacies) and

geochemical data to identify the cause of the observed variability. At a micron scale, XAS micron-scale imaging reveals clear differences in the distribution and abundance of sulfur-bearing phases in thin sections. This analysis is supplemented by mapping of trace element proxies of water-column and porewater chemical and redox conditions by LA-ICP-MS imaging with the aim of increasing understanding of how the conditions in which carbonate components form may contribute to the observed variable distribution of carbonate-associated sulfate (CAS).

A newly presented bulk-rock $\delta^{34}\text{S}_{\text{CAS}}$ dataset exhibits a typical pattern of high-frequency secular variation over short stratigraphic distances and exhibits higher mean values than previous $\delta^{34}\text{S}_{\text{CAS}}$ records from the same section. The data is supplemented by sedimentological evidence of reworking, trace element data on porewater and water column chemistry and redox conditions, and micron-scale elemental and species mapping. These data indicate that low $\delta^{34}\text{S}_{\text{CAS}}$ values at the base of the section are caused by sulfide oxidation in reworked shallow sedimentary porewaters, with minimal detrital input and very low Fe and Mn concentrations, to form isotopically light sulfate which is incorporated into precipitating phreatic carbonate cements. This research supports a need for caution when interpreting $\delta^{34}\text{S}_{\text{CAS}}$ datasets from shallow, reworked facies and suggest that further research is required to clarify the relationship between shallow sediment processes and variability in both $\delta^{34}\text{S}_{\text{CAS}}$ and rare earth element records.

Acknowledgments

I wish to express my gratitude to my PhD supervisors and current and former staff members in the Department of Geology. In particular David Chew, Balz Kamber, Catherine Rose, John Graham, Robbie Goodhue, George Sevastopulo and Chris Nicholas, who have assisted in bringing my PhD studies and unconventional career change to completion. John, Balz and Dave went above and beyond the expected in mentoring me and were deeply inspiring at undergraduate and postgraduate level as teachers. Dave also deserves particular gratitude for taking matters in hand and negotiating the continuance of my PhD with the Academic Registry after Catherine and Balz went to pastures new. George, thank you for taking the time to show interest and keep my project moving during the staff-turnovers and thanks to Chris and Dave for employment as a graduate researcher and lecturer respectively, both were thoroughly enjoyable experiences.

In the course of this project I have received support and input from the Biogeochemical team at Washington University in St Louis, including from David Fike, Alex Bradley, Jennifer Houghton and Stephanie Moore. Fernando Gomez of the University of Cordoba showed great generosity with his time during field work in the Argentine Precordillera, with a perfect combination of expertise in local geology, steak grilling and Malbec. I would like to thank the Department's technical and administrative staff; Cora McKenna, Gary O'Sullivan, Paul Guyett, Maura Morgan, Noel McGinley, Neil Kearney and, the Buddha in the basement, Francis Hendron. Thank you to my friends and other staff who made my experience as an undergraduate and postgraduate at TCD so enjoyable, including Finbarr, Kerrymin, Meabh, Claire, Mike, Kyle, Brendan, Eoghan and the Germans. Thank you also to Kevin and Thomas at Malone O'Regan Environmental for the patience as I juggled full time project work and the need to complete my PhD concurrently.

To my family and my friends, I am extremely grateful for your support and encouragement. In particular I'd like to thank my parents Davis and Mary, brothers Peter, John Davis and James and the gang of Roisin, Patrick and Joseph, with whom I hope to share the rediscovered joy and excitement that can be found in exploring nature past and present. Finally, and most especially, thank you Áine for being infinitely patient and supporting in the past ten years as we negotiated a more tumultuous period of change than expected with our young family, to arrive at this place with wider and happier horizons.

TABLE OF CONTENTS

Chapter 1: Introduction	3
1.1 Context of thesis	3
1.1.1 Geological Context	8
1.1.2 Summary	9
1.2 Layout and themes of the Thesis	10
1.3 Co-author statement.....	13
References	14
Chapter 2	20
ABSTRACT	20
2.1 Introduction.....	22
2.2 Geological Setting	28
2.3 Methods	31
2.4.1 Sedimentology.....	35
2.4.2 Geochemistry	39
2.5 Discussion.....	49
2.5.1 Contamination	49
2.5.2 Diagenesis.....	50
2.5.3 Depth change proxies recorded in carbonate chemistry at Cerro La Silla	55
2.5.4 Redox sensitive trace elements	61
2.6 Conclusions.....	67
Tables	69
Appendix 2.1 – Detailed Stratigraphic Log Cerro La Silla.....	83
References	84
Chapter 3	96
ABSTRACT	96
3.1 Introduction.....	98
3.2 Methods	101
3.3 Geological Setting	103
3.4 Results	104
3.4.1 Mapped Thin Sections	104
3.4.2 Geochemistry	108
3.4.3 Micron-scale analysis	108
3.5 Discussion.....	112
3.6 Conclusion	137
Tables.....	140
References	141
Chapter 4	147
ABSTRACT	147

4.1 Introduction	149
4.2 Geological Setting	152
4.3 Methods	153
4.3.1 Mass Spectrometer Analysis	153
4.3.2 X-ray Spectrometry	154
4.4 Results	159
4.4.1 Stratigraphy and carbonate petrography	159
4.4.2 Geochemical Results	161
4.4.3 Chemostratigraphic Data	161
4.4.4 Micron-scale analysis	161
4.5 Discussion	174
4.5.1 Micron-Scale Variability in sulfate, sulfide and trace-element distribution	174
4.5.2 Cement phases	175
4.5.3 Fossils	177
4.5.4 Allomicrite	178
4.5.6 Chemostratigraphic Bulk CAS data in the upper La Silla and basal San Juan Formations.....	180
4.6 Conclusions	185
References.....	188
Tables	196
<i>Chapter 5: Conclusions and general discussion.....</i>	<i>210</i>
References.....	214

Chapter 1: Introduction

1.1 Context of thesis

The geological record of sulfur isotopes preserved in the sulfur-bearing minerals of sedimentary rocks forms the basis for interpreting the evolution of the sulfur cycle, and its interaction with Earth-surface redox conditions throughout geologic history (Canfield and Teske, 1996; Canfield *et al.*, 2000; Habicht *et al.*, 2002). The research presented in this thesis aims to improve our ability to extract environmental information (both local and global) from sulfur isotope records, by investigating the origin of the poorly understood temporal and lateral variation that is observed in both carbonate-associated sulfate (CAS) and pyrite (pyr) derived sulfur isotope records ($\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$) (Kampschulte and Strauss, 2004; Hurtgen *et al.*, 2006; Ries *et al.*, 2009; Thompson and Kah, 2012; Jones and Fike, 2013). Whilst similar magnitudes of variation are observed in both CAS and pyrite sulfur isotope records at both a stratigraphic and micron scale¹, this research focuses predominantly on the stratigraphic and lateral variation observed in $\delta^{34}\text{S}_{\text{CAS}}$. Identifying the cause of this variation is critical for confident use of $\delta^{34}\text{S}_{\text{CAS}}$ records to interpret changes in biogeochemical cycling, surface redox conditions and microbial activity over geological time.

The sulfur cycle is governed by fluxes of sulfur species into and out of an oceanic sulfate reservoir ($\delta^{34}\text{S}_{\text{SO}_4}$), which in the modern ocean has a concentration of 28 mM (Kah *et al.*, 2004). There are three dominant controls on secular change to the sulfur isotope record:

- (i) the mean sulfur isotope fractionation associated with microbial reduction of sulfate to hydrogen sulfide and its subsequent formation of pyrite, both of which influence the $\delta^{34}\text{S}_{\text{pyr}}$ of buried pyrite. Distinct fractionation trends are generated by microbial activity, principally during sulfate reduction, but also through disproportionation and oxidation of sulfur species (Fry *et al.*, 1984; Fry *et al.*, 1985; Canfield and Thamdrup, 1994; Habicht and Canfield, 1997; Habicht *et al.*, 1998; Brunner and Bernasconi, 2005; Sim *et al.*, 2011a; Sim *et al.*, 2011b).

¹ $\delta^{34}\text{S} = ({}^{34}\text{S}/{}^{32}\text{S}_{\text{sample}}/{}^{34}\text{S}/{}^{32}\text{S}_{\text{std}} - 1) \times 10^3$. Values are expressed as $\delta^{34}\text{S}$ permil (‰) relative to the Vienna Canyon Diablo Troilite (V-CDT) standard.

- (ii) the proportion of all buried sulfur buried as pyrite (f_{pyr});
- (iii) the variation in the isotopic composition of the sulfate input to the ocean ($\delta^{34}\text{S}_{\text{in}}$) (Canfield, 2004; Wortmann and Chernyavsky, 2007; Fike and Grotzinger, 2008; Halevy *et al.*, 2012; Wortmann and Paytan, 2012).

These three controls form the steady-state description of isotopic mass balance in the global sulfur cycle:

$$\delta^{34}\text{S}_{\text{SO}_4} = \delta^{34}\text{S}_{\text{in}} + f_{\text{pyr}} * \delta^{34}\text{S}_{\text{pyr}}$$

Reconstructions of the behaviour of the sulfur cycle over geological time are based on sulfur isotope records of sulfate and sulfide from mineral phases in sedimentary rocks and from fluid inclusions (Horita *et al.*, 2002; Brennan *et al.*, 2004). Of the sedimentary rocks, marine carbonates offer a source of paired sulfur $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ and a more continuous $\delta^{34}\text{S}_{\text{SO}_4}$ record than the alternative, more restricted sources such as evaporites (Claypool *et al.*, 1980) or marine barites (Paytan *et al.*, 1998; Paytan *et al.*, 2004). Carbonate-associated sulfate is incorporated into the lattice of carbonate minerals during precipitation within the water column or near the sediment water interface without fractionation and it is assumed that $\delta^{34}\text{S}_{\text{CAS}}$ values and marine $\delta^{34}\text{S}_{\text{CAS}}$ are the same (Burdett *et al.*, 1989).

The modern marine sulfate reservoir has a calculated residence time of 13 Myr based on an estimated flux of 1.0×10^{14} g/yr into (and out of) the ocean and a 28 mM sulfate concentration (Kah *et al.*, 2004). However evidence from early Earth strata, suggest that this concentration has changed over time, from < 1 mM in the Archean, based on the precipitation sequence in evaporites lacking a sulfate phase (Grotzinger and Kasting, 1993), rising to > 2 mM after 1.2 Ga based on the increasing occurrence of sulfate evaporites (Kah *et al.*, 2001, 2004). Evidence of Phanerozoic sulfate concentrations has also been obtained from fluid inclusions in halite (Horita *et al.*, 2002; Lowenstein *et al.*, 2003; Brennan *et al.*, 2004; Timofeeff *et al.*, 2006). Secular variation in the $\delta^{34}\text{S}_{\text{CAS}}$ record is a further source of sulfate concentration estimates, with an inverse relationship in any given forcing between (a) the size of the reservoir and (b) the rate and magnitude of change in $\delta^{34}\text{S}_{\text{SO}_4}$ (Kah *et al.*, 2004; Gill *et al.*, 2007; Hurtgen, 2009; Gill *et al.*, 2011; Loyd *et al.*, 2012). Highly variable sulfur isotope records have therefore been interpreted as implying a lower seawater sulfate reservoir relative to the modern (Kah *et al.*, 2004., Fike *et al.*, 2006; Hurtgen *et al.*, 2009; Ries *et al.*, 2009).

There are multiple recorded occurrences of this high magnitude secular variability over short stratigraphic distances including variations ranging between 10 – 30‰ over an estimated 1 million years (Yan *et al.*, 2009; Hammarlund *et al.*, 2012) that have been interpreted as representing changes in the sulfur cycle over geological time (Fike *et al.*, 2006; Hurtgen *et al.*, 2006; Gill *et al.*, Fike and Grotzinger, 2008; Hurtgen *et al.*, 2009; Yan *et al.*, 2009; Gill *et al.*, 2011; Gorjan *et al.*, 2012; Hammarlund *et al.*, 2012; Jones and Fike, 2013). In the Argentine Precordillera, Thompson and Kah (2012) produced a $\delta^{34}\text{S}_{\text{CAS}}$ record for the Late Cambrian to Middle Ordovician La Silla and San Juan Formations at a ten metre resolution. Observed short term variation in the $\delta^{34}\text{S}_{\text{CAS}}$ record was interpreted as a global marine signal rapidly varying at a magnitude of 7‰ over a million years. This variability is interpreted as implying a marine sulfate reservoir of less than 2 mM (Thompson and Kah, 2012).

Invoking low sulfate concentrations to explain rapid temporal variability is however problematic when applied to particular data sets (Fike and Grotzinger, 2010; Jones and Fike, 2013). End-Ordovician $\delta^{34}\text{S}_{\text{SO}_4}$ records from evaporites suggest that marine sulfate concentrations were at that time > 5 mM (Lowenstein *et al.*, 2003; Brennan and Lowenstein, 2004), yet secular variability in sulfur and carbon isotope records from the coeval carbonate ramp facies of the Hirnantian glaciation at Anticosti Island, Quebec, show a continuous scatter in $\delta^{34}\text{S}_{\text{CAS}}$ of 5‰ through the stratigraphy with heavier pyrite values occurring in sections with textural features of energetic, shallow, potentially reworked facies and decreasing with increasing depth (Jones *et al.*, 2011). These changes are of too large a magnitude to produce variability on the observed timescales and cooccur with a 20‰ positive $\delta^{34}\text{S}_{\text{pyr}}$ excursion with no parallel excursion in CAS, indicating no increase in pyrite burial ($\delta^{34}\text{S}_{\text{in}}$) and a parallel 4‰ positive excursions in both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ (Jones *et al.*, 2011; Jones and Fike 2013).

Laterally discordant $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ records, up to 30‰ between coeval locations, are observed in the geological record at an inter-basinal scale (Fike and Grotzinger, 2008; Ries *et al.*, 2009; Fike and Grotzinger, 2010) and intra-basinal scale (Hurtgen *et al.*, 2006; Gill *et al.*, 2007; Li *et al.*, 2010;). This variability has also been interpreted as indicating low sulfate concentrations in the ocean, leading to gradients in sulfate concentrations, with differences up to ~ 20 ‰ in $\delta^{34}\text{S}_{\text{CAS}}$ between coeval locations (Hurtgen *et al.*, 2006; Li *et al.*, 2010). For example, the coeval Late Ediacaran Nama Group of Namibia and Ara Group of Oman record $\delta^{34}\text{S}_{\text{SO}_4}$ of $c. 38.9\text{‰} \pm 2.1\text{‰}$ and $\delta^{34}\text{S}_{\text{CAS}}$ of $\sim 27.3\text{‰} \pm 10.3\text{‰}$. The Ara Group carbonates exhibit laminated and microbial textures, interpreted as a quiet, periodically restricted basin

(Fike and Grotzinger, 2010), whilst the Nama Group strata shows textural evidence of wave reworking (Ries *et al.*, 2008). Most samples in the Nama Group exhibit more isotopically enriched $\delta^{34}\text{S}_{\text{pyr}}$ values than in cooccurring $\delta^{34}\text{S}_{\text{CAS}}$ (“super heavy pyrite”; Ries *et al.*, 2009). If this is related to low sulfate concentrations in the marine reservoir (Kah *et al.*, 2004), it requires different chemical gradients in the two locations (Fike and Grotzinger, 2008; Fike and Grotzinger, 2010) that are not supported by fluid-inclusion data in Ediacaran evaporites with sulfate concentrations of $\sim 16 - 24$ mM (Brennan *et al.*, 2004; Fike and Grotzinger, 2010).

Alternative causes of coeval variation in $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ include syn-depositional fractionation (Hurtgen *et al.*, 2006; Kamber and Whitehouse, 2007; Aller *et al.*, 2008; Fike *et al.*, 2008; Fike *et al.*, 2009; Aller *et al.*, 2010; Xiao *et al.*, 2010; Gao *et al.*, 2013; Fischer *et al.*, 2014) or post-depositional alteration by basinal brines or meteoric fluids (Gill *et al.*, 2008). Characteristics such as sedimentation rate, organic carbon loading, grain size and shape, and mineralogy potentially also influence the distribution, size and microecology of microbial redox zones and porewater exchange with the water column (Habicht and Canfield, 1997; Aller, 2014; Richardson 2019). Distribution of microbial activity in an undisturbed sediment column is determined by distribution of substrates and organisation of microbial communities (Fike *et al.*, 2015). Variation in the local microbial fauna, the rates at which they reduce sulfate and the abundance, availability and type of electron donors (Fike *et al.*, 2008; Fike *et al.*, 2009) impact the thickness of redox zones and abundance and isotopic values of sulfide. Isotopic enrichments of up to $\sim 10 - 20\%$ are observed in sulfides at a mm-scale in microbial mats (Fike *et al.*, 2008; Fike *et al.*, 2009) and are associated with rapid recycling of sulfur approaching the chemocline, with variations of $20 - 30\%$ over 1 mm identified ~ 1.5 cm below the chemocline (Fike *et al.*, 2008; Fike *et al.*, 2009). This variation may be attributable to differences in substrate availability (Sim *et al.*, 2011; Leavitt *et al.*, 2013).

Connectivity of pore-water sulfate with the water column during microbial sulfate fractionation determines whether open or closed system behaviour occurs and the fraction of sulfate consumed. Sulfate reduction causes an increase in $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ where closed system behaviour occurs, driving bulk $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ toward initial $\delta^{34}\text{S}_{\text{SO}_4}$ (Canfield, 2001; Aller, 2014). Available reactive iron is also required for the reaction of H_2S to pyrite, and the subsequent preservation of $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ as $\delta^{34}\text{S}_{\text{pyr}}$ (Berner, 1984; Rickard, 1995; Rickard and Luther, 1997). The impact of limited pore water exchange in sediment and resulting closed-system distillation has been identified in sedimentary pyrite as ^{34}S gradients within individual

pyrite crystals using Secondary Ion Mass Spectrometry (SIMS) analysis (Kamber and Whitehouse, 2007; Fischer *et al.*, 2014).

Studies in deltaic depositional environments also indicate that physical environmental characteristics may have an important, yet poorly understood, influence on the sulfur isotope signal recorded in marine sediments (Aller *et al.*, 2008; Canfield and Farquhar, 2009; Ries *et al.*, 2009; Aller *et al.*, 2010; Aller, 2014). Physical characteristics, such as sediment remobilisation by storms or tides, influence the concentration and isotopic value of porewater and sediment sulfur species. The redox stratigraphy may be disrupted by reworking, causing exchange of sulfur and iron pools between reduced and oxidized zones with resulting oxidation of H₂S (Aller *et al.*, 2008; Aller *et al.*, 2010; Gao *et al.*, 2013; Aller, 2014, Richardson *et al.* 2019; Rose *et al.*, 2019). Partial oxidation of H₂S may result in ³⁴S enrichment of the residual sulfide pool (Fry *et al.*, 1988) and ³⁴S depletion of local ³⁴S_{SO₄}. These processes could affect the $\delta^{34}\text{S}$ observed in sedimentary records with the resulting “super heavy” pyrite $\delta^{34}\text{S}_{\text{pyr}}$ values driven close to those of sulfate in the same sediment (Aller *et al.*, 2008; Aller *et al.*, 2010; Gao *et al.*, 2013). Bioturbation may also disrupt the redox stratigraphy, juxtaposing oxidized and reduced sediments or irrigating reduced sediments with oxygenated water, creating redox boundaries at burrow walls (Kristensen and Kostka, 2005; Aller *et al.*, 2010). This dynamic reorganisation of the redox column occurs in spatially extensive sediments, including deltaic deposits of the Amazon river and the Guiana coast, where reworked sediments preserve isotopically heavy $\delta^{34}\text{S}_{\text{pyr}}$ values from 0‰ to > 30‰, heavier than adjacent, low energy, oxidatively irrigated bioturbated areas (Kristensen and Kostka, 2005; Aller *et al.*, 2010; Gao *et al.*, 2013).

Textures of physical reworking and bioturbation are identifiable at a bed scale in the geological record and the $\delta^{34}\text{S}_{\text{CAS}}$ records of the coeval Nama Group and Ara Group discussed above can be hypothesized to have originated in contrasting depositional conditions. The undisturbed sediments of the Ara Group may have recorded seawater sulfate values, supported by consistent $\delta^{34}\text{S}$ values in interbedded CAS and anhydrite. The shallow, high energy facies in the Nama Group, exhibiting variable sulfate signals and super heavy pyrite (Ries *et al.*, 2009), may have been regularly reworked, creating the repeated oxidation and reduction cycles identified in the modern oceans (Aller *et al.*, 2010, 2014).

An assessment of the platform carbonates in the Argentine Precordillera permits an analysis of these processes at a number of scales from an intra-basinal scale (between stratigraphic

sections), lithofacies scale (between beds and hand samples) and microfacies scale (micron-scale observations). The current project focuses firstly on a strong definition of water-column and sediment conditions in the San Juan Formation, using rare earth element and yttrium (REE + Y) trace element data combined with redox-sensitive trace elements (authigenic Mo and U), integrated with petrographic evidence for the presence or absence of reworking of sediment (Chapter 2.). As carbonate rocks are typically composed of a varying range and abundance of components, including depositional micrite (allomicrite), fossils, cement phases and abiotic grains, this analysis is supplemented by a microfacies study of the micron-scale relationship of REE+Y data and the carbonate components that constitute the sample using LA-ICP-MS mapping with measurement of elemental concentrations using the Iolite add-in Monocle (Petrus *et al.*, 2017). In Chapter 4 a newly presented bulk $\delta^{34}\text{S}_{\text{CAS}}$ stratigraphic record from Cerro La Silla and its lithofacies is considered with petrographic and geochemical evidence of syn-depositional processes. This chapter incorporates a high-resolution microfacies study of sulfate distribution using synchrotron-based X-ray absorption spectromicroscopy (XAS) experiments. XAS permits a hitherto unobtainable micron-scale understanding of CAS distribution within samples (Richardson *et al.*, 2019; Rose *et al.*, 2019) and is here supplemented by LA-ICP-MS mapping applying the Iolite add-in Monocle (Petrus *et al.*, 2017) to provide elemental concentration data paired to the XAS distribution data.

1.1.1 Geological Context

The Argentine Precordillera carbonate platform of Cambro-Ordovician age is located in the north-south striking, thin-skinned thrust belt of the same name, and makes an ideal field area in which to conduct this research (see map of the study area in Chapter 2, Fig. 2.2). The field outcrops exhibit reworked and bioturbated beds in multiple coeval sections, including sections preserving primary $\delta^{34}\text{S}_{\text{CAS}}$ values (Thompson and Kah, 2012). The geological history and sedimentology of the platform is outlined in the Geological Setting sections of Chapters 2 - 4. The carbonate platform contains a number of formations with peritidal to subtidal facies with textural evidence of reworking and bioturbation (Keller, 1999). Based on its strong textural preservation at outcrop, the variety of identifiable depth-related depositional facies and the contiguous stratigraphic sections present, it was decided to sample the San Juan Formation at Cerro La Silla, Cerro La Chilca and the Talacasto Gorge at a metre-scale resolution. Nine hundred c. 200 g hand samples were collected at a metre resolution from these sections. Based on initial analysis of facies variability in each section and the

degree of preservation observed at both bed and thin-section scale it was decided to focus this study on the c. 400 m Cerro La Silla stratigraphic section.

1.1.2 Summary

In summary, sulfur isotope records from carbonate-associated sulfate (CAS), pyrite, marine barites and evaporites form the basis of interpretations of the evolution of the sulfur cycle and redox conditions throughout Earth's history (Canfield and Teske, 1996; Canfield *et al.*, 2000; Habicht *et al.*, 2002). However, 10 to 30‰ secular changes in $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ records (Fike and Grotzinger, 2008; Ries *et al.*, 2009; Fike and Grotzinger, 2010) and up to 30‰ lateral variations between coeval locations are observed in the geological record (Hurtgen *et al.*, 2006; Fike and Grotzinger, 2008; Ries *et al.*, 2009) and have been interpreted as representing temporal changes (Kah *et al.*, 2004; Fike *et al.*, 2006; Hurtgen *et al.*, 2009; Ries *et al.*, 2009) and lateral chemical gradients in ancient oceans (Hurtgen *et al.* 2006; Li *et al.*, 2010). These interpretations require the inference of low sulfate concentrations in ancient oceans with major implications for how we understand the evolution of the sulfur cycle, and its interaction with Earth-surface redox conditions throughout geologic history.

Varying depositional conditions, particularly sedimentary reworking, are seen to play a major role in generating and modifying the isotopic signatures of sulfur phases in modern environments (Aller, 2014) and these observations can be extrapolated to investigate records of sulfur cycling in ancient strata. This study therefore seeks to characterise the water and sediment porewater conditions that existed at the time of deposition at a micron and bed-scale by combining sedimentological observations with geochemical data including REE+Y, Mo_{auth} and U_{auth} data.

The analysis of lithofacies and microfacies seeks to identify the origin of this variation to provide new insights to refine our interpretations of chemostratigraphic $\delta^{34}\text{S}$ data. The goal is to ultimately clarify whether the observed variations were caused by either fractionation by physical processes during deposition or by early diagenetic alteration in sediment porewaters (Fike *et al.*, 2015). These interpretations have the potential to better constrain the behaviour of the sulfur cycle over geological timescales, improve our understanding of Early and Middle Ordovician marine chemistry and any potential sulfate and trace element alteration in sediment porewaters.

1.2 Layout and themes of the Thesis

This PhD thesis is composed of a collection of thematically-related manuscripts intended for peer-reviewed publication. A number of self-contained projects were devised, each forming a chapter of the thesis. Because each chapter represents an independent manuscript, comprehensive introductions and conclusions can be found in each. The last chapter provides a synopsis with conclusions and future outlook. All chapters have been drafted for future submission to relevant journals and have been formatted for the thesis.

Chapter 2 comprises an initial investigation of the water-column and sediment conditions during the deposition of the type section of the San Juan Formation at Cerro La Silla. I present a detailed trace element and $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ stratigraphy with an assessment of evidence of the preservation of unaltered geochemical data. Trace-element data include carbonate rare earth element and yttrium (REE+Y) data. Marine proxies that employ this REE+Y data display significant variability consistent with changing water column conditions and variable contamination by siliciclastic sediment input. It is concluded on the basis of the presented sedimentological and geochemical data that the water-column was oxic and porewaters varied between oxic and dysoxic as recorded in Mo_{auth} , U_{auth} and $(\text{Mo:U})_{\text{auth}}$ variability. The REE+Y patterns at no point approach the values expected in carbonates deposited under fully marine conditions however much of the stratigraphic section contains fauna typical of such conditions. Combined use of trace elements that are sensitive to redox change, marine mixing and sedimentological evidence of depth indicate that more marine conditions occurred in periods of raised sea level, due to greater mixing with the Iapetus ocean. The data suggest that existing $\delta^{34}\text{S}_{\text{CAS}}$ records from Cerro La Silla incorporate components formed in the water column and in shallow burial porewaters that might not reflect $\delta^{34}\text{S}_{\text{SO}_4}$ values of the global ocean. During deposition of the San-Juan Formation, the Precordillera platform is envisaged as a vast homoclinal ramp of subtidal flats. It is concluded that marginal shallow areas on this ramp, such as the one studied, are potentially vulnerable to local effects, particularly in periods of low sea level, and that investigation of further stratigraphic sections may be needed to establish whether these effects are confined to Cerro La Silla or are a platform-wide phenomenon. It is also observed that application of a siliciclastic correction to the data does not generate REE+Y profiles typical of marine carbonates despite the contradictory presence of fossils of marine organisms through much of the stratigraphic section. Micron scale LA-ICP-MS mapping is therefore applied to

selected thin sections in Chapter 3 to assist in identifying the cause of this apparent disparity between faunal and REE+Y data.

Chapter 3 further investigates the apparent contradiction between shale-normalised REE + Y trends at Cerro La Silla (that are typical of carbonate formed in brackish water) and the cooccurring fossils of marine faunae, including stenohaline crinoids, in the stratigraphic section. In particular it is considered whether there is evidence of cryptic early diagenetic alteration or of siliciclastic or other contaminant phases that might alter the shale-normalized REE slope or lower the Y/Ho ratio to move them away from primary seawater values. None of the analysed carbonates have the deep, upper crust-normalised patterns that are seen in fully open marine seawater and carbonate proxies thereof (e.g. Nothdurft *et al.*, 2004). Instead, the samples display REE + Y patterns that are slightly LREE-enriched to flat, with profiles intermediate between seawater and modern river water. We illustrate that a siliciclastic correction to allomicrite data, using LA-ICP-MS mapping measurements of semi-quantitative data, may be effective where variable siliciclastic contamination has occurred. The added value of the Iolite add-in Monocle is demonstrated by measurement of multi-element data extracted from the LA-ICP-MS maps from samples from above fair-weather wave base to below storm wave base. It is concluded that depositional micrite remains a potential source of primary marine geochemical data where appropriate micron scale screening is carried out, but should be used with caution and where preferred data sources such as marine radiaxial fibrous cement or microbial micrite (Kamber and Webb, 2001) are unavailable. A further value of LA-ICP-MS mapping is as a geochemical screen for further targeted analysis or for validating the impact on geochemical results of excessive or ineffective leaching during solution ICP-MS data sample preparation.

The impact of a number of porewater processes on phreatic cement composition is considered, including regular sediment reworking, very low levels of Fe and Mn, oxic cement precipitation and very low siliciclastic input. LA-ICP-MS mapping permits delimitation of possible brackish conditions to below c. 110 m in the stratigraphic section. This is consistent with the occurrence of crinoids above the deepening horizon at 110 m identified in the current study, and suggests that more marginal conditions may be limited to the very shallow, proximal portions of the carbonate platform at the base of the San Juan Formation and intertidal to sub-tidal facies of the uppermost La Silla Formation.

Chapter 4 investigates the micron-scale distribution of CAS, which is compared to trace element distribution and concentrations in four samples from three identified depositional facies. Facies range from reworked facies above fair-weather wave base to outer ramp facies below storm wave base. At the micron scale, mapping of the distribution and abundance of sulfur-bearing phases in thin sections by X-ray Absorption Near Edge Structure (XANES) spectroscopy and micro x-ray fluorescence (μ -XRF) imaging, is supplemented by mapping of trace element proxies of water-column and porewater chemical and redox conditions by LA-ICP-MS mapping. These analyses are assessed in light of a newly presented bulk rock $\delta^{34}\text{S}_{\text{CAS}}$ data set. The results reveal heterogeneity in CAS distribution at a micron scale and questions the assumption in bulk rock $\delta^{34}\text{S}_{\text{CAS}}$ analysis that CAS is evenly distributed in carbonate rocks. Instead, where $\delta^{34}\text{S}_{\text{CAS}}$ varies between component classes, the balance of each component class could partially control the resulting bulk-sample value.

This information is paired with the new bulk-rock $\delta^{34}\text{S}_{\text{CAS}}$ data, which exhibits a typical pattern of high-frequency secular variation over short stratigraphic distances and a more positive mean value by 4.4‰ than previous $\delta^{34}\text{S}_{\text{CAS}}$ records from the same section. It is concluded that phreatic cement precipitation in repeatedly reworked, oxic, brackish, low Fe and Mn porewaters occurred at the base of the San Juan Formation. This microfacies coincides with the lowest $\delta^{34}\text{S}_{\text{CAS}}$ values and the occurrence of similar very low $\delta^{34}\text{S}_{\text{CAS}}$ values in underlying existing datasets from the uppermost La Silla Formation. Repeated re-oxidation of the porewater sulfide pool during regular oxic reworking may drive the porewater sulfate pool toward lighter values and the lack of available Fe to fix sulfide produced during microbial sulfate reduction (MSR) may contribute to the magnitude of this process. Therefore, the occurrence of distinctively light $\delta^{34}\text{S}_{\text{CAS}}$ values in the upper La Silla Formation and at the base of the San Juan Formation is most likely to reflect porewater processes that drove the porewater $\delta^{34}\text{S}_{\text{CAS}}$ to lighter values than those of coeval seawater.

Chapter 5 is the synthesis of the results gathered from the observations presented in the core chapters of the thesis, and also discusses implications for future works on the topics considered.

1.3 Co-author statement

The three core chapters (2 - 4) of this thesis consist of three unsubmitted manuscripts. All three are co-authored and I am the lead author on all three of these works. I wrote the lead-authored manuscripts in their entirety. Detailed roles of the co-authors are listed below.

David Chew, TCD, my PhD supervisor, provided editorial comments on Chapter 2, Chapter 3 and Chapter 4. In addition David initially processed Laser Ablation – Inductively Coupled Mass Spectrometer (LA-ICP-MS) data in Iolite for the LA-ICP-MS maps used in Chapters 3 and 4.

David Fike, provided discussion and comments in relation to interpretation of XAS and bulk CAS data and facilitated my work at his laboratory to carry out bulk CAS extractions.

Balz Kamber, my former supervisor, provided editorial comments on Chapter 2 and was the primary discussion partner for the solution ICP-MS trace element data, including the discussion of REE + Y data interpretation.

Catherine Rose, my former supervisor, provided editorial comments on Chapter 2 and was the primary discussion partner for the interpretation of isotope data, X-ray Absorption Spectroscopy (XAS) data and also provided discussion in relation to trace element data. Catherine participated in field work assisted by Federico Gomez of Cordoba University and WashU graduate student Torr O'Brien, including the sampling that formed the basis of this study. Catherine also participated in the XAS experiments at the Advanced Photon Source, Argonne National Laboratories and processed synchrotron data with the assistance of Samuel Webb of the Stanford Synchrotron Radiation Lightsource.

George Sevastopulo, TCD, provided editorial comments on Chapter 2 and assistance with faunal interpretation and micro-imaging.

References

- ALLER, R.C. 2014. Sedimentary diagenesis, depositional environments, and benthic fluxes. In *Treatise on Geochemistry*, Vol. 8: The Oceans and Marine Geochemistry, ed. MJ Mottl, H Elderfield, pp. 293–334. Amsterdam, Elsevier. 2nd ed.
- ALLER, R.C., BLAIR, N.E., BRUNSKILL, G.J. 2008. Early diagenetic cycling, incineration, and burial of sedimentary organic carbon in the central Gulf of Papua (Papua New Guinea). *J. Geophys. Res.*, 113, F01S09.
- ALLER, R.C., MADRID, V., CHISTOSERDOV, A., ALLER, J.Y., HEILBRUN, C. 2010. Unsteady diagenetic processes and sulfur biogeochemistry in tropical deltaic muds: implications for oceanic isotope cycles and the sedimentary record. *Geochimica et Cosmochimica Acta*, 74, 4671–92.
- BERNER, R.A. 1984. Sedimentary pyrite formation: an update. *Geochimica et Cosmochimica Acta*, 48, 605–15.
- BRENNAN, S.T., LOWENSTEIN, T.K., HORITA, J. 2004. Seawater chemistry and the advent of biocalcification. *Geology*, 32, 473–76.
- BRUNNER, B., & BERNASCONI, S.M. 2005. A revised isotope fractionation model for dissimilatory sulfate reduction in sulfate reducing bacteria. *Geochimica et Cosmochimica Acta*, 69, 4759–71.
- BURDETT, J.W., ARTHUR, M.A., RICHARDSON, M. 1989. A Neogene seawater sulfate isotope age curve from calcareous pelagic microfossils. *Earth and Planetary Science Letters*, 94, 189–98.
- CANFIELD, D.E. 2001. Biogeochemistry of sulfur isotopes. *Rev. Mineral. Geochem*, 43, 607–36.
- CANFIELD, D.E. 2004. The evolution of the Earth surface sulfur reservoir. *American Journal of Science*, 304, 839–61.
- CANFIELD, D.E., & FARQUHAR, J. 2009. Animal evolution, bioturbation, and the sulfate concentration of the oceans. *PNAS*, 106, 8123–8127.
- CANFIELD, D.E., HABICHT, K.S. & THAMDRUP, B. 2000. The Archean sulfur cycle and the early history of atmospheric oxygen. *Science*, 288, 658–661.
- CANFIELD, D.E., & TESKE, A. 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. *Nature*, 382, 127–132.
- CANFIELD, D.E. & THAMDRUP, B. 1994. The production of ³⁴S-depleted sulfide during bacterial disproportionation of elemental sulfur. *Science*, 266, 1973–1975.

- CLAYPOOL, G. E., HOLSER, W. T., KAPLAN, I. R., SAKAI, H. & ZAK, I. 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology*, 28
- FIKE, D. A., BRADLEY, A. S. & ROSE, C. V. 2015. Rethinking the Ancient Sulfur Cycle. *Annual Review of Planetary Science*. 2015. 43: 593-622
- FIKE, D.A., FINKE, N., ZHA, J., BLAKE, G., HOEHLER, T.M. & ORPHAN, V.J. 2009. The effect of sulfate concentration on (sub) millimeter-scale sulfide $\delta^{34}\text{S}$ in hypersaline cyanobacterial mats over the diurnal cycle. *Geochimica et Cosmochimica Acta*, 73, 6187–6204.
- FIKE, D.A. & GROTZINGER, J.P. 2008. A paired sulfate–pyrite $\delta^{34}\text{S}$ approach to understanding the evolution of the Ediacaran–Cambrian sulfur cycle. *Geochimica et Cosmochimica Acta*, 72, 2636–2648.
- FIKE, D.A. & GROTZINGER, J.P. 2010. Reconstructing biogenic pyrite burial in evaporite basins: an example from the Ara Group, Sultanate of Oman. *Geology*, 38, 371–74.
- FIKE, D.A. & GROTZINGER, J.P., PRATT, L.M., SUMMONS, R.E. 2006. Oxidation of the Ediacaran ocean. *Nature*, 444, 744–747.
- FISCHER, W.W., FIKE, D.A., JOHNSON, J.E., RAUB, T.D., GUAN, Y. & KIRSCHVINK, J.L. 2014. SQUID–SIMS is a useful approach to uncover primary signals in the Archean sulfur cycle. *PNAS*, 111, 5468–5473.
- FRY, B., GEST, H., HAYES, J.M. 1984. Isotope effects associated with the anaerobic oxidation of sulfide by the purple photosynthetic bacterium *Chromatium vinosum*. *FEMS Microbiol. Lett.*, 22, 283–87.
- FRY, B., GEST, H., HAYES, J.M. 1985. Isotope effects associated with the anaerobic oxidation of sulfite and thiosulfate by the photosynthetic bacterium *Chromatium vinosum*. *FEMS Microbiol. Lett.*, 27, 227–32.
- FRY, B., RUF, W., GEST, H., HAYES, J.M. 1988. Sulfur isotope effects associated with oxidation of sulfide by O_2 in aqueous solution. *Chem. Geol.*, 73, 205–10.
- GAO, J, FIKE, D.A., ALLER, R.C. 2013. Enriched pyrite $\delta^{34}\text{S}$ signals in modern tropical deltaic muds. Presented at AGU Fall Meet., Dec. 9–13, San Francisco. Abstr. B31A-0352.
- GILL, B.C., LYONS, T.W., SALTZMAN, M.R. 2007. Parallel, high-resolution carbon and sulfur isotope records of the evolving Paleozoic marine sulfur reservoir. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 256:156–73.
- GILL, B.C., LYONS, T.W., FRANK, T.D. 2008. Behavior of carbonate-associated sulfate during meteoric diagenesis and implications for the sulfur isotope paleoproxy. *Geochim Cosmochim Acta* 72:4699–4711.

- GILL, B.C., LYONS, T.W., YOUNG, S.A., KUMP, L.R., KNOLL, A.H., SALTZMAN, M.R. 2011. Geochemical evidence for widespread euxinia in the Later Cambrian ocean. *Nature*, 469, 80–83.
- GORJAN, P., KAIHO, K., FIKE, D.A., XU, C. 2012. Carbon- and sulfur-isotope geochemistry of the Hirnantian (Late Ordovician) Wangjiawan (Riverside) section, South China: global correlation and environmental event interpretation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 337–38:14–22.
- GROTZINGER, J.P., KASTING, J.F. 1993. New constraints on Precambrian ocean composition. *The Journal of Geology*, 101, 235–43.
- HABICHT, K.S. & CANFIELD, D.E. 1997. Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments. *Geochimica et Cosmochimica Acta*, 61, 5351–5361.
- HABICHT, K.S., CANFIELD, D.E., RETHMEIER, J. 1998. Sulfur isotope fractionation during bacterial reduction and disproportionation of thiosulfate and sulfite. *Geochimica et Cosmochimica Acta*, 62, 2585–2595.
- HABICHT, K.S., GADE, M., THAMDRUP, B., BERG, P. & CANFIELD, D.E. 2002. Calibration of sulfate levels in the Archean ocean. *Science*, 298, 2372–4.
- HALEVY, I, PETERS, SE, FISCHER, WW. 2012. Sulfate burial constraints on the Phanerozoic sulfur cycle. *Science*, 337, 331–34.
- HAMMARLUND, E.U., DAHL, T., HARPER, W D.A.T., BOND, D.P.G., NIELSEN, A.T., BJERRUM, C.J., SCHOVSBO, N.H., SCHOENLAUB, H.P., ZALASIEWICZ, J.A., AND CANFIELD, D.E., 2012, A sulfidic driver for the end-Ordovician mass extinction: *Earth and Planetary Science Letters*, 331, 128–139.
- HORITA, J, ZIMMERMANN, H, HOLLAND, HD. 2002. Chemical evolution of seawater during the Phanerozoic: implications from the record of marine evaporites. *Geochimica et Cosmochimica Acta*, 66, 3733–56.
- HURTGEN, M.T., HALVERSON, G.P., ARTHUR, M.A. & HOFFMAN, P.F. 2006. Sulfur cycling in the aftermath of a 635-Ma snowball glaciation: Evidence for a syn-glacial sulfidic deep ocean. *Earth and Planetary Science Letters*, 245, 551–570.
- HURTGEN, M.T., PRUSS, S.B., KNOLL, A.H. 2009. Evaluating the relationship between the carbon and sulfur cycles in the later Cambrian ocean: an example from the Port au Port Group, Western Newfoundland, Canada. *Earth and Planetary Science Letters*, 281, 288–97.
- JONES, D.S., & FIKE, D.A. 2013. Dynamic sulfur and carbon cycling through the end-Ordovician extinction revealed by paired sulfate–pyrite $\delta^{34}\text{S}$. *Earth and Planetary Science Letters*, 363, 144–155.

- JONES, D.S., FIKE, D.A., FINNEGAN, S. FISCHER, W.W., SCHRAG, D.P., MCCAY, D. 2011. Terminal Ordovician carbon isotope stratigraphy and glacioeustatic sea-level change across Anticosti Island (Quebec, Canada). *Geol. Soc. Am. Bull.* 123, 1645–64.
- KAH, L.C., LYONS, T.W., CHESLEY, J.T. 2001. Geochemistry of a 1.2 Ga carbonate-evaporite succession, northern Baffin and Bylot Islands: implications for Mesoproterozoic marine evolution. *Precambrian Res.*, 111, 203–34.
- KAH, L.C., LYONS, T.W., FRANK, T.D. 2004. Low marine sulphate and protracted oxygenation of the Proterozoic biosphere. *Nature*, 431, 834–838.
- KAMBER, B.S., WHITEHOUSE, M.J. 2007. Micro-scale sulphur isotope evidence for sulphur cycling in the late Archean shallow ocean. *Geobiology*, 5, 5–17.
- KAMPSCHULTE, A & STRAUSS, H. 2004. The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulfate in carbonates. *Chemical Geology*, 204, 255-286.
- KELLER, M. 1999. Argentine Precordillera: Sedimentary and Plate Tectonic History of a Laurentian Crustal Fragment in South America. Special Paper 341: Argentine Precordillera: sedimentary and plate tectonic history of a Laurentian crustal fragment in South America. Geological Society of America.
- KRISTENSEN, E., & KOSTKA, J. E. (2005). Macrofaunal burrows and irrigation in marine sediment: Microbiological and biogeochemical interactions. In E. Kristensen, R. R. Haese, & J. E. Kostka (Eds.), *Interactions between macro- and microorganisms in marine sediments* (pp. 125-158). Washington DC: American Geophysical Union.
- LEAVITT, W.D., HALEVY, I., BRADLEY, A.S., JOHNSTON, D.T. 2013. Influence of sulfate reduction rates on the Phanerozoic sulfur isotope record. *PNAS*, 110, 11244–11249.
- LI, C., LOVE, G.D., LYONS, T.W., FIKE, D.A., SESSIONS, A.L., CHU, X. 2010. A new stratified redox model for the Ediacaran ocean. *Science*, 328, 80–83.
- LOWENSTEIN, T.K., HARDIE, L.A., TIMOFEEFF, M.N., DEMICCO, R.V. 2003. Secular variation in seawater chemistry and the origin of calcium chloride basinal brines. *Geology*, 31, 857–60.
- LOYD, S.J., MARENCO, P.J., HAGADORN, J.W., LYONS, T.W., KAUFMAN, A.J. *et al.* 2012. Sustained low marine sulfate concentrations from the Neoproterozoic to the Cambrian: insights from carbonates of northwestern Mexico and eastern California. *Earth and Planetary Science Letters*, 339–40, 79–94
- NOTHDURFT, L. D., WEBB, G. E. & KAMBER, B. S. 2004. Rare earth element geochemistry of Late Devonian reefal carbonates, Canning Basin, Western Australia:

confirmation of a seawater REE proxy in ancient limestones. *Geochimica et Cosmochimica Acta*, 68, 263–283.

PAYTAN, A., KASTNER, M., CAMPBELL, D., THIEMENS, M.H. 1998. Sulfur isotopic composition of Cenozoic seawater sulfate. *Science*, 282, 1459–1462.

PAYTAN, A., KASTNER, M., CAMPBELL, D., THIEMENS, M.H. 2004. Seawater sulfur isotope fluctuations in the Cretaceous. *Science*, 304, 1663–1665.

PETRUS, J. A., CHEW, D. M., LEYBOURNE, M. I. & KAMBER, B. S. 2017. A new approach to laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) using the flexible map interrogation tool ‘Monocle’. *Chemical Geology*, 463, 76–93.

RICHARDSON, J. A., NEWVILLE, M., LANZIROTTI, A., WEBB, S. M., ROSE, C. V., CATALANO, J. G. & FIKE, D. A. 2019. Depositional and diagenetic constraints on the abundance and spatial variability of carbonate-associated sulfate. *Chemical Geology*, 523, 59–72.

RICKARD, D. 1995. Kinetics of FeS precipitation. Part 1: Competing reaction mechanisms. *Geochimica et Cosmochimica Acta*, 59, 4367–4379.

RICKARD, D., LUTHER, G.W. 1997. Kinetics of pyrite formation by the H₂S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125°C: the mechanism. *Geochimica et Cosmochimica Acta*, 61, 135–47.

RIES, J.B., FIKE, D.A., PRATT, L.M., LYONS T.W., GROTZINGER J.P. 2009. Super-heavy pyrite ($\delta^{34}\text{S}_{\text{pyr}} > \delta^{34}\text{S}_{\text{SCAS}}$) in the terminal Proterozoic Nama Group, Southern Namibia: a consequence of low seawater sulfate at the dawn of animal life. *Geology* 37,743–746.

ROSE, C. V., WEBB, S. M., NEWVILLE, M., LANZIROTTI, A., RICHARDSON, J. A., TOSCA, N. J., CATALANO, J. G., BRADLEY, A. S. & FIKE, D. A. 2019. Insights into past ocean proxies from micron-scale mapping of sulfur species in carbonates. *Geology*, 47, 833–837

SIM, M.S., BOSAK, T., ONO, S. 2011a. Large sulfur isotope fractionation does not require disproportionation. *Science*, 333, 74–77.

SIM, M.S., ONO, S., DONOVAN, K., TEMPLER, S.P., BOSAK, T. 2011b. Effect of electron donors on the fractionation of sulfur isotopes by a marine *Desulfovibrio* sp. *Geochimica et Cosmochimica Acta*, 75, 4244–4259.

THOMPSON, C.K. & KAH, L.C. 2012. Sulfur isotope evidence for widespread euxinia and a fluctuating oxycline in Early to Middle Ordovician greenhouse oceans. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 313–314, 189–214.

- TIMOFEEFF, M.N., LOWENSTEIN, T.K., DA SILVA, M.A.M., HARRIS, N.B. 2006. Secular variation in the major-ion chemistry of seawater: evidence from fluid inclusions in Cretaceous halites. *Geochimica et Cosmochimica Acta*, 70:1977–94.
- WORTMANN, U.G., CHERNYAVSKY, B.M. 2007. Effect of evaporite deposition on Early Cretaceous carbon and sulphur cycling. *Nature*, 446, 654–56.
- WORTMANN, U.G., PAYTAN, A. 2012. Rapid variability of seawater chemistry over the past 130 million years. *Science*, 337, 334–336.
- XIAO, S., SCHIFFBAUER, J.D., MCFADDEN, K.A., HUNTER, J. 2010. Petrographic and SIMS pyrite sulfur isotope analyses of Ediacaran chert nodules: implications for microbial processes in pyrite rim formation, silicification, and exceptional fossil preservation. *Earth and Planetary Science Letters*, 297, 481–495.
- YAN D, CHEN D, WANG Q, WANG J, WANG Z. 2009. Carbon and sulfur isotopic anomalies across the Ordovician–Silurian boundary on the Yangtze Platform, South China. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 297, 32–39.

Chapter 2

Trace elements as a proxy for salinity and redox conditions across an Ordovician carbonate platform, San Juan Formation, Argentina

Stephen P. Coakley^{1*}, Balz S. Kamber¹, David A. Fike², Catherine V. Rose³

¹*Department of Geology, Trinity College Dublin, Dublin 2, IRE.*

²*Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, MO 63130, USA.*

³*School of Earth and Environmental Sciences, University of St Andrews, St Andrews, Fife KY16 9AL, UK.*

ABSTRACT

Carbonate-associated sulfate S isotope ($\delta^{34}\text{S}_{\text{CAS}}$) records from the Lower to Middle Ordovician San Juan Formation of the Argentine Precordillera vary by as much as 20‰ from coeval stratigraphic data. The San Juan Formation represents shallow subtidal to below storm wave base facies and its S isotope variations, when compared with coeval records, have been interpreted to reflect that of a global low-sulfate ocean with a deep-water euxinic reservoir. To further investigate these hypothetical marine conditions this study presents a detailed trace element and $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ stratigraphy from the type section of the San Juan Formation at Cerro La Silla. Diagnostic features of the carbonate rare earth element and yttrium (REE+Y) trends exhibit an appreciable variability in the various marine proxies, including low magnitude negative Ce anomalies, that are typically coupled to water column conditions fluctuating between oxic and dysoxic. Porewater conditions varied between oxic and dysoxic as recorded in Mo_{auth} , U_{auth} and $(\text{Mo:U})_{\text{auth}}$ variability. Notably, the REE+Y patterns at no point approach the magnitudes expected for deposition under fully marine conditions and contamination screening does not show evidence of siliciclastic suppression of those patterns. However, faunal paleoenvironmental proxies are consistent with open marine conditions for the majority of the sampled stratigraphy. Combined use of elements that are sensitive to redox change and salinity, sedimentological evidence of depositional depth and palaeontological indicators of marine conditions suggest that during periods of lowest sea level there was regular reworking of sediment with shallow phreatic cement formation in brackish, oxic to dysoxic porewater conditions. At the base of the stratigraphy elements

associated with siliciclastic input are at minimal levels and may indicate isolation of the depositional environment from basinal and terrestrial siliciclastic input.

Collectively, the new data suggest that the existing $\delta^{34}\text{S}_{\text{CAS}}$ records from the shallow conditions in the uppermost La Silla and basal San Juan Formations at Cerro La Silla may represent water column and shallow burial conditions that are not reflective of the global ocean. More marine water-column conditions and greater siliciclastic inputs occurred in periods of raised sea level, due to greater mixing with the open Iapetus ocean. The study also underlines the need for caution when applying siliciclastic correction to solution-ICP-MS REE+Y data in carbonates and the need for careful micron scale screening. This is particularly the case in the absence of supplementary palaeontological evidence. The Precordillera platform, during deposition of the San Juan Formation is envisaged as a vast homoclinal ramp of subtidal flats. A combined interpretation of palaeontological and REE+Y data suggests that marginal shallow areas, such as Cerro La Silla, were potentially vulnerable to local effects in periods of low sea level. Investigation of micron scale elemental distributions will assist in clarifying the causes of divergence between the geochemical evidence, provided by solution ICP-MS data and faunal evidence of paleoenvironmental conditions during deposition. In addition future assessment of coeval stratigraphic sections may be needed to establish whether the reconstructed seawater chemistry at the base of the section at Cerro La Silla is a local or platform-wide phenomenon.

Keywords: Argentina; carbon isotopes; Ordovician; Precordillera; sulfur; trace elements.

2.1 Introduction

Sulfur isotope records from carbonate-associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) frequently exhibit poorly understood stratigraphic and lateral variation (Fig. 2.1, Present *et al.*, 2015). Identifying the cause of this variation is critical for confident use of $\delta^{34}\text{S}_{\text{CAS}}$ records to interpret changes in biogeochemical cycling, surface redox conditions and microbial activity over geological time. During the Great Ordovician Biodiversification Event prior to the end-Ordovician mass-extinctions, $\delta^{34}\text{S}_{\text{CAS}}$ records from the La Silla and San Juan Formations of the Argentine Precordillera vary by as much as 20‰ from records in Missouri and Western Newfoundland (Saltzman *et al.*, 2015; Thompson and Kah, 2012). This variability has been attributed to non-conservative isotopic behaviour in a low-sulfate ocean, requiring extension of a stratified ocean with deep water euxinia to the Middle-Ordovician (Gill *et al.*, 2007; Thompson and Kah, 2012). Lateral S isotope variability in coeval Cambrian carbonates also has been interpreted to imply a stratified ocean (Hurtgen *et al.*, 2006; Li *et al.*, 2010; Gill *et al.*, 2011). As carbonate rocks are typically composed of a varying range and abundance of components, including depositional micrite (allomicrite), fossils, cement phases and abiotic grains, the chemical composition of a sample is also potentially influenced by the setting in which constituent components formed and, where values vary between those components, their relative abundance in a particular lithofacies (outcrop and hand sample observations) or microfacies (petrographic observations) (Richardson *et al.*, 2019; Rose *et al.*, 2019). The well-exposed sections of Ordovician carbonates in the Precordillera have produced important chemostratigraphic records that include the first well-constrained $\delta^{13}\text{C}$ records for the Early and Middle Ordovician from the La Silla and San Juan Formations (Buggisch *et al.*, 2003) and $\delta^{34}\text{S}_{\text{CAS}}$ records (Thompson and Kah, 2012).

The current study forms the first part of a larger project investigating the cause of $\delta^{34}\text{S}_{\text{CAS}}$ variability and the scale at which it originates, including: whether heterogeneous isotopic values are being averaged during bulk sample preparation; and whether observed variability in studied samples is primary or secondary. Samples will be placed within a well-characterised stratigraphic framework using three coeval sections of the Ordovician San Juan Formation that have been logged and sampled at a metre-scale resolution at Cerro La Silla, Talacasto and Cerro La Chilca (Fig 2.2). These sections, described in Chapter 2.2 and 2.4 below, exhibit good textural preservation and depth-related facies variability. A metre scale stratigraphic resolution will assist in clarifying whether the published frequency of secular variability in these sections is related to the limitations of the current c. 10m sampling

resolution (Thompson and Kah, 2012). The establishment of a metre scale $\delta^{13}\text{C}_{\text{carb}}$ stratigraphy in this study and occurrence of potentially correlatable K-Bentonite beds at Talacasto and Cerro La Chilca also offers the opportunity to study coeval lateral facies change between stratigraphic sections. The project will therefore permit greater understanding of: (i) lateral variability between coeval locations at a kilometre scale; (ii) secular variability at a metre scale; and (iii) the degree of variability within individual samples at a micron scale.

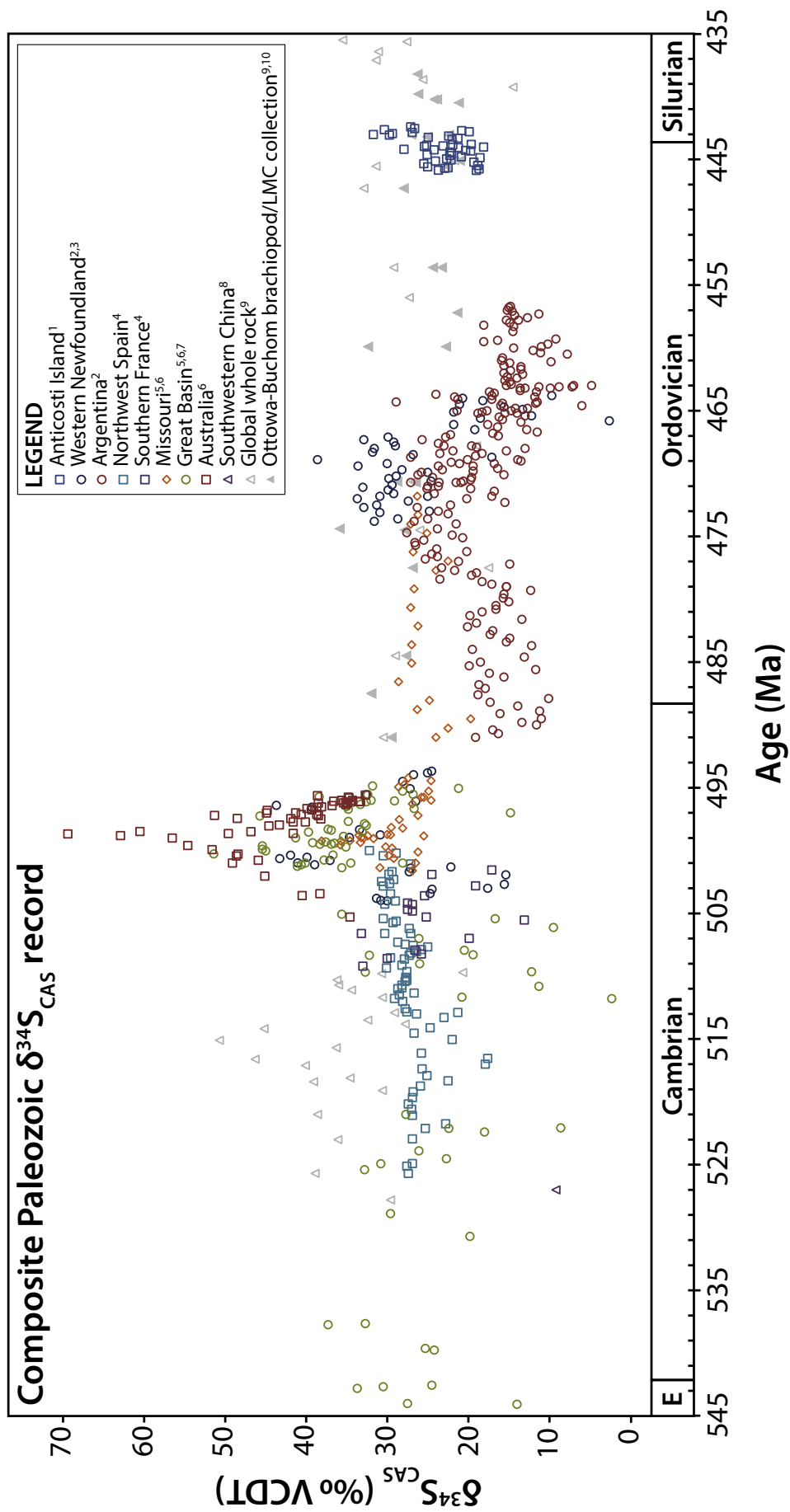
Samples were chosen for investigation of micron-scale sulphur species distribution using synchrotron-based X-ray spectromicroscopy described in Chapter 4 (Samples analysed indicated in Table 2-6). The initial sample set was selected focussing on samples that: (a) display textural component variability; (b) display contrasting textural preservation; and (c) potentially exhibit lateral chemical variability at a cm scale. To investigate the last of these, three thin sections were taken along a cross-section of a single bedding plane from within a single hand-sample. Initial results from bulk $\delta^{34}\text{S}_{\text{CAS}}$ analysis for the section at Cerro La Silla are also presented at Chapter 4, however the stratigraphic resolution of the $\delta^{34}\text{S}_{\text{CAS}}$ produced in the study was limited by delayed establishment of required facilities and staff change in the course of the project. In addition LA-ICP-MS elemental mapping was carried out as described in Chapters 3 and 4 with samples chosen to reflect representative facies through the stratigraphic section (Chapter 3) and to pair with samples analysed by synchrotron-based X-ray spectromicroscopy (Chapter 4) (Table 2-6).

Therefore, the chemostratigraphic analyses presented in this chapter focus first on developing a $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$ and trace element framework for the San Juan Formation at Cerro La Silla, using available expertise and facilities at TCD. $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ data from Talacasto and Cerro La Chilca were also produced as part of the current study and it is intended that these data will be published in future work, supplemented by $\delta^{34}\text{S}_{\text{CAS}}$, $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ data. The current chapter focusses on developing a strong definition of water-column and sediment conditions in the San Juan Formation at Cerro La Silla, using rare earth element and yttrium (REE + Y) trace element data combined with redox-sensitive trace elements (authigenic Mo and U), integrated with petrographic evidence for the presence or absence of reworking of sediment.

In modern seawater and estuaries, many aspects of the shale-normalized REE+Y pattern have been shown to alter in conditions of increasing salinity and depth toward a distinctive open

marine REE+Y profile with a steep slope ($\text{Pr}_n/\text{Yb}_n \ll 1$), a superchondritic Y/Ho ratio, a positive La anomaly (Bau and Dulski, 1996, 1999; Bolhar *et al.*, 2004); a moderate positive Gd anomaly (De Baar *et al.*, 1985; Byrne and Kim, 1990; Byrne *et al.*, 1996; Bau *et al.*, 1997; Zhang and Nozaki, 1998; Bolhar *et al.*, 2004) and a strong negative Ce anomaly (Zhang and Nozaki, 1998), here all calculated according to Lawrence and Kamber (2006) (Fig. 2.3). The REE+Y characteristics of ambient water are commonly faithfully recorded in carbonates (e.g. Webb and Kamber, 2000; Webb *et al.*, 2009) and REE+Y patterns in carbonate have become a useful proxy for relative water-column depth, for distinguishing between lacustrine and marine conditions (e.g. Bolhar and Van Kranendonk, 2007) and for identifying open ocean as opposed to restricted basin settings (Verdel *et al.*, 2018). In addition, both Ce and Eu act as redox proxies, with a pronounced positive Eu anomaly indicating anoxic bottom waters (Kamber *et al.*, 2014) and combined positive Ce and Eu anomalies developing in deep anoxic redox-stratified water columns (Frei *et al.*, 2008; Planavsky *et al.*, 2010). These two REE proxies are particularly useful when supplemented with data of other redox-sensitive elements, including the authigenic component Mo/U ratio ($(\text{Mo:U})_{\text{auth}}$) as a complementary indicator of sediment redox conditions (Algeo and Tribovillard, 2009). Combined with water-column REE+Y proxies, these redox proxies are applied to the San Juan Formation at Cerro La Silla to enable a better assessment of the extent to which its sediment geochemistry represents global seawater chemistry (Webb and Kamber, 2000; Kamber and Webb, 2001b; Nothdurft *et al.*, 2004; Webb *et al.*, 2009; Kamber *et al.*, 2014).

Fig. 2.1: The Paleozoic record of $\delta^{34}\text{S}_{\text{CAS}}$. The latest Cambrian and Ordovician record contains samples from three distinct datasets from Western Newfoundland, Missouri and the Argentine Precordillera with up to 20‰ variability between sampled sections. Records are from ¹Jones and Fike (2013), ²Thompson and Kah (2012), ³Hurtgen *et al.* (2009), ⁴Wotte *et al.* (2012), ⁵Gill *et al.* (2007), ⁶Gill *et al.* (2011), ⁷Loyd *et al.* (2012b), ⁸Goldberg *et al.* (2005), ⁹Kampschulte and Strauss (2004) and ¹⁰Wu *et al.* (2014).



2.2 Geological Setting

The San Juan Formation is exposed within the Cambro-Ordovician carbonates of the Argentine Precordillera platform, a north-south striking, fold-thrust belt between 28°S and 33°S in Northwest Argentina (Fig. 2.2). The Argentine Precordillera is one part of the amalgamated terranes of the Western South American margin (McDonough *et al.*, 1993; Varela and Dalla Salda, 1993; Kay *et al.*, 1996; Varela *et al.*, 1996). Rifting from Laurentia in the Early Cambrian, followed by drift and collision with the Gondwanan margin in the Middle to Late Ordovician (Thomas and Astini, 1999; Thomas and Astini, 2003; Thomas and Astini, 2007) is supported by the Laurentian faunal affinities of Precordillera fossils, the deposition of Famatinian K-bentonites in the San Juan Formation (Ramos, 2004), and records of a metamorphic event at c. 470 – 460 Ma in the Sierras Pampeanas and Famatina east of the Precordillera (Astini *et al.*, 1995; Ramos *et al.*, 1998; Benedetto *et al.*, 1999; Vujovich *et al.*, 2004; Voldman *et al.*, 2009).

At the base of the 2.5 km thick carbonate platform, the Early Cambrian Cerro Totorá and La Laja Formations represent rift-fill and shallow-shelf silicilastics and carbonates (Bordonaro, 1980; Bordonaro, 2003; Gomez *et al.*, 2007) and are overlain by the extensive peritidal complex of the Zonda and La Flecha Formations (Keller, 1999; Bordonaro, 2003). The late-Cambrian to Tremadocian La Silla Formation represents an overall shallowing-upward trend from a subtidal to intertidal-dominated unit and is composed of peloidal and intraclast grainstones, herringbone cross-bedded oolites, mudstones and dolomitic microbial laminites, with fauna generally limited to gastropods and trilobites (Cañas, 1995; Cañas, 1999; Keller, 1999; Bordonaro, 2003). The overlying San Juan Formation exhibits mudstones, bioclastic and intraclastic wackestone and packstone, grainstones, boundstones and intraclast breccia beds, which were deposited at depths from shallow subtidal to below storm wave-base. At the type-section at Cerro La Silla (Fig. 2.2), a sponge-algal boundstone reef is preserved in the lower section and a stromatoporoid framestone reef in the upper section (Fig. 2.4). The section at Cerro La Silla, sampled for this study, falls within the Talacasto sub-basin of the Eastern basin (Keller, 1999) and within the eastern tectofacies of Astini *et al.* (1995) and is considered a relatively shallow water section, distal from the platform margin (Keller, 1999). The drowning of the carbonate platform is recorded as a time transgressive deposition of shale, interpreted as a westward-prograding clastic wedge (Astini *et al.*, 1995), across much of the top of the San Juan Formation, linked to formation of a foreland basin and peripheral bulge (Ortega *et al.*, 1985; Sarmiento, 1986, 1990; Lehnert, 1995; Astini *et al.*, 1995).

Fig. 2.2: (A) Satellite image of the Argentine Precordillera. (B) Geological map of the study area in the northern Argentine Precordillera (adapted from Allmendinger and Judge, 2014). The La Silla and San Juan Formations were sampled at the Cerro La Silla section (1). Thermal maturation data presented are conodont alteration index (CAI) values (Voldman *et al.*, 2010).

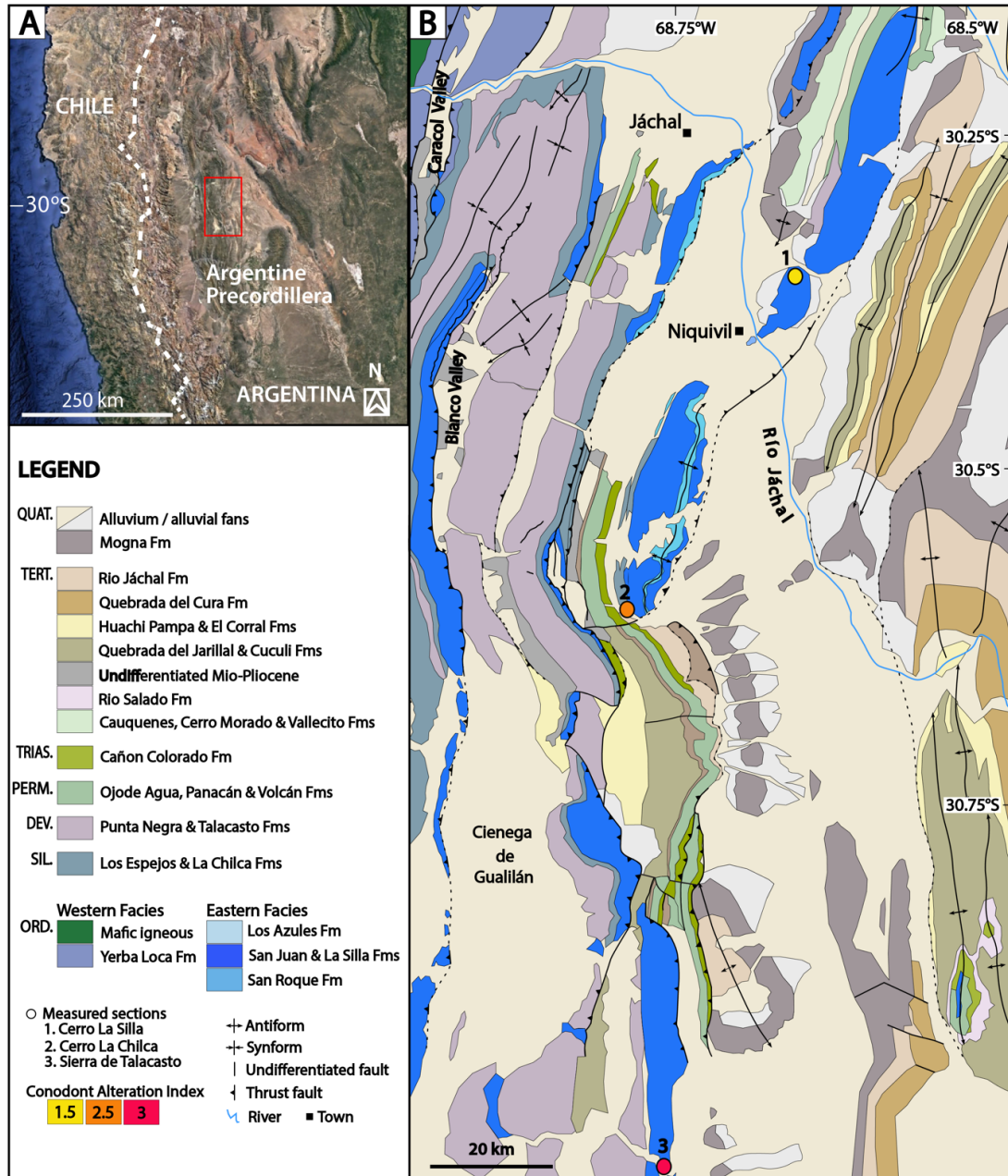
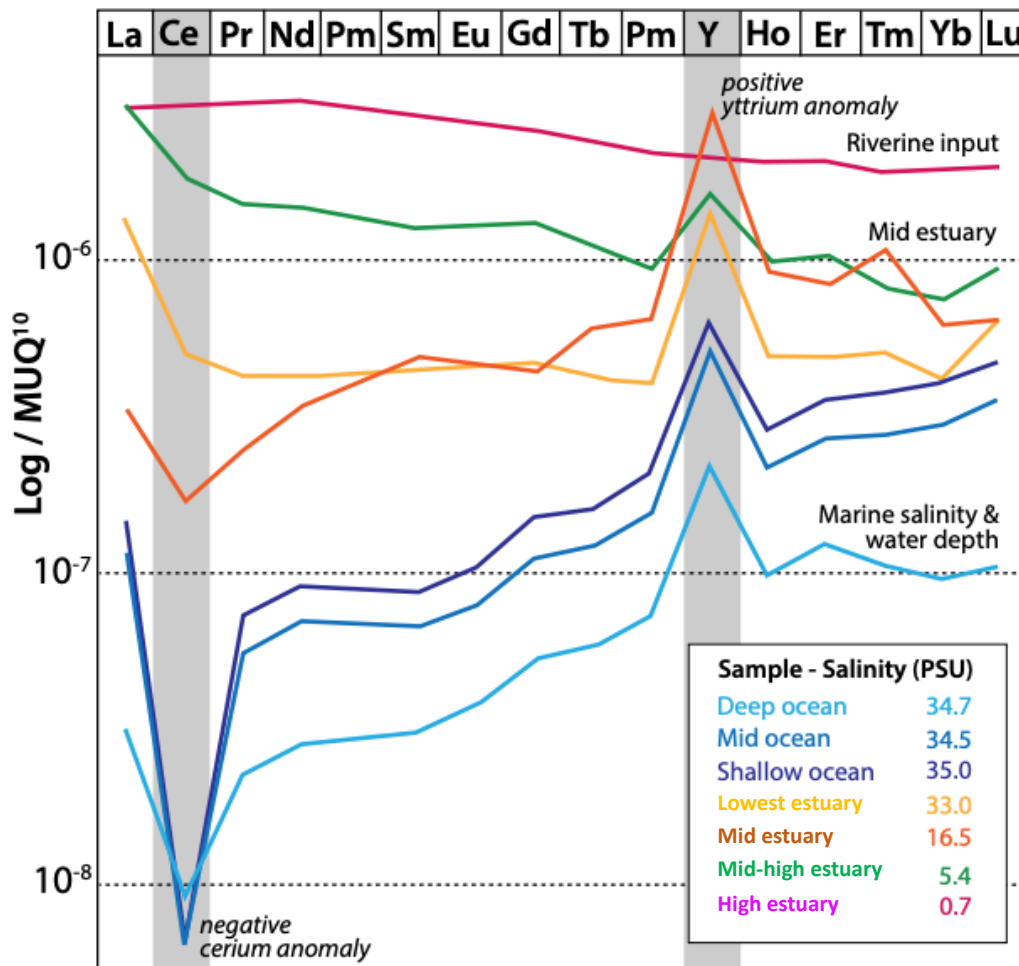


Fig. 2.3: Schematic of shale-normalized dissolved water REE+Y profiles and their alteration with salinity and water depth. Riverine freshwater profiles are flat and uniform, whilst estuarine and shallow marine waters record evolving profiles toward a distinctive marine REE+Y profile with a steep slope ($Pr_n/Yb_n \ll 1$), a superchondritic Y/Ho ratio, a positive La anomaly (Bau and Dulski, 1996, 1999, Bolhar *et al.*, 2004), a moderate positive Gd anomaly (De Baar *et al.*, 1985, Byrne and Kim, 1990, Byrne *et al.*, 1996; Bau *et al.*, 1997; Zhang and Nozaki, 1998; Bolhar *et al.*, 2004) and a strong negative Ce anomaly (Zhang and Nozaki, 1998).



2.3 Methods

In the field, 300 hand samples were taken from the stratigraphic section at Cerro La Silla (Fig. 2.2 and Fig. 2.4. See also detailed stratigraphic log at Appendix 2.1). From these samples, a subset of 275 hand samples were selected taking care to minimize leaching from modern-day weathering. All samples were slabbed with a rock saw to remove any weathered surfaces. Petrographic thin sections were cut from 32 samples. Cathodoluminescence (CL) screening of thin sections for Mn concentrations as an indication of diagenetic alteration was carried out at Trinity College Dublin (TCD) on a Reliotron cold cathode stage mounted on a Nikon binocular microscope (Hemming *et al.*, 1989). Material for elemental and isotopic analyses was obtained by drilling c. 100 mg of carbonate powder from each slab with a tungsten carbide dental drill, targeting well-preserved micritic textures in the slab.

A total of 224 samples were analysed for $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ in 3 laboratories. At TCD and Washington University in St Louis (WashU) c.100 μg samples of drilled carbonate powder were reacted for 4 hours at 72°C with an excess of 100% H_3PO_4 in He-flushed, sealed tubes. At the University of St Andrews (St Andrews), c. 0.3 mg of powdered samples were weighed into Labco Exetainers, flush filled with 6.0 He for 15 minutes then digested in 100% H_3PO_4 for 24 hours at 25°C. The resulting CO_2 analyte was sampled with a Finnigan Gas Bench II, and isotopic ratios were measured with a Delta Plus (TCD and St Andrews) and Delta V Advantage (WashU). Isotopic measurements were calibrated against NBS-19, NBS-20, and two in-house standards, with analytical errors of $< 0.2\text{‰}$ (1σ) $\delta^{13}\text{C}_{\text{carb}}$ and $< 0.4\text{‰}$ (1σ) $\delta^{18}\text{O}_{\text{carb}}$ (TCD), and $< 0.3\text{‰}$ (1σ) for $\delta^{13}\text{C}_{\text{carb}}$ and $< 0.5\text{‰}$ (1σ) $\delta^{18}\text{O}_{\text{carb}}$ (WashU). At St Andrews replicates ($n = 5$) of standard NBS-18 produced a mean $\delta^{13}\text{C}_{\text{carb}}$ value of -5.07‰ (± 0.15 1σ) compared to a certified value of -5.05‰ (± 0.035 1σ). All data are reported in delta notation as per mil (‰) deviations from Vienna Pee Dee Belemnite (VPDB).

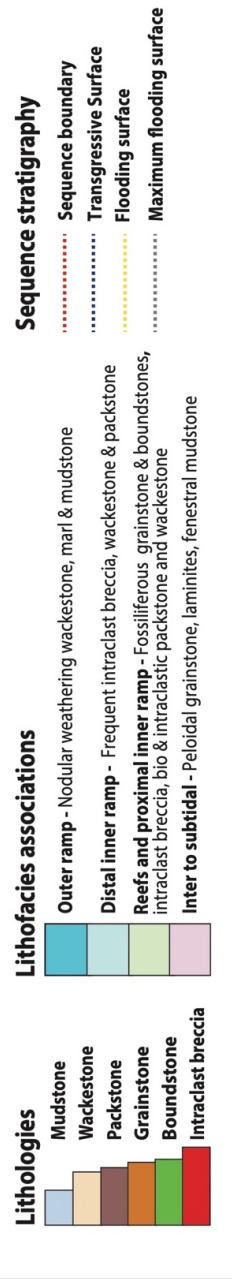
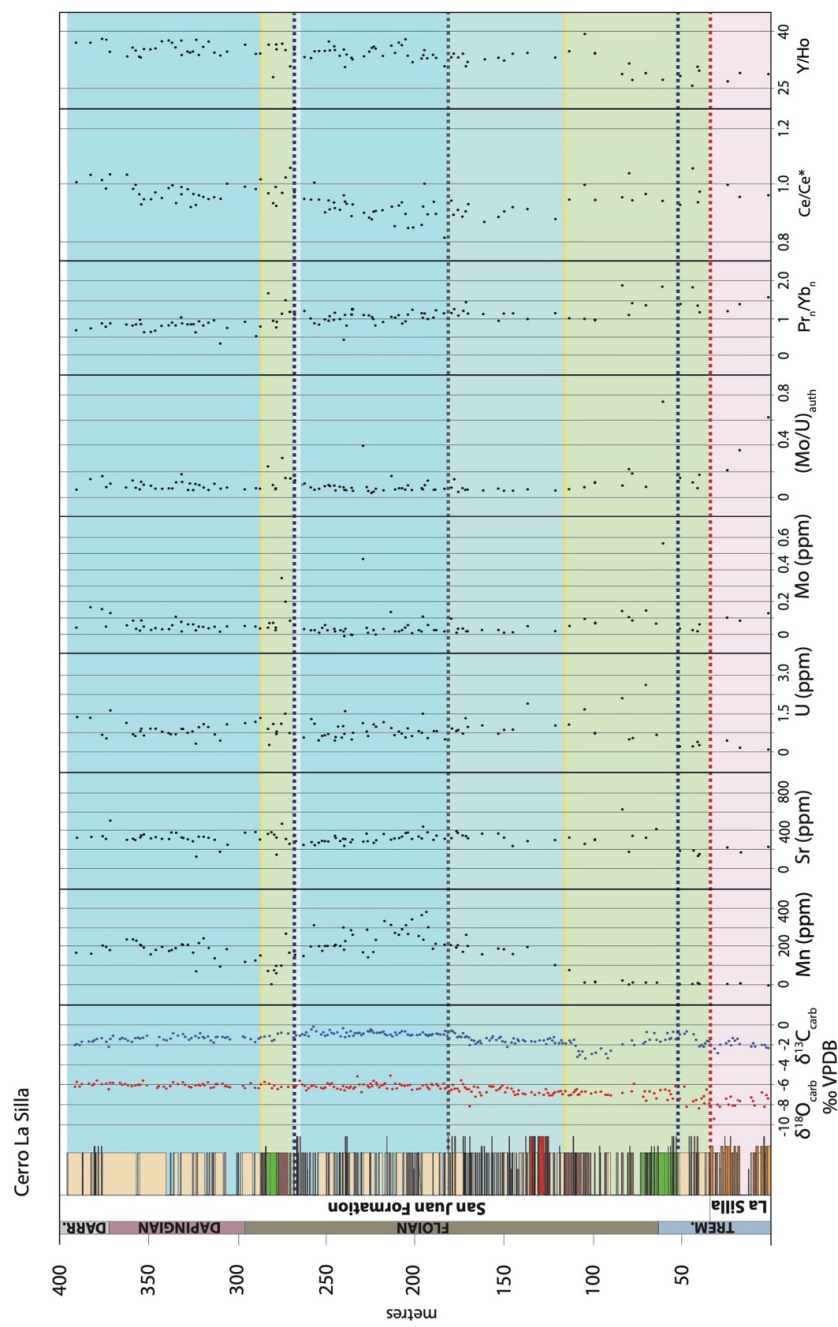
A subset of 109 carbonate samples were analysed using a Thermo Scientific iCap-Qs quadrupole ICP-MS at TCD for 52 major and trace elements, following the digestion methods of (Hahn *et al.*, 2015), and the ICP-MS analyses follow the experimental design of Eggins *et al.* (1997), with modifications described in Kamber (2009) and Babechuk *et al.* (2010). Element concentrations were externally calibrated using multiple digestions of USGS rock-standard W-2. In the absence of homogeneous natural carbonate reference materials with relevant REE concentrations, a selection of additional international silicate rock standards (including the low REE concentration BIR-1) were analysed to test accuracy relative to the laboratory long-term reproducibility (Kamber, 2009). At the preferred very high dilution

rates of the analyses ($> 5,000$), quadrupole ICP-MS analyses become matrix-insensitive and precise (to 2-3%) and accurate (to better than 5%) and REE+Y data can thus be obtained for carbonates with silicate calibration solutions (Allwood *et al.*, 2010). REE+Y data were normalized to the upper continental crust composite MuQ (Mud from Queensland, Australia; Kamber *et al.* (2005)). MUQ is a modern alluvial sediment composite produced and measured with a similar analytical protocol to the present study.

Digestion was carried out by single-step leaching in 5% HNO_3 for twelve hours. Dissolution in 5% HNO_3 ensures rapid total digestion of the carbonate. Aluminum silicates are generally resistant to nitric acid but full digestion of carbonates in 5% HNO_3 may potentially release contaminants from nitric soluble inclusions, such as apatite or from clay phases (Tostevin *et al.*, 2016). However, as solution ICP-MS analysis permits simultaneous measurement of multiple proxy elements for detrital contamination (Al, Zr, Hf, Nb, Ga, Th) in the same analysis as other trace elements of interest, those proxy elements may potentially be used to correct for the effects of siliciclastic contaminant in the resulting data. The effectiveness of this approach is considered in detail in the discussion section below, in particular in light of two recent studies using three-step leaching in 2% HNO_3 (Zhang *et al.*, 2015, Tostevin *et al.*, 2016) that have both produced their most sea-water like patterns from the second of three sequential leaching steps.

Several samples were also selected for *in situ* trace element analysis by LA-ICP-MS at TCD targeting petrographically defined carbonate component textures. These consisted of c. 40 μm thick polished thin sections. A Photon Machines Analyte Excite (193 nm Excimer) laser ablation system with a dual-volume ablation cell, coupled to a Thermo Scientific iCap-Qs quadrupole ICP-MS system, was used. Spot analyses with a 50 μm diameter were performed in 99.999% pure He. A total of 24 masses were analysed over an acquisition time per spot of 120s, consisting of 30s blank and 90s ablation, resulting in c. 90 usable repeats after signal stabilisation. Data were calibrated relative to analyses of NIST 612 (see Kamber and Webb (2007) for preferred values) with the 'trace element' data reduction scheme in Iolite (Paton *et al.*, 2011) and using ^{43}Ca as an internal elemental standard. NIST glasses have been demonstrated to be suitable standards for carbonates for refractory lithophile elements (Jochum *et al.*, 2012).

Fig. 2.4: Stratigraphy with chemostratigraphic proxies for the upper La Silla Formation and the San Juan Formation at Cerro La Silla, the type section of the San Juan Formation. Presented proxies include $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ ($< 0.3\text{‰}$ (1σ) for $\delta^{13}\text{C}_{\text{carb}}$ and $< 0.5\text{‰}$ (1σ) $\delta^{18}\text{O}_{\text{carb}}$) Mn, Sr, U, Mo, $(\text{Mo}/\text{U})_{\text{auth}}$ with the shale normalised REE + Y slope (Pr_n/Yb_n), the Ce anomaly Ce/Ce^* and the Y/Ho ratio. Trace and minor element data are accurate to better than 5%.



2.4 Results

2.4.1 Sedimentology

At Cerro La Silla (Fig. 2.4), the stratigraphic section sampled incorporated c. 35 metres of the upper La Silla Formation and c. 340 m of the overlying San Juan Formation. At the base of the measured section, the lithofacies of the uppermost La Silla Formation include pale grey, peloidal and fenestral wackestones, laminites and grainstones in a shallowing upward sequence. Peloids show an isopachous rim of phreatic cement with a later extensive phase of equant euhedral sparite precipitation, filling interclast space and fenestrae (Fig. 2.5). Gastropods were recorded at outcrop and are visible as relict textures in thin section. The recorded facies are consistent with intertidal flats previously described in the La Silla Formation that include fenestral mudstones formed in protected lagoonal conditions (Cañas, 1999; Keller, 1999; Bordonaro, 2003). The lowermost San Juan Formation begins 35m from the base of the measured section (Keller, 1999, Keller *et al.*, 1994) and includes fenestral mudstones and wackestones, consistent with inter to sub-tidal back-reef lagoonal deposits (Keller *et al.*, 1994; Lehnert, 1995; Keller, 1999). These facies exhibit cross-bedding indicative of shallow conditions above fair-weather wave base.

From c.50 m above the base of the section there is a transition to cross-bedded packstones, mottled grey to dark-grey wackestones and sponge-algal boundstone reef mounds (Cañas and Carrera, 1993; Keller and Flügel, 1996) (Fig. 2.4). Fossil fragmentation and intercalation of cross-bedded packstones and grainstones indicate turbulent, shallow conditions that occur with frequent graded beds with erosive bases and intraclasts up to 20 mm, that formed in high-energy storm events (intraclast breccias) (Fig. 2.5). The sequence from 50 m represents a sponge-algal reef and proximal facies above fair-weather wavebase, periodically affected by storms. The facies continues upsection to c. 80 m, before transitioning to crosslaminated bioclastic and intraclastic packstones and intraclast breccia storm-beds above fair-weather wave base (Fig. 2.4).

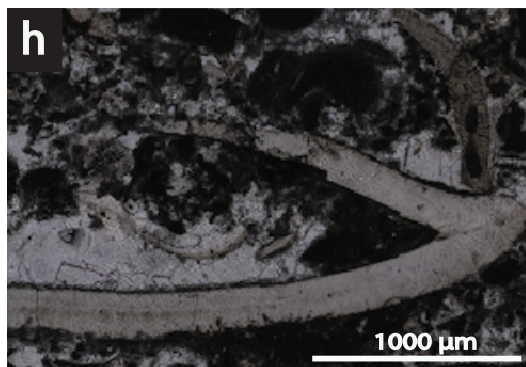
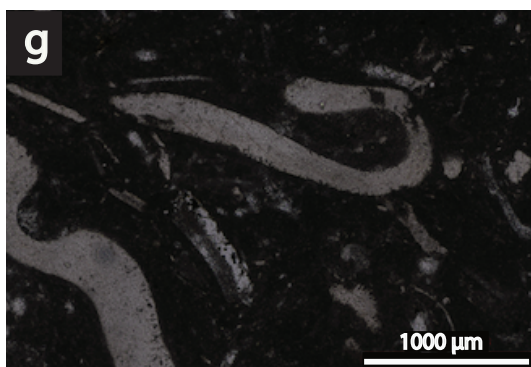
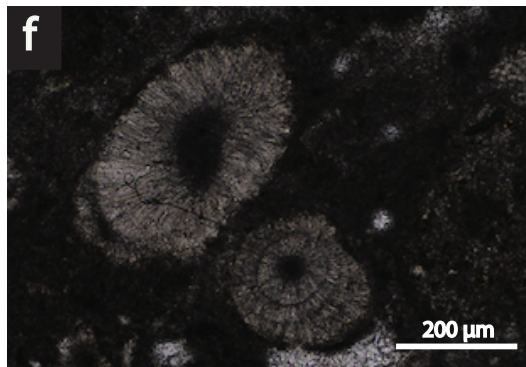
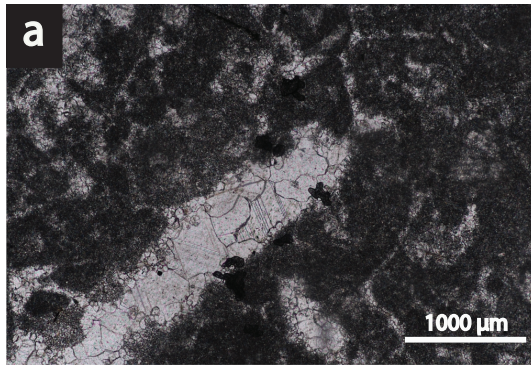
From c. 110 m there is a transition to grey, bioclastic wackestones and mudstones without cross-bedding, indicating transgressive deepening to below fair-weather wave base. Intraclast breccia beds persist, indicating that the facies remains above storm wave base (Fig. 2.4). This sequence represents a distal inner ramp facies (Keller, 1999) and the deepening event is marked by a change from warm-water to temperate water conodont forms (Lehnert, 1995).

Faunae visible at lithofacies and microfacies scale from 110 m include gastropods, rare orthoconic nautiloids, brachiopods, crinoids, trilobites and green algae species that indicate a marine facies remaining in the photic zone (Fig. 3.1h)(Keller, 1999).

Deepening to below storm wave base is represented by a transition to rare to absent intraclast breccia with stylolitic yellow-brown, silty wackestones that weather distinctively (e.g. the nodular limestones in Fig. 2.5e; Cañas, 1999; Keller, 1999) consistent with deposition on the deeper outer-ramp. The position of the lower boundary of the outer ramp facies, based on the cessation of intraclast breccia is conservatively placed at 178m (Fig. 2.4). Lehnert (1995) assigned this deepening phase to the base of the *O. evae* conodont zone, with a change to a colder, deepwater fauna.

Based on the recurrence of frequent intraclast breccia beds, the facies pass above storm wave base at c.261m, returning to the distal inner ramp facies. The facies shallow-up further to above fair-weather wave base at 263m, returning to reef and proximal ramp facies. Dark grey, mottled sponge-algal and stromatoporoid framestone reef mounds (Keller *et al.*, 1993), containing, crinoids, gastropods and brachiopods occur from 273m and have been interpreted as patch reefs (Fig. 2.4). The reef mounds are interbedded with and overlain by cross-bedded crinoidal packstones and grainstones representing channels and shoals in proximity to the reef (Fig. 3.1c; Keller, 1999). Above the reef from 285m there is a deepening to outer ramp facies below storm wave base that continues to the top of the section with the exception of a short, six-metre interval of grainstone at c. 372m. The top of the San Juan Formation, which elsewhere is represented by a transition to overlying deeper basinal facies of interbedded shales and organic-rich limestones, is not exposed at Cerro La Silla.

Fig. 2.5: Characteristic carbonate facies of the San Juan Formation at Cerro La Silla, Argentine Precordillera. (A) Peloidal wackestone from the upper La Silla Fm showing a grumeleuse micritic texture with peloids of microbial and moldic origin. Intergranular cement exhibits an initial thin isopachous phase and a later equant spar phase. (B) Sponge-algal reef mounds from the lower reef facies. (C) Reef mounds intercalated with cross-bedded grainstone within the lower reef facies (Fig. 2.4). (D) Deep water nodular weathered wackestone outcrop. (E) Normal graded intraclast breccia bed showing redeposited pale grey storm rip-up clasts in a dark wackestone matrix. Coin is 20 mm and intraclasts are 10 mm to 20 mm. (F) Algal *Nuia* wackestone deposited below fairweather wave base on the distal inner ramp. Note the good textural preservation of *Nuia* fossils and absence of an early cement rim on the fossils. (G) Trilobite packestone deposited below storm wavebase on the outer ramp. Fossils are texturally well preserved and lack an early cement rim. (H) Redeposited trilobite fragment with geopetal micrite fill from upper reef and proximal facies. Note the primary micritic fill, the early thin phreatic cement (that encloses both the fossil fragment and geopetal micrite fill) and the later intergranular drusy spar phase.



2.4.2 Geochemistry

Both $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ isotope systems only exhibit modest variability and both show coherent trends with an absence of outliers (Tables 2-1 and 2-2; Fig. 2.4). Moving up section, the $\delta^{13}\text{C}_{\text{carb}}$ starts out with relatively isotopically light values of c. -2 ‰ in the uppermost La Silla Formation, into the most variable portion of the section between c. -3 to -1‰ in the base of the San Juan Formation before becoming quite monotonous around -1‰ through the rest of the section. Oxygen isotopes also show only modest variations (Fig. 2.4).

The $\delta^{13}\text{C}_{\text{carb}}$ records from the measured section exhibit stratigraphic marker horizons and $\delta^{13}\text{C}_{\text{carb}}$ excursions that are identifiable in the two published records by Buggisch (2003) and Thompson and Kah (2012). Correlatable horizons include the two reef facies and the termination of the outcrop at the top of the measured section. Both the published $\delta^{13}\text{C}_{\text{carb}}$ records and that of the current study correlate well with each other above 110 m (Fig. 2.5). However, there are identifiable differences between the records in all three studies from the base of the measured section to 110 m. Key differences include:

- (i) The thickness of the lower reef, which is recorded as c. 10m by Buggisch (2003) and c. 25 m in the Thompson and Kah (2012) and current studies;
- (ii) In the $\delta^{13}\text{C}_{\text{carb}}$ record of Buggisch (2003) the most prominent negative excursion in the stratigraphic section (where $\delta^{13}\text{C}_{\text{carb}}$ approaches -3‰) occurs from c. 10 m above the lower reef. The $\delta^{13}\text{C}_{\text{carb}}$ then remains at similar, low values for c. 25 m before a rapid return to more positive values close to -1‰. In the current study the $\delta^{13}\text{C}_{\text{carb}}$ record is similar to that of Buggisch (2003). However, the lowermost reef is c.15m thinner in the Buggisch (2003) stratigraphy so that the $\delta^{13}\text{C}_{\text{carb}}$ record is consistently offset by 15 m from that in the current study. In the $\delta^{13}\text{C}_{\text{carb}}$ record of Thompson and Kah (2012) this excursion occurs within the lower reef and the return to more positive values occurs immediately above the top of the lower reef.

Above the lower reef mounds at Cerro La Silla the section drops downward precipitously, requiring careful lateral correlations whilst moving safely down the steep slope. It is therefore considered likely that the differences in the three stratigraphic records were produced by sampling and measurement challenges during field logging. The dataset in the current study

represents the most complete and accurate of the existing datasets as it records both the full 25 m thickness of the lower reef (as also recorded by Thompson and Kah, 2012) and the full negative excursion in $\delta^{13}\text{C}_{\text{carb}}$ above the reef (as previously recorded by Buggisch, 2003).

The dataset from the full measured section shows very limited covariation between $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ ($r^2 = 0.19$, $p\text{-value} < 0.0001$), typical of a well-preserved $\delta^{13}\text{C}_{\text{carb}}$ sequence (Banner and Hanson, 1990)(Fig. 2.6). Manganese and Sr concentrations show a modest positive rather than a negative covariation ($r^2 = 0.20$, $p\text{-value} = < 0.0001$), also consistent with good overall preservation of $\delta^{13}\text{C}_{\text{carb}}$ and trace element values (Banner and Hanson, 1990). Manganese concentrations through the section generally fall within the published range for well-preserved low Mg calcite (91 of 103 samples are < 300 ppm, Denison *et al.*, 1994, or < 100 ppm van Geldern *et al.*, 2006). However, Sr concentrations are lower than published values for well-preserved low magnesium calcite (at $\text{Sr} > 500$ ppm (van Geldern *et al.*, 2006) and $\text{Sr} > 900$ ppm (Denison *et al.*, 1994)). The mean Sr concentrations for the full section is 292 ppm (SD = 88 ppm, $n = 103$, range = 124 to 888 ppm). Only 2 of 103 samples are above the 500 ppm lower limit presented by van Geldern *et al.* (2006) as indicative of a well preserved $\delta^{13}\text{C}_{\text{carb}}$ record, whilst none exceed the 900 ppm lower limit published by Denison *et al.* (1994).

The minor element and REE+Y proxy ratios are shown as chemostratigraphic plots in figure 2.4. Lower reef facies REE+Y patterns are slightly LREE enriched to flat, with profiles that are similar to those formed in conditions intermediate between seawater and modern river water. Above 80 m the data show a fluctuating trend, with development of more seawater-like REE+Y patterns with seawater proxy REE+Y anomalies (Fig. 2.4) but these features remain much more subdued than the steep, upper crust-normalized patterns that are seen in fully open marine seawater and carbonate proxies thereof (e.g. Nothdurft *et al.*, 2004)(Fig. 2.7). The strong fluctuation in the relative magnitude of shale (MUQ)-normalized REE+Y features, (light rare earth element (LREE) depletion, La, Ce and Gd anomalies, superchondritic Y/Ho ratio) through the stratigraphy (Fig. 2.4) can potentially be attributable to a number of distinct causes, including variable contamination by siliciclastic material, phosphates or Fe-Mn oxides, diagenetic alteration, or a reflection of primary chemical changes in the composition of the water-column over time, as explored in the following discussion. To aid the distinction between primary REE+Y features versus contamination and/or secondary overprint, LA-ICP-MS analyses were also obtained on carefully targeted areas ($n = 48$) of representative samples (Table 2-4). The REE+Y patterns of the *in situ* data

are very similar in topology to the micro-drilled powder-derived solution data with none of the *in-situ* analysed patterns exhibiting the typical open marine REE+Y features of steep shale-normalized slopes, strong negative Ce anomalies and superchondritic Y/Ho ratios (Fig. 2.7).

Fig. 2.6: (A) $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ crossplot showing limited covariation throughout the Cerro La Silla section ($r^2 = 0.19$, p-value < 0.0001), consistent with good overall conservation of $\delta^{13}\text{C}_{\text{carb}}$ and trace element data in the studied samples (Banner and Hanson, 1990). (B) Mn and Sr concentrations exhibit a weak positive correlation ($r^2 = 0.20$, p-value $= < 0.0001$) consistent with good overall conservation of $\delta^{13}\text{C}_{\text{carb}}$ and trace element data in the studied samples (Banner and Hanson, 1990). (C) La v Ce anomaly crossplot shows both positive La and negative Ce anomalies but of a smaller magnitude than those expected for fully marine conditions (see Fig. 2.3).

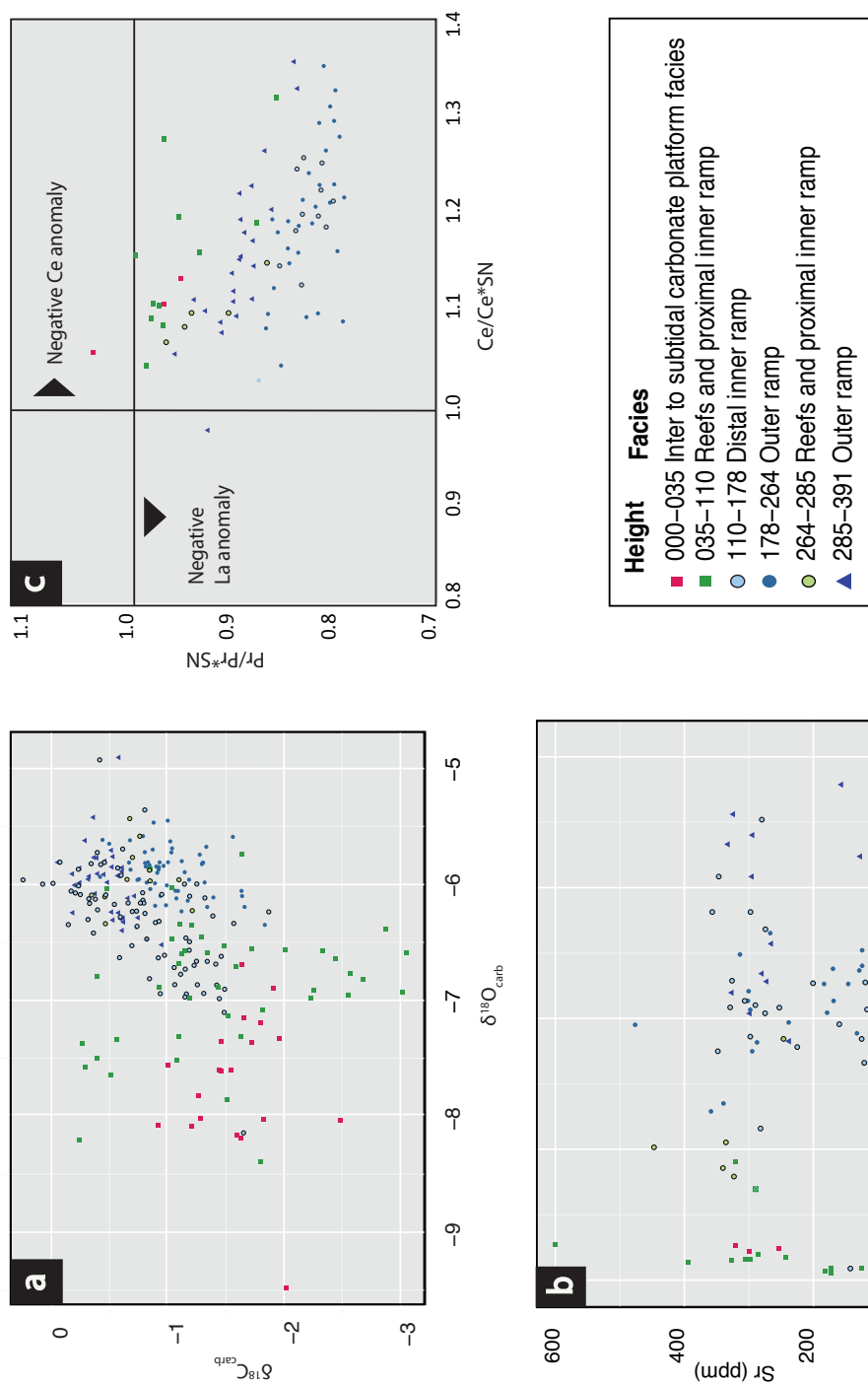


Fig. 2.7A: Median shale normalised REE+Y profiles from LA-ICP-MS analyses of micrite presented with bulk solution values from solution ICP-MS in the same samples at 104.4m, 135.7m and 204.4m

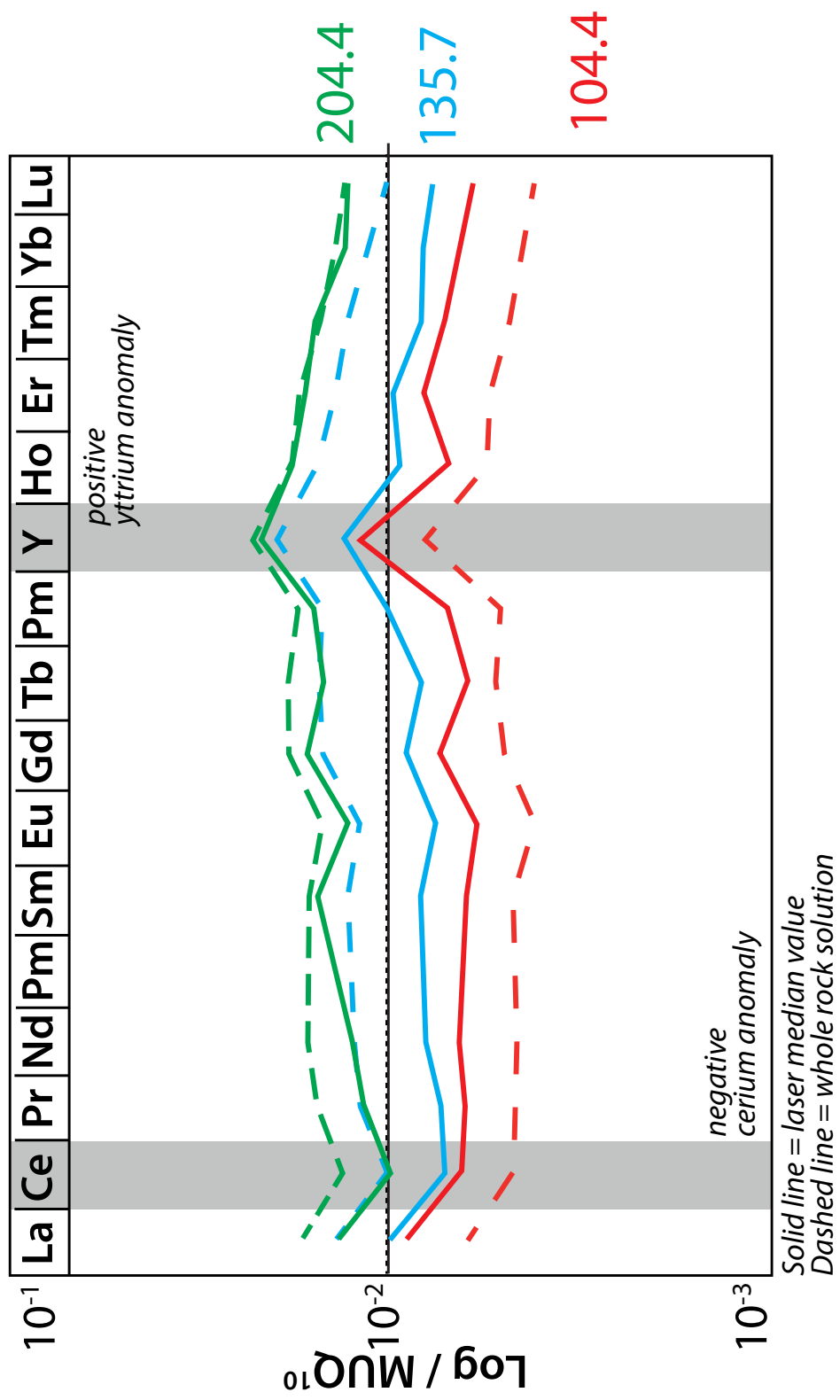


Fig. 2.7B: Shale normalised REE+Y profiles from LA-ICP-MS analysis of key carbonate components. Spot values for micrite from the sample at 104.4m in the stratigraphic section show REE + Y features consistent with solution-ICP-MS data from the same sample.

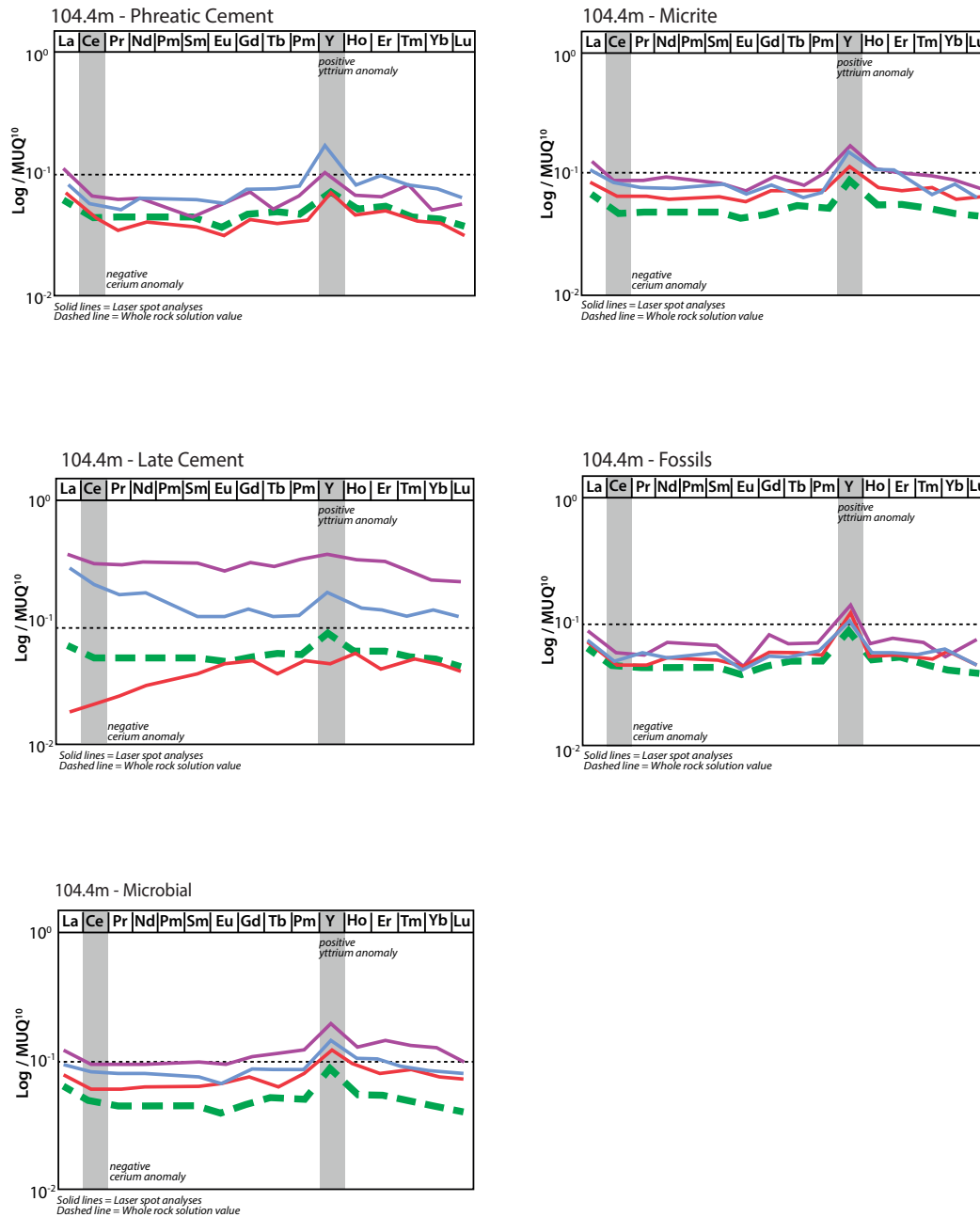


Fig. 2.7C: REE+Y profiles from LA-ICP-MS analysis of key carbonate components. Spot values of micrite from sample 135.7 m in the stratigraphic section show REE + Y features consistent with solution-ICP-MS data from the same sample.

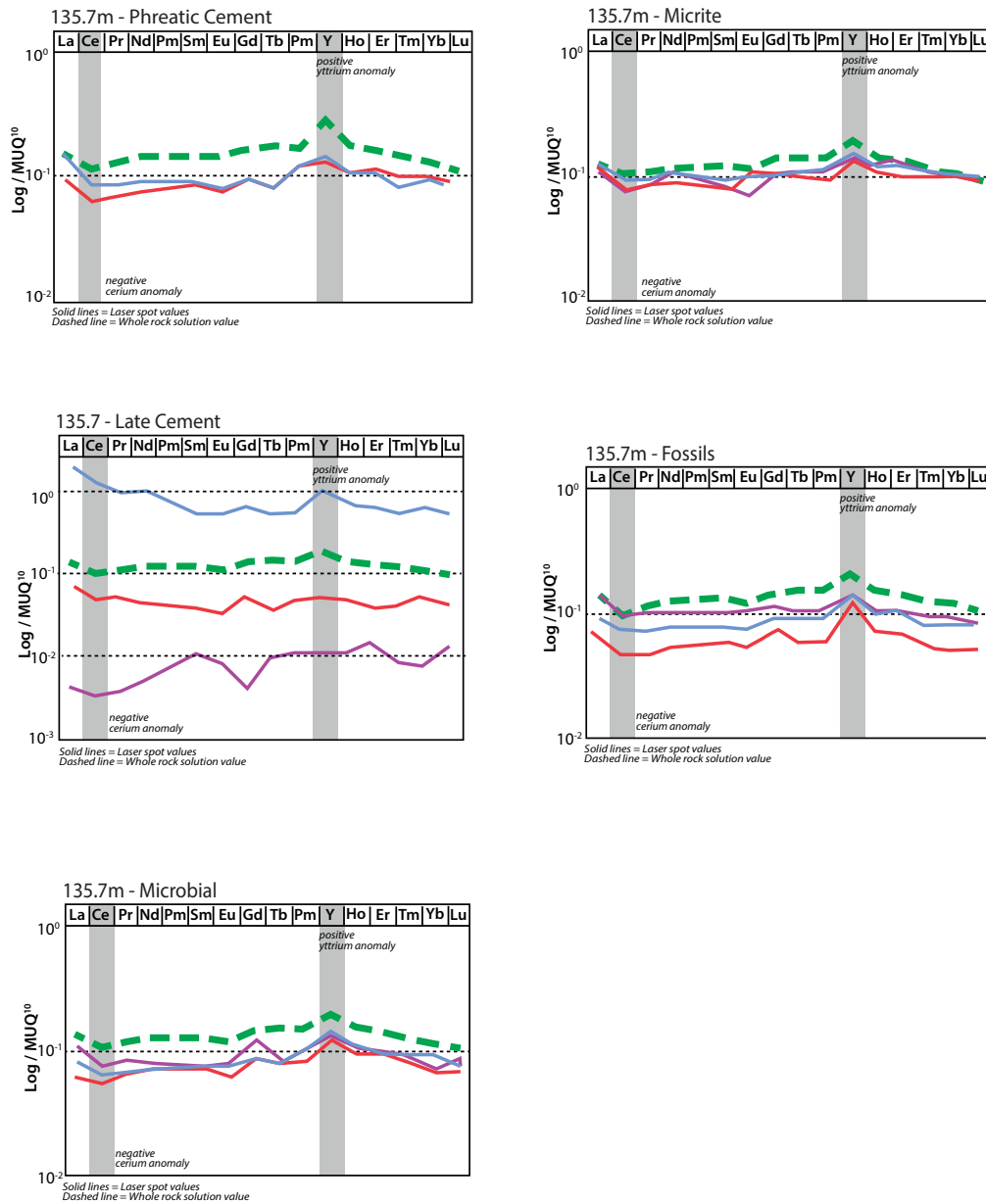
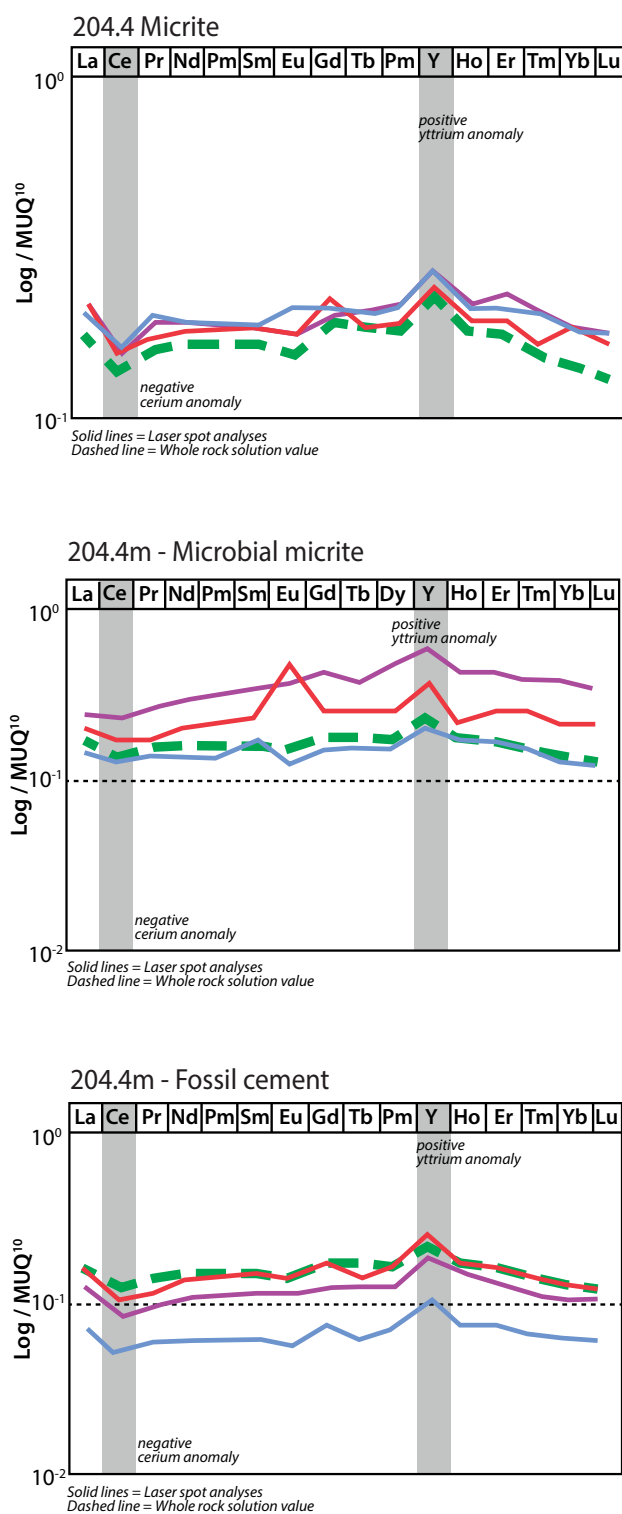


Fig. 2.7D: Shale normalised REE+Y profiles from LA-ICP-MS analysis of key carbonate components. Spot values of micrite for sample 204.4m in the stratigraphic section show REE + Y features consistent with solution-ICP-MS data from the same sample.



2.5 Discussion

2.5.1 Contamination

Contamination from fine-grained siliciclastic material and/or ferromanganese oxyhydroxides is a concern for the interpretation of many trace element data from carbonates. For the REE+Y, the situation is exacerbated because shale (Webb and Kamber, 2000; Nothdurft *et al.*, 2004; Tostevin *et al.*, 2016), phosphates (German and Elderfield, 1990; Reynard *et al.*, 1999) and ferro-manganese oxyhydroxides all have much higher REE+Y concentrations (Bau and Dulski, 1996), leaving carbonate vulnerable to even small degrees (c. 2% by mass) of contamination (Nothdurft *et al.*, 2004).

An advantage of solution-based analysis is that the weak acid (in this case 5% HNO₃) preferentially dissolves carbonate, leaving more resistant silicates and oxyhydroxides largely undigested. A common monitor of siliciclastic contamination is Al, which typically has very low concentrations in clean, pure carbonates. In the studied section, the Al concentration is generally low, ranging from 30 to 2,900 ppm (mean = 630 ppm, SD = 495 ppm, n = 104). This is well below published siliciclastic-contaminated carbonate Al concentrations of 4,200 ppm (Veizer, 1983). Notwithstanding this evidence for a generally low siliciclastic contribution, its presence as a contaminant is supported by moderate to strong covariation of Al with other crustal elements (r^2 = Al v. Ti = 0.86, Sc = 0.77, Zr = 0.52, Ga = 0.98, Fe = 0.68, Th = 0.10, P = 0.39; all p-values < 0.0001, n = 104). There is also a modest but significant correlation between total REE concentration with both Ga and Al (r^2 = 0.32 and 0.34 respectively, p-value < 0.0001, n = 104). This is expected because Ga and Al are geochemical twin elements and are strongly concentrated in clay minerals (e.g. Kamber *et al.*, 2005). The relatively strong correlation of Fe with Al (r^2 = 0.68) suggests that much of the Fe in the digested sample is from detritus and not from Fe substitution into the carbonate lattice. However, the clastic contributions as determined from either Al or Zr contents (both abundant in shale) are low in magnitude (Zr remains below 0.3 ppm compared to 199 ppm in MUQ), far below the 1% REE contribution from shale previously considered required to cause major reductions in the La and Ce anomalies or extent of LREE depletion in contaminated carbonate (Nothdurft *et al.*, 2004). None of the REE+Y proxy ratios commonly used, nor the U and Mo concentrations and enrichment factors show correlation with Al concentration. The geochemical evidence is therefore ambiguous as to whether the flat REE pattern and the subdued expressions of the typical marine REE features are attributable to

detrital contamination. However, based on the strong evidence of marine conditions provided by marine fauna above 110 m in the San Juan Formation, it is very unlikely that non-marine conditions, if present, persisted above the uppermost La Silla Formation and lowermost San Juan Formation. A secondary process of contamination or diagenetic alteration is likely to be responsible for the subdued expression of the marine REE+Y features above 110 m in the section. Therefore, the effects of clastic contamination on the REE+Y patterns were corrected for by deduction of the shale component, calculated based on the concentration of elements associated with siliciclastic sediment and a shale composite. In the current study Ga concentration was used as the most appropriate proxy for clastic contribution as follows:

$$\text{element}_{\text{sample}} - ((\text{Ga}_{\text{sample}}/\text{Ga}_{\text{MUQ}}) * \text{element}_{\text{MUQ}})$$

The resulting REE+Y patterns were compared to those of both the original data and additional patterns obtained by *in situ* LA-ICP-MS analyses, carried out on detritus-free carbonate components, including cement phases, microbial and fossil components (Fig. 2.7). Mean proxy results show agreement between LA-ICP-MS-derived REE+Y profiles and solution-derived micrite values (Table 2-4). The *in situ* value in micrite most closely approaches solution data values, confirming the precise sampling of the micritic component. However, the exception within the *in situ* data is the early cement and fossil values for sample 104.4, which returns larger Y/Ho, La and Ce anomalies than the solution data - at the lowest end of the range reported for marine hydrogenous deposits and retaining a flat shale normalized slope. There is also a strong positive correlation of total REE concentration with Fe, Mn, Sc, Ti and Mg ($r^2 = 0.70, 0.59$ and $0.66, 0.50$ and 0.42 respectively, see Table 2-3). These elements also occur in greater concentrations in facies representing distal and deeper platform settings supporting greater siliciclastic basinal inputs in those deeper settings.

2.5.2 Diagenesis

An assessment of the extent of diagenetic alteration was carried out by petrographic and cathodoluminescence screening and geochemical analysis. At the base of the section (Fig. 2.4) the upper La Silla Formation (0 – c.35 m) and basal San Juan Formation exhibit a thin rim of isopachous phreatic cement and a later extensive drusy calcite phase (Fig. 2.5). The samples are non-luminescent (Brand and Veizer, 1980; Veizer, 1983; Hemming *et al.*, 1989; Banner and Hanson, 1990; Banner, 1995) and, moving upsection, remain non to dull-luminescent with rare CL-brighter veins and fossils (these phases and any evidence of shale

contamination were avoided in sampling) (Banner and Hanson, 1990; Knoll *et al.*, 1995; Savard *et al.*, 1995). Further screening was carried out by assessing covariance in $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$, Mn and Sr data (Fig. 2.6). Meteoric fluids with carbon incorporated from organic matter are depleted in ^{18}O and ^{13}C relative to seawater and have a high oxygen to carbon ratio. Therefore during meteoric diagenesis $\delta^{18}\text{O}_{\text{carb}}$ alters at much lower water:rock volumes ($< \times 10$) than $\delta^{13}\text{C}_{\text{carb}}$ ($\times 1000$) or trace element concentrations ($\times 10,000$) (Brand and Veizer, 1981; Veizer, 1983; Banner and Hanson, 1990; Jacobsen and Kaufman, 1999). In an open system, $\delta^{13}\text{C}_{\text{carb}}$ values are expected to covary with $\delta^{18}\text{O}$ where water:rock interaction reaches volumes sufficient to alter $\delta^{13}\text{C}_{\text{carb}}$ (Brand and Veizer, 1980; Banner and Hanson, 1990). Oxygen isotope values are temperature sensitive and $\delta^{18}\text{O}$ is also expected to be more negative where diagenesis occurs during deeper burial (Dickson and Coleman, 1980; Brand and Veizer, 1981). In addition the much stronger partition coefficient of Mn relative to Sr for calcite results in its preferential concentration in calcite during meteoric diagenesis (Brand and Veizer, 1980). Where fluid:rock interaction is sufficient to alter $\delta^{13}\text{C}_{\text{carb}}$, Mn and Sr are expected to show a negative correlation. Mn:Sr ratios < 1 are also considered to represent well preserved carbonates (Brand and Veizer, 1980; Banner and Hanson, 1990). In the current study the data for the overall section suggests that diagenetic fluids, in a hypothesized open system, may have caused Sr loss and ^{18}O depletion, although water:rock interaction volumes may not have been insufficient to alter primary $\delta^{13}\text{C}_{\text{carb}}$ or REE+Y values (Banner and Hanson, 1990). This interpretation is supported by a lack of correlation between $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$, Mn, Sr or the marine REE + Y proxy ratios (Derry, 2010)(Fig. 2.6) and has been cited in previous studies to support the primary marine composition of carbon and sulfur isotope data from Cerro La Silla (Buggisch, 2003 and Thompson and Kah, 2012).

It should also be noted that there is strong evidence of sea-level change in the San Juan Formation at Cerro La Silla, an important factor in determining the penetration depth of meteoric lenses and resulting alteration, which is more effective during regression (Allan and Matthews, 1982; Melim *et al.*, 2002, 2004; Oehlert and Swart, 2014). As the facies switched between regressive and transgressive periods it is likely that sections of the c.400m thick stratigraphy underwent very different alteration regimes. Studies of ancient carbonates have identified characteristic behaviors of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$, originally identified in Pleistocene core (Allan and Matthews, 1982) in distinct zones of meteoric lenses during regressive periods (the freshwater phreatic zone; the fresh and marine water mixing zone and the marine phreatic zone (Allan and Matthews, 1982; Melim *et al.*, 2002; Melim *et al.*, 2004; Oehlert and Swart, 2014).

In the measured stratigraphic section the lowermost c. 51 metres of peritidal (including shallow lagoonal/backreef) carbonates have the strongest textural and geochemical evidence of possible alteration. The $\delta^{18}\text{O}_{\text{carb}}$ values reach $< 8\text{‰}$ and $\delta^{13}\text{C}_{\text{carb}}$ data are variable and reach minimum values $< 2.5\text{‰}$, with standard deviations of 0.65 and 0.50 respectively (Fig. 2.4). There is also an increase in Sr concentrations above this horizon.

The gradual increase in Sr coincides with a transgressive change to deeper water, evident in sedimentary facies and a change to temperate and subsequently colder water faunae moving up-section (Lehnert, 1995). Modern ocean deeper water Sr vertical and horizontal variability is in the region of 2% and 2-3% respectively with the deep ocean more enriched, however due to its long residence time relative to mixing Sr is considered a conservative element in the global oceans through geological time. Factors including temperature, salinity, continental run-off and nutrient supply (particularly in low latitude upwelling) have all been considered as potential drivers of lateral and depth variability in the ocean (see De Villers, 1999). In the relatively shallow ocean depth range represented by facies at Cerro La Silla (at all times within the photic zone based on green algae fossil occurrence (Keller, 1999)), vertical variability in the modern ocean is expected to be associated principally with growth and dissolution of planktonic acantharea (radiolarians) in the water column (de Villiers, 1999). The low abundance of fossils at the base of the section and subsequent development upsection of a more diverse marine fauna may also suggest a possible means of delivery of greater Sr levels to the sediment porewaters via dissolution of aragonite and release of Sr. The Sr concentrations in phreatic cements formed in sediment porewaters and components formed in the watercolumn are therefore further investigated by LA ICP-MS mapping in Chapter 3.

Meteoric cement formation and/or component alteration in these shallow facies is supported by low Sr (< 240 ppm) and low Sr/Ca ratios below c.51 m. In the deeper water carbonates below fairweather wavebase, Sr concentrations are more elevated with a mean of 300 ppm and rare negative excursions consistent with less extensive penetration by meteoric waters. Keller (1999) has argued that the base of the reef at c.51 m forms a transgressive surface and the evidence of decreased meteoric diagenesis from trace element, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ above this horizon are consistent with deepening during transgression. Very low Mn concentrations may also relate to catchments with exclusively carbonate drainage lithologies and resulting low concentrations of available Mn. Modern, broadly analogous sediments from Great Bahamas Bank depositional environments have minimal Fe and Mn levels, with source

dominated by small magnitude, autochthonous Saharan dust delivery to carbonate sediments rather than local sources (Swart *et al.*, 2014).

Manganese concentrations in the samples below 51 m are anomalously low at < 10 ppm in the La Silla Formation and rise slowly to < 25 ppm in the lower reef, increasing steeply only in the distal facies above 110 m. The low Mn concentrations restrict the Mn:Sr ratio below values expected in altered carbonates (> 1). A lack of Mn^{2+} availability during primary carbonate formation might be caused by conditions that preclude Mn oxide reduction in the watercolumn or sediment porewater and/or factors that influence the flux of Mn delivered to the ocean from riverine sources (including catchment lithology)(Swart *et al.* 2014). In the modern ocean, Mn is typically at greater concentrations in the shallow ocean due to riverine oxide and dust inputs (van Hulten et al., 2016). At Cerro La Silla Mn concentrations increase with depth and are at very low concentrations in shallow surface waters of the La Silla Formation. This is consistent with very low riverine and dust inputs during formation of the La Silla Formation.

A strong trend to lighter $\delta^{13}\text{C}_{\text{carb}}$ values also begins and persists through the reef and overlying facies, reaching minimum values of -3.0‰ between 91.8 m and 108.9 m, followed by a rapid increase of $\delta^{13}\text{C}_{\text{carb}}$ to -1.2‰ at c. 110 m. This excursion in $\delta^{13}\text{C}_{\text{carb}}$ is of a high magnitude, exhibits less short scale variability than expected as a result of diagenesis and shows no covariance with $\delta^{18}\text{O}_{\text{carb}}$. It has been correlated with a global marine $\delta^{13}\text{C}_{\text{carb}}$ excursion in previous studies (Buggisch *et al.*, 2003; Bergström *et al.*, 2008; Saltzman *et al.*, 2015).

A return to very low Mn concentrations (<<100 ppm) occurs over a short distance in the upper reef facies and overlying packstones, dropping from 200 ppm to 5 ppm, whilst Sr also decreases to 173 ppm at 280.6 m, so that the Mn:Sr ratio remains < 1. Diagenetic loss may explain the low Sr concentrations in these samples. Finally, close to the top of the sampled section $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ covary in a wackestone sequence from 352 m to 371 m ($r^2 = 0.68$, p-value < 0.05), with negative correlation of Mn and Sr between 353.9 m and 374.3 m ($r^2 = 0.60$, p-value < 0.05) and a negative excursion in the Sr/Ca data. A further negative correlation of Mn and Sr occurs from 371 m to 381m ($r^2 = 0.52$, p-value < 0.05). These samples underly and coincide with a six-metre interval of grainstone from 372 m to c.378 m that may represent a cryptic, short-lived regressive period that did not reach fairweather wave base, but permitted penetration of a meteoric lens.

The data illustrate that at least three of the shallower segments of the stratigraphic section display Sr variability whose scale is most consistent with diagenetic Sr loss or formation of phreatic cement in mixed-zone brackish porewaters and that is most clearly identified as negative excursions in Sr/Ca ratios. The extent of these zones may be constrained by combining macrotextural evidence of depth, microtextural evidence from cement fabrics, including the presence or extent of phreatic cements, and trace elements and isotopic variability. This evidence allows the influence of diagenesis to be distinguished from changes in marine chemical composition, both of which are affected by sea level change (Zhao and Zheng, 2017). However, to determine whether the REE+Y attributes of seawater chemistry examined in this study, namely the shale normalized slope, Y/Ho ratio and La, Gd and Ce anomalies (referred to as the marine “REE+Y proxies”), or the U_{EF} or Mo_{EF} , were altered they were also assessed for covariation with $\delta^{18}O$ and Sr, which would be expected to become more negative and be lost respectively during meteoric diagenesis. Results indicate that variation is very weak to absent throughout the stratigraphic section (Fig. 2.6 and Table 2-3). Calculated partition coefficients between calcite and water for REE + Y are > 100 (Zhong and Mucci, 1995; Webb and Kamber, 2000; Della Porta *et al.*, 2015; Zhao and Zheng, 2017), whilst diagenetic models indicate that water:rock ratios higher than $\times 10,000$ are necessary to significantly change the REE composition of calcites during meteoric diagenesis (Banner and Hanson, 1990). Support for the robust resistance of REE+Y to meteoric alteration profiles in aragonite, which has low partition coefficients of c.1-5 with seawater (Sholkovitz and Shen, 1995; Wyndham *et al.*, 2004), is also found in the recovery of conserved REE+Y patterns across a meteoric alteration front in Pleistocene corals where complete neomorphism of calcite from aragonite had occurred. This process resulted in a decrease in the concentration of Sr, Ba and U and increased Mn as predicted in meteoric diagenesis (Webb and Kamber, 2000).

An assessment for the possible influence of phosphates was also carried out as they are elevated in REE relative to carbonate and are prone to alteration by diagenesis (German and Elderfield, 1990; Reynard *et al.*, 1999). There is very low covariation of REE+Y proxies with P in the dataset, and P and total REE concentration shows low covariance ($r^2 = 0.29$). In addition, with the exception of an excluded sample at 171 m, which shows a much greater LREE and MREE enrichment than could be expected in marine carbonates, the patterns do not exhibit MREE enrichments as would be expected from diagenetic phosphate (Byrne *et al.*, 1996; Reynard *et al.*, 1999; Haley *et al.*, 2004; Lécuyer *et al.*, 2004; Baldwin *et al.*, 2011). For the bulk of the dataset, phosphate contribution is not considered to be controlling the

magnitude of the marine proxies. No correlation between other possible contaminants such as Fe-Mn oxides and the elemental proxies used in this study occur and the Fe and Mn concentrations remain below those of average carbonate 3800 ppm (Veizer, 1983).

Therefore, the geochemical data, assessed on the basis of typically used interpretative techniques, suggest that: (i) whilst diagenetic Sr loss has occurred, diagenetic water:rock interaction remained below the volumes required to alter the REE+Y data even within the rare zones exhibiting covariation of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ and (ii) that siliciclastic contamination has occurred that may have altered the REE+Y profile. This assessment is considered further below in light of the resulting contradictory evidence that emerges between REE+Y proxies that support non-marine conditions and palaeoecological evidence of diverse marine fauna in much of the San Juan Formation at Cerro La Silla.

2.5.3 Depth change proxies recorded in carbonate chemistry at Cerro La Silla

In the modern ocean the development of shale-normalized REE+Y profiles with distinctive features occurs when riverine freshwater, the major source of REE+Y, mixes with estuarine water of increasing salinity (Elderfield *et al.*, 1990; Lawrence *et al.*, 2006a; Lawrence *et al.*, 2006b; Lawrence and Kamber, 2006). Absorptive scavenging onto Fe-Mn oxyhydroxides, clays and organic material, which favours removal of LREE, steepens the shale-normalized profile and forms a distinctive seawater signal with features that change with depth (De Baar *et al.*, 1985; Bau *et al.*, 1997; Zhang and Nozaki, 1998) (Fig. 2.3). The utility of REE+Y data as relative paleo-depth and salinity proxies has been demonstrated by the recovery of data from carbonate rocks formed in diverse palaeoenvironments and time periods, including Neoproterozoic stromatolites (Kamber and Webb, 2001), Permian limestones (Webb and Kamber, 2000) and Devonian reefal carbonates (microbialites, skeletal grains, early marine cements and carbonate packstone and grainstone sediment; (Nothdurft *et al.*, 2004). In carbonates formed in fully-marine oxic conditions a typical REE+Y profile exhibits:

- (1) LREE depletion relative to heavy rare-earth elements (HREE) (Zhong and Mucci, 1995) expressed as a steep positive slope of shale-normalized REE+Y ($\text{Pr}_n/\text{Yb}_n \ll 1$), that develops with increased salinity and depth most rapidly in the top 500m of the water column (Kamber *et al.*, 2014);

(2) a strongly superchondritic Y/Ho ratio, which increases during cycling of REE+Y from surface waters to deep ocean water ($Y/Ho \geq 40 - 80$) (De Baar *et al.*, 1985; Bau *et al.*, 1997; Nozaki *et al.*, 1997);

(3) a positive La anomaly due to reduced adhesion to particles relative to neighbouring REE (Bau and Dulski, 1996; Bau, 1999; Bolhar *et al.*, 2004);

(4) a moderate positive Gd anomaly due to its greater stability in solution than neighbouring REE (De Baar *et al.*, 1985; Byrne and Kim, 1990; Byrne *et al.*, 1996; Bau *et al.*, 1997; Bolhar *et al.*, 2004; Zhang and Nozaki, 1998); and

(5) a strong negative Ce anomaly in oxic marine conditions (Zhang and Nozaki, 1998). Cerium³⁺ oxidizes in high free oxygen estuarine and marine conditions, forming Ce⁴⁺ that adsorbs to metal oxyhydroxide complexes (Bau and Koschinsky, 2009) and progressively becomes depleted relative to Pr (Fig. 2.3).

At Cerro La Silla the development of this marine trend is most apparent in covariation of Y/Ho, La*, Gd* and the shale normalized slope (see Table 2-3) and is identifiable despite the probable variable alteration of the REE+Y profile by shale related contamination.

In the peritidal upper La Silla Formation (0-35 m) and the lagoonal, back-reef facies at the base of the San Juan Formation (35-51 m), the shale-normalized slope is flat to mildly LREE-enriched ($Pr_n/Yb_n > 1.19$, min 1.19 max 1.87, mean = 1.50) with low Y/Ho ratios (< 30.75 , range 25.51 to 30.75, mean = 28.34) (Fig. 2.4 and 2.7). The magnitude of these features is incompatible with REE+Y data from uncontaminated fully marine carbonates. Y/Ho values of a similar magnitude (c.28) have in previous studies been attributed to formation in conditions of brackish, mixed seawater and freshwater (Frimmel, 2009; Baldwin *et al.*, 2011; Baldwin *et al.*, 2012; Zhao and Zheng, 2017). As facies deepen at 35 m the data retain characteristics consistent with freshwater-saltwater mixing - from 41.2 m, and within the lower reef from 51.3 m, the shale normalized slope is relatively flat with values higher than 1.12. The samples below the lower reef (below 51.3 m), form a distinct data subset with low Y/Ho ratios (< 31), low total REE concentration ($< 44,11.29$ ppb) (Fig. 2.4) and flat shale normalized slopes ($Pr_n/Yb_n > 1.19$) that plot far from the modern seawater field on an Y/Ho v Pr_n/Yb_n crossplot (Fig. 2.8). This segment corresponds to anomalously low Mn concentrations. In addition, an impoverished macrofauna dominated by gastropods is present

in the samples below the lower reef so that a marine paleoenvironment is not clearly established on a faunal basis. This facies may therefore represent a marginal, low salinity environment, based on faunal and REE+Y trends, or a facies where REE+Y removal from the water-column has not occurred in the expected manner. In the latter case, the flat profiles in the REE+Y data may be due to the absence or reduced operation of processes required to establish a marine profile. These include required inputs of organic matter, clays and Fe-Mn oxyhydroxide complexes to which the REE+Y adsorb and are exported from the water-column (Elderfield *et al.*, 1990). The very low clay and Mn concentrations in the samples, may therefore have contributed to the absence of a marine REE+Y profile. This interpretation is supported by the very low concentrations of detrital proxy elements, Fe and Mn in the limestones in the uppermost La Silla Formation and basal San Juan Formation. Measured total organic carbon (TOC) in four samples submitted for Rock-eval, and supporting TOC estimates based on the mass of insoluble residue after dissolution for bulk CAS analysis (See Chapter 4.3) are presented in Table 2-5. The TOC concentrations are consistent with ongoing organic matter deposition through the stratigraphy so that REE+Y stripping associated with organic matter may have occurred. However, the data also indicate a probable decreased carbonate wt% upsection of the lower reef facies, most likely associated with increasing siliciclastic inputs (Table 2-5).

The base of the San Juan Formation at Cerro La Silla has previously been interpreted as a change to fully marine conditions (Kelller, 1999). However, it does not exhibit the REE+Y anomalies associated with fully marine water - from the base of the San Juan Formation (35 m) to deepening at c.98.5 m the REE+Y anomaly values are reduced relative to fully marine waters with $Pr_n/Yb_n > 1$ (mean 1.48 min 1.19 max 1.87) and $Y/Ho < 31.5$ (min 25.51, max 31.5) and $Gd < 1.05$ (0.99-1.05) to 98.5m (Fig. 2.4 and 2.7). Shallow negative to shallow positive Ce and La anomalies remain near shale unity values on a Ce/Ce* vs La anomaly cross-plot (Bau and Dulski, 1996; Webb and Kamber, 2000; Nothdurft *et al.*, 2004) (Fig. 2.6). From above the flooding surface that occurs at c.98.5 m (Fig. 2.4), there is a clear trend to more seawater-like proxy values as sea-level rises, consistent with development of a marine REE+Y profile and as facies deepen there is a gradual, fluctuating increase towards the establishment of the REE+Y features more typical of marine carbonates. It therefore appears that there is a development of more marine conditions but the magnitude of these features may be partially suppressed by shale contamination. The Y/Ho ratio increases to 34.5 at 98.5 m with an excursion to 39.3 at 104.4 m (Fig. 2.4). The La anomaly is expressed consistently above 98.5 m, both below fairweather wave base (110 m) and below storm wave

base (178 m). The negative Ce anomaly is expressed in all but three samples up to the reef facies of the upper section above 273 m. The Gd anomaly is also expressed consistently up as far as the upper reef facies and there is a steep increase in total REE concentration from < 6.5 ppm at 98.5m above fairweather wave base to > 20 ppm at 135.7 m below fairweather wave base. These changes in the magnitude of the REE+Y seawater proxies with increasing depth as the facies pass below fair weather wave base coincide with a faunal change from warm water to temperate water conodont forms (Lehnert, 1995) consistent with cooler, transgressive waters. However, probably due to greater shale contaminant inputs in deeper water facies, all anomalies fall short of values expected in marine carbonates and the shale normalized REE+Y slope remains flat to shallow and close to unity during deepening (Fig. 2.4 and Fig. 2.7).

The magnitude of the REE+Y seawater proxy anomalies continues to increase as facies deepen to below storm wavebase at 178 m (Fig. 2.4 and Fig. 2.7). Y/Ho values below storm wavebase exhibit a wide range from 30.6 to 37.9 but with an elevated mean of 34.5 and include two samples with Y/Ho ratios > 37 (i.e. close to marine values) at 205.8 m and 249.1 m. The shale-normalized slope also reaches its steepest values below storm wave base (0.47 at 239.6 m), although all other values fall within a range of 0.85 to 1.25 (mean = 1.05). The La anomaly is consistently present but highly variable, within a range from 1.02 to 1.40 (mean = 1.26), and a weak negative Ce anomaly occurs between 0.82 and 1.0 (mean = 0.92). The Gd anomaly reaches maximum values of 1.11 but continues to exhibit values as low as 1.00 in the samples below storm wave base (mean = 1.07). The REE+Y features in these samples therefore most closely approach fully marine values. It is notable, however, that estimated based on modern photic zone depths, the deepest facies below storm wavebase are unlikely to have exceeded c.200 m depth as indicated by the presence of fossil green algae and the marine fauna present (Keller, 1999). The facies below storm wave base also correspond to a change in conodont fauna to cold-water elements that may be related to depth change (Lehnert, 1995).

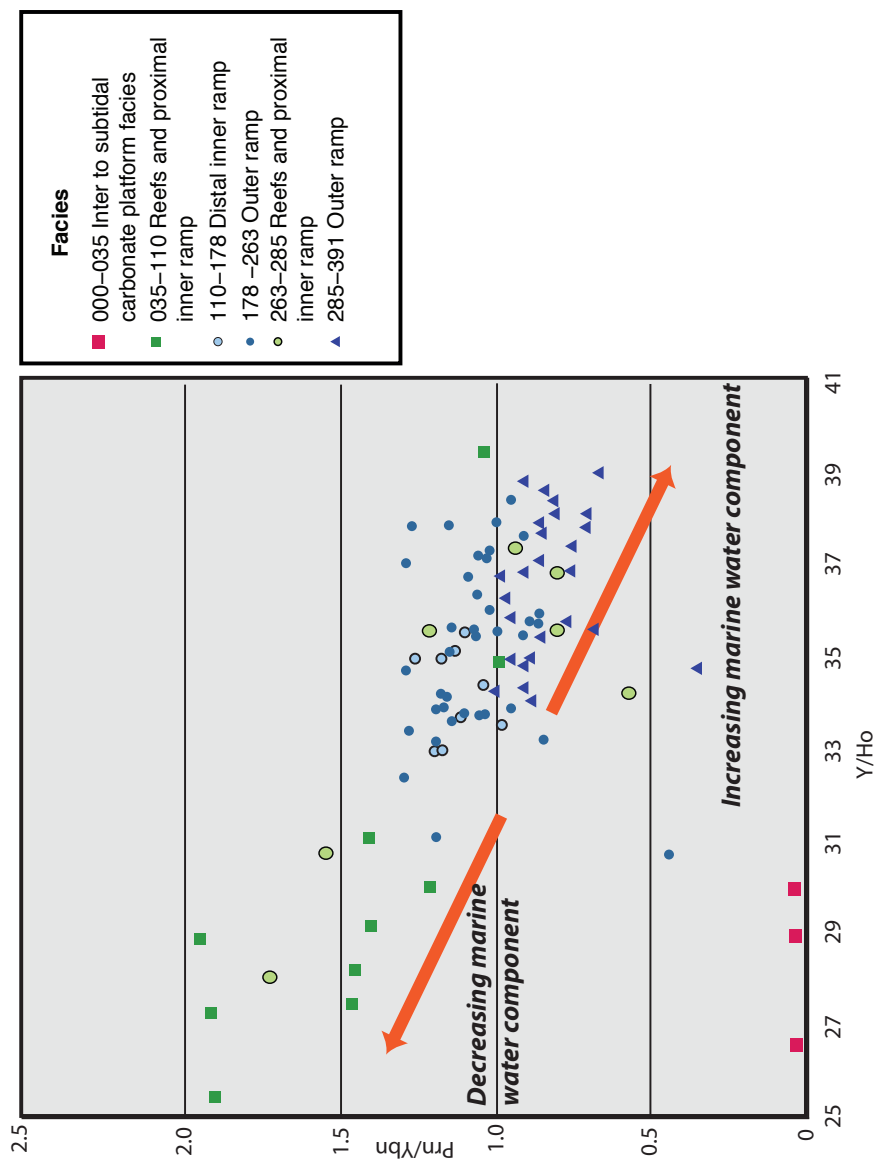
As facies return to shallower depths, approaching storm wavebase at 261m and above fairweather wave base as indicated by crossbedding from 263m, the REE + Y data exhibit a shallowing trend. Minimum Y/Ho values of 27.7 and 30.7 and maximum shale-normalized Pr_n/Yb_n slopes of 1.51 and 1.52 occur above fairweather wave base, below and within the upper reef at 270.7m and 280.6m, respectively (Fig. 2.4). The mean Y/Ho ratio remains elevated (mean = 34.2) but with flat shale-normalized slopes with Pr_n/Yb_n (0.82-1.52, mean

= 1.12). The magnitude of the La and Ce anomalies is also reduced at 280.6 m for La and at 270.7 m and 273.4 m for Ce (Fig. 2.4). The presence of cross-bedded facies, an elevated Y/Ho ratio and subdued La and Ce anomalies is consistent with shallowing with REE+Y profiles remaining partially suppressed by shale contamination. REE+Y seawater proxies approach, but do not attain, the lower magnitude observed in the proxy data of the lowermost San Juan Formation (Fig. 2.4).

Above 285 m, facies deepen to below storm wavebase and REE+Y proxies continue to fluctuate, remaining at values similar to those above fairweather wave base but with an overall trend toward marine values in Y/Ho (33.2 to 38.0, mean = 35.5) and Pr_n/Yb_n (0.36-1.06, mean = 0.85). Subsequently, deepening once more corresponds to increased REE+Y proxies, with a brief shift to lower values in what may be a short regressive period corresponding to a sequence of grainstones and underlying wackestones above 361 m. It is therefore likely that, with the exception of the base of the section, which may have a lower siliciclastic component and a greater diagenetic effect, the magnitude of the REE+Y marine systematics are suppressed by shale contamination in deeper water facies.

The overall trend of increasing and decreasing marine character of the REE+Y data at Cerro La Silla is still discernible and can therefore be related to relative sea-level changes identified through sedimentological evidence. However, the magnitude of much of the proxy data, which fall short of that expected in fully marine conditions is clearly contradicted by the occurrence of diverse marine fauna above c. 110 m above the base of the measured stratigraphic section.

Fig. 2.8: Plot of Y/Ho ratio vs Pr_n/Yb_n (shale normalized slope) for the data from Cerro La Silla, illustrating the correlation between both proxies and their plotting along a seawater/freshwater mixing line. The notable deviation from the highlighted trend occurs in the lowest Y/Ho and Pr_n/Yb values in the inter to subtidal facies at the base of the measured section (see Fig. 2.4).



2.5.4 Redox sensitive trace elements

Redox sensitive anomalies (Ce^* and Eu^*) can provide further useful paleoenvironmental information on redox conditions at a time of fluctuating sea-level. The extent of Ce-removal as oxidized Ce^{4+} depends on redox conditions within the watercolumn. The most negative anomalies occur in oxic seawater where Ce^{4+} is strongly depleted in the watercolumn, and increase with depth. Lower magnitude negative Ce anomalies may occur in dysoxic conditions where oxidation of Ce^{3+} to Ce^{4+} is partially inhibited. Where Ce^{4+} complexes drop below an oxycline into anoxic water, reduction to Ce^{3+} releases Ce to solution resulting in a positive Ce anomaly, enabling identification of redox chemoclines in ancient sediments (Frei *et al.*, 2008; Planavsky *et al.*, 2010). In anoxic conditions with active hydrothermal input Eu^{2+} - Cl^- complexes are also expected to remain in solution and be transported in the water-column (Derry and Jacobsen, 1990; Jacobsen and Pimentel-Klose, 1988) so that in reducing conditions positive Ce anomalies and negative Eu anomalies are expected to cooccur.

Ce anomalies throughout much of Cerro La Silla are weakly negative and show a limited range, consistent with weakly oxic conditions with respect to Ce or with oxic conditions with a Ce anomaly suppressed by siliciclastic contamination. A solitary weak positive Eu anomaly of 1.01 occurs in facies below storm wave base at 240.7 m, co-occurring with a low magnitude negative Ce anomaly (Fig. 2.4). However, throughout the remaining stratigraphy of the San Juan Formation at Cerro La Silla there is no positive Eu anomaly, indicating either a sufficiently oxic ocean to prevent long-distance transport of Eu^{2+} from oceanic hydrothermal vents or a mixing barrier that prevented expression of such an anomaly (Jacobsen and Pimentel-Klose, 1988; Derry and Jacobsen, 1990; Isley, 1995; Baldwin *et al.*, 2012). In addition there is no positive Ce anomaly at periods of inferred high-sealevel at Cerro La Silla and therefore no evidence of a migrating redoxcline. An increased connection to oceanic hydrothermal Eu sources in periods of high sea-level may be supported by the greater frequency of lower magnitude negative Eu anomalies (> 0.90) in the facies below storm wave base from 178 m. Alternatively, the more negative Eu anomaly may simply be an indication of solute supply from a coastal proximal riverine source, as can be observed along modern shorelines (e.g. Kamber *et al.*, 2005).

The REE+Y patterns therefore suggest either a transition from patterns indicating local sources of lower salinity, enriched in LREE, at inferred low sealevel periods, to patterns approaching but, likely due to contamination, not attaining more typical open-marine

topology during periods of inferred high sealevel. Control of this mixing by sea-level variation is supported by the dominance of lower magnitude and atypical patterns in the most proximal facies below the lower reef facies and the decreasing relative contribution of marine sources of REE+Y during regression. Further support can be found from a freshwater-seawater mixing line apparent in a plot of Y/Ho vs Pr_n/Yb_n (Fig. 2.8). Only samples in deeper facies from periods of raised sea level approach the values expected of fully marine carbonates.

Alternatively, variable siliciclastic input may account for a large component of the observed changes in REE+Y profiles. Although the correction applied based on Ga does not reveal a fully marine signature, it does indicate that deeper facies are increasingly marine. Low Mn and Fe concentrations in the samples may be indicative of atypical catchment conditions and low basinal inputs of siliciclastic material and/or oxidising conditions that limit reduction of Mn or Fe for incorporation to carbonates. A lack of clays and oxides will also decrease the magnitude of stripping of REE+Y from the water-column (Elderfield *et al.*, 1990).

Other redox sensitive elements, including Mo and U, provide complementary information on water and sediment redox conditions (Brumsack, 2006; Tribovillard *et al.*, 2006; Frei *et al.*, 2008; Planavsky *et al.*, 2010; Algeo and Rowe, 2012). Molybdenum and U are enriched in seawater relative to crustal values, behave conservatively in seawater and distribute evenly across all depths with long oceanic residence times (Tribovillard *et al.*, 2006; Algeo and Rowe, 2012). In suboxic, anoxic and euxinic sediment conditions, abiotic diffusion processes across the sediment-water interface may result in identifiable enrichments in Mo and U and in the ratio of authigenic Mo to U ($Mo:U_{auth}$) (Tribovillard *et al.*, 2006). Because the conditions that control the magnitude of fixation for both elements differ their ratio can provide valuable information on sediment redox conditions during deposition of the carbonates at Cerro La Silla. Under oxic–suboxic conditions, U is present mainly as soluble U^{+6} uranyl carbonate complexes ($UO_2(CO_3)_3^{4-}$) (Langmuir, 1978; Klinkhammer and Palmer, 1991; Calvert and Pedersen, 1993) and limited U enrichment relative to Mo enrichment occurs (Morford *et al.*, 2009b). Under anoxic conditions, U^{+6} is reduced to U^{+4} within the sediment (Anderson *et al.*, 1989; McManus *et al.*, 2005), forming the highly soluble uranyl ion UO_2^{2+} or less soluble uranous fluoride complexes. Uptake of U may then occur during organic-metal ligand formation in humic acids or by precipitation of uraninite (UO_2) or a precursor (Klinkhammer and Palmer, 1991; Zheng *et al.*, 2002). Uranium uptake occurs under less reducing conditions than Mo uptake (Morford *et al.*, 2009a). Molybdenum uptake

requires the presence of free sulfide to form thiomolybdate at the sediment-water interface (Algeo and Tribovillard, 2009), or of ferrous Fe and S to form Fe-Mo-S complexes in specific pH conditions (Helz *et al.*, 1996; Algeo and Tribovillard, 2009) or may be incorporated from Fe-Mn redox shuttling by release of molybdate ions (adsorbed to Fe-Mn oxyhydroxides in an oxic or dysoxic watercolumn) when those oxyhydroxides pass below the sediment redox chemocline (Tribovillard *et al.*, 2006; Morford *et al.*, 2009b). A greater relative enrichment of (Mo:U)_{auth} is therefore expected where free sulfide is present. Concentrations of enrichment are typically reported as enrichment factors (EF) - calculated by double normalisation to a shale standard (here MUQ):

$$X_{EF} = (X/Al)_{\text{sample}} / (X/Al)_{\text{MUQ}}$$

X and Al represent the weight concentrations of element X and Al, respectively.

However, the accuracy of enrichment factors depends on normalization to the immobile trace element Al, which occurs in very low quantities in carbonates and therefore calculating enrichment factors in carbonates poses a risk of artificially overestimating values, particularly where detrital Al contributions are high relative to authigenic Al (Van der Weijden, 2002, Tribovillard *et al.*, 2006). At Cerro La Silla Al concentrations range from 93 ppm to a maximum of 2,900 ppm. However, Mo_{detr} is problematically large in many of the samples above c. 110 m (on average contributing 10% of the Mo concentration and in some samples c. 50 %) so that there is a significant risk of distortion of carbonate enrichment trends due to Mo contributions from detrital components. In these circumstances, Mo_{auth} and U_{auth} trends and the (Mo/U)_{auth} ratio of the sediment was preferred as an indicator of enrichment relative to the modern seawater Mo/U ratio (~7.5–7.9) as utilized in a number of publications (Algeo and Tribovillard, 2009; Tribovillard *et al.*, 2012; Kalvoda *et al.*, 2018).

Suboxic sediments typically have higher U_{auth} enrichment values relative to Mo_{auth} (Algeo and Tribovillard, 2009), with greater relative U enrichment indicating increasingly anoxic conditions. Greater U_{auth} enrichment relative to Mo_{auth} occurs in all samples, indicating that a range of oxic to suboxic porewater conditions occurred as illustrated in the (Mo/U)_{auth} ratios plotted against stratigraphic variation (Fig. 2.4). The Ce and Eu anomalies, if primary marine features, indicate that watercolumn conditions above the variably oxic to suboxic porewaters also ranged from oxic to dysoxic during periods of raised and lower sea-level.

Combined evidence from REE+Y and $(\text{Mo}/\text{U})_{\text{auth}}$ and Mo data suggests that during the Ordovician, Cerro La Silla varied between a relatively shallow, possibly brackish, oxic to dysoxic watercolumn with oxic to dysoxic porewaters, to deeper platform conditions with a more marine, oxic water column and oxic-dysoxic porewaters. Alternatively, a lack of terrestrial or basinal siliciclastic clay or Fe-Mn oxyhydroxide inputs, or a lack of reduction of oxides to Mn^{2+} or Fe^{2+} might also contribute to locally anomalous REE+Y patterns and the minimal Mn concentrations in facies below 110 m.

The extent of primary brackish conditions as indicated by the REE+Y data is unlikely to be a reflection of water-column conditions, based on the contradictory faunal indicators of fully marine conditions. Faunae include at various horizons gastropods, brachiopods, orthoconic nautiloids, trilobites, crinoids, ostracods, sponge and *Girvanella*, *Nuia* and calcareous algae. Crinoids and brachiopods are considered to be indicators of marine conditions as they generally have a very low tolerance of marginal salinity conditions (Scholle *et al.*, 1983). Whilst there is some published support for tolerance of marginal conditions in echinoids (Salamon *et al.*, 2012) and brachiopods (Webby and Percival, 1983), those reports are exceptional and the presence of these taxa at Cerro La Silla suggest a watercolumn that did not deviate far from marine salinity concentrations.

Whilst there has been extensive published work on facies characterization in the San Juan Formation, the interpretation of its palaeoceanography has been hampered by incomplete preservation of its margins (Cañas, 1995; Keller, 1999). Cañas (1995) argued that the vast subtidal flats of the San Juan Formation were formed on a rimmed platform, although this interpretation appears to be limited now to the underlying La Silla Formation where oolite shoals have been interpreted as a platformward migration of barrier facies. Other researchers argue that the La Silla Formation was deposited in open-marine conditions (Pratt *et al.*, 2012). These reconstructions all infer a vast homoclinal ramp during deposition of the La Silla and San Juan Formation, based on the occurrence of deeper water facies to the west and a lack of sedimentological evidence of a slope (Keller, 1999). The $(\text{Mo}/\text{U})_{\text{auth}}$ ratio data at Cerro La Silla are more consistent with the latter interpretations than a partially restricted, rimmed basin, which would be expected to exhibit higher Mo concentrations relative to U (e.g Baldwin *et al.*, 2012).

It is possible that, during periods of low sealevel, increased volumes of freshwater from surface and groundwater have impacted local salinity levels at proximal sections on the homoclinal ramp (Keller, 1999). However, faunal evidence indicates that this was confined to low sea level intervals only (Zhao and Zheng, 2017). Whilst the modern, low bathymetric shelf off the Amazon river mouth exhibits a brackish gradient across hundreds of kilometres, the geographic conditions that generate this strong fluvial outflow (Dalrymple, 2007) are unlikely to have been present on the reconstructions of a low-lying, relatively isolated and dominantly subtidal carbonate terrane (Astini *et al.*, 1995). In addition the very low levels of siliciclastic associated elements support the interpretation that the La Silla Formation and lowermost San Juan Formation formed on a westward paleo-orientated homoclinal carbonate ramp isolated by distance, ocean conditions or a physical barrier to siliciclastic input. Phreatic cements formed in brackish water in these samples supports the inference of some sub-aerial exposure of carbonate terrestrial facies inboard of the La Silla Formation as a probable source of meteoric ground and surface water. Deepening above the lower reef coincides with a greater clay content and a less frequently reworked sediment redox column both of which would contribute to the increase of Mn, Fe and siliciclastic associated elements in the facies above 110 m.

A final but remote possibility is that, whilst steep shale-normalised slopes and negative Ce anomalies have been recovered from carbonate rocks as early as the Late Archean (Kamber and Webb, 2001) and these features have been shown in a number of studies to be relatively unchanged in seawater across much of the Earth's subsequent history (Shields and Webb, 2004), there is evidence in studies from the Lower Ordovician that suggests possible divergence from this trend. LREE-enriched, flat shale-normalized slopes have been recovered from Lower Ordovician shallow water carbonates in the current study, from Lower Ordovician dolomites of the Tarim Basin (Zhang *et al.*, 2009) and from Lower to Middle Ordovician cherts of the North Quilan basin, China (Du *et al.*, 2007) and may represent primary seawater values that diverge from this persistent trend.

Therefore, whilst the REE+Y data, screened with widely applied techniques for identification of contamination and diagenesis in chemostratigraphic studies, support the occurrence of brackish water column conditions throughout the deposition of the upper La Silla Formation and San Juan Formation, the wide faunal diversity strongly indicates that this is not a faithful marine signal for the majority of the San Juan Formation. It is problematic that the commonly used methods for assessment of contamination in solution-ICP-MS REE+Y studies may not

be adequate where no supporting faunal or other data is present – in particular this presents difficulties for their use in Proterozoic studies where similar results are obtained and there is some evidence of contamination. The cause of these difficulties identifying and correcting for contamination is therefore investigated further in Chapter 3 by use of micron-scale laser ablation thin section mapping, with further consideration of the dissolution method used (Tostevin *et al.*, 2016).

2.6 Conclusions

The limited diagenetic alteration of the well-exposed San Juan Formation carbonates at Cerro La Silla has made it an important source of proxy data of Ordovician seawater, including the first high-resolution C isotope records for the Floian (Buggisch *et al.*, 2003) and subsequent $\delta^{34}\text{S}_{\text{CAS}}$ reconstructions (Thompson and Kah, 2012). The REE+Y patterns of the San Juan Formation at Cerro La Silla at no point exhibit the characteristics expected for deposition under fully marine conditions. A full understanding of the palaeoceanography of the San Juan Formation is hampered by lack of preservation of its margins (Keller, 1999), however faunal indicators for much of the formation contradict the geochemical data and indicate an open-marine environment during formation of the majority of the studied stratigraphy.

Detailed paired sedimentology, trace element (including REE+Y) and carbon and oxygen isotope carbonate data through Cerro La Silla permits the identification of discrete zones of diagenesis, but using typical data assessment techniques the magnitude of fluid:rock interaction in all zones appears to have been insufficient to alter primary REE+Y values.

Evidence for siliciclastic contamination that suppresses the REE+Y profile of marine carbonates is more equivocal - throughout the section REE+Y anomalies are of a magnitude that indicate freshwater-marine water mixing that are contradicted by the cooccurring palaeoecological record. In those portions of the section that exhibit marine fauna but non-marine REE+Y, the sampled material is interpreted as recording a contaminated record rather than a brackish seawater record. Siliciclastic contamination occurs throughout the more distal facies at Cerro La Silla consistent with a greater basinal source with deepening and may be suppressing the expression of the marine REE+Y profile. Whilst the failure of screening techniques to clearly identify the siliciclastic contribution is less problematic in phanerozoic, fossil bearing sections, it is potentially a significant problem in Proterozoic samples.

In the lowermost section corresponding to the upper La Silla and lowermost San Juan Formations the evidence supports phreatic cement formation in brackish porewaters in the mixing zone (between a meteoric lens and seawater) during early burial. It is not clear whether these conditions extended to the water-column but the impoverished fauna suggests some divergence from typical marine conditions occurred. The carbonate samples have very low Mn and Fe concentrations consistent with oxidising reworked porewaters that reduced availability of Mn^{2+} and Fe^{2+} and an absence of siliciclastic content and underdeveloped

REE+Y profiles. This important feature of the uppermost La Silla Formation and lowermost San Juan Formation requires further attention in light of the marked negative $\delta^{34}\text{S}_{\text{CAS}}$ records that have been recovered from the La Silla Formation and its low faunal diversity.

It is therefore concluded that during formation of most of the San Juan Formation a well-mixed, extensive homoclinal ramp remained at relatively shallow water depths with Cerro La Silla representing a proximal section, at a distance from the open ocean. At the base of the section, during a period of relatively low sea-level, there may have been a much more limited degree of mixing occurring, supported by the impoverished fauna, with potential implications for anomalous REE+Y records in this study and $\delta^{34}\text{S}_{\text{CAS}}$ records obtained in previous studies from the section. In order to further investigate the cause of the potentially misleading REE+Y results that occur through much of the San Juan Formation, Chapter 3 utilises LA-ICP-MS mapping to disentangle at a micron scale the geochemical information recorded in different carbonate cement phases. It may also be valuable in future works to determine whether the observed evidence of decreased mixing with the ocean at the base of Cerro La Silla is consistent across the basin and sub-basins of the Precordillera platform, or whether it is limited to the location of Cerro La Silla distal from the platform margin. The work raises the related question of whether researchers need to be more cautious in using coeval S isotope records from disparate localities as comparable records of marine sulfur reservoirs. In particular, the results at the base of the section may have implications for the bulk $\delta^{34}\text{S}_{\text{CAS}}$ records considered in Chapter 4. Improved understanding of the regional, and in some cases the section-specific, water-column and sediment conditions may be needed to ensure that chemostratigraphic data represent historical carbon and sulfur budgets through Earth history.

ACKNOWLEDGEMENTS

Field and stable isotope work was supported by the Stephen Fossett Postdoctoral Fellowship and a Trinity Fellowship awarded to CVR, and a Packard Fellowship and a Hansewissenschaftskolleg Fellowship awarded to DAF. Trace element analyses were supported by an EU FP7 Marie Curie Actions – Career Integration Grant awarded to BSK. Thanks are extended to Fernando Gomez and Tor O’Brien for assisting with field work. We are very grateful to Robbie Goodhue at Trinity College Dublin, Dwight McCay at Washington University in St Louis, and Angus Calder at the University of St Andrews for helping with sample preparation and stable isotope measurements. We would also like to thank Cora McKenna for help and expertise with the trace element analyses at Trinity College Dublin.

Tables

Table 2-1 - Solution ICP-MS data, Cerro La Silla, ppb. Precision of 2-3%, accurate to 5%. Metres above base of section.

M	26Mg	27Al	31P	54Fe	55Mn	71Ga	88Sr	89Y	90Zr	98Mo	139La	140Ce	141Pr	146Nd
2.4	1,699,786	1,964,48	36,659	221,485	8,630	45	214,140	215	39	138	299	589	69	260
17.6	1,455,059	72,592	15,898	83,347	10,180	13	155,956	366	-	80	473	960	112	413
25.1	1,703,297	56,259	21,567	181,984	7,809	13	208,376	372	-	105	453	993	110	397
41.2	1,476,629	31,712	26,691	180,906	8,339	8	143,167	206	-	54	233	478	53	182
42.1	1,532,850	30,166	19,636	147,865	10,046	7	126,703	190	-	19	281	530	57	196
44.5	1,905,798	34,067	23,114	127,724	7,467	7	180,730	389	-	22	1,242	1,975	184	598
51.3	1,764,343	46,347	41,480	145,012	6,470	8	172,246	341	-	32	405	840	99	356
61.5	3,900,182	138,859	22,542	235,831	13,377	38	394,329	397	-	569	679	1,392	162	585
70.7	2,801,773	53,320	13,932	185,990	16,341	16	305,523	541	-	146	652	1,327	154	573
78.2	3,094,217	203,609	41,686	257,084	15,058	65	327,713	698	-	98	906	1,863	221	816
80	1,620,292	104,167	35,153	178,213	8,223	20	182,320	278	21	109	267	557	65	257
83.5	5,927,038	107,008	71,454	276,256	27,187	30	599,747	827	-	140	1,356	2,607	298	1,065
98.5	2,851,198	118,549	20,041	182,951	19,494	38	287,205	1,637	-	71	1,346	2,566	306	1,141
104.4	2,505,182	95,604	20,231	165,816	17,665	28	244,815	2,586	-	92	1,984	3,225	387	1,521
113.2	3,990,636	161,580	37,054	676,272	89,787	44	320,188	3,052	-	55	2,517	4,432	559	2,192
120.6	3,287,030	411,670	41,193	1,181,363	115,347	110	280,704	3,944	89	19	3,407	5,755	778	3,035
135.7	3,638,652	133,134	61,525	1,622,894	203,965	46	275,077	6,163	6	44	4,312	7,004	973	4,056
144.8	3,220,530	931,375	78,623	1,621,426	180,405	218	235,769	3,496	221	29	3,100	5,049	660	2,607
149.4	4,263,931	1,443,580	122,132	2,669,501	212,557	342	291,484	5,370	189	22	4,593	8,103	1,082	4,293
152.8	3,403,536	863,543	92,978	2,239,086	208,604	216	333,592	5,198	133	33	3,965	6,378	888	3,605
161.2	3,791,958	405,422	39,303	1,686,044	174,897	159	348,698	5,588	72	27	4,350	7,580	1,060	4,249
170	4,196,301	496,194	49,541	1,872,076	209,771	137	292,560	5,050	72	37	4,537	7,482	969	3,847
171	4,241,985	800,031	84,589	2,904,626	282,213	221	300,379	7,824	202	26	7,312	13,891	1,914	7,852
173.1	4,179,595	1,237,082	89,816	2,065,176	197,690	279	312,258	4,607	146	35	3,806	6,186	846	3,371
175.1	3,800,083	865,565	92,480	2,163,025	228,008	228	329,765	6,779	119	40	5,278	8,672	1,184	4,838
178.8	4,003,883	821,141	84,622	1,903,585	216,590	203	351,000	5,464	147	13	4,940	7,927	1,072	4,254
179.6	3,729,893	1,652,788	49,442	2,413,255	234,148	367	297,774	4,651	218	116	3,833	6,434	855	3,530
183.3	3,813,632	699,598	107,362	1,633,025	228,646	164	274,182	5,548	132	27	4,416	7,531	1,145	4,656
188.1	3,136,306	961,456	95,321	1,797,164	234,454	242	283,114	6,887	139	33	5,393	9,411	1,329	5,547
189.2	3,796,272	430,750	66,396	1,278,181	204,702	105	304,094	4,766	87	34	3,572	5,894	788	3,256
192.9	3,573,034	950,358	101,016	1,599,863	327,297	254	314,383	5,371	165	72	4,050	6,705	912	3,652
194.1	4,845,998	898,034	85,412	1,877,380	405,862	185	348,173	6,992	113	118	5,287	9,113	1,137	4,671
195.2	4,978,190	874,296	96,820	1,818,678	258,641	207	386,074	6,205	173	27	4,792	8,731	1,165	4,736
196	3,774,424	1,020,103	109,540	1,736,950	279,076	249	283,320	7,074	137	43	4,893	9,176	1,299	5,166
201.7	4,218,535	1,130,616	99,246	2,151,470	395,410	283	291,662	6,674	168	22	5,460	9,495	1,375	5,589
204.4	4,015,693	983,255	112,547	2,197,385	367,124	238	277,940	7,127	185	67	5,472	9,076	1,307	5,256
205.9	3,915,981	504,262	81,961	1,254,937	281,310	127	358,170	6,009	73	48	4,041	6,313	855	3,410
207.3	4,691,298	712,301	128,444	1,816,428	333,736	182	334,227	4,693	140	44	3,359	5,129	671	2,701
208.9	4,442,939	843,898	98,934	1,688,642	311,584	185	293,657	4,824	146	32	3,648	6,307	822	3,256
211.3	4,250,609	1,268,718	110,269	1,970,800	288,911	292	289,348	5,556	189	32	4,338	6,980	976	3,843
212.8	3,901,666	422,223	106,826	1,422,083	290,534	109	281,792	4,535	102	146	3,695	5,738	753	3,001
217.6	3,369,004	514,729	94,922	1,421,191	330,910	105	266,633	5,123	110	34	3,742	6,487	865	3,450
222.1	4,448,349	905,298	102,601	1,867,392	353,303	216	326,538	8,682	172	35	5,214	8,286	1,142	4,695
223.2	4,077,121	803,221	122,914	1,722,812	257,402	214	267,448	4,353	121	9	3,425	5,334	714	2,838
225.1	3,552,990	570,087	101,779	1,342,103	183,431	131	240,748	4,664	137	8	3,269	5,206	734	2,986
226.9	3,844,888	543,110	67,232	1,185,467	160,225	137	256,964	4,307	127	42	3,285	5,375	740	2,967
229.2	4,005,791	553,947	59,688	1,814,414	307,970	150	347,043	6,034	150	482	4,850	8,222	1,103	4,388
235.4	4,480,730	1,681,285	77,081	2,115,712	292,730	371	270,660	5,739	227	16	4,559	7,936	1,059	4,299
236.4	3,895,006	375,947	74,476	1,488,432	302,341	103	246,326	6,962	89	37	4,593	7,431	1,032	4,178
238.7	4,491,965	1,962,246	94,650	2,182,346	263,703	455	276,500	5,131	219	19	4,161	6,900	910	3,682
239.6	3,102,062	592,839	55,688	1,236,961	202,059	132	206,252	7,807	90	20	4,844	7,458	950	3,730
240.7	5,771,678	2,895,817	140,246	3,703,357	352,148	681	280,557	7,960	338	63	6,376	10,013	1,292	5,247
242.9	3,759,123	627,355	64,923	1,143,291	220,217	143	256,256	5,119	144	24	4,190	7,210	972	3,906

Table 2-1 cont.

M	149Sm	151Eu	159Tb	160Gd	161Dy	165Ho	167Er	169Tm	172Yb	175Lu	178Hf	238U
2.4	49	9	7	44	38	8	20	3	16	2	2	207
17.6	81	16	11	72	62	13	34	5	30	4	1	208
25.1	78	16	12	73	68	14	39	5	34	5	2	507
41.2	36	8	6	36	32	7	19	2	17	2	1	355
42.1	38	8	5	35	32	6	17	3	16	2	1	418
44.5	104	19	13	88	80	15	42	6	38	5	1	259
51.3	71	15	10	65	59	12	33	5	27	4	1	253
61.5	105	20	13	89	71	15	39	6	36	5	2	674
70.7	116	22	16	106	94	19	50	7	43	6	1	2,623
78.2	162	31	22	142	124	26	66	10	62	9	2	570
80	51	10	8	50	44	9	24	4	22	3	1	522
83.5	193	39	25	166	142	29	75	11	61	9	3	2,101
98.5	222	43	36	228	217	47	129	20	119	17	2	789
104.4	301	63	47	333	297	66	181	25	144	20	2	1,705
113.2	437	90	68	458	413	87	242	32	191	25	3	1,111
120.6	607	127	96	641	566	118	313	44	250	34	8	1,072
135.7	863	182	141	948	853	179	465	64	361	49	4	1,967
144.8	517	110	81	559	482	103	274	38	221	30	8	936
149.4	866	177	132	870	789	167	447	61	363	48	8	957
152.8	735	159	125	795	739	158	428	59	348	49	8	754
161.2	905	187	137	930	819	170	448	60	355	47	9	1,114
170	809	163	126	836	726	157	412	53	319	42	7	1,462
171	1,635	328	230	1,554	1,286	255	645	87	508	66	9	1,047
173.1	670	144	107	742	642	136	361	47	269	36	6	794
175.1	1,010	216	165	1,115	965	204	534	72	410	56	6	927
178.8	823	177	129	880	753	160	422	56	329	44	7	848
179.6	722	153	118	782	682	141	371	51	286	39	10	991
183.3	956	197	149	992	861	180	473	64	376	51	6	553
188.1	1,148	252	177	1,231	1,021	209	533	72	411	57	7	894
189.2	674	142	108	728	646	141	367	50	286	40	4	891
192.9	787	169	131	869	779	162	437	57	342	45	8	645
194.1	950	218	159	1,066	936	199	531	71	412	57	5	1,535
195.2	961	200	150	997	869	184	487	67	387	54	8	820
196	1,170	237	182	1,209	1,058	216	584	73	428	62	7	905
201.7	1,180	253	181	1,191	1,025	209	547	72	422	58	9	687
204.4	1,099	235	178	1,146	1,015	212	573	75	443	62	9	990
205.9	699	148	121	806	717	158	429	59	344	47	8	649
207.3	525	111	92	613	577	128	345	47	281	38	6	816
208.9	662	137	110	674	622	131	363	47	281	39	6	874
211.3	815	162	129	853	766	161	442	58	356	48	9	765
212.8	581	135	95	643	570	125	334	46	268	36	5	983
217.6	731	152	121	779	714	152	420	56	350	50	4	1,193
222.1	974	209	180	1,160	1,110	245	652	89	506	69	8	1,049
223.2	547	118	92	604	554	121	327	45	268	37	7	1,135
225.1	606	131	101	665	605	130	344	48	268	37	6	695
226.9	626	134	99	647	582	124	334	43	252	35	4	852
229.2	918	194	146	968	865	181	477	65	387	53	10	1,162
235.4	894	191	145	961	841	176	468	63	365	49	9	572
236.4	970	189	164	1,036	981	210	560	77	466	65	5	1,625
238.7	738	163	120	793	716	151	398	55	316	44	9	800
239.6	867	180	177	1,028	1,122	255	771	115	779	117	4	610
240.7	1,064	258	178	1,172	1,062	226	607	83	490	67	13	1,071
242.9	826	171	130	834	729	153	415	55	318	44	6	1,014

Table 2-1 cont.

M	26Mg	27Al	31P	54Fe	55Mn	71Ga	88Sr	89Y	90Zr	98Mo	139La	140Ce	141Pr	146Nd
245.7	4,108,172	508,680	79,200	1,173,778	224,693	129	290,619	3,872	104	40	2,685	4,464	606	2,472
246.9	3,981,494	780,863	66,404	1,215,331	221,454	183	295,833	4,557	125	36	3,389	5,363	710	2,889
248	3,488,911	624,034	75,750	1,322,517	219,622	148	252,106	4,966	113	26	3,487	5,633	761	3,082
249.1	3,368,216	380,320	57,051	1,095,587	216,868	100	249,560	5,102	85	55	3,294	5,442	722	2,971
250.6	3,970,919	470,987	95,904	1,109,467	190,269	115	260,610	3,616	67	42	2,685	4,540	601	2,354
253.1	3,614,964	656,966	51,459	1,348,040	218,856	155	251,595	3,520	109	16	2,397	3,900	510	2,067
257.3	3,540,401	723,914	95,347	1,888,622	332,877	145	242,462	4,588	141	30	3,042	5,194	656	2,739
258.5	3,072,299	1,337,671	96,472	2,019,892	228,175	353	254,022	6,421	168	43	4,597	8,412	1,117	4,630
259.8	4,742,424	1,707,892	84,643	2,646,116	176,217	364	225,589	5,591	132	52	4,403	7,620	985	3,956
261.3	4,053,396	1,307,937	71,456	1,855,960	180,167	304	254,785	5,645	150	71	4,354	7,754	1,019	4,186
268.2	3,392,476	801,404	79,611	1,622,460	183,731	197	253,297	4,258	101	91	3,308	5,810	747	3,072
270.7	3,475,230	446,417	40,495	1,810,772	287,172	137	290,399	6,237	91	208	6,410	12,872	1,500	6,070
273.4	3,866,138	93,256	15,729	592,465	104,152	28	446,899	3,086	40	350	2,391	4,635	552	2,218
275.4	2,671,388	337,532	44,075	488,858	67,224	79	290,211	3,341	245	46	2,094	3,920	497	2,006
277.4	3,318,945	300,876	46,532	698,462	108,153	85	336,089	4,443	92	29	2,598	4,797	625	2,482
278.2	3,705,570	523,655	88,152	793,521	87,858	123	343,682	3,923	83	77	2,545	4,788	598	2,429
280.6	1,910,189	327,382	66,968	310,872	9,569	65	173,358	467	70	67	657	1,322	161	602
282	3,934,629	455,931	77,130	605,959	82,404	92	325,395	2,656	90	38	1,648	3,037	378	1,500
287	3,923,234	523,130	41,646	810,987	167,722	121	287,960	9,030	121	35	5,348	9,354	1,116	4,461
290.1	3,219,296	273,370	100,754	565,968	133,473	52	341,706	3,823	70	42	2,444	4,544	579	2,387
295.8	3,500,550	259,581	26,801	342,567	129,366	59	359,759	3,614	21	56	1,965	3,606	453	1,864
304.5	2,679,094	205,707	51,563	784,496	196,774	52	238,996	8,083	-	50	3,945	6,189	746	2,967
308.6	2,690,815	1,287,675	61,209	1,022,260	118,500	301	181,044	2,130	137	28	1,510	2,903	369	1,467
311.4	3,229,438	558,897	73,758	785,395	151,643	133	263,409	1,945	136	47	1,418	2,573	322	1,271
314.9	2,887,604	299,914	56,290	558,301	205,088	85	299,513	3,155	13	36	1,842	3,372	436	1,759
318.5	2,887,602	245,851	55,434	672,105	256,247	67	313,229	3,336	211	50	2,292	4,267	542	2,170
321	3,839,527	689,662	68,873	1,097,091	239,237	183	302,048	4,079	112	55	2,272	3,962	497	1,980
322.1	1,394,292	475,049	112,283	549,727	81,423	112	124,057	1,116	116	25	781	1,442	184	746
323.7	3,227,902	621,233	86,376	781,577	183,985	158	266,613	2,660	71	70	1,685	3,124	408	1,628
326.1	3,133,408	619,615	97,749	956,541	229,173	162	278,640	3,178	230	64	2,261	4,125	526	2,033
327.3	3,097,542	281,655	72,754	884,914	221,459	75	281,960	2,738	144	18	2,275	3,838	466	1,832
329.6	3,824,226	854,625	96,572	1,359,152	234,629	235	290,342	3,479	160	92	2,727	5,213	658	2,626
330.8	2,623,591	385,080	83,965	745,195	206,055	105	334,326	2,356	99	116	1,495	2,708	335	1,353
333.6	3,583,428	544,751	91,535	759,920	197,766	138	334,101	3,088	103	57	2,245	4,010	504	1,953
336.3	3,054,952	267,918	54,972	547,506	184,325	71	276,282	2,307	71	33	1,563	2,777	341	1,372
337.8	3,250,430	486,097	73,963	685,117	214,634	126	277,170	3,602	78	38	2,268	4,000	499	2,025
341.5	2,822,353	299,959	55,295	739,479	194,462	84	298,480	3,337	136	35	1,950	3,340	427	1,708
345.3	2,438,329	694,631	43,001	673,153	174,518	170	280,926	5,639	176	30	4,028	6,394	790	3,125
347.5	3,386,355	349,902	86,048	652,230	208,958	88	314,888	3,159	68	49	1,872	3,428	445	1,799
351	8,931,433	1,062,994	213,162	2,450,985	717,748	274	887,816	11,345	254	103	7,134	12,103	1,600	6,485
353	3,969,560	2,314,715	142,602	2,229,479	244,963	568	314,941	5,688	155	113	3,515	7,219	951	3,884
353.9	2,756,006	610,810	50,583	895,103	227,842	166	293,850	4,333	220	28	3,183	5,965	754	3,035
354.9	2,413,511	307,219	67,875	904,959	245,886	73	262,728	3,094	151	31	2,161	3,820	466	1,864
357.4	3,653,069	878,272	106,890	942,886	261,704	235	284,465	3,983	137	92	2,562	4,885	605	2,426
361.7	2,822,157	886,821	90,872	1,469,782	261,574	214	267,137	4,695	163	62	3,175	6,386	760	3,080
370	4,809,056	320,803	57,470	595,201	196,133	84	476,898	5,128	17	130	3,474	6,675	792	3,193
372.5	2,707,573	256,094	57,837	392,206	211,827	65	300,944	3,813	103	51	2,086	3,774	485	2,020
374.3	2,861,973	617,722	113,163	970,527	221,532	151	305,204	4,892	227	163	3,467	5,974	720	2,897
380.7	2,992,585	401,412	62,524	656,678	174,749	98	296,754	4,853	175	173	2,740	5,003	618	2,595
388.7	2,954,884	539,359	66,214	649,407	179,776	118	288,166	3,772	174	46	2,063	3,659	461	1,924

Table 2-1 cont.

M	149Sm	151Eu	159Tb	160Gd	161Dy	165Ho	167Er	169Tm	172Yb	175Lu	178Hf	238U
245.7	529	113	89	585	522	109	296	40	231	31	4	616
246.9	602	140	100	643	598	125	349	43	260	37	4	583
248	674	148	115	745	672	142	380	50	296	40	4	541
249.1	649	136	111	704	653	136	380	48	278	39	4	729
250.6	497	104	82	525	478	103	287	38	232	31	3	671
253.1	441	96	79	489	474	101	280	36	223	30	3	483
257.3	597	131	103	686	624	132	351	48	275	37	4	1,117
258.5	1,025	220	163	1,065	945	195	529	67	410	56	9	1,354
259.8	792	177	126	864	733	155	409	56	312	43	7	675
261.3	913	197	145	958	835	170	459	58	348	47	7	595
268.2	623	135	99	677	572	121	323	43	243	33	4	809
270.7	1,286	254	183	1,274	1,024	203	506	67	383	51	9	1,541
273.4	462	96	71	498	416	88	235	32	183	26	3	1,121
275.4	427	91	71	459	424	90	248	34	201	29	2	1,178
277.4	536	112	94	607	586	126	350	48	293	44	6	717
278.2	505	112	84	563	505	107	300	39	234	34	3	1,122
280.6	115	21	15	100	90	17	49	7	41	5	3	295
282	314	66	54	354	327	73	208	30	177	25	3	891
287	984	195	186	1,169	1,203	265	778	116	743	107	4	1,362
290.1	507	109	87	577	518	112	305	41	244	35	2	1,230
295.8	411	91	74	472	441	99	273	37	226	32	3	1,133
304.5	652	137	140	819	960	233	730	118	787	124	2	1,104
308.6	303	63	48	326	289	63	168	24	143	20	6	505
311.4	259	53	43	280	258	56	154	22	131	19	3	711
314.9	378	82	65	436	396	85	238	33	194	28	4	1,016
318.5	448	83	72	489	440	93	256	35	216	30	4	1,108
321	429	81	78	487	485	108	315	44	270	40	3	926
322.1	156	33	25	174	150	33	91	12	77	11	3	330
323.7	348	75	59	377	346	77	210	28	173	24	3	854
326.1	443	92	73	457	425	92	258	34	217	31	5	779
327.3	374	74	61	383	359	79	219	29	186	25	3	901
329.6	540	110	83	517	478	103	279	39	238	33	6	977
330.8	289	62	48	318	294	63	176	24	149	21	2	737
333.6	403	84	67	428	391	86	246	33	209	30	4	663
336.3	282	58	49	299	286	62	176	24	152	22	2	735
337.8	427	89	71	463	440	96	270	38	230	32	3	836
341.5	373	79	64	424	410	89	261	35	223	32	3	944
345.3	669	138	118	730	719	161	471	67	433	65	5	934
347.5	382	80	67	424	414	90	254	35	217	31	2	687
351	1,379	296	236	1,580	1,457	321	894	119	716	99	9	2,259
353	831	176	137	892	813	172	467	65	400	56	8	1,033
353.9	648	120	105	690	605	129	347	46	288	41	4	869
354.9	389	79	67	421	400	88	125	32	205	30	3	661
357.4	532	109	88	564	517	112	316	42	264	37	5	773
361.7	653	140	111	725	670	141	384	54	326	47	6	1,182
370	652	138	107	726	677	148	409	57	335	48	5	1,628
372.5	442	95	74	501	461	101	275	38	228	33	4	1,004
374.3	577	135	99	653	584	129	358	50	302	44	3	1,150
380.7	556	122	98	639	612	131	364	51	308	43	4	1,387
388.7	413	93	75	487	458	102	282	41	240	35	3	1,370

Table 2-2 MUQ Normalized Values

Metres	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er
2.4	0.00921	0.00829	0.00823	0.00793	0.00707	0.00582	0.00687	0.0068	0.0064	0.00676	0.00618	0.00579
17.6	0.0145	0.0135	0.0132	0.0125	0.0117	0.00995	0.0114	0.0113	0.0105	0.0115	0.0104	0.00998
25.1	0.0139	0.014	0.013	0.0121	0.0114	0.0105	0.0115	0.0121	0.0116	0.0117	0.0115	0.0114
41.2	0.00716	0.00672	0.00628	0.00554	0.00523	0.00497	0.0057	0.00574	0.00542	0.00646	0.00567	0.00578
42.1	0.00864	0.00746	0.00675	0.00596	0.00557	0.00516	0.00554	0.00512	0.00535	0.00597	0.00507	0.0051
44.5	0.0382	0.0278	0.0218	0.0182	0.0151	0.0123	0.0139	0.0135	0.0135	0.0122	0.0125	0.0124
51.3	0.0124	0.0118	0.0117	0.0108	0.0103	0.00934	0.0102	0.0103	0.01	0.0107	0.00993	0.00989
61.5	0.0209	0.0196	0.0192	0.0178	0.0153	0.0127	0.014	0.0133	0.012	0.0125	0.012	0.0116
70.7	0.0201	0.0187	0.0183	0.0174	0.0169	0.0138	0.0167	0.0165	0.0159	0.017	0.0153	0.0149
78.2	0.0279	0.0262	0.0262	0.0248	0.0236	0.0197	0.0223	0.022	0.0211	0.0219	0.021	0.0197
80	0.00822	0.00783	0.00764	0.0078	0.00743	0.00622	0.00793	0.00774	0.0075	0.00873	0.00724	0.00701
83.5	0.0417	0.0367	0.0352	0.0324	0.028	0.0249	0.0261	0.0252	0.0241	0.026	0.0236	0.0223
98.5	0.0414	0.0361	0.0362	0.0347	0.0323	0.0273	0.0358	0.0368	0.0368	0.0514	0.0389	0.0384
104.4	0.061	0.0454	0.0457	0.0462	0.0438	0.0403	0.0523	0.0479	0.0503	0.0812	0.054	0.0536
113.2	0.0774	0.0623	0.0661	0.0666	0.0636	0.0576	0.072	0.0691	0.0701	0.0958	0.0716	0.072
120.6	0.105	0.081	0.0919	0.0922	0.0882	0.0812	0.101	0.0967	0.0961	0.124	0.0967	0.093
135.7	0.133	0.0985	0.115	0.123	0.126	0.116	0.149	0.143	0.145	0.193	0.147	0.138
144.8	0.0954	0.071	0.078	0.0792	0.0751	0.0698	0.088	0.0821	0.0819	0.11	0.0847	0.0812
149.4	0.141	0.114	0.128	0.13	0.126	0.113	0.137	0.134	0.134	0.169	0.137	0.133
152.8	0.122	0.0897	0.105	0.11	0.107	0.101	0.125	0.127	0.126	0.163	0.129	0.127
161.2	0.134	0.107	0.125	0.129	0.132	0.119	0.146	0.138	0.139	0.175	0.139	0.133
170	0.14	0.105	0.115	0.117	0.118	0.104	0.131	0.128	0.123	0.159	0.129	0.122
171	0.225	0.195	0.226	0.239	0.238	0.209	0.244	0.232	0.218	0.246	0.209	0.191
173.1	0.117	0.087	0.0999	0.102	0.0974	0.0919	0.117	0.108	0.109	0.145	0.111	0.107
175.1	0.162	0.122	0.14	0.147	0.147	0.137	0.175	0.167	0.164	0.213	0.167	0.159
178.8	0.152	0.112	0.127	0.129	0.12	0.113	0.138	0.13	0.128	0.172	0.131	0.125
179.6	0.118	0.0905	0.101	0.107	0.105	0.0975	0.123	0.119	0.116	0.146	0.116	0.11
183.3	0.136	0.106	0.135	0.141	0.139	0.126	0.156	0.151	0.146	0.174	0.147	0.14
188.1	0.166	0.132	0.157	0.169	0.167	0.16	0.193	0.179	0.173	0.216	0.171	0.158
189.2	0.11	0.0829	0.0931	0.0989	0.0979	0.0903	0.115	0.109	0.11	0.15	0.116	0.109
192.9	0.125	0.0943	0.108	0.111	0.114	0.107	0.137	0.132	0.132	0.169	0.133	0.13
194.1	0.163	0.128	0.134	0.142	0.138	0.139	0.168	0.161	0.159	0.22	0.163	0.158
195.2	0.147	0.123	0.138	0.144	0.14	0.127	0.157	0.151	0.147	0.195	0.151	0.145
196	0.15	0.129	0.154	0.157	0.17	0.151	0.19	0.183	0.18	0.222	0.177	0.173
201.7	0.168	0.134	0.163	0.17	0.172	0.161	0.187	0.183	0.174	0.21	0.171	0.162
204.4	0.168	0.128	0.154	0.16	0.16	0.15	0.18	0.18	0.172	0.224	0.174	0.17
205.9	0.124	0.0888	0.101	0.104	0.102	0.094	0.127	0.123	0.122	0.189	0.13	0.127
207.3	0.103	0.0721	0.0793	0.0821	0.0763	0.0707	0.0964	0.0931	0.0979	0.147	0.105	0.102
208.9	0.112	0.0887	0.0972	0.0989	0.0962	0.0871	0.106	0.111	0.106	0.151	0.107	0.108
211.3	0.133	0.0982	0.115	0.117	0.119	0.103	0.134	0.13	0.13	0.174	0.132	0.131
212.8	0.114	0.0807	0.0891	0.0912	0.0845	0.0859	0.101	0.0964	0.0968	0.142	0.102	0.0991

Table 2-2 Cont.

Metres	Tm	Yb	Lu	Y/Ho	PRn/Ybn	La*	Ce/Ce*	Gd *	Eu*	Total REE
2.4	0.00574	0.00506	0.00436	28.6	1.63	1.04	0.969	0.997	0.834	1410
17.6	0.00902	0.0092	0.00834	28.9	1.44	0.985	0.966	0.995	0.859	2280
25.1	0.00991	0.0106	0.00937	26.6	1.22	0.935	1.01	0.975	0.903	2300
41.2	0.00484	0.00526	0.00483	29.7	1.19	0.885	0.943	1.02	0.921	1110
42.1	0.00496	0.00492	0.00464	30.7	1.37	0.998	0.976	1.05	0.952	1230
44.5	0.0114	0.0117	0.0111	25.5	1.87	1.22	1.06	0.991	0.842	4410
51.3	0.00883	0.00824	0.0082	28.2	1.42	0.91	0.933	0.996	0.909	2000
61.5	0.0115	0.011	0.00933	27.2	1.74	0.937	0.947	1.01	0.868	3220
70.7	0.0143	0.0133	0.0123	29.1	1.37	0.999	0.975	1	0.822	3190
78.2	0.0196	0.0191	0.018	27.3	1.37	0.956	0.949	0.992	0.853	4460
80.0	0.00714	0.00681	0.00647	31.5	1.12	1.12	1.05	1.04	0.826	1370
83.5	0.0212	0.0189	0.0189	28.7	1.87	1	0.958	1	0.919	6080
98.5	0.0382	0.0367	0.0346	34.5	0.988	1.05	0.954	1.02	0.809	6440
104.4	0.0488	0.0445	0.0409	39.3	1.03	1.37	1	1.12	0.893	8590
113.2	0.0626	0.0589	0.0518	35	1.12	1.19	0.951	1.07	0.881	11700
120.6	0.0856	0.0769	0.0702	33.4	1.2	1.15	0.884	1.07	0.893	15800
135.7	0.125	0.111	0.101	34.3	1.03	1.33	0.919	1.09	0.886	20500
144.8	0.0743	0.068	0.0609	33.9	1.15	1.26	0.924	1.1	0.902	13800
149.4	0.119	0.112	0.0988	32.2	1.15	1.15	0.909	1.04	0.876	22000
152.8	0.115	0.107	0.0997	32.9	0.982	1.26	0.891	1.05	0.896	18400
161.2	0.119	0.109	0.0964	32.9	1.15	1.13	0.876	1.08	0.89	21300
170	0.103	0.0981	0.0863	32.1	1.17	1.27	0.937	1.06	0.86	20500
171	0.171	0.156	0.135	30.7	1.45	1.11	0.911	1.04	0.887	37600
173.1	0.0931	0.0828	0.0727	33.9	1.21	1.23	0.892	1.12	0.912	17400
175.1	0.142	0.126	0.115	33.2	1.11	1.28	0.915	1.1	0.897	24700
178.8	0.109	0.101	0.0905	34.1	1.25	1.25	0.898	1.09	0.919	22000
179.6	0.0997	0.0879	0.0799	32.9	1.15	1.31	0.951	1.08	0.891	18000
183.3	0.126	0.116	0.104	30.9	1.17	1.1	0.818	1.06	0.881	22000
188.1	0.142	0.127	0.115	33	1.24	1.21	0.904	1.11	0.938	26800
189.2	0.0977	0.0879	0.081	33.8	1.06	1.33	0.945	1.09	0.889	16700
192.9	0.111	0.105	0.0923	33.1	1.03	1.22	0.901	1.08	0.895	19100
194.1	0.139	0.127	0.116	35.1	1.06	1.35	1.01	1.1	0.955	24800
195.2	0.131	0.119	0.11	33.7	1.16	1.17	0.932	1.06	0.888	23800
196	0.143	0.132	0.127	32.8	1.17	1.02	0.859	1.06	0.866	25800
201.7	0.14	0.13	0.119	31.9	1.25	1.13	0.858	1.05	0.918	27100
204.4	0.147	0.136	0.126	33.6	1.13	1.16	0.855	1.04	0.902	26100
205.9	0.116	0.106	0.0954	37.9	0.955	1.29	0.901	1.1	0.869	18100
207.3	0.0925	0.0865	0.0779	36.7	0.918	1.39	0.941	1.11	0.867	14600
208.9	0.0924	0.0864	0.0797	37	1.12	1.2	0.929	1	0.863	17100
211.3	0.113	0.11	0.0971	34.5	1.05	1.18	0.861	1.06	0.844	19900
212.8	0.0895	0.0825	0.0744	36.3	1.08	1.34	0.928	1.1	0.974	16000

Table 2-2 Cont.

Metres	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er
217.6	0.115	0.0912	0.102	0.105	0.106	0.0966	0.123	0.122	0.121	0.161	0.125	0.125
222.1	0.16	0.117	0.135	0.143	0.142	0.133	0.182	0.182	0.188	0.273	0.201	0.193
223.2	0.105	0.075	0.0844	0.0862	0.0795	0.0751	0.095	0.0926	0.0941	0.137	0.099	0.0972
225.1	0.101	0.0732	0.0867	0.0907	0.0881	0.0837	0.104	0.102	0.103	0.146	0.107	0.102
226.9	0.101	0.0756	0.0875	0.0902	0.091	0.0851	0.102	0.0998	0.0988	0.135	0.102	0.0991
229.2	0.149	0.116	0.13	0.133	0.133	0.124	0.152	0.148	0.147	0.189	0.148	0.141
235.4	0.14	0.112	0.125	0.131	0.13	0.121	0.151	0.146	0.143	0.18	0.144	0.139
236.4	0.141	0.105	0.122	0.127	0.141	0.12	0.163	0.165	0.167	0.219	0.172	0.166
238.7	0.128	0.0971	0.108	0.112	0.107	0.104	0.125	0.121	0.122	0.161	0.124	0.118
239.6	0.149	0.105	0.112	0.113	0.126	0.114	0.162	0.179	0.19	0.245	0.209	0.229
240.7	0.196	0.141	0.153	0.159	0.155	0.164	0.184	0.18	0.18	0.25	0.185	0.18
242.9	0.129	0.101	0.115	0.119	0.12	0.109	0.131	0.131	0.124	0.161	0.125	0.123
245.7	0.0826	0.0628	0.0716	0.0751	0.0768	0.072	0.092	0.0897	0.0886	0.122	0.0897	0.0878
246.9	0.104	0.0754	0.0839	0.0878	0.0874	0.0892	0.101	0.101	0.102	0.143	0.103	0.104
248	0.107	0.0792	0.0899	0.0936	0.098	0.0942	0.117	0.116	0.114	0.156	0.116	0.113
249.1	0.101	0.0765	0.0854	0.0903	0.0943	0.0867	0.111	0.112	0.111	0.16	0.111	0.113
250.6	0.0826	0.0639	0.071	0.0715	0.0723	0.0661	0.0825	0.0824	0.0812	0.114	0.0847	0.0853
253.1	0.0737	0.0549	0.0603	0.0628	0.0641	0.0609	0.0769	0.0793	0.0805	0.111	0.0826	0.083
257.3	0.0936	0.0731	0.0776	0.0832	0.0867	0.0833	0.108	0.104	0.106	0.144	0.108	0.104
258.5	0.141	0.118	0.132	0.141	0.149	0.14	0.167	0.164	0.16	0.202	0.16	0.157
259.8	0.135	0.107	0.116	0.12	0.115	0.113	0.136	0.127	0.124	0.176	0.127	0.121
261.3	0.134	0.109	0.12	0.127	0.133	0.125	0.151	0.146	0.142	0.177	0.14	0.136
268.2	0.102	0.0817	0.0883	0.0933	0.0905	0.0858	0.106	0.1	0.0971	0.134	0.0992	0.0959
270.7	0.197	0.181	0.177	0.184	0.187	0.162	0.2	0.185	0.174	0.196	0.167	0.15
273.4	0.0736	0.0652	0.0653	0.0674	0.0672	0.0609	0.0783	0.0721	0.0707	0.0969	0.0719	0.0696
275.4	0.0644	0.0551	0.0587	0.061	0.0621	0.0578	0.0721	0.0716	0.0721	0.105	0.0742	0.0736
277.4	0.0799	0.0675	0.0739	0.0754	0.0779	0.0714	0.0954	0.0951	0.0995	0.139	0.103	0.104
278.2	0.0783	0.0673	0.0707	0.0738	0.0734	0.0715	0.0886	0.0846	0.0857	0.123	0.0879	0.089
280.6	0.0202	0.0186	0.019	0.0183	0.0167	0.0132	0.0157	0.0152	0.0153	0.0147	0.0138	0.0145
282	0.0507	0.0427	0.0447	0.0456	0.0457	0.0418	0.0557	0.0548	0.0555	0.0834	0.0602	0.0617
287	0.165	0.132	0.132	0.136	0.143	0.124	0.184	0.187	0.204	0.284	0.217	0.231
290.1	0.0752	0.0639	0.0684	0.0725	0.0737	0.0696	0.0908	0.0879	0.0879	0.12	0.0917	0.0905
295.8	0.0605	0.0507	0.0536	0.0566	0.0598	0.0577	0.0742	0.0745	0.0749	0.113	0.081	0.081
304.5	0.121	0.0871	0.0881	0.0902	0.0948	0.0875	0.129	0.142	0.163	0.254	0.191	0.217
308.6	0.0464	0.0408	0.0436	0.0446	0.044	0.0401	0.0513	0.0487	0.049	0.0669	0.052	0.0497
311.4	0.0436	0.0362	0.0381	0.0386	0.0376	0.0338	0.0441	0.0437	0.0438	0.0611	0.0462	0.0456
314.9	0.0566	0.0474	0.0516	0.0534	0.055	0.0523	0.0685	0.0655	0.0672	0.0991	0.0697	0.0707
321	0.0699	0.0557	0.0588	0.0602	0.0623	0.0514	0.0766	0.0787	0.0823	0.128	0.0886	0.0935
318.5	0.0705	0.06	0.0641	0.0659	0.0651	0.0526	0.0769	0.0723	0.0747	0.105	0.0763	0.0761
322.1	0.024	0.0203	0.0218	0.0227	0.0227	0.0208	0.0273	0.0251	0.0255	0.0351	0.0271	0.0271
323.7	0.0518	0.0439	0.0482	0.0495	0.0505	0.0478	0.0593	0.0592	0.0587	0.0835	0.0629	0.0623
326.1	0.0696	0.058	0.0622	0.0618	0.0644	0.0587	0.0718	0.0734	0.0722	0.0998	0.0754	0.0765

Table 2-2 Cont.

Metres	Tm	Yb	Lu	Y/Ho	Prn/Ybn	La*	Ce/Ce*	Gd *	Eu*	Total REE
217.6	0.111	0.108	0.101	33.6	0.95	1.18	0.915	1.05	0.867	18100
222.1	0.175	0.156	0.141	35.5	0.866	1.33	0.913	1.09	0.865	24500
223.2	0.088	0.0824	0.0753	36	1.02	1.31	0.909	1.08	0.899	15000
225.1	0.0935	0.0824	0.0754	35.8	1.05	1.27	0.883	1.08	0.905	15100
226.9	0.0843	0.0775	0.0723	34.6	1.13	1.23	0.891	1.05	0.906	15200
229.2	0.128	0.119	0.108	33.4	1.09	1.2	0.907	1.07	0.896	22800
235.4	0.123	0.112	0.101	32.7	1.12	1.22	0.931	1.08	0.899	22000
236.4	0.15	0.143	0.132	33.1	0.851	1.26	0.892	1.04	0.807	22000
238.7	0.108	0.0972	0.0896	33.9	1.11	1.29	0.938	1.07	0.932	19100
239.6	0.225	0.24	0.238	30.6	0.468	1.35	0.944	1.02	0.808	22400
240.7	0.162	0.151	0.137	35.2	1.01	1.4	0.963	1.08	1.01	28100
242.9	0.108	0.0979	0.0907	33.5	1.17	1.2	0.912	1.03	0.88	20000
245.7	0.0778	0.0711	0.0633	35.4	1.01	1.27	0.921	1.08	0.89	12800
246.9	0.0844	0.0799	0.0747	36.3	1.05	1.36	0.941	1.05	0.972	15200
248	0.0974	0.0911	0.0815	35	0.987	1.29	0.918	1.07	0.909	16200
249.1	0.0951	0.0857	0.0797	37.5	0.997	1.33	0.948	1.05	0.868	15600
250.6	0.0746	0.0713	0.0633	35	0.995	1.18	0.906	1.05	0.876	12600
253.1	0.0712	0.0685	0.0606	34.9	0.88	1.32	0.946	1.04	0.884	11100
257.3	0.0947	0.0846	0.0754	34.9	0.917	1.39	1.01	1.1	0.904	14600
258.5	0.132	0.126	0.114	32.9	1.05	1.22	0.955	1.05	0.912	23400
259.8	0.11	0.0961	0.0885	36.2	1.21	1.24	0.951	1.1	0.945	20600
261.3	0.114	0.107	0.0969	33.1	1.12	1.24	0.957	1.06	0.914	21400
268.2	0.0835	0.0749	0.0681	35.2	1.18	1.29	0.978	1.1	0.916	15800
270.7	0.132	0.118	0.104	30.7	1.51	1.2	1.06	1.08	0.868	32100
273.4	0.0633	0.0563	0.0523	35.2	1.16	1.2	1.03	1.11	0.885	11900
275.4	0.0675	0.0619	0.0582	36.9	0.948	1.18	0.976	1.06	0.887	10600
277.4	0.0948	0.0902	0.0892	35.3	0.819	1.13	0.933	1.07	0.857	13300
278.2	0.0763	0.0721	0.0684	36.6	0.98	1.21	0.996	1.1	0.929	12800
280.6	0.013	0.0125	0.0104	27.7	1.52	0.982	0.94	0.998	0.815	3200
282	0.058	0.0545	0.0516	36.2	0.82	1.18	0.976	1.08	0.861	8190
287	0.228	0.229	0.218	34.1	0.577	1.32	1.03	1.07	0.793	26000
290.1	0.081	0.0752	0.0718	34.2	0.909	1.23	0.991	1.1	0.891	12500
295.8	0.0725	0.0695	0.0647	36.6	0.771	1.26	1	1.07	0.897	10000
304.5	0.231	0.242	0.253	34.7	0.364	1.44	1.01	1.04	0.808	18500
308.6	0.0464	0.044	0.0398	33.6	0.991	1.11	0.957	1.09	0.881	7690
311.4	0.0424	0.0402	0.0386	34.5	0.948	1.18	0.963	1.06	0.856	6860
314.9	0.0639	0.0598	0.0573	37.1	0.863	1.18	0.953	1.11	0.897	9340
321	0.0856	0.083	0.0808	37.7	0.708	1.25	0.97	1.05	0.764	11000
318.5	0.0687	0.0664	0.0608	35.9	0.965	1.17	0.964	1.1	0.78	11400
322.1	0.0244	0.0236	0.022	33.7	0.924	1.2	0.97	1.13	0.887	3920
323.7	0.0553	0.0532	0.0481	34.6	0.907	1.13	0.936	1.06	0.896	8560
326.1	0.0674	0.0669	0.0623	34.5	0.93	1.1	0.927	1.02	0.872	11100

Table 2-2 cont.

Metres	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er
327.3	0.07	0.054	0.0551	0.0557	0.0544	0.0474	0.0602	0.0615	0.061	0.086	0.065	0.0651
329.6	0.0839	0.0733	0.0778	0.0798	0.0785	0.0699	0.0813	0.0839	0.0812	0.109	0.0843	0.0828
330.8	0.046	0.0381	0.0396	0.0411	0.042	0.0398	0.05	0.0488	0.05	0.074	0.0516	0.0523
333.6	0.069	0.0564	0.0596	0.0593	0.0586	0.0535	0.0674	0.0675	0.0664	0.0969	0.0707	0.073
336.3	0.0481	0.0391	0.0403	0.0417	0.041	0.0366	0.0471	0.049	0.0485	0.0724	0.0509	0.0522
337.8	0.0698	0.0563	0.059	0.0615	0.0621	0.0567	0.0727	0.0716	0.0748	0.113	0.0787	0.0801
341.5	0.06	0.047	0.0504	0.0519	0.0542	0.0501	0.0667	0.0645	0.0696	0.105	0.073	0.0774
345.3	0.124	0.0899	0.0934	0.095	0.0973	0.0882	0.115	0.119	0.122	0.177	0.132	0.14
347.5	0.0576	0.0482	0.0526	0.0547	0.0556	0.0511	0.0667	0.0673	0.0703	0.0992	0.0735	0.0754
351	0.219	0.17	0.189	0.197	0.2	0.189	0.248	0.238	0.247	0.356	0.263	0.265
353	0.108	0.102	0.112	0.118	0.121	0.112	0.14	0.138	0.138	0.179	0.141	0.139
353.9	0.0979	0.0839	0.0892	0.0922	0.0942	0.0765	0.108	0.106	0.103	0.136	0.106	0.103
354.9	0.0665	0.0537	0.055	0.0566	0.0565	0.0501	0.0661	0.0679	0.0679	0.0972	0.0724	0.0372
357.4	0.0788	0.0687	0.0715	0.0737	0.0774	0.0692	0.0887	0.0888	0.0877	0.125	0.0915	0.0937
361.7	0.0977	0.0898	0.0898	0.0936	0.0949	0.0891	0.114	0.112	0.114	0.147	0.115	0.114
370	0.107	0.0939	0.0936	0.097	0.0947	0.0878	0.114	0.108	0.115	0.161	0.122	0.121
372.5	0.0642	0.0531	0.0573	0.0614	0.0643	0.0605	0.0788	0.0752	0.0783	0.12	0.0829	0.0817
374.3	0.107	0.084	0.0851	0.088	0.0839	0.086	0.103	0.0995	0.0992	0.154	0.106	0.106
380.7	0.0843	0.0704	0.0731	0.0789	0.0809	0.0777	0.1	0.0993	0.104	0.152	0.108	0.108
388.7	0.0635	0.0515	0.0545	0.0585	0.0601	0.059	0.0765	0.0758	0.0777	0.118	0.0833	0.0838

Table 2-2 cont.

Metres	Tm	Yb	Lu	Y/Ho	Prn/Ybn	La*	Ce/Ce*	Gd *	Eu*	Total REE
327.3	0.0564	0.0573	0.0518	34.5	0.961	1.3	0.991	1.02	0.837	10200
329.6	0.0757	0.0733	0.0666	33.8	1.06	1.14	0.968	0.991	0.871	13600
330.8	0.0467	0.0459	0.0431	37.4	0.864	1.25	0.997	1.08	0.901	7340
333.6	0.0654	0.0643	0.0603	35.8	0.926	1.15	0.943	1.05	0.87	10700
336.3	0.047	0.0467	0.0439	37.2	0.863	1.27	1	1.02	0.841	7460
337.8	0.074	0.0709	0.0656	37.5	0.833	1.29	0.994	1.07	0.872	10900
341.5	0.0687	0.0686	0.0654	37.5	0.735	1.26	0.958	1.1	0.873	9410
345.3	0.13	0.133	0.133	35	0.701	1.37	0.979	1.03	0.848	17900
347.5	0.069	0.0669	0.0625	35.2	0.786	1.19	0.955	1.06	0.863	9540
351	0.232	0.22	0.202	35.3	0.858	1.26	0.938	1.1	0.888	34400
353	0.128	0.123	0.115	33.2	0.914	1.06	0.948	1.06	0.887	19600
353.9	0.0912	0.0886	0.0844	33.7	1.01	1.17	0.973	1.07	0.782	16000
354.9	0.0636	0.0632	0.0606	35	0.871	1.28	1	1.03	0.833	10100
357.4	0.0829	0.0813	0.0757	35.7	0.879	1.17	0.992	1.05	0.854	13100
361.7	0.107	0.1	0.0951	33.3	0.896	1.18	1.04	1.07	0.887	16700
370	0.111	0.103	0.0984	34.6	0.909	1.23	1.04	1.1	0.887	17400
372.5	0.0738	0.0701	0.0674	37.7	0.817	1.29	0.993	1.1	0.893	10600
374.3	0.0973	0.093	0.0903	38	0.915	1.34	1.02	1.09	0.968	16000
380.7	0.0993	0.0948	0.0881	37	0.771	1.34	1.04	1.08	0.897	13900
388.7	0.0797	0.0739	0.0706	37.1	0.738	1.34	1.01	1.09	0.909	10300

Table 2-3 Correlation of selected elemental concentrations and rare earth element and yttrium parameters through the section, n = 106, p-values < 0.001

	Ti	Sc	Zr	Ga	Fe	Mn	Th	P	Al	Total REE	Y/Ho	Pr _n /Yb _n	Gd*	La*	Ce*	Eu*
Y/Ho	0.02	0.04	0.12	0.02	0.02	0.16	0.01	0.10	0.02	0.03	-	-	-	-	-	-
Pr_n/Yb_n	0.02	0.05	0.06	0.02	0.02	0.12	0.02	0.04	0.02	0.02	0.50	-	-	-	-	-
Gd/Gd*	0.06	0.11	0.10	0.07	0.11	0.14	0.004	0.01	0.07	0.13	0.38	0.13	-	-	-	-
La/La*	0.07	0.08	0.14	0.07	0.13	0.25	0.01	0.08	0.07	0.18	0.46	0.34	0.30	-	-	-
Ce/Ce*	0.05	0.03	0.003	0.02	0.06	0.09	0.02	0.03	0.02	0.13	0.01	0.02	0.01	0.01	-	-
Eu/Eu*	0.13	0.11	0.04	0.12	0.13	0.02	0.01	0.09	0.14	0.04	0.02	0.04	0.12	0.02	0.02	-
U_{EF}	0.18	0.21	0.25	0.17	0.19	0.17	0.07	0.20	0.18	0.12	0.06	0.07	0.01	0.08	0.05	0.01
Mo_{EF}	0.18	0.19	0.25	0.18	0.17	0.22	0.07	0.25	0.17	0.17	0.17	0.18	0.08	0.20	0.07	0.01
Al	0.86	0.77	0.52	0.98	0.68	0.28	0.1	0.39	-	-	-	-	-	-	-	-
Total REE	0.03	0.66	0.33	0.37	0.70	0.58	0.25	0.28	0.33	-	-	-	-	-	-	-

Table 2-4 – Sample type vs marine proxy value calculated from solution and Mean LA-ICP-MS Component Values

Height	Sample Type	Y/Ho	Pr _n /Yb _n	Gd/Gd*	La/La*	Ce/Ce*	Eu/Eu*
104.4	Solution	39.26	1.03	1.12	1.37	1.00	0.89
	Solution - detrital correction	39.63	1.03	0.97	1.38	1.00	0.86
	Cement 1	48.34	0.91	1.20	2.22	1.24	0.98
	Cement 2	28.63)	1.11	1.26	1.64	1.09	1.04
	Microbial	37.44	0.84	1.09	1.24	0.97	0.96
	Micrite	38.09	0.98	1.14	1.34	1.03	0.89
	Fossil	44.22	0.91	1.08	1.77	1.08	0.80
135.7	Solution	34.34	1.03	1.09	1.33	0.91	0.89
	Solution – Detrital	34.47	1.03	1.02	1.33	0.92	0.87
	Cement 1	34.46	0.81	1.18	1.69	1.01	0.93
	Cement 2	28.69	0.75	0.95	1.48	0.93	0.86
	Microbial	36.16	0.95	1.26	1.37	0.92	0.94
	Micrite	31.77	0.84	1.04	1.75	1.14	1.10
	Fossil	35.40	0.96	1.26	1.38	0.92	1.03
204.4	Solution	33.62	1.13	1.04	1.16	0.85	0.90
	Solution - Detrital	34.20	1.15	1.04	1.18	0.84	0.89
	Cement 1	N/A	N/A	N/A	N/A	N/A	N/A
	Cement 2	N/A	N/A	N/A	N/A	N/A	N/A
	Microbial	34.50	0.82	1.11	1.43	1.55	1.04
	Micrite	33.17	1.01	1.09	1.17	0.87	0.99
	Fossil	37.45	0.95	1.14	1.55	0.94	0.96

Table 2-5 – Carbonate wt% and Total Organic Carbon % as calculated from four samples submitted for rock-eval and calculation based on deduction of inorganic residue mass from total mass.

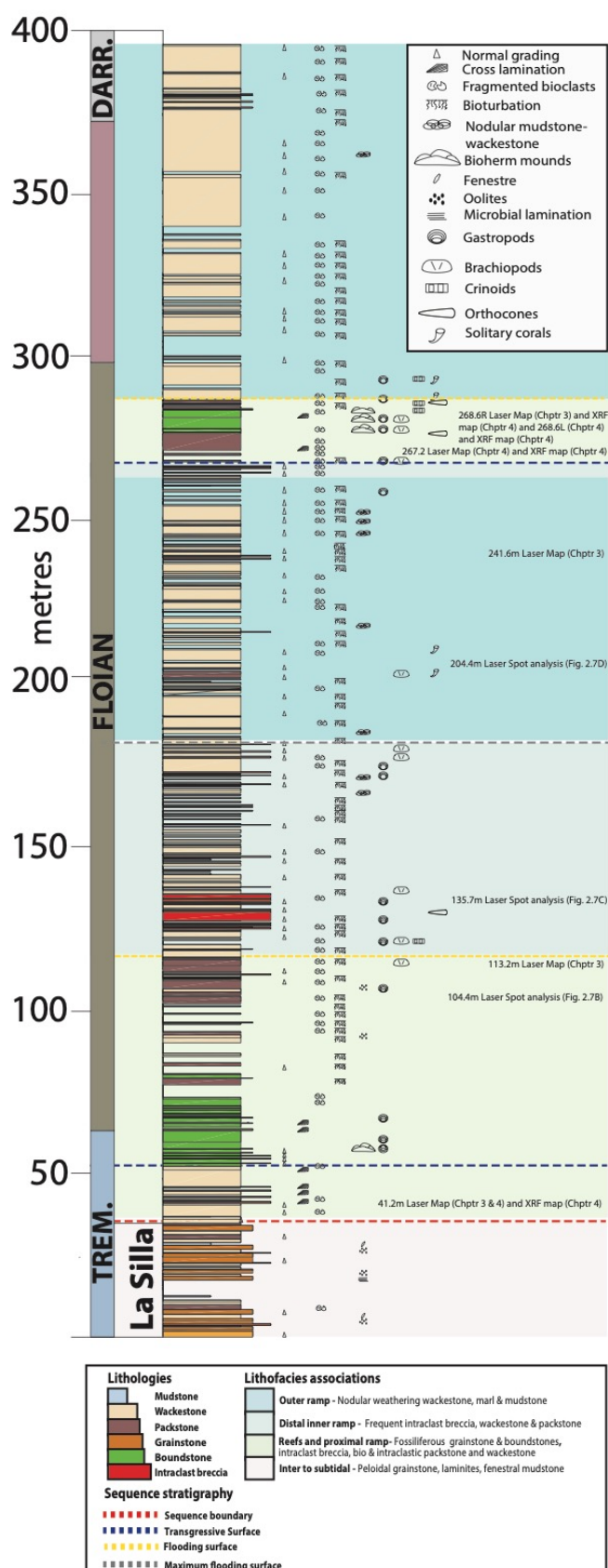
Metres	Carbonate % Rock-eval	% Carbonate (Sample less insoluble residue)	Leco TOC wt%	Est. TOC % (insoluble residue)
35.9		98.11		0.014
60.4	96.62		0.05	
61.5		96.74		0.016
65.6		99.60		0.004
69.9		89.96		0.035
70.2		84.08		0.051
82.4		75.88		0.048
90.1		70.80		0.073
90.9		94.60		0.019
92.8		93.08		0.019
100.8		89.37		0.051
101.9		79.81		0.038
115.5		83.80		0.043
129.00	92.85		0.03	
130.2		97.98		0.011
157.8		97.66		0.008
185.9		94.37		0.022
190.3		94.21		0.025
220.1		97.35		0.011
229.2		95.87		0.014
242.9		84.55		0.141
245.7		85.04		0.048
256.2	95.16		0.04	
270.7		94.33		0.022
287		75.94		0.074
310.3		95.45		-
323.7		93.38		0.038
329.6		76.25		0.039
358.6		95.76		0.014
363.3		94.65		0.012
373.7	92.09		0.04	
375.5		96.85		0.011
376.3		87.88		0.044
388.4		96.50		0.014

Table 2-6 Samples chosen for micron-scale analysis. UTM data, Zone 19J.

Sample Stratigraphic Height	Eastings	Northings	LA-ICP-MS Spot Analyses	Laser Map	XRF Map
41.2	0534022 m E	6642304 m S		Chapter 3 & 4	Chapter 4
104.4	0533574 m E	6642014 m S	Chapter 2		
113.2	0533562 m E	6642022 m S		Chapter 3	
135.7	0533528 m E	6642030 m S	Chapter 2		
204.4	0533438 m E	6642065 m S	Chapter 2		
241.6	0533388 m E	6642079 m S		Chapter 3	
267.2	0533377 m E	6642077 m S		Chapter 4	Chapter 4
268.6R	0533374 m E	6642081 m S		Chapter 3 & 4	Chapter 4
268.6L	0533374 m E	6642081 m S		Chapter 3 & 4	Chapter 4

Appendix 2.1 – Detailed Stratigraphic Log Cerro La Silla

Cerro La Silla



References

- ALGEO, T. J. & ROWE, H. 2012. Paleooceanographic applications of trace metal concentration data. *Chemical Geology*, 324–325, 6–18.
- ALGEO, T. J. & TRIBOVILLARD, N. 2009. Environmental analysis of palaeoceanographic systems based on molybdenum–uranium covariation. *Chemical Geology*, 268, 211–225.
- ALLAN, J. R. & MATTHEWS, R. K. 1982. Isotope signatures associated with early meteoric diagenesis. *Sedimentology*, 29, 797–817
- ALLWOOD, A. C., KAMBER, B. S., WALTER, M. R., BURCH, I. W. & KANIK, I. 2010. Trace elements record depositional history of an Early Archean stromatolitic carbonate platform. *Chemical Geology*, 270, 148–163.
- ALLMENDINGER, R. W. & JUDGE, P. A. 2014, The Argentine Precordillera: A foreland thrust belt proximal to the subducted plate: *Geosphere*. V, 10 (6)
- ANDERSON, R. F., FLEISCHER, M. Q. & LEHURAY, A. P. 1989. Concentration, oxydation state and particle flux of Uranium in the Black Sea. *Geochim. Cosmochim. Acta.*, 53, 2215–2224.
- ASTINI, R. A., BENEDETTO, J. L. & VACCARI, N. E. 1995. The early Paleozoic evolution of the Argentine Precordillera as a Laurentian rifted, drifted, and collided terrane: A geodynamic model. *Geological Society of America Bulletin*, 107, 253–0273
- BABECHUK, M. G., KAMBER, B. S., GREIG, A., CANIL, D. & KODOLANYI, J. 2010. The behavior of tungsten during mantle melting revisited with implications for planetary differentiation time scales. *Geochimica et Cosmochimica Acta*, 74, 1448–1470.
- BALDWIN, G. J., THURSTON, P. C. & KAMBER, B. S. 2011. High precision rare earth element, nickel, and chromium chemistry of chert microbands pre-screened with in-situ analysis. *Chemical Geology*, 285, 133–143.
- BALDWIN, G. J., TURNER, E. C. & B.S., K. 2012. A new depositional model for glaciogenic Neoproterozoic iron formation: insights from the chemostratigraphy and basin configuration of the Rapitan iron formation¹. *Canadian Journal of Earth Sciences*, 49, 455–476.
- BANNER, J. L. 1995. Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis. *Sedimentology*, 42, 805–824.
- BANNER, J. L. & HANSON, G. N. 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochimica et Cosmochimica Acta*, 54, 3123–3137.

- BAU, M. 1999. Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. *Geochimica et Cosmochimica Acta*, 63, 67-77.
- BAU, M. & DULSKI, P. 1996. Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. *Precambrian Research*, 79, 37-55.
- BAU, M. & DULSKI, P. 1999. Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic seawater. *Chemical Geology*, 155, 77-90.
- BAU, M., MÖLLER, P. & DULSKI, P. 1997. Yttrium and lanthanides in eastern Mediterranean seawater and their fractionation during redox-cycling. *Marine Chemistry*, 56, 123-131.
- BAU, M. & KOSCHINSKY, A. 2009. Oxidative scavenging of cerium on hydrous Fe oxide: Evidence from the distribution of rare earth elements and yttrium between Fe oxides and Mn oxides in hydrogenetic ferromanganese crusts. *Geochem. J.*, 43, 37-47.
- BENEDETTO, J. L., SÁNCHEZ, T. M., CARRERA, M. G., BRUSSA, E. D. & SALAS, M. J. 1999. Paleontological constraints on successive paleogeographic positions of Precordillera terrane during the early Paleozoic. Special Paper 336: Laurentia-Gondwana connections before Pangea. Geological Society of America.
- BERGSTRÖM, S. M., CHEN, X., GUTIERREZ-MARCO, J. C. & DRONOV, A. 2008. The new chronostratigraphic classification of the Ordovician System and its relations to major regional series and stages and to $\delta^{13}\text{C}$ chemostratigraphy. *Lethaia*, 42.
- BOLHAR, R., KAMBER, B. S., MOORBATH, S., FEDO, C. M. & WHITEHOUSE, M. J. 2004. Characterisation of early Archaean chemical sediments by trace element signatures. *Earth and Planetary Science Letters*, 222, 43-60.
- BOLHAR, R. & VAN KRANENDONK, M. J. 2007. A non-marine depositional setting for the northern Fortescue Group, Pilbara Craton, inferred from trace element geochemistry of stromatolitic carbonates. *Precambrian Research*, 155, 229-250.
- BORDONARO, O. L. 1980. El Cámbrico en la Quebrada de Zonda. *Revista de la Asociación Geológica Argentina*. San Juan:: Asociación Geológica Argentina.
- BORDONARO, O. L. 2003. Review of the Cambrian stratigraphy of the Argentine Precordillera. *Geologica Acta*, 1, 11-21.
- BRAND, U. & VEIZER, J. 1980. Chemical diagenesis of a multicomponent carbonate system-1: trace elements. *Journal of Sedimentary Petrology*, 50, 1219-1236.

- BRAND, U. & VEIZER, J. 1981. Chemical diagenesis of a multicomponent carbonate system; 2, Stable isotopes. *Journal of Sedimentary Research*, 51, 987–997.
- BRUMSACK, H. J. 2006. The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 232, 344–361.
- BUGGISCH, W., KELLER, M. & LEHNERT, O. 2003. Carbon isotope record of the Late Cambrian and Early Ordovician carbonates of the Argentine Precordillera. *Palaeogeography, Palaeoclimatology, Palaeoecology*.
- BYRNE, R. & KIM, K.-H. 1990. Rare earth element scavenging in seawater. *Geochimica et Cosmochimica Acta*, 54, 2645–2656.
- BYRNE, R. H., LIU, X. & SCHUF, J. 1996. The influence of phosphate coprecipitation on rare earth distribution in natural waters. *Geochimica et Cosmochimica Acta*, 60, 3341–3346.
- CALVERT, S. E. & PEDERSEN, T. F. 1993. Geochemistry of Recent oxic and anoxic marine sediments: Implications for the geological record. *Mar. Geol.*, 113, 67–88.
- CAÑAS, F. L. 1995. Early Ordovician carbonate platform facies of the Argentine Precordillera: Restricted shelf to open platform evolution. In: COOPER, J. D., DROSER, M. L. & FINNEY, S. C. (eds.) *Ordovician odyssey: Short papers for the Seventh International Symposium on the Ordovician System*. Pacific Section: SEPM (Society for Sedimentary Geology)
- CAÑAS, F. L. 1999. Facies and sequences of the Late Cambrian–Early Ordovician carbonates of the Argentine Precordillera: A stratigraphic comparison with Laurentian platforms. *Special Paper 336: Laurentia–Gondwana connections before Pangea*. Geological Society of America.
- DALRYMPLE, R. W. C., KYUNGSIK 2007. Morphologic and facies trends through the fluvial–marine transition in tide-dominated depositional systems: A schematic framework for environmental and sequence-stratigraphic interpretation. *Earth Science Reviews* 81 135–174.
- DE BAAR, H. J. W., BACON, M. P., BREWER, P. G. & BRULAND, K. W. 1985. Rare earth elements in the Pacific and Atlantic Oceans. *Geochimica et Cosmochimica Acta*, 49, 1943–1959.
- DELLA PORTA, G., WEBB, G. E. & MCDONALD, I. 2015. REE patterns of microbial carbonate and cements from Sinemurian (Lower Jurassic) siliceous sponge mounds (Djebel Bou Dahar, High Atlas, Morocco). *Chem. Geol.*, 400, 65–86.
- DENISON, R. E., KOEPNICK, R. B., FLETCHER, A., HOWELL, M. W. & CALLAWAY, W. S. 1994. Criteria for the retention of original seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in ancient shelf limestones. *Chemical Geology*, 112, 131–143.

- DERRY, L. A. 2010. A burial diagenesis origin for the Ediacaran Shuram–Wonoka carbon isotope anomaly. *Earth and Planetary Science Letters*, 294, 152-162.
- DERRY, L. A. & JACOBSEN, S. B. 1990. The chemical evolution of Precambrian seawater: Evidence from REEs in banded iron formations. *Geochimica et Cosmochimica Acta*, 54, 2965-2977.
- DE VILLIERS, S. 1999. Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans. *Earth and Planetary Science Letters*, 171 (4), 623-624.
- DICKSON, J. A. D. & COLEMAN, M. L. 1980. Changes in carbon and oxygen isotope composition during limestone diagenesis. *Sedimentology*, 27, 107-118.
- DU Y., ZHU, J., GU S., XU, Y., YANG J., 2007. Sedimentary geochemistry of the Cambrian-Ordovician cherts: Implication on archipelagic ocean of North Qilian orogenic belt. *Sci China Ser D-Earth Sci*. 50 (11)
- EGGINS, S. M., WOODHEAD, J. D., KINSLEY, L. P. J., MORTIMER, G. E., SYLVESTER, P., MCCULLOCH, M. T., HERGT, J. M. & HANDLER, M. R. 1997 A simple method for the precise determination of > 40 trace elements in geological samples by ICP-MS using enriched isotope internal standardisation. *Chemical Geology*, 134, 311-326.
- ELDERFIELD, H., UPSTILL-GODDARD, R. & SHOLKOVITZ, E. R. 1990. The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochimica et Cosmochimica Acta*, 54, 971–991.
- FIKE, D. A., BRADLEY, A. S. & ROSE, C. V. 2015. Rethinking the Ancient Sulfur Cycle. *Annual Review of Planetary Science*. 2015. 43, 593-622
- FREI, R., DAHL, P. S., DUKE, E. F., FREI, K. M., HANSEN, T. R., FRANDSSON, M. M. & JENSEN, L. A. 2008. Trace element and isotopic characterization of Neoproterozoic and Paleoproterozoic iron formations in the Black Hills (South Dakota, USA): Assessment of chemical change during 2.9–1.9Ga deposition bracketing the 2.4–2.2Ga first rise of atmospheric oxygen. *Precambrian Research*, 162, 441-474.
- FRIMMEL, H. E. 2009. Trace element distribution in Neoproterozoic carbonates as paleoenvironmental indicators. *Chemical Geology*, 258 (3-4) 338-353
- GERMAN, C. R. & ELDERFIELD, H. 1990. Application of the Ce anomaly as a paleoredox indicator: the ground rules. *Palaeoceanography* 5.
- GILL, B.C., LYONS, T.W., SALTZMAN, M.R. 2007. Parallel, high-resolution carbon and sulfur isotope records of the evolving Paleozoic marine sulfur reservoir. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 256, 156–73.

- GILL, B.C., LYONS, T.W., YOUNG, S.A., KUMP, L.R., KNOLL, A.H., SALTZMAN, M.R. 2011. Geochemical evidence for widespread euxinia in the Later Cambrian ocean. *Nature*, 469, 80–83.
- GOLDBERG, T., POULTON, S.W. & STRAUSS, H. 2005. Sulphur and oxygen isotope signatures of late Neoproterozoic to early Cambrian sulphate, Yangtze Platform, China: Diagenetic constraints and seawater evolution. *Precambrian Research*, 137, 223-241.
- GOMEZ, F. J., OGLE, N., ASTINI, R. A. & KALIN, R. M. 2007. Paleoenvironmental and Carbon-Oxygen Isotope Record of Middle Cambrian Carbonates (La Laja Formation) in the Argentine Precordillera. *Journal of Sedimentary Research*, 77, 826-842
- HALEY, B. A., KLINKHAMMER, G. P. & J, M. 2004. Rare earth elements in pore waters of marine sediments. . *Geochimica Et Cosmochimica Acta*, 68, 1265-1279.
- HELZ, G. R., MILLER, C. V., CHARNOCK, J. M., MOSSELMANS, J. L. W., PATTRICK, R. A. D., GARNER, C. D. & VAUGHAN, D. J. 1996. Mechanisms of molybdenum removal from the sea and its concentration in black shales: EXAFS evidences. *Geochim. Cosmochim. Acta*, 60, 3631–3642.
- HEMMING, N. G., MEYERS, W. J. & GRAMS, J. C. 1989. Cathodoluminescence in Diagenetic Calcites: The Roles of Fe and Mn as Deduced from Electron Probe and Spectrophotometric Measurements. *Journal of Sedimentary Research (SEPM)*, 59, 404-411.
- HAHN, K. E., TURNER, E. C., BABECHUK, M. G. & KAMBER, B. S. 2015. Deep-water seep-related carbonate mounds in a Mesoproterozoic alkaline lake, Borden Basin (Nunavut, Canada). *Precambrian Research*, 271, 173-197.
- HURTGEN, M.T., HALVERSON, G.P., ARTHUR, M.A. & HOFFMAN, P.F. 2006. Sulfur cycling in the aftermath of a 635-Ma snowball glaciation: Evidence for a syn-glacial sulfidic deep ocean. *Earth and Planetary Science Letters*, 245, 551-570.
- HURTGEN, MT, PRUSS, SB, KNOLL, AH. 2009. Evaluating the relationship between the carbon and sulfur cycles in the later Cambrian ocean: an example from the Port au Port Group, Western Newfoundland, Canada. *Earth and Planetary Science Letters*, 281, 288–97.
- ISLEY, A. E. 1995. Hydrothermal plumes and the delivery of iron to banded iron-formation. *The Journal of Geology*, 103, 169–185.
- JACOBSEN, S. B. & KAUFMAN, A. J. 1999. The Sr, C and O isotopic evolution of Neoproterozoic seawater. *Chemical Geology*, 161, 37-57.
- JACOBSEN, S. B. & PIMENTEL-KLOSE, M. R. 1988. A Nd isotopic study of the Hamersley and Michipicoten banded iron formations: the source of REE and Fe in Archean oceans. *Earth and Planetary Science Letters*, 87, 29-44.

- JOCHUM, K. P., SCHOLZ, D., STOLL, B., WEIS, U., WILSON, S. A., YANG, Q. C., SCHWALB, A., BORNER, N., JACOB, D. E. & ANDREAE, M. O. 2012. Accurate trace element analysis of speleothems and biogenic calcium carbonates by LA-ICP-MS. *Chemical Geology*, 318, 31-44.
- JONES, D.S., & FIKE, D.A. 2013. Dynamic sulfur and carbon cycling through the end-Ordovician extinction revealed by paired sulfate–pyrite $\delta^{34}\text{S}$. *Earth and Planetary Science Letters*, 363, 144–155.
- KALVODA, J., KUMPAN, T., HOLA, M., BABEK, O., KANICKY, V., SKPDA, R. 2018. Fine-scale LA-ICP-MS study of redox oscillations and REEY cycling during the latest Devonian Hangenberg Crisis (Moravian Karst, Czech Republic). *Palaeogeography, Palaeoclimatology, Palaeoecology*, 493, 30-43.
- KAMBER, B. S. & WEBB, G. E. 2001. The geochemistry of late Archaean microbial carbonate: implications for ocean chemistry and continental erosion history. *Geochimica et Cosmochimica Acta*, 65, 2509-2525.
- KAMBER, B. S., GREIG, A. & COLLERSON, K. D. 2005. A new estimate for the composition of weathered young upper continental crust from alluvial sediments, Queensland, Australia. *Geochimica et Cosmochimica Acta*, 69, 1041-1058.
- KAMBER, B.S., WHITEHOUSE, M.J. 2007. Micro-scale sulphur isotope evidence for sulphur cycling in the late Archean shallow ocean. *Geobiology*, 5, 5–17.
- 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.
- KAMPSCHULTE, A & STRAUSS, H. 2004. The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulfate in carbonates. *Chemical Geology*, 204, 255-286.
- KAY, S. M. O., S.; ABBRUZZI, J. M. 1996. Zircon and whole rock Nd-Pb isotopic evidence for a Grenville age and Laurentian origin for the basement of the Precordilleran terrane in Argentina. *Abstracts with Programs. Geological Society of America*.
- KELLER, M. 1999. Argentine Precordillera: Sedimentary and Plate Tectonic History of a Laurentian Crustal Fragment in South America. *Special Paper 341: Argentine Precordillera: sedimentary and plate tectonic history of a Laurentian crustal fragment in South America. Geological Society of America*.
- KELLER, M., CAÑAS, F. L., LEHNERT, O. & VACCARI, N. E. 1994. The Upper Cambrian and Lower Ordovician of the Precordillera (Western Argentina): Some stratigraphic reconsiderations. *Newsletters Stratigraphy*, 31, 115-132.

- KELLER, M., EBERLEIN, S. & LEHNERT, O. 1993. Sedimentology of Middle Ordovician carbonates in the Argentine Precordillera: Evidence for regional relative sea-level changes. *Geologische Rundschau*, 82, 362–377.
- KELLER, M. & FLÜGEL, E. 1996. Early Ordovician reefs from Argentina: Stromatoporoid vs. stromatolite origin. *Facies* 34, 177–192.
- KLINKHAMMER, G. P. & PALMER, M. R. 1991. Uranium in the oceans: where it goes and why. *Geochim. Cosmochim. Acta* 55, 1799–1806., 55, 1799–1806.
- KNOLL, A. H., KAUFMAN, A. J. & A, S. M. 1995 The carbon isotopic composition of Proterozoic carbonates: Riphean successions from northwestern Siberia (Anabar massif, Turukhansk uplift) *American Journal of Science*, 295, 823–850.
- LANGMUIR, D. 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta*, 42, 547–569.
- LAWRENCE, M. G., GREIG, A., COLLERSON, K. D. & KAMBER, B. S. 2006a. Rare Earth Element and Yttrium Variability in South East Queensland Waterways. *Aquatic Geochemistry*, 12, 39–72.
- LAWRENCE, M. G., JUPITER, S. D. & KAMBER, B. S. 2006b. Aquatic geochemistry of the rare earth elements and yttrium in the Pioneer River catchment, Australia. *Mar. Freshwater Res.*, 57, 725.
- LAWRENCE, M. G. & KAMBER, B. S. 2006. The behaviour of the rare earth elements during estuarine mixing—revisited. *Marine Chemistry*, 100, 147–161.
- LÉCUYER, C., REYNARD, B. & GRANDJEAN, P. 2004. Rare earth element evolution of Phanerozoic seawater recorded in biogenic apatites. *Chemical Geology* 204, 63–102.
- LI, C., LOVE, G.D., LYONS, T.W., FIKE, D.A., SESSIONS, A.L., CHU, X. 2010. A new stratified redox model for the Ediacaran ocean. *Science*, 328, 80–83.
- LEHNERT, O. 1995. Ordovizische Conodonten aus der Präkordillere Westargentinien: Ihre Bedeutung für Stratigraphie und Paläogeographie. *Erlanger Geologische Abhandlungen* 125, 1–193.
- LOYD, S.J., MARENCO, P.J., HAGADORN, J.W., LYONS, T.W., KAUFMAN, A.J. *et al.* 2012. Sustained low marine sulfate concentrations from the Neoproterozoic to the Cambrian: insights from carbonates of northwestern Mexico and eastern California. *Earth and Planetary Science Letters*, 339–40, 79–94
- MORFORD, J. L., MARTIN, W. R., FRANÇOIS, R. & CARNEY, C. M. 2009, A model for uranium, rhenium, and molybdenum diagenesis in marine sediments based on results from coastal locations. *Geochim. Cosmochim. Acta*, 73, 2938–2960.

- MELIM, L. A., SWART, P. K. & EBERLI, G. P. 2004. Mixing Zone Diagenesis in the subsurface of Florida and the Bahamas. *Journal of Sedimentary Research*, 74, 904-913.
- MELIM, L. A., WESTPHAL, H., SWART, P. K., EBERLI, G. P. & MUNNECKE, A. 2002. Questioning carbonate diagenetic paradigms: evidence from the Neogene of the Bahamas. *Marine Geology* 185, 27–53.
- MOURA, R. L. A.-F., G. M.; MORAES, F. C.; BRASILEIRO, P. S.; SALOMON, P. S.; MAHIQUES, M. M.; , BASTOS, A. C. A., M. G.; SILVA JR., J. M.; ARAUJO, B. F.; BRITO, F. P.; RANGEL, T. P.; OLIVEIRA, B. C. V.; BAHIA, R. G. P., R. P.; DIAS, R. J. S.; SIEGLE, E.; FIGUEIREDO JR., A. G.; PEREIRA, R. C.; LEAL, C. V.; HAJDU, E. A., N. E.; GREGORACCI, G. B.; NEUMANN-LEITÃO, S.; YAGER, P. L.; FRANCINI-FILHO, R. B.; FRÓES, A.; CAMPEÃO, M. S., B. S.; MOREIRA, A. P. B.; OLIVEIRA, L.; SOARES, A. C.; ARAUJO, L.; OLIVEIRA, N. L.; TEIXEIRA, J. B.; & VALLE, R. A. B. T., C. C.; REZENDE, C. E.; THOMPSON, F. L. 2016. An extensive reef system at the Amazon River mouth. *Science Advances*, 2.
- MCDONOUGH, M. R., RAMOS, V. A., ISACHSEN, C. E., BOWRING, S. A. & VUJOVICH, G. I. 1993. Nuevas edades de circones del basamento de la sierra de Pie de Palo, Sierras Pampeanas Occidentales de San Juan: sus implicancias para los modelos del supercontinente proterozoico de Rodinia. *Actas, XII Congreso Geológico Argentino y II Congreso de Exploración de Hidrocarburos*. Mendoza: Asociación Geológica Argentina e Instituto Argentino de Petróleo y Gas.
- MCMANUS, J., BERELSON, W. M., KLINKHAMMER, G. P., HAMMOND, D. E. & HOLM, C. 2005. Authigenic uranium: relationship to oxygen penetration depth and organic carbon rain. *Geochim. Cosmochim. Acta*, 69, 95–108
- NOTHDURFT, L. D., WEBB, G. E. & KAMBER, B. S. 2004. Rare earth element geochemistry of Late Devonian reefal carbonates, Canning Basin, Western Australia: confirmation of a seawater REE proxy in ancient limestones. *Geochimica et Cosmochimica Acta*, 68, 263-283.
- NOZAKI, Y., ZHANG, J. & AMAKAWA, H. 1997. The fractionation between Y and Ho in the marine environment. *Earth and Planetary Science Letters*, 148, 329-340.
- OEHLERT, A. M. & SWART, P. K. 2014. Interpreting carbonate and organic carbon isotope covariance in the sedimentary record. *Nat. Commun.*, 5.
- ORTEGA, G., CAÑAS, F. L. & HÜNICKEN, M. A. 1985. Sobre la presencia de *Isograptus victoriae* Harris en la Formación Gualcamayo, La Rioja, Argentina. *Revista Técnica Yacimientos Petrolíferos Fiscales Bolivia*, 9, 215–221.

- PATON, C., HELLSTROM, J., PAUL, B., WOODHEAD, J. & HERGT, J. 2011. Iolite: Freeware for the visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry*, 26, 2508.
- PLANAUSKY, N., BEKKER, A., ROUXEL, O. J., KAMBER, B., HOFMANN, A., KNUDSEN, A. & LYONS, T. W. 2010. Rare Earth Element and yttrium compositions of Archean and Paleoproterozoic Fe formations revisited: New perspectives on the significance and mechanisms of deposition. *Geochimica et Cosmochimica Acta*, 74, 6387-6405.
- PRATT, B. R., RAVIOLO M. M. & BORDONORO, O. L. 2012. Carbonate platform dominated by peloidal sands: Lower Ordovician La Silla Formation of the eastern Precordillera, San Juan, Argentina *Sedimentology*, 59, 843–866.
- PRESENT TM, P. G., BURKE A, FISCHER WW, ADKINS JF. 2015. Large Carbonate Associated Sulfate isotopic variability between brachiopods, micrite, and other sedimentary components in Late Ordovician strata. *Earth and Planetary Science Letters*, 432, 187–198.
- RAMOS, V. A., DALLMEYER, R. D. & I., V. G. 1998. Time constraints on the early Palaeozoic docking of the Precordillera, central Argentina. In: PANKHURST, R. J. & RAPELA, C. W. (eds.) *The proto-Andean margin of Gondwana*.
- RAMOS, V. A. 2004. Cuyania, an exotic block to Gondwana: review of a historical success and the present problems. *Gondwana Research*, 7, 1009–1026.
- REYNARD, B., LÉCUYER, C. & GRANDJEAN, P. 1999. Crystal-chemical controls on rare earth element concentrations in fossil biogenic apatite and implications for paleoenvironmental reconstructions. *Chemical Geology*, 233-241.
- RICHARDSON, J. A., NEWVILLE, M., LANZIROTTI, A., WEBB, S. M., ROSE, C. V., CATALANO, J. G. & FIKE, D. A. 2019. Depositional and diagenetic constraints on the abundance and spatial T variability of carbonate-associated sulfate. *Chemical Geology*, 523, 59–72.
- ROSE, C. V., WEBB, S. M., NEWVILLE, M., LANZIROTTI, A., RICHARDSON, J. A., TOSCA, N. J., CATALANO, J. G., BRADLEY, A. S. & FIKE, D. A. 2019. Insights into past ocean proxies from micron-scale mapping of sulfur species in carbonates. *Geology*, 47, 833-837.
- SALAMON, M. A. N., R., LACH, R., BRACHANIEC, T., GORZELAK, P. 2012. Ophiuroids Discovered in the Middle Triassic Hypersaline Environment. *PLoS ONE* 7, e49798.

- SALTZMAN, M. R., EDWARDS, C. T., ADRAIN, J. M. & WESTROP, S. R. 2015. Persistent oceanic anoxia and elevated extinction rates separate the Cambrian and Ordovician radiations. *Geology*, 43, 807-810.
- SARMIENTO, G. N. 1986. La biozona de *Amorphognathus variabilis*–*Eoplacognathus pseudoplanus* (Conodonta), Llanvirniano inferior, en el flanco oriental de la Sierra de Villicum. *Actas, 1as Jornadas sobre Geología de Precordillera*. San Juan, Argentina: Universidad Nacional de San Juan.
- SARMIENTO, G. N. 1990 Conodontes Ordovícicos de Argentina *Treballs Museu Geologia Barcelona*, 1, 135–161.
- SAVARD, M., VEIZER, J. & HINTON, R. 1995 Cathodoluminescence at low Fe and Mn concentrations: A SIMS study of zones in natural calcites. *Journal of Sedimentary Research*. A65, 208-2136.
- SCHOLLE, P. A., BEBOUT, D. G. & MOORE C. H. Carbonate Depositional Environments. 1983. AAPG.
- SHIELDS, G. A. & WEBB, G. E. 2004. Has the REE composition of seawater changed over geological time? *Chemical Geology*, 204, 1 (2), 103-107
- SHOLKOVITZ, E. & SHEN, G. T. 1995. The incorporation of rare earth elements in modern coral. *Geochimica et Cosmochimica Acta*, 59, 2749-2756.
- SWART, P. K., OEHLERT, A. M., MACKENZIE, G. J., EBERLI, G. P. & REIJMERT, J. J. G. 2014. The fertilization of the Bahamas by Saharan dust: A trigger for carbonate precipitation? *Geology*, 42 (8), 671–674.
- THOMAS, W. A. & ASTINI, R. A. 1999. Simple-shear conjugate rift margins of the Argentine Precordillera and the Ouachita embayment of Laurentia. *Geological Society of America Bulletin*, 111, 1069-1079.
- THOMAS, W. A. & ASTINI, R. A. 2003. Ordovician accretion of the Argentine Precordillera terrane to Gondwana: a review. *Journal of South American Earth Sciences*, 16, 67–79.
- THOMAS, W. A. & ASTINI, R. A. 2007. Vestiges of an Ordovician west-vergent thinskin Oclitic thrust belt in the Argentine Precordillera, southern Central Andes. *Journal of Structural Geology*, 29, 1369–1385.
- THOMPSON, C.K. & KAH, L.C. 2012. Sulfur isotope evidence for widespread euxinia and a fluctuating oxycline in Early to Middle Ordovician greenhouse oceans. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 313-314, 189-214.

- TOSTEVIN, R., SHIELDS, G. A., TARBUCK, G. M., HE, T., CLARKSON, M. O. & WOOD, R. A. 2016. Effective use of cerium anomalies as a redox proxy in carbonate-dominated marine settings. *Chemical Geology*, 438, 146-162.
- TRIBOVILLARD, N., ALGEO, T. J., LYONS, T. & RIBOULLEAU, A. 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. *Chemical Geology*, 232, 12–32.
- VAN DER WEIJDEN, C. H. 2002. Pitfalls of normalisation of marine geochemical data using a common divisor. *Marine Geology*, 184, 167–187.
- VAN GELDERN, R., JOACHIMSKI, M., DAY, J., JANSEN, U., ALVAREZ, F., YOLKIN, E. A. & MA, X. 2006. Carbon, oxygen and strontium isotope records of Devonian brachiopod shell calcite. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 240, 47-67.
- VAN HULTEN, M., DUTAY, J. C., MIDDAG, R., DE BAAR, H., ROY-BARMAN, M., GEHLEN, M., TAGLIABUE, A. & STERL, A. 2016. Manganese in the world ocean: A first global model. *Biogeosciences Discussion*. <https://doi.org/10.5194/bg-2016-282>
- VERDEL, C., PHELPS, B. & WELSH, K. 2018. Rare earth element and $^{87}\text{Sr}/^{86}\text{Sr}$ step-leaching geochemistry of central Australian Neoproterozoic carbonate. *Precambrian Research*, 310, 229-242.
- VEIZER, J. 1983. Chemical diagenesis of carbonates: theory and application of trace element technique. Short Course Notes Society of Economic Paleontologists and Mineralogists.
- VOLDMAN, G. G., ALBANESI, G. L. & RAMOS, V. A. 2009. Ordovician metamorphic event in the carbonate platform of the Argentine Precordillera: Implications for the geotectonic evolution of the proto-Andean margin of Gondwana. *Geology*, 37, 311–314.
- VUJOVICH, G. I., VAN STAAL, C. R. & DAVIS, W. 2004. Age constraints on the tectonic evolution and provenance of the Pie de Palo complex, Cuyania Composite terrane, and the Famatinian orogeny in the Sierra Pie de Palo, San Juan, Argentina. *Gondwana Research*, 7, 1041–1056.
- VARELA, R. & DALLA SALDA, L. H. 1993. Geocronología Rb-Sr de metamorfitas y granitoides del tercio sur de la Sierra de Pie de Palo, San Juan, Argentina *Revista de la Asociación Geológica Argentina*, 47, 271–275.
- VARELA, R., LOPEZ DE LUCHI, M. G., C, C. & DALLA SALDA, L. H. 1996. Geocronología de gneises y granitoides de la Sierra de Umango, La Rioja *Actas, XIII Congreso Geológico Argentino y III Congreso de Exploración de Hidrocarburos*. Buenos Aires, Argentina: Asociación Geológica.
- WEBB, G. E. & KAMBER, B. S. 2000. Rare earth elements in Holocene reefal microbialites: a new shallow seawater proxy. *Geochimica et Cosmochimica Acta*, 64, 1557-1565.

- WEBB, G. E., NOTHDURFT, L. D., KAMBER, B. S., KLOPROGGE, J. T. & ZHAO, J. X. 2009. Rare earth element geochemistry of scleractinian coral skeleton during meteoric diagenesis: a sequence through neomorphism of aragonite to calcite. *Sedimentology* 56(5), 1433-1463.
- WEBBY, B. D., PERCIVAL, I. G. 1983. Ordovician trimerellacean brachiopod shell beds. *Lethaia*, 16, 215-232.
- WOTTE, T., SHIELDS-ZHOU, G. A. & STRAUSS, H. 2012. Carbonate-associated sulfate: Experimental comparisons of common extraction methods and recommendations toward a standard analytical protocol. *Chemical Geology*, 326-327, 132-144.
- WU, N., FARQUHAR, J. & STRAUSS, H. 2014. $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ records of Paleozoic seawater sulfate based on the analysis of carbonate associated sulfate. *Earth and Planetary Science Letters*, 399, 44-51.
- WYNDHAM, T., MCCULLOCH, M., FALLON, S. & ALIBERT, C. 2004. High-resolution coral records of rare earth elements in coastal seawater: biogeochemical cycling and a new environmental proxy. *Geochimica et Cosmochimica Acta* 68, 2067–2080.
- ZHANG, J. & NOZAKI, Y. 1998. Behavior of rare earth elements in seawater at the ocean margin: a study along the slopes of the Sagami and Nankai troughs near Japan. *Geochimica et Cosmochimica Acta*, 62, 1307-1317.
- ZHANG, T., SHEN, Y., ZHAN, R., SHEN, S. & CHEN, X. 2009. Large perturbations of the carbon and sulfur cycle associated with the Late Ordovician mass extinction in South China. *Geology*, 37, 299-302.
- ZHAO, M. & ZHENG, Y. 2017. A geochemical framework for retrieving the linked depositional and diagenetic histories of marine carbonates. *Earth and Planetary Science Letters*, 460, 213-221.
- ZHENG, Y., ANDERSON, R. F., VAN GEEN, A. & FLEISCHER, M. Q. 2002. Preservation of nonlithogenic particulate uranium in marine sediments. *Geochim. Cosmochim. Acta*, 66, 3085–3092.
- ZHONG, S. & MUCCI, A. 1995. Partitioning of rare earth elements (REEs) between calcite and seawater solutions at 25°C and 1 atm, and high dissolved REE concentrations. *Geochim. Cosmochim. Acta*, 59, 443–453.

Chapter 3

Application of micron-scale trace element mapping to discriminate water column conditions from syndepositional porewater processes recorded in marine limestones

Stephen P. Coakley^{1*}, Catherine V. Rose², David M. Chew¹,

¹ *Department of Geology, Trinity College Dublin, Dublin 2, IRE.*

² *School of Earth and Environmental Sciences, University of St Andrews, St Andrews, Fife KY16 9AL, UK.*

ABSTRACT

Marine carbonates of the Early to Middle Ordovician San Juan Formation from the Cerro La Silla stratigraphic section in the Argentine Precordillera display shale-normalised rare earth element and yttrium (REE + Y) trends in solution-ICP-MS data that are considered typical of carbonates formed in brackish water. None of the analysed carbonates have the deep, upper crust-normalised patterns that are seen in open marine seawater and carbonate proxies thereof. The samples instead display REE + Y patterns that are slightly light rare earth element-enriched or depleted to flat, with profiles similar to those intermediate between seawater and modern river water. However, in the majority of the samples from the San Juan Formation these data cooccur with a faunal assemblage of marine fossils including brachiopods and stenohaline crinoid fossils. As siliciclastic contamination may suppress marine REE+Y profiles, and as the solution ICP-MS data does not show unequivocal evidence of such contamination, further investigation was undertaken at a micron scale to identify the cause of the shale-normalized REE+Y data's divergence from primary marine values.

The value of the LA-ICP-MS mapping tool Monocle, an Iolite add-in, is demonstrated by measurement of multiple elements in different components in LA-ICPM-MS maps from four samples from above fair-weather wave base to below storm wave base. With these data, siliciclastic correction using Th in allomicrocline to quantify shale contributions is more effective in the analyzed samples than a similar attempted correction using solution ICP-MS

data. The corrected data reveal that the majority of the samples in the San Juan Formation incorporated components that recorded a marine REE+Y signature suppressed by siliciclastic contamination. However, many samples also retain flat shale-normalized slopes post-correction, in particular in the shallow water facies that exhibit minimal siliciclastic contamination at the base of the stratigraphic section in the La Silla Formation and lowermost San Juan Formation. Alternative causes for these REE+Y results are therefore investigated, including factors that impact the redox-related uptake and release of trace elements from clays, organic matter and Fe-Mn oxyhydroxides and oxic precipitation of cements in brackish porewaters during early burial.

The resulting data indicates that LA-ICP-MS mapping, with measurement of elemental concentrations using Monocle, is potentially useful for geochemical screening to identify and target least-altered components in carbonate rocks and for validation of solution ICP-MS results to rule out excessive or ineffective leaching during the digestion of samples for solution ICP-MS analysis. This technique constitutes a stronger method for correction than from existing solution ICP-MS and spot analysis data sets. The results also demonstrate that LA-ICP-MS mapping is potentially useful for deriving geochemical data from complex phases such as allomicrite and may assist in their use as a source of geochemical data in circumstances where an effective screening and appropriate correction for siliciclastic contamination is undertaken and where preferred sources such as marine radiaxial fibrous cement or microbial micrite are unavailable.

3.1 Introduction

The well-exposed sections of Ordovician carbonates in the Argentine Precordillera have produced important chemostratigraphic records that include the first well constrained carbon isotope ($\delta^{13}\text{C}_{\text{carb}}$) records for the Early and Middle Ordovician (Buggisch *et al.*, 2003) along with a sulfur isotope archive in carbonate associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) whose negative values compared to coeval data form a key component of recent reinterpretations of the Ordovician sulfur cycle (Fig. 2.1 Thompson and Kah, 2012; Present, 2015; Kah *et al.*, 2016). To investigate anomalously light $\delta^{34}\text{S}_{\text{CAS}}$ signals from the Tremadocian to Darwillian San Juan Formation, Chapter 2 presented a suite of solution-ICP-MS trace element analyses, paired with $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ data from the type section of the San Juan Formation at Cerro La Silla. These included rare earth element and yttrium analyses that have been shown to faithfully record seawater redox conditions in carbonates (Webb and Kamber, 2000; Webb *et al.*, 2009).

In the modern ocean when riverine freshwater, the major source of REE+Y, mixes with estuarine water of increasing salinity, absorptive scavenging onto Fe-Mn oxyhydroxides, clays and organic material favours removal of light rare earth elements (LREE) (Elderfield *et al.*, 1990; Lawrence *et al.*, 2006a; Lawrence *et al.*, 2006b; Lawrence and Kamber, 2006). This steepens the (shale-normalised) REE+Y profile and forms a distinctive seawater signal with features that initially develop with progressively greater estuarine salinity and subsequently alter with seawater depth (De Baar *et al.*, 1985; Bau *et al.*, 1997; Zhang and Nozaki, 1998) (Fig. 2.2). These characteristics in fully-marine, oxic conditions include:

- (1) LREE depletion relative to heavy rare-earth elements (HREE) (Zhong and Mucci, 1995), expressed as a steep positive slope of shale-normalised REE+Y ($\text{Pr}_n/\text{Yb}_n \ll 1$), that develops with increased salinity and depth, most rapidly in the top 500 m of the water column (Kamber *et al.*, 2014);
- (2) a strongly superchondritic Y/Ho ratio, which increases during cycling of REE+Y from surface waters to deep ocean water ($\text{Y}/\text{Ho} \geq 40 - 80$) (Bau and Dulski, 1996; Bau and Dulski, 1999; Bolhar *et al.*, 2004). The majority of geologic materials have near chondritic values of 24-34, whilst modern seawater has Y/Ho ratio > 44 (De Baar *et al.*, 1985; Bau and Dulski, 1996; Bau *et al.*, 1997; Nozaki *et al.*, 1997);

- (3) a positive La anomaly due to reduced adhesion to particles relative to neighbouring REE (Bau and Dulski, 1996; Bau, 1999; Bolhar *et al.*, 2004);
- (4) a moderate positive Gd anomaly due to its greater stability in solution than neighbouring REE (De Baar *et al.*, 1985; Byrne and Kim, 1990; Byrne *et al.*, 1996; Bau *et al.*, 1997; Zhang and Nozaki, 1998; Bolhar *et al.*, 2004); and
- (5) a strong negative Ce anomaly in oxic marine conditions (Zhang and Nozaki, 1998). Ce^{3+} oxidised in highly oxic estuarine and marine conditions forms Ce^{4+} that adsorbs to metal oxyhydroxide complexes (Bau and Koschinsky, 2009) and progressively becomes depleted relative to Pr.

As marine carbonate rocks are composed, in varying abundance, of cement, micrite (including depositional/allomicrite), abiotic grains and fossils (Richardson *et al.*, 2019), the samples were petrographically and geochemically screened to identify component types, potential contaminants and diagenetic alteration, before the selection of allomicrite for sampling as a ubiquitous phase across all studied depositional facies (Chapter 2). On review of the resulting solution-ICP-MS data it was concluded in Chapter 2, based on the concentration and covariation trends of elements associated with diagenetic alteration (i.e. Mn and Sr as discussed in detail in Chapter 2), that the carbonate record is not significantly altered in samples. However, few of the resulting REE + Y patterns approach values expected from fully-marine carbonates. Plots of Pr_n/Yb_n vs Y/Ho presented in Fig. 2.8 from solution-ICP-MS data illustrate that no data points achieve both the Pr_n/Yb_n ratio $\ll 1$ and the Y/Ho value > 40 expected in uncontaminated, unaltered marine carbonates. In addition, the other seawater-diagnostic characteristics of the REE + Y profile are subdued, including Y/Ho , the La anomaly, the Gd anomaly and the shale-normalised slope (Table 2-1). The REE + Y spectra are instead typical of carbonates formed in fluctuating seawater-freshwater mixing conditions (Fig. 2.4; Bolhar and Van Kranendonk, 2007; Verdel *et al.*, 2018), whilst ratios of authigenic redox sensitive Mo and U ($\text{Mo}:\text{U}_{\text{auth}}$) are consistent with some variation in the redox conditions in sediment pore-waters (Algeo and Tribovillard, 2009). Screening and a correction for siliciclastic contamination produce results that are equivocal. Therefore, the presence of marine fauna throughout much of the measured section requires further consideration.

A progressive development of water column salinity from the flat shale-normalised slopes typical of near-marine conditions to more marine conditions is represented by the covarying change of Pr_n/Yb_n and Y/Ho toward marine values in Fig. 2.4. However, brackish conditions are contradicted by the presence of marine faunae including crinoids above 110 m in the stratigraphic section. Crinoids are considered to be physiologically limited to marine salinities (e.g. Binyon, 1972). It therefore appears likely that cryptic siliciclastic contamination may be present and subduing the marine REE + Y signature. LA-ICP-MS mapping is well suited to investigating and quantifying the causes of the subdued profile as it enables rapid visualization of the spatial distribution of major and trace element concentrations within and between identifiable sample components (Ubide *et al.*, 2015) and now has the added advantage of permitting quantitative data extraction, using the Iolite add-in Monocle (Petrus *et al.*, 2017). This chapter therefore uses LA-ICP-MS elemental image mapping to investigate whether the scale of the REE + Y anomalies in the samples is indeed due to brackish conditions or to alternative processes controlling the uptake and release of REE+Y, cryptic contamination (i.e. not clearly discernable in the solution ICP-MS dataset) or early diagenetic alteration (Haley *et al.*, 2004; Caetano-Filho *et al.*, 2018) or deviation of Early to Middle Ordovician seawater from REE+Y compositions typical of modern seawater (Du *et al.*, 2007; Zhang *et al.*, 2009).

3.2 Methods

In the field, 300 samples were collected from the stratigraphic section at Cerro La Silla (see Fig. 2.2 and Fig. 2.4). In the laboratory all samples were trimmed of weathered surfaces and veins and a subset of 275 hand samples were selected to minimise modern-day weathering and slabbed. Petrographic thin sections were cut from 32 samples. Cathodoluminescence (CL) screening of thin sections for Mn concentrations (as an indicator of diagenetic alteration) was carried out at Trinity College Dublin (TCD) on a Reliotron cold cathode stage, mounted on a Nikon binocular microscope (Hemming *et al.*, 1989). Material for elemental and isotopic analyses was obtained by drilling c. 100 mg of carbonate powder from each slab with a dental drill, targeting well-preserved micritic textures in the slabs.

Mass Spectrometer Analysis

A total of 224 samples were analysed for $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ and a subset of 109 carbonate samples were analysed by solution quadrupole ICP-MS at TCD for 52 major and trace elements, following the digestion methods of Hahn *et al.* (2015). The ICP-MS analyses followed the experimental design of Eggins *et al.* (1997), with modifications described in Kamber (2009) and Babechuk *et al.* (2010) (Chapter 2). Several samples were also selected for *in situ* trace element analysis by LA-ICP-MS (spot ablations) at TCD for a total of 24 masses as also described in Chapter 2. REE+Y data were normalized to the upper continental crust composite MuQ (Mud from Queensland, Australia, (Kamber *et al.*, 2005)). MUQ is a modern alluvial sediment composite analysed using a similar experimental protocol to the solution data produced in this study.

LA-ICP-MS Mapping

A total of 16 individual element maps and two element ratio maps were created from two separate LA-ICP-MS mapping experiments for each of the thin sections 41.2, 113.2, 268.6R and 268.6L. Eight isotopes and nine isotopes were mapped respectively in each experiment with ^{43}Ca employed as an internal elemental standard in each experiment. The following sixteen isotopes were measured: ^{24}Mg , ^{34}S , ^{43}Ca , ^{51}V , ^{55}Mn , ^{57}Fe , ^{88}Sr , ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{165}Ho , ^{172}Yb , ^{232}Th , ^{238}U . The elemental maps were acquired using a Photon Machines Analyte Excite 193 nm ArF Excimer laser-ablation system with a Helex 2-volume ablation

cell coupled to an Agilent 7900 ICP-MS at the iCrag laboratory in the Department of Geology, Trinity College Dublin. The ICP-MS was tuned using NIST 612 standard glass to yield Th/U ratios of unity and low oxide production rates (ThO^+/Th^+ typically $< 0.15\%$). 0.5 l/min He carrier gas was fed into the cell body and 0.2 l/min He was fed into the cup. The aerosol was subsequently mixed with 0.56 l/min Ar make-up gas and a small volume of N_2 (c. 6 ml/min) to enhance signal sensitivity and reduce oxide formation were added to the aerosol in a c. 1.5 cm^3 mixing bulb.

A laser fluence of $3.5 \text{ J/cm}^2\text{s}$, a repetition rate of 38 Hz, a $47 \text{ }\mu\text{m}$ spot size and a scan speed of $30 \text{ }\mu\text{m/s}$ was employed. The LA-ICP-MS trace element image mapping procedure is similar to that adopted by Ubide *et al.* (2015) and Chew *et al.* (2016) and is outlined briefly below. Image maps were made by “rastering” the sample under the ablation site. To produce the full map, adjacent lines (or “rasters”) were ablated in a successive manner. The final ablated area was rectangle-shaped to facilitate production of trace element maps using the “Image from Integrations” module in Iolite. Although the system has a fast washout (90% signal reduction in less than 0.25s), 10 seconds were allowed for washout between lines to avoid any carry-over from standards to samples and vice versa. NIST612 glass reference material was used as the calibration standard and ablated with the same parameters as the samples. Data reduction and production of trace element distribution maps was undertaken with the Iolite software (Paton *et al.*, 2011) using the “Trace Elements” data reduction scheme in “Semi-Quantitative” mode (which in Iolite corresponds to not employing an internal standard isotope). Following data reduction, trace element distribution maps were built with the Iolite module “Images from Integrations”. Semi-quantitative major and trace element data were measured using the Monocle data extraction add-in tool for Iolite (Petrus *et al.*, 2017) and subsequently normalised to a Ca content of 400,400 ppm. To avoid sampling bias, regions of interest (ROI) were defined based on petrographic rather than geochemical criteria, targeting petrographically identifiable component classes, including fossils, peloidal micrite and cements. ROI were outlined using the drawing tool in Monocle at a scale of c. $625 \text{ }\mu\text{m}^2$ and not less than 40 pixels in order to increase measurement precision, which is a function of pixel counting statistics (Petrus *et al.*, 2017).

3.3 Geological Setting

The study area is described in detail in Chapter 2.2 with map at Fig. 2.2.

3.4 Results

The measured stratigraphic section is described in Chapter 2.4.1 (Fig. 2.4 and Appendix 2.1).

3.4.1 Mapped Thin Sections

A representative sample was chosen for LA-ICP-MS mapping from each of the four depositional facies described above (intertidal and subtidal above fairweather wave base (sample 41.2 m); distal ramp facies below fair-weather wave base (113.2 m); outer ramp (241.6 m); reef and proximal facies (268.6R) (Fig. 3.2)). The stratigraphically lowermost representative thin section was prepared from the hand sample at 41.2 m (Fig. 3.2a), located at c. 6m above the base of the San Juan Formation (Fig. 2.4) and taken from the intertidal to subtidal facies. The thin section is composed of allomicritic syn-depositional infill (M), with extensive cement precipitation including phreatic cement and components neomorphosed to pseudospar (Ps). An initial isopachous phreatic cement occurs as a thin rim on clasts and fills the tight pore space between clasts (C1). There is a later extensive occluding equant and drusy calcite cement phase (C2) (Fig. 3.2a). The pseudospar exhibits relict textures of infill of gastropod shells (Gs) and cement has replaced the originally aragonite gastropod shells so that relict shell morphology is visible (Gs) (Fig 3.2a).

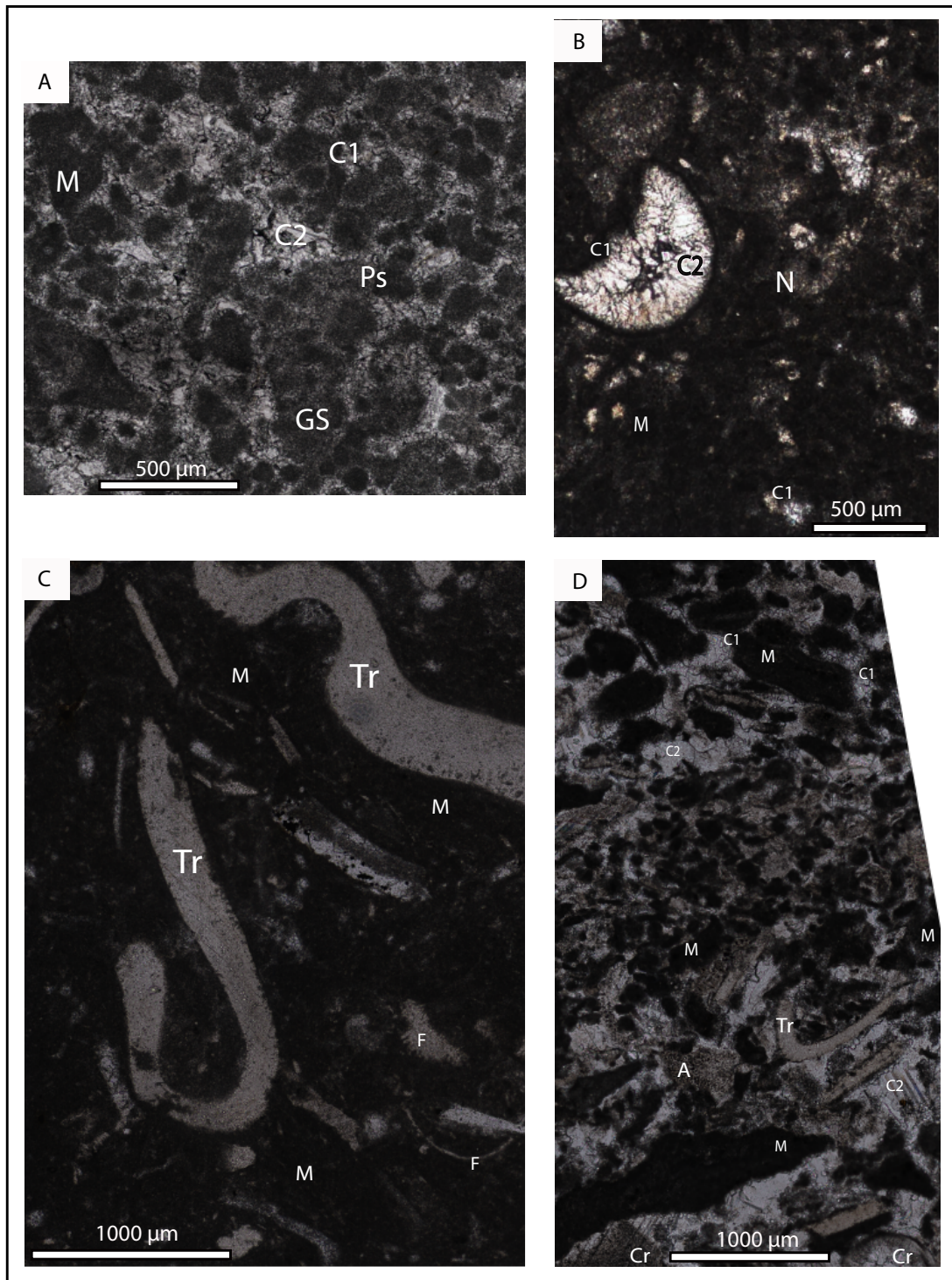
The portion of the second thin section (113.2 m; Fig. 3.2b) that was mapped is composed of texturally well-preserved Nuia fauna, allomicrite and microspar. The source lithofacies is the distal inner ramp with microfacies within thin sections including bioturbated, bioclastic wackestone with clotted microbial textures and numerous bioclasts. These include marine fauna such as brachiopods, trilobites, crinoids, nuia, gastropods and sponge spicules. The mapped area has a more extensive allomicrite component than sample 41.2 and less extensive cement phases (Fig. 3.2b). The C1 cement phase is absent on well-preserved clasts located within allomicrite. The mapped portion has four distinct components: allomicrite (M); nuia (N); isopachous microspar (C1) cement; and a later occluding (C2) cement (Fig. 3.2b).

The third sample was taken from a bioclastic packstone at 241.6 m (Fig. 3.2c), within the outer-ramp facies deposited below storm wave base. The area mapped by LA-ICP-MS is composed of trilobite (Tr) and other fossil fragments (F) in allomicrite (M) (Fig. 3.2c). The thin section also exhibits a diverse range of bioclasts, bioturbation and stylolites. Clasts are supported in a micrite matrix. Fossils include typical marine fauna such as brachiopods,

trilobites, crinoids, naia, sponge spicules and gastropods and are relatively intact and well preserved compared to samples above fair-weather wave base, consistent with a lack of wave reworking of the sediment below storm wave base. There are no visible phreatic cements although an occluding isopachous spar cement occurs locally.

The fourth thin sections studied, 268.6R (Fig. 3.2d) was taken from the bed at 268.6 m in the reef and proximal inner ramp facies. It consists of a peloidal bioclastic wackestone and includes algal (A), crinoid (Cr), trilobite (Tr) and other fragmented bioclasts, allomicritic peloids (M) and intraclasts and extensive cement phases. There are two visible cement phases: an isopachous phase on the rim of allochems (C1), and a later extensive, occluding spar (C2). Preservation is variable in the samples, with some trilobite and microbial fossil fragments exhibiting strong textural preservation. The mapped segment of the thin section includes a number of these carbonate components, including intraclasts, allomicrite, cement phases, trilobites and microbial clasts (Fig. 3.2d).

Fig. 3.2: Mapped microfacies in thin section at Cerro La Silla: (8a) Sample 41.2, a peloidal packstone composed of peloids including allomicritic syn-depositional infill (*M*), partially neomorphosed to pseudospar (*Ps*), with an initial isopachous phreatic cement occurring as a thin rim on peloids and filling the narrow pore space between clasts (*C1*) and a later extensive occluding equant and drusy calcite cement phase (*C2*). *C1* and *C2* cements occur including within the originally aragonite gastropod (*Gs*) shells and relict shell morphology is visible with allomicritic infill. The sample is from the intertidal and subtidal facies above fair weather wave base. (8b) Sample 113.2, a bioclastic packstone composed of texturally well-preserved *Nuia* fauna, allomicrite (*M*), isopachous microspar (*C1*) and a later occluding cement (*C2*). Sample from below fairweather wave base and above storm wave base. (8c) Sample 241.6 m, a bioclastic packstone composed of trilobite (*Tr*) and other fossil fragments (*F*) in an allomicrite matrix (*M*). Sample from outer-ramp facies deposited below storm wave base. (8d) Sample 268.6R, Peloidal bioclastic wackestone with algal (*A*), crinoid (*Cr*), trilobite (*Tr*) and other fragmented bioclasts. Other components include allomicritic peloids (*M*), an isopachous phreatic cement phase on the rim of allochems (*C1*) and a later extensive, occluding spar (*C2*). Sample from proximal inner ramp facies.



3.4.2 Geochemistry

Geochemical results are presented in Table 3-1 (Monocle elemental concentration measurements for samples 41.2, 113.2, 241.6 and 268.6R) and Tables 3-2 to 3-5 (calculated elemental covariation data and ratios from Monocle for samples 41.2, 113.2, 241.6 and 268.6R). Table 2-1 of Chapter 2 presents the carbon and oxygen isotope ratios and solution ICP-MS elemental values.

3.4.3 Micron-scale analysis

The LA-ICP-MS maps created for each sample illustrate that variability in elemental concentrations, including REE, occurs both between carbonate components and within components at a micron scale (maps discussed in this chapter are presented in Figs 3.3-3.6 in section 4 for samples 41.2, 113.2, 241.6 and 268.6R respectively).

As carbonates typically exhibit low concentrations of REE+Y and a quadrupole ICP-MS employs sequential detection of isotopes, the REE+Y analyte list was limited to Pr, La, Ce, Nd, Y and Ho. This suite of elements nevertheless permits calculation of the following REE+Y proxies (after Lawrence *et al.*, 2006a):

$$\text{Shale-Normalized Slope} = (\text{Pr}_n/\text{Yb}_n)$$

$$\text{Y/Ho ratio} = \text{Y}/\text{Ho}$$

$$\text{Ce anomaly} = \text{Ce}_n/(\text{Pr}_n * (\text{Pr}_n/\text{Nd}_n))$$

$$\text{La anomaly} = \text{La}_n/(\text{Pr}_n * (\text{Pr}_n/\text{Nd}_n)^2)$$

As Y has the highest abundance of the measured REE + Y it is used to approximate the relative abundance of the REE + Y between the carbonate components in the four samples mapped.

Mean calculated measurements by component in all four thin sections mapped are presented in Table 3-1. The values discussed in the text are mean Monocle values unless otherwise specified, the number of measurements are specified in the text (i.e. n =) and in the title row of Table 3-1.

In sample 41.2 the shale-normalized slope (Pr_n/Yb_n) is LREE-enriched to flat in all components. The allomicrite, C1 cement and C2 cement, have mean values of $\text{Pr}_n/\text{Yb}_n = 1.29$

(SD = 0.30, n = 12), 1.30 (SD = 0.41, n = 13) and 1.57 (SD = 0.85, n = 11) respectively (Table 3-1). The Y/Ho ratios (Fig. 3.3c) of these same components are 38 (SD = 12, n = 12), 34.5 (SD = 9.7, n = 13) and 37.7 (SD = 13, n = 11) and are lower (albeit with a large deviation), than the Y/Ho values > 40 that usually occur in marine carbonates from the open ocean (Nothdurft *et al.*, 2004, Webb *et al.*, 2009, Webb and Kamber, 2000). The concentration of Y (as a proxy for the REE + Y concentration) is 0.166 ppm in allomicrite (SD = 0.104 ppm, n = 12), 0.184 ppm in the C1 cement (SD = 0.042 ppm, n = 13) and 0.20 ppm in the C2 cement (SD = 0.14 ppm).

In sample 113.2 (Fig. 3.4), Y exhibits much higher concentrations than in sample 41.2. Highest concentrations occur in allomicrite (2.98 ppm, SD = 0.49 ppm, n = 21), with lower concentrations in the phreatic C1 cement (2.55 ppm, SD = 0.61 ppm, n = 10) and occluding C2 cement (1.80 ppm, SD 0.61, n = 3). Thorium (Fig 3.4b), as a proxy for the siliciclastic content in allomicrite, has a concentration of 0.50 ppm (SD 0.11, n = 21), decreasing to 0.32 ppm (SD = 0.08, n = 10) in the C1 cement and 0.15 ppm (SD = 0.11, n = 3) in the C2 cement. The shale-normalized REE slope (Fig. 3-4e) and Y/Ho ratio (Fig. 3.4c) are similar in the allomicrite phase to those in sample 113.2 and to sample 41.2, with $Pr_n/Yb_n = 1.33$ (SD = 0.10, n = 21) and Y/Ho = 33.66 (SD = 0.65, n = 21) (Table 3-1). However, Y/Ho ratios have a wider range (15-55) and mean Sr concentration (Fig. 3-4f), which is discussed in depth below as a proxy for diagenetic alteration, is 325 ppm (SD = 17 ppm, n = 21), a 1.5 fold increase on sample 41.2, while the Mn (Fig. 3.4f) concentration is 120 ppm (SD = 39 ppm, n = 21), with a Mn/Sr ratio < 1.

The third mapped thin section at 241.6 m, has an allomicrite phase with the highest measured Y concentration at 6.76 ppm (SD = 0.49 ppm, n = 6, see Monocle measurements in Table 3-1) and the highest Th concentrations (Fig. 3.5b) in allomicrite of 1.04 ppm (SD = 0.14 ppm, n = 6). As Th occurs in very low concentrations in carbonates, this supports siliciclastic contamination contributing to the REE – discussed in detail in relation to potential contamination and diagenesis effects below. In figure 3.5b Th can be seen to be heterogenous and located in the allomicrite phase. The shale-normalised REE slope (Pr_n/Yb_n) (Fig. 3.5e) has a lower mean value than samples 41.2 and 113.2 at 0.877 (SD = 0.083), whilst the Pr_n/Yb_n ratio in fossil components is 0.742 (SD = 0.068, n = 12). The fossil components also record a higher Sr (Fig. 3.5f) and lower Mn (Fig. 3.5h) concentration than the adjacent allomicrite; Sr mean concentrations in allomicrite are 326 ppm (SD = 13 ppm, n = 6), and in fossil cements are 403 ppm (SD = 64 ppm, n = 13) while Mn concentrations are 350 ppm (SD = 20 ppm, n = 6) in allomicrite and 287 ppm (SD = 33 ppm, n = 12) in the fossil cement (Table

3-1). The Ce anomaly in both components is flat (Table 3-1), whilst the Y/Ho ratio is < 40 , with a mean Y/Ho ratio of 34.30 (SD= 1.03, $n = 6$) (Fig. 3.5c) in the allomicrite and increasing in the C1 phase to Y/Ho = 36.94 (SD = 2.09). However, figure 3.5c indicates that the Y/Ho range in the sample may be wider and includes values up to 50. There is a large decrease in Fe (Fig. 3.4g) between the allomicrite (2061 ppm, SD = 194 ppm, $n = 6$) and the cement phases (666 ppm, SD = 301 ppm, $n = 12$).

Sample 268.6 contains allomicrite, a phreatic C1 cement, a C2 occluding cement and a number of fossil fragments. The REE + Y patterns from sample 268.6 in allomicrite have a shallow Pr_n/Yb_n (Fig. 3.6e) slope of 0.737 (SD = 0.069, $n = 6$), with similar values in the other components (Table 3-1). The Y/Ho (Fig. 3.6c) ratios in the sample are close to marine values, reaching a Y/Ho ratio of 37.38 (SD = 2.03, $n = 6$) in the allomicrite (the full range in the LA-ICP-MS map is 25-55). Ce anomaly values are flat to very slightly positive (1.12, SD = 0.10, $n = 6$) in fossil components to 1.082 (SD = 0.027, $n = 7$) in allomicrite. Y concentrations are highest in the allomicrite and fossils (4.95 ppm, SD 0.55 ppm, $n = 7$ and SD = 4.66 ppm, SD = 0.28 ppm, $n = 6$ respectively). The Sr concentrations (Fig. 3.6f) is 312 ppm (SD = 24 ppm, $n = 7$) in allomicrite and the Mn concentration (Fig. 3.6h) is 162.3 ppm (SD = 3.5 ppm, $n = 7$). Mn/Sr ratios are < 1 .

The covariation of measured elements within the allomicrite phase in each sample is presented in Tables 3-2 to 3-5, and further considered in the Discussion section.

Table 3-1: Mean carbonate component element concentrations with standard deviations measured using Monocle (Petrus *et al.*, 2017) and calculated REE + Y proxy values (Lawrence *et al.*, 2006a) from samples 41.2, 113.2, 241.6 and 268.6R.

Component	41.2 Allonite (n=12)	41.2 C1 Cement (n=13)	41.2 C2 Cement (n=11)	113.2 Allonite (n=21)	113.2 C1 Cement (n=10)	113.2 C2 Cement (n=3)	241.6 Allonite (n=6)	241.6 C1 Cement (n=12)	268.6R Allonite (n=7)	268.6 C1 Cement (n=4)	268.6 C2 Cement (n=4)	268.6 Fossil Cement (n=6)
Pr+Nd	1.293	1.30	1.57	1.327	1.27	1.494	0.877	0.742	0.737	0.8543	0.83	0.760
SD	0.304	0.41	0.85	0.101	0.17	0.097	0.083	0.068	0.069	0.303	0.14	0.071
Ho+Yb	1.20	1.46	1.5	1.212	1.26	1.43	1.139	1.171	1.19	1.134	1.13	1.151
SD	0.29	0.59	1.1	0.094	0.13	0.11	0.048	0.068	0.08	0.059	0.302	0.049
Y	0.166	0.184	0.20	2.98	2.55	1.798	6.76	5.8	4.95	3.8	3.89	4.66
SD	0.104	0.042	0.14	0.49	0.61	0.609	0.49	1.5	0.55	1.2	0.79	0.28
Y/Ho	38	34.5	37.699	33.66	33.50	36.31	34.30	36.94	37.38	34.3	36.09	36.07
SD	12	9.7	13.089	0.65	3.03	5.33	1.03	2.09	2.03	1.3	2.04	2.04
La anom.	1.52	1.47	1.37	1.281	1.3436	1.332	1.523	1.73	1.63	1.79	1.77	1.765
SD	0.33	0.44	0.35	0.083	0.0801	0.049	0.094	0.14	0.13	0.38	0.13	0.108
Ce anom.	1.23	1.19	1.15	1.08	1.053	1.052	0.988	1.007	1.082	1.115	1.116	1.1101
SD	0.17	0.22	0.15	0.13	0.033	0.034	0.011	0.031	0.027	0.099	0.037	0.0308
Th (ppm)	0.048	0.020	0.012	0.50	0.312	0.15	1.04	0.32	0.39	0.098	0.248	0.026
SD	0.015	0.014	0.012	0.11	0.078	0.11	0.14	0.27	0.11	0.061	0.028	0.13
U (ppm)	0.451	0.317	0.48	1.51	1.33	1.160	1.162	0.51	0.745	0.65	1.12	1.11
SD	0.051	0.075	0.19	0.13	0.35	0.076	0.107	0.33	0.079	0.29	0.04	0.03
Mn (ppm)	12.0	10.1	9.6	88.4	83.0	74.6	350.30	287	162.3	161	184	156.0
SD	1.2	1.1	1.1	3.8	6.4	8.4	20.06	33	3.5	27	19	10.7
Fe (ppm)	157	139	129	865	601	593	2061	666	1025	465	733	686
SD	31	31	19	179	148	76	194	301	58	85	92	250
Sr (ppm)	203	152	120	325	344	385	326	403	312	318	248	327
SD	23	16	39	17	42	50	13	64	24	112	79	32
Mn/Sr	0.060	0.0669	0.090	0.273	0.247	0.195	1.0786	0.74	81.2	80	91.8	78.0
SD	0.012	0.0088	0.034	0.015	0.051	0.034	0.1004	0.22	1.8	13	9.6	5.4

3.5 Discussion

The LA-ICP-MS Monocle measurements (Table 3-1) are broadly consistent with those of previous solution and spot LA-ICP-MS results from Cerro La Silla (Chapter 2, Table 2-1). Shale-normalized REE + Y data from the LA-ICP-MS maps, LA-ICP-MS spot ablation data and solution-ICP-MS experiments display flat slopes with subdued anomalies that are not consistent with primary marine REE + Y signatures. Instead they are typical of carbonates formed in variable seawater-freshwater mixing conditions or those impacted by siliciclastic contamination (Chapter 2). Crinoid fossils are identifiable in thin sections (Fig. 3.2d) and extant and extinct crinoid species are considered almost exclusively stenohaline (Binyon, 1972). Hence, the distribution and covariance of the mapped elements determined in Monocle is further assessed for clear evidence of contamination, porewater processes or later diagenesis that are not discernible in the solution-ICP-MS or spot ablation data, before considering the implications for the interpretation of water-column chemistry.

Petrographically, samples 41.2, and 268.6R (Fig. 3.2a and 3.2d), both deposited above fair weather wave base, and sample 113.2 from the distal inner-ramp facies (Fig. 3.2b) and deposited below fair weather wave base but above storm wave base, all exhibit an allomicrite phase (M), an isopachous rim of phreatic cement (C1) and a later occluding spar (C2), but do not show textural evidence of contamination. In sample 41.2 the allomicrite phase has been partially neomorphosed to pseudospar (Ps). Sample 241.6 was deposited below storm wave base on the outer ramp. It contains only one cement phase (C1) and allomicrite (M) (Fig 3.2c). All samples contain fossil fragments in varying states of preservation, although these are only identifiable as gastropods textures in sample 41.2 due to extensive aragonite recrystallisation (Fig. 3.2a).

Contamination from fine-grained siliciclastic material, phosphates and/or ferromanganese oxyhydroxides is a concern for the interpretation of many trace element data from carbonates. For the REE+Y, the situation is exacerbated because shale (Webb and Kamber, 2000; Nothdurft *et al.*, 2004; Tostevin *et al.*, 2016), phosphates (German and Elderfield, 1990; Reynard *et al.*, 1999) and ferro-manganese oxyhydroxides all have relatively much higher REE+Y concentrations than marine carbonate (Bau and Dulski, 1996), leaving carbonate vulnerable to even small degrees (c. 2% by mass) of contamination (Nothdurft *et al.*, 2004).

Thorium is a useful monitor of siliciclastic contamination, as it typically has very low concentrations in uncontaminated carbonates. Thorium concentrations vary between samples and are highest in each sample in the allomicrite phase. The allomicrite phase Th content (Table 3-1 and Fig. 3.3b) ranges from 0.048 ppm (SD = 0.015 ppm, n = 12) for the pseudospar after allomicrite in sample 41.2, increasing in sample 113.2 (Fig. 3.4b) to 0.50 ppm (SD = 0.11, n = 21) and in sample 268.6R to 0.39 ppm (SD = 0.11 ppm, n = 7) (Fig. 3.6b). It is highest in sample 241.6 (1.04 ppm, SD = 0.14 ppm, n = 7) (Fig 3.5.b). In Chapter 2, an upper concentration threshold for Al of 4,200 ppm (Veizer, 1983) was used to discriminate carbonates with low concentrations of siliciclastic contamination in the presented solution ICP-MS dataset (Table 2-3). Based on the MUQ shale composite this is equivalent to a concentration of 0.52 ppm Th, so that samples 41.2 and 268.6 are considered relatively clean, sample 113.2 is marginally above this concentration threshold and sample 241.6 has an appreciable shale component. This increase in shale contamination in basinward facies is consistent with basinal siliciclastic input to the platform in all but the shallowest locations.

Of the samples studied, sample 41.2 (Fig. 3.3b), in the intertidal to subtidal facies, has the lowest Th concentrations in all three constituent components. It is low in the pseudosparitic allomicrite at 0.048 ppm (SD = 0.015 ppm, n = 12) decreasing to very low concentrations in the cement phases (Table 3-1 and Fig. 3.3), implying minimal detrital material within the sample. The LA-ICP-MS map for sample 41.2 (Fig. 3.3) also illustrates that the allomicrite is internally heterogenous, and that the mapped concentrations of Th in the C1 and C2 cements are very low and difficult to distinguish. However, despite the very low concentrations of siliciclastic input, there is a moderate covariation of Th and Fe in the pseudosparitic allomicrite ($r^2 = 0.59$, n = 12, p-value < 0.01), that suggests that a component of the Fe present is detrital. In any case the REE + Y profile is not discernably impacted by the low levels of siliciclastic contaminant in the sample, as Th shows minimal correlation with REE concentrations (Y v Th, $r^2 = 0.10$, n = 12, p-value 0.32) or with the Y/Ho or shale-normalized REE slope as shown in Table 3-2.

Petrographic and geochemical information was used to assess evidence for alteration of the primary geochemistry, including thin section petrography and application of elemental thresholds that permit the identification of carbonate samples that have undergone levels of fluid-rock interaction sufficient to alter $\delta^{13}\text{C}_{\text{carb}}$ values (Veizer, 1983). Trace elements, including the REE + Y, alter at higher fluid-rock ratios than $\delta^{13}\text{C}_{\text{carb}}$ (although relative concentrations of the elements in the sediment and fluid must be considered) (Brand and

Veizer, 1980; Brand and Veizer, 1981; Banner and Hanson, 1990). Sr is abundant in seawater and marine carbonates and lost with progressive recrystallization. Mn is typically preferentially incorporated or retained during fluid-rock interaction in reducing conditions (Brand and Veizer, 1980). Where fluid-rock interaction is sufficient to alter $\delta^{13}\text{C}_{\text{carb}}$, Mn and Sr are expected to show a negative correlation with Mn/Sr ratios > 1 (Brand and Veizer, 1981). Samples that fall below the thresholds for $\delta^{13}\text{C}_{\text{carb}}$ alteration are therefore described as well-preserved in this study.

Mn concentrations are very low in all components in sample 41.2 (Fig. 3.3h), at 12.0 ppm (SD = 1.2 ppm, $n = 12$) in the allomicrite, 10.1 ppm (SD = 1.1, $n = 13$) in the C1 cement phase and 9.6 ppm (SD = 1.1 ppm, $n = 11$) in the C2 cement. Mn/Sr ratios remain $\ll 1$, far below the published thresholds for well-preserved low Mg calcite (< 300 ppm, Denison *et al.*, 1994) or < 100 ppm (van Geldern *et al.*, 2006) and hence are *prima facie* consistent with strong preservation.

Whilst Sr concentrations may vary between environments in the modern ocean (as discussed in Chapter 2.5.2) (de Villiers, 1999), they also vary at a micron scale within sample at 41.2m. Very low Sr concentrations of 203 ppm (SD = 23 ppm, $n = 12$) in the allomicrite phase decreases sequentially to 152 ppm (SD = 16 ppm, $n = 13$) in the C1 cement and 120 ppm (SD = 39 ppm, $n = 11$) in the C2 cement, suggesting that porewater Sr concentrations decreased progressively, reducing Sr concentrations to well below the concentration expected in well preserved marine low Mg calcite (Sr > 500 ppm, (van Geldern *et al.*, 2006) and Sr > 900 ppm (Denison *et al.*, 1994)). This is consistent with precipitation of cements in brackish mixed porewater conditions or greater secondary recrystallization occurred in the interclastic phreatic cement phases. All components in sample 41.2 exhibit anomalously low Mn concentrations and the samples are also non-luminescent under optical CL (Brand and Veizer, 1980; Veizer, 1983; Hemming *et al.* 1989; Banner and Hanson, 1990; Banner, 1995b) consistent with a lack of Mn in the sediment. Moving up-section, the optical CL response remains non to dully-luminescent with rare brighter veins and fossils (Banner and Hanson, 1990; Knoll *et al.*, 1995; Savard *et al.*, 1995). The combined anomalously low concentrations of Mn with low Sr, indicate that the phreatic cements present precipitated in oxic porewater conditions (Brand and Veizer, 1980).

Greater REE + Y concentrations in the allomicrite in sample 41.2 (Fig. 3.3) correlate with greater Fe (Y v Fe $r^2 = 0.63$, $n = 12$, p-value < 0.01) and Mn ($r^2 = 0.42$, $n = 12$, p-value $<$

0.01) and lower Sr ($r^2 = -0.46$, $n = 12$) (where “-” denotes a negative correlation). There is a weak negative correlation of Sr with Fe ($r^2 = -0.31$, $n = 12$) and Mn ($r^2 = -0.35$, $n = 12$). This is consistent with fine grained siliciclastic present within the allomicrite contributing to the minimal levels of Fe, Mn and REE present and with the minimal, heterogenous distribution of Fe in the allomicrite phases. The very low concentrations of Mn in the sample and the presence of cross bedding at outcrop are consistent with intermittently reworked, oxic conditions during formation of phreatic cement. Post-depositional incorporation of Fe, Mn or REE released from oxy-hydroxides is therefore expected to be minimal due to the probable repetitive cycling between oxic and reducing porewater conditions during cement precipitation (Haley *et al.*, 2004; Hood *et al.*, 1989, Caetano-Filho *et al.*, 2018). As allomicrite preserves the highest Sr concentrations of the various components it remains the most likely phase to preserve primary marine values in sample 41.2.

Overall in the sample there appears to have been either extensive elemental (including REE) loss, or a lack of available REE+Y to incorporate into phreatic cements during cement formation under predominantly oxic conditions and isolated from siliciclastic input. Sr in allomicrite shows no correlation with either Pr_n/Yb_n ($r^2 = -0.02$, $n = 12$), Y/Ho ($r^2 = 0.08$, $n = 12$) or with the La and Ce anomalies (Table 3-2). There is no clearly identifiable post-lithification alteration of the REE+Y pattern of a magnitude likely to alter initial REE+Y profiles in the phreatic cements.

Table 3-2: Covariation of REE + Y seawater proxies with selected trace elemental data (ppm) within the allomicrite phase of sample 41.2. All data are Monocle measurements, n = 12.

	Pr _n /Yb _n	Ho _n /Yb _n	Y	Y/H _o	La/La*	Ce/Ce*	Th ppm	U ppm	Mn	Fe	Sr	Mn/Sr
Pr _n /Yb _n	-	0.52	0.04	-0.18	-0.21	-0.37	-0.05	<0.01	<0.01	-0.01	-0.02	<0.01
Ho _n /Yb _n	-	-	0.02	-0.76	-0.02	-0.06	-0.07	0.07	0.03	<0.01	<0.01	0.03
Y	-	-	-	-0.10	0.07	<0.01	0.10	0.15	0.42	0.63	-0.46	0.19
Y/Ho	-	-	-	-	-0.03	<0.01	0.01	-0.19	-0.23	-0.15	0.08	-0.23
La/La*	-	-	-	-	-	0.89	0.14	<0.01	-0.05	0.05	0.04	0.05
Ce/Ce*	-	-	-	-	-	-	0.15	<0.01	<0.01	0.02	<0.01	<0.01
Th	-	-	-	-	-	-	-	0.19	<0.01	0.59	0.06	<0.01
U	-	-	-	-	-	-	-	-	-	0.46	0.02	0.15
Mn	-	-	-	-	-	-	-	-	-	0.53	-0.35	1
Fe	-	-	-	-	-	-	-	-	-	-	-0.31	0.53
Sr	-	-	-	-	-	-	-	-	-	-	-	0.31
Mn/Sr	-	-	-	-	-	-	-	-	-	-	-	<0.01

Sample 113.2, was deposited below fair weather wave base in the distal inner ramp facies and exhibits a weak expression of the shale-normalized REE + Y slope and the Y/Ho ratio in all components measured with Monocle (Table 3-1, Fig. 3.4c and 3.4e). The REE + Y slope in allomicrite is flat to slightly LREE enriched (mean Pr_n/Yb_n = 1.327, SD = 0.101, n = 10). Th as a proxy for siliciclastic contamination in allomicrite in sample 113.2 exhibits concentrations marginally below the upper threshold for clean carbonate rocks of 0.52 ppm (allomicrite mean Th = 0.50 ppm, SD = 0.11 ppm, n = 10). However, the Th map indicates that due to very fine-scale heterogeneity the range may in fact be higher (Fig. 3.4b). The impact of shale contamination is discernable in the negative correlation of Th with the shale normalized REE + Y slope (Th v Pr_n/Yb_n = -0.36), the positive correlation of the slope in the heavy rare earth elements with Th (Th v Ho_n/Yb_n r² = 0.78) and the negative correlation of the La anomaly with Th (r² = -0.37).

To compensate for the impact of contamination and seek to identify primary values a correction was made whereby the REE + Y contribution from the siliciclastic component was removed. This was achieved by using the Th abundance in the sample, and assuming an elemental/Th ratio identical to that of MUQ as follows:

$$\text{Element}_{\text{sample}} - ((\text{Th}_{\text{sample}}/\text{Th}_{\text{MUQ}}) * \text{Element}_{\text{MUQ}})$$

There is a discernable correction toward more sea water like values in the resulting Y/Ho ratio, which increases from 33.66 to 45.55, consistent with the marine conditions suggested by the marine fauna present (Table 3-6). However, correction with MUQ does not increase the shale normalized slope, which may be related to the composition of the marine shale inputs deviating from that of the MUQ composite (Table 3-6).

Within the allomicrite, increased Fe concentrations coincide with greater concentrations of redox sensitive U (Fe v U, $r^2 = 0.46$, $n = 10$) and more positive Ce anomalies (Fe v Ce anomaly, $r^2 = 0.55$, $n = 10$) (Fig. 3.3). However, Fe does not correlate with Th, suggesting that the correlation might not be related to siliciclastic contamination. Fe, U and Ce are expected to be incorporated to cements forming in reducing conditions and the release of Ce from Fe and Mn oxyhydroxides in reducing porewaters is as a potential mechanism for reduced Ce anomalies and flat shale-normalized slopes in carbonate cements (Haley *et al.*, 2004).

There is evidence in the allomicrite phase in sample 113.2 that could be interpreted as a low magnitude of diagenetic alteration – Sr concentrations of 325 ppm (SD = 17 ppm, $n = 10$) (Fig. 3.3f) are below the concentrations suggested for unaltered carbonates of 500 ppm (van Geldern *et al.*, 2006). The allomicrite value agrees well with the solution ICP-MS concentration of 320 ppm (Table 2-1). C1 cement Sr concentrations of 344 ppm (SD = 42 ppm, $n = 10$) and C2 concentrations of 385 ppm (SD = 50 ppm, $n = 3$) indicate that the impact of brackish porewaters is no longer present in the samples. Sr concentrations may have increased progressively in marine phreatic cements due to greater concentrations of Sr in porewaters with recrystallisation of biogenic carbonates (Gieskes *et al.*, 1986).

Mn concentrations (allomicrite = 88.4 ppm, SD 3.8, $n = 10$) (Fig. 3.3h) are within the range of those expected in well preserved carbonates (< 300 ppm, Denison *et al.*, 1994) or (< 100 ppm, van Geldern *et al.*, 2006)). Sr concentration correlates negatively with the La anomaly suggesting that microcrystalline cement formed in low Sr porewaters may be present within the mapped allomicrite or that some Sr loss has occurred, whilst incorporating La ($r^2 = -0.37$, $n = 10$) (all correlation coefficients are otherwise < 0.12 with the exception of Mn/Sr) (Table 3-3). Negative correlation of U and REE + Y suggest that overall those REE + Y unaffected by redox conditions may have been lost in the early diagenetic process but that redox sensitive Ce has been incorporated to cements.

The REE+Y profile as incorporated during primary cement formation is expected to be conserved in any subsequent recrystallisation in meteoric porewaters, consistent with previous studies that indicate that primary REE + Y features are conserved in Pleistocene corals even where complete recrystallisation from aragonite to calcite has occurred and despite large decreases in the concentration of Sr, Ba and U and increased Mn as predicted in meteoric diagenesis (Webb and Kamber, 2000).

Table 3-3: Covariation of REE + Y seawater proxies with selected trace elemental data (ppm) within the allomicrite phase of sample 113.2. All data are Monocle measurements, n = 10.

Element and proxy values	Ho _n /Yb _n	Y	Y/Ho	La/La*	Ce/Ce*	Th	U	Mn	Fe	Sr	Mn/Sr
Pr _n /Yb _n	0.49	-0.51	<0.001	<0.001	-0.16	-0.36	0.05	0.08	<0.01	0.02	<0.01
Ho _n /Yb _n	-	-0.12	-0.07	0.29	0.78	0.78	0.03	-0.08	-0.06	-0.12	-0.07
Y	-	-	<0.01	-0.02	<0.01	0.19	-0.39	-0.23	-0.12	<0.01	-0.02
Y/Ho	-	-	-	-0.07	<0.01	<0.01	-0.02	-0.07	<0.01	<0.01	-0.02
La/La*	-	-	-	-	0.23	-0.37	0.08	-0.06	0.23	-0.37	0.08
Ce/Ce*	-	-	-	-	-	-0.05	0.31	<0.01	0.55	-0.05	0.31
Th	-	-	-	-	-	-	-0.24	0.05	0.02	-0.24	0.05
U	-	-	-	-	-	-	-	<0.01	0.43	<0.01	<0.01
Mn	-	-	-	-	-	-	-	-	0.24	0.22	0.21
Fe	-	-	-	-	-	-	-	-	-	<0.01	0.10
Sr	-	-	-	-	-	-	-	-	-	-	-0.46
Mn/Sr	-	-	-	-	-	-	-	-	-	-	-

The third sample, 241.6 (Fig. 3.5) from below storm wave base on the distal ramp exhibits two dominant components: (i) fossils containing neomorphosed spar and (ii) an allomicrite matrix. REE concentrations based on Y concentrations, are relatively high in allomicrite at 6.76 ppm (SD = 0.49 ppm, n = 6). A strong correlation in Th v Y ($r^2 = 0.67$, n = 6; Table 3-4) supports the presence of siliciclastic contamination. A key result, that is not clearly shown in the solution ICP-MS data, is that the flattening of the shale-normalized REE slope (greater Pr_n/Yb_n) correlates with higher Th ($r^2 = 0.44$, n = 6). The recorded allomicrite Pr_n/Yb_n ratio also has a mean value closer to the steeper slope expected in marine conditions at 0.877 (SD = 0.083, n = 6), despite apparent suppression by siliciclastic contamination. The fossil spar has a corresponding value of 0.742 (SD = 0.068, n = 12). The Y/Ho map indicates that there may be locally higher values, approaching 50 in trilobite fossils. There is no Ce anomaly in either cement or the allomicrite, whilst the Y/Ho ratio in the allomicrite remains < 40 (Y/Ho = 34.30, SD = 1.03) and is higher in the C1 phase (Y/Ho = 36.94, SD = 2.09). There is a strong correlation between Fe and Th ($r^2 = 0.72$, n = 6; Table 3-4). The large decrease in Fe abundance (Table 3-1 and Fig. 3.5g) between the micrite (2061 ppm, SD = 194 ppm, n = 6)

and the cement phases (666 ppm, SD = 301, n = 12) is particularly prominent and also supports the REE being derived predominantly from siliciclastic material in the allomicrite.

Critically, this siliciclastic correction in allomicrite produces seawater-like shale-normalized REE slopes and Y/Ho ratios ($Pr_n/Yb_n = 0.74$ and $Y/Ho = 47.62$) (Table 3-6). The corrected Y/Ho value agrees well with the upper boundary of the mapped range for Y/Ho of 50, indicating that the REE+Y marine signature of this sample has been strongly suppressed by detrital contamination. These corrected values are consistent with a shallow oxic water column. It is notable that the correction, based on LA-ICP-MS mapping data, is of much greater magnitude than the equivalent correction in the solution-ICP-MS data.

Sr concentrations in the sample range from 326 ppm (SD = 13 ppm, n = 6) in allomicrite to 403 ppm (SD = 64 ppm, n = 12) in the cement phase within fossil fragments. This is consistent with a better preserved biogenic carbonate input and a lack of brackish porewater cements (Gieskes *et al.*, 1986). The nearest solution ICP-MS sample at 240.7 m has a Sr concentration of 281 ppm, which is lower than the LA ICP-MS map values and may be due to the much greater shale contribution by volume to the solution ICP-MS sample in the outer ramp facies, supported by the negative correlation of Th and Sr ($r^2 = -0.54$) in the allomicrite (Table 3-4).

Table 3-4 Covariation of REE + Y seawater proxies with selected trace elemental data (ppm) within the allomicrite phase of sample 241.6, all data are Monocle measurements, n = 10.

	Ho _n /Yb _n	Y	Y/Ho	La/La*	Ce/Ce*	Th	U	Mn	Fe	Sr	Mn/Sr
Pr _n /Yb _n	0.49	0.13	0.02	-0.18	-0.26	0.44	0.13	0.51	0.08	0.49	0.13
Ho _n /Yb _n	-	-0.25	-0.14	-0.21	0.01	-0.17	0.05	0.01	-0.25	-0.14	-0.21
Y	-	-	<0.01	0.05	-0.02	0.67	0.05	0.24	0.71	-0.13	0.21
Y/Ho	-	-	-		-0.01	-0.16	-0.04	0.64	0.31	-0.01	-0.16
La/La*	-	-	-	-	0.31	<0.01	<0.01	-0.01	<0.01	<0.01	0.31
Ce/Ce*	-	-	-	-	-	-0.29	0.04	-0.1	0.12	0.11	-0.29
Th	-	-	-	-	-	-	0.35	0.63	0.72	-0.54	0.63
U	-	-	-	-	-	-	-	0.81	0.23	-0.87	0.83
Mn	-	-	-	-	-	-	-	-	0.31	-0.88	0.99
Fe	-	-	-	-	-	-	-	-	-	-0.23	0.29
Sr	-	-	-	-	-	-	-	-	-	-	-0.94

Sample 268.6 (Fig. 3.6) is taken from a bioclastic packstone in the upper reef and proximal facies. It contains an allomicritic phase, a C1 isopachous phreatic cement, a C2 later occluding cement and fossil fragments with varying states of preservation. The REE + Y

patterns from the allomicrite phase have a shallow slope (Fig. 3.6e) at $\text{Pr}_n/\text{Yb}_n = 0.737$ (SD = 0.069, $n = 7$), with a similar slope measured in the fossil fragments (0.760, SD = 0.071, $n = 6$; Table 3-1). The Y/Ho ratios in the allomicrite are close to marine values at 37.3 (SD = 2.03, $n = 6$). The Ce anomaly is flat (Table 3-1).

The REE + Y data indicate that Y, as a proxy for REE concentration, is in greater abundance in areas of higher Sr ($Y \text{ v } Sr = 0.43$; Table 3-5 and Fig. 3.6f). This is consistent with REE loss during diagenesis. In addition, the effect of siliciclastic contamination is also discernable in a Th v Y plot ($r^2 = 0.51$, $n = 7$; Table 3-5). The strong negative correlation of U and Sr ($r^2 = -0.87$, $n = 7$) is also likely to be due to siliciclastic contamination based on the much greater U concentrations in shale compared to carbonate. The effect of siliciclastic contamination is illustrated by the siliciclastic-corrected marine Y/Ho ratio of 43, which falls within the upper values occurring in the Y/Ho map at Fig. 3.6c. Correction of the shale normalized slope in the sample is ineffective, though unnecessary given the shale normalized slopes < 1 are produced in the uncorrected data (Table 3-6).

Sr concentration evolution between components is consistent with relatively strong conservation of marine values compared to other samples above fairweather wave base. Sr concentrations in fossils and allomicrite are 327 (SD = 32 ppm, $n = 6$) and are at similar concentrations in allomicrite and the C1 initial phreatic cement. Subsequent Sr loss in diagenesis or the very high standard deviation due to the low volume of C2 cement present may explain the lower values in the later C2 cement of 248 ppm (SD = 79 ppm, $n = 4$). As this sample is above fairweather wave base it is more vulnerable to diagenetic alteration that may cause Sr loss. Whilst, the solution ICP-MS concentration in the nearest sample at 268.2 m diverges from the allomicrite LA ICP-MS data, there is a wide variability in Sr values in this segment of the stratigraphic section (see Table 2-1) and this may represent a divergence between samples due to their compositions.

Table 3-5 Covariation of REE + Y seawater proxies with selected trace elemental data (ppm) within the allomicrite phase of sample 268.6R, all data are Monocle measurements, n = 7.

	Ho _n /Yb _n	Y	Y/Ho	La/La*	Ce/Ce*	Th	U	Mn	Fe	Sr	Mn/Sr
Pr_n/Yb_n	<0.01	<0.02	0.20	-0.03	-0.26	-0.13	-0.16	0.01	<0.01	0.28	0.01
Ho_n/Yb_n	-	-0.07	0.58	0.25	0.25	-0.09	-0.04	-0.13	-0.04	0.34	-0.13
Y	-	-	-0.03	-0.16	-0.07	0.51	-0.08	-0.04	0.76	0.43	-0.04
Y/Ho	-	-	-	0.13	0.06	-0.04	-0.06	-0.17	-0.13	0.32	-0.17
La/La*	-	-	-	-	0.73	<0.01	-0.06	-0.55	-0.32	<0.01	-0.55
Ce/Ce*	-	-	-	-	-	0.05	<0.01	-0.59	-0.13	<0.01	-0.59
Th	-	-	-	-	-	-	0.05	-0.11	0.45	0.09	-0.11
U	-	-	-	-	-	-	-	0.13	<0.01	-0.87	0.83
Mn	-	-	-	-	-	-	-	-	0.02	-0.29	0.13
Fe	-	-	-	-	-	-	-	-	-	0.09	0.02
Sr	-	-	-	-	-	-	-	-	-	-	-0.3

Phosphate contamination (phosphates incorporate REE+Y disproportionately during diagenesis) is a further complicating factor. However there is no evidence for phosphate contamination in the solution ICP-MS data, and no evidence of a bell-shaped REE+Y profile that characterizes phosphate addition (Byrne *et al.*, 1996; Reynard *et al.*, 1999; Haley *et al.*, 2004; Lécuyer *et al.*, 2004; Baldwin *et al.*, 2011).

A review of the corrected allomicrite data, presented in Table 3-6, therefore indicates that whilst the magnitude of the uncorrected recorded proxy features is incompatible with REE+Y data from fully marine carbonates, this is partially attributable to siliciclastic contamination in samples 113.2, 241.6 and 268.6, which reduces the Y/Ho ratio. When a siliciclastic correction is applied to these three samples, the resulting Y/Ho ratios > 40 are consistent with shallow marine values expected in marine carbonates. Siliciclastic correction does not generate interpretable results for sample 41.2, although the lack of covariation in siliciclastic components and evidence of the minimal siliciclastic contamination at the base of the section indicates that correction for shale input is not appropriate.

LA-ICP-MS mapping indicates that sample 41.2 may have formed in more marginal, lower salinity waters or, based on the prominent low Mn, low Sr and low Th phreatic cement phases, have formed in brackish, regularly reworked and oxidising conditions with minimal siliciclastic input. Importantly the corrections for siliciclastic contamination using the LA-ICP-MS mapping data in samples 113.2, 241.6 and 268.6 all confirm that the samples formed in a marine, saline water-column in contradiction of the solution-ICP-MS based correction. Whilst the fluctuating trend with depth change is observed in both datasets, based

on the LA-ICP-MS mapping, the salinity in the San Juan Formation above 113m is likely to be very close to modern marine values. Studies of cherts (Du *et al.*, 2007) and dolomites (Zhang *et al.*, 2009) in Ordovician carbonate sequences have suggested that flatter, more LREE-enriched profiles may have been present in the global ocean during the Ordovician but such an interpretation is not supported by the corrected data from the outer ramp at Cerro La Silla, which produces marine values analogous to those in modern oceans. This is consistent with the hypothesis of Shields and Webb (2004) of unchanging REE + Y oceanic conditions through the Paleozoic. The persistent occurrence of the shallow shale- normalized REE slopes below 110 m may be due to combined lower salinity in shallow porewaters and potentially to greater influence of local inputs and brackish conditions on REE in periods of a very shallow water depth in a marginal, inter to subtidal setting, at the base of the section.

An important observation is that the LA-ICP-MS mapping provides a more accurate correction that reveals the true marine origin of three of the four samples. It is possible that this is due to either refractive behaviour of siliciclastic Th in the weak acid used to dissolve samples for solution analysis or to differences relative to the Ga abundance used to correct the solution values, which may require further consideration in future studies. Unintentional leaching of non-carbonate associated species from siliciclastic or other components has been previously cited as the cause of shallow REE slopes in carbonates (Tostevin *et al.*, 2016). Solution-based analysis using weak acid (in Chapter 2, a 5% HNO₃ dissolution was used) preferentially dissolves carbonate, leaving more resistant silicates and oxyhydroxides largely undigested. However, where leaching of siliciclastic material does occur it is likely to represent partial dissolution only and the resulting calculated elemental ratios may not be representative of the composition of the source shale. The effectiveness of siliciclastic correction to solution ICP-MS carbonate datasets requires further consideration in light of the probable under-correction for such contamination in the solution ICP-MS dataset produced in Chapter 2.

A key consideration when assessing results obtained from LA-ICP-MS and solution ICP-MS data is whether the chosen experimental technique is appropriate given their relative strengths and whether the technique has accurately sampled the targeted carbonate phase. Wet chemistry, which can lack in strong spatial discrimination, offers an alternative solution to LA-ICP-MS sampling of carbonate phases. However, particulate contaminants in the sampled carbonate may lead to unintentional leaching of elements.

Where it is possible to dissolve carbonate without unintentional leaching of non-carbonate phases such as siliciclastic phases, solution ICP-MS can effectively separate the carbonate components from siliciclastic components for analysis. Whilst spatial discrimination in sampling is greatly improved by micro-drilling powders for dissolution, micro-drilling is subject to the same limitation of laser sampling in terms of the potential to sample through the two-dimensional component into underlying different phases. Unintentional leaching of non-carbonate associated species from siliciclastic or other components has been previously cited as the cause of shallow REE slopes in carbonates, including in studies using weaker 2% HNO₃ dissolution (Tostevin *et al.*, 2016). These studies obtained best results (most seawater-like REE patterns) where a sequence of leaching steps were applied, including an initial discarded leach, interpreted as representing less refractive siliciclastics, a middle, most seawater like leach, and a final leach that exhibited evidence of more refractive siliciclastic contamination. LA-ICP-MS sampling accuracy depends on a number of factors including: the size of the sample area relative to the laser spot size; the dwell-time required to sample targeted elements and resulting ablation depth; and the depth of the targeted phase. In complex heterogeneous carbonates it remains possible that carbonate phases targeted from a two dimensional view may ablate adjoining or underlying carbonate, siliciclastic or other phases or minute contaminants. However, a key strength of LA-ICP-MS mapping, when compared to spot analysis, is its short dwell-time as the laser raster across the sample decreases the risk of ablation through thin carbonate phases. The resulting map may be combined with identification and measurement using Monocle to identify least contaminated components.

Relative to the other samples in the study, it is apparent from the petrographic evidence of phreatic cements abundance and their very low Mn and Sr concentrations that sample 41.2 may have undergone a greater degree of cement formation in shallow brackish, oxidising porewaters than the other investigated samples. Very low Fe content and low concentrations of siliciclastic associated elements suggest that the depositional environment was not receiving siliciclastic inputs. A lack of clay or Fe-Mn oxides in the watercolumn removes one of the principal pathways for the removal of REE from the watercolumn that creates the distinctive marine signature in modern seawater (Elderfield *et al.*, 1990). These results raise the issue of whether the samples at the base of the stratigraphic section are representative of porewater or global marine chemistry.

Whilst Sr concentration is known to vary locally in modern oceans with depth and laterally,

the magnitude and rapidity of the variation at Cerro La Silla is not consistent with a secular variation to a primary marine signature of an element with such a long residence times (de Villiers, 1999). In addition, whilst it is possible to interpret the Mo:U_{auth} data from the solution ICP-MS experiments (Chapter 2) as indicating dysoxic to euxinic porewater conditions, such conditions would be expected to incorporate greater Mn concentrations if present than the minimal Mn concentrations recorded (Haley *et al.*, 2004, Caetano-Filho *et al.*, 2018), and it may be the case that instead the Mo:U_{auth} ratio has been altered at the base of the section. As previously noted, in sample 41.2 there is a correlation of increased (but very low) REE concentrations with greater Mn and Fe and lower Sr. As the Mn, Fe and REE concentrations are very low sediment porewater conditions are likely to have been dominated by oxic conditions during cement formation and this correlation in allomicroite is not likely to represent anoxic inclusion of Mn or REE from reducing porewaters (Haley *et al.*, 2004, Caetano-Filho *et al.*, 2018).

The LA-ICP-MS map derived results are therefore consistent with solution data below 51 m, where the shale-normalised REE slope is flat ($> 1.19 \text{ Pr}_n/\text{Yb}_n$), with low Y/Ho ratios (< 31), that plot far from the modern seawater field on an Y/Ho v Pr_n/Yb_n crossplot (Fig. 2.8). The solution samples below 51m also display anomalously low Mn concentrations (< 10 ppm at the base of the section in the uppermost La Silla Formation, rising slowly to < 25 ppm in the lower reef of the San Juan Formation and correlating with low Sr concentrations (< 240 ppm). The probable influence of brackish porewater cement at the base of the section is supported by $\delta^{18}\text{O}_{\text{carb}}$ values that reach $< 8\text{‰}$ (SD = 0.65‰) and $\delta^{13}\text{C}_{\text{carb}}$ data that are more variable and reach minimum values of $< 2.5\text{‰}$ (SD = 0.50‰) (Fig. 2.4).

Where carbonate forms in more reducing conditions low Sr will co-occur with incorporation of available species reduced species in the porewaters including Mn^{2+} , Fe^{2+} and REE+Y released from organic material, Fe-Mn oxyhydroxides and colloids. Anoxic porewaters have been shown to contain middle rare earth element (MREE)-enriched patterns in marine burial, that may be due to reduction of Fe-oxides (of terrestrial provenance) in reducing porewaters (Haley *et al.*, 2004; Caetano-Filho *et al.*, 2018). It has been argued that this process would potentially release Ce into early marine burial suboxic pore fluids from oxide crusts on water column particles and would reduce the negative Ce anomaly to close to unity. In this regard the concentrations of a number of redox sensitive elements covary in the results for sample 113.2 deposited below fairweather wave base (Fe v U , $r^2 = 0.46$, $n = 10$, Fe v Ce anomaly, $r^2 = 0.55$, $n = 10$; Table 3-3) and it is possible that this may indicate incorporation of redox

sensitive elements in the reducing zone in the sediment redox column due to reductive release from organic matter or Fe-Mn oxyhydroxides (Haley *et al.*, 2004, Caetano-Filho *et al.*, 2018).

LREE-enriched particulate materials from the water column trapped and bound in seafloor sediments (coated grain skeletal packstone/wackestone) and fluvially-derived LREE-enriched organic colloids in stromatolites in continental fringing reefs have been cited in previous studies as the cause of similar LREE-enriched patterns ((Nothdurft *et al.*, 2004; Frimmel, 2009). Given the growing use of REE+Y as a proxy in ancient water-column chemistry, further study of shallow porewater processes may be needed to clarify how these elements are incorporated to crystallizing carbonates in different early diagenetic conditions in recent and modern carbonates (Caetano-Filho *et al.*, 2018).

After correction for siliciclastic content the LA-ICP-MS derived data in the current study supports the following interpretation of the solution ICP-MS results through the full stratigraphic section (Fig. 3.7): (a) Below 110 m brackish porewater conditions were present in frequently reworked, oxidizing sediment porewaters with very low siliciclastic inputs that increase with deepening moving upsection. Brackish conditions may have extended to the water-column based on the impoverished fauna encountered in the shallow facies at the base of the section; (b) By 110 m, with deepening below fair weather wave base the sediment redox column was less frequently disrupted and reducing conditions occurred with greater basinal clay input with basinward facies migration to more marine conditions. This is supported by the marine Y/Ho ratios indicated in these rocks post siliciclastic correction; (c) The deepening to below storm wave base led to a much greater basinal shale input and undisrupted redox column as recorded in sample 241.6. Again, the effectiveness of the siliciclastic correction of both the Y/Ho ratio and the shale normalised slope illustrate the much greater siliciclastic component in this outer ramp setting (d) Siliciclastic input decreased slightly at the upper reef and the data briefly show a return to very low Mn levels, consistent with oxic burial conditions, but also retain a greater magnitude of a more marine REE+Y signature, strongly supported by the corrected data when compared to the data from the base of the stratigraphic section.

The LA-ICP-MS mapping therefore provides a result that is consistent with the presence of crinoids, which in the modern ocean are stenohaline and restricted to marine salinity conditions. The absence of crinoids below the lower reef and proximal facies (i.e. below the sample at 113m) and in the inter to subtidal facies at the base of the section, which retain

very flat shale- normalized REE slopes and low Y/Ho ratios with minimal siliciclastic contamination, requires further investigation. As noted, this might indicate that the hyposaline conditions in the porewater were not limited to cement but may have also occurred in the shallow water-column, an interpretation supported by the very low levels of Mn and Sr that is also present in the allomicritic peloids and relict gastropod shells.

Fig. 3.3 Laser ablation ICP-MS maps from sample 41.2: (A) Thin section, plane polarized light, component labelling is presented at figure 3.2a; (B) Th concentrations as ppm; (C) Y/Ho ratio; (D) U concentrations as ppm; (E) Prn/Ybn; (F) Sr concentration as ppm; (G) Fe as ppm; (H) Mn as ppm.

Cerro La Silla - Sample 41.2

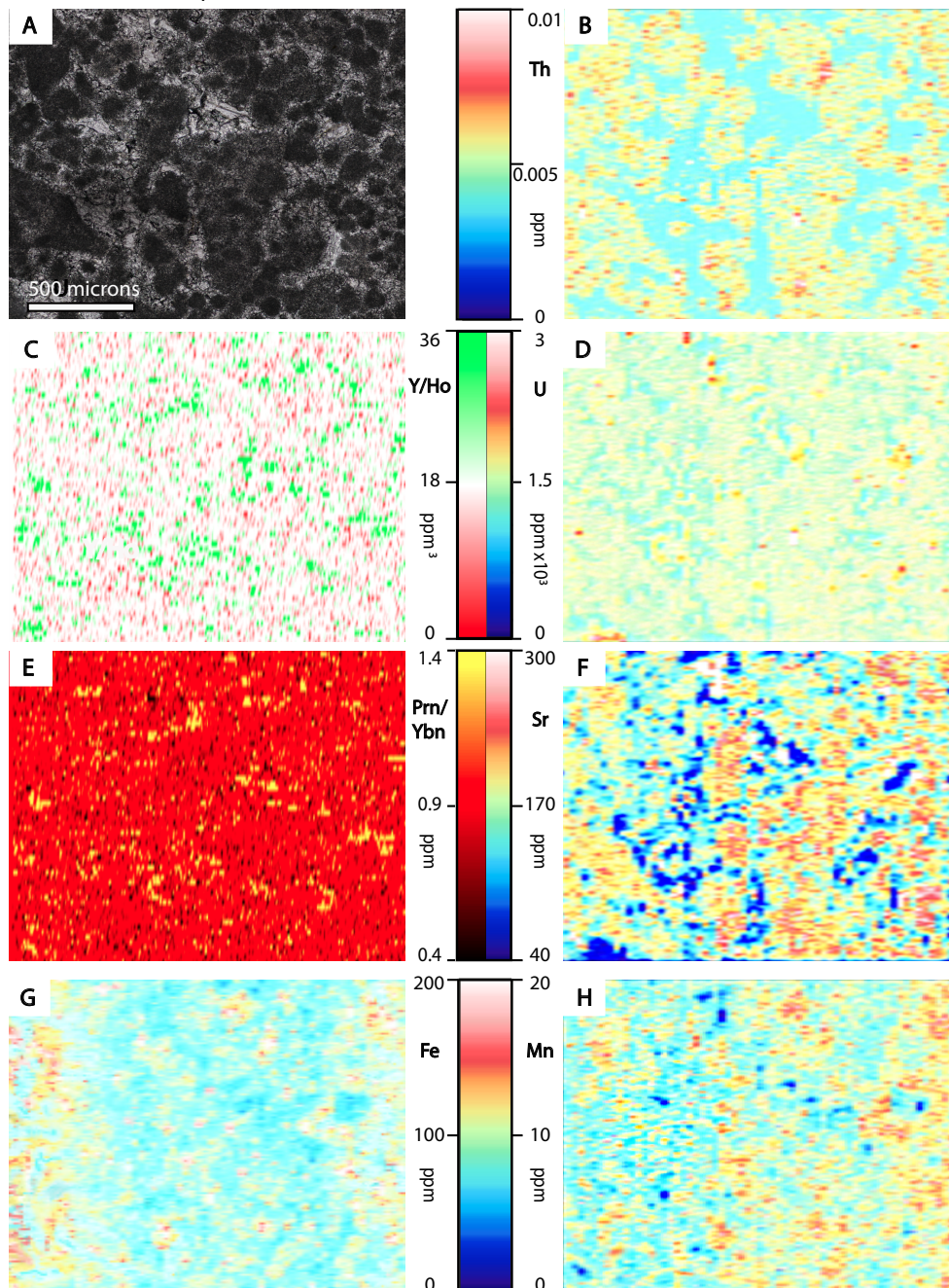


Fig. 3.4: Laser ablation ICP-MS maps from sample 113.2: (A) Thin section, plane polarized light, component labelling is presented at figure 3.2b; (B) Th concentrations as ppm; (C) Y/Ho ratio; (D) U concentrations as ppm; (E) Prn/Ybn; (F) Sr concentration as ppm; (G) Fe as ppm x 10³; (H) Mn as ppm.

Cerro La Silla - Sample 113.2

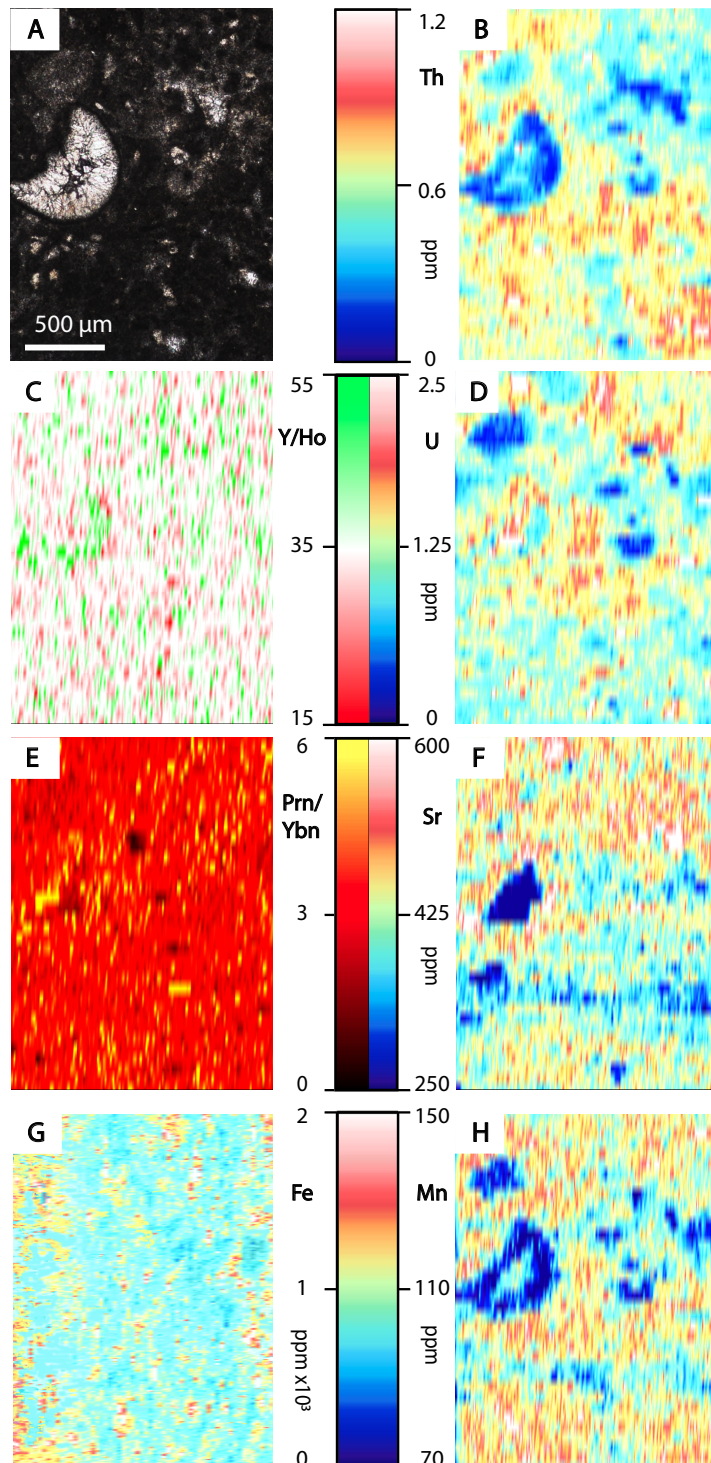


Fig. 3.5: Laser ablation ICP-MS maps from sample 241.6: (A) Thin section, plane polarized light, component labelling is presented at Fig. 3.2; (B) Th concentrations as ppm; (C) Y/Ho ratio; (D) U concentrations;³. (E) Prn/Ybn; (F) Sr concentration; (G) Fe as ppm x 10³; (H) Mn as ppm.

Cerro La Silla - Sample 241.6

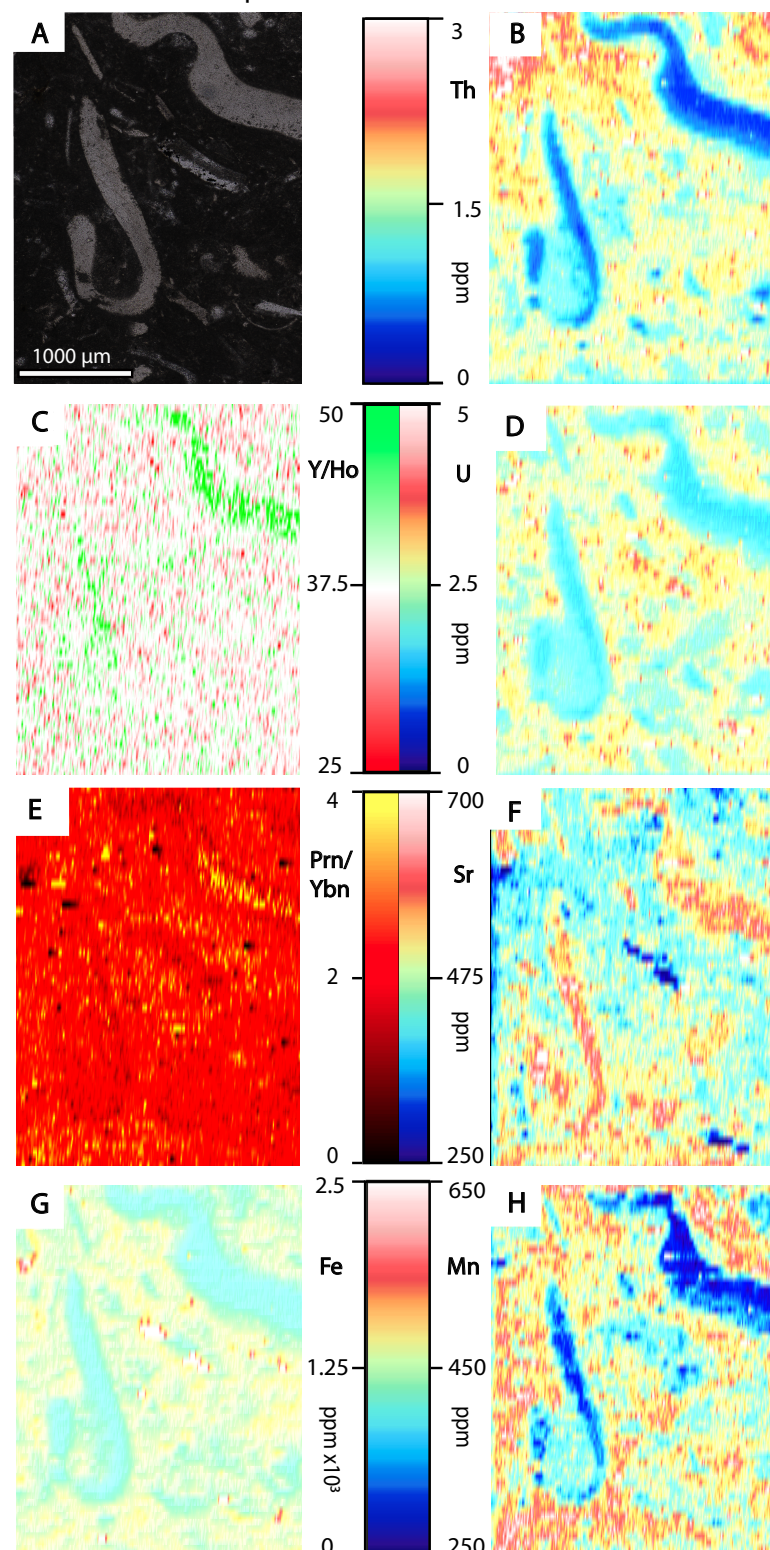


Fig. 3.6: Laser ablation ICP-MS maps from sample 268.6R: (A) Thin section, plane polarized light, component labelling is presented at Fig. 3.2; (B) Th concentrations as ppm; (C) Y/Ho ratio; (D) U concentrations as ppm; (E) Prn/Ybn; (F) Sr concentration; (G) Fe as ppm x 10³; (H) Mn as ppm.

Cerro La Silla - Sample 268.6R

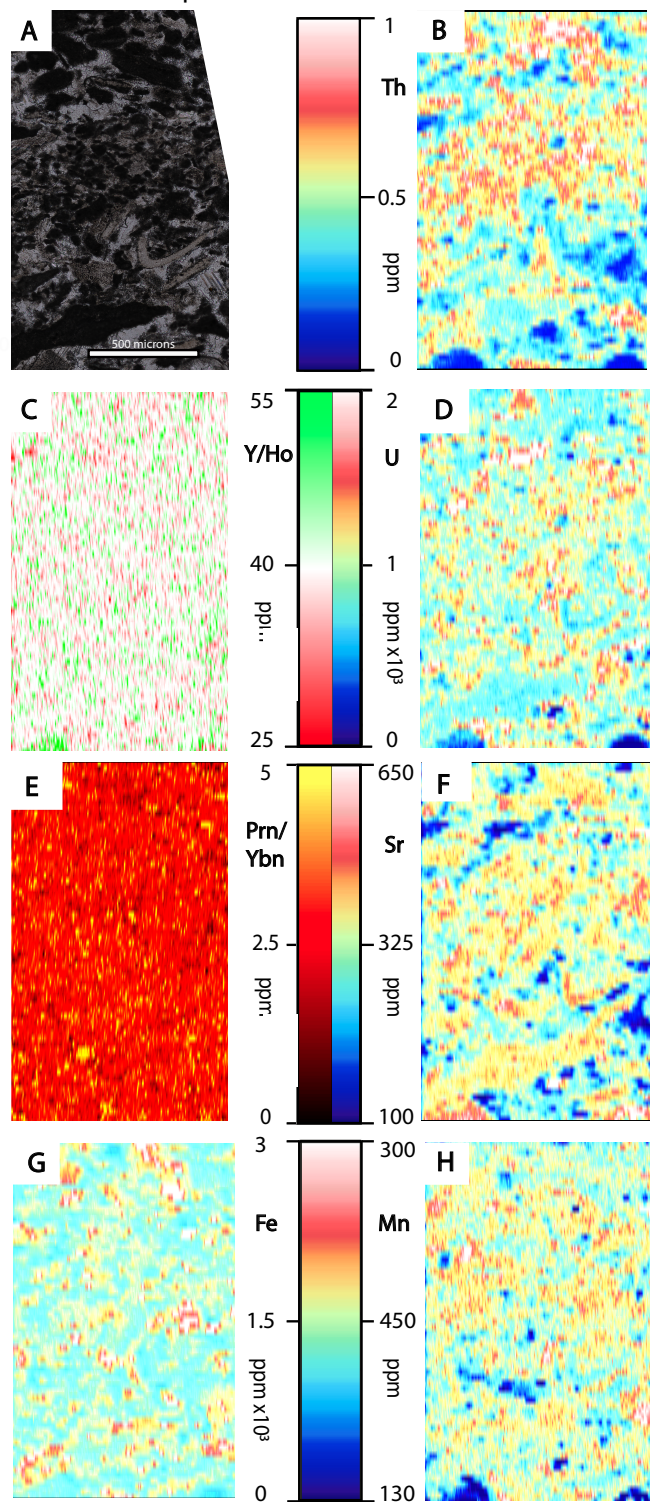
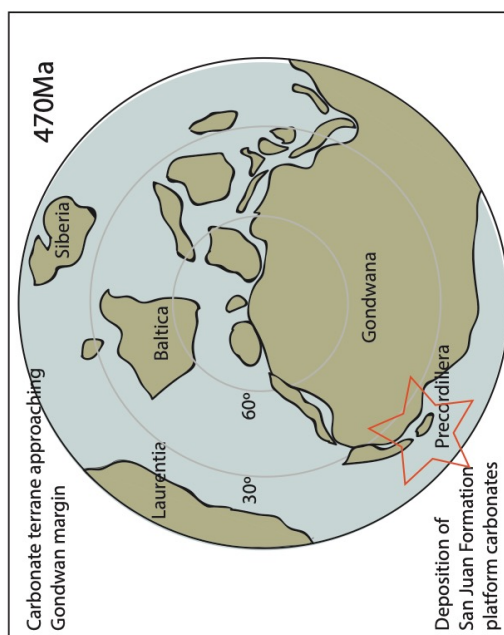
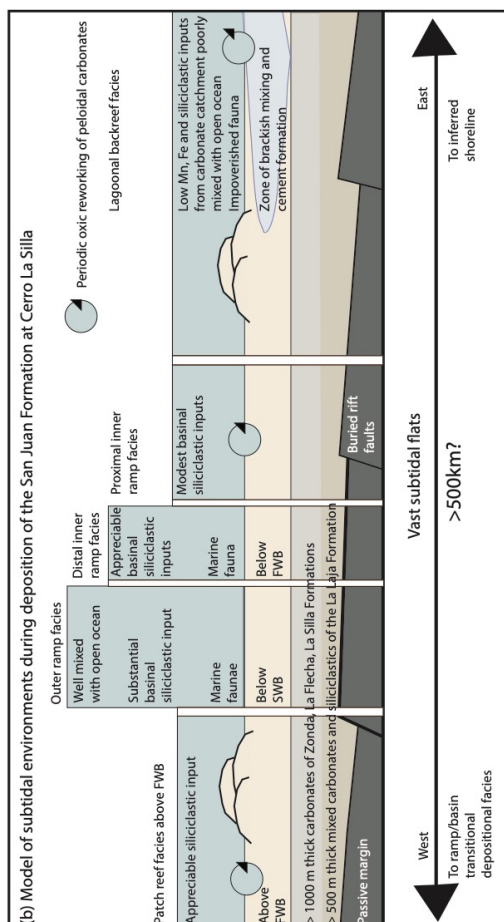
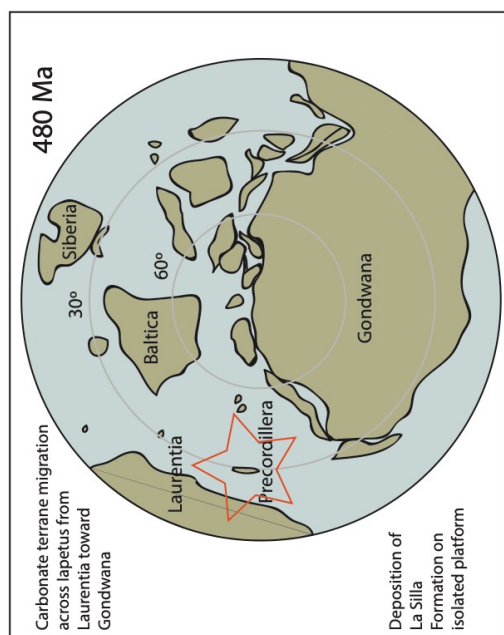
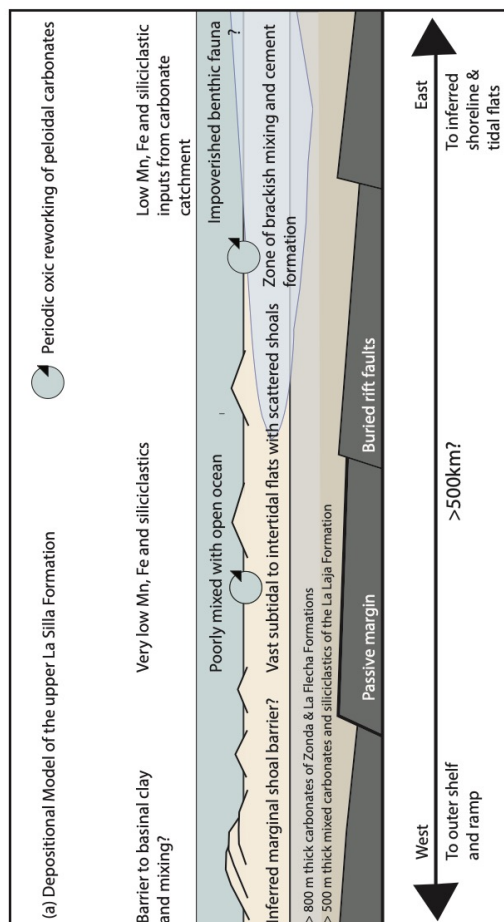


Fig. 3.7: Paleoenvironmental (after Keller, 1999 and Canas, 1999) and paleogeographical (after modified from Cocks & Torsvik, 2002) reconstructions of (a) the La Silla Formation during deposition and (b) the San Juan Formation at Cerro La Silla. The La Silla Formation was deposited on a passive margin during the drift of the Precordillera terrane across the Iapetus. It exhibits remarkably low siliciclastic content. LA-ICP-MS derived data in the current study supports brackish conditions in frequently reworked, oxidizing sediment porewaters with very low siliciclastic inputs that increase with deepening. Brackish conditions may have extended to the water-column based on the impoverished fauna encountered in the shallow facies at the base of the section; (b) The San Juan Formation was deposited as the Precordillera terrane approached the Gondwanan margin and exhibits greater depth related facies change. Deepening below fairweather wave base caused the sediment redox column to be less frequently disrupted and reducing conditions occurred with greater basinal clay input with basinward facies migration to more marine conditions. This is supported by the marine Y/Ho ratios indicated in these rocks post siliciclastic correction; Deepening to below storm wave base led to a much greater basinal shale input and undisrupted redox column as recorded in sample 241.6. Siliciclastic input decreased slightly at the upper reef and the data briefly show a return to very low Mn levels, consistent with oxic burial conditions, but also retain a greater magnitude of siliciclastic associated elements suggesting more marine conditions than those at the base of the measured section.



3.6 Conclusion

The current study demonstrates that LA-ICP-MS mapping is potentially a useful test of the fidelity of solution values and clarifies certain aspects of the depositional conditions during formation of the uppermost La Silla and lowermost San Juan Formations. Where it is proposed to carry out data corrections or screening for siliciclastic contamination in solution data the concentration of shale derived elements can be confirmed using *in situ* analysis to ensure that the correction is of sufficient magnitude. The ability to visualize and measure concentration variability is potentially particularly useful for correcting for siliciclastic contributions within heterogeneous phases such as allomicrite (which has been questioned as a reliable source of primary REE+Y data in recent studies (e.g. Della Porta *et al.*, 2015)). It seems that the greater magnitude of the correction of the LA-ICP-MS mapping data compared to the solution-ICP-MS data is due to disproportionate release of different elements from siliciclastic contamination due to variable refractive behaviour in the weak acid used to dissolve carbonate samples for solution analysis in this study. A solution-based analysis using weak acid (in Chapter 2, a 5% HNO₃ dissolution was used) is intended to dissolve carbonate, leaving more resistant silicates and oxyhydroxides largely undigested. However, any dissolution of siliciclastic associated elements that does occur is likely to be incomplete and to disproportionately favour less refractive elements, distorting the resulting correction.

Previous studies of carbonate sediments have used LA-ICP-MS mapping to create transects of cement phases that, when normalised to length of the transect, provided indications of the relative contribution of different phases to whole rock measurements (Hood *et al.*, 2018). The added value of the Monocle-derived LA-ICP-MS data is that *in situ* measurements can now be carried out. Measurements can be based on petrographic sampling criteria as in this study, or on an iterative identification of the least contaminated or altered components or areas within those components. Using this technique allomicrite remains a potential source of geochemical data where preferred sources such as marine radiaxial fibrous cement or microbial micrite (Kamber and Webb, 2001) are unavailable.

Combined use of LA-ICP-MS mapping and semi-quantitative data measured using Monocle provide evidence of alteration of the REE+Y profile in samples 113.2, 241.6 and 268.6 due to siliciclastic contamination of carbonate phases. The data from these samples exhibit (i)

some degree of covariation consistent with siliciclastic contamination (ii) shallow, shale normalized slopes and Y/Ho ratios considered typical of formation in shallow, brackish waters.

However, LA-ICP-MS mapping combined with measurement using Monocle enabled validation of the results using the key parameters (the shale normalized slope and the Y/Ho ratio). In sample 241.6 the Y/Ho correction in allomicrite produced marine values (Y/Ho = 47.62) that agreed with the uppermost carbonate Y/Ho values in the mapped range for the sample (Y/Ho of 50). The shale normalised slope is also corrected to a steeper slope consistent with carbonate formation in seawater ($Pr_n/Yb_n = 0.74$) indicating that the REE+Y marine signature of this sample has been strongly suppressed by detrital contamination. Likewise, sample 268.6 exhibits a corrected marine Y/Ho ratio of 43, which also approaches the upper values of the Y/Ho map for the sample. The samples therefore are likely to have formed in a shallow, oxic marine watercolumn contrary to the brackish signature suggested by the uncorrected data. Comparison of the data from LA-ICP-MS mapping with solution ICP-MS data from allomicrite powder (Chapter 2) indicates that the former provides a more faithful measure of siliciclastic derived elements and more accurate correction where there is possible partial dissolution of siliciclastic components.

This study therefore shows that LA-ICP-MS mapping is a relatively rapid and accessible method for either (i) screening for the most appropriate components for micro-drilling or LA-spot analysis in heterogeneous media, or (ii) to identify primary values or validate solution values that show possible siliciclastic contamination by siliciclastic correction. In the carbonates of the San Juan Formation at Cerro La Silla, the LA-ICP-MS mapping permits delimitation of brackish conditions to below c. 113m, based on an improved ability to identify and correct for siliciclastic contamination. This result is consistent with the identification of crinoids in the current study above this stratigraphic level, and suggests that more marginal conditions may be limited to the very shallow, proximal portions of the carbonate platform. In that segment of the section it appears that brackish, repeatedly oxidising conditions with minimal siliciclastic input occurred, factors that are discussed in relation to $\delta^{34}S_{CAS}$ records in Chapter 4.

In Chapters 2 and 3, siliclastic contamination that subdues the expression of marine REE+Y in solution-ICP-MS data was identified above the lower reef facies in the mid to upper San Juan Formation at Cerro La Silla. By contrast, the upper La Silla Formation and lowermost

San Juan Formation has minimal concentrations of shale associated elements, including Al and Fe. Micron scale analysis of components by LA-ICP-MS mapping (Chapter 3) identified variability in elemental concentrations across component types, including peloids, allomicrite, fossils and phreatic cement phases. Most notably, the mapped sample from the basal San Juan Formation has much lower concentration of Fe, Th and Mn across all recorded phases (peloidal allomicrite and phreatic cements) than occur in components or cement phases from all mapped samples in the mid to upper San Juan Formation (113.2, 241.6, and 268.6R). Combined interpretation of textural and geochemical data therefore suggests that the minimal concentrations of these elements may be related to formation in shallow, oxic, reworked conditions, isolated from siliciclastic input. These conditions are consistent with reconstructions of the Precordillera in the Late Cambrian-Early Ordovician as a vast homoclinal carbonate ramp, deposited in an isolated passive margin waterbody, outboard of a low relief, predominantly subtidal, carbonate terrane.

ACKNOWLEDGEMENTS

Field and stable isotope work was supported by the Stephen Fossett Postdoctoral Fellowship and a Trinity College Dublin Fellowship awarded to Catherine Rose. The solution trace element analysis laboratory at TCD was in part established with funding from CIG PCIG9-GA-2011-293712 awarded to BSK. The laboratory's operation is supported with funding from Science Foundation Ireland (SFI) Grant Number 13/RC/2092, co-funded under the European Regional Development Fund. Thanks are extended to Fernando Gomez and Tor O'Brien for assisting with field work. We would also like to thank Cora McKenna and Kerstin Dorst for help and expertise with the solution-IPMS and LA-ICP-MS mapping analyses at Trinity College Dublin.

Tables

Table 3-6: Siliciclastic Th and MUQ (shale composite) based correction (see text) to mean carbonate REE+Y data concentrations in allomicrite measured using Monocle (Petrus *et al.*, 2017) and calculated shale normalized slope (Prn/Ybn) and Y/Ho ratio (Lawrence *et al.*, 2006a) from samples 41.2, 113.2, 241.6 and 268.6R. Uncorrected values, with standard deviation, are bracketed. Correction is not meaningful in sample 41.2 due to the minimal siliciclastic levels present. Y/Ho ratio correction return more plausible shallow marine values in the remaining samples, whilst correction to the shale normalized slope provides a plausible result only in sample 241.6.

Component	41.2 Allomicrite (n=12)	113.2 Allomicrite (n=21)	241.6 Allomicrite (n=6)	268.6R Allomicrite (n=7)
Pr_n/Yb_n	>15	3.000 (1.327 SD 0.101)	0.721 (0.877 SD 0.083)	2.376 (0.737 SD 0.069)
Y/Ho	>100	45.55	47.62	43.08
SD		(33.66 SD 0.65)	(34.30 SD 1.03)	(37.38 SD 2.03)

References

- ALGEO, T. J. & TRIBOVILLARD, N. 2009. Environmental analysis of palaeoceanographic systems based on molybdenum–uranium covariation. *Chemical Geology*, 211–225.
- ALLMENDINGER, R. W. & JUDGE, P. A. 2014, The Argentine Precordillera: A foreland thrust belt proximal to the subducted plate: *Geosphere*. V, 10 (6)
- BABECHUK, M. G., KAMBER, B. S., GREIG, A., CANIL, D. & KODOLANYI, J. 2010. The behavior of tungsten during mantle melting revisited with implications for planetary differentiation time scales. *Geochimica et Cosmochimica Acta*, 74, 1448–1470.
- BALDWIN, G. J., THURSTON, P. C. & KAMBER, B. S. 2011. High precision rare earth element, nickel, and chromium chemistry of chert microbands pre-screened with in-situ analysis. *Chemical Geology*, 285, 133–143.
- BANNER, J. L. 1995. Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis. *Sedimentology* 42, 805–824.
- BANNER, J. L. & HANSON, G. N. 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochimica et Cosmochimica Acta*, 54, 3123–3137.
- BAU, M. 1999. Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. *Geochimica et Cosmochimica Acta*, 63, 67–77.
- BAU, M. & DULSKI, P. 1996. Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. *Precambrian Research*, 79, 37–55.
- BAU, M. & DULSKI, P. 1999. Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic seawater. *Chemical Geology*, 155, 77–90.
- BAU, M. & KOSCHINSKY, A. 2009. Oxidative scavenging of cerium on hydrous Fe oxides. Evidence from the distribution of rare earth elements and yttrium between Fe oxides and Mn oxides in hydrogenetic ferromanganese crusts. *Geochem. J.*, 43, 37–47.
- BAU, M., MÖLLER, P. & DULSKI, P. 1997. Yttrium and lanthanides in eastern Mediterranean seawater and their fractionation during redox-cycling. *Marine Chemistry*, 56, 123–131.
- BINYON, J (1972). *Physiology of echinoderms*, Pergamon Press, Oxford.
- BOLHAR, R., KAMBER, B. S., MOORBATH, S., FEDO, C. M. & WHITEHOUSE, M. J. 2004. Characterisation of early Archaean chemical sediments by trace element signatures. *Earth and Planetary Science Letters*, 222, 43–60.

- BOLHAR, R. & VAN KRANENDONK, M. J. 2007. A non-marine depositional setting for the northern Fortescue Group, Pilbara Craton, inferred from trace element geochemistry of stromatolitic carbonates. *Precambrian Research*, 155, 229-250.
- BRAND, U. & VEIZER, J. 1980. Chemical diagenesis of a multicomponent carbonate system-1: trace elements. *Journal of Sedimentary Petrology*, 50, 1219–1236.
- BRAND, U. & VEIZER, J. 1981. Chemical diagenesis of a multicomponent carbonate system; 2, Stable isotopes. *Journal of Sedimentary Research*, 51, 987–997.
- BUGGISCH, W., KELLER, M. & LEHNERT, O. 2003. Carbon isotope record of the Late Cambrian and Early Ordovician carbonates of the Argentine Precordillera. *Palaeogeography, Palaeoclimatology, Palaeoecology*.
- BYRNE, R. & KIM, K.-H. 1990. Rare earth element scavenging in seawater. *Geochimica et Cosmochimica Acta*, 54, 2645-2656.
- BYRNE, R. H., LIU, X. & SCHUF, J. 1996. The influence of phosphate coprecipitation on rare earth distribution in natural waters. *Geochimica et Cosmochimica Acta*, 60, 3341-3346.
- CAETANO-FILHO, S., PAULA-SANTOS, G. M., DIAS-BRITO, D. 2018. Carbonate REE plus Y signatures from the restricted early marine phase of South Atlantic Ocean (late Aptian - Albian): The influence of early anoxic diagenesis on shale-normalized REE plus Y patterns of ancient carbonate rocks. *Palaeogeography Palaeoclimatology Palaeoecology*, 500, 69-83
- CHEW, D. M., BABECHUK, M. G., COGNÉ, N., MARK, C., O’SULLIVAN, G. J., HENRICHS, I. A., DOEPKE, D. & MCKENNA, C. A. 2016. (LA,Q)-ICP-MS trace-element analyses of Durango and McClure Mountain apatite and implications for making natural LA-ICP-MS mineral standards. *Chemical Geology*, 435, 35-48.
- COCKS, L.R.M. & TORSVIK, T.H., 2002. Earth Geography from 500 to 400 million years ago: a faunal and palaeomagnetic review. *J. Geol. Soc. Lond.*, 159, 631-644
- DE BAAR, H. J. W., BACON, M. P., BREWER, P. G. & BRULAND, K. W. 1985. Rare earth elements in the Pacific and Atlantic Oceans. *Geochimica et Cosmochimica Acta*, 49, 1943- 1959.
- DELLA PORTA, G., WEBB, G. E. & MCDONALD, I. 2015. REE patterns of microbial carbonate and cements from Sinemurian (Lower Jurassic) siliceous sponge mounds (Djebel Bou Dahar, High Atlas, Morocco). *Chem. Geol.*, 400, 65–86.
- DENISON, R. E., KOEPNICK, R. B., FLETCHER, A., HOWELL, M. W. & CALLAWAY, W. S. 1994. Criteria for the retention of original seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in ancient shelf limestones. *Chemical Geology*, 112, 131-143.
- DE VILLIERS, S. 1999. Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans. *Earth and Planetary Science Letters*, 171 (4), 623-624.

- DU Y., ZHU, J., GU S., XU, Y., YANG J., 2007. Sedimentary geochemistry of the Cambrian-Ordovician cherts: Implication on archipelagic ocean of North Qilian orogenic belt. *Sci China Ser D-Earth Sci.* 50 (11)
- EGGINS, S. M., WOODHEAD, J. D., KINSLEY, L. P. J., MORTIMER, G. E., SYLVESTER, P., MCCULLOCH, M. T., HERGT, J. M. & HANDLER, M. R. 1997. A simple method for the precise determination of > 40 trace elements in geological samples by ICP-MS using enriched isotope internal standardisation. *Chemical Geology*, 134, 311-326.
- ELDERFIELD, H., UPSTILL-GODDARD, R. & SHOLKOVITZ, E. R. 1990. The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochimica et Cosmochimica Acta*, 54, 971–991.
- FRIMMEL, H. E. 2009. Trace element distribution in Neoproterozoic carbonates as paleoenvironmental indicators. *Chemical Geology*, 258 (3-4), 338-353.
- GERMAN, C. R. & ELDERFIELD, H. 1990. Application of the Ce anomaly as a paleoredox indicator: the ground rules. *Paleoceanography* 5.
- GIESKES, J. M., ELDERFIELD, H. & PALMER, M. R. 1986. Strontium and its isotopic composition in interstitial waters of marine carbonate sediments. *Earth and Planetary Science Letters*, 77 (2), 229-235.,
- HAHN, K. E., TURNER, E. C., BABECHUK, M. G. & KAMBER, B. S. 2015. Deep-water seep-related carbonate mounds in a Mesoproterozoic alkaline lake, Borden Basin (Nunavut, Canada). *Precambrian Research*, 271, 173-197.
- HALEY, B. A., KLINKHAMMER, G. P. & J, M. 2004. Rare earth elements in pore waters of marine sediments. *Geochimica Et Cosmochimica Acta* 68, 1265-1279.
- HEMMING, N. G., MEYERS, W. J. & GRAMS, J. C. 1989. Cathodoluminescence in Diagenetic Calcites: The Roles of Fe and Mn as Deduced from Electron Probe and Spectrophotometric Measurements. *Journal of Sedimentary Research (SEPM)*, 59, 404-411.
- HOOD, A. G., MEYERS, W. J. & GRAMS, J. C. 1989. Cathodoluminescence in Diagenetic Calcites: The Roles of Fe and Mn as Deduced from Electron Probe and Spectrophotometric Measurements. *Journal of Sedimentary Research (SEPM)*, 59, 404-411.
- HOOD, A. G., PLANAVSKY, N. J., WALLACE, M. W., WANG, X. & GRAMS, J. C. 2018. The Effects of Diagenesis on Geochemical Paleoredox Proxies in Sedimentary Carbonates. *Geochimica et Cosmochimica Acta*, 232, 265-287.
- KAH, L. C., THOMPSON, C. K., HENDERSON, M. A. & ZHAN, R. 2016. Behavior of marine sulfur in the Ordovician. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 458, 133-153.

- KAMBER, B. S. 2009. Geochemical fingerprinting: 40 years of analytical development and real world applications. *Applied Geochemistry*, 24, 1074-1086.
- KAMBER, B. S., GREIG, A. & COLLERSON, K. D. 2005. A new estimate for the composition of weathered young upper continental crust from alluvial sediments, Queensland, Australia. *Geochimica et Cosmochimica Acta*, 69, 1041-1058.
- KAMBER, B. S. & WEBB, G. E. 2001. The geochemistry of late Archaean microbial carbonate: implications for ocean chemistry and continental erosion history. *Geochimica et Cosmochimica Acta*, 65, 2509-2525.
- 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.
- KELLER, M. 1999. Argentine Precordillera: Sedimentary and Plate Tectonic History of a Laurentian Crustal Fragment in South America. Special Paper 341: Argentine Precordillera: sedimentary and plate tectonic history of a Laurentian crustal fragment in South America. Geological Society of America.
- KNOLL, A. H., KAUFMAN, A. J. & A, S. M. 1995 The carbon isotopic composition of Proterozoic carbonates: Riphean successions from northwestern Siberia (Anabar massif, Turukhansk uplift) *American Journal of Science*, 295 823–850.
- LAWRENCE, M. G., GREIG, A., COLLERSON, K. D. & KAMBER, B. S. 2006a. Rare Earth Element and Yttrium Variability in South East Queensland Waterways. *Aquatic Geochemistry*, 12, 39-72.
- LAWRENCE, M. G., JUPITER, S. D. & KAMBER, B. S. 2006b. Aquatic geochemistry of the rare earth elements and yttrium in the Pioneer River catchment, Australia. *Mar. Freshwater Res.*, 57, 725.
- LAWRENCE, M. G. & KAMBER, B. S. 2006. The behaviour of the rare earth elements during estuarine mixing—revisited. *Marine Chemistry*, 100, 147-161.
- LÉCUYER, C., REYNARD, B. & GRANDJEAN, P. 2004. Rare earth element evolution of Phanerozoic seawater recorded in biogenic apatites. *Chemical Geology* 204, 63–102.
- NOTHDURFT, L. D., WEBB, G. E. & KAMBER, B. S. 2004. Rare earth element geochemistry of Late Devonian reefal carbonates, Canning Basin, Western Australia: confirmation of a seawater REE proxy in ancient limestones. *Geochimica et Cosmochimica Acta*, 68, 263-283.
- NOZAKI, Y., ZHANG, J. & AMAKAWA, H. 1997. The fractionation between Y and Ho in the marine environment. *Earth and Planetary Science Letters*, 148, 329-340.

- PATON, C., HELLSTROM, J., PAUL, B., WOODHEAD, J. & HERGT, J. 2011. Iolite: Freeware for the visualisation and processing of mass spectrometric data. . *Journal of Analytical Atomic Spectrometry*, 26, 2508-2518.
- PETRUS, J. A., CHEW, D. M., LEYBOURNE, M. I. & KAMBER, B. S. 2017. A new approach to laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) using the flexible map interrogation tool 'Monocle'. *Chemical Geology*, 463, 76-93.
- PRESENT, T. M., PARIS, G., BURKE, A., FISCHER, W. W. & ADKINS, J. F. 2015. Large Carbonate Associated Sulfate isotopic variability between brachiopods, micrite, and other sedimentary components in Late Ordovician strata. *Earth and Planetary Science Letters*, 432, 187-198.
- REYNARD, B., LÉCUYER, C. & GRANDJEAN, P. 1999. Crystal-chemical controls on rare earth element concentrations in fossil biogenic apatite and implications for paleoenvironmental reconstructions. *Chemical Geology*, 233-241.
- RICHARDSON, J. A., NEWVILLE, M., LANZIROTTI, A., WEBB, S. M., ROSE, C. V., CATALANO, J. G. & FIKE, D. A. 2019. Depositional and diagenetic constraints on the abundance and spatial T variability of carbonate-associated sulfate. *Chemical Geology*, 523, 59–72.
- SAVARD, M., VEIZER, J. & HINTON, R. 1995 Cathodoluminescence at low Fe and Mn concentrations: A SIMS study of zones in natural calcites. *Journal of Sedimentary Research*. , A65, 208-2136.
- SHIELDS, G. A. & WEBB, G. E. 2004. Has the REE composition of seawater changed over geological time? *Chemical Geology*, 204, 1(2), 103-107
- THOMPSON, C. K. & KAH, L. C. 2012. Sulfur isotope evidence for widespread euxinia and a fluctuating oxycline in Early to Middle Ordovician greenhouse oceans. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 313-314, 189-214.
- TOSTEVIN, R., SHIELDS, G. A., TARBUCK, G. M., HE, T., CLARKSON, M. O. & WOOD, R. A. 2016. Effective use of cerium anomalies as a redox proxy in carbonate-dominated marine settings. *Chemical Geology*, 438, 146-162.
- UBIDE, T., MCKENNA, C. A., CHEW, D. M. & KAMBER, B. S. 2015. High-resolution LA-ICP-MS trace element mapping of igneous minerals: In search of magma histories. *Chemical Geology*, 409.
- VAN GELDERN, R., JOACHIMSKI, M., DAY, J., JANSEN, U., ALVAREZ, F., YOLKIN, E. A. & MA, X. 2006. Carbon, oxygen and strontium isotope records of Devonian brachiopod shell calcite. *Palaeogeography, Palaeoclimatology, Palaeoecology*. 240, 47-67.

- VEIZER, J. 1983. Chemical diagenesis of carbonates: theory and application of trace element technique. Short Course Notes Society of Economic Paleontologists and Mineralogists.
- VERDEL, C., PHELPS, B. & WELSH, K. 2018. Rare earth element and $^{87}\text{Sr}/^{86}\text{Sr}$ step-leaching geochemistry of central Australian Neoproterozoic carbonate. *Precambrian Research*, 310, 229-242.
- WEBB, G. E. & KAMBER, B. S. 2000. Rare earth elements in Holocene reefal microbialites: a new shallow seawater proxy. *Geochimica et Cosmochimica Acta*, 64, 1557-1565.
- WEBB, G. E., NOTHDURFT, L. D., KAMBER, B. S., KLOPPROGGE, J. T. & ZHAO, J. X. 2009. Rare earth element geochemistry of scleractinian coral skeleton during meteoric diagenesis: a sequence through neomorphism of aragonite to calcite. *Sedimentology*, 56, 1433-1463.
- ZHANG, J. & NOZAKI, Y. 1998. Behavior of rare earth elements in seawater at the ocean margin: a study along the slopes of the Sagami and Nankai troughs near Japan. *Geochimica et Cosmochimica Acta*, 62, 1307-1317.
- ZHANG, T., SHEN, Y., ZHAN, R., SHEN, S. & CHEN, X. 2009. Large perturbations of the carbon and sulfur cycle associated with the Late Ordovician mass extinction in South China. *Geology*, 37, 299-302.
- ZHONG, S. & MUCCI, A. 1995. Partitioning of rare earth elements (REEs) between calcite and seawater solutions at 25°C and 1 atm, and high dissolved REE concentrations. *Geochimica Et Cosmochimica Acta* 59, 443–453.

Chapter 4

Micron-scale spatial distribution and speciation of sulfur and trace elements in sedimentary carbonates.

Stephen P. Coakley¹, David Chew¹, Matthew Newville², Antonio Lanzirotti², David A. Fike³, Catherine V. Rose⁴

¹Department of Geology, Trinity College Dublin, Dublin 2, IRE;

²Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, USA;

³Dept. of Earth and Planetary Sciences, Washington University in St. Louis, 1 Brookings Drive, St. Louis, MO 63130, USA;

⁴School of Earth and Environmental Sciences, University of St Andrews, St Andrews, Fife KY16 9AL, UK.

ABSTRACT

Sulfur isotopes ($\delta^{34}\text{S}$) records from carbonate associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) have been interpreted as a record of seawater sulfate that permit insights into biogeochemical cycling, surface redox conditions and microbial activity over geological time. However, with increasing use of $\delta^{34}\text{S}_{\text{CAS}}$ records as a paleoenvironmental proxy it has become clear that they frequently exhibit poorly understood stratigraphic and lateral variation. Existing bulk-rock $\delta^{34}\text{S}_{\text{CAS}}$ records from the Lower to Middle Ordovician San Juan Formation of the Argentine Precordillera, from shallow subtidal to below storm wave base facies, are up to 20‰ more negative than coeval records from Missouri and Western Newfoundland. The isotopic difference between these data has been interpreted as representing a global low-sulfate ocean with a deep-water euxinic reservoir. However, carbonate rocks are often composed, in varying abundance, of cement, micrite, abiotic grains and fossils and it is therefore important to identify the key components and their relative contribution to the bulk geochemical signal. Here we examine four samples from the San Juan Formation at Cerro La Silla, Argentine Precordillera, at the micron scale by mapping of the distribution and abundance of sulfur-bearing phases using X-ray Absorption Near Edge Structure (XANES) spectroscopy and micro x-ray fluorescence ($\mu\text{-XRF}$) imaging, supplemented by mapping of trace element proxies of water-column and porewater chemistry and redox conditions by LA-ICP-MS. At a micron scale, carbonates exhibit clear differences in the distribution of carbonate-associated sulfate (CAS) between the key components, which can be related to elemental concentrations and processes occurring during formation, from deposition at the sediment-water interface and lithification in evolving porewaters during burial.

Micron-scale results are considered in the context of a newly presented bulk-rock $\delta^{34}\text{S}_{\text{CAS}}$ dataset that exhibits a typical pattern of high-frequency secular variation over short stratigraphic distances and a more positive mean value by 4.4‰ than previous $\delta^{34}\text{S}_{\text{CAS}}$ records from the same section. The results question the assumption in bulk rock $\delta^{34}\text{S}_{\text{CAS}}$ analysis that CAS is evenly distributed in carbonate rocks and suggest that $\delta^{34}\text{S}_{\text{CAS}}$ may vary between different components, which may as a result partially control the bulk isotopic value.

At the base of the San Juan Formation, the micron scale petrographic analysis and elemental distribution supports distinctive, non-marine formation for a large proportion of the carbonate components in the samples. There is an absence of evidence of siliciclastic contamination and an extensive early phreatic cement phase with distinctive low concentrations of Mn, Fe and trace elements. Combined interpretation of textural and geochemical data suggests that the sample formed in shallow, oxic, reworked conditions, isolated from siliciclastic input. These conditions are consistent with reconstructions of the Precordillera in the Late Cambrian-Early Ordovician as a vast homoclinal carbonate ramp, deposited in an isolated passive margin waterbody, outboard of a low relief, predominantly subtidal, carbonate terrane. In addition these conditions coincide with lower $\delta^{34}\text{S}_{\text{CAS}}$ values in the upper La Silla and lowermost San Juan Formation. In the outlined depositional conditions, the absence of Fe for pyrite formation would result in a greater magnitude of porewater sulfide available for oxidation during oxidative reworking and consequently a local porewater sulfate pool with lower $\delta^{34}\text{S}$ than the marine $\delta^{34}\text{S}_{\text{SO}_4}$ value during phreatic cement precipitation. The results are also consistent with a depositional environment isolated from siliciclastic inputs, with greater clay occurring during the subsequent deposition of the San Juan Formation above 110 m in the stratigraphic section, with deepening. Alternatively, primary factors such as a catchment composition that sample a greater magnitude of sulfides derived from weathering of siliciclastic or igneous lithologies (compared to the catchment contributing to up-section, more positive samples) might contribute to lower $\delta^{34}\text{S}_{\text{CAS}}$ values in brackish porewaters, in a partially restricted basin or in a low-sulfate ocean with more rapid response time than the modern ocean. Currently there is no evidence of a potential siliciclastic land-mass inboard of the carbonate platform and the very low levels of siliciclastic components suggest that the required catchment conditions might not have been present.

This research emphasizes the need for caution when interpreting bulk $\delta^{34}\text{S}_{\text{CAS}}$ datasets, especially those derived from shallow, reworked facies. The use of $\delta^{34}\text{S}_{\text{CAS}}$ as a proxy for secular redox change requires a strong understanding of $\delta^{34}\text{S}_{\text{CAS}}$ variation at a micron scale and how it relates to facies variability.

4.1 Introduction

Geological reconstructions of global ocean chemistry and atmospheric oxygen concentrations over Earth history frequently rely on the abundance and stable isotopic composition of sulfur-bearing ($\delta^{34}\text{S}$) and carbon-bearing ($\delta^{13}\text{C}$) compounds (Garrels and Lerman, 1981; Berner, 2006). Changing redox conditions in Earth-surface environments over geological timescales are reflected in the marine sulfur cycle and recorded as burial ratios between redox-sensitive sulfide and sulfate (Berner and Raiswell, 1983) in sedimentary rocks (Canfield and Teske, 1996; Canfield *et al.*, 2000; Habicht *et al.*, 2002). Carbonate-associated sulfate (CAS) is sulfate trapped within the calcium carbonate mineral matrix at typical trace concentrations of tens to hundreds of ppm in ancient carbonates and hundreds to thousands of ppm in modern carbonates (Staudt and Schoonen, 1995). This sulfate is extracted and used as a proxy in the majority of existing studies by bulk sampling and leaching (Wotte *et al.*, 2012). Measurement of $\delta^{34}\text{S}$ in CAS ($\delta^{34}\text{S}_{\text{CAS}}$) has been interpreted as a primary record of $\delta^{34}\text{S}$ in seawater sulfate ($\delta^{34}\text{S}_{\text{water}}$) from the Archean to the Cenozoic (Burdett *et al.*, 1989; Kampschulte and Strauss, 2004; Gill *et al.*, 2007; Fike and Grotzinger, 2008; Ries *et al.*, 2009; Hurtgen *et al.*, 2009; Turchyn *et al.*, 2009; Gill *et al.*, 2011; Thompson and Kah, 2012; Jones and Fike, 2013; Crowe *et al.*, 2014; Osburn *et al.*, 2015; Kozik *et al.*, 2019). $\delta^{34}\text{S}_{\text{SO}_4}$ is of particular value when paired with $\delta^{34}\text{S}_{\text{pyr}}$ data from carbonate rocks and the abundance of carbonate rocks provides a more continuous $\delta^{34}\text{S}_{\text{SO}_4}$ record than either evaporites (Claypool *et al.*, 1980) or marine barites (Paytan *et al.*, 1998, 2004).

The increased use of $\delta^{34}\text{S}_{\text{CAS}}$ for the purposes of paleoenvironmental reconstruction has highlighted frequent occurrences of discordant stratigraphic and coeval records that are poorly understood (Fig. 2.1) (Kampschulte and Strauss, 2004; Fike and Grotzinger, 2008; Ries *et al.*, 2009; Osburn *et al.*, 2015; Present *et al.*, 2015; Rose *et al.*, 2019). As seawater sulfate has a multi-million year residence time (Berner, 2001), the high-frequency secular variation observed, which can up to 10‰ between samples ca. 10 metres apart (Riccardi *et al.*, 2006; Jones and Fike, 2013; Edwards *et al.*, 2018), is unlikely to be due to changes in the marine sulfate reservoir alone (Jones and Fike, 2013; Fike *et al.*, 2015). The rapidity of observed changes in the oceanic sulfate reservoir would require very low sulfate concentrations in ancient oceans relative to the 28 mM in modern oceans (Kah *et al.*, 2004; Ries *et al.*, 2009) and has led to inference of sulfate concentrations as low as 2 mM in the Ordovician ocean (Thompson and Kah, 2012). Similarly, low seawater sulfate is invoked to

explain lateral geochemical gradients in sulfur isotope values in ancient oceans (Hurtgen *et al.*, 2006; Li *et al.*, 2010).

Micron-scale variability may potentially contribute to bulk rock values of $\delta^{34}\text{S}_{\text{CAS}}$ depending on the cumulative effect of the following factors: (a) differences in the composition of the sediment, as carbonate rocks are typically composed of a varying range and abundance of components, including lime mud (frequently referred to as depositional micrite or allomicrite), fossils, cement phases and abiotic grains (Kampschulte *et al.*, 2001; Kampschulte and Strauss, 2004; Gill *et al.*, 2011; Wotte *et al.*, 2012; Paris *et al.*, 2014; Present *et al.*, 2015; Rennie *et al.*, 2018; Richardson *et al.*, 2019; Rose *et al.*, 2019). The modal abundance and preservation state of components in any one sample therefore has the potential to determine bulk $\delta^{34}\text{S}$ in the rock record (Present *et al.*, 2015, Rose *et al.*, 2019); (b) the extent of alteration of those components by syndepositional physical and chemical processes, including contamination (Aller *et al.*, 2014); or (c) diagenetic processes affecting those components (occurring after the precipitation/sedimentation of carbonate, including lithification) (Aller, 2004; Derry, 2010). Examples of diagenetic fluids that may affect marine carbonates include chemically evolved porewaters, meteoric fluids, dolomitizing fluids, and basinal brine fluids. Several studies have assessed the effect of diagenesis on CAS of bulk rock samples (Hurtgen *et al.*, 2006; Gill *et al.*, 2008; Rennie and Turchyn, 2014; Fichtner *et al.*, 2017).

Studies in modern deltaic environments however also suggest that the physical environmental characteristics of a depositional environment may have an important yet poorly understood influence on the sulfur isotope signal recorded in marine sediments (Aller *et al.*, 2008; Canfield and Farquhar, 2009; Ries *et al.*, 2009; Aller *et al.*, 2010; Aller, 2014). Physical characteristics, such as sediment remobilisation by storms or tides, influence the concentration and isotopic value of porewater and sediment sulfur species. The established sediment redox stratigraphy may be disrupted by reworking, causing exchange of sulfur and iron pools between reduced and oxidized zones with resulting oxidation of H_2S (Aller *et al.*, 2008, 2010; Gao *et al.*, 2013; Aller, 2014; Richardson *et al.* 2019; Rose *et al.*, 2019). The type of depositional environment in which sediment forms may affect the extent of such physical reworking, or of shale contribution to the sediment, biotic diversity or penetration depth of seawater or altering fluids and rates of cement precipitation (Strauss, 1997; Fike *et al.*, 2015; Pasquier *et al.*, 2017; Rose *et al.*, 2019). These characteristics are potentially

discernible in carbonate rocks as lithofacies (outcrop and hand sample observations) and microfacies (petrographic observations).

Accurate petrographic characterization and understanding of micron-scale variability in sulfate concentrations and $\delta^{34}\text{S}_{\text{CAS}}$ is therefore a fundamental step to aid current understanding. Micron-scale factors that might cause the observed variability in $\delta^{34}\text{S}_{\text{CAS}}$ were until recently undecipherable due to an absence of techniques that could determine the CAS abundance of individual components within a petrographic context (Present *et al.*, 2015; Rose *et al.*, 2019). Micro X-Ray Fluorescence (μ -XRF) imaging and X-Ray Absorption Near Edge Structure (XANES) spectroscopy now make possible the non-destructive detection of low abundance S-species at μm -scale spatial resolution within a petrographic context (Richardson *et al.*, 2019; Rose *et al.*, 2019). S-species have a wide range of oxidation states that corresponds to ~ 14 eV range of absorption edge energies in XANES spectroscopy (Hedman *et al.*, 1986), providing an ideal platform for multi-energy μ -XRF imaging that can distinguish between the various S species. Initial investigations by Rose *et al.* (2019) indicate sulfate abundance is spatially variable within an individual Ordovician carbonate thin section, with CAS concentrations ranging from ~ 10 to 200 ppm. Paired LA-ICP-MS mapping is a useful supplementary tool to μ -XRF, permitting a spatial understanding of major and trace element concentration and distribution information from LA-ICP-MS mapping that may be petrographically paired with the textures in the analyzed thin section. We examine samples from the Cerro La Silla section that spans the late Tremadocian (Keller *et al.*, 1994; Albanesi and Ortega, 2002) to mid-Darriwilian and coincides with the great Ordovician biodiversification event preceding the Hirnantian glaciation. The section is stratigraphically, petrographically and biostratigraphically well-characterized (Herrera and Benedetto, 1991; Canas, 1999; Keller, 1999). Previous chemostratigraphic studies analysed carbon and bulk sulfur isotopes (Buggisch *et al.*, 2003; Thompson and Kah, 2012), showing high frequency $\delta^{34}\text{S}_{\text{CAS}}$ variation over a short stratigraphic distance that has been interpreted as a global marine signal rapidly varying at a magnitude of 7‰ over a million years (Thompson and Kah, 2012). To be feasible, this very rapid scale of variation in sulphate, which has a multi-million year residence time in the global ocean, requires a low sulphate concentration of 2 mM in the Ordovician global ocean sulfate reservoir (Bernier, 2001; Kah *et al.*, 2004). Here we investigate the potential origin of $\delta^{34}\text{S}_{\text{CAS}}$ variability at a micron scale with the benefit of paired μ -XRF, LA-ICP-MS mapping and observations from Chapters 2 and 3 that pertain to the paleogeographic and paleoenvironmental conditions on the Precordillera platform during deposition of the upper La Silla Formation and San Juan Formations.

4.2 Geological Setting

The geological setting is described in detail in Chapter 2.2 with a map of the field area (Fig 2.3).

4.3 Methods

In the field, 300 hand samples were taken from the stratigraphic section at Cerro La Silla (Fig. 2.2 and Fig. 4.1). In the laboratory all samples were trimmed of weathered surfaces and veins and a subset of 275 hand samples were selected to minimise leaching from modern-day weathering and then slabbed. Trimmed samples were cut into 8 cm³ cubes and 104 samples were crushed to fine powder in a rock crusher and agate ball mill for sulfate extraction. Petrographic thin sections were made from 32 samples. Cathodoluminescence (CL) screening of thin sections for Mn concentrations as an indication of diagenetic alteration was carried out at Trinity College Dublin (TCD) on a Reliotron cold cathode stage, mounted on a Nikon binocular microscope (Hemming *et al.*, 1989). Material for elemental and isotopic analyses was obtained as described in Chapter 2 by drilling c. 100 mg of carbonate powder from each slab with a dental drill, targeting well-preserved micritic textures in the plaquettes.

4.3.1 Mass Spectrometer Analysis

A total of 224 samples were analysed for $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ in three laboratories as described in Chapter 2. A subset of 109 carbonate samples were analysed by solution quadrupole ICP-MS at TCD as described in Chapter 2 for 52 major and trace elements, following the digestion methods of Hahn *et al.* (2015), while the ICP-MS analyses follow the experimental design of Eggins *et al.* (1997), with modifications described in Kamber (2009) and Babechuk *et al.* (2010). Several samples were also selected for *in situ* trace element analysis (spot ablations) by LA-ICP-MS at TCD for a total of 24 masses as described in Chapter 2. REE+Y data were normalized to the upper continental crust composite MuQ (Mud from Queensland, Australia, (Kamber *et al.*, 2005). MUQ is a modern alluvial sediment composite analysed using a similar experimental protocol to the solution data produced in this study.

A set of 21 of the 104 powder samples were selected for bulk carbonate-associated sulfate analysis for $\delta^{34}\text{S}_{\text{CAS}}$ at WashU. Approximately 40-80g of powdered sample was used for each sulfate extraction, following a modified version of the procedure of Burdett *et al.* (1989). The powder was soaked in three rinses of 10% NaCl solution for 24 h and rinsed three times in deionized water. It was then reacted with an excess of 3 N HCl to dissolve the carbonate matrix and liberate CAS. The solution was filtered from the insoluble residue via vacuum

filtration and centrifugation in three steps, finishing with a 0.2 mm filter. Saturated barium chloride solution was added to the filtrate to precipitate barium sulfate for 72h. The precipitate was then rinsed with deionized water and isolated by centrifugation. The resulting barium sulfate was dried in the lab at room temperature. Isotopic analysis of the sulfate phase was performed using a Costech ECS 4010 elemental analyser coupled to a Thermo Finnigan Delta V Plus mass spectrometer. For each analysis approximately 100 μg of BaSO_4 was loaded into a tin capsule and combusted at 1000 °C. Sulfate sample combustion was catalyzed by the addition of 2 mg of vanadium pentoxide to the sample capsules. Evolved SO_2 gas entered the mass spectrometer in continuous flow mode. Sulfur isotope composition was calibrated against NBS-127, IAEA-S1, and IAEA-S3. Sulfur isotope values are reported in permil (‰) relative to V-CDT (Vienna Canyon Diablo Troilite). Analytical precision was determined to be $< 0.16\text{‰}$ using routine analysis of international $\delta^{34}\text{S}$ standards and internal lab standards.

4.3.2 X-ray Spectrometry

One sample from 41.2 m and 267.2 m and two samples from 268.6 m were chosen for analysis by combined $\mu\text{-XRF}$ mapping and S K-edge XANES (X-ray Absorption Near Edge Structure) data collection at the GeoSoilEnviroCARS (GSECARS) micro-probe beamline 13-ID-E at the Advanced Photon Source at Argonne National Laboratory. X-rays were generated from the 7 GeV APS electron storage ring running at 102 mA, and a 2.1 m long, 36 mm period (57 pole) undulator. A liquid nitrogen cooled, Si(111) double-crystal monochromator was used to select X-rays of the desired energy, and this monochromatic beam was focused to $\sim 2 \times 2 \mu\text{m}$ using silicon Kirkpatrick-Baez focusing mirrors. At the S K-edge (2.472 keV), the flux at the sample was approximately 5×10^{10} photons s^{-1} . Although the beam was nominally monochromatic, a small amount of 3rd harmonic intensity (X-rays with energy 7.4 keV) was allowed through the monochromators and mirrors in order to deliberately excite elements between S and Fe. Resulting X-ray fluorescence was measured with a Vortex Me-4 silicon drift-diode detector array with digital signal processing electronics from XIA. The sample and path for incident beam and for fluorescence from sample to the detector was kept in a bag purged with helium to reduce attenuation of the X-rays by air. For XRF mapping, the sample was moved back and forth through the beam, collecting full XRF spectra at 30 to 100 msec intervals. Pre-defined regions of the XRF spectrum corresponding to the $\text{K}\alpha$ emission lines for S, Ca, Mn, and Fe were extracted from

the full spectra at each point to make maps of elemental distribution. Although these were not corrected and standardized to give absolute abundances, there are no significant artefacts to complicate the relative concentrations shown in each map.

On completion of each μ -XRF map, XANES data were collected from point selection on mapped sample areas before completion of each experiment. Sulfur K-edge XANES measurements were optimized to produce distinguishable absorbance spectra from the analysis of samples containing sulfate, sulfide, or both. XANES measurements were stepped in energy across the S K edge, nominally at 2.472 keV (Fig. 4.2). Steps of 0.15 eV were taken in the energy range between 2.465 and 2.495 eV to give fine resolution in distinguishing sulfate from sulfide and other S phases (Fig. 4.2). These spectra are sensitive to an array of S species. Four maps of the distribution and relative abundance of CAS within complex sedimentary carbonates were produced with the intention of improving understanding of how this proxy is incorporated, and subsequently altered, in geologic samples.

All X-Ray absorption spectroscopy data were processed using standard methods in SIXPACK (Webb, 2005). Data were background subtracted using a linear pre-edge region (up to 2.465 keV) and a linear post-edge (after 2.495 keV). Processing of XRF maps was performed in the MicroAnalysis Toolkit (Webb, 2011). Images were corrected as needed for incident intensity variations and then the data was smoothed using a 5x5 Gaussian kernel with a 0.80 pixel FWHM to improve counting statistics and signal to noise.

Fig. 4.1 Stratigraphic record with chemostratigraphic proxies for the upper La Silla Formation and the San Juan Formation at Cerro La Silla, the type section of the San Juan Formation. $\delta^{18}\text{O}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{carb}}$, (error $< 0.3\text{‰}$ (1σ) $\delta^{13}\text{C}_{\text{carb}}$ and $< 0.5\text{‰}$ (1σ) $\delta^{18}\text{O}_{\text{carb}}$). Mn, Sr solution-ICP-MS data (precision 2-3%, accurate to 5%) and $\delta^{34}\text{S}_{\text{CAS}}$ (precision $< 0.16\text{‰}$). The figure includes both $\delta^{34}\text{S}_{\text{CAS}}$ data from this study (black markers) and previous studies (red markers, Thompson and Kah, 2012).

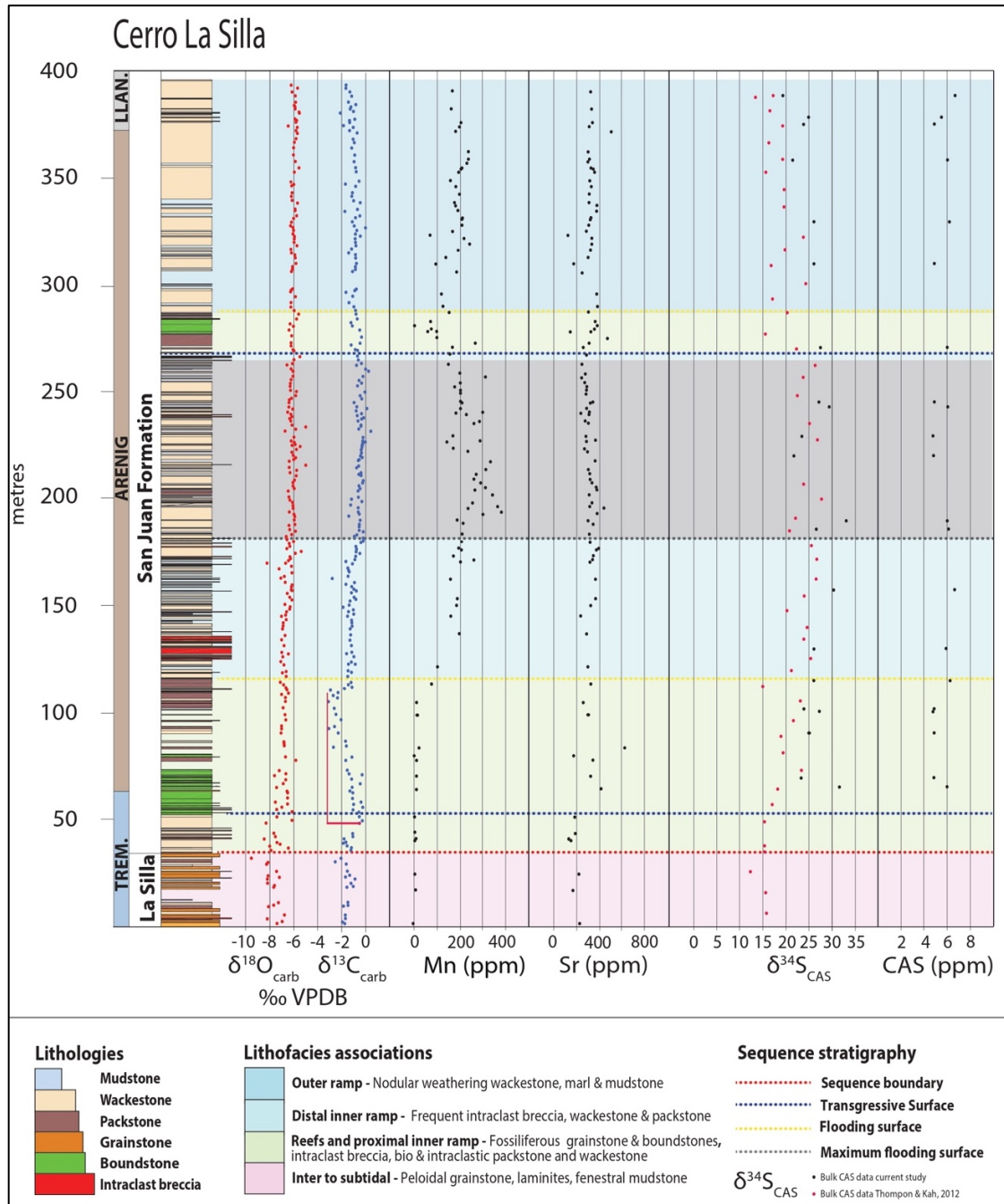
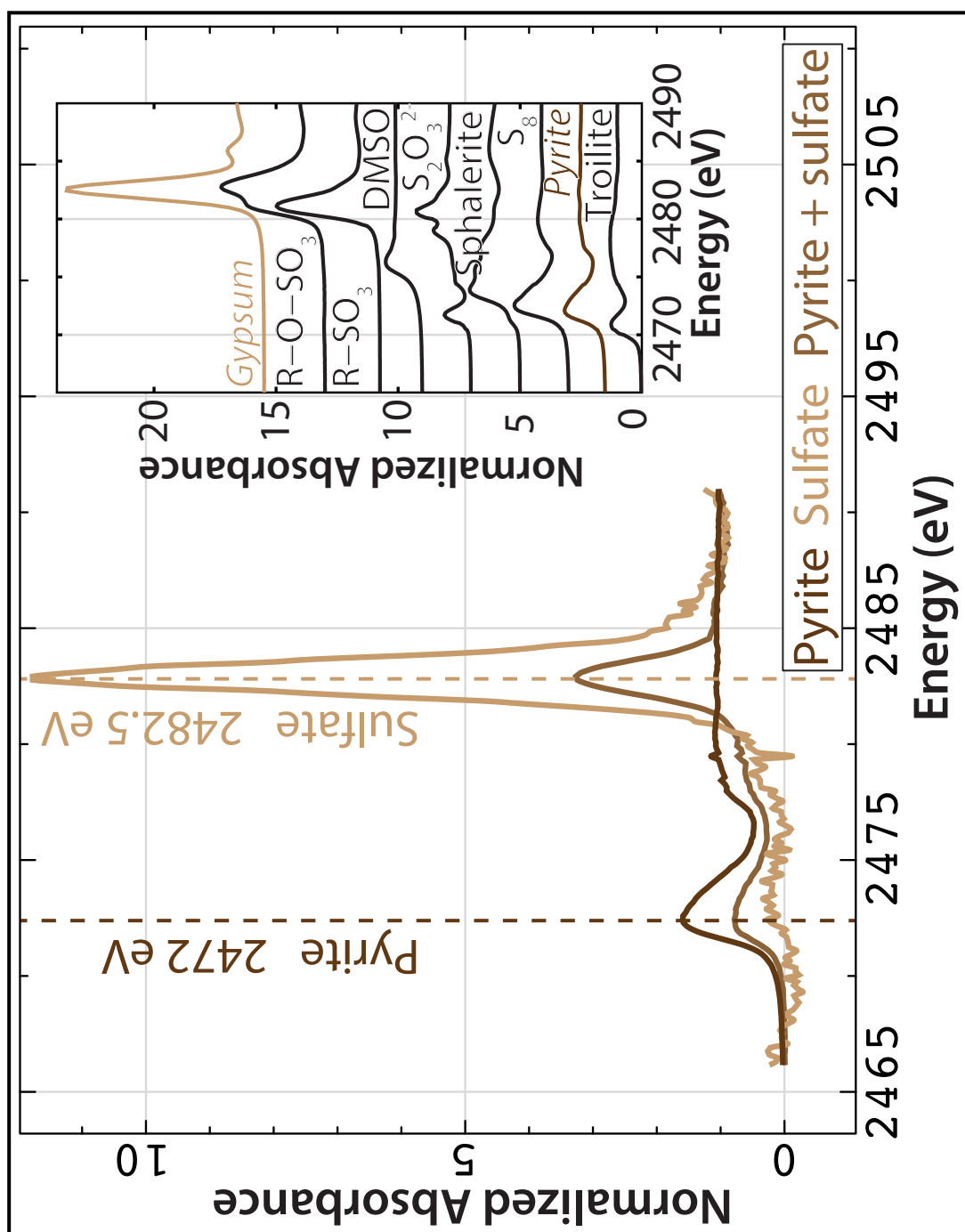


Fig 4.2: X-ray Absorption Near-edge Structure (XANES) measurements across the S K-edge resolved sulfate from sulfide and other S phases. Spectra position are from a crinoidal grainstone analysed in Rose *et al.* (2019).



4.3.3 LA-ICP-MS Mapping

A total of 16 individual element maps and two element ratio maps were created from two separate LA-ICP-MS mapping experiments over the same mapped area for each of the thin sections 41.2, 268.6R and 268.6L. Eight isotopes and nine isotopes were mapped respectively in each experiment with ^{43}Ca employed as an internal elemental standard in each experiment. The following sixteen isotopes were measured: ^{24}Mg , ^{34}S , ^{43}Ca , ^{51}V , ^{55}Mn , ^{57}Fe , ^{88}Sr , ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{165}Ho , ^{172}Yb , ^{232}Th , ^{238}U . LA-ICP-MS mapping methodology is described in detail in Chapter 3.

4.4 Results

4.4.1 Stratigraphy and carbonate petrography

Sample 41.2 was taken from the lowermost San Juan Formation, which begins 35 m from the base of the measured section (Keller *et al.*, 1994; Keller, 1999) and includes fenestral mudstones and wackestones, interpreted as consistent with back-reef lagoonal deposits (Keller *et al.*, 1994; Lehnert, 1995; Keller, 1999). Petrographical observations (Fig. 4.3A) show that sample 41.2 is composed of peloidal syndepositional moldic pseudospar (Ps) with relict textures of micritic infill (M) of gastropods; an initial phreatic isopachous spar cement (C1) on the rims of peloids/filling the tight pore space between clasts; and a subsequent mosaic cement occluding remaining porespace (C2). The C2 spar has replaced the aragonite gastropod shells and relict shell morphology is visible (Gs).

From c. 50 m above the base of the section there is a transition to cross-bedded packstones, mottled grey to dark-grey wackestones and sponge-algal boundstone reef mounds (Fig. 2.5B) (Cañas and Carrera, 1993; Keller and Flügel, 1996). Fossil fragmentation and intercalcation of cross-bedded packstones (Fig. 2.5c) and grainstones indicate turbulent, shallow conditions and occur with frequent graded beds with erosive bases and intraclasts up to 20 mm, interpreted together as formed in high-energy storm events (“intraclast breccia”) (Figs 4.1 and 2.5D). The sequence from 50 m is interpreted as representing a sponge-algal reef and proximal facies above fair-weather wavebase (Fig. 4.1) that was periodically affected by storms. This facies continues up section to c. 80 m, before transitioning to cross-laminated bioclastic and intraclastic packstones and intraclast breccia storm-beds above fair-weather wave base.

Evidence for transitional deepening to below fairweather wave base is shown by a lack of crossbedding above c. 110 m (Fig. 4.1), with persistent intraclast breccia beds indicating that facies remain above storm wave base. This facies corresponds to the mid-ramp facies of Keller (1999) and the deepening event is marked by a change from warm-water to temperate water conodont forms (Lehnert, 1995). Fauna above 110 m in the mid-ramp facies include gastropods, rare orthoconic nautiloids, brachiopods, crinoids, trilobites and green algae species that indicate a marine facies remaining in the photic zone (Keller, 1999). Deepening to below storm wave base occurs at c. 178m (Fig. 4.1) and is represented by facies with very rare to absent intraclast breccia and with stylolitic yellow-brown, silty wackestones with

distinctive weathering such as the nodular limestone on Fig. 2.5E (Cañas, 1999; Keller, 1999). Lehnert (1995) assigned this deepening phase to the base of the *O. evae* conodont zone, with a faunal change to colder, deepwater fauna. Facies pass above storm wave base at 261m, rapidly followed by further shallowing to above fair-weather wavebase at 263m.

Sample 267.2 was taken from a fossiliferous packstone bed above fairweather wavebase. The thin section (Fig. 4.3B) includes a large (c. 2 mm) trilobite fragment (Tr) with good textural preservation, a dasyclad green algae fossil (Al), fossil fragments and a syndepositional micrite fill (M). Many peloidal micritic components occur. An isopachous phreatic cement phase (C1) is located on the rims of allochems and a later occluding cement (C2) fills the porespace. There is evidence that some of the components may have been reworked, with both a thin allomicrite coating and internal fill (Gp) encased in the C1 cement phase with the large trilobite fragment (Fig. 4.3B). Evidence of micro-borings and micritisation is also present on a number of fossil margins, with varying penetration into shells from their edges (Bo).

The two thin sections 268.6L and 268.6R (Figs 4.3C and 4.3D) were taken from a single hand sample 6cm apart along an individual bedding plane. Both thin sections consist of a peloidal bioclastic wackestone and include microbial (Mb), crinoid, (Cr) trilobite (Tr) and other fragmented bioclasts, micritic peloids and intraclasts (M) and extensive cement phases. There are two visible cement phases: a phreatic isopachous phase on the rim of allochems (C1), and a later extensive (C2) occluding spar.

Dark grey, mottled sponge-algal and stromatoporoid framestone reef mounds (Keller *et al.*, 1993), containing crinoids, gastropods and brachiopods occur from 273m and have been interpreted as patch reefs (Fig. 4.1). The reef mounds are interbedded and overlain by cross-bedded crinoidal packstones and grainstones representing channels and shoals in proximity to the reef (Keller, 1999)(Fig. 4.1). Above the reef facies from 285m there is a deepening to facies below storm wave base that continues to the top of the section with the exception of a short, six-metre interval of grainstone at c. 372m (Fig. 4.1). The top of the San Juan Formation, a transition to overlying deeper basinal facies of interbedded shales and organic rich limestones, is not exposed at Cerro La Silla.

4.4.2 Geochemical Results

Geochemical results are presented in Table 4-1 (carbon, oxygen and sulfur isotope ratios and solution ICP-MS elemental values), Table 4-2 (Monocle elemental semi-quantitative concentration measurements) and Table 4-3 (Elemental covariation data derived from Monocle). The stable isotope chemostratigraphy for $\delta^{18}\text{O}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ is shown in Fig. 4.1.

4.4.3 Chemostratigraphic Data

The carbon and oxygen isotope systematics only exhibit modest variability and little covariation (Fig. 2.6; $r^2 = 0.19$, p-value < 0.0001 , $n = 273$) as described in Chapter 2.4.2. Bulk $\delta^{34}\text{S}_{\text{CAS}}$ results exhibit a mean value of 25.5‰ (SD = 3.2‰, $n = 34$) with a range of 18.9 to 32.9‰ and exhibit secular variation at both long and short stratigraphic distances through the section (Fig. 4.1). There is a clear overall negative trend moving up-section. Values between 23‰ and 32‰ occur in the lower reef, with a short increase to 32.8‰ at 190.3m before decreasing to a nadir value of 18.9‰ at the top of the section. The combined dataset from the full measured section shows no covariation between $\delta^{34}\text{S}_{\text{CAS}}$ and either $\delta^{18}\text{O}_{\text{carb}}$ or $\delta^{13}\text{C}_{\text{carb}}$ ($r^2 = < 0.01$, p-value 0.75, $n = 17$; and $r^2 = < 0.01$, p-value 0.79, $n = 17$). Manganese and Sr trace element data are shown in chemostratigraphic plots in figure 2.4. The Mn and Sr data are considered consistent with post-depositional fluid:rock interaction of insufficient magnitude to alter $\delta^{13}\text{C}_{\text{carb}}$ (herein referred to as well-preserved). A further discussion of the preservation state is contained in Chapter 2 paras. 2.4.2 and 2.5.2.

4.4.4 Micron-scale analysis

The distribution of sulfate and sulfide in thin sections 41.2, 268.6R, 268.6L and 267.2 are presented as XRF maps in Figs 4.4 to 4.7. Statistical covariation analysis of samples 41.2, 268.6R, 268.6L and 267.2 was carried out across the mapped region for the elements analysed by XRF mapping and are presented in the SOM.

A selection of LA-ICP-MS maps (Mn, Sr, Th, U and Fe) that correspond to the areas mapped by XRF for thin sections 41.2, 268.6R and 268.6L are also shown in Figs 4.4 to 4.7. Measurements of the semiquantitative data in the selected regions of interest (ROI) for the 16 recorded isotopes was carried out using the data extraction tools in Monocle and are

presented at Table 4-2. Combined, the LA-ICP-MS and x-ray spectrometry maps give a strong initial visual indication of the heterogeneity in major and trace elements, sulfate and sulfide between and, in some cases, within the micrite, fossil and cement components.

In sample, 41.2 sulfate (Fig. 4.4B) is locally in moderate abundance in the C1 cement on clast edges and in micron-scale, recrystallized fossil fragments (which are also low in sulfide) within the micritic peloid clusters. Sulfide (Fig. 4.4C) is mostly absent from the cement phases in sample 41.2 and is relatively low in abundance in the peloidal pseudosparitic micrite, with discrete higher concentration points within the peloidal material that have no discernable textural basis and are likely to represent rare disseminated sulfides.

The LA-ICP-MS Sr map (Fig. 4.4H) for sample 41.2 records low Sr values in all constituent components, decreasing from a maximum measurement of 171.8 ppm (SD = 3.2 ppm) in the allomicrite to 60.7 ppm (SD = 1.8 ppm) in the C2 cement and with a mean overall concentration of 128 ppm (SD = 41 ppm, n = 35). Mn concentrations (Fig. 4.4I) in all components in sample 41.2 are very low with a mean value of 8.65 ppm (SD = 0.95 ppm, n = 13) in allomicrite, a mean of 8.62 ppm (SD = 0.79 ppm, n = 11) in the C1 spar and a mean of 8.15 ppm (SD = 0.69 ppm, n = 13) in the C2 spar. Fe concentrations are very low and range from a mean 129 ppm in the C2 spar (SD = 19 ppm, n = 13) to 157 ppm (SD = 31 ppm, n = 11).

In samples 268.6L (Fig. 4.5) and 268.6R (Fig. 4.6), sulfate (Fig. 4.5B and 4.6B) is moderately enriched in the peloidal micritic phase and fossil fragments, less enriched (with the exception of local discrete points) in early cements and depleted in the later cement. Both samples show a similar strong distribution of disseminated sulfides (Figs 4.5C and 4.6C) on clast edges with multiple discrete points of enrichment throughout the peloidal micritic phase. Lower concentrations occur in the C1 cement and lower again in the C2 cement phase. Sulfide occurs alternating with sulfate at a fine scale (<10 μ m) in the brachiopod fragment in 268.6L, with local enrichment cooccurring with microbial textures at the upper face of the fossil fragment at the top of the map (Fig. 4.5C). A trend of decreasing Sr from fossils, allomicrite and C1 cements, which are of a similar magnitude, to the C2 cement is evident in samples 268.6R (Fig. 4.6G). In the same sample Sr has a mean value across all components of 306 ppm (SD = 64 ppm, n = 21) but is higher in the allomicrite phase at 313 ppm (SD = 24 ppm, n = 7) and fossil components at 327 ppm (SD = 33 ppm, n = 6). Strontium abundances are only slightly depleted in the early C1 cement at 318 ppm (SD = 12, n = 4) and significantly

more depleted in the C2 cement at 243 ppm (SD = 79 ppm, n = 4). Mn (Fig. 4.6F) has a mean overall value of 164 ppm (SD = 17 ppm, n = 21) and mean values ranging from 156 ppm (SD 11, n = 5) in fossils, to a mean value of 183 ppm (SD = 19 ppm, n = 4) in the C2 cement. The full set of semi-quantitative data from Monocle for sample 268.6R indicates that Mn and Sr for all combined components have a negative correlation ($r^2 = 0.83$, p-value < 0.001). This correlation is expected in diagenetic conditions with Sr loss and Mn incorporation occurring during early burial (Banner and Hanson, 1990). When broken down by component, this correlation is much weaker in the allomicrite phase ($r^2 = 0.29$) but is strongly evident in fossils ($r^2 = 0.65$) the C1 cement ($r^2 = 0.99$) and C2 cement ($r^2 = 0.62$). Fe concentrations are relatively higher in sample 268.6R from 465 ppm in C1 cement (SD = 85 ppm, n = 4) to 1025 ppm in allomicrite (SD = 58 ppm, n = 7).

Sample 267.2 exhibits a similar sulfate distribution (Fig. 4.7B) to sample 268.6R and 268.6L with moderate enrichment in the allomicritic phase (M) and fossil fragments, less enrichment (with the exception of local discrete points) in early cements (C1) and depletion in the later cement (C2). The samples also display a distribution of sulfide (Fig. 4.7C) similar to the samples at 268.6L and 268.6R, with relatively higher sulfide concentrations in allomicrite, although sulfide on the edge of the large trilobite fragment (Tr) is not notable despite a clear occurrence of a Si-rich micrite coating (Fig. 4.7D). The trilobite fossil displays a number of discrete linear penetrations of sulfide on the left side of the fossil (Bo) and low concentrations of sulfide (Fig. 4.7). In addition, sulfate variability in the trilobite fragment is observed to decrease moving from the inner to the outer lower-right edge where sulfide concentrations display a decrease across the shell that appears to be inversely correlated with sulfate concentration. Locally increased abundance of sulfate is visible within the peloid in the bottom right of the sample. A trend of decreasing Sr from fossils to allomicrite, C1 cement and C2 cement is evident in both samples 268.6R (Fig. 4.6F) and 267.2 (Fig. 4.7F).

Fig. 4.3: (a) Sample 41.2 Peloidal gastropod (Gs) packstone above fairweather wave-base. Components include allomicrite peloids (M) neomorphosed to pseudospar (Ps), C1 isopachous cement, C2 occluding mosaic spar; (b) Sample 267.2 Peloidal bioclastic packstone above fairweather wave-base. Components include allomicrite peloids (M), geopetal fill (Gp) and fossils including trilobite (Tr) and dasyclad algae (Al), C1 isopachous cement, C2 occluding mosaic spar; (c & d) Samples 268.6R and 268.6L Peloidal bioclastic packstone above fairweather wave-base. Components include allomicrite peloids (M), brachiopod (Br), microbial (Mb), crinoid, (Cr) and trilobite (Tr) fossils. Evidence of micro-boring and related micritisation is also present on a number of fossil margins, with varying penetration into shells from their edges (Bo). There are two visible cement phases: a phreatic isopachous phase on the rim of allochems (C1), and a later extensive (C2) occluding spar.

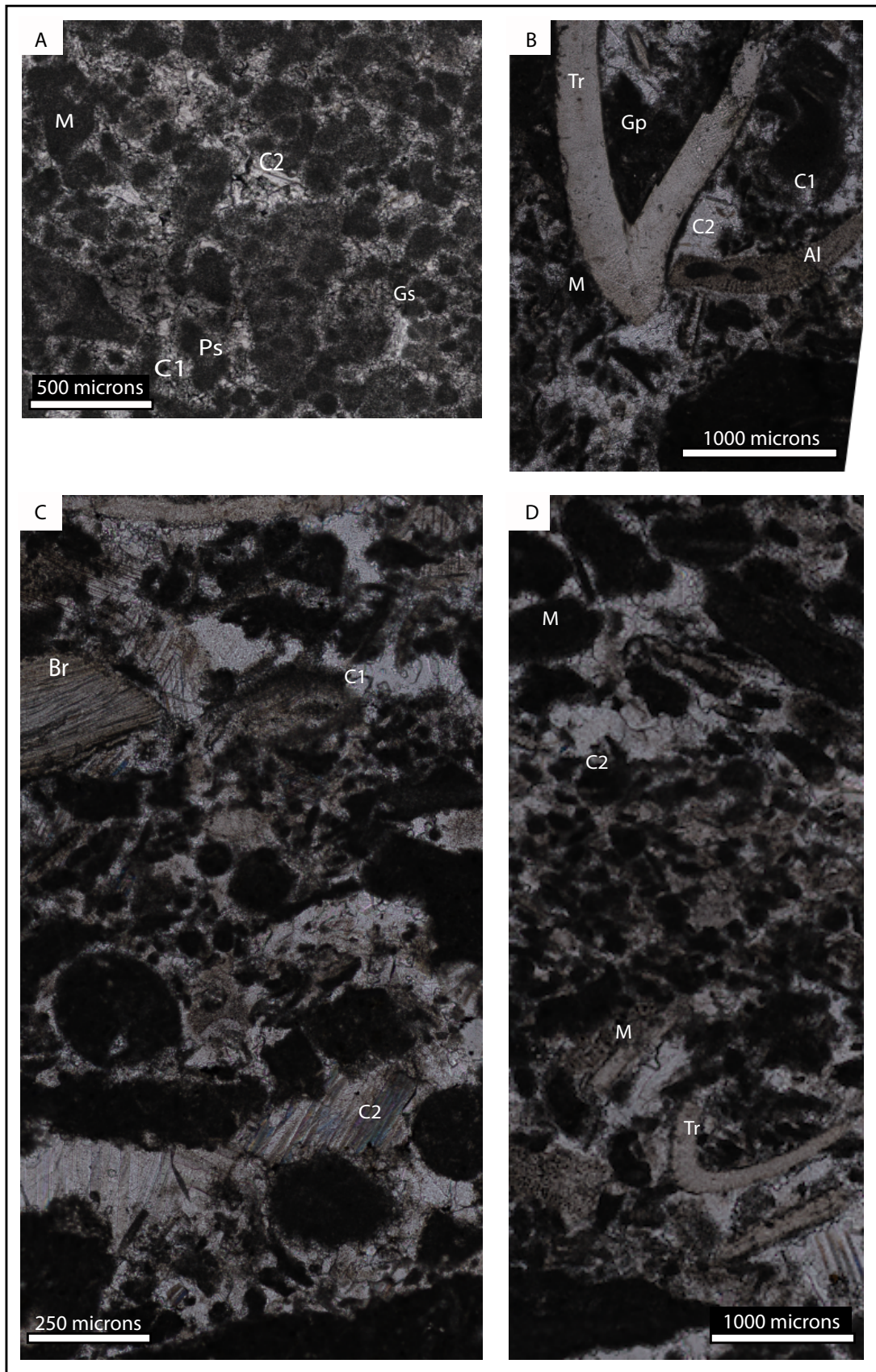
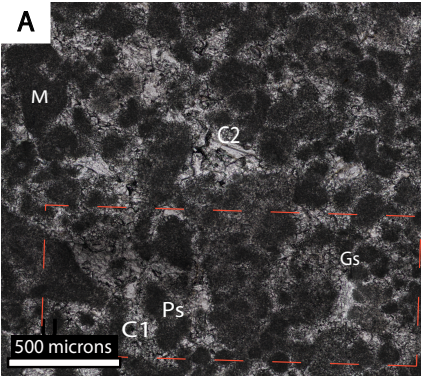
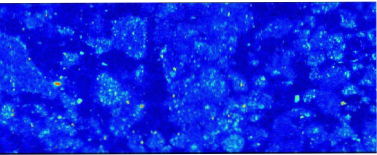


Fig 4.4: Sample 41.2: (A) Peloidal gastropod packstone above fairweather wave base. X-ray spectrometry maps of speciation distribution and LA-ICP-MS maps of elemental concentrations are shown as follows: (B) Sulfate, which is more abundant in fossils and allomicrite and much lower in the C1 and C2 phases. The C1 isopachous cement phase exhibits higher sulfate abundances than the low, near detection limit, levels in the later C2 occluding equant spar; (C) Sulfide is largely absent from the C1 and C2 intergranular cements and is at greater levels in the allomicrite and fossils; (D) Distribution of elemental Fe, (E) Distribution of Si; and (F) Th concentrations are very low in the sample and heterogeneous in allomicritic peloids; (G) LA-ICP-MS elemental map for U; (H) Sr concentrations are low and decrease from fossils and allomicrite to C1 and C2 cements in the LA-ICP-MS maps. Comparison of the XRF and LA-ICP-MS maps show a clear correlated trend of decreasing sulfate abundance from the highest Sr components to lowest Sr components (I) LA-ICP-MS elemental map for Mn. Concentrations are very low in all components.

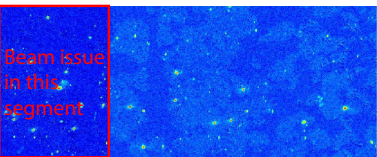
Cerro La Silla - Sample 41.2



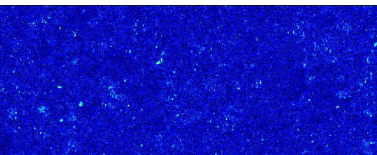
B. Sulfate



C. Sulfide



D. Fe



E. Si

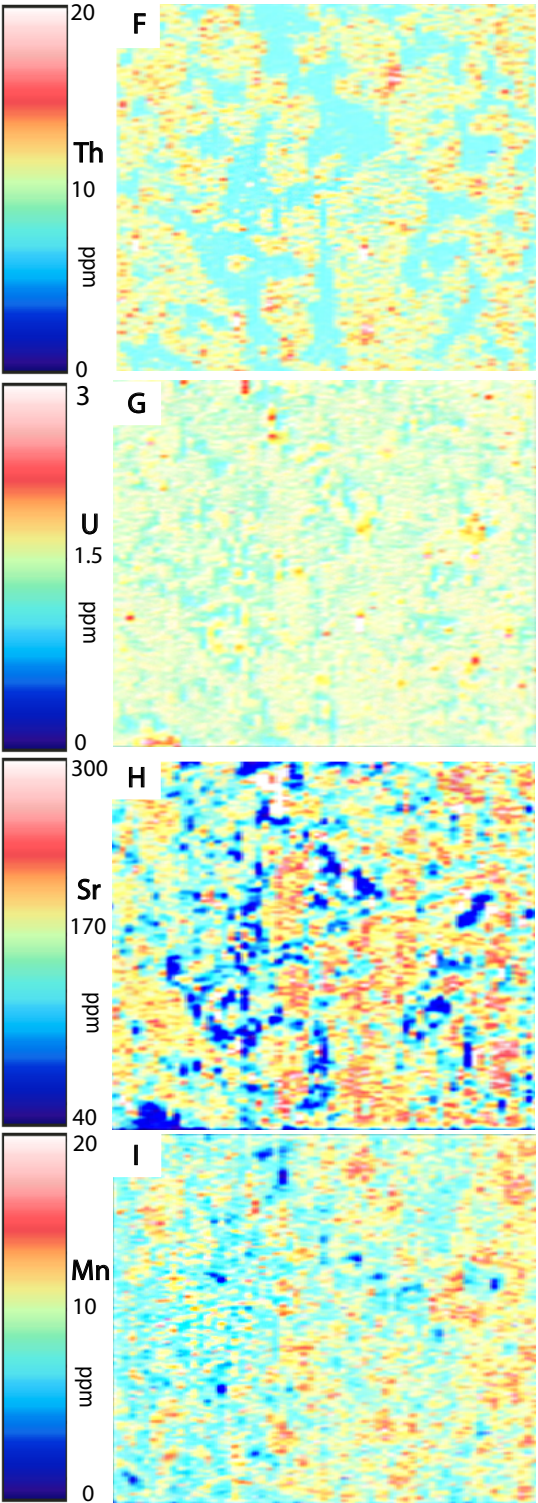
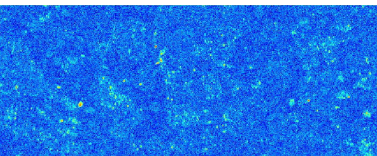


Fig 4.5: Sample 268.6L: (A) Peloidal bioclastic packstone above fairweather wave base. Components include allomicrite peloids (M), brachiopod (Br), C1 isopachous cement, C2 occluding mosaic spar. X-ray spectrometry maps of speciation distribution and LA-ICP-MS elemental maps are shown as follows: (B) Sulfate, which is more abundant in fossils and allomicrite and much lower in the C1 and C2 phases. The texturally well-preserved brachiopod fragment in sample 268.6L, shows very high relative sulfate levels. The C1 isopachous cement phase also exhibits higher sulfate abundances than the low levels in the later C2 occluding equant spar; (C) Sulfide is largely absent from the C1 and C2 intergranular cements and is at greater levels in the allomicrite and fossils. It occurs alternating with sulfate at a fine scale ($< 10\ \mu\text{m}$) in the brachiopod fragment. Local enrichment in sulfide cooccurs with microbial textures at the upper face of the fossil at the top of the map (Mb); (D) Distribution of elemental Fe; (E) Distribution of Si; and (F) Concentration of Th are greater but heterogenous in allomicritic peloids; (G) LA-ICP-MS elemental map for U; (H) Sr concentrations decrease from fossils and allomicrite to C1 and C2 cements in the LA-ICP-MS maps. Sr concentrations are high in the texturally well-preserved brachiopod as are sulfate concentrations. Comparison of the XRF and LA-ICP-MS maps show a clear correlated trend of decreasing sulfate abundance from the highest Sr components to lowest Sr components (I) LA-ICP-MS elemental map for Mn.

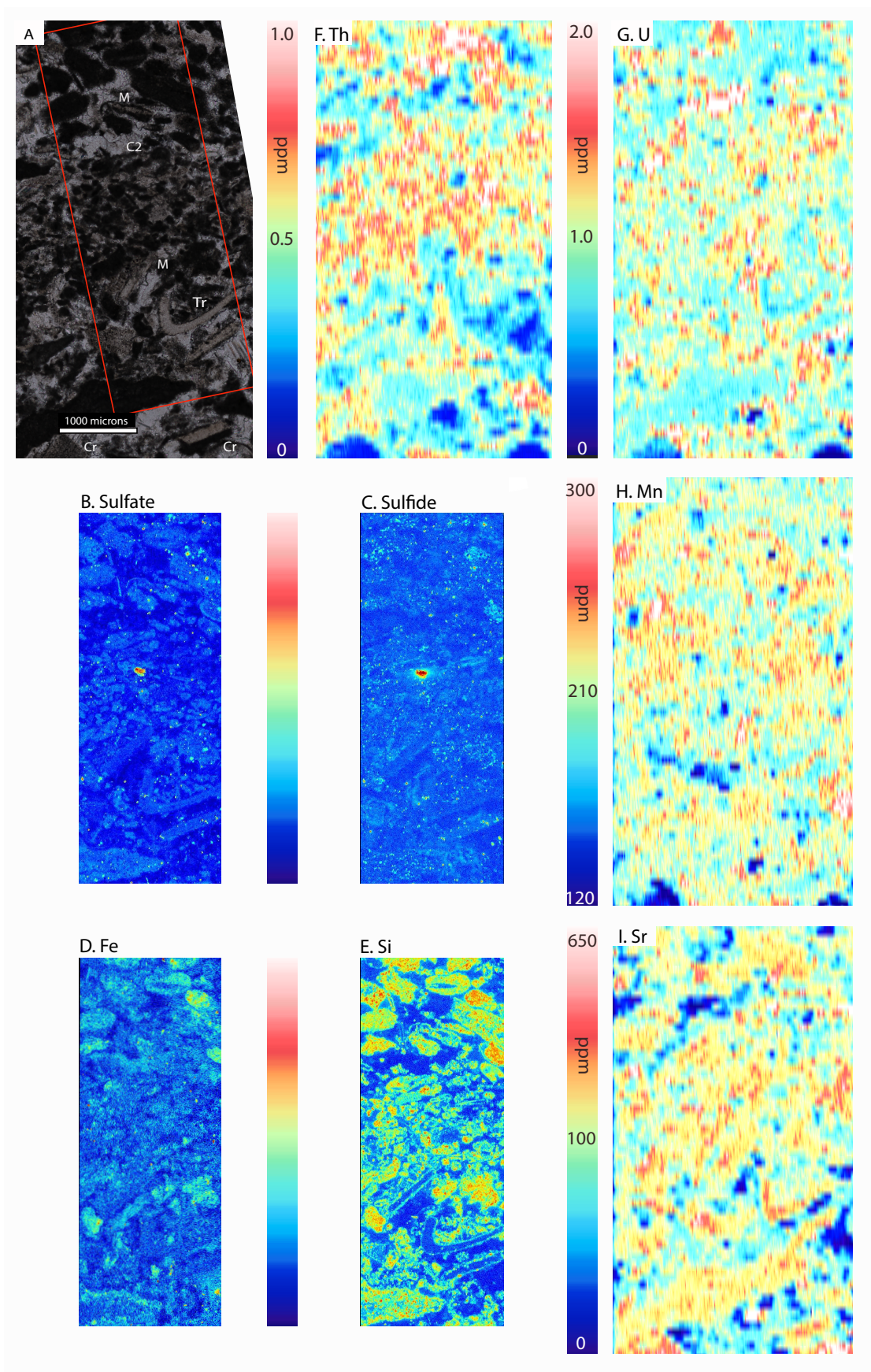


Fig. 4.6: Sample 268.6R: (A) Peloidal bioclastic packstone above fairweather wave base. Components include allomicrite peloids (M), trilobite fragments (Tr), C1 isopachous cement, C2 occluding mosaic spar. X-ray spectrometry maps of speciation distribution and LA-ICP-MS elemental maps are shown as follows: (B) Sulfate, which is more abundant in fossils and allomicrite and much lower in the C1 and C2 phases. The C1 isopachous cement phase also exhibits higher sulfate abundances than the low concentrations in the later C2 occluding equant spar; (C) Sulfide is at relatively low levels in the C1 and C2 intergranular cements and is at greater levels in the allomicrite and fossils. (D) Concentrations of elemental Fe, (E) Si and (F) Th are greater but heterogenous in allomicritic peloids; (G) LA-ICP-MS elemental map for U; (H) Sr concentrations decrease from fossils and allomicrite to C1 and C2 cements in the LA-ICP-MS maps. Lower Mn and higher Sr abundances are apparent in the two crinoid fossils at the base of the slide. A comparison of the XRF and LA-ICP-MS maps shows a clear correlated trend of decreasing sulfate abundance from the highest Sr components to lowest Sr components (I) LA-ICP-MS elemental map for Mn.

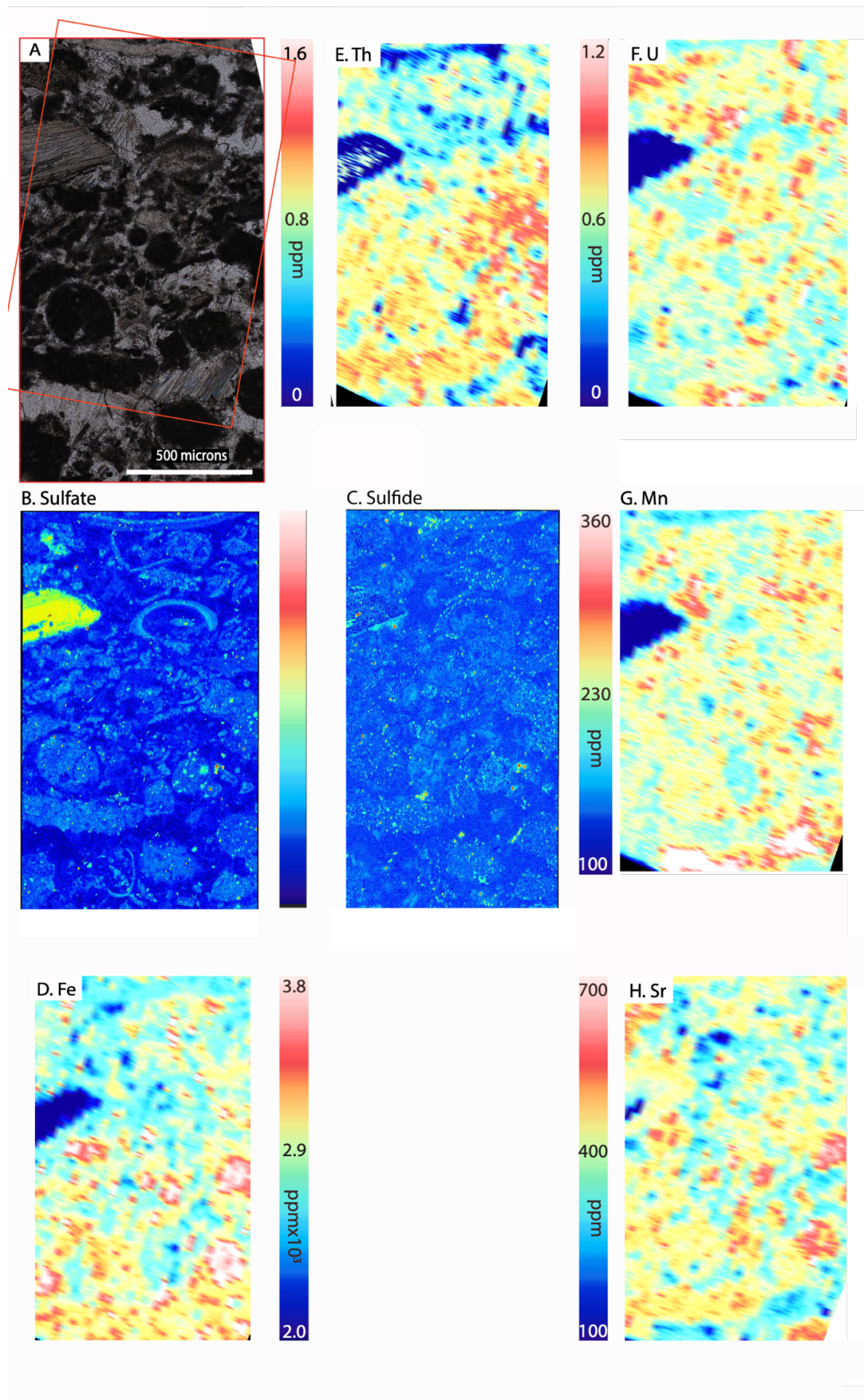
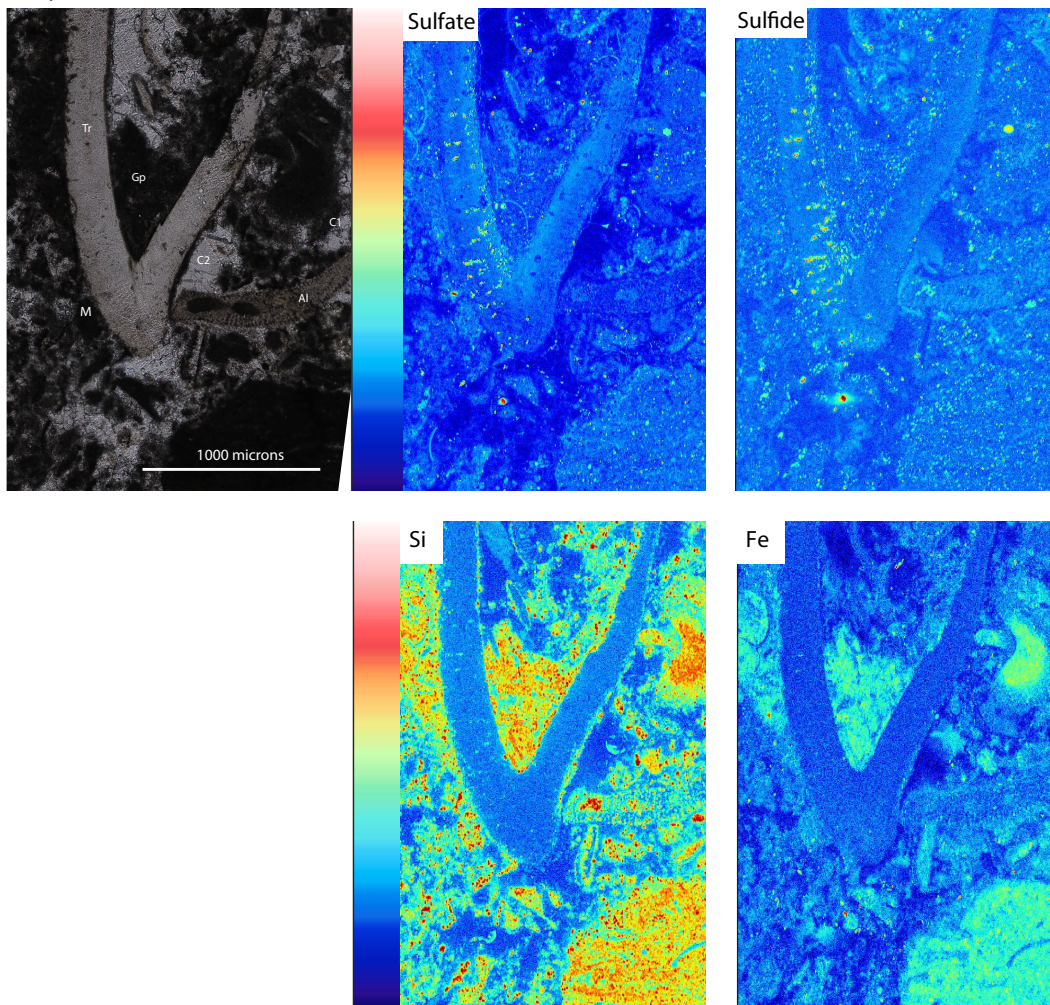


Fig 4.7: Sample 267.2: (A) Peloidal bioclastic packstone above fairweather wave base. Components include allomicrite peloids (M), geopetal fill (Gp) and thin coating on fossils. Fossils include trilobite (Tr) and dasyclad algae (Al)). C1 isopachous cement, C2 occluding mosaic spar. XRF maps are shown as follows: (B) Sulfate, which is more abundant in fossils and allomicrite and much lower in the C1 and C2 phases. There is internal heterogeneity within the micrite fill; (C) Sulfide is largely absent from the C1 and C2 intergranular cements and is at greater levels in the allomicrite and fossils. The large trilobite fragment displays a number of discrete linear penetrations of sulfide on the left side of the fossil (Bo). Sulfate abundance in the large trilobite fragment in sample 267.2 is also observed to decrease moving from the inner to the outer edge with sulfide concentrations displaying an inverse correlated increase (marked by arrows in Tr fossil); (D) Concentrations of elemental Fe; (E) Si; and (F) Th are greater but heterogenous in allomicritic peloids; (G) LA-ICP-MS elemental map for U; (H) Sr concentrations decrease from fossils and allomicrite to C1 and C2 cements in the LA-ICP-MS maps. Comparison of the XRF and LA-ICP-MS maps show a clear correlated trend of decreasing sulfate abundance from the highest Sr components to lowest Sr components (I) LA-ICP-MS elemental map for Mn.

Sample 267.2



4.5 Discussion

4.5.1 Micron-Scale Variability in sulfate, sulfide and trace-element distribution

A range of carbonate components in varying abundances are present in the mapped samples, including fossils, allomicrite and cements phases. The extent of the variability visible in the distribution of sulfate and sulfide in all examined thin sections underlines the need to assess these data at a micron scale with textures and geochemical data that provide information on the water column conditions and porewater processes occurring during and post-deposition (Richardson *et al.*, 2019; Rose *et al.*, 2019). In order to use $\delta^{34}\text{S}_{\text{CAS}}$ data to reconstruct marine geochemistry through the geological record it is critical to identify which of the components preserve primary marine chemical data – either as texturally well preserved primary carbonate components, i.e. those that precipitate within seawater, or within sediment that is in open connectivity with seawater (Claypool, 2004; Richardson *et al.*, 2019), or as primary components that have undergone some diagenetic alteration but insufficient to alter the primary $\delta^{34}\text{S}_{\text{CAS}}$ (Brand and Veizer, 1980).

Recent studies utilizing XRF mapping and XANES have enabled quantification of sulfate concentrations and distributions in carbonates (Rose *et al.*, 2019). The value of LA-ICP-MS mapping as a supplementary tool is predominantly to understand trace and major element distribution between and within components with the added value of extracting semi-quantitative data using Monocle (Petrus *et al.*, 2017). Compared to x-ray spectrometry, the spatial resolution of LA-ICP-MS is larger as it is limited by the large analytical beam size (typically 47 μm in this study) required for low abundance REE measurements in carbonates. However it permits rapid acquisition of elemental distribution data for a range of elements and has a relatively shallow ablation depth compared to spot analysis which may be advantageous in analysis of thin carbonate phases (Petrus *et al.*, 2017).

The extent to which the mapped components incorporate primary marine geochemical signals and the impact of altering processes in those components is considered below for each component class before the discussion of the implications for $\delta^{34}\text{S}_{\text{CAS}}$ for the measured stratigraphic section. The formation process of marine carbonates is broadly understood, from formation of primary components, abiotic or biotic in the water column or at the seafloor, through deposition and lithification (Richardson *et al.*, 2019). Lithification proceeds through precipitation of pore-filling cements and neomorphism (recrystallisation) of

components, which may occur at different rates and in porewaters of different and evolving chemical compositions, depending on multiple factors during shallow to deep burial (e.g. Swart, 2015). Progressive oxidation of organic matter in sediments is expected to occur as it moves through various redox zones during burial, thereby contributing to the evolving porewater conditions (Aller, 2014). The rate of contemporaneous cement formation will determine the redox conditions and chemistry recorded in the precipitating cements or in cements in recrystallised components (Rose *et al.*, 2019). We consider the sulfate, sulfide and trace element composition of our samples within this framework, beginning with cements to better understand the lithification processes that have occurred, before consideration of the preservation state of the depositional phases present (fossils and allomicrite) and comparison of these results to bulk $\delta^{34}\text{S}_{\text{CAS}}$ data from the stratigraphic section.

4.5.2 Cement phases

All four samples in this study exhibit petrographically identifiable cement phases including an initial C1 isopachous rim on clasts and a subsequent C2 occluding spar of both equant and drusy morphologies (Fig. 4.3). Whilst cement phases may form on the seafloor, they more typically form initially in shallow sub-surface porewaters (Flügel and Munnecke, 2010) with later occlusion of any remaining porosity. Early marine cements that form at the sediment water-interface are not present in the studied samples. The isopachous cement rims are consistent with phreatic, sub-surface, precipitation during shallow burial, followed by an occluding cement phase whose timing, other than its formation subsequent to the C1 cement based on its pore filling position, is not petrographically constrainable. However, in a number of samples its similar composition to the C1 phreatic cement phase suggests that it precipitated in the same but more evolved shallow meteoric porewaters.

In sample 41.2 at the base of the stratigraphic section there are very low concentrations of siliciclastic associated Th with low concentrations of Mn and Sr (Figs. 3.3 and 4.4). Concentrations decrease from fossils and allomicrite to C1 and C2 cements (Fig. 4.4F to 4.7F), consistent with an increasing meteoric component in porewaters with burial. Sr concentrations decrease from the allomicrite phase (154 ppm, SD 4.2) to very low concentrations in the C1 and C2 cements (130 ppm, SD 7.6 and 104 ppm, SD 32 respectively). The bulk data from micrite powder in the same sample contains 143 ppm Sr, suggesting that the bulk sample may contain predominantly mixed allomicrite and C1 cement. Whilst primary mechanisms for variation of Sr in the global ocean were considered

in Chapter 2 (De Villiers, 1999), the use of micron scale LA-ICP-MS mapping in Chapter 3 clarifies that the sequential decrease in Sr from the allomicrite to the C1 and C2 cements (see Chapter 3) is most likely to be attributable to brackish porewater formation of phreatic cements in this sample (41.2). Combined solution ICP-MS and LA-ICP-MS mapping analysis carried out in Chapter 3 established that both Mn and Fe concentrations are very low in samples below the lower reef in the San Juan Formation and in the upper La Silla Formation where there is evidence of both phreatic cement precipitation in brackish porewaters and minimal evidence of siliciclastic inputs.

The allomicrite and C1 isopachous cement phases in sample 41.2 exhibit higher sulfate abundances than the low, near detection limit, concentrations in the later occluding cements (Figs. 4.4B to 4.7B). This progressive decrease in sulfate in cement phases is consistent with the depletion of sulphate by MSR in porewaters during burial but, when considered in light of the progressive Sr decrease indicating brackish porewater, may also represent mixing of watercolumn sulfate with low sulfate brackish porewaters during progressive early burial. Sulfide is largely absent from the C1 and C2 intergranular cements (Figs. 4.4C to 4.7C) in sample 41.2 and is at greater concentrations in the peloidal allomicrite. Low sulfide concentrations may relate to low levels of MSR occurring in porewaters due to absence of organic matter (Habicht and Canfield, 1997), an absence of Fe^{2+} to fix the H_2S produced by MSR or the absence of anoxic burial conditions for MSR (Aller, 2014). Manganese is only found in trace quantities in oxic seawater and primary marine carbonates. It is preferentially retained relative to Sr during meteoric diagenesis and is abundant in anoxic fluids so that its abundance can increase in carbonates recrystallized in the presence of anoxic fluids (Brand and Veizer, 1980). The extremely low Mn concentrations and the reduced Sr concentrations in sample 41.2 therefore suggest that cement formation occurred in brackish, oxic porewaters in conditions with very little siliciclastic input (Figs 4.4E and 4.4F). This is likely to have occurred in shallow, energetic conditions, here evidenced by cross-bedded textures through the backreef, reef and proximal shallow ramp facies. In such circumstances any sulfate reduction that does occur during quiescent periods in anoxic conditions is likely to produce H_2S that would be available for reoxidation during reorganisation of the sediment redox column in reworking events and in the absence of Fe or Mn to fix the sulphide produced.

A similar trend of decreasing Sr from allomicrite and fossils toward lower concentrations in the C1 cement and C2 cement is evident in samples 267.2, 268.6R and 268.6L. However, the full set of semi-quantitative data from Monocle for sample 268.6R indicates that Mn and Sr concentrations are greater across all components than in the samples below 110 m. In Chapter 3 samples 113.2 m, 241.6 m and 268.6 m retain relatively high Sr concentrations compared

to sample 41.2. Mn and Sr for all combined components exhibit a strong negative correlation ($r^2 = -0.83$, $p\text{-value} < 0.001$). This correlation is expected in diagenetic conditions with Sr loss and Mn incorporation occurring during burial (Brand and Veizer, 1980). In addition, Mn concentrations are higher in the samples than in the samples at the base of the stratigraphic section and are consistent with marine formation as are the concentrations of shale associated elements. When broken down by component, this correlation does not occur in allomicrite ($r^2 = 0.30$) and is strongly evident in the C1 cement ($r^2 = -0.99$) and C2 cement ($r^2 = -0.62$). Both Sr and Mn are at a level suggesting very minor alteration within the published range for well-preserved marine low Mg calcite by Denison (< 300 ppm, (Denison *et al.*, 1994) but above the more conservative threshold of < 100 ppm (van Geldern *et al.*, 2006). Sample 268.6R therefore exhibits both limited Sr decrease in primary components and Mn gain, most apparent in the C1 and C2 cement phases.

4.5.3 Fossils

The bioclast components present vary between the mapped thin sections. Samples 267.2, 268.6R and 268.6L are faunally diverse and include fragmented ostracods, trilobites, gastropods, brachiopods and crinoids. Recrystallised fossil fragments frequently occur as microspar within the micritic matrix. Daschylad algae also occur indicating deposition within the photic zone. Gastropod fossils are common and constitute a dominant component in sample 41.2 where they have been extensively recrystallised from primary aragonite to low Mg calcite.

The preservation potential of fossils depends in part on their primary composition, with originally low-Mg calcite brachiopods exhibiting stronger textural preservation in the San Juan Formation samples than aragonitic faunae such as gastropods. This is most clearly observed in the large trilobite fragment in sample 267.2, and in the laminated brachiopod fragment in sample 268.6L which are texturally better preserved than the gastropod fossil in sample 41.2. In that sample gastropods are only discernible petrographically based on relict shell textures within the C1 and C2 cements and the allomicritic casts of their former shell-fill. Diagenetic proxies for diagenetic alteration of fossils, such as cooccurrence of higher Sr and lower Mn are also highlighted well in the LA-ICP-MS maps of 268.6L and 268.6R, (Fig. 4.5 and Fig. 4.6) for example in sample 268.6R (Fig. 4.6) two crinoid fossils at the base of the slide show low Mn and high Sr concentrations, indicating strong preservation.

In the XRF maps of samples 267.2, 268.6L and 268.6R, sulfate is more abundant in fossils and allomicrite than in the cement phases (including the cements within relict gastropod fossils) for the reasons discussed in section 4.5.2. Specific fossils show higher concentrations of sulfate, including the well-preserved brachiopod fragment in sample 268.6L, which shows very high relative sulfate abundances. Sulfate abundance in the large trilobite fragment in sample 267.2 is observed to decrease moving from the inner to the outer edge with sulfide concentrations displaying an inverse correlated increase. Sulfide occurs within fossils in all samples and on grain surfaces and is present in samples 268.6L and 268.6R in the ostracod fossil fragments and in the large trilobite fragment in 267.2, which displays a number of discrete linear penetrations of sulfide on the left side of the fossil (Fig. 4.7). This may be related to shell boring based on the morphology of the sulfide running inward from the shell edges. In smaller fossils micritic envelopes indicate that boring faunae were present. Sulfide also occurs alternating with sulfate at a fine scale ($< 10\ \mu\text{m}$) in the brachiopod fragment in 268.6L. Local enrichment in sulfide cooccurs with microbial textures at the upper face of the fossil at the top of the map (Fig. 4.6). In sample 41.2 there are no texturally well-preserved fossils – however, as discussed at Chapter 4.5.3 in the recrystallized gastropods there is a correlated minimal level of sulfate, sulfide, Sr, Mn and Fe consistent with phreatic cement formation from oxic, brackish porewaters.

Overall the clearest potential source of unaltered data in the XRF maps is the well preserved brachiopod fragment, with its strong textural preservation, high Sr concentration and high sulfate abundance. This is consistent with similar observations in Richardson (2019) and supports the potential of low-Mg brachiopod shell material as a source of primary sulfate sulfur isotope information. However, more research is needed on extant brachiopods, as biotic effects during sulfate incorporation to the organism, including the potential occurrence of sulfur isotope fractionation, are not currently well understood (Burdett *et al.*, 1989; Cuif *et al.*, 2003; Cusack *et al.*, 2008; Yoshimura *et al.*, 2013).

4.5.4 Allomicrite

Allomicrite is present in all samples, as shell in-fill, peloids and coated grains. The depositional nature of the allomicrite fill can be clearly seen in geopetal infilling textures (for example within the large trilobite fragment in sample 267.2). Allomicrite shows varying degrees of textural preservation between samples, including neomorphism of allomicrite to pseudospar in sample 41.2.

Allomicrite presents interpretative problems due to visible internal heterogeneity of sulfate and sulfide. As noted in Rose *et al.* (2019), quantifying spatial variability within sulfate in micritic textures is critical because micrite is often targeted as a homogeneous component assumed to passively record ocean biogeochemical signals (Kaufman *et al.*, 1991; Saltzman *et al.*, 1998; Kump *et al.*, 1999). In all samples sulphide is more abundant in the micrite phase than in the cement phase, which may be due to greater organic matter and therefore MSR occurring in the former. Sulfide is also relatively low in the micrite in sample 41.2 compared to micrite in the other samples in this study, and this may be related to the lack of Fe in the sample, lack of organic matter or disruption of reducing conditions required for anaerobic microbial sulfate reduction. There is evidence from the C1 and C2 cement composition (section 4.5.2) that much of the cement formation occurred in oxic porewater conditions.

In sample 41.2 microspar precipitation is evident through much of the allomicrite texture. This corresponds to a low and more homogenised abundance of sulfate in the XRF map compared to the other samples in the study. There are very low Mn and Sr concentrations in the LA-ICP-MS maps and a near absence of shale input. As there is evidence that cement phases in the sample were formed in frequently reworked, oxic conditions, in the absence of Fe and Mn, greater sulphide oxidation is expected where periodic reorganisation of the redox column occurs (Aller, 2014). This is likely to contribute to a greater magnitude of sulfide oxidation to secondary sulfate within the components in sample 41.2. Alternatively, Fe and Mn starved conditions may have meant pyrite was not formed whilst sulfate was consumed by MSR. Sulfide oxidation has been suggested as a probable cause of light $\delta^{34}\text{S}_{\text{CAS}}$ values recorded in highly variable data in micro-drilled samples from Anticosti Island (Present *et al.*, 2015, Richardson, 2019). By contrast the allomicrite phase in sample 268.6R and 268.6L retains relatively high Sr and moderate Mn concentrations and siliciclastic indicators of a greater siliciclastic input.

Strontium abundances in fossils and micrite in sample 268.6R are near 400 ppm, consistent with slightly altered calcite compared to a level of > 500 ppm for well-preserved low-Mg calcite (van Geldern *et al.*, 2006). Mn is also at a level suggesting very minor alteration within the published range for well-preserved low Mg calcite by Denison (< 300 ppm, (Denison *et al.*, 1994) but above the more conservative threshold of < 100 ppm (van Geldern *et al.*, 2006).

In samples 267.2, 268.6L and 268.6R the allomicrite contains a relatively high abundance of sulfate compared to the cement components and a similar abundance to many of the fossil components. Composition of sulfate and sulfide is however heterogeneous within the allomicrite phase. In these samples the distribution of sulfide on clast edges with multiple discrete points of enrichment throughout the peloidal allomicritic phase indicates the probable presence of pyrite.

The correlation of Th, Si and sulfide within the allomicrite may also be evidence of the oxidation of shale derived organic matter during MSR to produce sulfide and, in the presence of Fe, form pyrite.

Allomicrite-derived $\delta^{34}\text{S}_{\text{CAS}}$ in samples lithified in frequently reworked oxic conditions (sample 41.2), are therefore potentially more heavily influenced by more negative $\delta^{34}\text{S}_{\text{CAS}}$ derived from sulfide oxidation. This is supported by near-absence of Fe in the solution samples at the base of the section and in sample 41.2, and the near absence of pyrite in sample 41.2, and suggests that the samples may not be a faithful archive of seawater sulfate. The $\delta^{34}\text{S}_{\text{CAS}}$ values in any homogenised bulk samples would be likely to record the light $\delta^{34}\text{S}_{\text{CAS}}$ values of the allomicrite and cement phases. However, where depositional conditions are less disrupted and have a greater Fe component (samples 267.2, 268.6R and 268.6L), oxidised sulfide does not contribute to the sulfate pool and allomicrite values are likely to be closer to those of marine-derived CAS (e.g. Kampschulte and Strauss, 2004; Wotte *et al.*, 2012).

4.5.6 Chemostratigraphic Bulk CAS data in the upper La Silla and basal San Juan Formations

The bulk CAS data in this study exhibits typical high-frequency secular variation over short stratigraphic distances (see Fig. 4.1). Similar scatter is found in previous bulk rock sample studies from diverse locations and time periods (Hurtgen *et al.*, 2002; Kampschulte and Strauss, 2004; Ries *et al.*, 2009; Thompson and Kah, 2012; Wotte *et al.*, 2012; Jones and Fike, 2013; Osburn *et al.*, 2015; Young *et al.*, 2016; Edwards *et al.*, 2018; Richardson *et al.*, 2019; Rose *et al.* 2019) and in micro-drilled samples (Present *et al.*, 2015). Researchers have sought to explain this variation in $\delta^{34}\text{S}_{\text{CAS}}$ datasets by a number of mechanisms, including the oxidation of pyritic sulfide during acidification/sample preparation (Wotte *et al.*, 2012), syn-depositional physical reworking or bioturbation as observed in modern sediments (Aller *et al.*, 2010), diagenesis (Derry, 2010) or primary marine processes (Thompson and Kah, 2012).

Bulk $\delta^{34}\text{S}_{\text{CAS}}$ values measured in the Argentine Precordillera platform in previous studies have yielded more negative values than those in coeval records (Thompson and Kah, 2012), with an offset of approximately 10‰ from datasets in Missouri and up to 20‰ from coeval datasets from Western Newfoundland (Thompson and Kah, 2012; Present *et al.*, 2015). These previous bulk data from Cerro La Silla are included as red data points in Fig. 4.1, and it is apparent that both data sets show a similar overall trend but that values produced in this study (mean 25.5‰, SD 3.2, $n = 34$, range 18.9‰ to 32.9‰) are generally more positive than those produced previously (mean 21.1‰, SD 4.4, range 13.5‰ to 27.6‰ (Thompson and Kah, 2012)) with a higher mean value by 4.4‰.

Disseminated sulfides are visible in the XRF maps, although their occurrence is limited in cement suites, and it has been shown that oxidation of granular sulfide ($< 300 \mu\text{m}$) during acid extraction can alter bulk CAS at sulfide abundances $> 1 \text{ wt}\%$ (Marengo *et al.*, 2008; Wotte *et al.*, 2014). However, pyrite generally occurs at $< 1 \text{ wt}\%$ (e.g. Jones and Fike, 2013; Richardson *et al.*, 2019; Rose *et al.*, 2019) and the concentration is not known in the samples in this study. Therefore, variable sulfide oxidation during sulfate extraction might have contributed to the short scale variability observed in both data sets, and to the mean offset between the two datasets, but is unlikely to produce the full scale of variability observed. The impact of this process is difficult to quantify in any given sample as it is partly dependent on stringent lab control of pH during the acidification step (Wotte *et al.*, 2014). Brine rinses during bulk-rock CAS extraction are intended to remove secondary sulfate. In the current study three brine rinses were undertaken to remove secondary sulfate phases prior to bulk CAS extraction as recommended during lab extraction and subsequently published by Edwards *et al.* (2019) (in a modification of the protocol of Wotte *et al.* (2012)). It is notable that there is a $\delta^{34}\text{S}_{\text{CAS}}$ offset of 4.4‰ towards heavier $\delta^{34}\text{S}_{\text{CAS}}$ values in the dataset of this study, compared to the previous $\delta^{34}\text{S}_{\text{CAS}}$ dataset produced at Cerro La Silla, which used a bleach rinse rather than employ additional brine rinses (Thompson and Kah, 2012). Overall, the isotopically lighter CAS mean values in the current study are more consistent with the existing $\delta^{34}\text{S}_{\text{CAS}}$ Cambro-Ordovician records from Missouri (Gill *et al.*, 2007, 2011), subject to the specific exceptions outlined below in relation to the upper La Silla and lowermost San Juan Formations.

When the full chemostratigraphic dataset is examined, the lack of covariation between $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$, interpreted in isolation, suggests that there is a relatively low level of diagenetic alteration throughout the full stratigraphic section, with insufficient fluid-rock

interaction with meteoric waters to alter $\delta^{13}\text{C}_{\text{carb}}$ (Banner and Hanson, 1990). This occurs with Mn and Sr trace element data whose magnitude and lack of negative correlation would be considered as indicative of good overall preservation and a lack of extensive diagenesis (Fig. 2.6). Manganese concentrations through the section also lie within the published range for well-preserved low Mg calcite. However, Sr concentrations are lower than published values for well-preserved low Mg calcite. Therefore, whilst the chemostratigraphic data for the section potentially supports some interaction of sediment with diagenetic fluids in a hypothesised open system, causing Sr loss and ^{18}O depletion, the magnitude of that water:rock interaction volume was likely insufficient to alter primary $\delta^{13}\text{C}_{\text{carb}}$ (Banner and Hanson, 1990). These features of the bulk chemostratigraphic record at Cerro La Silla have been cited in previous studies as supporting the primary marine nature of bulk $\delta^{34}\text{S}_{\text{CAS}}$ data from the section (Thompson and Kah, 2012). The response of CAS during recrystallisation of primary components in meteoric fluids has been studied in Pleistocene limestones in which recrystallisation from aragonite to meteoric low Mg calcite occurs across a sharp reaction front. Strontium and Na concentrations, which are depleted in meteoric water relative to seawater decreased across the front, as did values of $\delta^{18}\text{O}$ (Gill *et al.*, 2008). $\delta^{34}\text{S}_{\text{CAS}}$ values across the reaction front varied within a narrow range from 20.6 to 22.6‰, close to the 20.8–22.0‰ range of coeval Pleistocene seawater (Burdett *et al.*, 1989; Paytan *et al.*, 1998). This range was maintained despite sulfate concentrations dropping from a mean concentration of 3234 ± 1180 ppm ($n = 33$) in the aragonite to 308 ± 261 ppm ($n = 16$) in the calcite. The data suggest that CAS may be rock-buffered in the presence of meteoric waters due to their low sulfate concentrations (Gill *et al.*, 2008). Whilst carbonate dissolution and recrystallisation caused by interaction with basinal brines or meteoric fluids may also alter $\delta^{34}\text{S}_{\text{CAS}}$ post-deposition (Veizer, 1983; Banner and Hanson, 1990; Knauth and Kennedy, 2009; Derry, 2010), there is no evidence of late stage cements in the analysed samples (Gill *et al.*, 2008; Derry, 2010; Fischer *et al.*, 2014; Xiao *et al.* 2010). In addition, bulk data analysis does not adequately consider petrographic information, including the variable occurrence and composition of phreatic cement phases present in samples through the stratigraphic section outlined in Chapters 4.5.2 and 4.5.3.

An unusual aspect of the $\delta^{34}\text{S}_{\text{CAS}}$ dataset at Cerro La Silla is the markedly negative $\delta^{34}\text{S}_{\text{CAS}}$ record previously recorded in the La Silla Formation (Fig. 2.1 and Fig. 4.1). In Chapters 2 and 3, the upper La Silla Formation and lowermost San Juan Formation samples from both solution ICP-MS and LA-ICP-MS analysis, exhibit very low concentrations of siliciclastic-associated elements, including Al and Fe. This is consistent with a carbonate ramp isolated

from shale inputs and with previous studies' reports of very pure carbonate rocks occurring in the La Silla Formation (Pratt *et al.*, 2012). Micron scale analysis of components by LA-ICP-MS mapping (Chapter 3) identified variability in elemental concentrations across component types, including peloids, allomicrite, fossils and phreatic cement phases, in the analysed samples from Cerro La Silla, however, mapped sample from the lowermost San Juan Formation (sample 41.2) has a much lower concentration of Fe, Th and Mn across all recorded phases (peloidal allomicrite and phreatic cements) than the concentrations recorded across similar components in all mapped samples in the mid to upper San Juan Formation (241.6 m, 267.2 m and 268.6 m)(Table 3-1). Combined interpretation of textural and geochemical data in these samples in Chapter 3 suggests that the upper La Silla Formation and lowermost San Juan Formation at Cerro La Silla formed in shallow, regularly reworked, oxic and possibly brackish conditions, with minimal siliciclastic input. Early phreatic cementation occurred in brackish porewaters and is identifiable as a decreasing concentration of Sr from allomicrite to the C1 and C2 cements (refer to Chapter 3). An image of the interpreted depositional environment is presented at Fig. 3.7.

There is evidence that in segments of the stratigraphic section phreatic phases were precipitated in shallow porewaters whose chemical composition may have evolved from the primary marine composition, including in brackish porewaters at the base of the section. Where stratigraphic covariation trends are relied upon as the basis for a conclusion of a lack of alteration throughout a full stratigraphic section, it has the potential to overlook micro-facies evidence, such as that identified in thin section at the base of the section at Cerro La Silla. The occurrence of isopachous phreatic cement in the study is consistent with either meteoric, marine or mixed zone precipitation. In sample 41.2 at the base of the section these cements are more extensive with low sulfate and sulfide concentrations and decreasing Sr concentrations moving from allomicrite to C1 and C2 cements. In those samples precipitation of phreatic cements in oxic early, mixed zone conditions, combined with minimal concentrations of Fe and Mn, may have caused deviation of porewater $\delta^{34}\text{S}_{\text{CAS}}$ values from seawater sulfate values due to sulfide oxidation. The occurrence of these environmental conditions may be related to the history of the Precordillera, where carbonates formed on a vast, homoclinal, carbonate ramp on the passive, westward margin of a drifting carbonate platform terrane (Astini *et al.*, 1995). This carbonate terrane (Cuyania) is interpreted by researchers as having migrated in isolation across the Iapetus Ocean in the Cambro-Ordovician, with carbonates forming to the west of the low relief, predominantly subtidal, carbonate terrane (Astini *et al.*, 1995).

The atypical depositional conditions of the La Silla Formation offer a cause of more negative CAS in the upper La Silla Formation and lowermost San Juan Formation. Based on the near absence of siliciclastic components the platform was isolated from both marine and terrestrial siliciclastic inputs until the increased flooding of the platform with marine water during transgression above the lower reef facies. Decreased manganese and iron oxide or clays would decrease the preferential stripping of LREE from the water-column, contributing to the flat REE+Y profiles recorded in Chapter 2. The samples studied by LA-ICP-MS mapping from the shallow depositional facies at Cerro La Silla (sample 41.2 and 268.6) both show, at a micron scale, a correlation between decreasing sulfate abundance and decreasing Sr concentration moving from allomicticrite and C1 to later cements. This trend is also consistent with evolving porewater with decreasing sulfate concentrations either related to cement formation in low sulfate mixed marine and meteoric porewaters or decreasing sulfate concentrations as MSR progressed. More negative local values may be associated with increased riverine or groundwater input of sulfate derived from weathered sulfides (Halevy *et al.*, 2012). Such increased groundwater or riverine influx of low $\delta^{34}\text{S}$ sulfate could potentially reduce sulfate values particularly in partially restricted water body or low sulfate ocean. However, Fe concentrations and pyrite, expected to occur where weathered sulfides contribute to the riverine sulfate, are very low in sample 41.2 through all components suggesting either a lack of MSR (no anoxic conditions or no organic matter) or lack of pyrite formation due to absence of Fe. Catchment $\delta^{34}\text{S}_{\text{CAS}}$ values, controlled by the relative pyrite vs evaporite inputs, can vary based on lithologies sampled by local freshwater inputs, particularly in restricted basins or low sulfate oceans (Halevy *et al.*, 2012). However, basement lithologies are not exposed in the Precordillera and may not have been encountered by surface or groundwaters due to their significant depth beneath over a kilometer of carbonate rocks. The carbonate platform is therefore unlikely to have had an increased flux of negative $\delta^{34}\text{S}$ in riverine sulfate from siliciclastic or igneous contributions.

Whilst the current study based on a combination of outcrop sedimentology, petrology and micron scale analytical techniques is limited to the uppermost 35 metres of the La Silla Formation, the factors discussed may also require investigation in the underlying La Silla Formation (Thompson and Kah, 2012).

4.6 Conclusions

Combined high resolution mapping of the distribution of CAS and bulk analysis of $\delta^{34}\text{S}_{\text{CAS}}$, in samples from Cerro La Silla provide evidence of the impact of syndepositional to early diagenetic processes occurring in sediment porewaters on the $\delta^{34}\text{S}_{\text{CAS}}$ record. Supported by evidence of porewater conditions developed in Chapters 2 and 3, the data from this chapter give an indication of the conditions in which $\delta^{34}\text{S}_{\text{CAS}}$ data may diverge from primary marine values.

At the base of the stratigraphic section in the uppermost La Silla Formation and basal San Juan Formation, sediments were starved of siliciclastic input, reflected in the near absence of elements associated with fine grained siliciclastic contamination of carbonates. The samples also display a markedly low concentrations of Fe and Mn, elements which are also delivered to shallow seawater as oxides and associated with weathering of siliciclastic and igneous catchment areas.

In addition very low Mn levels are consistent with oxic porewater conditions and REE+Y profiles may indicate a brackish, low Sr, phreatic cement component, which occurs extensively in samples at the base of the section.

High resolution μ -XRF imaging and XANES spectroscopy at the S K- edge illustrates that the variation in sulfate abundance begins at the micron-scale between adjacent components in these samples and the observed variability undermines the assumption that bulk rock-extracted $\delta^{34}\text{S}_{\text{CAS}}$ is a consistent proxy for seawater values (Burdett *et al.*, 1989). The combined use of XRF mapping, to identify sulfur distribution and abundances, and of LA-ICP-MS mapping to quantify cooccurring elemental concentrations of proxies for diagenesis (e.g. Mn and Sr) and contamination (e.g. Th, Al or Ga) indicates that lowest $\delta^{34}\text{S}_{\text{CAS}}$ values are associated with atypical sediment porewater conditions. Low Fe, regularly reworked oxic sediments provide a pathway for oxidation of sulfide produced by MSR. Low Fe and pyrite in sample 41.2 support the possible occurrence of this process, which may contribute ^{34}S depleted sulfate to the porewater sulfate pool. In addition, notably higher abundances of sulfate are present in the brachiopod fragment in sample 268.6L, consistent with high abundances of sulfate occurring in brachiopod shells in samples from the Ordovician of Anticosti Island (Richardson *et al.*, 2019; Rose *et al.*, 2019) and supporting the potential of low Mg-calcite fossils such as brachiopods as sources of sulfate records (Kampschulte and Strauss, 2004; Present *et al.*, 2015). This application would be subject to developing our understanding of any biotic fractionation in extant species and how they relate to fossil values

in the geological record (Burdett *et al.*, 1989; Cuif *et al.*, 2003; Cusack *et al.*, 2008; Yoshimura *et al.*, 2013).

An offset in the mean bulk $\delta^{34}\text{S}_{\text{CAS}}$ by 4.4‰ to more positive values in the current bulk dataset compared to that produced in previous studies from the same section (Thompson and Kah, 2012) may be a product of the distinct methodologies used and the potential oxidation of sulfide during sample preparation (Wotte *et al.*, 2012).

It cannot be assumed that shallow water facies throughout the geological record are similar to those at Cerro La Silla and there are potentially highly variable and interrelated factors related to depositional facies that might influence the abundance and values of sulfide and sulfate recorded in microfacies and lithofacies. The extent of the impact of sulfide oxidation in similar oxic, reworked facies in the fossil record may need to be considered in future works with a consideration of the viability of shallow, reworked facies, as sources of marine $\delta^{34}\text{S}_{\text{CAS}}$ records. In the majority of existing $\delta^{34}\text{S}_{\text{CAS}}$ datasets from energetic shallow conditions the extent to which shallow porewater or extraction-related processes have impacted the bulk CAS record is likely to be an open question. As a result, an unquantified component of the stratigraphic and lateral variability recognized in the geological record may be due principally to these processes rather than to secular change in the marine sulfate reservoir. This attaches a large degree of uncertainty to the complex marine mechanisms currently inferred to explain apparent anomalously rapid or large coeval changes in the sulfur isotope value of the marine sulfate reservoir.

Whilst XRF mapping offers the potential for a much greater understanding of sulfur species distributions, it is a relatively inaccessible analytical technique for routinely validating the primary nature of $\delta^{34}\text{S}_{\text{CAS}}$ stratigraphic data. Further investigation of the potential of LA-ICP-MS mapping as a tool for coincidence mapping of elements associated with sulfate or sulfide abundance (obtained by development of XRF mapping datasets) offers one potential means of developing a more routine, accessible LA-ICP-MS-based protocol to delineate likely sulfate or sulfide distributions.

ACKNOWLEDGEMENTS

Field and stable isotope work was supported by the Stephen Fossett Postdoctoral Fellowship and a Trinity Fellowship awarded to CVR, and a Packard Fellowship and a Hansewissenschaftskolleg Fellowship awarded to DAF. The element analysis laboratory at

TCD was in part established with funding from CIG PCIG9-GA-2011-293712 awarded to BSK. The laboratory's operation is supported with funding from Science Foundation Ireland (SFI) Grant Number 13/ RC/2092, co-funded under the European Regional Development Fund. Thanks are extended to Fernando Gomez and Tor O'Brien for assisting with field work. We are very grateful to Robbie Goodhue at Trinity College Dublin, Dwight McCay at Washington University in St Louis, and Angus Calder at the University of St Andrews for helping with sample preparation and stable isotope measurements. We would also like to thank Cora McKenna and Kerstin Drost for help and expertise with the trace element analyses and LA-ICP-MS mapping at Trinity College Dublin.

References

- ALBANESI, G. L. & ORTEGA, G. 2002. Advances on conodont-graptolite biostratigraphy of the Ordovician System of Argentina. In: ACENÓLAZA, F. G. (ed.) Aspects on the Ordovician System in Argentina.: Tucumán.
- ALLER, R. C. 2004. Conceptual models of early diagenetic processes: The muddy seafloor as an unsteady, batch reactor. *Journal of Marine Research*, 62, 815-835.
- ALLER, R. C., MADRID, V., CHISTOSERDOV, A., ALLER, J. Y. & HEILBRUN, C. 2010. Unsteady diagenetic processes and sulfur biogeochemistry in tropical deltaic muds: Implications for oceanic isotope cycles and the sedimentary record. *Geochimica et Cosmochimica Acta*, 74, 4671-4692.
- ALLER, R.C. 2014. Sedimentary diagenesis, depositional environments, and benthic fluxes. In *Treatise on Geochemistry*, Vol. 8: The Oceans and Marine Geochemistry, ed. MJ Mottl, H Elderfield, pp. 293–334. Amsterdam, Elsevier. 2nd ed.
- ASTINI, R. A., BENEDETTO, J. L. & VACCARI, N. E. 1995. The early Paleozoic evolution of the Argentine Precordillera as a Laurentian rifted, drifted, and collided terrane: A geodynamic model. *Geological Society of America Bulletin*, 107, 253-273.
- BANNER, J. L. & HANSON, G. N. 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochimica et Cosmochimica Acta*, 54, 3123-3137.
- BERNER, R.A., 2001. Modelling atmospheric O₂ over phanerozoic time. *Geochim. Cosmochim. Acta* 65, 685–694.
- BERNER, R. A. 2006. GEOCARBSULF: A combined model for Phanerozoic atmospheric O₂ and CO₂. *Geochimica et Cosmochimica Acta*, 70, 5653-5664.
- BERNER, R.A., RAISWELL, R., 1983. Burial of organic carbon and pyrite sulfur in sediments over phanerozoic time: a new theory. *Geochim. Cosmochim. Acta* 47, 855–862.
- BRAND, U. & VEIZER, J. 1980. Chemical diagenesis of a multicomponent carbonate system-1: trace elements. *Journal of Sedimentary Petrology*, 50, 1219–1236.
- BUGGISCH, W., KELLER, M. & LEHNERT, O. 2003. Carbon isotope record of Late Cambrian to Early Ordovician carbonates of the Argentine Precordillera. *Palaeogeography Palaeoclimatology Palaeoecology*, 195, 357-373.
- BURDETT, J. W., ARTHUR, M. A. & RICHARDSON, M. 1989. A Neogene seawater sulfur isotope age curve from calcareous pelagic microfossils. *Earth and Planetary Science Letters*, 94, 189-198.
- CANFIELD, D.E. & FARQUHAR, J. 2009. Animal evolution, bioturbation, and the sulfate concentration of the oceans. *PNAS*, 106, 8123–8127.

- CANÑAS, F. L. 1999. Facies and sequences of the Late Cambrian-Early Ordovician carbonates of the Argentine Precordillera: A stratigraphic comparison with Laurentian platforms. Special Paper 336: Laurentia-Gondwana connections before Pangea. Geological Society of America.
- CANÑAS, F. L. & CARRERA, M. G. 1993. Early Ordovician microbial-sponge-receptaculitid bioherms of the Precordillera, western Argentina. *Facies*, 29, 169–178.
- CANFIELD, D. E., HABICHT, K. S. & THAMDRUP, B. 2000. The Archean sulfur cycle and the early history of atmospheric oxygen. *Science*, 288, 658-61.
- CANFIELD, D. E. & TESKE, A. 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulfur-isotope studies. *Nature*, 382, 127-32.
- CLAYPOOL, G. E., HOLSER, W. T., KAPLAN, I. R., SAKAI, H. & ZAK, I. 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology*, 28.
- CROWE, S. A.U, PARIS, G., KATSEV, S., JONES, C. A., KIM, S., ZERKLE, A. L., NOMOSATRYO, S., FOWLE, D. A., ADKINS, J. F., SESSIONS, A. L., FARQUHAR, J. & CANFIELD, D. E. 2014, Sulfate was a trace constituent of Archean seawater. *Science*, 346 (6210) 735-739.
- CUIF, J.-P., DAUPHIN, Y., DOUCET, J., SALOME, M., SUSINI, J., 2003. XANES mapping of organic sulfate in three scleractinian coral skeletons. *Geochim. Cosmochim. Acta* 67, 75–83.
- CUSACK, M., DAUPHIN, Y., CUIF, J.-P., SALOMÉ, M., FREER, A., YIN, H., 2008. Micro-XANES mapping of sulphur and its association with magnesium and phosphorus in the shell of the brachiopod, *Terebratulina retusa*. *Chem. Geol.* 253, 172–179.
- DENISON, R. E., KOEPNICK, R. B., FLETCHER, A., HOWELL, M. W. & CALLAWAY, W. S. 1994. Criteria for the retention of original seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in ancient shelf limestones. *Chemical Geology*, 112, 131-143.
- DERRY, L. A. 2010. A burial diagenesis origin for the Ediacaran Shuram-Wonoka carbon isotope anomaly. *Earth and Planetary Science Letters*, 294 152-162.
- EDWARDS, C.T., FIKE, D.A., SALTZMAN, M.R., LU, W., LU, Z., 2018. Evidence for local and global redox conditions at an Early Ordovician (Tremadocian) mass extinction. *Earth Planet. Sci. Lett.* 481, 125–135.
- EDWARDS, C.T., FIKE, D.A., SALTZMAN, M.R., 2019. Testing carbonate-associated sulfate (CAS) extraction methods for sulfur isotope stratigraphy: A case study of a Lower–Middle Ordovician carbonate succession, Shingle Pass, Nevada, USA. *Chemical Geology*, 529, 2019, 119297

- EGGINS, S. M., WOODHEAD, J. D., KINSLEY, L. P. J., MORTIMER, G. E., SYLVESTER, P., MCCULLOCH, M. T., HERGT, J. M. & HANDLER, M. R. 1997. A simple method for the precise determination of > 40 trace elements in geological samples by ICP-MS using enriched isotope internal standardisation. *Chemical Geology*, 134, 311-326.
- FICHTNER, V., STRAUSS, H., IMMENHAUSER, A., BUHL, D., NEUSER, R.D., NIEDERMAYR, A., 2017. Diagenesis of carbonate associated sulfate. *Chem. Geol.* 463, 61–75.
- FIKE, D. A., BRADLEY, A. S. & ROSE, C. V. 2015. Rethinking the Ancient Sulfur Cycle. *Annual Reviews of Earth and Planetary Sciences*, 43, 593–622.
- FIKE, D. A. & GROTZINGER, J. P. 2008. A paired sulfate-pyrite $\delta^{34}\text{S}$ approach to understanding the evolution of the Ediacaran-Cambrian sulfur cycle. *Geochimica et Cosmochimica Acta*, 72 2636-2648.
- FISCHER, W.W., FIKE, D.A., JOHNSON, J.E., RAUB, T.D., GUAN, Y. & KIRSCHVINK, J.L. 2014. SQUID–SIMS is a useful approach to uncover primary signals in the Archean sulfur cycle. *PNAS*, 111, 5468–5473.
- FLÜGEL, E., MUNNECKE, A., 2010. *Microfacies of Carbonate Rocks: Analysis, Interpretation and Application*. Springer.
- GAO, J, FIKE, D.A., ALLER, R.C. 2013. Enriched pyrite $\delta^{34}\text{S}$ signals in modern tropical deltaic muds. Presented at AGU Fall Meet., Dec. 9–13, San Francisco. Abstr. B31A-0352.
- GARRELS, R. M. & LERMAN, A. 1981. Phanerozoic cycles of sedimentary carbon and sulfur. *Proc Natl Acad Sci U S A*, 78, 4652-6.
- GILL, B.C., LYONS, T.W., SALTZMAN, M.R., 2007. Parallel, high-resolution carbon and sulfur isotope records of the evolving Paleozoic marine sulfur reservoir. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 256, 156–173.
- GILL, B.C., LYONS, T.W., FRANK, T.D., 2008. Behavior of carbonate-associated sulfate during meteoric diagenesis and implications for the sulfur isotope paleoproxy. *Geochim. Cosmochim. Acta* 72, 4699–4711.
- GILL, B. C., LYONS, T. W., YOUNG, S. A., KUMP, L. R., KNOLL, A. H. & SALTZMAN, M. R. 2011. Geochemical evidence for widespread euxinia in the Later Cambrian ocean. *Nature*, 469, 80-83.
- HABICHT, K.S. & CANFIELD, D.E. 1997. Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments. *Geochimica et Cosmochimica Acta*, 61, 5351–5361.
- HABICHT, K. S., GADE, M., THAMDRUP, B., BERG, P. & CANFIELD, D. E. 2002. Calibration of sulfate levels in the archaean ocean. *Science*, 298, 2372-4.

- HALEVY, I, PETERS, SE, FISCHER, WW. 2012. Sulfate burial constraints on the Phanerozoic sulfur cycle. *Science*, 337, 331–34.
- HAHN, K. E., TURNER, E. C., BABECHUK, M. G. & KAMBER, B. S. 2015. Deep-water seep-related carbonate mounds in a Mesoproterozoic alkaline lake, Borden Basin (Nunavut, Canada). *Precambrian Research*, 271, 173-197.
- HEDMAN, B., FRANK, P., PENNER-HAHN, J.E., ROE, A.L., HODGSON, K.O., CARLSON, R.M.K., BROWN, G., CERINO, J., HETTEL, R., TROXEL, T., WINICK, H., YANG, J., 1986. Sulfur K-edge X-ray absorption studies using the 54-pole wiggler at SSRL in undulator mode. *Nucl. Instrum. Methods Phys. Res., Sect. A* 246, 797–800.
- HEMMING, N. G., MEYERS, W. J. & GRAMS, J. C. 1989. Cathodoluminescence in Diagenetic Calcites: The Roles of Fe and Mn as Deduced from Electron Probe and Spectrophotometric Measurements. *Journal of Sedimentary Research (SEPM)*, 59, 404-411.
- HERRERA, Z.A. AND BENEDETTO, J.L., 1991. Early Ordovician brachiopod faunas from the Precordillera basin, Western Argentina: biostratigraphy and paleobiogeographical affinities. In: MacKinnon, D.I. *et al.*, (eds.) *Brachiopods through time*, p. 283-301. Balkema Ed.
- HURTGEN, M.T., ARTHUR, M.A., SUITS, N.S., KAUFMAN, A.J., 2002. The sulfur isotopic composition of Neoproterozoic seawater sulfate: implications for a snowball Earth? *Earth Planet. Sci. Lett.* 203, 413–429. [https://doi.org/10.1016/S0012-821X\(02\)00804-X](https://doi.org/10.1016/S0012-821X(02)00804-X).
- HURTGEN, M. T., HALVERSON, G. P., ARTHUR, M. A. & HOFFMAN, P. F. 2006. Sulfur cycling in the aftermath of a 635-Ma snowball glaciation: Evidence for a syn-glacial sulfidic deep ocean. *Earth and Planetary Science Letters*, 245, 551-570.
- HURTGEN, M.T., PRUSS, S.B., KNOLL, A.H., 2009. Evaluating the relationship between the carbon and sulfur cycles in the later Cambrian ocean: an example from the Port au Port Group, western Newfoundland, Canada. *Earth Planet. Sci. Lett.* 281, 288–297. <https://doi.org/10.1016/J.EPSL.2009.02.033>.
- JONES, D. S. & FIKE, D. A. 2013. Dynamic sulfur and carbon cycling through the end-Ordovician extinction revealed by paired sulfate-pyrite $\delta^{34}\text{S}$. *Earth and Planetary Science Letters*, 363, 144–155.
- JONES, D.S., FIKE, D.A., FINNEGAN, S., FISCHER, W.W., SCHRAG, D.P., MCCAY, D., 2011. Terminal Ordovician carbon isotope stratigraphy and glacioeustatic sea-level change across Anticosti Island (Québec, Canada). *Bull. Geol. Soc. Am.* 123, 1645–1664.
- KAH, L. C., LYONS, T. W. & FRANK, T. D. 2004. Low marine sulfate and protracted oxygenation of the proterozoic biosphere. *Nature*, 431, 834-838.

- KAMBER, B. S. 2009. Geochemical fingerprinting: 40 years of analytical development and real world applications. *Applied Geochemistry*, 24, 1074-1086.
- KAMBER, B. S., GREIG, A. & COLLERSON, K. D. 2005. A new estimate for the composition of weathered young upper continental crust from alluvial sediments, Queensland, Australia. *Geochimica et Cosmochimica Acta*, 69, 1041-1058.
- KAMPSCHULTE, A & STRAUSS, H. 2004. The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulfate in carbonates. *Chemical Geology*, 204, 255-286.
- KAMPSCHULTE, A., BRUCKSCHEN, P., STRAUSS, H., 2001. The sulphur isotopic composition of trace sulphates in Carboniferous brachiopods: implications for coeval seawater, correlation with other geochemical cycles and isotope stratigraphy. *Chem. Geol.* 175, 149–173.
- KAUFMAN, A. J., HAYES, J. M., KNOLL, A. H. GERMS, G. J. B. 1991. Isotopic compositions of carbonates and organic carbon from upper Proterozoic successions in Namibia: stratigraphic variation and the effects of diagenesis and metamorphism. *Precambrian Research*, 49.
- KELLER, M. 1999. Argentine Precordillera: Sedimentary and Plate Tectonic History of a Laurentian Crustal Fragment in South America. Special Paper 341: Argentine Precordillera: sedimentary and plate tectonic history of a Laurentian crustal fragment in South America. Geological Society of America.
- KELLER, M., CAÑAS, F. L., LEHNERT, O. & VACCARI, N. E. 1994. The Upper Cambrian and Lower Ordovician of the Precordillera (Western Argentina): Some stratigraphic reconsiderations. *Newsletters Stratigraphy*, 31, 115-132.
- KELLER, M., EBERLEIN, S. & LEHNERT, O. 1993. Sedimentology of Middle Ordovician carbonates in the Argentine Precordillera: Evidence for regional relative sea-level changes. *Geologische Rundschau*, 82, 362–377.
- KELLER, M. & FLÜGEL, E. 1996. Early Ordovician reefs from Argentina: Stromatoporoid vs. stromatolite origin. *Facies* 34, 177–192.
- KNAUTH, L.P. & KENNEDY, M. J., 2009. The late Precambrian greening of the Earth. *Nature* 460 (7256) 728-32.
- KOZIK, N.P., YOUNG, S.A., BOWMAN, C.N., SALTZMAN, M.R., THEM, T.R., 2019. Middle–Upper Ordovician (Darriwilian–Sandbian) paired carbon and sulfur isotope stratigraphy from the Appalachian Basin, USA: Implications for dynamic redox conditions spanning the peak of the Great Ordovician Biodiversification Event. *Palaeogeogr.*

- KUMP, L. R., ARTHUR, M. A., PATZKOWSKY, M. E., GIBBS, M. T., PINKUS, D. S. & SHEEHAN, P. M. 1999. A weathering hypothesis for glaciation at high atmospheric pCO₂ during the Late Ordovician. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 152, 173–187.
- LEHNERT, O. 1995. Ordovizische Conodonten aus der Präkordillere Westargentinien: Ihre Bedeutung für Stratigraphie und Paläogeographie. *Erlanger Geologische Abhandlungen*, 125, 1-193.
- LI, C., LOVE, G. D., LYONS, T. W., FIKE, D. A., SESSIONS, A. L. & CHU, X. 2010. A New Stratified Redox Model for the Ediacaran Ocean. *Science*, 328 80-83.
- MARENCO, P.J., CORSETTI, F.A., HAMMOND, D.E., KAUFMAN, A.J., BOTTJER, D.J., 2008. Oxidation of pyrite during extraction of carbonate associated sulfate. *Chem. Geol.* 247, 124–132.
- OSBURN, M.R., OWENS, J., BERGMANN, K.D., LYONS, T.W., GROTZINGER, J.P., 2015. Dynamic changes in sulfate sulfur isotopes preceding the Ediacaran Shuram Excursion. *Geochim. Cosmochim. Acta* 170, 204–224. <https://doi.org/10.1016/J.GCA.2015.07.039>.
- PARIS, G., ADKINS, J.F., SESSIONS, A.L., WEBB, S.M., FISCHER, W.W., 2014. Neoproterozoic carbonate-associated sulfate records positive $\Delta^{33}\text{S}$ anomalies. *Science* 346, 739–741.
- PASQUIER, V., SANSJOFRE, P., RABINEAU, M., REVILLON, S., HOUGHTON, J., FIKE, D.A., 2017. Pyrite sulfur isotopes reveal glacial–interglacial environmental changes. *Proc. Natl. Acad. Sci.* 114, 5941–5945. <https://doi.org/10.1073/pnas.1618245114>.
- PAYTAN, A., KASTNER, M., CAMPBELL, D. & THIEMENS, M. H. 1998. Sulfur isotopic composition of Cenozoic seawater sulfate. *Science*, 282, 1459-1462.
- PAYTAN, A., KASTNER, M., CAMPBELL, D. & THIEMENS, M. H. 2004. Seawater sulfur isotope fluctuations in the Cretaceous. *Science* 304, 1663-1665.
- PETRUS, J. A., CHEW, D. M., LEYBOURNE, M. I. & KAMBER, B. S. 2017. A new approach to laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) using the flexible map interrogation tool ‘Monocle’. *Chemical Geology*, 463, 76-93.
- PRESENT, T. M., PARIS, G., BURKE, A., FISCHER, W. W. & ADKINS, J. F. 2015. Large Carbonate Associated Sulfate isotopic variability between brachiopods, micrite, and other sedimentary components in Late Ordovician strata. *Earth and Planetary Science Letters*, 432, 187-198.
- RENNIE, V. C. F., TURCHYN, A. V., 2014. The preservation of $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_2}$ in carbonate-associated sulfate during marine diagenesis: a 25 Myr test case using marine sediments. *Earth Planet. Sci. Lett.* 395, 13–23.

RENNIE, V.C.F., PARIS, G., SESSIONS, A.L., ABRAMOVICH, S., TURCHYN, A.V., ADKINS, J.F., 2018. Cenozoic record of $\delta^{34}\text{S}$ in foraminiferal calcite implies an early Eocene shift to deep-ocean sulfide burial. *Nat. Geosci.* 1.

RICCARDI, A.L., ARTHUR, M.A., KUMP, L.R., 2006. Sulfur isotopic evidence for chemocline upward excursions during the end-Permian mass extinction. *Geochim. Cosmochim. Acta* 70, 5740–5752.

RICHARDSON, J. A., NEWVILLE, M., LANZIROTTI, A., WEBB, S. M., ROSE, C. V., CATALANO, J. G. & FIKE, D. A. 2019. Depositional and diagenetic constraints on the abundance and spatial variability of carbonate-associated sulfate. *Chemical Geology*, 523, 59–72.

RIES, J. B., FIKE, D. A., PRATT, L. M., LYONS, T. W. & GROTZINGER, J. P. 2009. Super-heavy pyrite ($\delta^{34}\text{S}_{\text{pyr}} > \delta^{34}\text{S}_{\text{CAS}}$) in the terminal Proterozoic Nama Group, Southern Namibia: A consequence of low seawater sulfate at the dawn of animal life. *Geology*, 37(8), 743–746.

ROSE, C. V., WEBB, S. M., NEWVILLE, M., LANZIROTTI, A. A., TOSCA, N. J., CATALANO, J. G., BRADLEY, A. S. & FIKE, D. A. 2019. Insights into past ocean proxies from micron-scale mapping of sulfur species in carbonates. *Geology*, 47, 833–837.

SALTZMAN, M. R., RUNNEGAR, B. & LOHMANN, K. C. 1998. Carbon isotope stratigraphy of upper Cambrian (Steptoean stage) sequences of the eastern Great Basin: Record of a global oceanographic event. *Bulletin of the Geological Society of America*, 110, 285–297.

STAUDT, W. J., SCHOONEN, M. A. A., 1995. Sulfate Incorporation Into Sedimentary Carbonates. 332–345. <https://doi.org/10.1021/bk-1995-0612.ch018>.

STRAUSS, H., 1997. The isotopic composition of sedimentary sulfur through time. *Palaeogeography, Palaeoclimatology, Palaeoecology*. 132, 97–118.

SWART, P.K., 2015. The geochemistry of carbonate diagenesis: The past, present and future. *Sedimentology*. 62, 5, 1233–13–4

SWART, P. K., OEHLERT, A. M., MACKENZIE, G. J., EBERLI, G. P. & REIJMERT, J. J. G. 2014. The fertilization of the Bahamas by Saharan dust: A trigger for carbonate precipitation? *Geology*, 42 (8), 671–674.

THOMPSON, C. K. & KAH, L. C. 2012. Sulfur isotope evidence for widespread euxinia and a fluctuating oxycline in Early to Middle Ordovician greenhouse oceans. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 313–314, 189–214.

TURCHYN, A.V., SCHRAG, D.P., COCCIONI, R., MONTANARI, A., 2009. Stable isotope analysis of the cretaceous sulfur cycle. *Earth Planet. Sci. Lett.* 285, 115–123.

- VAN GELDERN, R., JOACHIMSKI, M., DAY, J., JANSEN, U., ALVAREZ, F., YOLKIN, E. A. & MA, X. 2006. Carbon, oxygen and strontium isotope records of Devonian brachiopod shell calcite. *Palaeogeography, Palaeoclimatology, Palaeoecology*. 240, 47-67.
- VEIZER, J. 1983. Chemical diagenesis of carbonates: theory and application of trace element technique. *Short Course Notes*. Society of Economic Paleontologists and Mineralogists.
- WEBB, S. M. 2005. SIXpack: a graphical user interface for XAS analysis using IFEFFIT. *Physica Scripta*, 2005.
- WEBB, S. M. 2011. The MicroAnalysis Toolkit: X-ray Fluorescence Image Processing Software. *AIP Conference Proceedings*, 1365.
- WOTTE, T., SHIELDS-ZHOU, G. A. & STRAUSS, H. 2012. Carbonate-associated sulfate: Experimental comparisons of common extraction methods and recommendations toward a standard analytical protocol. *Chemical Geology*, 326-327, 132-144.
- XIAO, S., SCHIFFBAUER, J.D., MCFADDEN, K.A., HUNTER, J. 2010. Petrographic and SIMS pyrite sulfur isotope analyses of Ediacaran chert nodules: implications for microbial processes in pyrite rim formation, silicification, and exceptional fossil preservation. *Earth and Planetary Science Letters*, 297, 481-495.
- YOSHIMURA, T., TAMENORI, Y., SUZUKI, A., NAKASHIMA, R., IWASAKI, N., HASEGAWA, H., KAWAHATA, H., 2013. Element profile and chemical environment of sulfur in a giant clam shell: Insights from μ -XRF and X-ray absorption near-edge structure. *Chem. Geol.* 352, 170-175.
- YOUNG, S.A., GILL, B.C., EDWARDS, C.T., LESLIE, S.A., 2016. Middle-Late Ordovician (Darriwilian-Sandbian) decoupling of global sulfur and carbon cycles: Isotopic evidence from eastern and southern Laurentia. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 458, 118-132.

Tables

Table 4-1: Isotope Ratio and Solution ICP-MS data, Cerro La Silla. Error is $< 0.3\text{‰}$ (1σ) for $\delta^{13}\text{C}_{\text{carb}}$ (‰ VPDB) and $< 0.5\text{‰}$ (1σ) $\delta^{18}\text{O}_{\text{carb}}$ (‰ VPDB) Solution-ICP-MS data in ppb (precision 2-3%, accurate to 5%) and $\delta^{34}\text{S}_{\text{CAS}}$ (‰ VCDT) (precision $< 0.16\text{‰}$).

Height	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	$\delta^{34}\text{S}_{\text{CAS}}$	27Al	54Fe	55Mn	88Sr
0	-1.72	-7.36					
1.4	-1.96	-7.33					
2.4	-1.91	-6.90		1,964,48	221,485	8,630	214,140
3.4	-1.63	-8.19					
5	-1.64	-6.69					
9.1	-1.82	-8.02					
10	-1.45	-7.60					
11	-1.45	-7.60					
17.6	-1.54	-7.60		72,592	83,347	10,180	155,956
18.8	-1.00	-7.56					
20.2	-1.22	-8.08					
21.3	-0.92	-8.08					
22.4	-1.66	-7.15					
23.6	-1.29	-8.02					
25.1	-1.50	-7.40		56,259	181,984	7,809	208,376
26.2	-1.46	-7.35					
28.5	-1.60	-8.17					
29.9	-2.48	-8.03					
31.6	-2.02	-9.48					
34.7	-1.26	-7.82					
35.9	-1.21	-6.35					
37.1	-1.51	-7.86					
37.7	-1.82	-7.08					
38.9	-1.63	-7.31					
40.2	-1.80	-8.39					
41.2	-1.08	-7.51		31,712	180,906	8,339	143,167
42.1	-1.08	-7.51		30,166	147,865	10,046	126,703
44.5				34,067	127,724	7,467	180,730
45.7	-0.51	-7.64					
47.4	-0.24	-8.21					
48.6	-0.48	-6.03					
51.3	-0.56	-7.34		46,347	145,012	6,470	172,246
52.5	-0.54	-6.25					
53.5	-1.03	-6.03					

Height	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	$\delta^{34}\text{S}_{\text{CAS}}$	27Al	54Fe	55Mn	88Sr
55	-0.26	-7.37					
56.2	-0.93	-6.89					
57.1	-1.03	-6.47					
58.1	-0.39	-7.50					
59.4	-1.10	-6.34					
61.5	-1.00	-6.60		138,859	235,831	13,377	394,329
62.1	-1.29	-6.45					
64.3	-1.10	-7.31					
65.6	-0.40	-6.79	31.36				
68.2	-1.12	-6.60					
69.9	-0.27	-7.51	23.15				
70.7	-1.34	-6.59		53,320	185,990	16,341	305,523
71.8	-1.52	-7.14					
76.9	-1.64	-5.74					
78.2	-1.14	-6.57		203,609	257,084	15,058	327,713
80.0				104,167	178,213	8,223	182,320
82.6	-2.63	-6.39					
83.5	-1.59	-6.71		107,008	276,256	27,187	599,747
85.4	-1.68	-6.69					
90.1	-2.23	-6.98	24.67				
91.8	-3.02	-6.93					
92.8	-2.55	-6.96					
95.6	-2.01	-6.56					
98.5	-2.44	-6.64		118,549	182,951	19,494	287,205
100.8	-2.57	-6.77	27.06				
101.9			23.71				
104.4	-3.05	-6.59		95,604	165,816	17,665	244,815
106.1	-2.33	-6.58					
107.6	-2.68	-6.82					
108.2	-2.25	-6.91					
108.9	-2.88	-6.38					
109.9	-1.72	-6.56					
110.8	-1.10	-6.69					
112.4	-1.43	-6.88					
113.2	-1.19	-6.98		161,580	676,272	89,787	320,188
115.5	-1.48	-6.53	25.85				
117.1	-1.42	-6.87					
117.9	-1.18	-6.57					
119.2	-1.46	-6.62					
120.6				411,670	1,181,363	115,347	280,704

Height	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	$\delta^{34}\text{S}_{\text{CAS}}$	27Al	54Fe	55Mn	88Sr
121.5	-1.41	-6.69					
122.1	-0.84	-6.81					
123	-1.15	-6.97					
124.3	-0.94	-6.94					
125.5	-1.06	-6.72					
126.4	-1.57	-6.34					
127.8	-1.16	-6.95					
130.2	-1.15	-6.73					
132.7	-1.31	-6.94					
134.6	-1.25	-6.66					
135.7	-1.23	-6.70		133,134	1,622,894	203,965	275,077
136.8	-1.25	-6.61					
138.2	-1.25	-6.87					
139.4	-1.11	-6.78					
141.8	-1.19	-6.49					
142.5	-1.06	-6.87					
143.7	-1.49	-6.90					
144.8	-0.97	-6.61		931,375	1,621,426	180,405	235,769
145.7	-1.39	-6.27					
147.3	-1.00	-6.92					
148.3	-1.87	-6.24					
149.4	-1.34	-6.66		1,443,580	2,669,501	212,557	291,484
151	-1.25	-6.00					
151.9	-0.79	-6.16					
152.8	-0.93	-6.32		863,543	2,239,086	208,604	333,592
154.4	-1.16	-6.46					
156.2	-0.78	-6.07					
157	-0.95	-6.09					
157.8	-1.14	-6.00	29.96				
158.6	-1.65	-6.39					
159.9	-0.92	-6.63					
161.2	-2.75	-6.51		405,422	1,686,044	174,897	348,698
162.7	-1.44	-6.99					
164.8	-1.32	-6.12					
166	-1.49	-7.10					
168.3	-1.11	-6.60					
169.3	-1.65	-8.14					
170	-0.89	-6.33		496,194	1,872,076	209,771	292,560

Height	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	$\delta^{34}\text{S}_{\text{CAS}}$	27Al	54Fe	55Mn	88Sr
171	-0.74	-6.36		800,031	2,904,626	282,213	300,379
172	-0.79	-6.14					
173.1	-0.46	-5.81		1,237,082	2,065,176	197,690	312,258
174	-0.80	-5.36					
175.1	-0.69	-6.53		865,565	2,163,025	228,008	329,765
176.3	-0.80	-6.25					
177.8	-0.40	-6.22					
178.8	-0.23	-5.87		821,141	1,903,585	216,590	351,000
179.6	-0.15	-6.35		1,652,788	2,413,255	234,148	297,774
180.8	-0.95	-6.52					
182.1	-0.71	-6.10					
183.3	-0.18	-6.24		699,598	1,633,025	228,646	274,182
184.3	-0.53	-5.76					
185.9	-0.53	-6.31	26.15				
187.1	-0.48	-5.98					
188.1	-0.46	-5.80		961,456	1,797,164	234,454	283,114
189.2	-0.48	-6.16		430,750	1,278,181	204,702	304,094
190.3	-1.38	-6.12	32.82				
191	-0.52	-5.85					
192.2	-0.61	-5.86					
192.9	-0.62	-6.29		950,358	1,599,863	327,297	314,383
194.1	-0.66	-6.12		898,034	1,877,380	405,862	348,173
195.2	-0.57	-5.92		874,296	1,818,678	258,641	386,074
196	-1.22	-6.27		1,020,103	1,736,950	279,076	283,320
197.5	-0.32	-5.96					
198.3	-1.12	-6.49					
199.1	-0.62	-6.32					
201.7	-0.61	-6.40		1,130,616	2,151,470	395,410	291,662
203.1	-0.61	-5.89					
203.6	-0.45	-5.91					
204.4	-0.58	-5.93		983,255	2,197,385	367,124	277,940
205.9	-0.24	-5.99		504,262	1,254,937	281,310	358,170
207.3	-0.18	-5.91		712,301	1,816,428	333,736	334,227
208.9	-0.39	-5.77		843,898	1,688,642	311,584	293,657
210.6	-0.58	-6.24					
211.3	-0.37	-5.77		1,268,718	1,970,800	288,911	289,348
212.8	-0.74	-6.29		422,223	1,422,083	290,534	281,792
213.9	-0.58	-4.91					

Height	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	$\delta^{34}\text{S}_{\text{CAS}}$	27Al	54Fe	55Mn	88Sr
215.9	-0.60	-6.30					
216.9	-0.51	-5.71					
217.6	-0.24	-5.86		514,729	1,421,191	330,910	266,633
219.1	-0.32	-5.93					
220.1	-0.38	-6.08	21.26				
221.1	-0.40	-5.91					
222.1	-0.29	-5.62		905,298	1,867,392	353,303	326,538
223.2	-0.36	-5.42		803,221	1,722,812	257,402	267,448
224.3	-0.20	-6.01					
225.1	-0.04	-5.81		570,087	1,342,103	183,431	240,748
225.9	-0.25	-6.09					
226.9	-0.23	-6.01		543,110	1,185,467	160,225	256,964
229.2	0.43	-5.83	22.97	553,947	1,814,414	307,970	347,043
230.1	-0.58	-6.63					
231.4	-0.35	-5.82					
232.6	-0.41	-4.93					
233.6	-0.38	-6.13					
234.7	-0.60	-6.28					
235.4	-0.33	-6.13		1,681,285	2,115,712	292,730	270,660
236.4	-0.17	-6.06		375,947	1,488,432	302,341	246,326
237.2	-0.70	-6.23					
238.7	-0.33	-6.16		1,962,246	2,182,346	263,703	276,500
239.6	-0.82	-6.47		592,839	1,236,961	202,059	206,252
240.7	0.08	-6.00		2,895,817	3,703,357	352,148	280,557
241.6	-0.73	-6.37					
242.9	-0.95	-6.16	29.18	627,355	1,143,291	220,217	256,256
243.7	-0.31	-6.30					
245.7	-0.47	-6.09	27.00	508,680	1,173,778	224,693	290,619
246.9	-0.39	-5.73		780,863	1,215,331	221,454	295,833
248	-0.07	-5.81		624,034	1,322,517	219,622	252,106
249.1	-0.61	-5.69		380,320	1,095,587	216,868	249,560
250.6	-0.66	-6.16		470,987	1,109,467	190,269	260,610
251.6	-0.32	-6.30					
253.1	-0.54	-6.18		656,966	1,348,040	218,856	251,595
255.5	-0.21	-6.07					
257.3	0.24	-5.96		723,914	1,888,622	332,877	242,462
258.5	-0.01	-5.99		1,337,671	2,019,892	228,175	254,022
259.8	-0.73	-6.23		1,707,892	2,646,116	176,217	225,589

Height	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	$\delta^{34}\text{S}_{\text{CAS}}$	27Al	54Fe	55Mn	88Sr
260.5	-0.77	-6.16					
261.3	-0.36	-6.42		1,307,937	1,855,960	180,167	254,785
262.3	-0.59	-5.93					
263.4	-0.57	-5.86					
265.1	-0.68	-5.43					
267.2	-0.65	-5.95					
268.2	-0.85	-5.96		801,404	1,622,460	183,731	253,297
270.7	-1.21	-6.44	27.24	446,417	1,810,772	287,172	290,399
271.5	-0.46	-6.10					
273.4	-0.35	-6.08		93,256	592,465	104,152	446,899
275.4				337,532	488,858	67,224	290,211
277.4	-0.47	-6.32		300,876	698,462	108,153	336,089
279.4	-1.10	-5.95		523,655	793,521	87,858	343,682
280.6	-1.21	-6.22		327,382	310,872	9,569	173,358
282.8	-0.70	-5.75		455,931	605,959	82,404	325,395
284.8	-0.77	-5.57					
286.1	-0.85	-5.87		523,130	810,987	167,722	287,960
288.2	-0.98	-6.18					
290.1	-1.34	-6.19		273,370	565,968	133,473	341,706
292.6	-1.03	-5.72					
294.2	-1.64	-5.82					
295.8	-0.89	-6.18		259,581	342,567	129,366	359,759
296.8	-0.75	-5.96					
304.5	-1.07	-6.12		205,707	784,496	196,774	238,996
305.8	-0.85	-6.04					
306.7	-0.89	-5.99					
308.6	-0.80	-5.72		1,287,675	1,022,260	118,500	181,044
310.3	-	-	25.84				
311.4	-0.81	-5.85		558,897	785,395	151,643	263,409
312.2	-0.84	-5.83					
313.3	-1.39	-6.11					
314.9	-1.17	-6.14		299,914	558,301	205,088	299,513
316.7	-0.79	-5.58					
318.5	-0.91	-5.90		245,851	672,105	256,247	313,229
319.4	-0.83	-5.81					
321	-0.42	-5.94		689,662	1,097,091	239,237	302,048
322.1	-0.85	-5.87		475,049	549,727	81,423	124,057
323.7	-0.74	-5.96		621,233	781,577	183,985	266,613

Height	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	$\delta^{34}\text{S}_{\text{CAS}}$	27Al	54Fe	55Mn	88Sr
324.9	-0.04	-5.55					
326.1	-0.94	-6.10		619,615	956,541	229,173	278,640
327.3	-1.09	-6.06		281,655	884,914	221,459	281,960
329.6	-0.81	-5.82	25.77	854,625	1,359,152	234,629	290,342
330.8	-0.50	-5.65		385,080	745,195	206,055	334,326
332.2	-1.70	-5.63					
333.6	-0.67	-5.81		544,751	759,920	197,766	334,101
336.3	-0.44	-5.62		267,918	547,506	184,325	276,282
337.8	-0.99	-6.01		486,097	685,117	214,634	277,170
340	-1.12	-6.23					
341.5	-1.07	-6.06		299,959	739,479	194,462	298,480
344.2	-0.82	-5.98					
345.3	-1.66	-6.19		694,631	673,153	174,518	280,926
347.5	-0.54	-6.00		349,902	652,230	208,958	314,888
351	-0.76	-6.14		1,062,994	2,450,985	717,748	887,816
353	-0.88	-5.47		2,314,715	2,229,479	244,963	314,941
353.9				610,810	895,103	227,842	293,850
354.9	-0.90	-5.85		307,219	904,959	245,886	262,728
356.1	-0.96	-5.84					
357.4	-0.92	-5.87		878,272	942,886	261,704	284,465
358.6	-	-	20.98				
359.3	-0.91	-5.75					
361.7	-1.18	-5.96		886,821	1,469,782	261,574	267,137
363.3	-1.00	-5.81					
364.9	-0.92	-5.85					
366.2	-1.04	-5.69					
367.2	-0.68	-5.87					
369.00	-0.68	-5.62					
370.5	-1.31	-5.16		320,803	595,201	196,133	476,898
371.3	-1.02	-5.63					
372.5	-1.83	-6.35		256,094	392,206	211,827	300,944
373.7	-1.29	-5.83					
374.3	-1.33	-5.68		617,722	970,527	221,532	305,204
375.5	-0.87	-5.70	23.16				
376.4	-0.93	-5.81					
378.3	-2.09	-6.01	24.43				
378.9	-1.00	-5.45					
379.8	-1.30	-5.81					

Height	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	$\delta^{34}\text{S}_{\text{CAS}}$	^{27}Al	^{54}Fe	^{55}Mn	^{88}Sr
380.7	-1.21	-5.76		401,412	656,678	174,749	296,754
381.2	-1.15	-5.89					
382.2	-0.79	-5.06					
383.5	-1.40	-5.83					
386	-1.12	-5.80					
387.6	-1.30	-5.81					
388.7	-1.63	-6.06	19.04	539,359	649,407	179,776	288,166
390.4	-1.56	-5.59					
391.3	-1.64	-6.10					

Table 2: Monocle data (ppm)

Sample 41.2												
ROI	Sample	55Mn	2 SE	57 Fe	2 SE	88 Sr	2 SE	232 Th	2 SE	238 U	2 SE	Pix els
ROI09	Micrite	9.46	0.34	132.8	8.9	145.6	3.5	0.0442	0.0062	0.335	0.017	93
ROI13	Micrite	9.39	0.29	99.7	3.4	163.8	3.4	0.0275	0.0035	0.332	0.014	102
ROI14	Micrite	8.59	0.34	90.4	2.6	164.4	5.6	0.0344	0.0071	0.317	0.028	84
ROI15	Micrite	8.99	0.29	142.4	6.2	152.5	4.4	0.0373	0.0035	0.360	0.015	54
ROI16	Micrite	8.32	0.25	112.2	6.3	149.3	4.4	0.0311	0.0042	0.324	0.016	87
ROI18	Micrite	9.27	0.45	135.8	8.9	136.8	3.4	0.0382	0.0043	0.370	0.034	68
ROI23	Micrite	8.93	0.36	106.1	3.7	154.8	3.2	0.0280	0.0034	0.314	0.014	99
ROI29	Micrite	9.78	0.41	103.1	4.4	155.7	5.2	0.0313	0.0051	0.324	0.016	91
ROI36	Micrite	10.08	0.35	155.6	5.3	171.6	6.5	0.0465	0.0058	0.469	0.058	54
ROI37	Micrite	11.72	0.37	163.2	8.2	126.1	3.2	0.0352	0.0048	0.345	0.014	51
ROI38	Micrite	7.59	0.21	94.2	2.4	171.8	3.2	0.02721	0.00297	0.305	0.011	87
ROI01	Cement C2	9.13	0.28	131.0	3.5	60.7	1.8	0.0159	0.0035	0.864	0.107	144
ROI04	Cement C2	8.669	0.303	96.0	3.9	90.4	7.1	0.0042	0.0021	0.243	0.027	68
ROI07	Cement C2	8.24	0.37	83.7	4.8	83.3	11.3	0.0181	0.0073	0.460	0.045	49
ROI08	Cement C2	8.06	0.24	91.1	5.5	66.8	4.1	0.0000	0.0000	0.486	0.035	43
ROI10	Cement C2	8.53	0.34	117.1	6.2	90.0	8.6	0.00305	0.00203	0.282	0.022	44
ROI12	Cement C2	7.54	0.28	118.6	4.5	138.1	12.6	0.0031	0.0015	0.399	0.061	40
ROI20	Cement C2	8.68	0.49	145.9	5.5	139.2	8.1	0.0277	0.0054	0.3439	0.0196	52
ROI22	Cement C2	6.67	0.35	114.1	3.4	171.8	12.8	0.0066	0.0024	0.317	0.023	57
ROI24	Cement C2	8.19	0.28	98.3	3.8	67.5	3.5	0.00158	0.00105	0.388	0.027	66
ROI26	Cement C2	7.86	0.27	77.4	2.5	59.0	2.3	0.0030	0.0013	0.591	0.049	63
ROI30	Cement C2	7.25	0.22	103	4.03	139.9	9.7	0.0045	0.0029	0.219	0.017	70
ROI35	Cement C2	8.48	0.44	147.5	6.2	108.1	5.7	0.0150	0.0046	0.322	0.028	40
ROI39	Cement C2	8.70	0.35	111.3	4.7	124.1	7.7	0.0309	0.0059	0.336	0.042	47
ROI02	Cement C1	8.73	0.36	133.0	4.8	123.3	6.5	0.0094	0.0034	0.222	0.022	75
ROI03	Cement C1	8.63	0.33	109.9	3.2	130.3	6.9	0.0123	0.0038	0.201	0.024	50
ROI06	Cement C1	8.33	0.44	93.1	4.3	128.8	11.5	0.0032	0.0016	0.254	0.023	59
ROI17	Cement C1	8.68	0.31	102.6	3.8	101.0	9.1	0.0074	0.0029	0.228	0.022	49
ROI19	Cement C1	8.71	0.35	110.2	4.6	119.6	11.3	0.0079	0.0029	0.230	0.039	46
ROI21	Cement C1	7.99	0.32	154.6	5.3	153.1	5.2	0.0321	0.0061	0.304	0.021	41
ROI25	Cement C1	8.26	0.401	89.9	3.1	133.8	7.2	0.0254	0.0038	0.311	0.015	93
ROI28	Cement C1	8.85	0.36	113.0	4.99	125.13	5.96	0.0145	0.0038	0.247	0.026	102
ROI31	Cement C1	7.53	0.25	95.7	4.3	126.2	8.9	0.0074	0.0028	0.361	0.027	84
ROI32	Cement C1	8.36	0.37	122.1	3.9	136.7	5.7	0.0235	0.0061	0.226	0.026	54
ROI34	Cement C1	10.72	0.63	189.7	9.1	152.6	5.4	0.0412	0.0054	0.380	0.019	87
Mean	All	8.65	0.34	116.7	4.9	128	6.4	0.0200	0.0038	0.343	0.029	
Mean	Micrite	9.28	0.33	121.4	5.5	153.8	4.2	0.0346	0.0046	0.345	0.022	
Mean	C1	8.62	0.37	119.4	4.7	130.1	7.6	0.0167	0.0039	0.269	0.024	
Mean	C2	8.15	0.32	110.4	4.5	103.0	7.3	0.0103	0.0031	0.404	0.039	
Sample 268.6R												
	TS Petrog	55Mn ppm	2SE	57Fe ppm	2SE	88Sr ppm	2SE	232Th ppm	2SE	238U ppm	2SE	Pix els
ROI03	Cement C1	154.52	2.98	512	18	333.9	10.2	0.165	0.012	0.560	0.016	51
ROI07	Cement C1	191.4	5.5	489	36	186	20	0.117	0.017	0.841	0.061	39
ROI18	Cement C1	169.44	3.96	521	19	296	23	0.089	0.011	0.921	0.062	55
ROI19	Cement C1	127.2	5.3	338.7	10.1	457.7	10.4	0.0216	0.0037	0.272	0.025	102
ROI11	Cement C2	189.1	4.1	618	46	171	14	0.225	0.021	1.246	0.076	67
ROI13	Cement C2	171.7	3.7	828	57	339	16	0.249	0.014	0.667	0.035	62
ROI14	Cement C2	165.50	2.97	783.1	80.4	288.0	8.8	0.2875	0.0205	0.821	0.049	39
ROI15	Cement C2	208.0	5.5	707	43	193	11	0.230	0.015	1.181	0.078	45
ROI32	Micrite	158.5	1.3	1057	54	347.3	3.2	0.451	0.012	0.627	0.016	186
ROI05	Micrite	164.5	4.9	2070	309	316	13	0.548	0.039	0.804	0.041	70
ROI06	Micrite	160.9	2.8	680	49	306.2	7.9	0.476	0.021	0.875	0.055	69
ROI21	Micrite	157.3	2.2	947	45	312.5	4.7	0.400	0.013	0.6875	0.0295	82
ROI22	Micrite	166.3	2.5	579	46	267.3	6.1	0.281	0.012	0.753	0.025	50
ROI23	Micrite	165.8	1.7	1217	62	316.8	4.3	0.329	0.011	0.718	0.016	129
ROI24	Micrite	162.90	1.96	624	31	323.4	9.7	0.230	0.013	0.749	0.027	94
ROI25	Fossil	155.6	2.5	897.3	50.1	335.6	4.6	0.4855	0.0199	0.606	0.019	42
ROI27	Fossil	173.6	2.6	1029	95	292	14	0.1921	0.0202	0.812	0.03002	64
ROI28	Fossil	154.0	2.7	466	27	303.2	19.8	0.205	0.015	0.972	0.058	41
ROI30	Fossil	158.9	3.7	779	85	302.7	9.8	0.324	0.015	0.807	0.022	68
ROI31	Fossil	153.9	2.9	457	28	356.8	5.9	0.0963	0.0088	0.667	0.038	47
ROI33	Fossil	140.1	3.4	487.1	10.4	372.9	7.5	0.237	0.014	0.663	0.023	47
Mean All		164.2	3.3	766	57	305.6	64	0.269	0.016	0.774	0.038	
Mean Allomic		162.3	2.5	1025	85	312.7	7.1	0.388	0.017	0.7447	0.0298	
Mean C1		160.6	4.4	465	21	318.3	15.8	0.098	0.011	0.648	0.041	
Mean C2		183.6	4.1	734	57	248	12	0.248	0.018	0.9788	0.0596	
Mean Fossil		156	2.9	686	49	327.2	10	0.257	0.016	0.754	0.032	

Table 3 Elemental covariation Monocle data

41.2 m	Component	55Mn	57 Fe	88Sr	232 Th	238U
57Fe	Full Set	0.35	-			
88Sr	Full Set	0.01	0.10	-		
232 Th	Full Set	0.38	0.30	0.38	-	
238 U	Full Set	0.01	<0.01	-0.19	<0.01	-
57Fe	Micrite	0.52	-			
88Sr	Micrite	-0.33	-0.29	-		
232 Th	Micrite	0.16	0.52	-0.03	-	
238 U	Micrite	0.17	0.48	0.01	0.57	-
57Fe	Cement C1	0.49	-			
88Sr	Cement C1	0.06	0.45	-		
232 Th	Cement C1	0.25	0.59	0.68	-	
238 U	Cement C1	0.11	0.13	0.31	0.32	-
57Fe	Cement C2	0.08	-			
88Sr	Cement C2	-0.30	0.18	-		
232 Th	Cement C2	0.23	0.22	0.06	-	
238 U	Cement C2	0.11	<0.01	-0.35	<0.01	-
268.6R	Component	55Mn	57 Fe	88Sr	232 Th	238U
57Fe	Full Set	0.02	-			
88Sr	Full Set	-0.83	<0.01	-		
232 Th	Full Set	<0.01	0.52	<0.01	-	
238 U	Full Set	0.63	<0.01	-0.75	<0.01	-
57Fe	Micrite	0.02	-			
88Sr	Micrite	0.30	0.10	-		
232 Th	Micrite	0.11	0.45	0.15	-	
238 U	Micrite	0.13	<0.01	0.20	0.05	-
57Fe	Cement C1	0.56	-			
88Sr	Cement C1	-0.99	-0.55	-		
232 Th	Cement C1	0.30	0.69	-0.35	-	
238 U	Cement C1	0.81	0.70	-0.74	0.21	-
57Fe	Cement C2	-0.39	-			
88Sr	Cement C2	-0.62	0.92	-		
232 Th	Cement C2	-0.64	-0.61	0.43	-	
238 U	Cement C2	0.66	-0.91	-0.99	-0.47	
57Fe	Fossils cement	0.59	-			
88Sr	Fossils cement	-0.61	-0.24	-		
232 Th	Fossils cement	<0.01	0.27	-0.01	-	
238 U	Fossils cement	0.07	-0.02	-0.51	0.12	-

Supplementary Materials

Table A1 Elemental covariation XRF data Sample 267.2 2472 eV

	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Ga	As
Si	-	0.03	0.04	0.25	-0.24	0.21	0.19	0.04	0.25	0.02	0.01	0.01	0
S	-	-	0.99	0.75	0.06	0.66	0.59	0.6	0.25	0.52	0.54	0.51	0.47
Cl	-	-	-	0.79	0.06	0.74	0.68	0.68	0.28	0.62	0.63	0.61	0.57
K	-	-	-	-	0.16	0.86	0.82	0.79	0.37	0.74	0.75	0.73	0.69
Ca	-	-	-	-	-	0.01	0.02	0.08	-0.04	0.05	0.05	0.05	0.05
Ti	-	-	-	-	-	-	0.96	0.92	0.45	0.91	0.91	0.9	0.86
Cr	-	-	-	-	-	-	-	0.94	0.45	0.96	0.96	0.95	0.93
Mn	-	-	-	-	-	-	-	-	0.42	0.94	0.94	0.92	0.9
Fe	-	-	-	-	-	-	-	-	-	0.42	0.41	0.4	0.4
Cu	-	-	-	-	-	-	-	-	-	-	0.99	0.99	0.98
Zn	-	-	-	-	-	-	-	-	-	-	-	0.99	0.98
Ga	-	-	-	-	-	-	-	-	-	-	-	-	0.99
As	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A2 Elemental covariation XRF data Sample 267.2 2481 eV

	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Ga	As
Si	-	0.05	0.05	0.38	-0.26	0.42	0.5	0.08	0.26	0.08	0.03	0.02	0.01
S	-	-	0.85	0.57	0.04	0.63	0.42	0.4	0.09	0.35	0.43	0.41	0.27
Cl	-	-	-	0.61	0.04	0.54	0.47	0.45	0.08	0.44	0.54	0.52	0.36
K	-	-	-	-	0.16	0.68	0.65	0.51	0.14	0.49	0.55	0.52	0.41
Ca	-	-	-	-	-	-0.08	-0.09	0.08	-0.09	0	0.02	0.02	0.02
Ti	-	-	-	-	-	-	0.79	0.59	0.23	0.64	0.69	0.66	0.58
Cr	-	-	-	-	-	-	-	0.59	0.25	0.69	0.73	0.72	0.64
Mn	-	-	-	-	-	-	-	-	0.16	0.62	0.68	0.65	0.59
Fe	-	-	-	-	-	-	-	-	-	0.16	0.13	0.11	0.12
Cu	-	-	-	-	-	-	-	-	-	-	0.84	0.82	0.8
Zn	-	-	-	-	-	-	-	-	-	-	-	0.91	0.86
Ga	-	-	-	-	-	-	-	-	-	-	-	-	0.85
As	-	-	-	-	-	-	-	-	-	-	-	-	-

Table B1 Elemental covariation XRF data Sample 268.6L 2472 eV

	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Ga	As
Si	-	0.03	0.04	0.36	-0.27	0.51	0.62	0.09	0.19	0.19	0.06	0.03	0.02
S	-	-	0.92	0.64	0.04	0.56	0.43	0.44	0.11	0.39	0.68	0.59	0.29
Cl	-	-	-	0.69	0.03	0.58	0.48	0.48	0.04	0.43	0.67	0.65	0.34
K	-	-	-	-	0.17	0.65	0.61	0.47	0.09	0.45	0.6	0.57	0.32
Ca	-	-	-	-	-	-0.09	-0.11	0.09	-0.05	-0.02	0.01	0.02	0.02
Ti	-	-	-	-	-	-	0.74	0.48	0.17	0.52	0.65	0.6	0.37
Cr	-	-	-	-	-	-	-	0.43	0.18	0.49	0.55	0.53	0.34
Mn	-	-	-	-	-	-	-	-	0.15	0.41	0.55	0.53	0.35
Fe	-	-	-	-	-	-	-	-	-	0.16	0.12	0.05	0.09
Cu	-	-	-	-	-	-	-	-	-	-	0.6	0.58	0.4
Zn	-	-	-	-	-	-	-	-	-	-	-	0.77	0.5
Ga	-	-	-	-	-	-	-	-	-	-	-	-	0.51
As	-	-	-	-	-	-	-	-	-	-	-	-	-

Table B2 Elemental covariation XRF data Sample 268.6L 2481 eV

	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Ga	As
Si	-	0.02	0.04	0.37	-0.28	0.5	0.59	0.09	0.18	0.19	0.06	0.04	0.02
S	-	-	0.74	0.52	0.02	0.49	0.38	0.37	0.07	0.35	0.55	0.49	0.27
Cl	-	-	-	0.72	0.03	0.63	0.54	0.48	0.04	0.5	0.75	0.7	0.4
K	-	-	-	-	0.12	0.68	0.65	0.46	0.09	0.5	0.64	0.61	0.37
Ca	-	-	-	-	-	-0.1	-0.12	0.09	-0.06	-0.03	0.01	0.02	0.02
Ti	-	-	-	-	-	-	0.75	0.45	0.16	0.53	0.65	0.61	0.4
Cr	-	-	-	-	-	-	-	0.42	0.17	0.51	0.6	0.57	0.39
Mn	-	-	-	-	-	-	-	-	0.15	0.39	0.52	0.49	0.34
Fe	-	-	-	-	-	-	-	-	-	0.15	0.12	0.06	0.1
Cu	-	-	-	-	-	-	-	-	-	-	0.6	0.58	0.42
Zn	-	-	-	-	-	-	-	-	-	-	-	0.77	0.55
Ga	-	-	-	-	-	-	-	-	-	-	-	-	0.54
As	-	-	-	-	-	-	-	-	-	-	-	-	-

Table C1 Elemental covariation XRF data Sample 268.6R 2472 eV

	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Ga	As
Si	-	0.05	0.03	0.24	-0.23	0.3	0.34	0.06	0.17	0.06	0.02	0.01	0.01
S	-	-	0.97	0.83	0.06	0.76	0.68	0.65	0.17	0.62	0.72	0.67	0.5
Cl	-	-	-	0.85	0.06	0.79	0.72	0.68	0.13	0.67	0.76	0.72	0.55
K	-	-	-	-	0.14	0.85	0.81	0.72	0.16	0.71	0.78	0.74	0.59
Ca	-	-	-	-	-	-0.01	-0.02	0.1	-0.03	0.03	0.04	0.04	0.04
Ti	-	-	-	-	-	-	0.92	0.78	0.21	0.83	0.88	0.84	0.73
Cr	-	-	-	-	-	-	-	0.77	0.2	0.84	0.87	0.84	0.75
Mn	-	-	-	-	-	-	-	-	0.18	0.76	0.81	0.79	0.7
Fe	-	-	-	-	-	-	-	-	-	0.18	0.17	0.15	0.15
Cu	-	-	-	-	-	-	-	-	-	-	0.91	0.89	0.85
Zn	-	-	-	-	-	-	-	-	-	-	-	0.93	0.87
Ga	-	-	-	-	-	-	-	-	-	-	-	-	0.87
As	-	-	-	-	-	-	-	-	-	-	-	-	-

Table C2 Elemental covariation XRF data Sample 268.6R 2481 eV

	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Ga	As
Si	-	0.14	0.29	0.73	-0.21	0.73	0.76	0.14	0.17	0.18	0.11	0.08	0.01
S	-	-	0.41	0.2	0	0.29	0.13	0.07	0.2	0.06	0.27	0.09	0.01
Cl	-	-	-	0.31	-0.03	0.25	0.23	0.07	0.07	0.07	0.13	0.18	0.04
K	-	-	-	-	0.03	0.54	0.54	0.12	0.1	0.13	0.1	0.07	0.01
Ca	-	-	-	-	-	-0.12	-0.13	0.09	-0.02	-0.04	-0.03	0	0
Ti	-	-	-	-	-	-	0.57	0.11	0.17	0.14	0.15	0.07	0.01
Cr	-	-	-	-	-	-	-	0.11	0.15	0.14	0.09	0.07	0.01
Mn	-	-	-	-	-	-	-	-	0.09	0.03	0.04	0.02	0.01
Fe	-	-	-	-	-	-	-	-	-	0.1	0.1	0.02	0.03
Cu	-	-	-	-	-	-	-	-	-	-	0.08	0.08	0.01
Zn	-	-	-	-	-	-	-	-	-	-	-	0.2	0.01
Ga	-	-	-	-	-	-	-	-	-	-	-	-	0.01
As	-	-	-	-	-	-	-	-	-	-	-	-	-

Chapter 5: Conclusions and general discussion

Sulfur isotope records from carbonate associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) are a valuable source of information on the behaviour of the sulfur cycle and its interaction with redox conditions over earth history (Canfield and Teske, 1996, Canfield *et al.*, 2000, Habicht *et al.*, 2002). Carbonates occur in diverse marine depositional environments over much of the geological record and offer a source of paired sulfur $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ data. The strength of carbonates as a source of $\delta^{34}\text{S}_{\text{CAS}}$ in diverse palaeoenvironments requires researchers to develop an understanding of how processes that impact $\delta^{34}\text{S}$ vary between those environments or more specifically between depositional conditions occurring in those environments. Such physical processes in modern environments include sedimentation rate, organic carbon loading, grain size and shape (Habicht and Canfield, 1997; Aller, 2014). Studies in modern deltaic depositional environments indicate that physical environmental characteristics may have an important, yet poorly understood influence on the sulfur isotope signal recorded by marine sediments (Aller *et al.*, 2008; Canfield and Farquhar, 2009; Ries *et al.*, 2009; Aller *et al.*, 2010; Aller, 2014). The hypothesis that these processes may have caused a component of the $\delta^{34}\text{S}_{\text{CAS}}$ variability recorded within or between ancient depositional facies requires investigation in particular due to the scale and rapidity of the identified lateral and secular changes in $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ data, which is frequently incompatible with the long residence time of sulfur in the oceanic sulfate reservoir.

This study tests the hypothesis, firstly by characterising the depositional environment by sedimentological interpretation of lithofacies and microfacies scale textural observations. Textural information is supplemented in Chapter 2 by $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$ and solution-ICP-MS trace-element data. This data assists in constraining the extent of diagenetic alteration within different segments of the stratigraphic section and indicates that post-depositional diagenetic alteration is unlikely to have been of a magnitude considered sufficient to alter trace element data. However, when REE + Y data are considered it is also apparent that despite a lack of evidence for a large magnitude of diagenetic alteration or of siliciclastic contamination, none of the analysed carbonates have the deep, upper crust-normalised patterns that are seen in fully open marine seawater and carbonate proxies thereof (e.g. Nothdurft *et al.*, 2004). The samples instead display REE + Y patterns that are slightly LREE-enriched to flat, with profiles intermediate between seawater and modern river water.

The REE+Y data also display variability that, interpreted as a primary marine signal, indicates changing water column conditions through the stratigraphy and is consistent with a gradient of brackish to saline conditions (Lawrence *et al.*, 2006a). However, the results are clearly contradicted by the occurrence of open-marine taxa through much of the stratigraphic section. Chapter 2 therefore concludes that the samples required further micron-scale analysis to clarify the origin of the divergence of the paleoenvironments indicated by the REE+Y data and the faunal assemblage. In particular the low Mn and Fe concentrations in the La Silla Formation require further attention in light of the distinctly negative $\delta^{13}\text{C}_{\text{CAS}}$ data produced from the La Silla Formation in previous studies of the stratigraphic section at Cerro La Silla (Thompson and Kah, 2012).

Chapter 3 further investigates the origin of the flat REE+Y profiles in the samples, using LA-ICP-MS mapping and the measurement tool Monocle (Petrus *et al.*, 2017). The investigation considers whether there is evidence of alteration or siliciclastic or other contaminant phases that might alter the shale-normalized REE slope or lower the Y/Ho ratio. As the allomicrite phase was analyzed in the solution-ICP-MS study (Chapter 2), representative samples were mapped by LA-ICP-MS analysis with focus in particular on the micron scale variability occurring within the potentially heterogeneous allomicrite phase. Elemental concentration measurements from the LA-ICP-MS map data were made using the Iolite add-in Monocle and the resulting values are within the range of those expected in marine carbonates, with the exception of the carbonates below 110 m (above fairweather wave base) at the base of the section. The effectiveness of the dissolution in 5% HNO_3 is considered and it is concluded that partial, disproportionate leaching of siliciclastic associated elements has led to a correction that is unreliable and of insufficient magnitude in the solution data.

A correction based on the LA-ICP-MS mapping results supports the interpretation of the facies conditions from the upper La Silla Formation to the top of the section (within the San Juan Formation) set out in Fig. 3.7. Below 110 m brackish porewater conditions were present in frequently reworked, oxidizing sediment porewaters with very low siliciclastic inputs that increase with deepening moving upsection. Brackish conditions may have extended to the water-column based on the impoverished fauna encountered in the shallow facies at the base of the section. By 110 m, with deepening below fair-weather wave base, the sediment redox column was less frequently disrupted. Reducing conditions in the sediment column and greater basinal clay input occurred with migration to more marine facies conditions. With deepening to below storm wave base, much greater basinal shale input and an undisrupted

redox column are recorded in sample 241.6. Siliciclastic input decreased slightly at the upper reef and the data briefly show a return to very low Mn levels, consistent with oxic burial conditions.

The results illustrate the value of LA-ICP-MS mapping as a geochemical screen for further targeted analysis where there is a texturally indistinguishable, but geochemically variable, phase such as allomicrite. This variability would not be identifiable by LA-ICP-MS spot analysis based on petrographic criteria alone. The current study also reveals the potential of LA-ICP-MS mapping as a screen for identification of the impact on geochemical results of leaching during solution ICP-MS data sample preparation.

The micron-scale distribution of CAS is investigated in Chapter 4, paired with trace element distribution and concentrations in four LA-ICP-MS maps from three identified depositional facies. At the micron scale, mapping of the distribution and abundance of sulfur-bearing phases in thin sections by X-ray Absorption Near Edge Structure (XANES) spectroscopy and micro x-ray fluorescence (μ -XRF) imaging, is supplemented by overlapping mapping of trace element proxies of water-column and porewater chemical and redox conditions by LA-ICP-MS mapping. These data are assessed in light of the newly presented bulk rock $\delta^{34}\text{S}_{\text{CAS}}$ analysis and provide evidence of the impact of syndepositional to early diagenetic processes occurring in sediment porewaters on the $\delta^{34}\text{S}_{\text{CAS}}$ record. Supported by evidence of porewater conditions developed in Chapters 2 and 3, the data from Chapter 4 contribute to a growing body of work that seeks to identify depositional factors which may cause $\delta^{34}\text{S}_{\text{CAS}}$ data to diverge from primary marine values. At the base of the section depositional sediment with very low Fe concentrations, periodically reworked in oxic conditions provide a pathway for oxidation of sulfide produced by MSR. Low Fe and pyrite in sample 41.2 support the possible occurrence of this process, which may contribute ^{34}S depleted sulfate to the porewater sulfate pool (Aller, 2014). An offset in the mean bulk $\delta^{34}\text{S}_{\text{CAS}}$ by 4.4‰ to more positive values in the current bulk dataset compared to that produced in previous studies from the same section (Thompson and Kah, 2012) may be a product of the distinct methodologies used and the impact of oxidation of sulfides during sample preparation (Wotte *et al.*, 2012).

Whilst it cannot be assumed that shallow water facies datasets produced throughout the geological record are similar to those at Cerro La Silla, there are nonetheless potentially highly variable and interrelated factors related to depositional facies that might influence the abundance and values of sulfide and sulfate recorded in microfacies and lithofacies. This

attaches a degree of uncertainty to the complex marine mechanisms currently inferred to explain anomalously rapid or large coeval changes in the sulfur isotope value of the marine sulfate reservoir. The development of methods to identify and exclude those samples impacted by syndepositional processes will improve our understanding of the sulfur isotope record through geological time. XRF mapping offers the potential for a much stronger understanding of sulfur species distributions but is not appropriate for routine investigation of multiple samples or multiple sample sets from existing datasets. As such, it may be valuable to further investigate the potential of LA-ICP-MS mapping as a more routine tool for mapping – this may be feasible by development of coincidence mapping of elements associated with sulfate or sulfide abundance, obtained by initial development of reference XRF mapping datasets.

References

- ALLER, R.C., BLAIR, N.E., BRUNSKILL, G.J. 2008. Early diagenetic cycling, incineration, and burial of sedimentary organic carbon in the central Gulf of Papua (Papua New Guinea). *J. Geophys. Res.*, 113, F01S09.
- ALLER, R.C., MADRID, V., CHISTOSERDOV, A., ALLER, J.Y., HEILBRUN, C. 2010. Unsteady diagenetic processes and sulfur biogeochemistry in tropical deltaic muds: implications for oceanic isotope cycles and the sedimentary record. *Geochimica et Cosmochimica Acta*, 74, 4671–92.
- ALLER, R.C. 2014. Sedimentary diagenesis, depositional environments, and benthic fluxes. In *Treatise on Geochemistry*, Vol. 8: The Oceans and Marine Geochemistry, ed. MJ Mottl, H Elderfield, pp. 293–334. Amsterdam, Elsevier. 2nd ed.
- BERNER, R.A., 2001. Modelling atmospheric O₂ over phanerozoic time. *Geochim. Cosmochim. Acta* 65, 685–694.
- CANÑAS, F. L. 1999. Facies and sequences of the Late Cambrian-Early Ordovician carbonates of the Argentine Precordillera: A stratigraphic comparison with Laurentian platforms. Special Paper 336: Laurentia-Gondwana connections before Pangea. Geological Society of America.
- CANFIELD, D.E. & FARQUHAR, J. 2009. Animal evolution, bioturbation, and the sulfate concentration of the oceans. *PNAS*, 106, 8123–8127.
- CANFIELD, D. E., HABICHT, K. S. & THAMDRUP, B. 2000. The Archean sulfur cycle and the early history of atmospheric oxygen. *Science*, 288, 658-61.
- CANFIELD, D. E. & TESKE, A. 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. *Nature*, 382, 127-32.
- HABICHT, K.S. & CANFIELD, D.E. 1997. Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments. *Geochimica et Cosmochimica Acta*, 61, 5351–5361.
- HABICHT, K. S., GADE, M., THAMDRUP, B., BERG, P. & CANFIELD, D. E. 2002. Calibration of sulfate levels in the archean ocean. *Science*, 298, 2372-4.
- HURTGEN, M. T., HALVERSON, G. P., ARTHUR, M. A. & HOFFMAN, P. F. 2006. Sulfur cycling in the aftermath of a 635-Ma snowball glaciation: Evidence for a syn-glacial sulfidic deep ocean. *Earth and Planetary Science Letters*, 245, 551-570.
- NOTHDURFT, L. D., WEBB, G. E. & KAMBER, B. S. 2004. Rare earth element geochemistry of Late Devonian reefal carbonates, Canning Basin, Western Australia:

confirmation of a seawater REE proxy in ancient limestones. *Geochimica et Cosmochimica Acta*, 68, 263-283.

LAWRENCE, M. G., GREIG, A., COLLERSON, K. D. & KAMBER, B. S. 2006a. Rare Earth Element and Yttrium Variability in South East Queensland Waterways. *Aquatic Geochemistry*, 12, 39-72.

PETRUS, J. A., CHEW, D. M., LEYBOURNE, M. I. & KAMBER, B. S. 2017. A new approach to laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) using the flexible map interrogation tool 'Monocle'. *Chemical Geology*, 463, 76-93.

THOMPSON, C.K. & KAH, L.C. 2012. Sulfur isotope evidence for widespread euxinia and a fluctuating oxycline in Early to Middle Ordovician greenhouse oceans. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 313-314, 189-214.

WOTTE, T., SHIELDS-ZHOU, G. A. & STRAUSS, H. 2012. Carbonate-associated sulfate: Experimental comparisons of common extraction methods and recommendations toward a standard analytical protocol. *Chemical Geology*, 326-327, 132-144.