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Development of a SEM-EDS method for quantifying free mica in building materials.

Declaration

I declare that this thesis has not been submitted as an exercise for a degree at this or any other University and the scanning electron microscopy with energy dispersive spectroscopy analysis is entirely my own work.

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I wish to acknowledge that the XRD analysis was conducted with the support of Dr. Robbie Goodhue and the Methylene Blue testing was performed at the Testall Ltd. laboratory.

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Summary

Following the publication of Irish Standard IS 465:2018, a standard developed to provide guidelines for those intending to provide assessment and testing services for dwellings suspected of being affected by defective concrete blocks, a need was highlighted for a technique to accurately and non-subjectively quantify free mica. Utilising the latest technology in field emission scanning electron microscopy coupled with energy dispersive X-ray microanalysis (FE SEM-EDS), we developed and published a method during the course of this thesis, for forensically investigating and measuring excessive levels of deleterious materials in sand and in the hardened cement matrix of concrete blocks, testing which can be subjective or problematic using other methods. Our method requires the generation of high-resolution backscattered electron (BSE) images using the FE SEM, from highly polished samples, where the characteristic needle-like morphology of free mica can easily be identified. Additional information on the size, shape and chemical composition of the free mica fines, is gathered using energy dispersive spectroscopy (EDS or EDX). The combination of high-magnification images, high-resolution elemental maps, and mineral liberation software allows accurate identification and quantification of free mica within the sand fines and cement matrix.

Thirty-two samples of building sands were independently collected from pits and builders' suppliers around Ireland who know the provenance of the sand. Sub-samples of concrete blocks were extracted from two semi-detached dwellings in Co. Donegal, exhibiting the characteristic damage patterns from free mica or suspected of containing high concentrations of free mica. The sampling locations were the gable end, external leaf and internal leaf (standard 4 inch blocks used on their edge) and one of the 'big 12' load bearing blocks which are commonly used on their flat, at the base of the exterior foundation walls.

Mica concentrations vary considerably in the sand samples tested. SEM-EDS analysis for the quantification of the percentage of free mica among the total fines gave the following results breakdown for the sand samples tested – in seven samples it was <1.0 %, in a further fifteen it was between 1 – 5%, in five it was between 5 – 10% and four samples contained >10% mica. For the quantification of the same sand samples using XRD, the results correlated well with the SEM-EDS and the mica concentrations also vary considerably – in five samples it was

not detected, in nine it was 0.3 – 1.0 %, in a further eight samples it was 1 – 5%, in five samples it was 5 – 10% and 5 samples contained >10% mica. Comparison of the SEM-EDS and XRD analysis results show that while the correlation is strong (with an R^2 value of 0.955), there appears to be systematic over estimation of the mica by XRD. The correlation of the SEM-EDS and MB free mica analysis is poor (with an R^2 value of 0.096) and there appears to be a systematic underestimation of the mica by MB.

The inhomogeneous nature of concrete blocks is a more complicated matrix to analyse. Averaging twelve of more fields of view at 1200x magnification, we were able to quantify the percentage of free mica among both the total fines and the cement matrix in the fields of view tested. The size of the area tested by SEM-EDS is small relative to the concrete block area, so the result demonstrates a fully quantitative value for these analysed areas and represents a semi-quantitative value relative to an entire concrete block.

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First and foremost, I wish to thank my supervisor, Dr. Robbie Goodhue for agreeing to supervise this project. I'm very grateful for his advice and support throughout my research time. Funding was awarded by iCRAG through Science Foundation Ireland (SFI) under Grant Number 13/RC/2092 and co-funded under the European Regional Development Fund and by iCRAG industry partners, so my thanks to them for this funding. Robbies work over the course of the project tracking down sand and concrete block samples for us to work on, is effort that is very much appreciated. My thanks also, for supplying sand samples, goes to the GSI (Geological Survey of Ireland). Robbie was of immense influence in enlisting the support of the GSI to access quarries, this support enabled us to expand the locations covered by the research. Thanks goes to the homeowners in County Donegal and Donegal County Council for support provided in accessing concrete samples.

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On a personal note, thank you to my family, especially Alan, for your advice, support and for helping to free up my time during the period of this research and thesis preparation. To Aoife, Rory, and Aisling, three rays of sunshine, thanks for all the fun.

Abstract

Leona O'Connor, MSc in Geology. Development of a SEM-EDS method for quantifying free mica in building materials.

The publication of Irish Standard IS 465:2018 highlighted the need for a technique to accurately and non-subjectively quantify free mica. The standard was developed to assist those who intend to provide assessment and testing services for dwellings that are suspected of being affected by defective concrete blocks. Utilising the latest technology in field emission scanning electron microscopy coupled with energy dispersive X-ray microanalysis (FE SEM-EDS), we developed and published a method during the course of this thesis, for forensically investigating and measuring excessive levels of deleterious materials in sand and in the hardened cement matrix of concrete blocks, testing which can be subjective or problematic using other methods. Our method requires the generation of high-resolution backscattered electron (BSE) images using the FE SEM, from highly polished samples, where the characteristic needle-like morphology of free mica can easily be identified. Additional information on the size, shape and chemical composition of the free mica fines, is gathered using energy dispersive spectroscopy (EDS or EDX). The combination of high-magnification images, high-resolution elemental maps, and mineral liberation software allows accurate identification and quantification of free mica within the sand fines and cement matrix.

Thirty-two samples of building sands were independently collected from pits and builders' suppliers around Ireland who know the provenance of the sand. Sub-samples of concrete blocks were extracted from two semi-detached dwellings in Co. Donegal, exhibiting the characteristic damage patterns from free mica or suspected of containing high concentrations of free mica. The sampling locations were the gable end, external leaf and internal leaf (standard 4 inch blocks used on their edge) and one of the 'big 12' load bearing blocks which are commonly used on their flat, at the base of the exterior foundation walls.

Mica concentrations vary considerably in the sand samples tested. SEM-EDS analysis for the quantification of the percentage of free mica among the total fines gave the following results breakdown for the sand samples tested – in seven samples it was <1.0 %, in a further fifteen it was between 1 – 5%, in five samples it was between 5 – 10% and four samples contained >10% mica. For the quantification of the same sand samples using XRD, the results correlated well with the SEM-EDS (R^2 0.955), the mica concentrations also vary considerably – in five samples it was not detected, in nine samples it was 0.3 – 1.0 %, in a further eight it was 1 – 5%, in five it was 5 – 10% and five samples contained >10% mica. Methylene blue comparative testing of the sand samples demonstrated poor correlation (R^2 0.096) with all of the sand tested ≦1g / kg.

The inhomogeneous nature of concrete blocks is a more complicated matrix to analyse, averaging twelve of more fields of view at 1200x magnification we were able to quantify the percentage of free mica among both the total fines and the cement matrix in the fields of view tested. The size of the area tested by SEM-EDS is small relative to the concrete block area, but the result demonstrates a quantitative value for the analysed areas.

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Introduction

Geoscience is proving that it has a positive role to play in problem solving, quality control and providing evidence-based rationales for defining and setting standards for the construction sector. In recent years, critical problems were highlighted in the construction industry and improving our understanding of building materials is beneficial to industry and society in general. Confidence is afforded to the consumer, when the product or service they purchase is manufactured according to quality standards or using accredited quality systems. The construction industry requires well defined standards for raw material and manufacturing, yet many knowledge gaps exist which require research before limits can be defined.

It is of societal benefit to fill this knowledge gap; it could help prevent homeowners in future from experiencing the difficulties experienced by others in the past. In 2013, structural distress in dwellings in County Donegal, Ireland was widely communicated to the public, through media reports, political representatives, local action groups and individual homeowners. The reports communicated concerns related to the alleged compromised structural integrity of these dwellings, the crumbling concrete blockwork with a particular cracking pattern in the external walls and the distress of the people living in these dwellings. These issues were formally raised with the Department of the Environment, Community and Local Government by the end of that year and in 2015 the Minister of State visited some the affected dwellings to witness first-hand the problems being experienced there. Following this, The Minister of State established an Expert Panel to investigate the problems in Counties Donegal and Mayo, related to the concrete blockwork of certain dwellings. The findings of the Expert Panel were issued in June 2017, in the Report of the Expert Panel on Concrete Blocks[1]. They observed that the presence of muscovite mica in abundant quantities in the aggregate constituent of the concrete blocks was suggested as being one of the main factors contributing to the deterioration of the concrete blocks.

Following the publication of Irish Standard IS 465:2018, a standard developed to provide guidelines for those intending to provide assessment and testing services for dwellings suspected of being affected by defective concrete blocks, a need was highlighted for a technique to accurately and non-subjectively quantify free mica. Utilising the latest technology in field emission scanning electron microscopy coupled with energy dispersive X-ray microanalysis (FE SEM-EDS), we developed and published a method during the course of this thesis, for forensically investigating and measuring excessive levels of deleterious materials in sand and in the hardened cement matrix of concrete blocks, testing which can be subjective or problematic using other methods.

A viable, quantitative analytical method, for the determination of the percentage of <63 µm muscovite fines (termed free mica) was required. The method needed to be applicable for both sand analysis and for quantifying free mica in the inhomogeneous cement matrix of hardened concrete blocks. During this research, a method was developed and published (O'Connor and Goodhue, 2019). The method requires the generation of high-resolution backscattered electron (BSE) images of the samples using field emission scanning electron microscopy (FE-SEM), where the characteristic needle-like morphology of mica can easily be identified. Additional information on the size, shape and chemical composition of the free mica fines, is gathered using energy dispersive spectroscopy (EDS or EDX). The combination of high-magnification images, high-resolution elemental maps and mineral liberation software allows accurate identification and quantification of free mica within the sand fines and cement matrix.

Sampling of building sand from quarries and building suppliers around Ireland was undertaken to provide a database for mineralogical mapping. The sand was tested for the presence of a deleterious material, muscovite mica, to improve the understanding of sand material quality. For similar analysis, samples of concrete blocks were cored from structurally weakened dwellings, in order to identify and quantify if excessive levels of deleterious material were used during the concrete block manufacturing.

Chapter 1 The nature of the problem

In 2013, structural distress in dwellings in County Donegal and Mayo, Ireland was widely communicated to the public, through media reports, political representatives, local action groups and individual homeowners. The reports communicated concerns related to the alleged compromised structural integrity of these dwellings, the crumbling concrete blockwork, a particular cracking pattern in the external wall render and the distress of the people living in these dwellings. These issues were formally raised with the Department of the Environment, Community and Local Government by the end of that year, and in 2015, the Minister of State visited some the affected dwellings to witness himself the problems being experienced there. Following this, The Minister of State established an Expert Panel to investigate the problems in Counties Donegal and Mayo, related to the concrete blockwork of certain dwellings. The findings of the Expert Panel were issued in June 2017, in the Report of the Expert Panel on Concrete Blocks[1] who observed that “The presence of muscovite mica in abundant quantities in the aggregate constituent of the concrete blocks was suggested as being one of the main factors contributing to the deterioration of the concrete blocks”.

It was reported that the locations in County Donegal affected, were mainly confined to specific regions, primarily in the Inishowen Municipal District, with Letterkenny Municipal District reporting a smaller number of dwellings affected. Investigators found the time scale of reported problems stretched back to dwellings constructed from 1984 up until 2011, but by far the greatest number of dwellings affected in County Donegal, appeared to have been constructed between 1999 and 2008. The report also noted that the issues were from many property types, from one-off single storey, dormer or two storey detached houses to large and small scale semi-detached housing developments. It was reported by some of the homeowners who were consulted by the Expert Panel, that during the prolonged cold winter of 2009 and 2010 the cracking started or became more pronounced, while others noted problems with cracking years before this. A survey conducted by the Mica Action Group advised the Panel that on average they found it was 5.3 years from construction to homeowners reporting cracking damage to their dwellings.

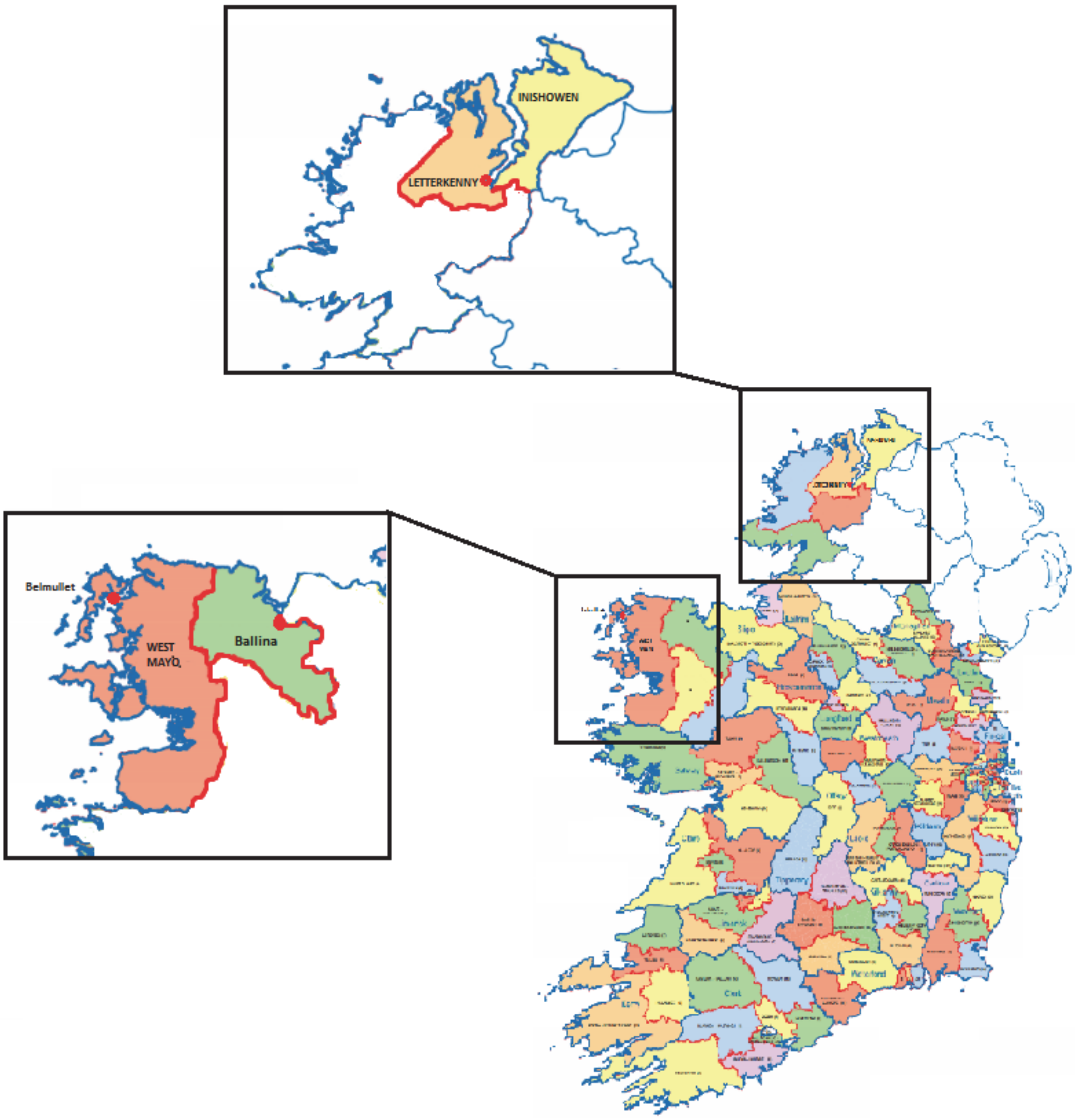

Figure 1: Map of Ireland indicating the locations in Donegal where concerns relating to defective blockwork were reported, image curtesy of the Report of the Expert Panel on Concrete Blocks.

The Expert Panel observations, relating to the nature of the problem in Donegal, noted that dwellings exhibited a particular pattern of cracking of the outer render on the horizontal and vertical plane, with the most severe cracks appearing in the vertical axis near corners (see Fig. 2 & 3). Some dwellings experienced displaced window frames, limiting their use, related to the movement of the external outer leaf concrete blocks. The external walls directly exposed to the prevailing wind and rain were generally reported as having the worst structural distress and were where the problems were first noticed by some homeowners. In instances where the render had fallen off and the outer leaf concrete block was exposed, it was possible for the concrete blocks to be fragmented by hand. Other surplus blocks from construction left exposed to the elements on one premises, also fragmented by hand. The panel noted that in general, the inner concrete block leaf of the damaged dwellings was unaffected.

Figure 2: Severe vertical cracks in the gable end of a dwelling in County Donegal found to have high levels of mica in the concrete blocks used for its construction.

Figure 3: Gable end of a two storey semi-detached dwelling exhibiting the typical vertical and horizontal cracking pattern on the outer render, and a significant vertical crack through the quoin.

During the course of their investigations into the construction defects, the Panel researched building designs, the concrete products, and the workmanship, using supplied engineering reports, photographic evidence and on-site visits. They felt there was little indicating that construction caused the distress, though some deviations to standards were noted. This coupled with the geographical spread of the houses and variety of the builders used, and the fact that dwellings both affected and unaffected were located closely and exposed to the same prevailing winds and rain, pointed to a problem with a building material. Similarly, with design related issues, the Panel noted that the dwellings affected appeared to be traditional concrete block constructions, though again they observed there were some deviations from the codified recommendations for masonry use in Ireland.

The Expert Panel also considered the significance of the report from Met Eireann, regarding the severe weather events of the winters of 2009 and 2010. Many factors including exceptional rainfall, up to twice the national average for the winter of 2009 and daily variation in temperatures of 10˚C in 2009 and one of 20˚C in 2010 (from -10˚C to +10˚C in 24 hours) among other weather factors like multiple consecutive days where the maximum and minimum temperature did not exceed 0˚C in Donegal. One other weather factor worth noting from the Expert Report, is the Driving Rain Index Map which categorises the exposure to driving rain as severe, moderate or sheltered. The dwellings affected in Donegal are mainly in severe exposure zones, see Fig. 4. Appendix 2 in the Report of the Expert Panel on Concrete Blocks presents a comprehensive Met Eireann weather report prepared for the Expert Panel.

In total, 63 technical reports were reviewed by the Expert Panel during the course of their investigation into the crumbling blockwork, contributing to their conclusion that high concentrations of muscovite were a likely cause of the failure. The reports received were a combination of consulting engineer reports and laboratory reports supplied by the Mica Action Group and other stakeholders. Eight recommendations were made by the Expert Panel at the conclusion of their technical review into the nature of the problem, based on the information and reports supplied to them.

The recommendations range from providing technical guidelines to homeowners ensuring a consistent assessment protocol is followed, to recommendations for preventing this problem from recurring. The first recommendation, regarding the testing and categorisation, emphasises the need for a simple standardised protocol to be developed. The Panel suggested that the National Standard Authority of Ireland should address the following points: -

(a) assess and categorise the damage.

(b) establish the extent of the problem.

(c) identify the scope of any testing required; and

(d) aid selection of an appropriate remedial solution.

Recommendation eight from the Expert Panel stated that due to legacy failures involving construction products, in spite of the current knowledge, further research should be undertaken to gain a greater understanding of the effects of pyrite and excessive amounts of muscovite mica in concrete blocks in order to avoid future adverse effects in buildings, with the Irish Centre for Research in Applied Geoscience (iCRAG) recommended at a research body to action this.

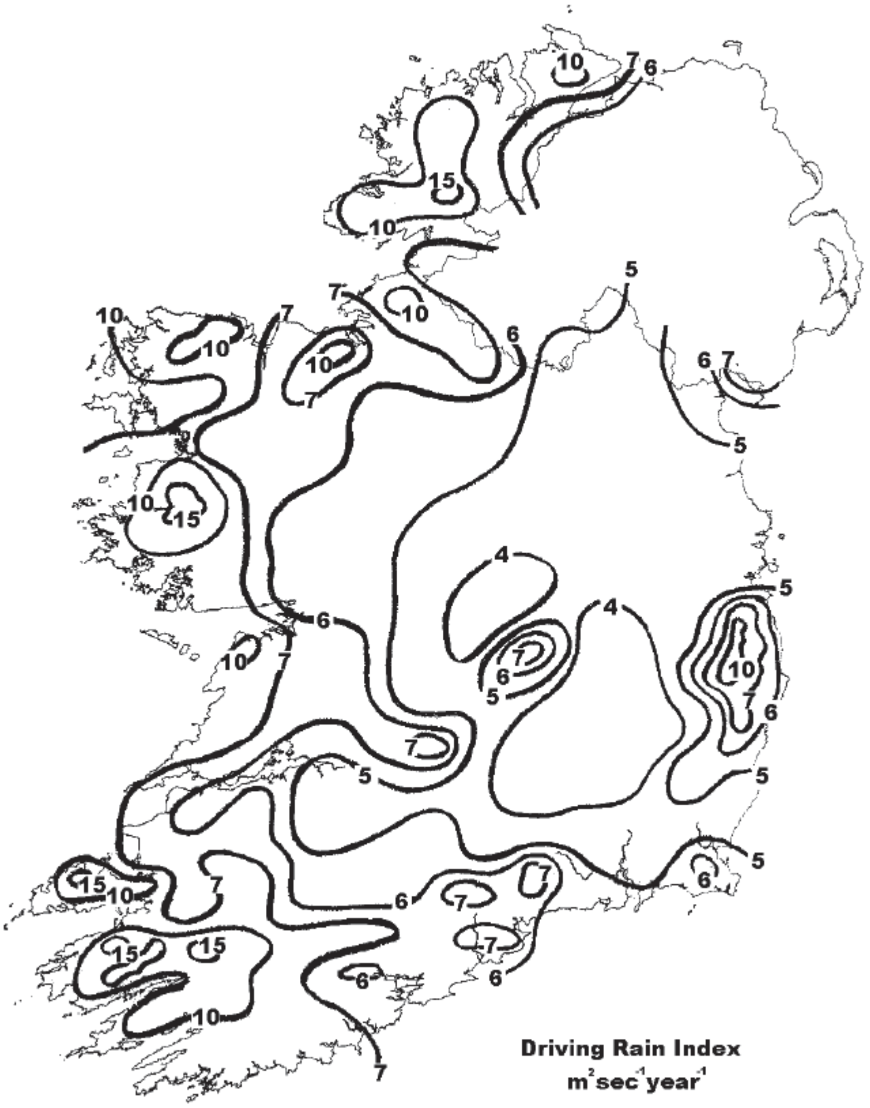

Figure 4: Driving Rain Index Map of Ireland, courtesy of the Report of the Expert Panel on Concrete Blocks, 2017.

The NSAI Expert panel on concrete blocks were consulted in late 2016 on their interpretation of a previous standard, S.I.288 in relation to statements made on RTE Prime Time which was broadcast on 31st May 2016. From September 11th, 2017 until its publication on 15th November 2018 the panel worked on the new national standard I.S. 465:2018 'Assessment, testing and categorisation of damaged buildings incorporating concrete blocks containing certain deleterious materials'.

The Irish National standard IS 465:2018[2] defines deleterious materials as the constituents of an aggregate that may compromise or include materials which could have an adverse effect on the properties of any concrete into which that aggregate was incorporated. The standard IS 465:2018 lists that adverse effects mainly include the following:

- chemical interference with the setting of cement.
- physical prevention of good bond between the aggregate and cement paste.
- modification of the properties of the fresh concrete to the detriment of the durability or strength of the hardened material.
- interaction between the cement paste and the aggregate which continues after hardening, sometimes causing expansion and cracking of the concrete.
- weakness and poor durability of the aggregate themselves.

Lea's Chemistry of Cement and Concrete[3] defines muscovite mica and biotite mica as "common constituents of many rock types, including granites, gneisses and sandstones, forming distinctive platy crystals. When mica occurs as discrete (or 'free') flaky grains in fine aggregates, it usually increases the water demand of concrete and also reduces the cohesiveness of the mix, which can adversely affect the final strength and durability of the hardened concrete". Technical research published in the UK[3], Sweden[4], USA[5] and South Africa[6], on the topics surrounding the implications for concrete made with high levels of muscovite baring aggregate, provide a plausible concrete block deterioration mechanism. Described in their research, is how the concrete aggregate and fines with high levels of mica in it, attracts a disproportionate amount of water compared to other aggregate. Also reported is the reduction in workability and strength of the concrete. Susceptibility to loss of integrity in freeze thaw conditions also results[7,1]. The small particle size of free mica, the low concentration of <63 µm fines in concrete aggregate (which is generally < 3% by weight), the abundance of muscovite in coarse aggregate and the inclusion of other non-muscovite mica minerals precludes or limits the viability of other standard analytical techniques[8,9,10,11,12].

Johansson, E et al (2007) presents a method for estimation of free mica particles in aggregate fine fraction by image analysis of grain mounts, using a modified point counting approach with micro photos of grain mounts and an analysis software package. Manual mineral identification is utilised by this technique and it is well known that the number of grains counted is imperative to the reliability of free mica content estimation in samples. The method is proposed as complimentary method to be used alongside other analytical methods for estimation of free mica.

Kondelchuk.D, et al (2008) details the use of two analytical methods considered sensitive to mica presence in aggregate; the sand equivalent test method and methylene blue (MB) test. Their research concluded that the sand equivalent test and MB test methods both showed susceptibility to free mica content in the fine fraction and gave a strong correlation in terms of mica content. They stated, both methods could be used as an indicating technique for quantitative determination of free mica fines in the unbound granular material but that there was a lack of laboratory methods available for estimating free mica in aggregates.

Novikov. E, (2008) studies the behaviour of mica-rich aggregates under the temperature climate conditions. His research shows that aggregates with a high mica content (> 30 vol. %) can absorb and store 20-30% more water when compared with aggregate with low concentrations of mica (< 20 vol. %). No critical concentration of mica was determined as further research was deemed necessary. Novikov's report shows the freeze-thaw cycling analysis confirmed that unbound mica-rich aggregates are frost susceptible, samples with the highest mica content (> 40%) showing the highest frost heave and highest heaving rate, resulting in deterioration in structures and loss of bearing capacity during a thaw.

Muller et al (1971) found that the deleterious effects of mica used for the manufacture of concrete depends more on the nature of the micaceous particles than on their quantity, with the presence of muscovite profoundly changing the concrete making properties of fine aggregate whereas biotite caused only small effects.

Schmitt (1990) documents that aggregate constituents such as micas, coatings, and water-soluble impurities are primarily present as minor constituents of concrete aggregates and, depending on composition, physical properties, and abundance may be harmful.

Ash, J.E. et al (1992) applies backscattered electron imaging to concrete materials and describes the application of the technique to concrete and mortar in order to determine a measure of porosity and the degree of hydration. Ash reaffirms Dewers[13] conclusions in that samples of the same concrete will have totally different properties dependent upon its position in a structure. The material close to the surface requires careful application to ensure durability.

Scrivener, K.L. (2004) describes the benefits of BSE imaging for the study of cement and concrete, highlighting its use to examine the microstructure of cement hydration, the microstructure development associated with atypical hydration (e.g. curing), and microstructural differences between cement paste produced in isolation versus part of a cement or mortar (e.g. interfacial transition zone). Scrivener emphasised the future advancement in quantitative BSE analysis needed to overcome the length of time required for quantitative analysis and emphasised the time restriction challenges for researchers with multi-user SEM facilities.

Stutzman. P, (2004) in scanning electron microscopy imaging of hydraulic cement microstructure, details the measurements made possible by the capabilities of SEM imaging coupled with X-ray microanalysis for bulk and surface phase composition of hydraulic cement. His research shows how by gaining better insight into hydration characteristics and cement-chemical admixture interactions, the information may be used to assist developing new hydraulic cements.

In I.S. 465:2018, the suspected safe/dangerous limits for mica are not specified in relation to the risk factor assessment for mica degradation in concrete blocks. A lack of data from quantitative methods exists to support such limits being set (pers. Comm. Goodhue). I.S. 465:2018 requires that the quantity of mica and the risk it poses is quantified by the Competent Person (professional geologist / petrographer).

Traditional non-SEM methods which are used have limitations. Thin section petrography of hardened concrete or resin-mounted fines suffer from a layering effect where multiple grains are stacked in the 30 µm thickness, obscuring individual grain boundaries. X-ray diffraction of powders generated from bulk concrete may not reflect the <63 µm fines as coarse aggregate is incorporated into the sample (pers. Comm. Goodhue).

The clear need for an analytical test method for quantifying the percentage of free mica in concrete sand and also within the cement matrix of hardened concrete blocks has been established. With both sand and concrete blocks highlighted by the Expert Panel as construction materials likely associated with the structural failures in County Donegal, this new method may prove to be beneficial for future prevention of failures in addition to identifying affected dwellings for remediation. The establishment of a database relating to the percentage of free mica in sand, from sources located around Ireland and intended for use in mortar, render and concrete block manufacturing, is beneficial data for current and future research and collaborations. This thesis provides a database of free mica in sands using the SEM-EDS method, which will be added to beyond the duration of this research project.

XRD (X-ray diffraction) was used as a second analytical tool to quantify the percentage of muscovite in <63μm fines sieved from the sand, allowing cross-reference with the SEM-EDS technique. This analysis was undertaken with the support of Dr. Robbie Goodhue. This is an analytical technique which identifies unknown phases by producing a 2d trace from a powdered crystalline substance and compares it to a comprehensive library. With this technique, the identification and quantification of the percentage of muscovite in the <63μm fines portion was measured and compared to the SEM-EDS results. The technique is discussed further in chapter 2.

As proposals exits to include methylene blue (MB) testing in relevant Irish Standards, it is included to provide some baseline data for building sands in Ireland as there is no experience of its use here yet (pers. Comm. Goodhue), 72 % of the sand sampled collected were independently tested using a third party laboratory, Testall Ltd. The test method used is based on BS EN 933-9:2009 +A1:2013 'Tests for geometrical properties of aggregates Part 9: Assessment of fines – Methylene blue test'. The principle of this method is, in increments to successively add a solution of methylene blue to the test sample in water. The standard method describes that the adsorption of the dye solution by the test sample is checked after each addition of solution using a filter paper to check for free dye. When the point of free dye detection is reached the methylene blue value (MB or MB_F) is quantified as grams of dye adsorbed per kilogram of the size fraction tested.

Chapter 2 Materials and method development

2.1 Sand samples

The range of samples analysed in the project include mica-rich sands from metamorphic terrains; sands which contain traces of detrital mica from reworked sandstones; and, samples which do not contain XRD-detectable mica from reworked reef limestones. This variability reflects the range of sands utilised in Ireland and is a justification for the project as no database of building sands exists in Ireland.

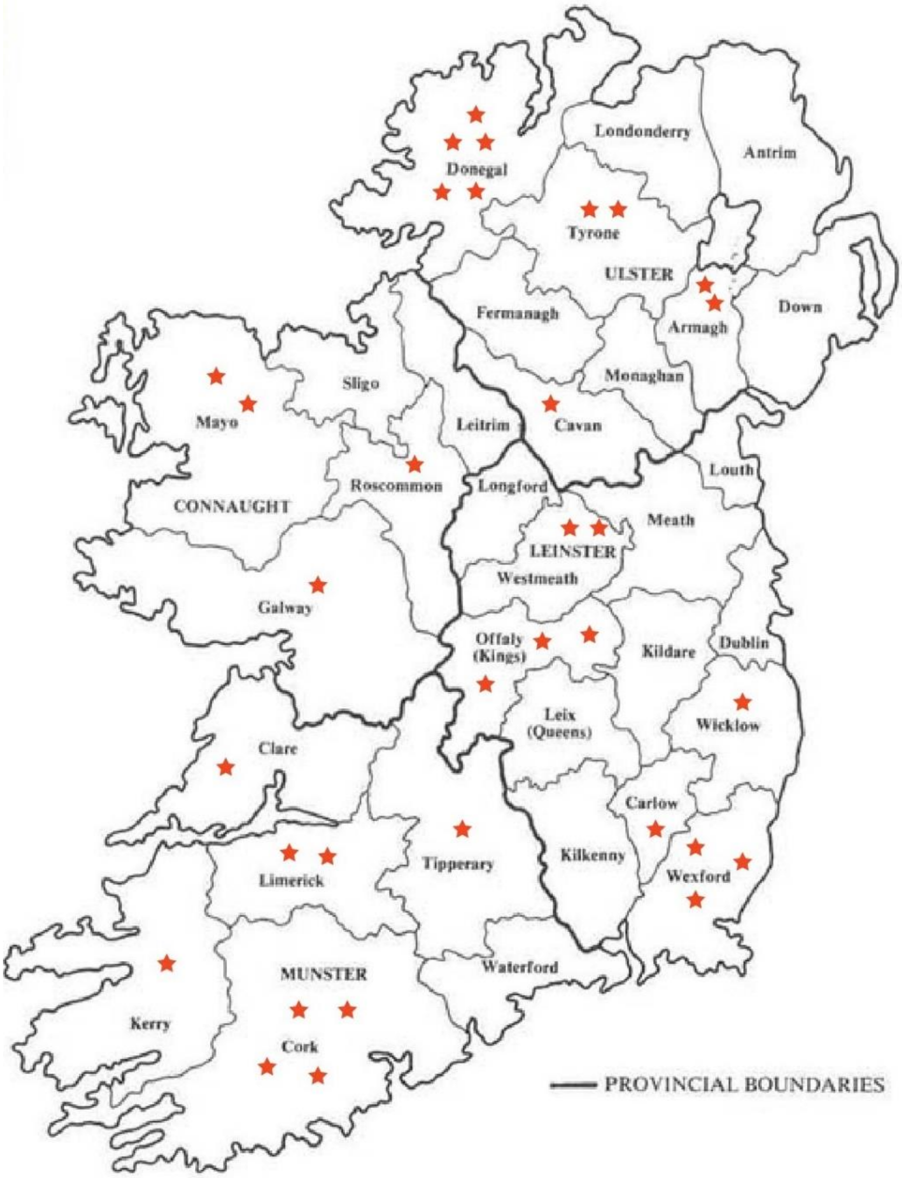

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Figure 5: Map of Ireland with the markers representing counties that were sampled for sand, the stars are not placed at the location of the source.

Figure 5 presents a map of Ireland which includes stars representing the counties that we sampled for sand, the markers are not placed at the location of the source to protect the identity of our sources.

2.2 Sand sample preparation for SEM-EDS analysis

For our investigation, thirty-two samples of building sand were independently collected from pits and builders suppliers around Ireland who know the provenance of the sand. The sampling location names are pseudonymised to protect the privacy of the sampling locations and for data protection purposes. Table 1 details information on the sampling locations based on the county in Ireland the sand was sampled from and product type tested. The samples were prepared by oven drying the sand at 45 °C before dry sieving to retain the <63 µm fraction. The sand was mixed thoroughly before a representative sub-sample was extracted and set in low-fluorine cold setting resin using round one-inch pucks (Fig 6), which were subsequently left to cure. The hardened resin pucks, with the sand embedded within were polished until the sand was exposed. Highly polished pucks are essential for good quality SEM-EDS sand analysis.

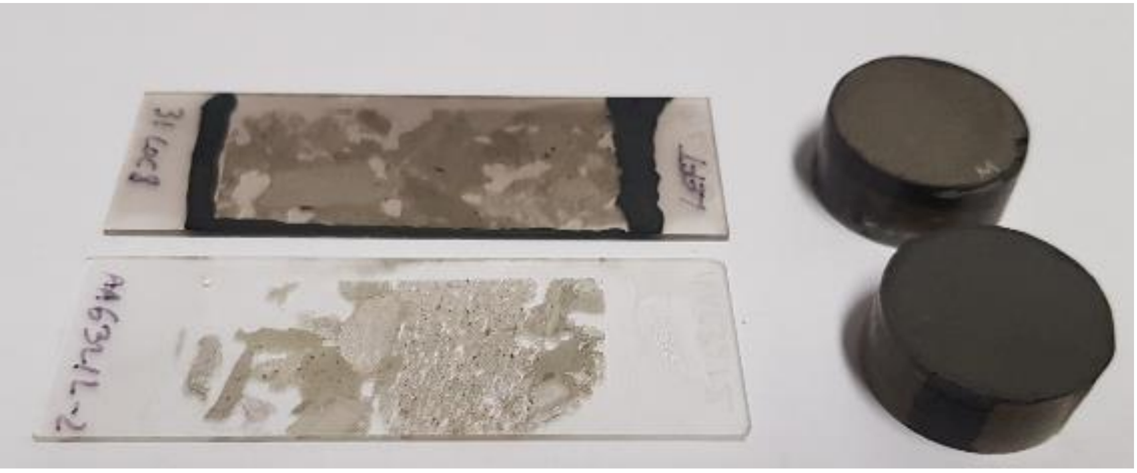


Figure 6: Polished thin sections of concrete blocks on the left (carbon coated to the rear, the boundary painted with colloidal graphite) and two polished round one inch pucks of sand embedded in resin, with a narrow rim and side strip of colloidal graphite applied.

Table 1: Counties in Ireland sampled, and sand type collected.

Sample Reference	County	Product description
AH-1	Armagh	Washed Building sand
AH-2	Armagh	Plastering sand
CE-1	Clare	*Building sand*
CK-1	Cork	*Concrete sand*
CK-2	Cork	*Concrete sand*
CK-3	Cork	*Building sand*
CK-4	Cork	*Sand*
CN-1	Cavan	Concrete sand
CW-1	Carlow	*Building sand*
DL-1	Donegal	*Building sand*
DL-2	Donegal	*Building sand*
DL-3	Donegal	*Building sand*
DL-4	Donegal	Sand
DL-5	Donegal	Concrete sand
GY-1	Galway	*Building sand*
KY-1	Kerry	Building sand
LK-1	Limerick	Concrete sand (4 mm)
LK-2	Limerick	Building sand (2 mm)
MO-1	Mayo	Asphalt sand
MO-2	Mayo	Concrete sand
OY-1	Offaly	*Building sand*
OY-2	Offaly	*Building sand*
OY-3	Offaly	*Building sand*
RN-1	Roscommon	Building sand
TE-1	Tyrone	Concrete sand
TE-2	Tyrone	Plastering sand
TS-1	Tipperary	*Concrete sand*
WH-1	Westmeath	Concrete sand
WH-3	Westmeath	*Building sand*
WW-1	Wicklow	*Building sand*
WX-1	Wexford	*Building sand*
WX-2	Wexford	*Building sand*
WX-3	Wexford	*Building sand*

2.3 XRD sample preparation and method

For XRD, the <63 µm sieved samples were prepared by placing them in a bulk cavity mount (with a 24 mm diameter and 2 mm depth) which were loaded into the Bruker D5000. The system has a 2.2 kW Cu long fine focus (0.4 x 12mm filament) and the following optical configuration was used: 2.5° primary soller, 1 mm aperture diaphragm, 1 mm scattered radiation diaphragm, no secondary soller, 0.2 mm detector diaphragm and a secondary curved graphite monochromator ahead of the scintillation counter. A scan each sample was made from 2 to 70 °2θ at a speed of 2 seconds / 0.01° step at 40 kV and 40 mA. Sample rotation was used.

The XRD trace was interpreted using Bruker AXS, Diffrac.EVA phase-matching software, 2012 Release, Version 3.0, with the industry-standard powder diffraction file database from the International Centre for Diffraction Data, Pennsylvania.

The XRD trace and interpreted phase information was used in Rietveld refinement software, Sietronics Siroquant Version 4.0, Release 5, with database v3.0g. to yield a semi-quantitative result. A theoretical trace is created, and parameters are optimised to fit it to the XRD traces. The merit of this fit is quantified by χ^2 and the R-Factor. The concentrations of minerals are presented as mass percent and are normalised to 100%. The software does not take account of any amorphous content.

2.4 Methylene blue (MB) sample preparation and method

The test (I.S. EN 933-9:2009+A1:2013, Tests for geometrical properties of aggregates Part 9: Assessment of fines – Methylene blue test) involves incremental addition of liquid methylene blue (MB) to a sample in water suspension. The >200 g 0/2 mm sample was pre-dried at <45 °C and weighed. After each addition of a measured volume of MB, the absorption by the sample is checked until excess dye is detected. The amount of dye used (in g per kg of sample) is then calculated.

The water content of a second subsample is determined by drying it to constant mass and the mass difference is used to ‘correct’ the data, but only makes negligible value differences: for example, a sample with an absorption of

20 ml of methylene blue dye would have a MB value of 1.0 with a water content of 0% and 1.05 with a water content of 5%.

For the purpose of the project, sand samples dried to constant mass were used for the MB test and the water content of three subsamples of DL-3, CN-1 and AH-2 were determined. Table 2 presents the corrected data for the samples, which is in the 3rd decimal and would be rounded to zero in each case. Table 7 presents the full set of MB g/kg (dry) results.

Table 2: MB data corrected for water content

Code	Water content (%)	MB g/kg (dry)	MB g/kg corrected
DL-3	0.26	0.3	0.30078
CN-1	0.51	0.5	0.50255
AH-2	0.27	1	1.00270

2.5 Concrete block sample preparation for SEM-EDS analysis

Sub-samples of concrete blocks were extracted from two semi-detached dwellings in Co. Donegal, exhibiting the characteristic damage patterns from free mica or suspected of containing high concentrations of free mica. The sampling locations were the gable end, external leaf and internal leaf (standard 4 inch blocks used on their edge) and one of the ‘big 12’ load bearing blocks which are commonly used on their flat, at the base of the exterior foundation walls. All concrete samples were cored horizontally, at mid-block height, with a 100 mm dry rig and the thin sections were produced from the long axis in the Department of Geology, Trinity College Dublin. It is recommended to prepare thin sections from more than one plane, due to the aspect ratio of free mica and the possibility of preferential alignment when concrete blocks are manufactured. The thin section results in this thesis are from single plane samples. The concrete samples were dried, impregnated with a low-fluorine cold setting resin, mounted to a glass slide, trimmed and reduced to a thickness of 30 µm, using a rotating plate polisher. A high quality polished thin section is critical to successful quantitative SEM-EDX analysis of the cement matrix containing mica.

2.6 Carbon Coating thin sections and pucks

The SEM-EDS analysis is performed under high vacuum (HV) at 20 kV, therefore steps are required to create a conductive sample surface in order to eliminate charging artefacts. The thin section and pucks are cleaned by wiping gently with ethanol, the surface is dusted off using a nitrogen air gun to remove any residual fibres. Carbon tracks are painted on the sample boundary and edges, then left to dry. Once dried, the samples are placed into the Cressington 208 carbon coater. When a suitable vacuum is achieved, 12 nm of carbon is applied to the sample surfaces (Fig.6). This step, which creates a conductive sample surface, is imperative for high quality SEM imaging[14,15].

2.7 BSE Imaging on the SEM

A Tescan MIRA3 variable pressure scanning electron microscope (VP-SEM) and a Tescan S8000 MIRA4 were used to take the backscattered electron (BSE) images. Elements with a high atomic mass number (heavy elements) appear brighter in the image and the darker areas in the BSE image, are elements with lower atomic mass numbers (light elements). The SEM has a Schottky field emission source and an electron gun maintained at high vacuum, the sample chamber is pressurised once the samples are inserted. The energy range, which spans from 1 – 30 kV, on the SEM was set to 20 kV for the cement matrix/sand fines imaging and EDS analysis. At 20 kV, sufficient energy is applied to the samples, to excite the atoms in the elements of interest within the cement matrix and sand fines, to generate the EDS spectrum. With a focused and destigmatise corrected image in resolution/analysis mode and using a WD & Z (working distance and z height) of 15 mm, the electron beam is aligned at 20 kV. Beam alignment includes automatic adjustments to the metal apertures and magnetic lenses in the gun and column, which is performed to create a thin, focused and stable electron beam. The image is refocused and degaussed as required during the working day. Due to the variation in fines/aggregate and cement hydration products, no one contrast and brightness setting is found to suit all images, so these settings vary. The image parameters are noted: resolution (width) pixels, resolution (height) pixels, the magnification, pixel dwell time (µs), image width (µm) and image height (µm) in the acquired images. The characteristic needle-like morphology of free mica, can easily be observed in the BSE image of sand fines set in resin, taken at 138 times magnification (Fig. 7). Free mica is different to the more irregular or rounded shapes of the other mineral fines.

TE-1a

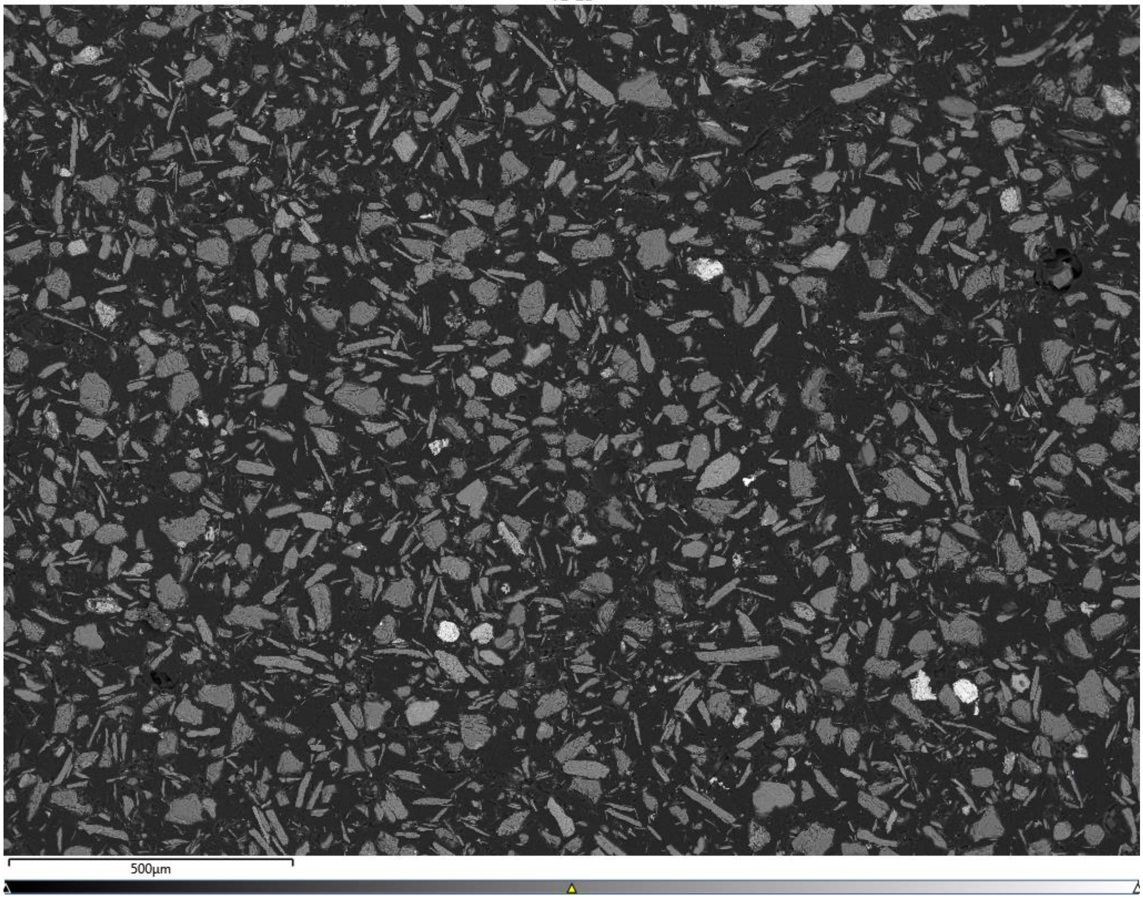


Figure 7: Backscattered electron (BSE) image, a single field of view at 138x magnification, of sand fines embedded in a resin puck. The needle-like morphology of free mica fines can easily be observed and are distinguishable from the other more irregular shaped and rounded fines. Image parameters; 2000 µm (length) x 1500 µm (breadth), 200 µs pixel dwell time and BSE frame time of 157 s. The black area in the image is the resin and grey/white features are sand fines.

The BSE image of sand fines embedded in resin (Fig 7), at 138x magnification, gives an overview of < 63 µm sieved sand fines in a polished resin puck. The black coloured area in the BSE image is resin, it may be identified by grey-level thresholding as a single feature due to its uniform colour in order to remove its surface area from the image area calculations. Thus, leaving only fines, which may be classified by the chemical and morphological free mica criteria defined by the user on the SEM EDS software, enabling the quantification of the percentage of < 63 µm free mica fines among the total fines.

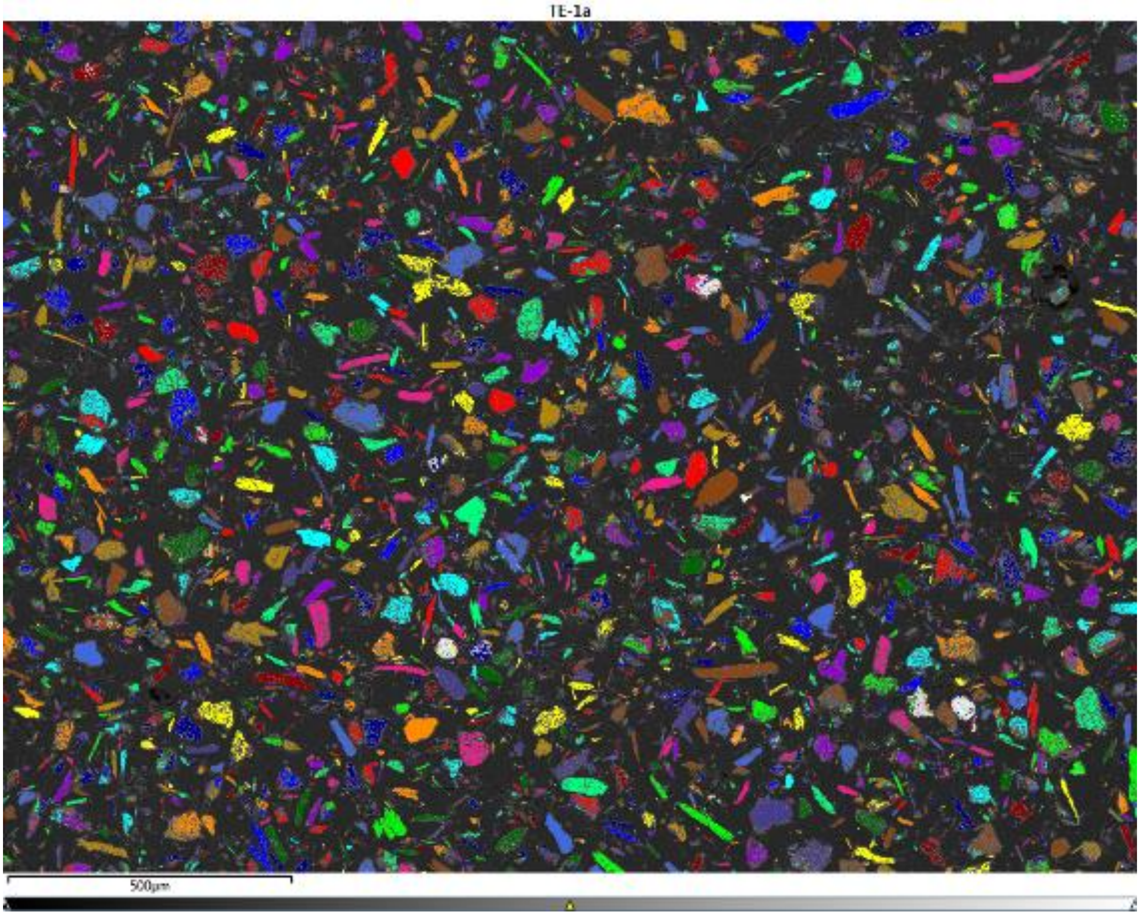


Figure 8: Backscattered electron (BSE) image, single field of view at 138x magnification, of sand fines embedded in a resin puck. The black area in the image is resin, all the sand fines are highlighted in multi-colour using thresholding (6832 fines in total identified by the software). Image parameters; 2000 µm (length) x 1500 µm (breadth).

The colours imposed by the thresholding software (Fig. 8) are used to highlight all the sand fines embedded in resin in the BSE image. The colours in this image are not used to display elemental composition, as is the case with the coloured single element and layered multi-elemental maps created with the SEM-EDS. The fines, coloured during this thresholding analysis step, are highlighted as areas to be assessed for free mica using the chemical and morphological criteria set.

The sand tested in this research was sieved to retain the <63 µm fraction. SEM images from a range of magnifications, ranging from 138–700x were acquired. It was determined that using magnifications between 250x and 600x magnification were suitable for imaging the < 63 µm fines fraction for quantitative analysis, montaging multiple images at 500x magnification for larger area analysis as required. The BSE and EDS pixel dwell times were set at 200 µs and 5000 µs respectively, BSE and EDS resolution were set to 1024 and 512, giving an EDS live frame time of approximately 16 minutes. Figure 8 shows all the sand features identified by grey-level thresholding. The classification criteria for size, shape and chemistry applied to the fines are calculated and the result displayed (Fig. 9), the <63 µm area fines are displayed in red. Chapter 3 presents the results of the sand samples examined, individual sand sample results are available in appendix A.

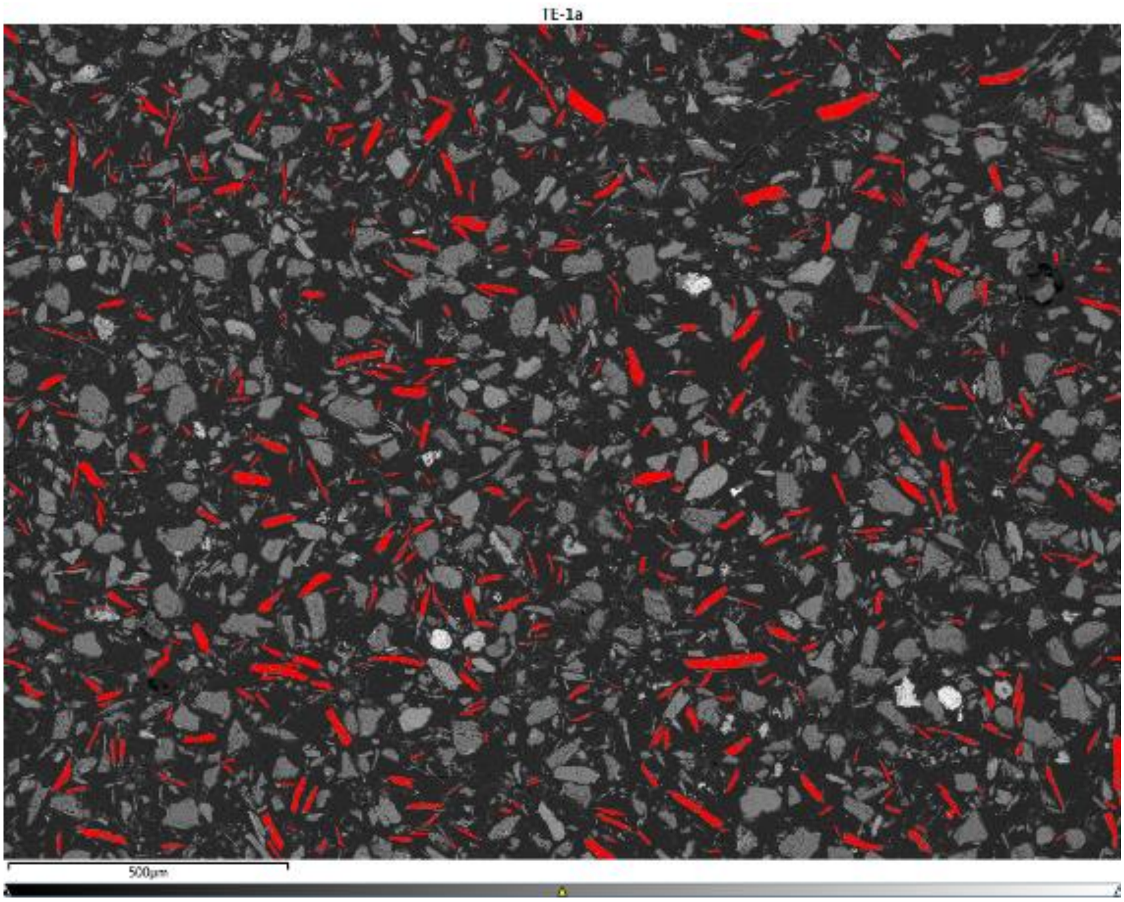


Figure 9: Feature image result; BSE image with free mica highlighted in red (138x magnification). The percentage of free mica among the total fines in this field of view is 20.4 %.

The BSE image in Fig. 10 is the cement matrix from a polished thin section at 1200x magnification, with free mica easily identified by its morphology. It is clear from comparing Fig. 7 (sand fines in a resin puck) and Fig. 10 (cement matrix) that the inhomogeneous nature of concrete is a far more complex matrix to analyse and highlights the additional complications of working with hardened concrete blocks.

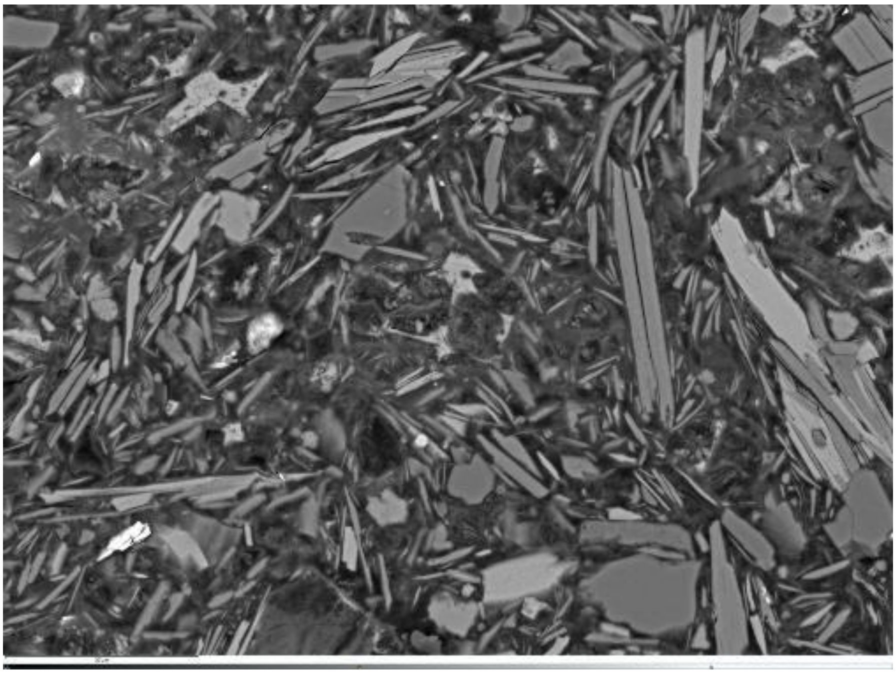


Figure 10: Backscattered electron SEM image, 1200x magnification, of free mica and other fines in the cement matrix of a hardened concrete block. Image dimensions, length 553 µm x breadth 445 µm.

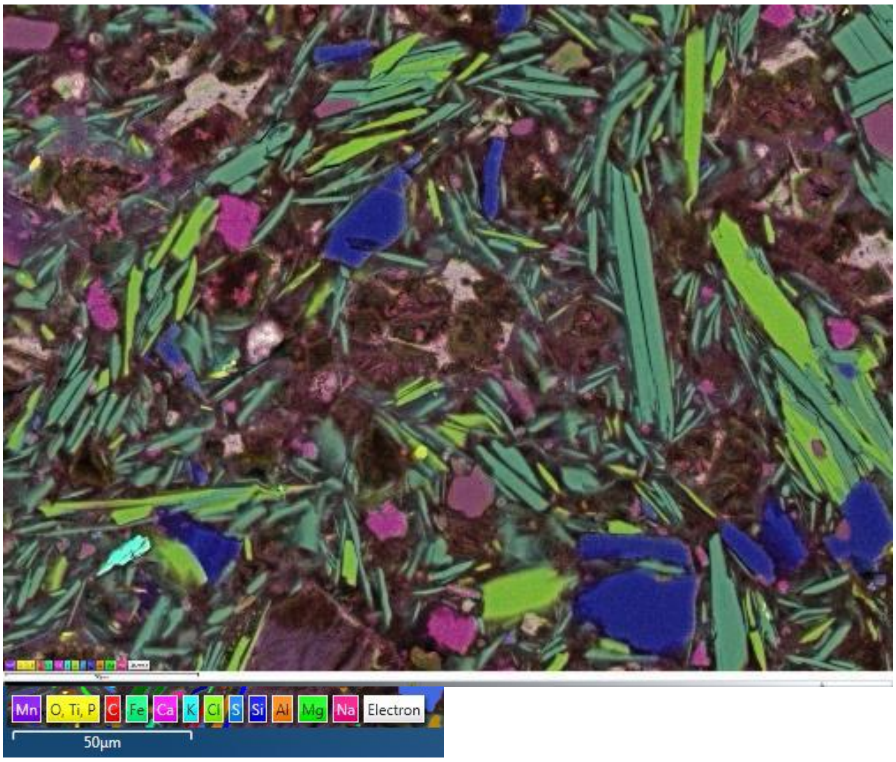


Figure 11: Layered EDS analysis map of free mica and other fines at 1200x magnification, in the cement matrix of a hardened concrete block. Free mica is highlighted in dark green, quartz is highlighted in blue and the cement paste binding the fines together is the purple background. A false colour is attributed to each element displayed in this map. Image dimensions, length 553 µm x breadth 445 µm.

2.8 SEM–EDS Operating conditions and calibration:

The Tescan MIRA3 variable pressure FE-SEM and Tescan S8000 MIRA4 FE-SEM are used with two Oxford X-Max 150 mm^2 Energy Dispersive X-Ray analysers (EDS) detectors which are controlled using Oxford Instruments Aztec X-Ray microanalysis software. The SEM settings included a beam intensity of ten, absorbed current of ~300 pA and a working distance of 15 mm. Cobalt was used to perform a quantitative optimisation of the electron beam prior to sample analysis and also at intervals during the day to monitor beam current drift.

Quantitative analysis of free mica within the sand fines was possible after the instrument was calibrated for selected elements, from the reference minerals in a certified Smithsonian mineral puck[14]. The elements of known weight percentage (Wt %) in the calibration were Si (in microcline), Al, Ti, Mg and Ca (in augite), Fe and Mn (in pyrope), Na and K (in anorthoclase), and Cr (in synthetic Cr_2O_3) and Ni (in synthetic Ni). Diopside and anorthoclase were subsequently used as quality control checks against this calibration. Precision was < 1% for all elements measured with accuracy better than 2%. A calibration using a certified SIRA grid is performed to demonstrate the accuracy of length measurements on the SEM image, with five 10 µm lengths on the grid selected, which resulted in an average measurement of 10.04 µm. Ten measurements using the 2 µm lengths are displayed in Fig. 12, averaging 2.01 µm.

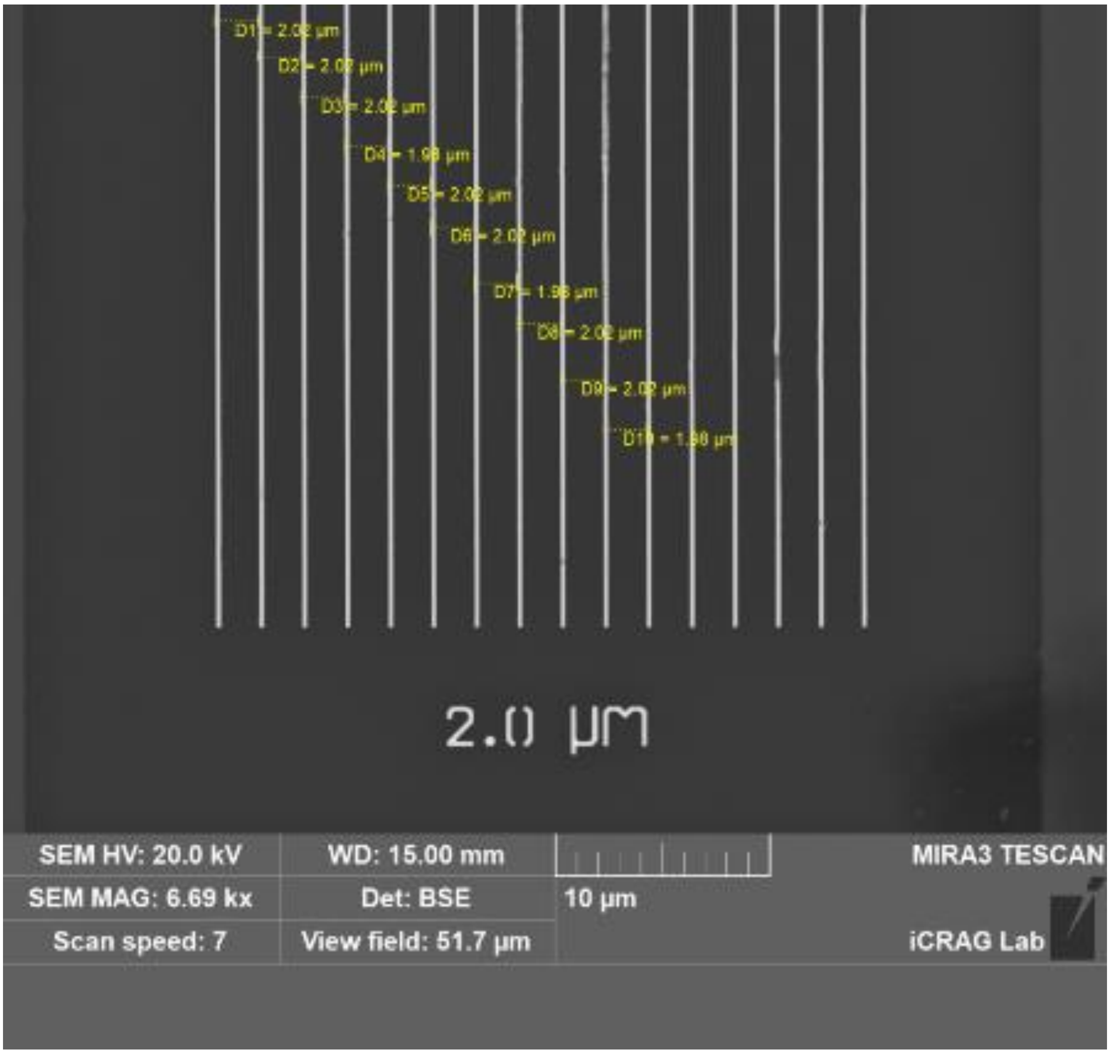


Figure 12: Certified SIRA grid for SEM length measurement calibration. The BSE image acquired at 6690x magnification demonstrates the accuracy of the length measurements on the SEM. The certified distance between each line is 2.0 µm and the measured distance is displayed in yellow on the image.

2.9 SEM-EDS Analysis

Elements are identified by their characteristic x-ray energies (KeV) and quantified by their peak intensities. Using the EDS, element maps are acquired from the same field of view as the BSE image, with the Map function on the Oxford Instruments Aztec software. Each element selected for analysis, is attributed a colour, and the individual element maps are combined by the software to generate a multi-coloured layered EDS element map (Fig. 11). The elements selected for EDS mapping are C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn and Fe (examples of K and Mg individual element maps are displayed in Fig. 13-14), additional or fewer elements may be displayed in the map, as data for the full elemental spectrum is automatically acquired.

Image dimensions, length 553 µm x breadth 445 µm for Fig. 13-14.

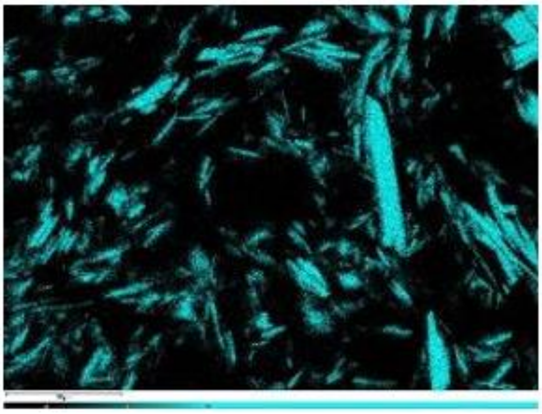


Figure 13: Potassium EDS map of fines in the cement matrix of a hardened concrete block.

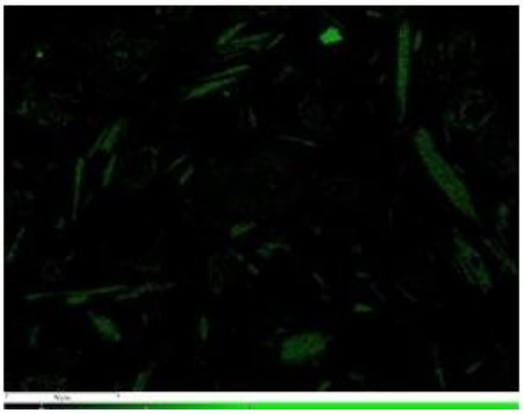


Figure 14: Magnesium EDS map of fines in the cement matrix of a hardened concrete block.

2.10 SEM-EDS Data processing:

The histogram of the BSE image is utilised by making adjustment to the upper and lower thresholds. The histogram, from black to white, covers a range from 0 to 32767. Identifying the threshold range for mica and other fines, distinguishes them from the epoxy resin matrix in the sand fines pucks and from the cement matrix in the polished concrete thin sections. By selecting a feature of interest in the BSE image, namely a mica fine, the software identifies its' gray-level, and can highlight all similar gray-level features in the image, manual adjustments may also be utilised to adjust threshold limits visually. In order to facilitate the extraction of the maximum statistical information on all fines identified in the BSE images, the threshold limits are set to include non- mica fines as well as mica fines in the sand/resin puck and cement matrix areas tested. The sieved mixed sand analysis yields the total number and area of fines tested, enabling calculation of the percentage of free mica within the total sand tested. For the concrete thin section, the area percentage of free mica can be expressed in terms of its abundance within the cement matrix in the fields of view tested. By excluding the cement paste, using its grayscale on the histogram, and focusing only on the fines, the percentage of free mica among the other fines in the fields of view tested can be determined.

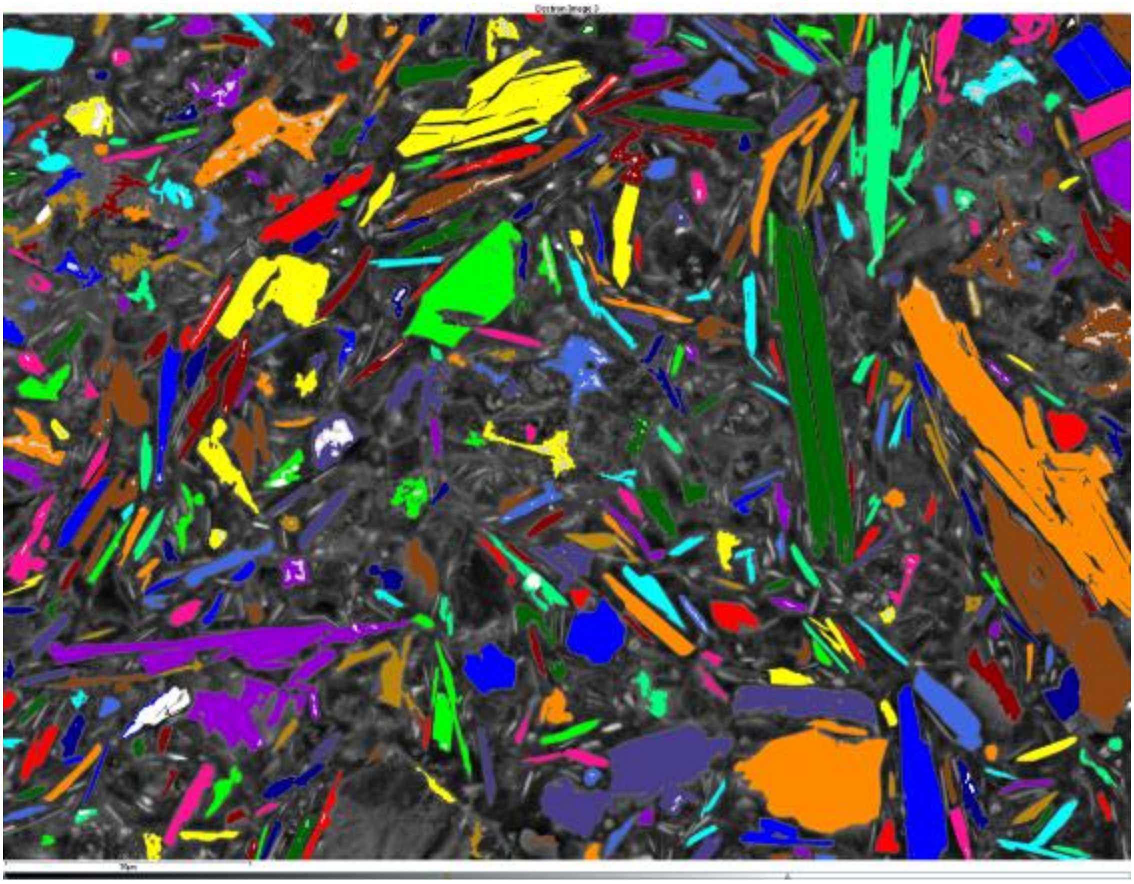


Figure 15: Backscattered electron SEM image with fines highlighted (multicoloured), by threshold adjustments, in the cement matrix of a hardened concrete block. 1200x magnification, Image dimensions, length 553 µm x breadth 445 µm.

Figure 15 is a high magnification (1200x) BSE image of cement matrix overlaid with features identified by thresholding, with the multi-coloured areas highlighting the unclassified fines. Classification of these features (or fines) follows, depending on the size, shape and chemistry classification criteria set. As free mica has a very characteristic morphology, it appears needle-like in the BSE image, the following measurements are set to identify free mica from the other fines; aspect ratio, breath, length and shape. Fines, with an aspect ratio less than 2.8 and shape factor less than 2 are rejected, length and/or breadth measurement are set to identify fines < 63µm. A circle has a shape value of 1, elongated and irregular features have larger values, shape is defined as $P^2/4\pi A$, where P is the perimeter, and A is the area[16]. The chemistry criteria used is, Potassium must be detected and Magnesium may be used to distinguish between muscovite and other mica minerals. Biotite and phlogopite can be distinguished from muscovite by EDS. Biotite and phlogopite consist of Si, Al, K, Mg, Fe and Ti whereas muscovite contains only a minor amount of Fe, and no Mg[17]. Figure 16 shows the cement matrix result, the <63 µm free mica is highlighted in red over the SEM image, the area of the fines is measured, enabling the calculation of the free mica percentage in the field of view of cement matrix tested. It must be noted that the 63 µm is a sieve mesh size, so some elongate grains >63 µm in diameter could have passed through into the sand batches used in manufacturing, such a feature is highlighted in green (Fig. 16), and such features are included in the <63 µm free mica calculation.

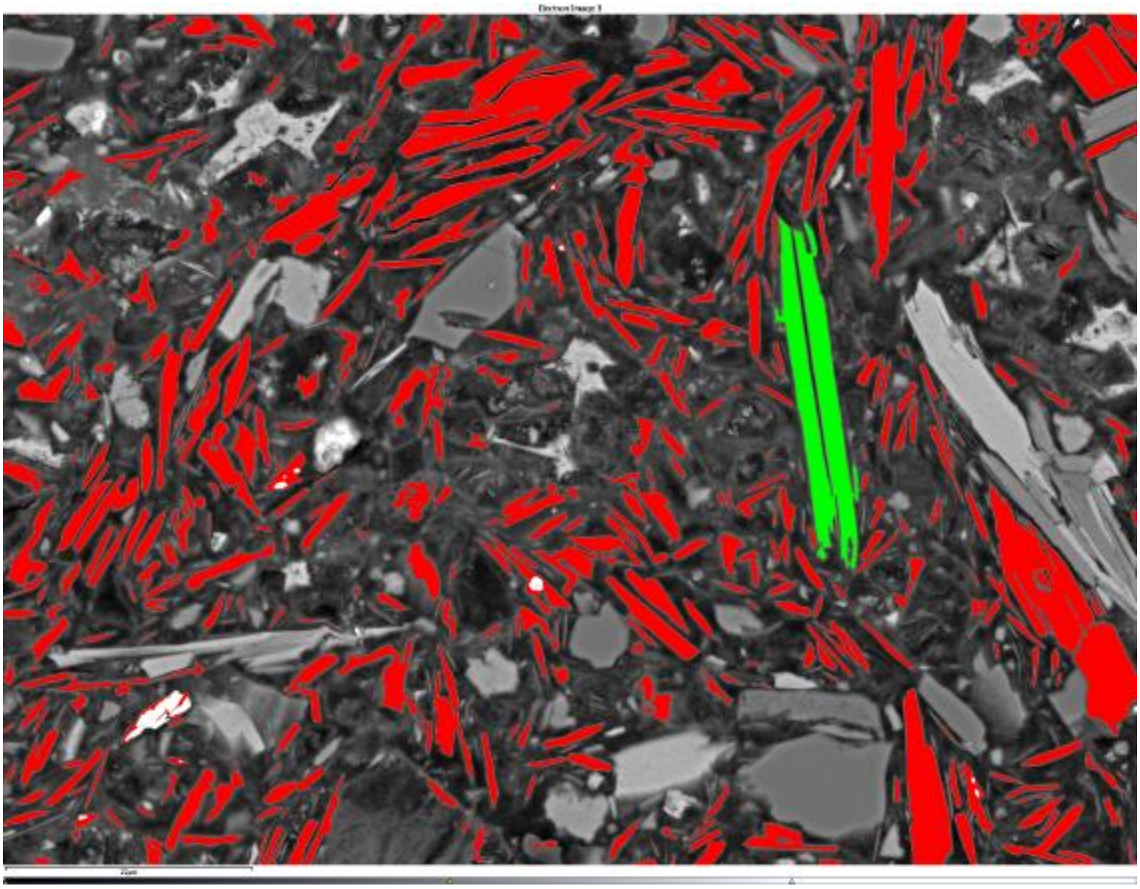


Figure 16: BSE image with the result of the extracted features displayed in colour, using potassium, shape and <63 µm criteria to identify free mica.

Twelve or excess fields of view of cement matrix, at 1200x magnification per thin section were chosen for analysis, avoiding large aggregate and focusing on the cement paste in between the aggregate. Lange et al (1994)[18] worked on twelve BSE images per block for porosity determination in concrete. ASTMC457, provides information on the minimum area of finished surfaces for macroscopically performed measurements. The 1σ graphs of the results, % of free mica in the total fines, for the cement matrix and sand (displayed in chapter 3), assisted determining the optimum number of fields of view for analysis.

2.11 Interpretation of XRD results

The XRD method relies on the ability of the operator to accurately identify the minerals present in a sample. The interpretative process uses the XRD generated diffraction trace and the database of minerals that provides lines which plot over the trace. The operator uses the peak positions and relative intensities to match various peaks in the sample to known mineral species. Several complications exist including peak overlap between minerals and orientation effects which give variable peak intensities depending on the crystallite shape and how the bulk cavity mount is loaded. Additionally, the degree of crystallinity of a mineral can vary between samples: a poorly crystalline mica will produce a low-intensity broad diffraction peak, a highly crystalline mica will produce an intense narrow peak.

The limit of detection for XRD is not fixed, but sample dependant – a concentration of 0.5% of a highly-crystalline mineral (e.g. muscovite) in a pure limestone or sandstone may be detected, while a concentration of >2% of a poorly crystalline illite may not be detected in a sample with a high amorphous content (e.g. organic carbon rich mudstone). Typically, LOD's are considered for most minerals by XRD as 0.5 – 2.0%.

Quantification of the identified minerals is an interactive and iterative process which involves selecting crystallographic parameters (e.g. cell sizes, crystallinity, orientation effects) for each of the minerals in the sample, to refine a calculated pattern until it closely resembles the measured XRD trace. The operator selected minerals from the Siroquant database which includes the crystallographic parameters. The quantification relies on the accurate identification of the minerals by the operator and on their presence in the database, which is not as comprehensive as the ICDD database. Some compromise is necessary, and the key one for this project was the selection of muscovite as opposed to other mica minerals.

Chapter 3 Results

3.1 Sand - SEM-EDS Results

The percentage of <63 µm free mica fines, identified and quantified by the SEM-EDS method for thirty-two sand samples obtained directly from pits and through builders suppliers around Ireland who knew the provenance of the sand, for the mineralogical assessment of sand is set out in the figures and tables below. The individual sand sample results are presented in Appendix A. The figures below include a combination of backscattered electron (BSE) SEM images, BSE images with all fines highlighted using the thresholding software, and thirdly BSE images with free mica identified by the developed method highlighted in red. The colours attributed by the thresholding software to the BSE images are for the purpose of identifying fines for classification or showing classified fines. Colours imposed by the energy dispersive spectroscopy (EDS) software are different, they represent the elemental composition in the area measured. False colours are attributed to each element, in single / layered EDS element maps of the sand, a colour given to illustrates its location measured in the map. One high and one low percentage micaceous sand sample, TE-1 and OY-1 respectively, are discussed below.

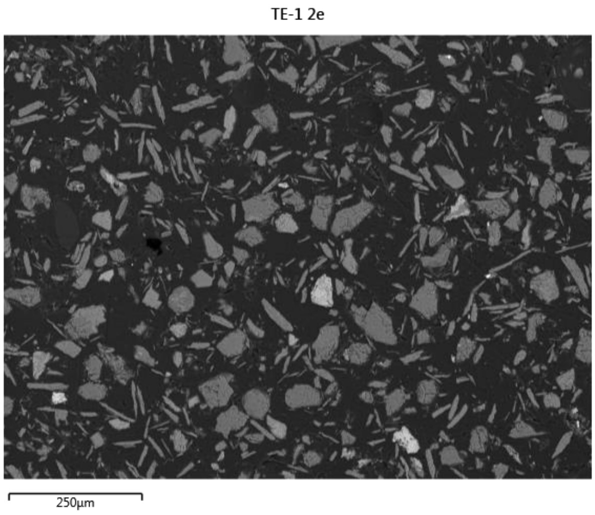


Figure 17: High mica bearing sand in a resin puck, TE-1 (2e) Co. Tyrone. A single BSE image at 250x magnification, 1110 µm (length**)** x 829 µm (breadth) of 2625 sand fines.

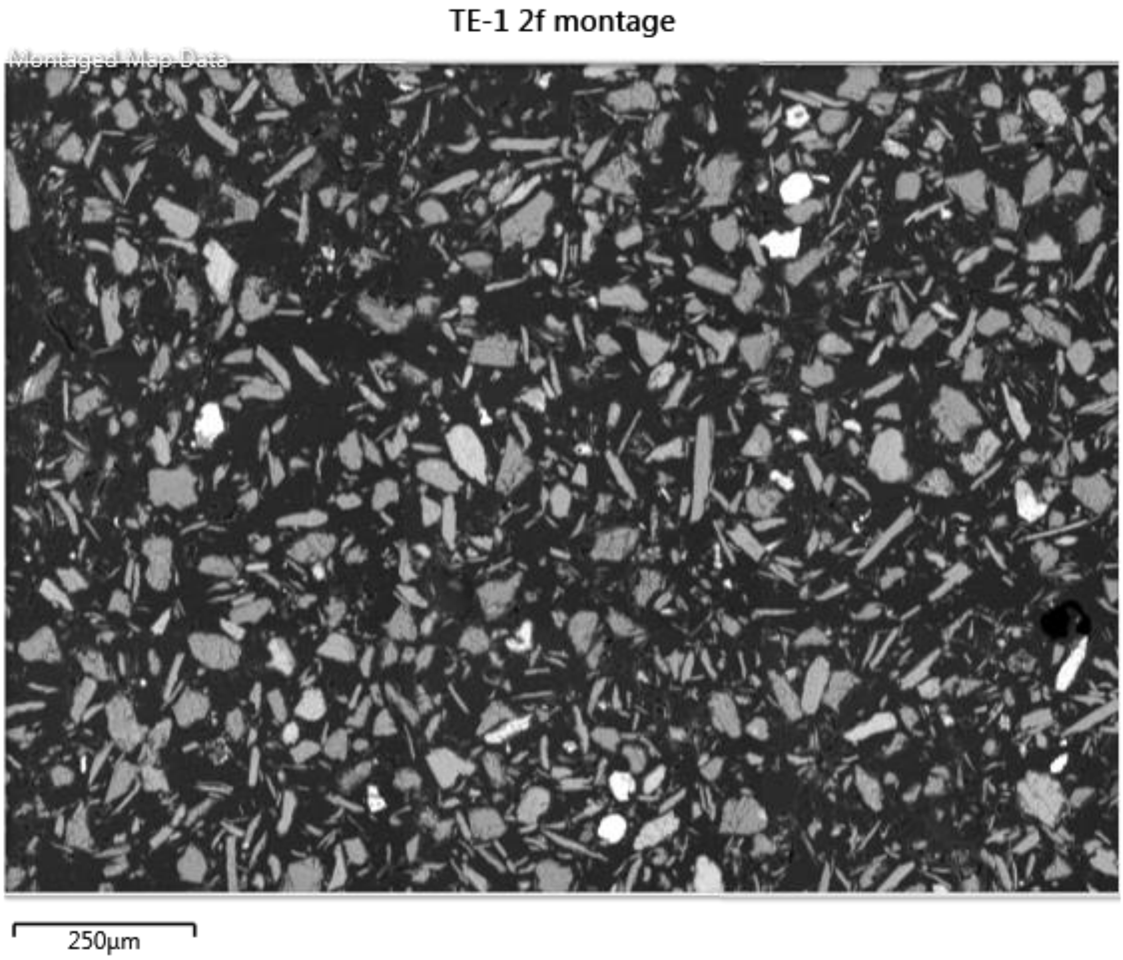


Figure 18: Highly micaceous sand sample TE-1 (2f), Co. Tyrone. BSE montage image of sand in a resin puck, a montage of nine images at 500x magnification. Montage image dimensions 1540 µm (length) x 1150 µm (breadth) of 9391 sand fines.

In the single field of view BSE image, 250x magnification (Fig 17), 2625 sand fines were identified by the software. 9391 sand fines were identified in the montage BSE image (Fig 18), which is nine fields of view at 500x magnification. For the purpose of this research, it was decided to base the sand quantification on up to approximately 10,000 fines per sample, as a result montages of between nine and twelve fields of view at 500x magnification are the templates used for SEM-EDS analysis to quantify the percentage of free mica fines in the total fines tested.

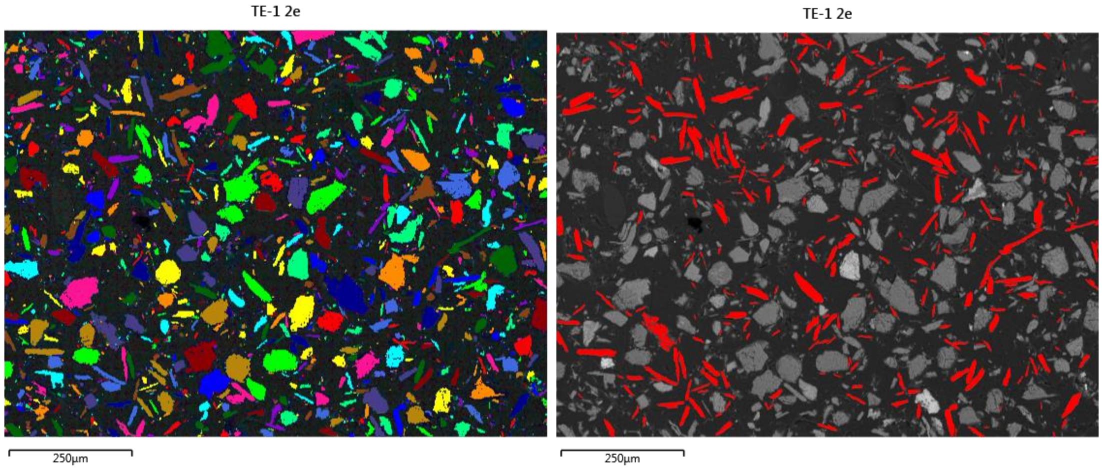


Figure 19: Highly micaceous resin puck sand sample, TE-1 (2e) Co. Tyrone. BSE images of a single field of view at 250x magnification, 1110 µm (image length) x 829 µm (image width) of 2625 sand fines. (Left image): All sand fines identified in colour by thresholding. (Right image): Free mica fines among total fines result is 21.65 % and is highlighted in red.

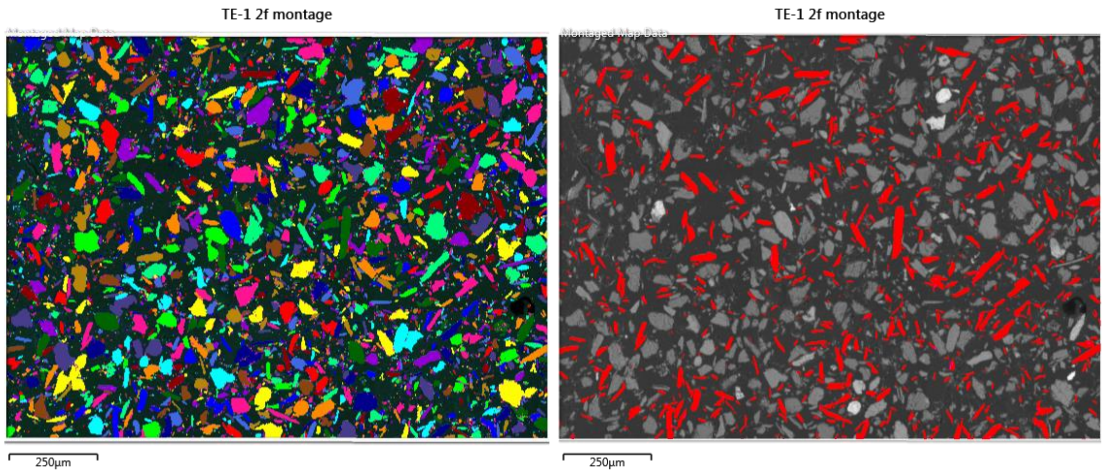
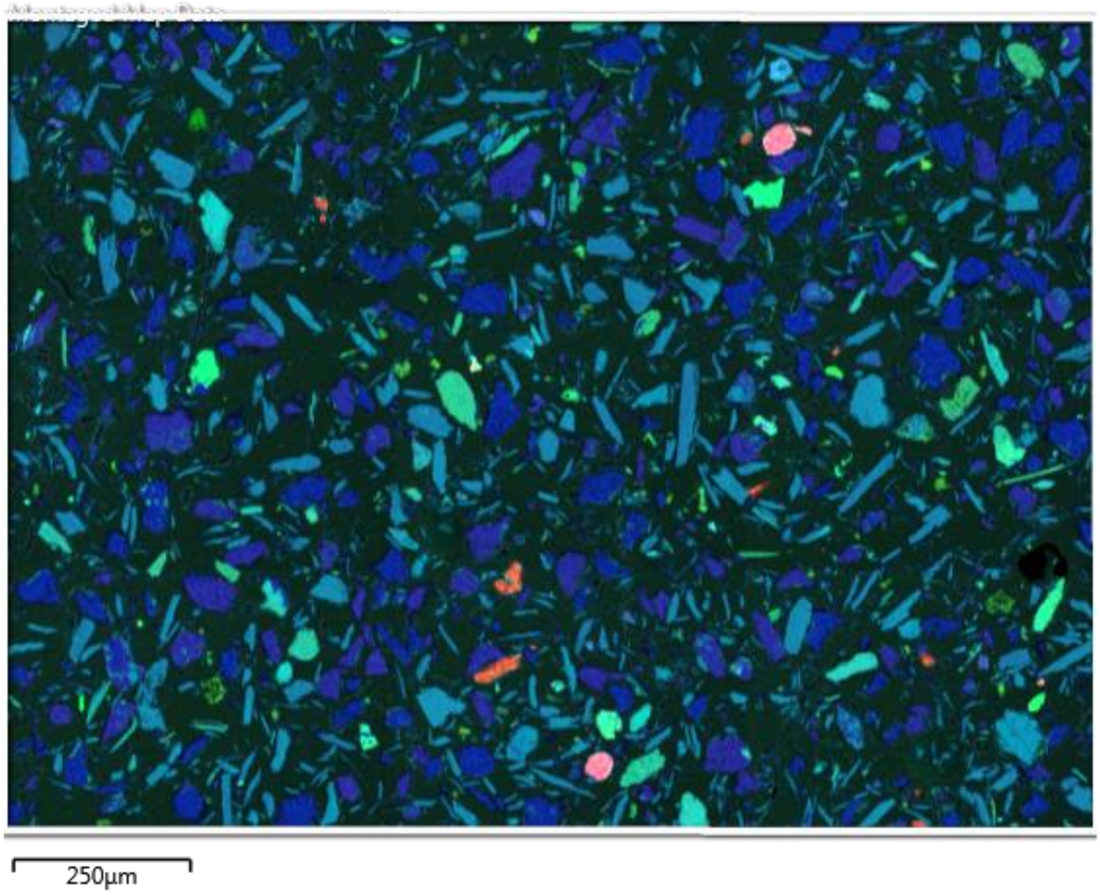
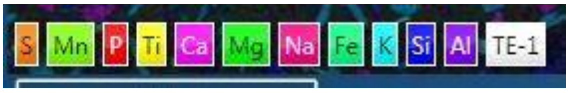


Figure 20: Resin puck sand sample TE-1 (2f), Co. Tyrone. BSE images of sand, a montage of nine images at 500x magnification. Montage image dimensions 1540 µm (length) x 1150 µm (breadth) of 9391 sand fines. (Left image) all fines for classification are highlighted using thresholding. (Right image); Free mica fines among total fines result is 21.64% and is identified in red.

The percentage of free mica among the total fines result, measured from different fields of view in the same highly micaceous sand sample TE-1, namely TE-1 2E (Fig. 19) and TE-1 2F (Fig.20), are comparable at 21.65 % and 21.64 % respectively.

TE-1 2f montage





Element key

Figure 21: Energy dispersive spectroscopy (EDS) map of highly micaceous sand sample in resin, TE-1 2f. Free mica is illustrated in light blue in the elemental map based on the colour attributed to potassium (K). The element key shows the false colours attributed to each element.

The layered multi-element EDS map (Fig. 21) displays the elemental composition corresponding to the BSE images in Figures 18 & 20. A selection of single element maps, used to create the layered multi-element energy dispersive spectroscopy map (Fig. 21) are presented below in Figure 22. In these single element maps, the false colour attributed to potassium in particular, covers considerably more surface area when compared to the potassium single element map for OY-1 (Fig.23). This, along with the shape, size, aspect ratio and other relevant elemental classifications set, demonstrates visually that the sand sample TE-1 contains a higher concentration of free mica among the total fines (namely 21.64 %). Tables 3 – 4 presents the percentage free mica among the total fines results for TE-1 and OY-1.

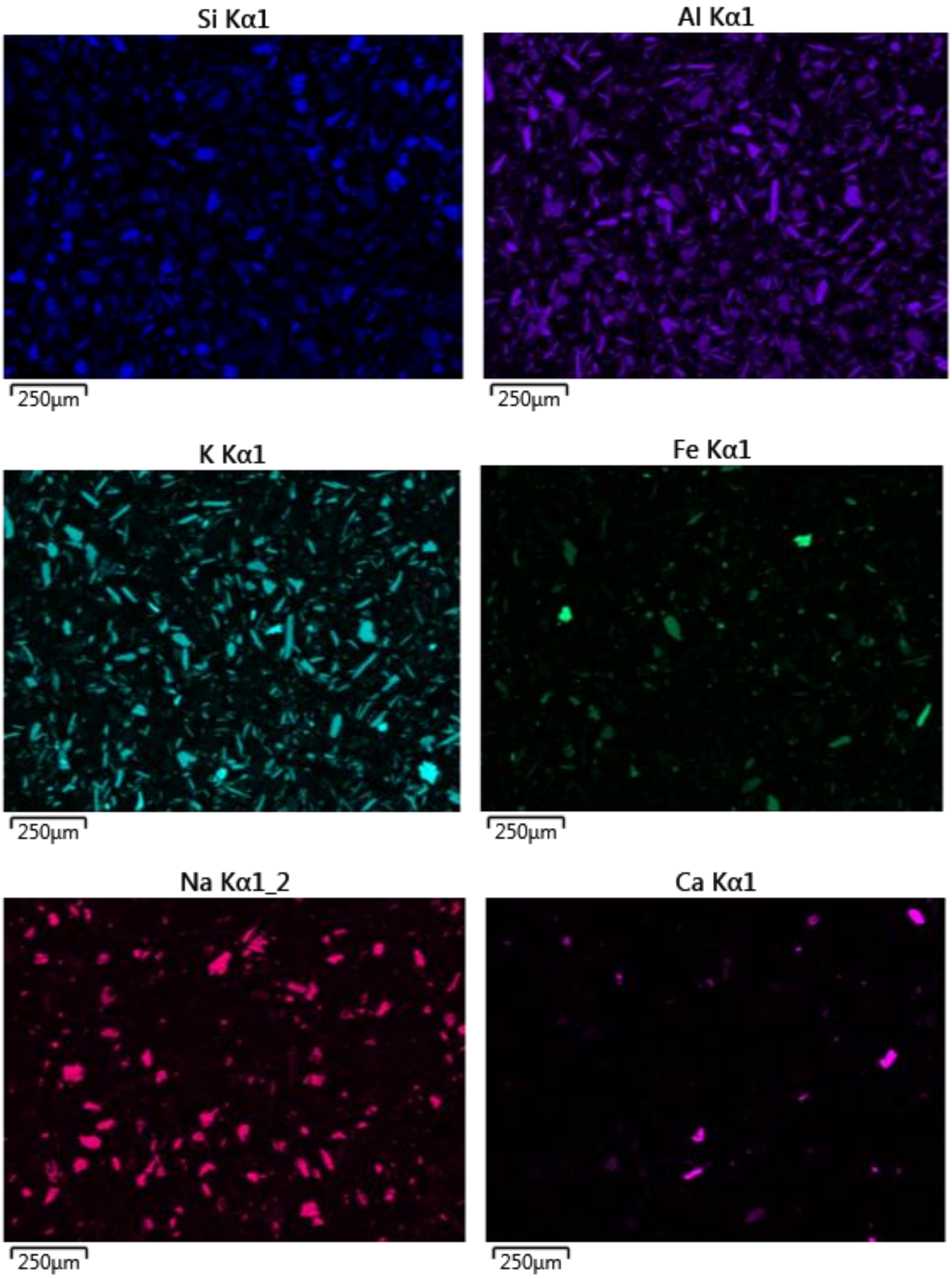
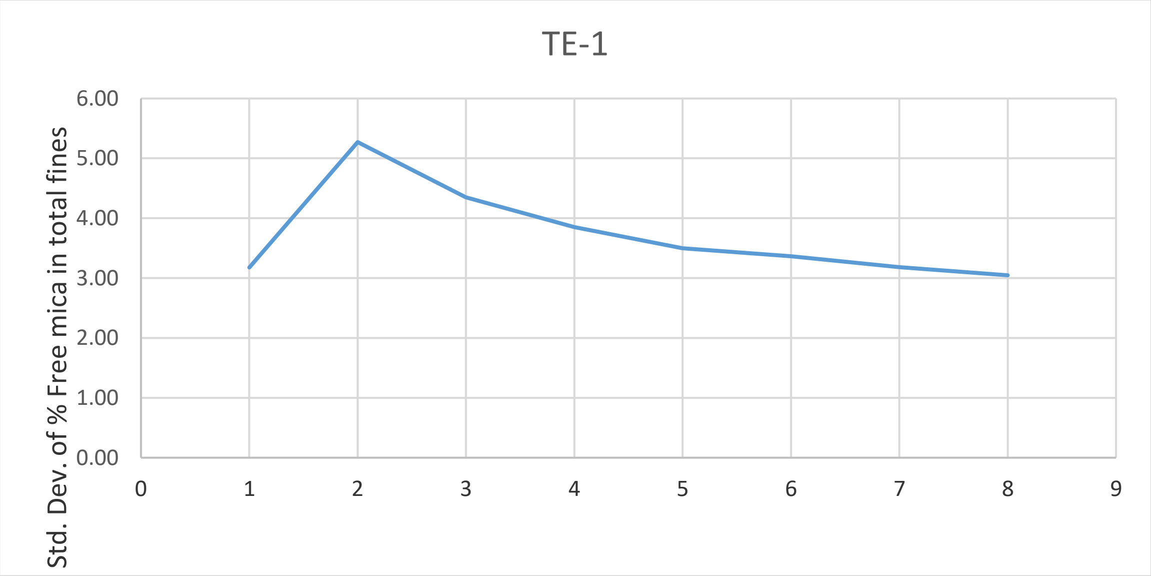


Figure 22: Highly micaceous sand sample TE-1 2f. The false coloured single element EDS maps of sand fines in the resin puck**.**

Table 3: Sample TE-1, % free mica in sand by SEM-EDS

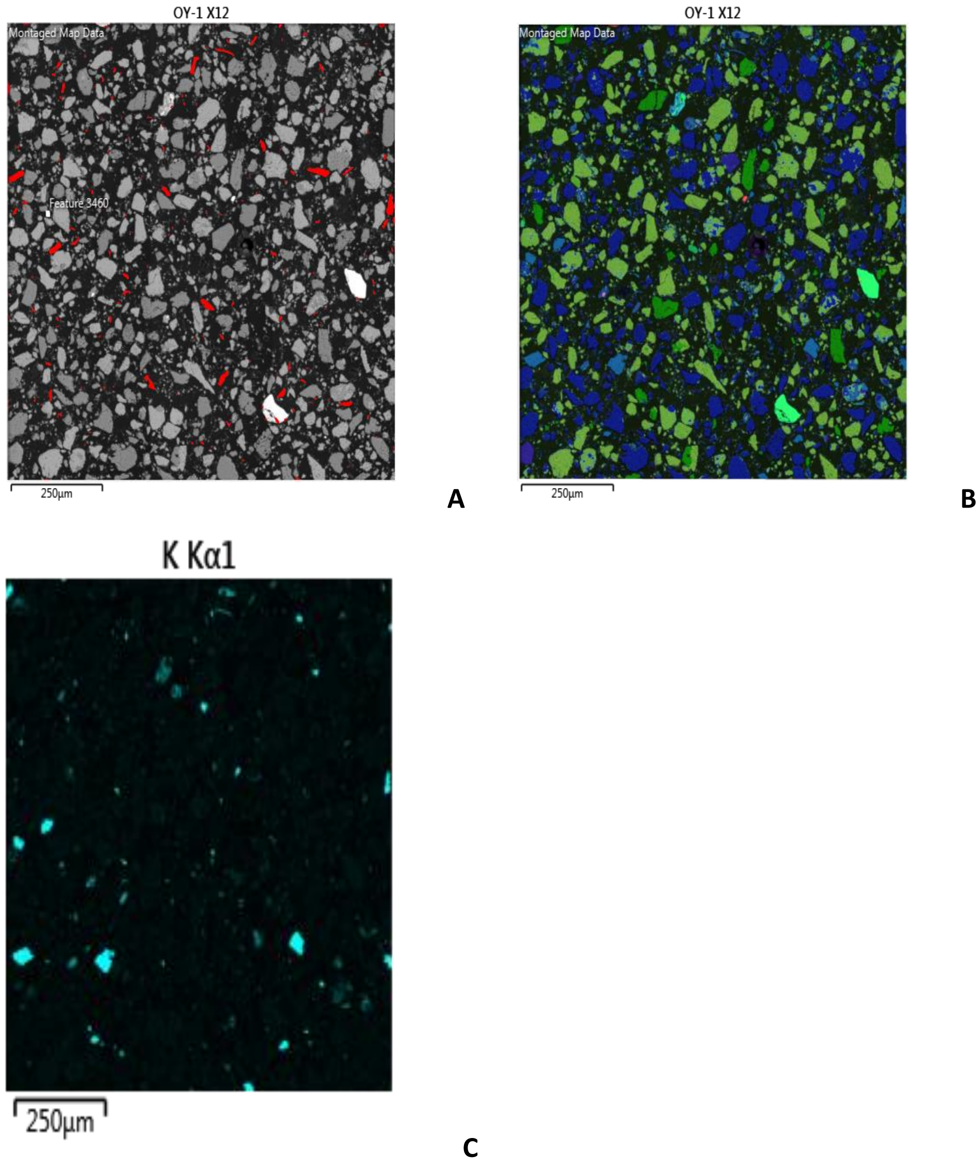
Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines tested	No. of free mica fines	% area free mica in total fines	1σ % free mica in total fines
TE-1 2a	637000	154000	28900	2175	208	18.77	
TE-1 2b	358000	76100	17700	1396	133	23.26	3.18
TE-1 2c	229000	50900	14900	1029	132	29.27	5.27
TE-1 2d	229000	45800	10300	1160	130	22.49	4.35
TE-1 2e	917000	206000	44600	2625	315	21.65	3.85
TE-1 2f	1800000	433000	93700	9030	823	21.64	3.50
TE-1 1a	3000000	473000	94800	6832	400	20.04	3.36
TE-1 1e	636411	162000	33300	2422	160	20.56	3.18
TE-1 1f	357938	83800	17000	1526	127	20.29	3.05
MEAN						22.00	
STD DEV						3.05	



Graph 1: 1σ (standard deviation) of % free mica among the total fines

BSE and EDS images of a low micaceous sand sample OY-1 (Fig. 23) are displayed below. The difference between the two sand samples TE-1 and OY-1 are worth noting again. The BSE image for OY-1 (Fig 23A) shows more rounded and irregularly shaped fines, as opposed to fines meeting the needle-like morphology of free mica which can easily be identified in the BSE image for TE-1 (Fig 18). A comparison of the potassium single element maps for TE-1 (Fig.22) and OY-1 (Fig. 23C) show the significantly lower surface area of potassium in

OY-1. All information which correlates with the lower calculated value of 3.4% free mica among the total fines for sand sample OY-1, calculated by the Oxford Feature software.

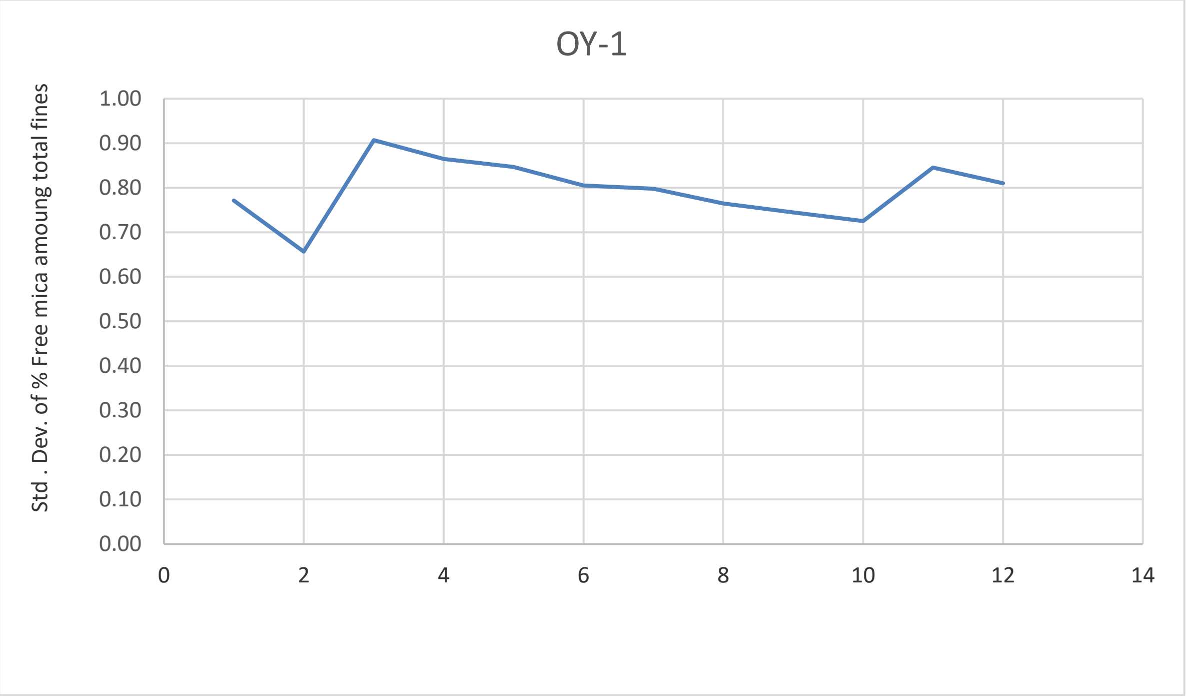


C

Figure 23: Low micaceous sand sample in resin OY-1, Co. Offaly. (A); Backscattered electron image of sand, a montage of 12 images at 500x magnification, the result of 3.4% free mica among the total fines is highlighted in red. (B); Layered multi-element EDS map of the sand. The false colour element key is consistent with Fig. 21 (C) Potassium single element map of the sand.

Table 4: OY-1, % free mica in total fines by SEM-EDS

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
OY-1 X1	357,938	115,000	3710	1570	34	3.23	
OY-1 X2	357,938	118,000	2520	1600	31	2.14	0.77
OY-1 X3	357,938	148,000	3030	2041	31	2.05	0.66
OY-1 X4	229,495	84,100	847	1587	22	1.01	0.91
OY-1 X5	116,920	47,700	617	909	19	1.29	0.86
OY-1 X6	116,920	52,700	580	1761	24	1.10	0.85
OY-1 X7	116,920	40,300	966	1389	18	2.40	0.80
OY-1 X8	116,920	48,700	525	1437	15	1.08	0.80
OY-1 X9	116,920	57,900	746	1606	16	1.29	0.76
OY-1 X10	116,920	45,700	521	1336	16	1.14	0.74
OY-1 X11	7,850,000	1,990,000	44000	43147	883	2.21	0.72
OY-1 X12	1,120,000	382,000	13000	8530	176	3.40	0.84
OY-1 X13	821,000	349,000	5990	8883	85	1.72	0.81
MEAN						1.85	
STD DEV						0.81	



Graph 2: 1σ of % free mica among the total fines

The 1σ graph for OY-1 (Graph 1) was used to determine that 6 measurements were viable for statically representative results. Table 5 below presents the averaged results of the percentage of free mica measured among the total sand fines tested using the SEM-EDS method, individual SEM-EDS sample data reported in appendix A.

Table 5: % free mica results in total <63 µm sieved sand fines by SEM-EDS.

Sample Reference	County	Product	SEM-EDS % free mica among total fines
AH-1	Armagh	Washed Building sand	1.66
AH-2	Armagh	Plastering sand	5.54
CE-1	Clare	*Building sand*	1.61
CK-1	Cork	*Concrete sand*	1.22
CK-2	Cork	*Concrete sand*	0.74
CK-3	Cork	*Building sand*	3.16
CK-4	Cork	*Sand*	5.55
CN-1	Cavan	Concrete sand	2.21
CW-1	Carlow	*Building sand*	0.29
DL-1	Donegal	*Building sand*	3.96
DL-2	Donegal	*Building sand*	4.08
DL-3	Donegal	*Building sand*	6.80
DL-4	Donegal	Sand	16.88
DL-5	Donegal	Concrete sand	6.01
KY-1	Kerry	Building sand	1.84
LK-1	Limerick	Concrete sand (4 mm)	1.20
MO-1	Mayo	Asphalt sand	2.45
MO-2	Mayo	Concrete sand	4.24
OY-1	Offaly	*Building sand*	1.85
OY-2	Offaly	*Building sand*	0.63
OY-3	Offaly	*Building sand*	1.23
RN-1	Roscommon	Building sand	0.03
TE-1	Tyrone	Concrete sand	22.00
TE-2	Tyrone	Plastering sand	16.55
TS-1	Tipperary	*Concrete sand*	0.28
WH-1	Westmeath	Concrete sand	0.07
WH-3	Westmeath	*Building sand*	0.21
WW-1	Wicklow	*Building sand*	3.20
WX-1	Wexford	*Building sand*	11.66
WX-2	Wexford	*Building sand*	5.28
WX-3	Wexford	*Building sand*	2.02

Mica concentrations in sand samples vary considerably – in 7 samples it was <1.0 %, in a further 15 it was between 1 – 5%, in 5 it was between 5 – 10% and 4 samples contained >10% mica.

3.2 Sand - XRD Results:

In sand samples containing more than one mica (i.e. a granite derived sand with muscovite and biotite), the quantification employed in this work assumes just one mica. Without this limitation detailed XRD analysis of separated clay fractions, involving multiple treatments and repeated analysis (e.g. glycolation, heating) would have severely restricted the number of samples which could have been analysed. As part of an extended project certain sand samples with high mica concentrations will be targeted for additional detailed analysis, but this was beyond the scope of the project.

The results presented in table 6 give the percentages of the minerals quantified by Rietveld refinement in the <63 µm fractions of sand samples. The feldspar minerals have been grouped for simplicity and concentrations of Na, K and Ca feldpars (i.e. albite, microcline, anorthite) are added and termed ‘feldspar’. Overall, the dominant minerals are quartz, felspar, calcite, chlorite, mica and dolomite, with localised subordinate occurrences of hornblende, hematite, cordierite, garnet and vermiculite.

In line with the SEM-EDS analysis results, the XRD mica concentrations also vary considerably – in 5 samples it was not detected, in 9 it was 0.3 – 1.0 %, in a further 8 it was 1 – 5%, in 5 it was 5 – 10% and 5 samples contained >10% mica among the total fines.

Table 6: XRD < 63 µm quantitative data (%)

	Quartz	Calcite	Dolomite	Albite	Microcline	Anorthite	Mica	Chlorite	Cordierite	Vermiculite	Hematite	Hornblende	Garnet
AH-1	75.1	3.9	7.2	11.6			2.1						
AH-2	29.6	1.0		23.2			6.9	29.3	6.2	3.8			
CE-1	83.0	1.0		9.6			0.4	6.1					
CK-2	84.2	0.7		5.8			0.6	6.3			2.4		
CK-3	66.0	0.3		14.4			3.0	16.3					
CK-4	71.4			12.9			3.2	12.5					
CN-1	56.8			29.7			1.4	12.1					
CW-1	47.7	26.7	15.9	7.0			0.3	2.4					
DL-1	44.1			30.9	8.0		9.0					8.0	
DL-2	52.9			22.9			9.4	6.7				7.8	0.3
DL-3	37.8		0.8	24.4			10.6	16.4				9.9	
DL-4	22.2			23.9			29.3	16.2				8.4	
DL-5	43.7			30.6			4.1	13.7				7.9	
GY-1	36.2	47	9.2	7.6									
KY-1	80.6			112.0			2.5	5.7					
LK-1	88.3	1.1		3.7			0.7	6.1					
LK-2	78.6	1.7		4.9	9.4		1.3	4.1					
MO-1	73.1	1	1.7	12.4	5.5		0.4	2.8				3	
MO-2	1	4.9	2.4	18.7	5.4	22.7	7.7	2.9				0.5	
OY-1	35.2	50.2	7.6	5.1			0.4	1.2					
OY-2	47.2	40.4	4.6	7.5			0.3						
OY-3	51.9	20.7	5.7	11.3	1.1			4.4			4.9		
RN-1	29.6	65	5.1	0.3									
TE-1	44			7.7			42.6	4				1.7	
TE-2	48.3			19.2			19.2	9.7				3.7	
TS-1	65.7	24.2	3.8	5.7			0.6						
WH-1	37	52.3	7.9	2.9									
WH-3	38.3	49	4.9	5.1				2.7					
WW-1	57.5	6.8		27.4			5.1	3.2					
WX-1	47.1			15			12.7	23.2					
WX-2	62.6			22	2.7		4.2	8.4					
WX-3	85.2	4.4	3.2	6.5			0.7						

3.3 Sand - methylene blue (MB) Results:

Table 7 presents the MB g/kg (dry) results.

Table 7: MB results (dry)

Code	County	Product description	MB g/kg
AH-1	Armagh	Washed Building sand	0.5
AH-2	Armagh	Plastering sand	1.0
CE-1	Clare	*Building sand*	0.3
CK-3	Cork		0.3
CN-1	Cavan	Concrete sand	0.5
CW-1	Carlow		0.3
DL-1	Donegal	*Building sand*	0.3
DL-2	Donegal	*Building sand*	0.3
DL-3	Donegal	*Building sand*	0.3
DL-4	Donegal	Sand	0.3
KY-1	Kerry	Building sand	0.5
LK-1	Limerick	Concrete sand (4 mm)	0.3
MO-1	Mayo	Asphalt sand	0.5
MO-2	Mayo	Concrete sand	0.3
OY-1	Offaly		0.5
TE-1	Tyrone	Concrete sand	0.3
TE-2	Tyrone	Plastering sand	0.3
WH-1	Westmeath	Concrete sand	0.3
WH-3	Westmeath		0.3
WW-1	Wicklow		0.5
WX-1	Wexford		0.5
WX-2	Wexford		0.3
WX-3	Wexford		0.3

3.4 Concrete block results

The large area EDS montaged map below is an area of concrete block with image dimensions 4.79 mm (length) x 2.49 mm (breadth), this two dimensional map gives an overview of how the coarse aggregate, fines, cement matrix and resin interact in a concrete block thin section sample. The small red box highlighted in Figure 24, is representative of the location and area size selected for analysis in the concrete block thin sections reported throughout this chapter, an image size achieved at approximately 1200x magnification on the SEM. Multiple such areas are randomly selected for testing per thin section, avoiding large aggregate and resin, to give a representative calculation of the percentage of <63 µm free mica within the cement matrix of the hardened concrete blocks. The black area in the map is resin, impregnated into the concrete pores during the thin section sample preparation and the larger coloured areas are the coarse aggregate. The area directly in and around the highlighted red box, is cement matrix and fines. The fines are visible as very small multi-coloured shapes, the cement matrix as an even purple colour**.** Concrete is an inhomogeneous product, so sample navigation on the SEM at low magnification is required, to identify such suitable analysis areas.

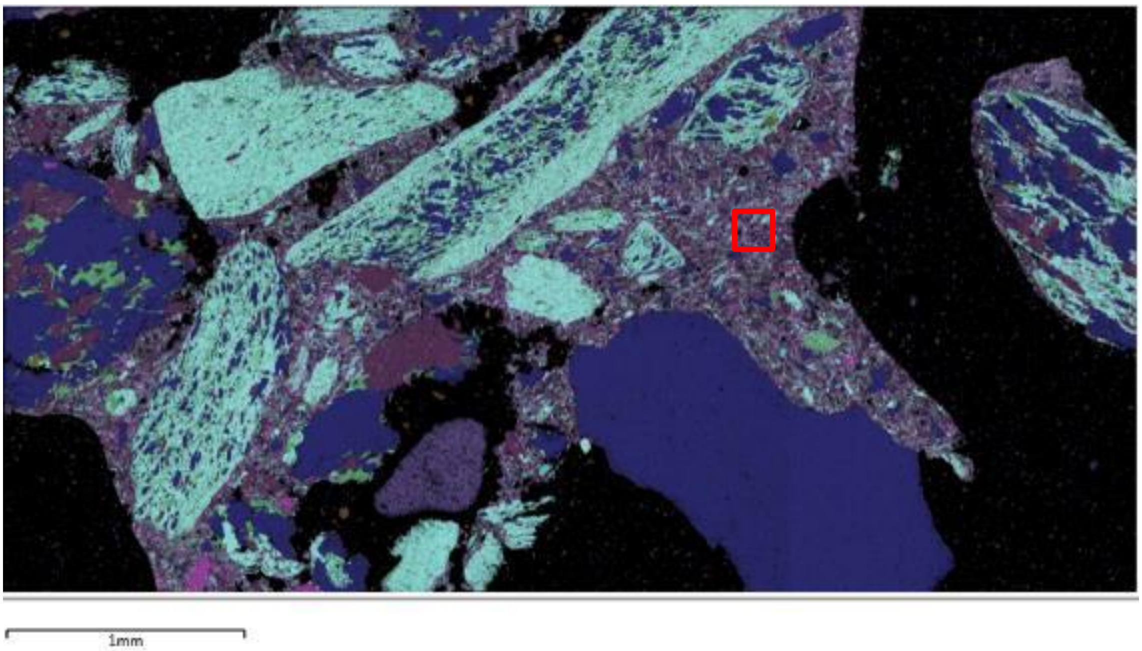


Figure 24: Concrete block sample; EDS layered image, 4.47 mm x 2.49 mm (image length x breadth). The black area is pore space filled with resin. The coloured areas represent the elemental composition in the fines, coarse aggregate and cement matrix. Fig. 25 below displays the associated single coloured EDS element maps with the element colour code used.

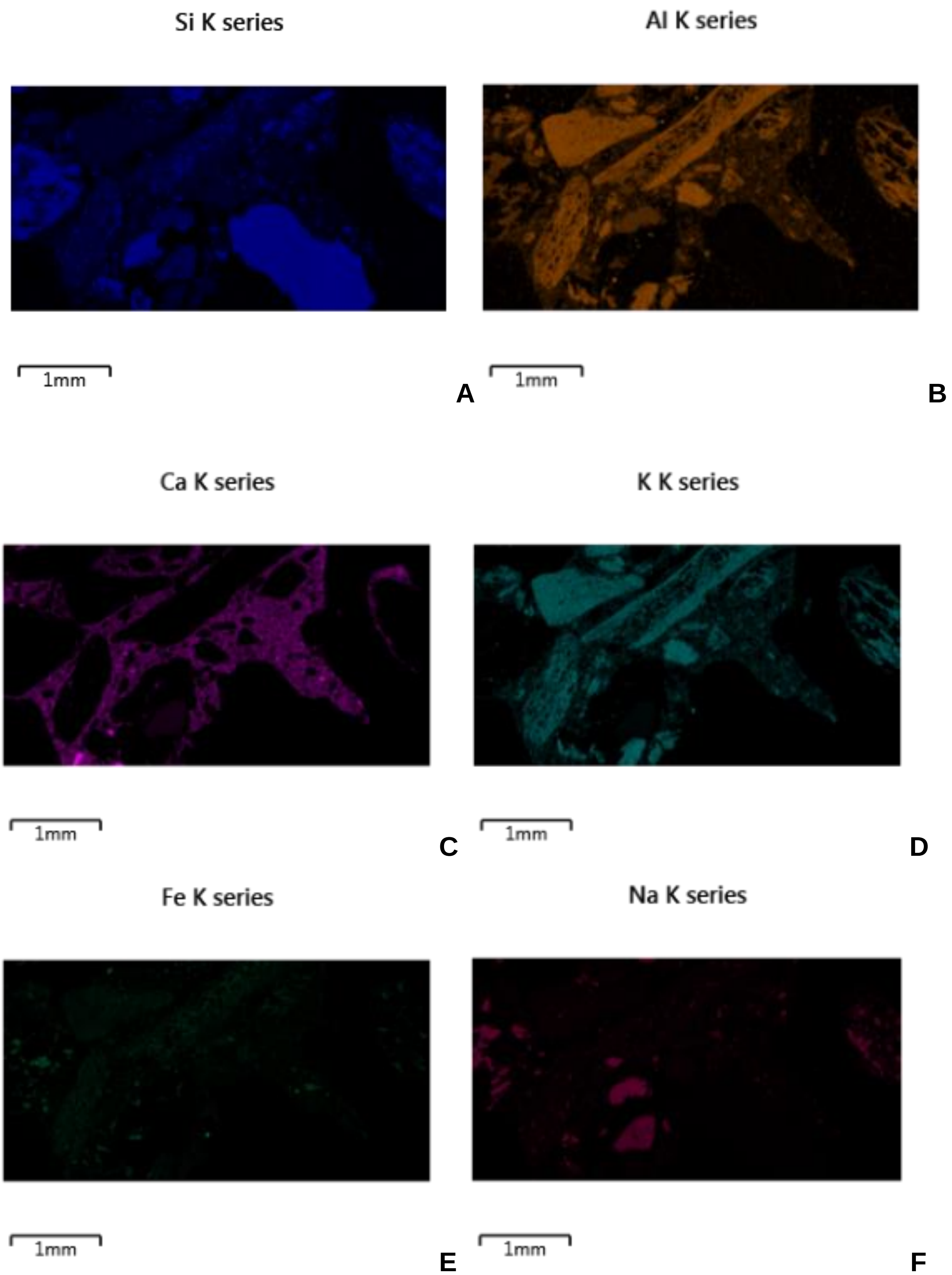


Figure 25: Concrete block sample. (A—F); A selection of single element EDS maps, used to generate the large area layered EDS montage map (Fig 24).

The false colours attributed to the single element EDS maps above are kept consistent to these same elements throughout the concrete block sample results in this chapter

In the first field of view of cement matrix tested, for sample AA63210 (Fig 26A), the characteristic needle-like morphology of free mica is clearly visible. From this same field of view, 950 features were identified using gray-level thresholding, with a total measured area of 10,644.41 μm^2 (Fig. 26B). The total area for this field of view was 172 µm (image height) x 230 µm (image width) = 39,790 μm^2. Thus the (area) percentage of <63 µm fines may be calculated as follows:

$$\frac{10{,}644.41\ \mu m^2}{39{,}790\ \mu m^2} \times 100 = 26.75\%$$

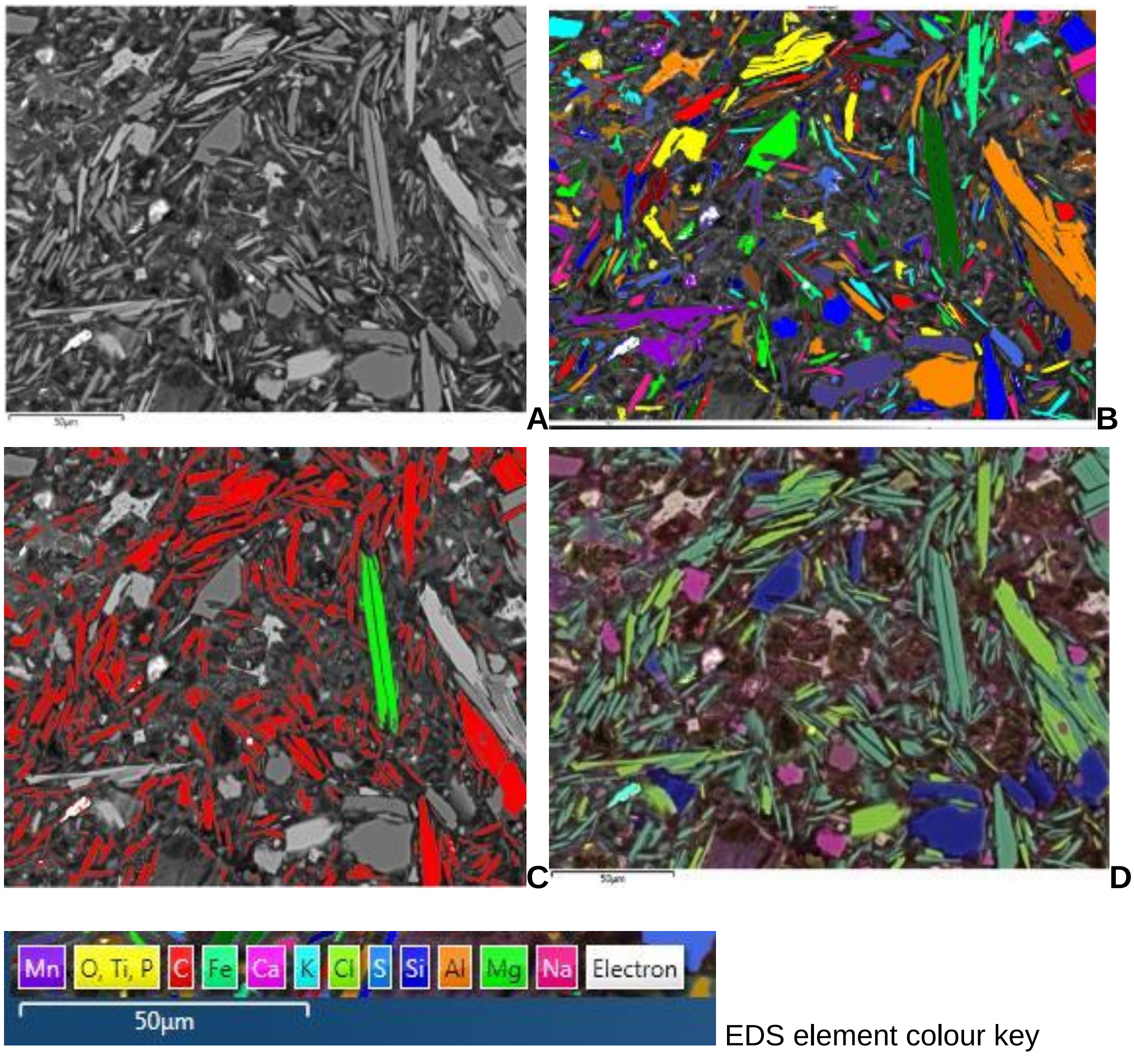
From the same field of view in the cement matrix, 478 features met the morphological and chemical criteria for free mica, with a total measured area of 6090.31 μm^2 (Fig. 26C). The percentage of free mica within the <63 µm fines may be calculated as follows:

$$\frac{6090.31\ \mu m^2}{10{,}644.41\ \mu m^2} \times 100 = 57.22\%$$

Finally, the percentage of free mica within the cement matrix (based on a single field of view, Fig. 6) is calculated as follows:

$$\frac{6090.31\ \mu m^2}{39{,}790\ \mu m^2} \times 100 = 15.70\%$$

Avoiding large aggregate and using the same analysis conditions, analysis was completed on an additional thirteen random fields of view of cement matrix from the same thin section, i.e. from the same concrete block, and the results are displayed in Table 8. A 1σ graph of the results, assists determining the number of fields of view suitable for representative analysis of the sample. The average percentage of free mica within the <63 µm fines for AA63210 is 64.13% ±9.04%. Concrete is a very heterogeneous material, and the concrete block is large in comparison to the fields of view tested, therefore the average percentage of free mica fines in the cement paste of the hardened concrete block, calculated at 14.06% ±2.10%, gives a semi-quantitative measurement value in relation to the entire block. The result is fully quantitative for the fields of view tested.



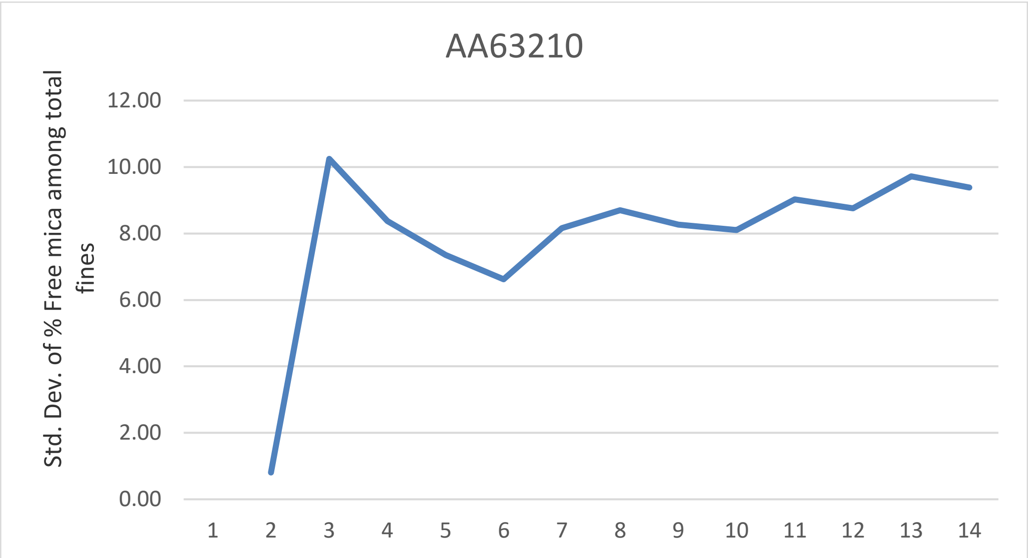
EDS element colour key

Figure 26: Concrete block AA63210. Image dimensions, (length) 553 µm x (breadth) 445 µm. (A); BSE image at 1200x magnification, the needle-like morphology of free mica is clearly visible in the image. (B) BSE image with thresholding used to identify all fines. (C); BSE image with free mica fines identified in red and green. (D); the corresponding layered EDS multi-element map with potassium bearing mica highlighted in dark green.

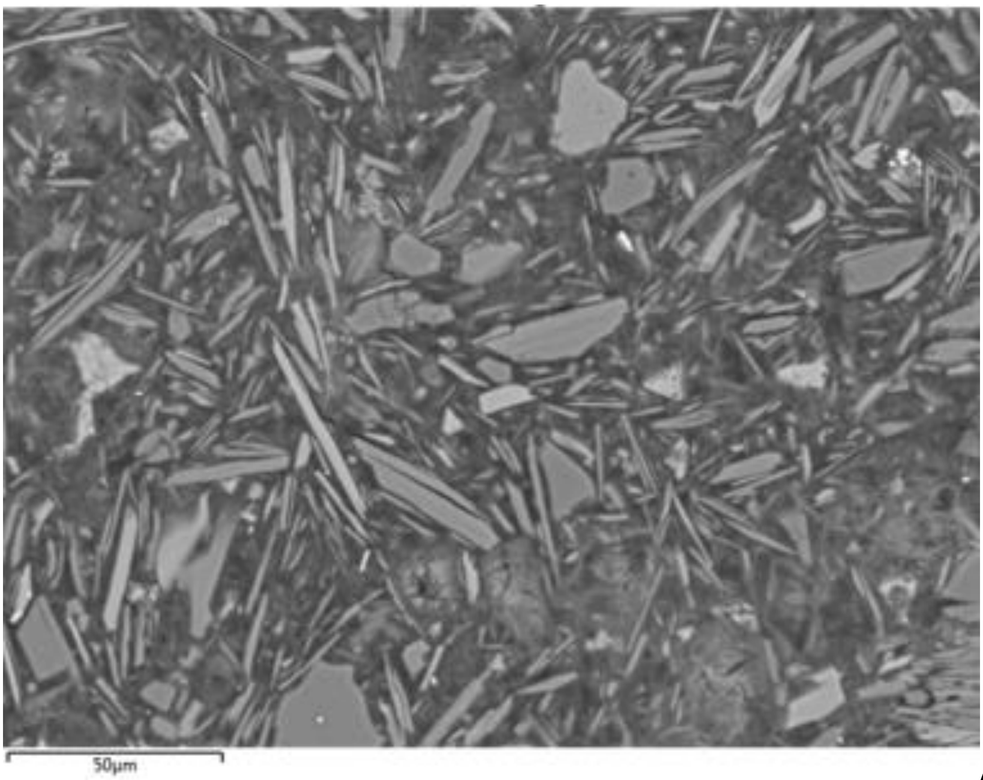
The BSE image (Fig. 26A) show the highly micaceous composition of the cement matrix in the polished thin section sample AA63210, free mica is identifiable by its needle-like morphology. With the fines for classification highlighted (Fig. 26B), these fines are then scanned for the presence of free mica morphology and elemental composition, with the result displayed in red and green (Fig. 26C). Figure 26D displays the elemental composition of the map with potassium rich areas in dark green. The colour attributed to K in the element colour key appears a slightly different tone in the EDS image due to the contribution of colour from the other elements present in the fines. The results of the analysis of multiple fields of view at 1200x magnification, from one concrete block thin section, are reported in Table 8. The 1σ graph which plots the standard deviation of the percentage of free mica among the total fines (Table 8) is reported in Graph 3.

Table 8: Concrete block sample AA62321, % free mica by SEM-ED

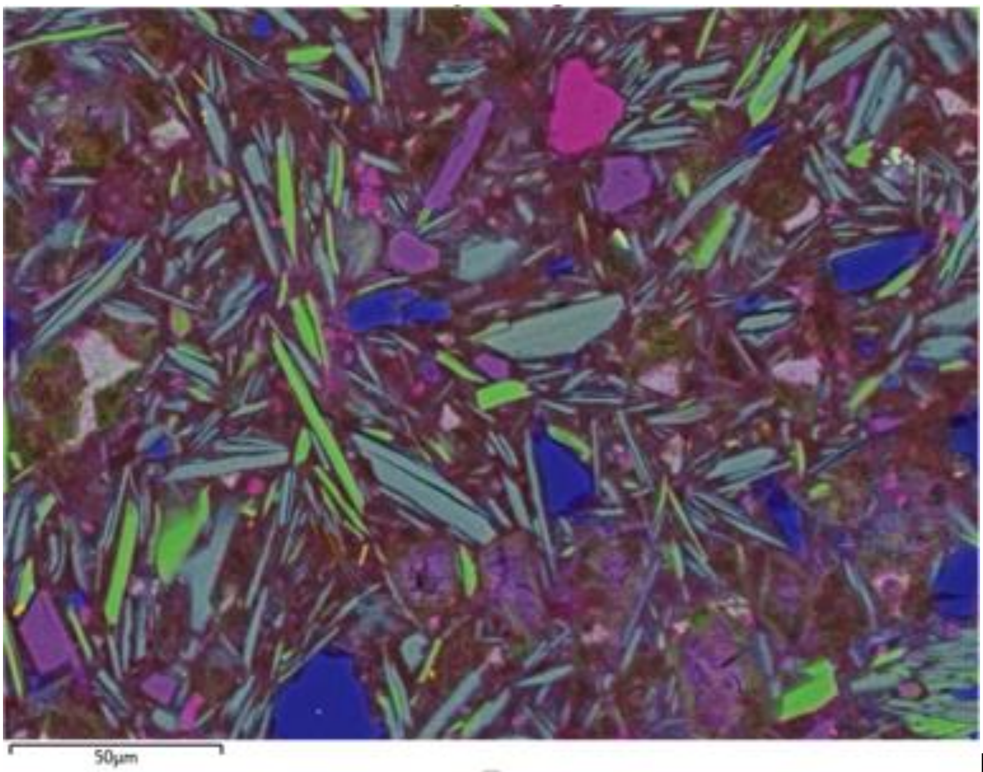
Code	Total image area, μm²	Total fines area, μm²	Free mica fines area, μm²	% Free mica in hardened cement matrix	% Free mica among total fines	Std. Dev. of % Free mica among total fines
1	39,790	12,106	6,168	15.70	57.22	
2	39,790	10,499	6,127	15.40	58.36	0.81
3	42,364	6,448	4,869	11.49	75.51	10.25
4	42,364	8,211	5,291	12.49	64.44	8.37
5	42,186	8,063	5,364	12.71	66.53	7.35
6	42,364	7,262	4,815	11.37	66.30	6.62
7	42,364	13,884	6,969	16.45	50.20	8.16
8	42,364	7,044	5,273	12.45	74.86	8.7
9	42,364	8,916	6,111	14.42	68.54	8.27
10	42,364	10,891	6,284	14.83	57.70	8.1
11	42,364	10,995	5,309	12.53	48.28	9.02
12	42,364	10,810	7,367	17.39	68.15	8.76
13	42,364	9,230	7,454	17.60	80.76	9.72
14	42,364	8,380	5,113	12.07	61.02	9.38
MEAN				14.06	64.13	
STD DEV				2.1	9.04	



Graph 3: The 1σ graph of the % of free mica among the total fines in the cement matrix of a hardened concrete block.



A



B

EDS element colour key

Figure 27: Concrete block sample AA63210. Image dimensions, (length) 553 µm x (breadth) 445 µm. (A) BSE image at 1200x magnification of the cement paste of a hardened concrete block. (B); corresponding layered EDS multi-element map with free mica in dark green.

The results in Table 9 give the average percentages of < 63 µm free mica in the cement matrix of four hardened concrete blocks tested. The results are based on averages of 12 or more fields of view per thin section. The individual concrete block results, for the percentage of free mica measured among the total fines and are reported in appendix B.

Table 9: Average % < 63 µm free mica in the cement matrix of hardened concrete blocks.

Concrete block reference	Average image area, µm²	Total fines area, µm²	Free mica fines area, µm²	% Free mica in hardened cement matrix	% Free mica among total fines
AA63210	41984	9481	5894	14	64
31LOCRight	33973	11300	3334	10	30
31LOCLeft	43204	13804	3662	9	27
AA68189 External leaf	39782	12352	2874	7	24

Three of the concrete blocks tested report similar levels of <63 µm free mica in the cement matrix of the hardened concrete block, the results range from 7 – 10%, with a fourth sample reporting 14 %. The same three concrete block thin sections report similar percentages of <63 µm free mica fines among the total fines in the cement matrix, results are between 24 – 30 %, with one significantly higher result of 64 %.

Chapter 4 Discussion

Mica concentrations vary considerably in the sand samples tested. SEM-EDS analysis for the quantification of the percentage of free mica among the total fines gave the following results breakdown for the sand samples tested – in seven samples it was <1.0 %, in a further fifteen it was between 1 – 5 %, in five it was between 5 – 10 % and four samples contained >10 % mica. For the quantification of the same sand samples using XRD, the mica concentrations also vary considerably – in five samples it was not detected, in nine it was 0.3 – 1.0 %, in a further eight it was 1 – 5 %, in five it was 5 – 10 % and 5 samples contained >10 % mica. As a proposal exits to include methylene blue (MB) testing in relevant Irish Standards, the technique was included to provide some baseline data for building sands in Ireland tested using the technique, as there is no experience of its use here yet (pers. Comm. Goodhue). The sand samples were dried prior to being sub-contracted for MB testing which is not in line with standard recommendations for the MB test, however this only makes negligible value differences: for example, a sample with an absorption of 20 ml of methylene blue dye would have a MB value of 1.0 g / kg with a water content of 0 % and 1.05 g / kg with a water content of 5%. For the determination of free mica by MB testing, mica concentrations do not vary considerably – in twenty-three samples sub-contracted for analysis, from the same batches used for XRD and SEM-EDS analysis, all of the results are between 0.3 – 1.0 g / kg. Fifteen samples reported values of 0.3 g / kg, in seven it was 0.5 g / kg and one MB analysis reported 1.0 g / kg of free mica. The results of the three analysis techniques used in this research are displayed (Tables 10 & 11).

Table 10: SEM-EDS, XRD & MB results grouped by mica distribution

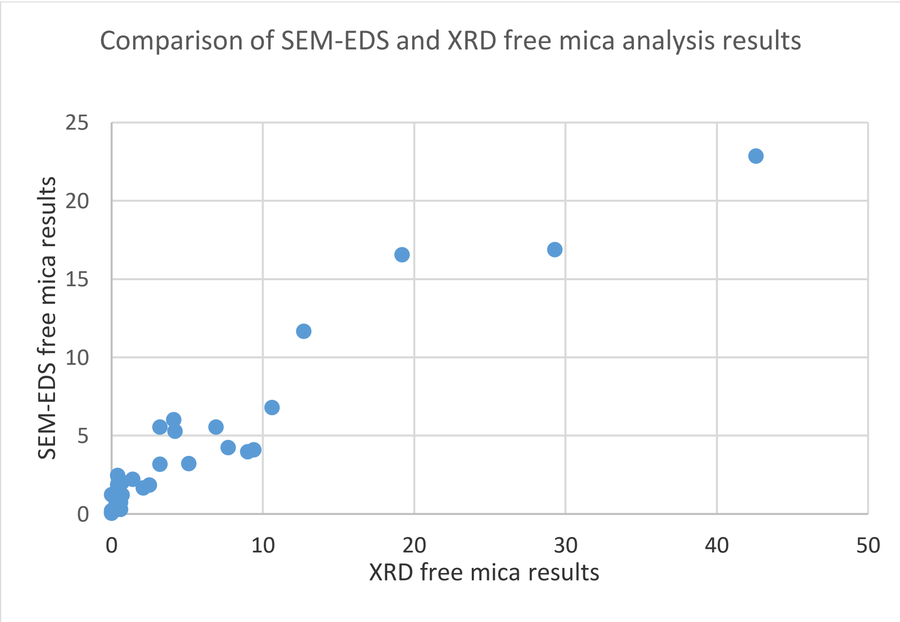
	XRD	SEM-EDS	MB
Not detected	**5**		
< 1%	9	7	23
1 – 5%	8	15	
5 – 10%	5	5	
>10%	5	4	

Table 11: SEM-EDS, XRD and MB mica concentrations.

CODE	County	XRD <63 µm (%)	SEM-EDX (%)	MB g / kg
AH-1	Armagh	2.1	1.7	0.5
AH-2	Armagh	6.9	5.5	1.0
CE-1	Clare	0.4	1.6	0.3
CK-1	Cork	*	1.2	*
CK-2	Cork	0.6	0.7	*
CK-3	Cork	3.2	3.2	0.3
CK-4	Cork	3.2	5.6	*
CN-1	Cavan	1.4	2.2	0.5
CW-1	Carlow	0.3	0.3	0.3
DL-1	Donegal	9.00	4.0	0.3
DL-2	Donegal	9.40	4.1	0.3
DL-3	Donegal	10.60	6.8	0.3
DL-4	Donegal	29.30	16.9	0.3
DL-5	Donegal	4.10	6.0	*
KY-1	Kerry	2.5	1.8	0.5
LK-1	Limerick	0.7	1.2	0.3
LK-2	Limerick	1.3	*	*
MO-1	Mayo	0.4	2.5	0.5
MO-2	Mayo	7.7	4.2	0.3
OY-1	Offaly	0.4	1.9	0.5
OY-2	Offaly	0.3	0.6	*
OY-3	Offaly	0	1.2	*
RN-1	Roscommon	0	0.0	*
TE-1	Tyrone	42.6	22.9	0.3
TE-2	Tyrone	19.2	16.6	0.3
TS-1	Tipperary	0.6	0.3	*
WH-1	Westmeath	0	0.1	0.3
WH-3	Westmeath	0	0.2	0.3
WW-1	Wicklow	5.1	3.2	0.5
WX-1	Wexford	12.7	11.7	0.5
WX-2	Wexford	4.2	5.3	0.3
WX-3	Wexford	0.7	2.0	0.3

Note 1: * denotes not tested

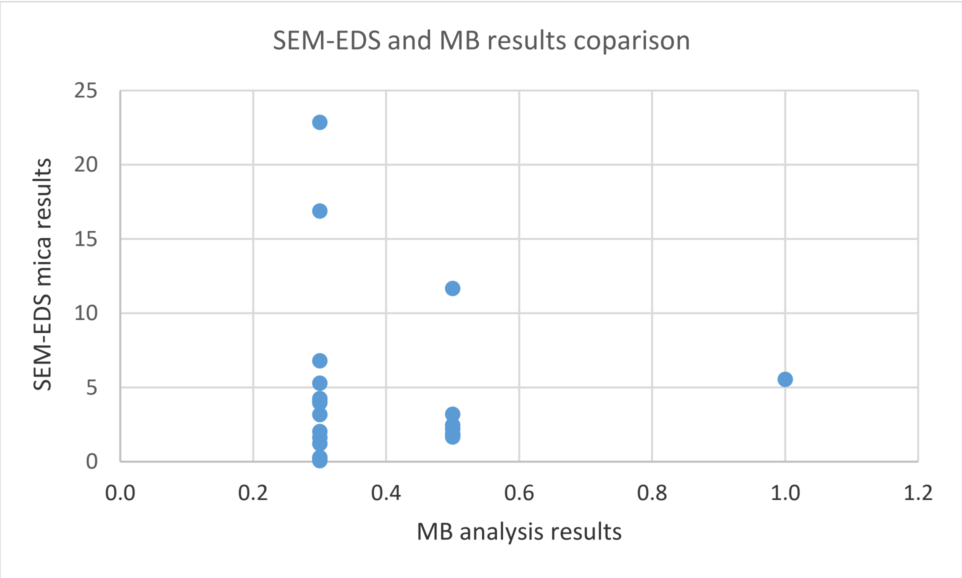
The capability of SEM-EDS as an analytical technique for free mica identification and quantification is clear. The power of utilising both morphology and elemental analysis means that the technique can differentiate between mica species. Fines are discarded from the results by the software if they fail to meet any aspect of the size, shape or elemental user defined criteria. The technique could also be expanded to include classification of other minerals within the sand, depending on the required testing or end-use of the material. The current version of the Oxford Instruments software is limited to a maximum of 60,000 features, which placed a restriction on the size of the maps that could be processed. Newer versions of the software reportedly can process up to 200,000 features and this number will increase further with time. Field emission SEM-EDS quantitative analysis is an expensive technique which requires a skilled operator and there are time restrictions when working in a shared analysis facility. A comparison of the SEM-EDS and XRD analysis results is displayed (Graph 4). While the correlation is strong (with an R^2 value of 0.955), there appears to be systematic over estimation of the mica by XRD.



Graph 4: Comparison of SEM-EDS and XRD analysis results**.**

While XRD is a powerful method for identification of minerals and providing semi-quantitative results, it suffers from some subjectivity, a lower limit of detection of 0.5 – 2.0% and crystallinity and orientation effects which are likely to reduce the accuracy of semi-quantitative results. Without more detailed and time-consuming preparation and investigation it may not differentiate between mica species. However, the XRD data gives mineralogical context to the occurrence of free-mica and allows some comparison and cross-referencing of the SEM-EDX result.

Comparison of the SEM-EDS and MB is displayed (Graph 5). The correlation of the SEM-EDS and MB free mica analysis is poor (with an R^2 value of 0.096) and there appears to be a systematic underestimation of the mica by MB.



Graph 5: Comparison of SEM-EDS and MB analysis results.

Sand samples collected from Donegal, Tyrone and Wexford displayed the highest concentrations of mica, from the collected sand tested in this research. While not all counties were sampled during the course of this project and the low number of locations tested are not representative of a county, what it is worth noting is that in general the highest sand concentrations reported were from metamorphic terrains, which is unsurprising as mica is frequently concentrated in metamorphic rocks.

Chapter 5 Conclusions

In recent years' critical problems were highlighted in the construction industry and geoscience is proving that it has a positive role to play in problem solving, quality control and providing evidence based rational for defining and setting standards for the sector. Utilising the latest technology in field emission scanning electron microscopy coupled with energy dispersive X-ray microanalysis (FE SEM-EDX), we set out a method we developed and published during the course of this thesis (Appendix E), for forensically investigating and measuring excessive levels of deleterious materials in sand and in the hardened cement matrix of concrete blocks. Our method requires the generation of high resolution backscattered electron (BSE) images using field emission scanning electron microscopy, from highly polished resin containing sand puck samples and thin sections of concrete, where the characteristic needle-like morphology of free mica can easily be identified. Additional information on the size, shape and chemical composition of the free mica fines, is gathered using energy dispersive spectroscopy (EDS or EDX). The combination of high-magnification images, high-resolution elemental maps, and mineral liberation software allows accurate identification and/or quantification of free mica within the sand fines and cement matrix. This method offers a viable analytical technique for testing deleterious materials in simple and complex matrices, testing which can be subjective or problematic using other methods.

Mineralogical mapping of sand fines from pits and builders suppliers in Ireland, who knew the provenance of the sand, was carried out using SEM-EDS, XRD and methylene blue testing. The results from the SEM-EDS and XRD show good correlation between both sets of results. Demonstrated from these results, is that mica concentrations vary considerably in sand around Ireland based on the limited number of samples we collected. In general, methylene blue testing demonstrated poor correlation when compared with both SEM-EDS and XRD testing, most notably in high mica bearing sands.

Further research in these materials and techniques supports expanding our knowledge base, assists improving the quality of standards produced by providing evidence based rational and reinforces the concept of getting it right the first time with the use of earths limited raw materials to support environmental protection.

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Appendix A

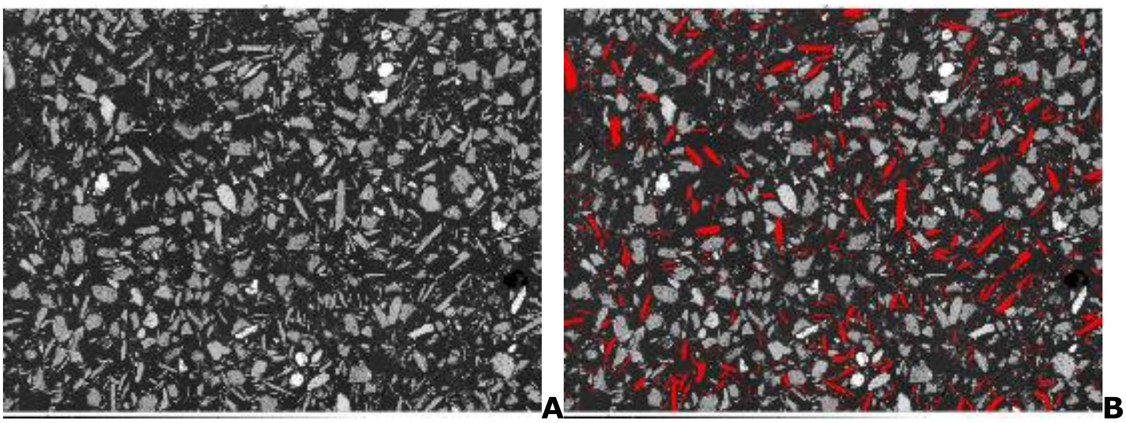
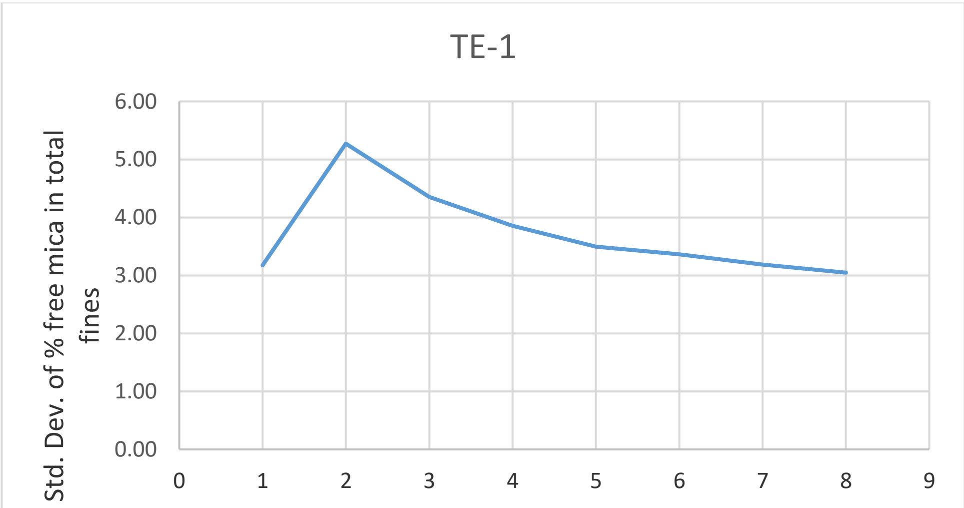


Figure 28: Sand sample TE-1 (2f), Co. Tyrone. (A); Backscattered electron (BSE) image of sand, a montage of nine images at 500x magnification. Montage image dimensions 1540 µm (length) x 1150 µm (breadth) of 9391 sand fines. (B); Free mica fines are identified in red over the BSE image.

Table 12: Sample TE-1, % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines tested	No. of free mica fines	% area free mica in total fines	Std. Dev % free mica in total fines
TE-1 2a	637000	154000	28900	2175	208	18.77	
TE-1 2b	358000	76100	17700	1396	133	23.26	3.18
TE-1 2c	229000	50900	14900	1029	132	29.27	5.27
TE-1 2d	229000	45800	10300	1160	130	22.49	4.35
TE-1 2e	917000	206000	44600	2625	315	21.65	3.85
TE-1 2f	1800000	433000	93700	9030	823	21.64	3.50
TE-1 1a	3000000	473000	94800	6832	400	20.04	3.36
TE-1 1e	636411	162000	33300	2422	160	20.56	3.18
TE-1 1f	357938	83800	17000	1526	127	20.29	3.05
MEAN						22.00	
STD DEV						3.05	



Graph 6: 1σ (standard deviation) of free mica in total fines.

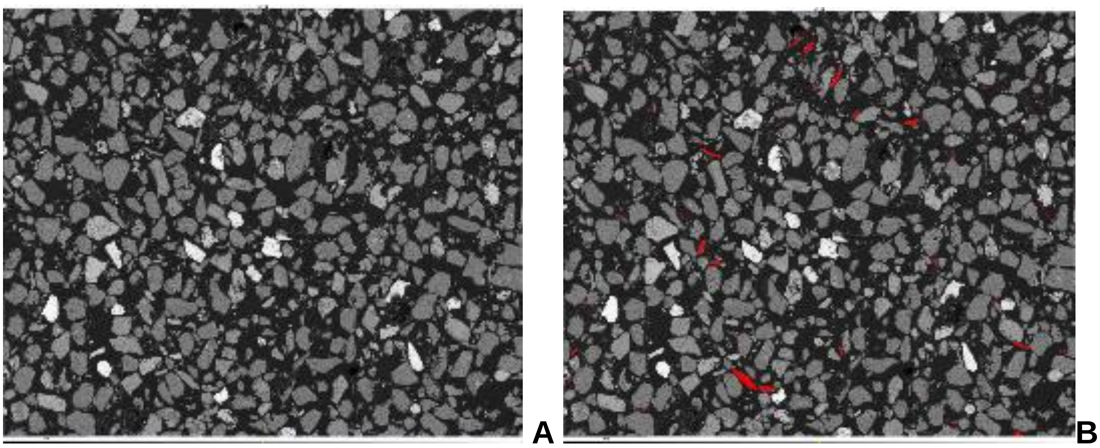
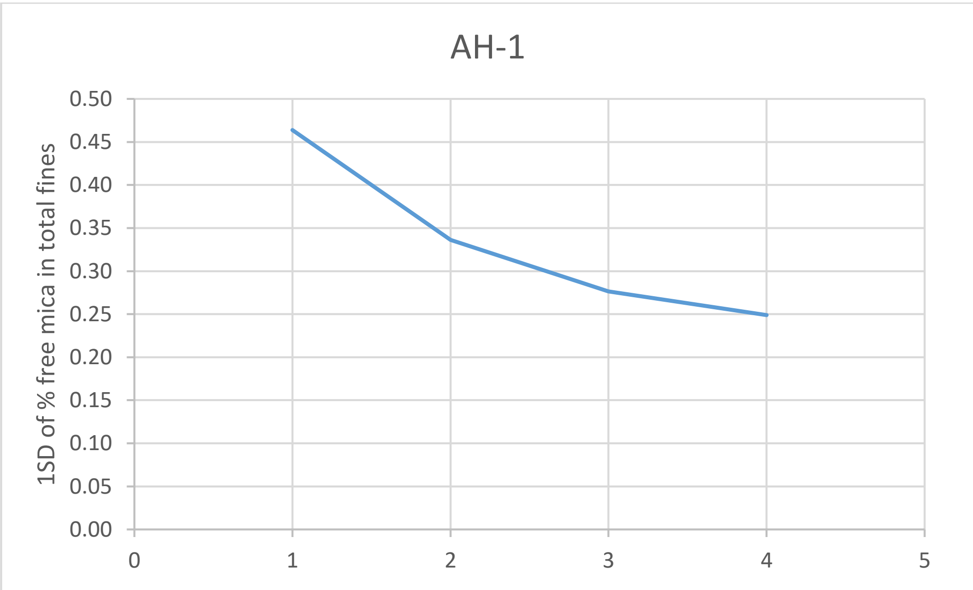


Figure 29: Sand sample AH-1 (1f Co. Armagh). (A); Backscattered electron montage of nine images at 500x magnification, 1540 µm (image length) x 1150 µm (image breadth). (B); Free mica fines are highlighted in red, identified by Oxford Instruments Aztec Feature mineral liberation software.

Table 13: Sample AH-1, % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
AH-1 1a	637000	229000	4620	1663	28	2.02	
AH-1 1b	358000	130000	1770	1182	19	1.36	0.46
AH-1 1c	358000	137000	2140	1032	16	1.56	0.34
AH-1 1e	358000	126000	1990	1074	24	1.58	0.28
AH-1 1f	1800000	679000	12100	6400	94	1.78	0.25
MEAN						1.66	
STD DEV						0.25	



Graph 7: 1σ (standard deviation) of free mica in total fines.

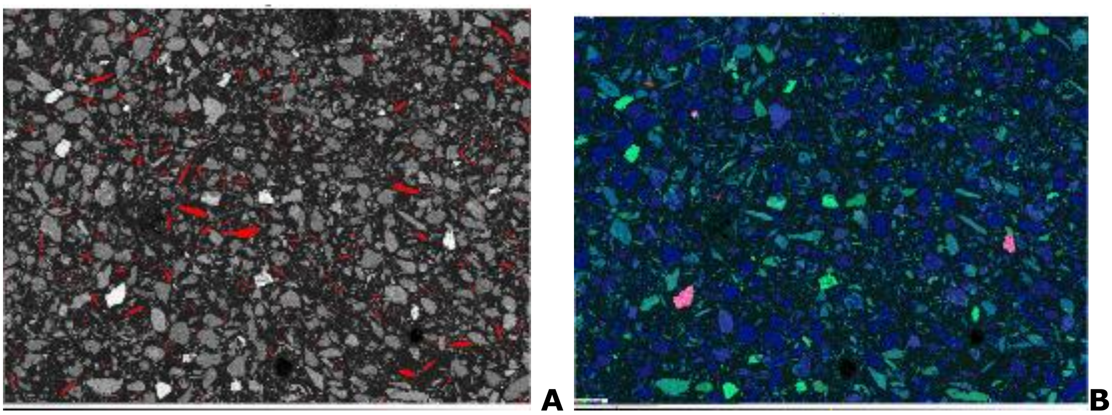
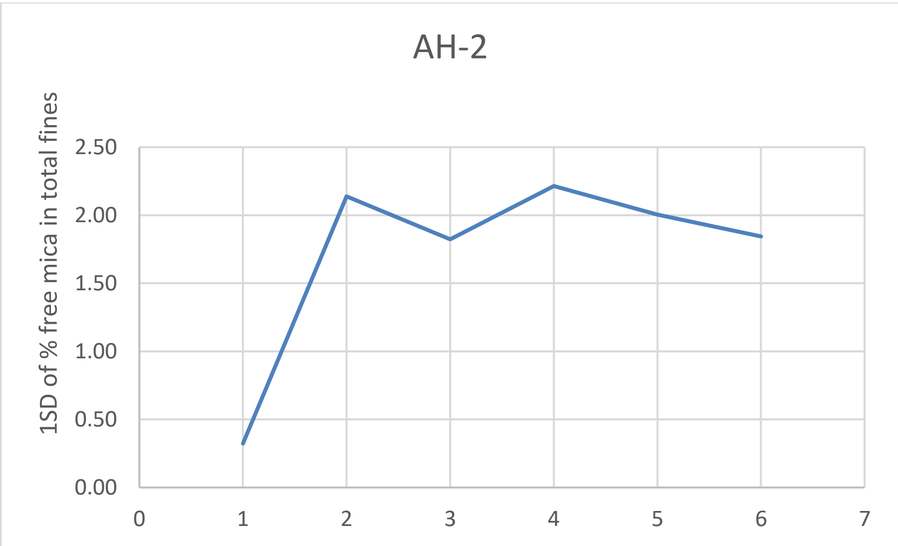


Figure 30: Sand sample AH-2 (1f Co. Armagh). (A); Backscattered electron image (1540 µm (image length) x 1150 µm (image breadth), a montage of nine images at 500x magnification. B; Layered energy dispersive spectroscopy (EDS) multi-element map.

Table 14: Sample AH-2, % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
AH-2 1a	637000	183000	6950	4021	106	3.80	
AH-2 1b	358000	89800	3000	3207	74	3.34	0.32
AH-2 1c	358000	103000	7470	2751	70	7.25	2.14
AH-2 1d	229000	69100	4040	2124	59	5.85	1.82
AH-2 1e	229000	81700	6970	2123	44	8.53	2.21
AH-2 1f	1800000	523000	26100	17621	461	4.99	2.01
AH-2 1g	3140000	949000	47500	29322	696	5.01	1.85
MEAN						5.54	
STD DEV						1.85	



Graph 8: 1σ (standard deviation) of free mica in total fines.

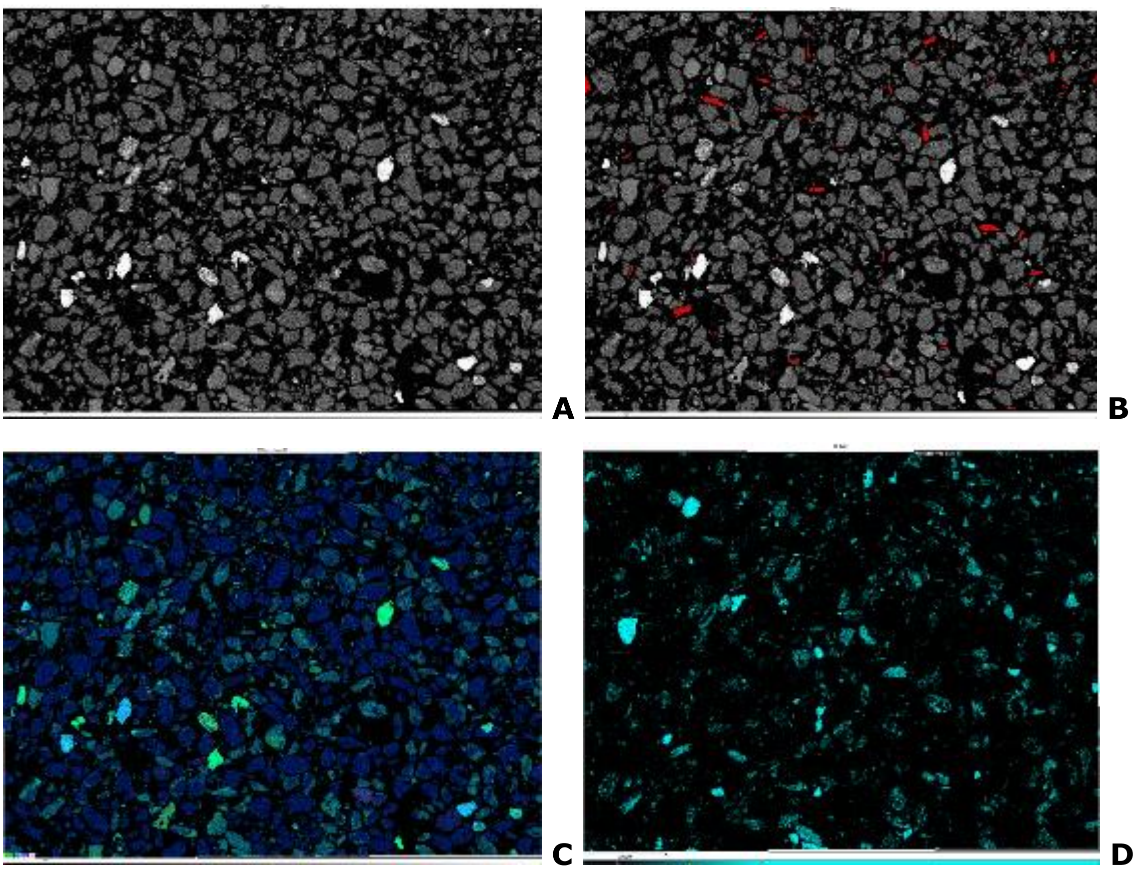
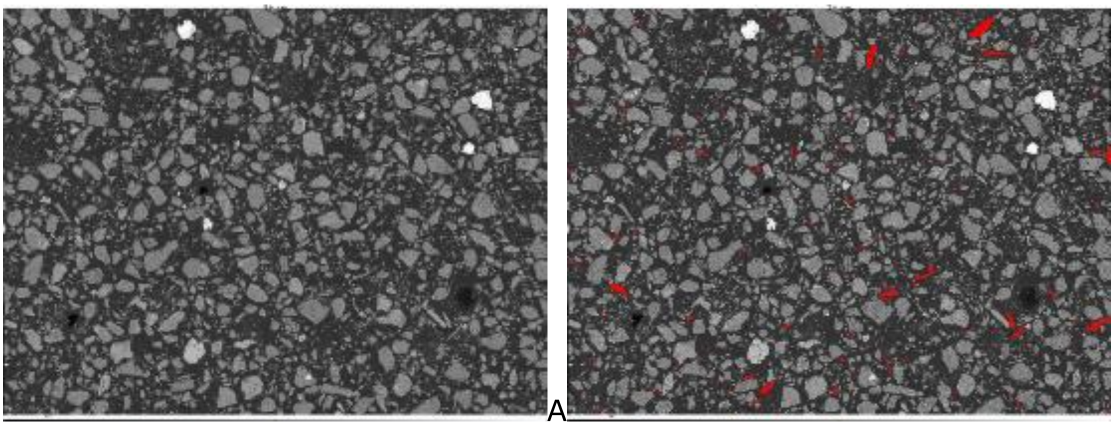


Figure 31: Sand sample CE-1 (1f Co. Clare). (A); Backscattered electron image (a montage of nine images at 500x magnification), 1540 µm (image length) x 1150 µm (image breadth). (B); free mica highlighted in red identified by Oxford Instruments Aztec Feature mineral liberation software. (C); Layered energy dispersive spectroscopy (EDS) multi-element map. (D); Potassium single element EDS map.

Table 15: CE-1, % free mica in sand by SEM-EDS.

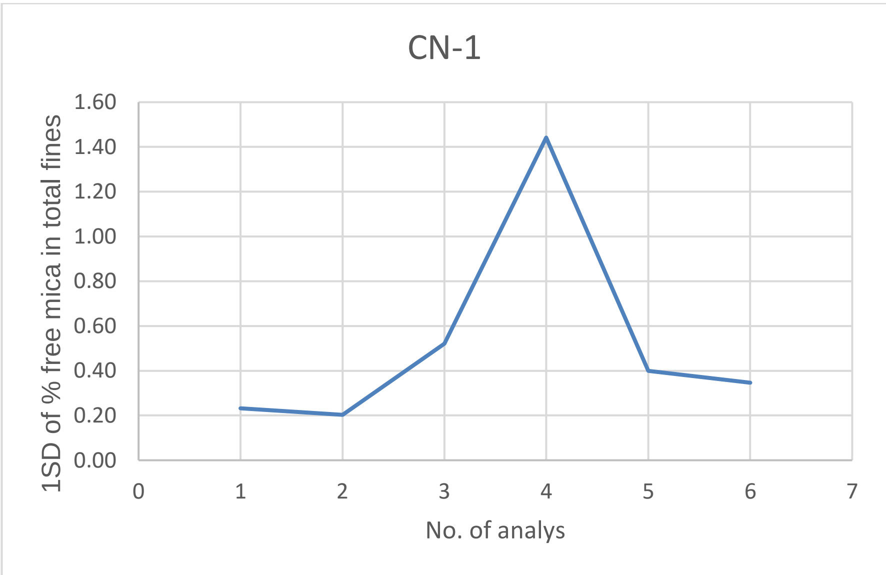
Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
CE-1 1a	637000	182000	5570	3328	28	3.06	
CE-1 1b	358000	102000	1070	2804	22	1.05	1.42
CE-1 1c	358000	84600	650	1680	20	0.77	1.25
CE-1 1d	229000	72200	1140	2068	27	1.58	1.02
CE-1 1f	1800000	621000	9990	14535	179	1.61	0.88
MEAN						1.61	
STD DEV						0.88	



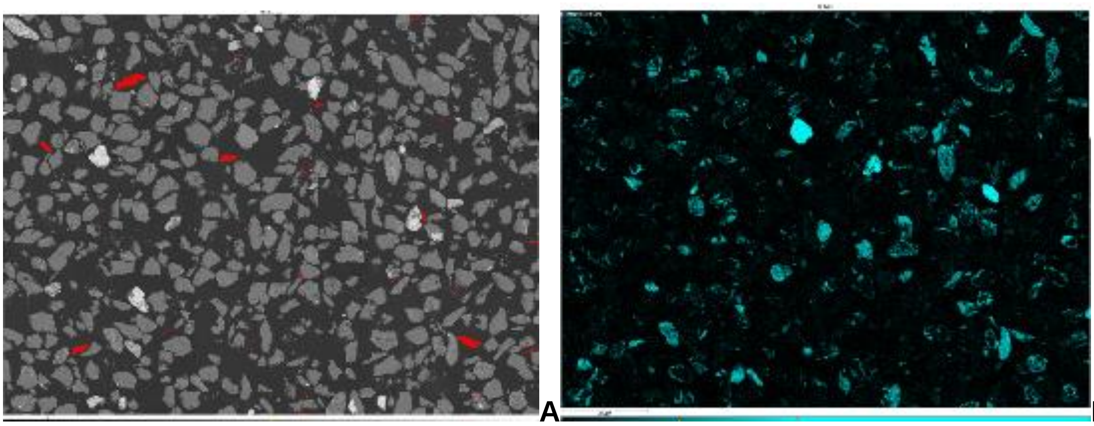
FFigure 32: Sand sample CN-1, Co. Cavan. (A); Backscattered electron image of sand (a montage of 9 images at 500x magnification. (B); in red free mica is identified by Oxford Instruments Aztec Feature mineral liberation software.

Table 16: CN-1, % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. μm)	Total fines area (sq. μm)	Free mica fines area (sq. μm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
CN-1	3000000	499000	10300	2424	37	2.06	
CN-1 2a	637000	235000	4080	4093	63	1.74	0.23
CN-1 2b	358000	128000	2590	2927	54	2.02	0.20
CN-1 2c	229000	86300	1110	2292	38	1.29	0.52
CN-1 2d	229000	81500	2710	2071	47	3.33	1.44
CN-1 2e	229000	84800	2340	1927	45	2.76	0.40
CN-1 2f	1800000	648000	14700	14990	294	2.27	0.35
MEAN						2.21	
STD DEV						0.67	



Graph 9: 1σ (standard deviation) of free mica in total fines.

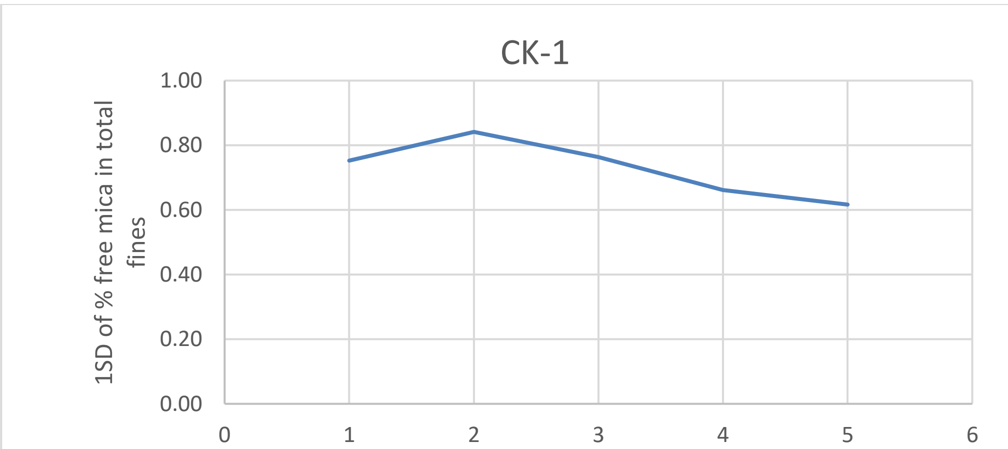


A B

Figure 33: Sand sample CK-1, Co. Cork. (A); Backscattered electron image montage of nine images at 500x magnification, 1540 µm (image length) x 1150 µm (image breadth) with free mica highlighted in red. (B); Potassium (K) EDS map.

Table 17: CK-1, % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
CK-1 2a	637000	214000	1740	1038	16	0.81	
CK-1 2b	358000	131000	2460	641	7	1.88	0.75
CK-1 2c	229000	80600	175	537	8	0.22	0.84
CK-1 2d	229000	83800	1370	641	11	1.63	0.76
CK-1 2e	229000	89900	1060	549	13	1.18	0.66
CK-1 2f	1800000	622000	9760	4508	63	1.57	0.62
MEAN						1.22	
STD DEV						0.62	



Graph 10: 1σ (standard deviation) of free mica in total fines.

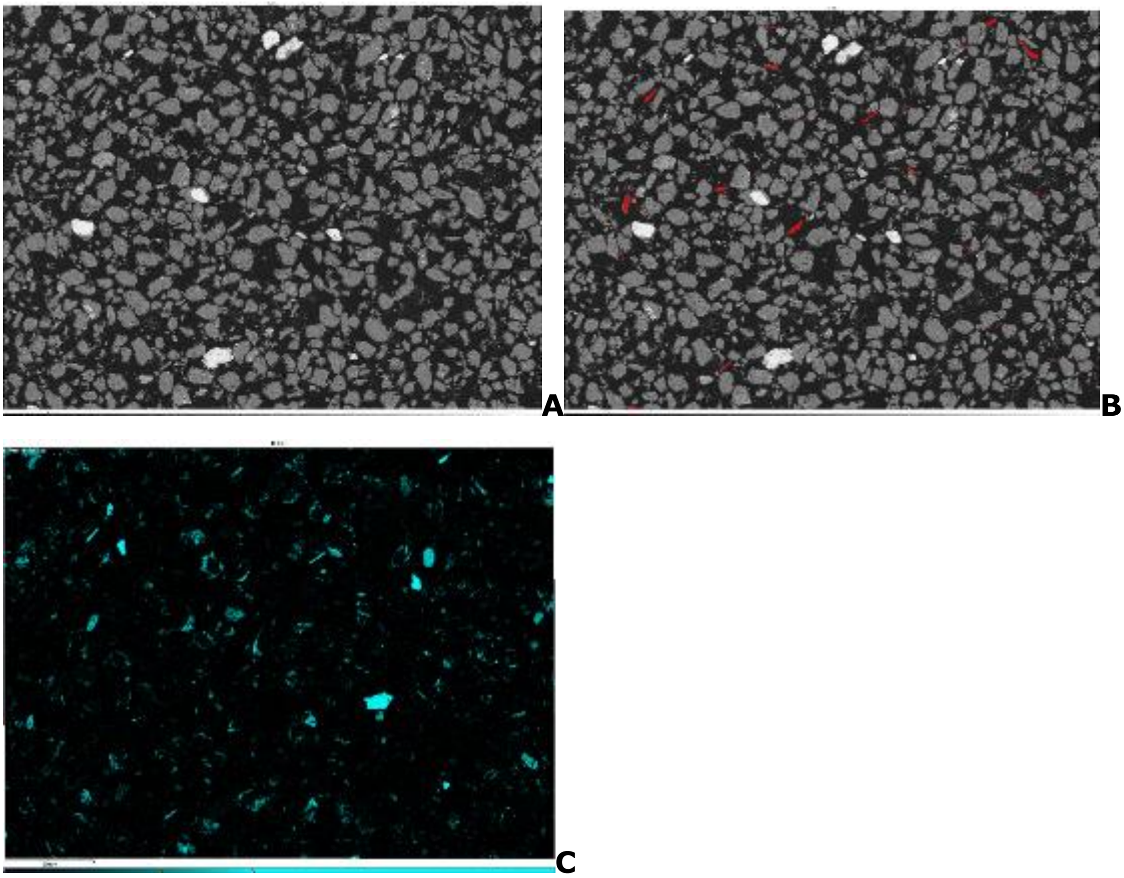


Figure 34: Sand sample CK-2. (Co. Cork). (A); Backscattered electron image of sand montage of 9 images at 500x magnification. (B); Free mica is highlighted in red. (C); Potassium EDS single element map.

Table 18: CK-2, % free mica in sand by SEM-EDX.

Code	Total area analysed (sq. μm)	Total fines area (sq. μm)	Free mica fines area (sq. μm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
CK-2 1a	637000	233000	2090	2092	18	0.90	
CK-2 1b	358000	125000	1353	1458	15	1.08	0.13
CK-2 1c	229000	82700	193	1122	10	0.23	0.45
CK-2 1d	229000	79700	480	1155	7	0.60	0.37
CK-2 1e	229000	72500	572	1215	6	0.79	0.32
CK-2 1f	1800000	509000	4390	12879	83	0.86	0.29
MEAN						0.74	
STD DEV						0.29	

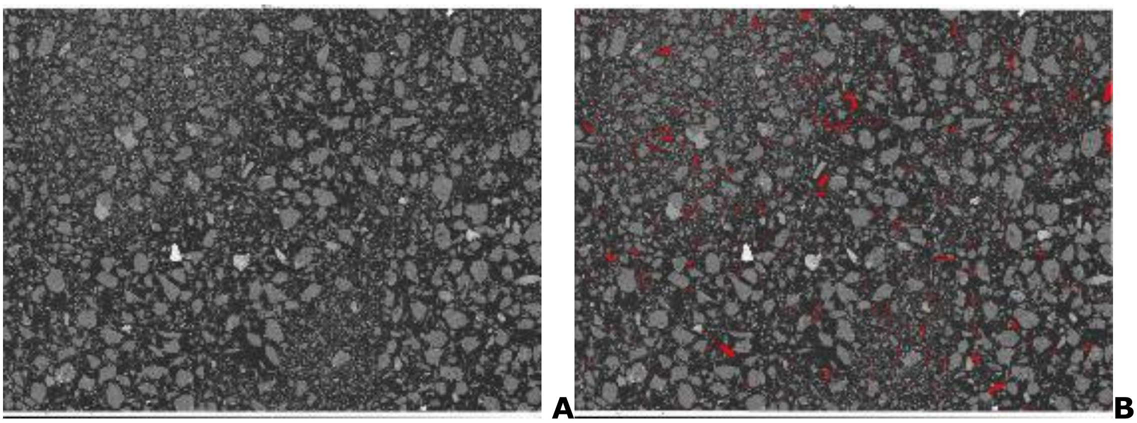
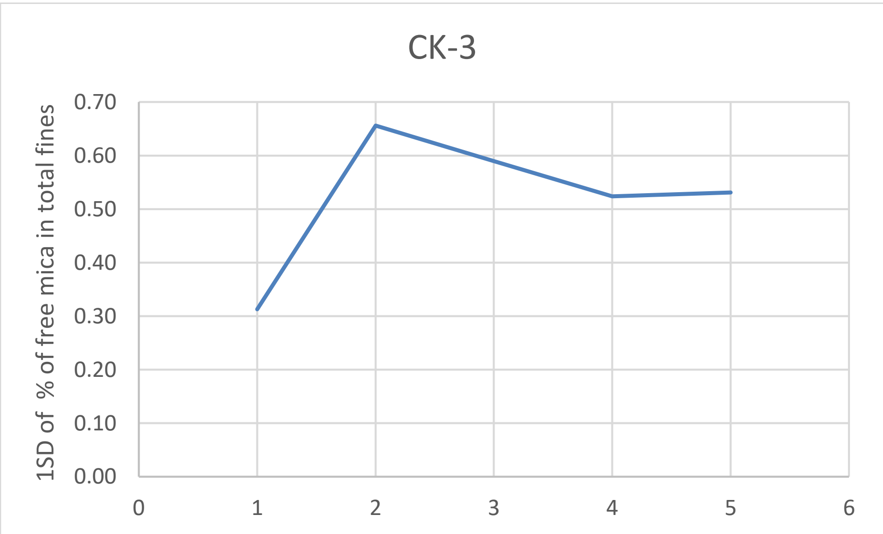


Figure 35: Sand sample CK-3, Co. Cork (A). Backscattered electron image of sand montage of 9 images at 500x magnification. (B) In red free mica is identified by Oxford Instruments Aztec Feature mineral liberation software.

Table 19: CK-3, % free mica in sand by SEM-EDX.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
CK-3 1a	637000	216000	4980	6144	135	2.31	
CK-3 1b	358000	119000	3270	3953	111	2.75	0.31
CK-3 1c	229000	86200	3100	2585	85	3.60	0.66
CK-3 1d	229000	77600	2620	2806	93	3.38	0.59
CK-3 1e	229000	79500	2600	2708	82	3.27	0.52
CK-3 1f	1800000	605000	22200	22091	727	3.67	0.53
MEAN						3.16	
STD DEV						0.53	



Graph 11: 1σ (standard deviation) of free mica in total fines.

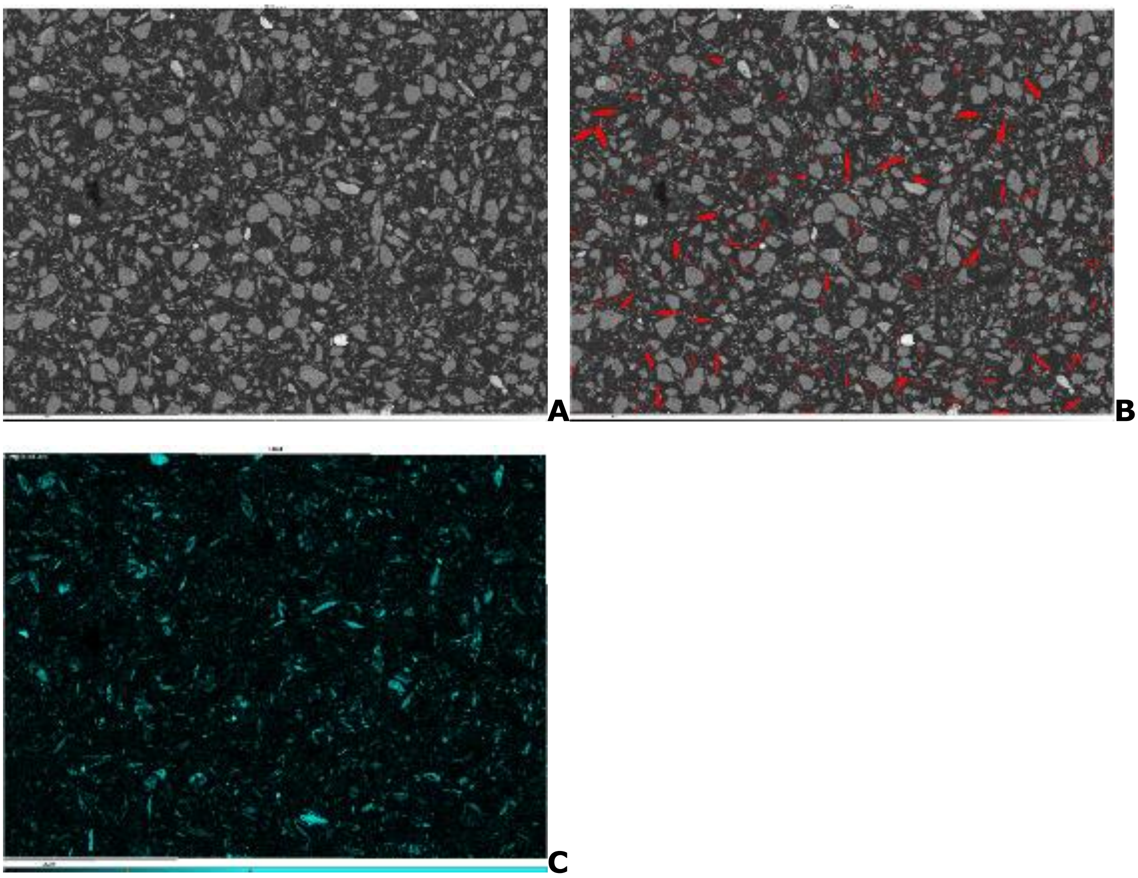


Figure 36: Sand sample CK-4 (Co. Cork). (A); Backscattered electron image of sand montage of 9 images at 500x magnification. (B); Free mica is identified in red. C; Potassium EDS single element map.

Table 20: CK-4, % free mica in sand by SEM-EDX.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
CK-4 1a	637000	195000	10400	4702	110	5.33	
CK-4 1b	358000	103000	5280	3153	90	5.13	0.15
CK-4 1c	229000	73900	4340	2211	81	5.87	0.39
CK-4 1f	1800000	539000	31600	17994	555	5.86	0.38
MEAN						5.55	
STD DEV						0.38	

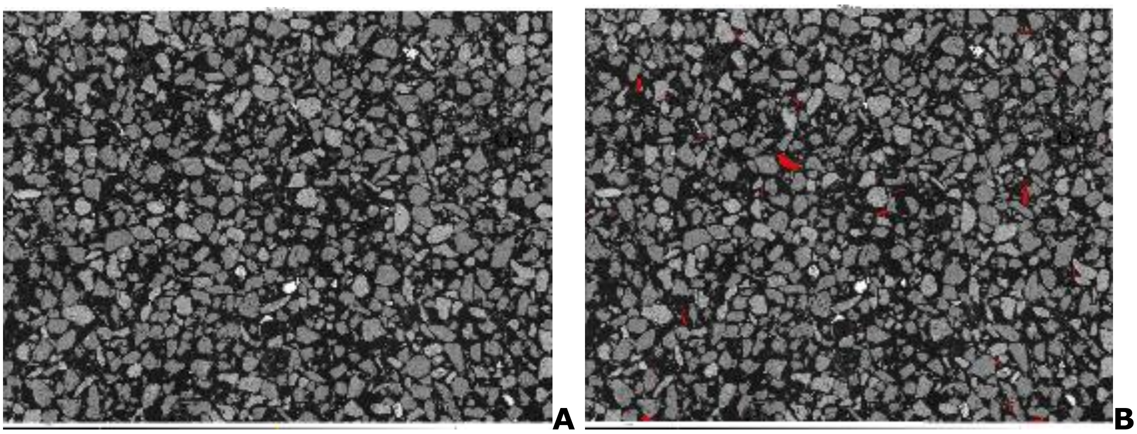


Figure 37: Sand sample CW-1 (Co. Carlow). (A); Backscattered electron image of sand montage of 9 images at 500x magnification. (B); Free mica is identified in red.

Table 21: CW-1, % free mica in sand by SEM-EDX.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
CW-1 1a	637000	257000	346	2611	11	0.13	
CW-1 1b	358000	163000	303	1621	10	0.19	0.04
CW-1 1c	229000	106000	183	1191	7	0.17	0.03
CW-1 1d	229000	105000	115	1212	6	0.11	0.03
CW-1 1e	229000	108000	575	1081	15	0.53	0.17
CW-1 1f	1800000	791000	4820	9358	66	0.61	0.22
MEAN						0.29	
STD DEV						0.22	

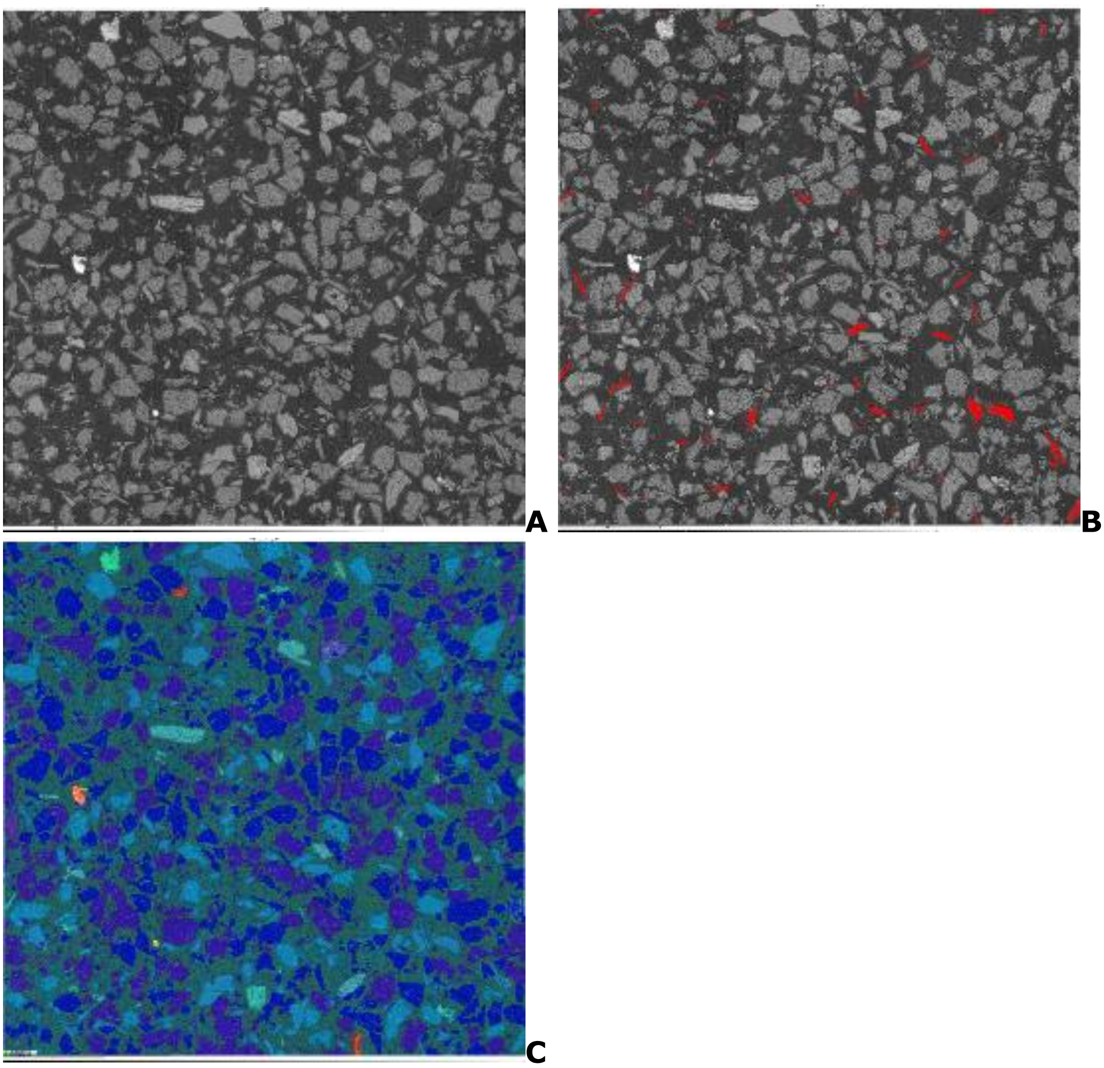
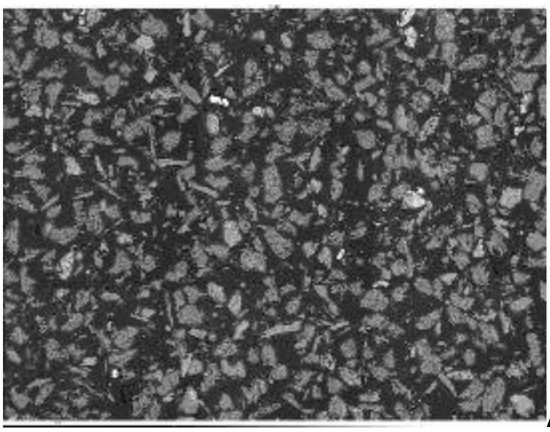


Figure 38: Sand sample DL-1 (Co Donegal). (A); Backscattered electron image of sand montage of 12 images at 500x magnification. (B); Free mica is identified in red. (C); Layered multi-element EDS map.

Table 22: DL-1, % free mica in sand by SEM-EDX.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	SD of the % free mica in total fines
DL-1a	229000	72300	4190	1719	23	5.80	
DL-1b	229000	56900	1640	2082	22	2.88	2.06
DL-1c	229000	61300	2240	1637	21	3.65	0.55
DL-1d	229000	55900	2940	1966	15	5.26	1.14
DL-1e	2480000	427000	14300	16824	164	3.35	1.35
DL-1f	1650000	480000	13500	14850	137	2.81	0.38
MEAN						3.96	
STDEV						1.27	



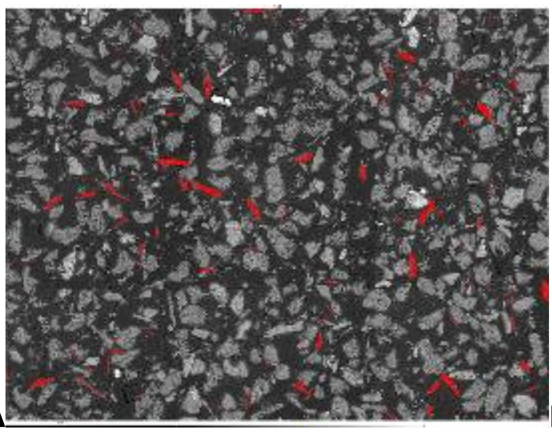
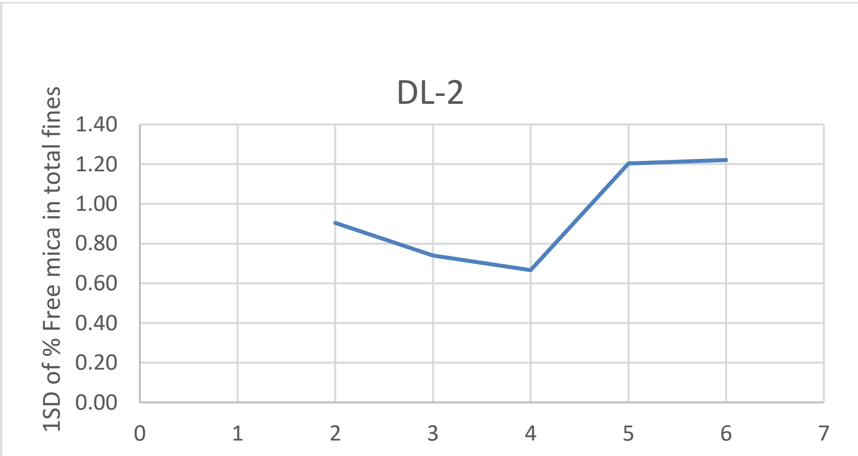


Figure 39: Sand sample DL-2 (Co. Donegal) (A); Backscattered electron image of sand montage, of 9 images at 600x magnification. B; in red free mica is identified.

Table 23: DL-2, % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. μm)	Total fines area (sq. μm)	Free mica area (sq. μm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
DL-2 1b	229000	58700	1650	2162	29	2.81	
DL-2 1c	229000	56000	2290	2008	21	4.09	0.90
DL-2 1d	229000	40600	1140	2624	22	2.81	0.74
DL-2 1e	358000	84200	3200	2339	35	3.80	0.67
DL-2 1f	1250000	244000	14000	14256	204	5.74	1.20
DL-2 1g	847000	183000	9630	8692	133	5.26	1.22
MEAN						4.08	
STD DEV						1.22	



Graph 12: 1σ (standard deviation) of free mica in total fines.

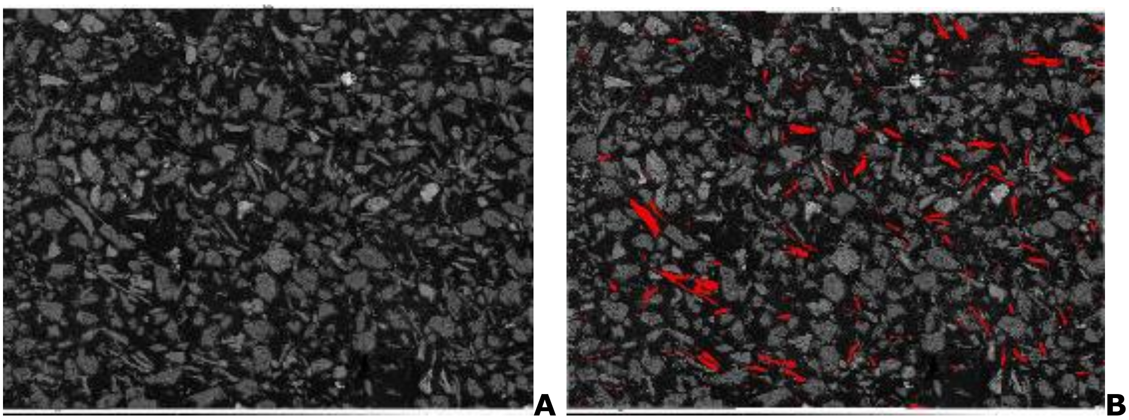
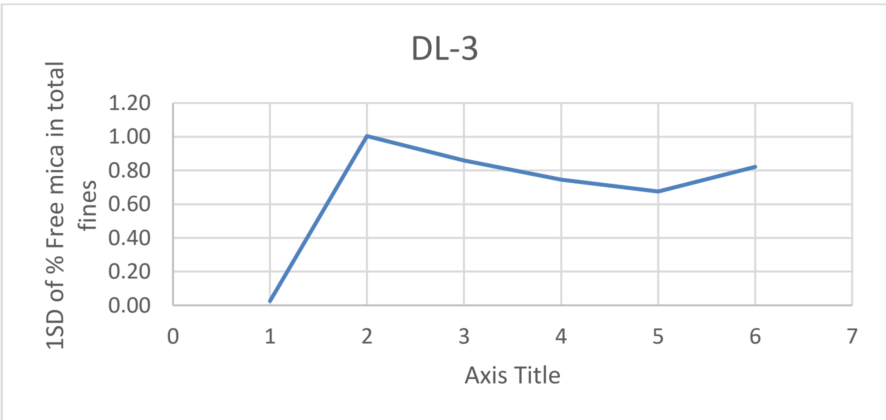


Figure 40: Sand sample DL-3 (Co. Donegal). (A); Backscattered electron image of sand, a montage of 9 images at 600x magnification. (B); in red free mica is identified.

Table 24: DL-3: % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
DL-3 1a	229000	52900	3100	2335	42	5.86	
DL-3 1b	229000	54600	3180	2162	44	5.82	0.03
DL-3 !c	290000	65300	4950	2121	37	7.58	1.00
DL-3 1d	229000	61100	4240	2196	46	6.94	0.86
DL-3 1e	358000	106000	6930	2527	54	6.54	0.74
DL-3 1f	2559000	698000	47600	22195	456	6.82	0.67
DL-3 1g	1160000	325000	26100	12393	281	8.03	0.82
MEAN						6.80	
STD DEV						0.82	



Graph 13: 1σ (standard deviation) of free mica in total fines.

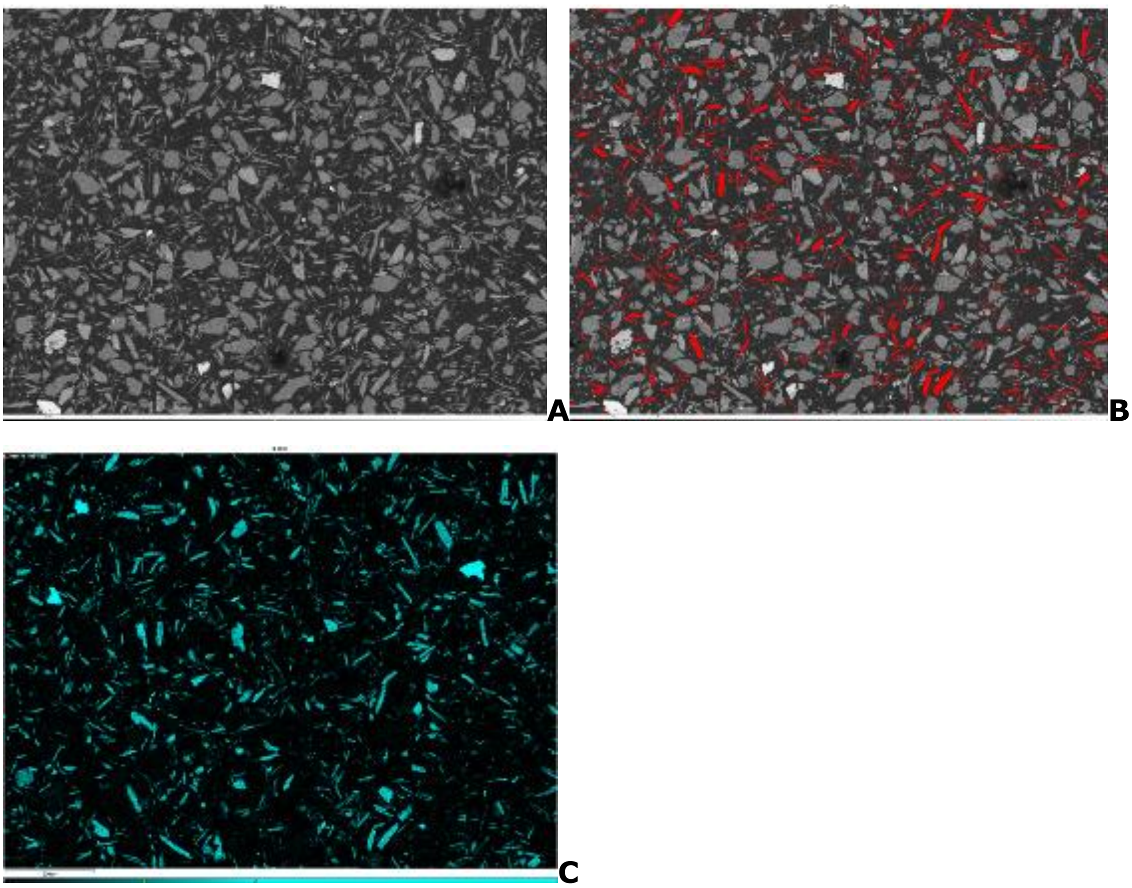
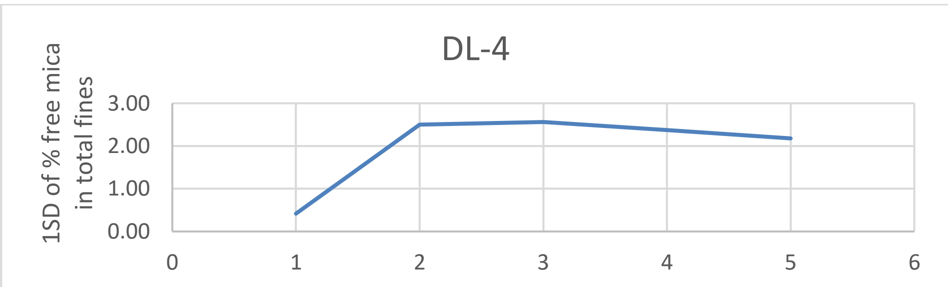


Figure 41: Sand DL-4 (Co. Donegal). A); BSE image of sand (montage of 9 images at 500x magnification. (B); Free mica fines are identified in red. (C); Potassium EDS map.

Table 25: DL-4, % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
DL-4 1a	637000	184000	28600	2481	321	15.54	
DL-4 1b	358000	98300	14700	1674	186	14.95	0.42
DL-4 1c	229000	61400	12000	1305	184	19.54	2.50
DL-4 1d	229000	73300	14500	1576	196	19.78	2.56
DL-4 1e	229000	80200	12500	1514	165	15.59	2.37
DL-4 1f	1800000	532000	84500	9335	1115	15.88	2.18
MEAN						16.88	
STD DEV						2.18	



Graph 14: 1σ (standard deviation) of free mica in total fines.

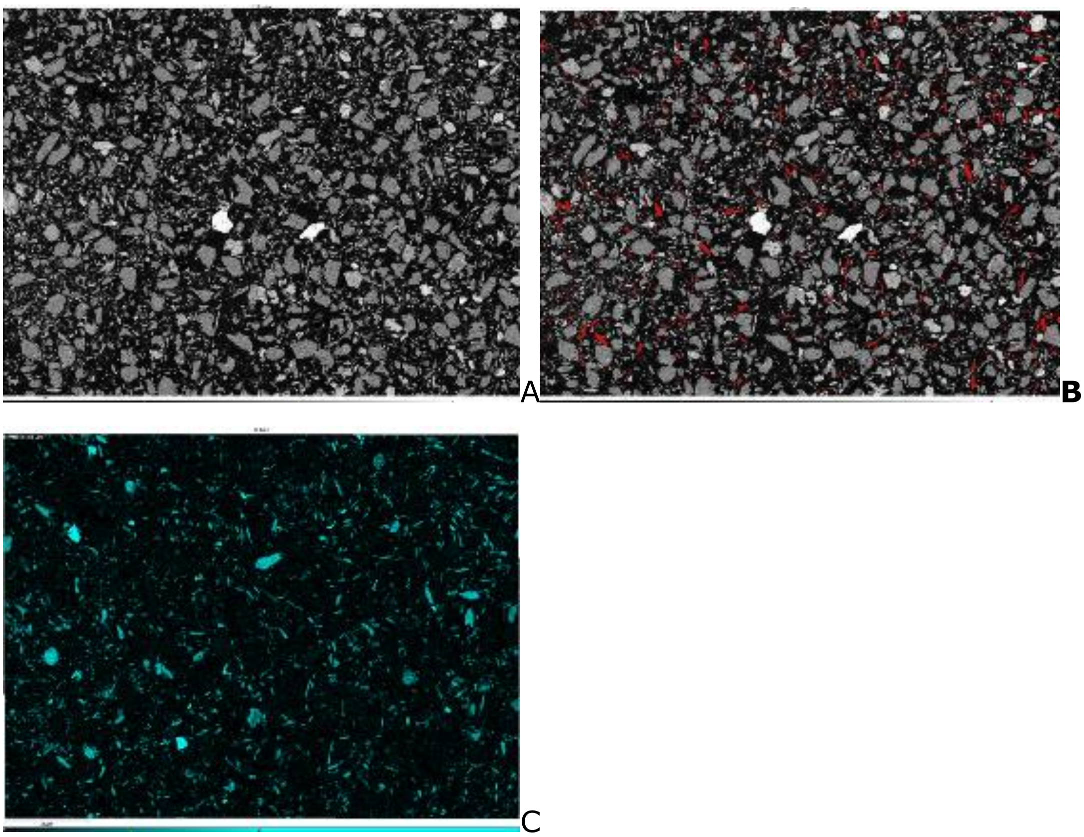
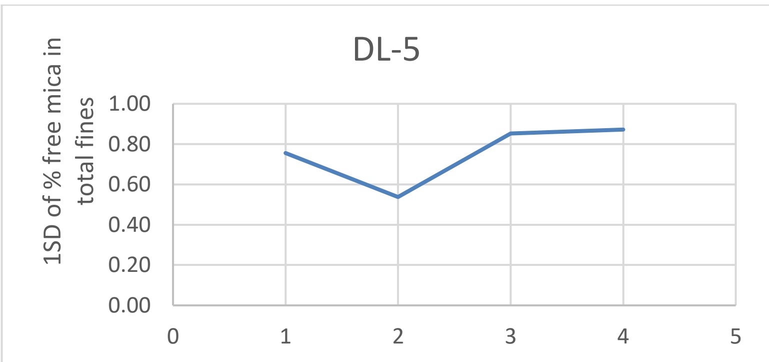


Figure 42: Sand DL-5, (Co. Donegal). (A); BSE image of sand, a montage of 9 images at 500x magnification. (B); Free mica is identified in red. (C); Potassium EDS map.

Table 26: DL-5, % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
DL-5 1a	637000	211000	10200	3399	160	4.83	
DL-5 1b	358000	125000	7380	2686	155	5.90	0.76
DL-5 1c	229000	76200	4020	2285	108	5.28	0.54
DL-5 1d	229000	89000	3450	1667	85	3.88	0.85
DL-5 1f	1800000	361000	21700	13081	718	6.01	0.87
MEAN						4.32	
STD DEV						0.87	



Graph 15: 1σ (standard deviation) of free mica in total fines.

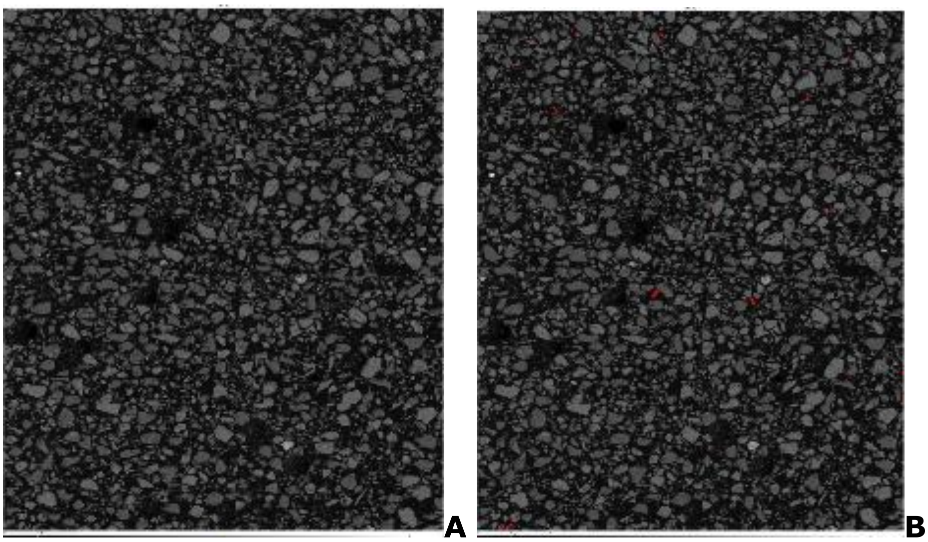
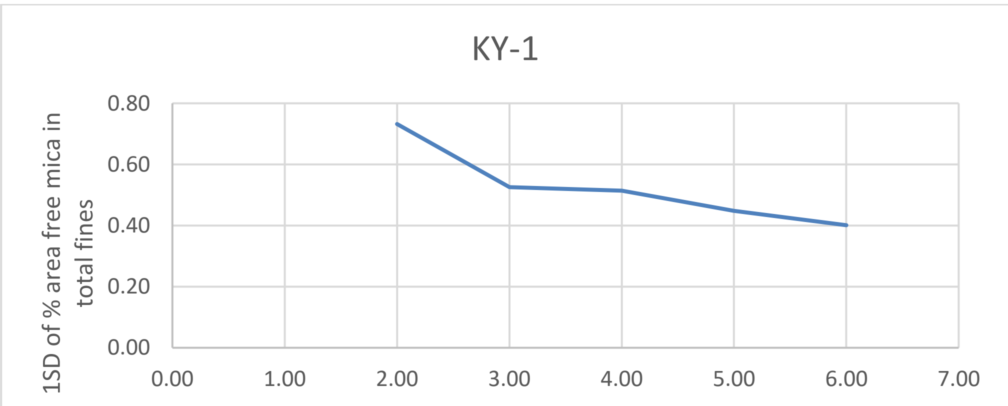


Figure 43: Sand sample KY-1, Co. Kerry. (A); Backscattered electron image of sand, a montage of 8 images at 371x magnification. (B); Free mica is identified in red.

Table 27: KY-1, % free mica in sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
KY-1 2a	637000	177000	2220	2290	35	1.25	
KY-1 2b	358000	107000	2450	1471	34	2.29	0.73
KY-1 2c	229000	79700	1290	1093	23	1.62	0.53
KY-1 2d	229000	65600	1500	1124	24	2.29	0.51
KY-1 2e	229000	72500	1260	1075	17	1.74	0.45
KY-1 2f	1800000	516000	9450	8773	153	1.83	0.40
MEAN						1.84	
STD DEV						0.40	



Graph 16: 1σ (standard deviation) of free mica in total fines.

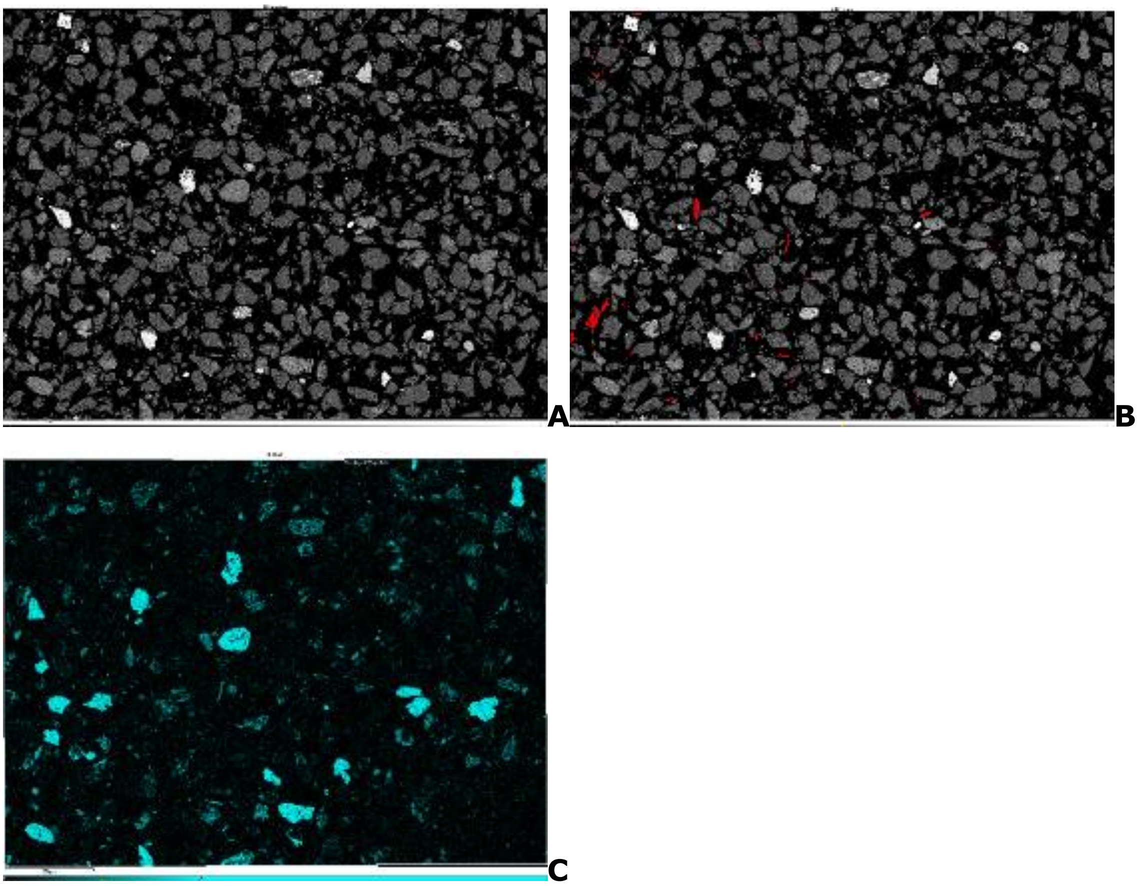


Figure 44: Sand sample LK-1, Co. Limerick. (A); Backscattered electron image of sand, a montage of 9 images at 500x magnification. (B); Free mica is identified in red. (C); Potassium EDS map.

Table 28: LK-1% free mica in sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
LK-1 1b	358000	121000	1530	2142	17	1.26	
LK-1 1c	358000	77300	1250	1614	24	1.62	0.25
LK-1 1d	229000	60900	359	1792	13	0.59	0.52
LK-1 1e	229000	76300	1270	1972	14	1.66	0.50
LK-1 1f	1800000	536000	4580	11664	75	0.85	0.47
MEAN						1.20	
STD DEV						0.47	

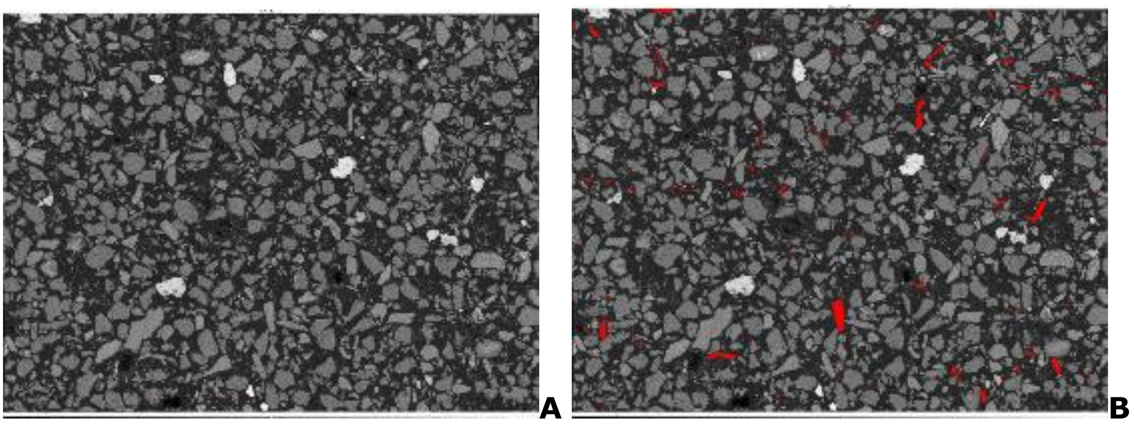
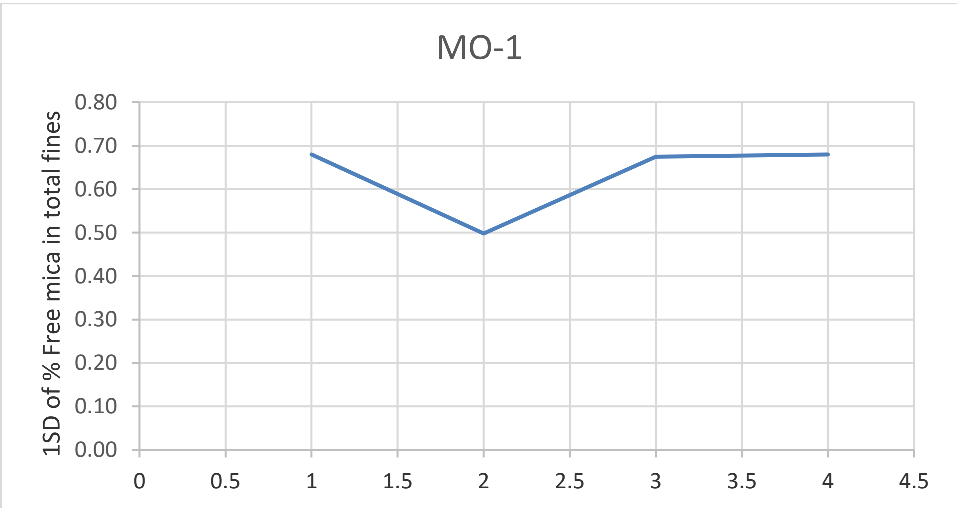


Figure 45: Sand sample MO-1, Co. Mayo. (A); Backscattered electron image of sand, a montage of 9 images at 500x magnification. (B); Free mica fines are highlighted in red.

Table 29: MO-1, % free mica in total fines by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
MO-1 1a	637000	254000	3730	3032	35	1.47	
MO-1 1b	358000	135000	3280	2338	35	2.43	0.68
MO-1 1d	229000	83700	1820	1657	22	2.17	0.50
MO-1 1e	229000	73100	2267	1729	20	3.10	0.67
MO-1 1f	1800000	570000	17500	13145	153	3.07	0.68
MEAN						2.45	
STD DEV						0.68	



Graph 17*:* 1σ (standard deviation) of free mica in total fines.

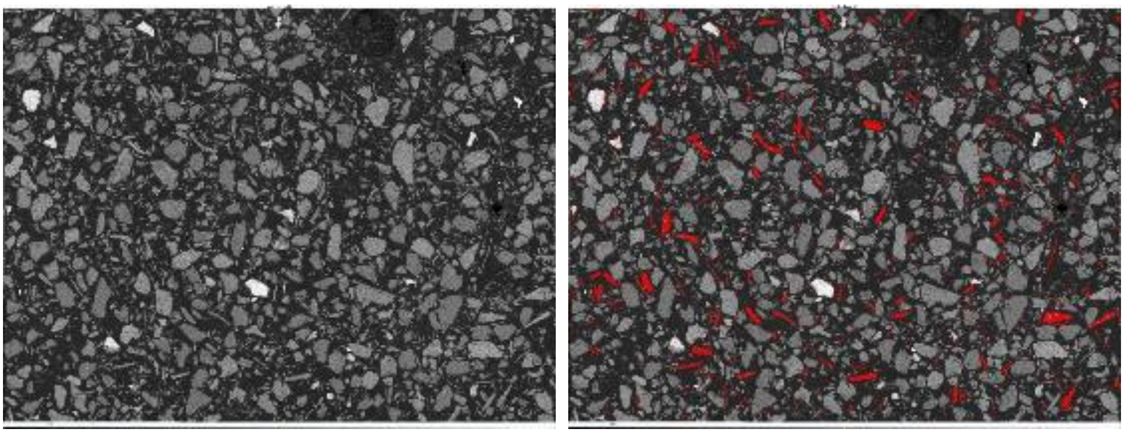
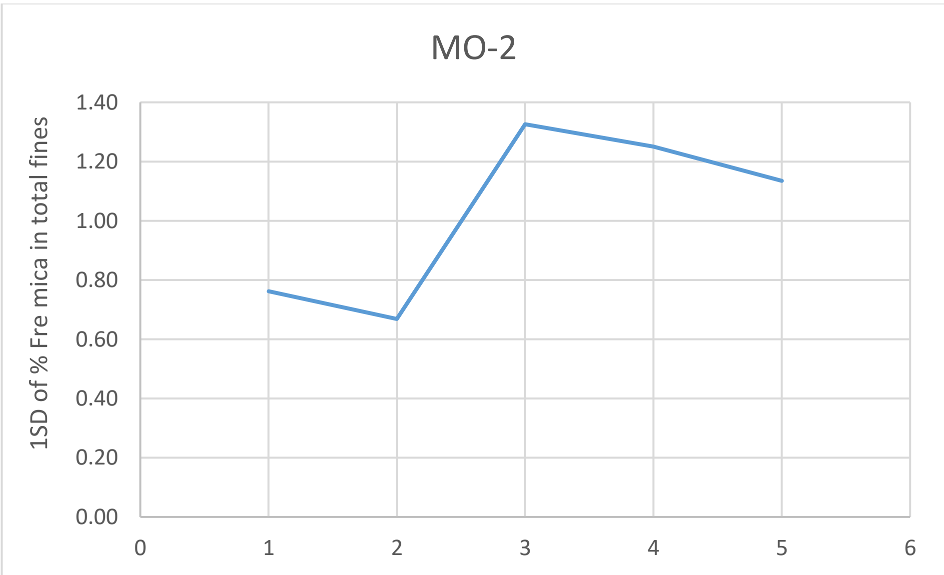


Figure 46: Sand sample MO-2, Co. Mayo. (A); Backscattered electron image of sand, a montage of 9 images at 500x magnification. (B) Free mica is highlighted in red.

Table 30: MO-2, % free mica in total fines by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
MO-2 1a	637000	195000	7970	3411	114	4.09	
MO-2 1b	358000	110000	3310	2258	75	3.01	0.76
MO-2 1c	229000	73000	3090	1936	71	4.23	0.67
MO-2 1d	229000	68300	4230	1910	72	6.19	1.33
MO-2 1e	2229000	71800	2350	1847	62	3.27	1.25
MO-2 1f	1800000	551000	25500	13836	427	4.63	1.13
MEAN						4.24	
STD DEV						1.13	



Graph 18: 1σ (standard deviation) of free mica in total fines.

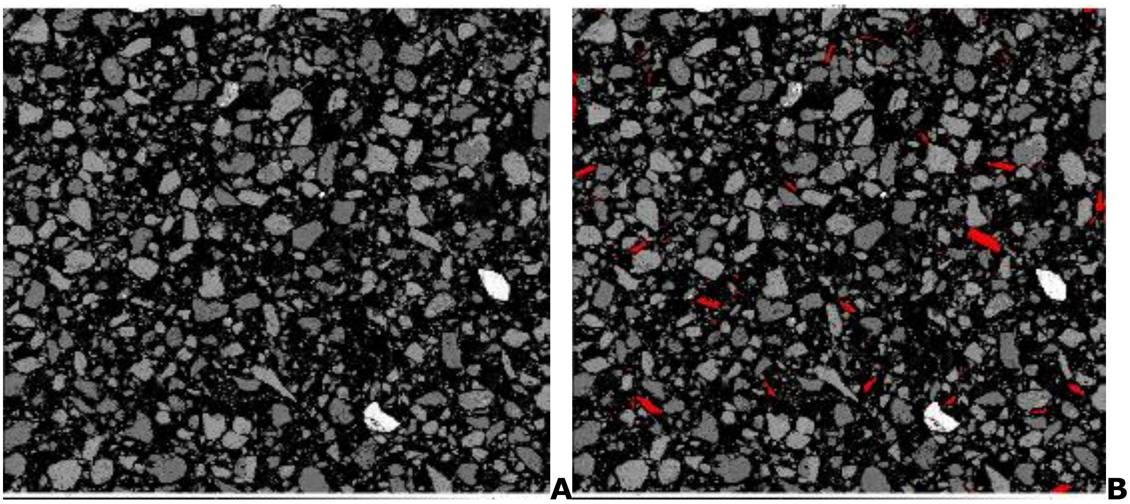
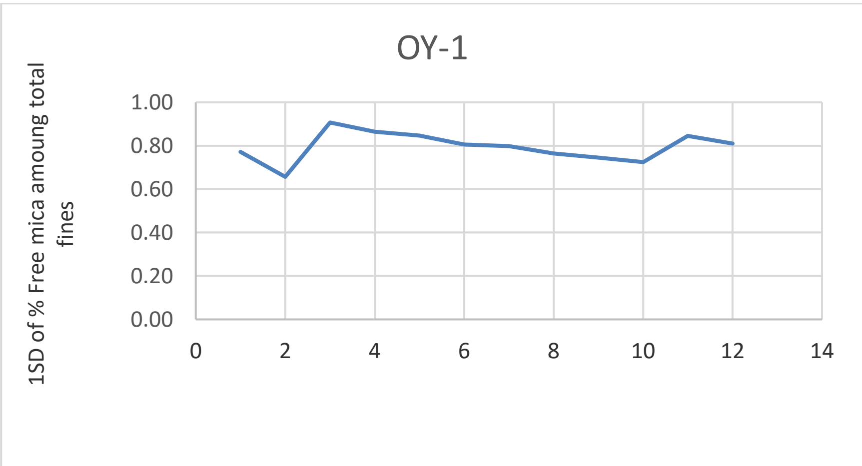


Figure 47: Sand sample OY-1, Co. Offaly. (A); Backscattered electron image of sand, a montage of 12 images at 500x magnification. (B) Free mica is identified in red by Oxford Instruments Aztec Feature mineral liberation software.

Table 31: OY-1, % free mica in total fines

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
OY-1 X1	357,938	115,000	3710	1570	34	3.23	
OY-1 X2	357,938	118,000	2520	1600	31	2.14	0.77
OY-1 X3	357,938	148,000	3030	2041	31	2.05	0.66
OY-1 X4	229,495	84,100	847	1587	22	1.01	0.91
OY-1 X5	116,920	47,700	617	909	19	1.29	0.86
OY-1 X6	116,920	52,700	580	1761	24	1.10	0.85
OY-1 X7	116,920	40,300	966	1389	18	2.40	0.80
OY-1 X8	116,920	48,700	525	1437	15	1.08	0.80
OY-1 X9	116,920	57,900	746	1606	16	1.29	0.76
OY-1 X10	116,920	45,700	521	1336	16	1.14	0.74
OY-1 X11	7,850,000	1,990,000	44000	43147	883	2.21	0.72
OY-1 X12	1,120,000	382,000	13000	8530	176	3.40	0.84
OY-1 X13	821,000	349,000	5990	8883	85	1.72	0.81
MEAN						1.85	
STD DEV						0.81	



Graph 19: 1σ (standard deviation) of free mica in total fines.

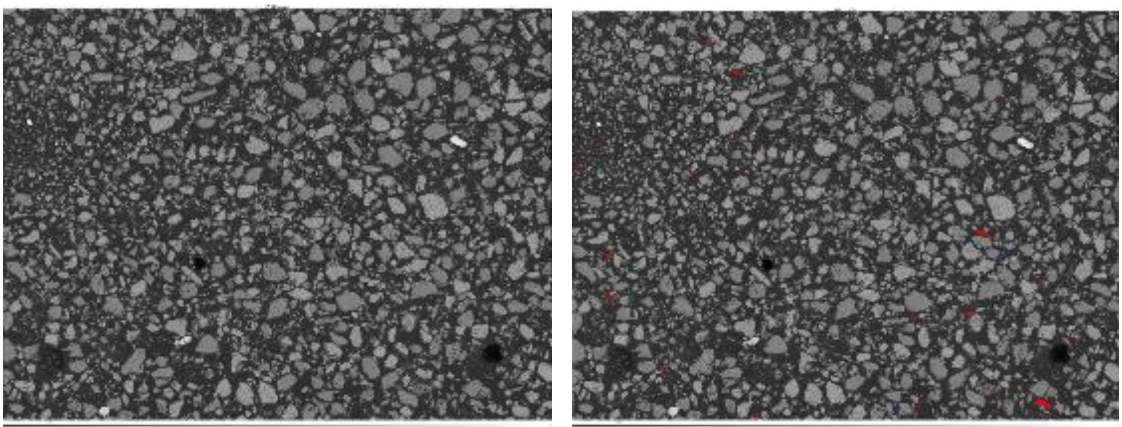
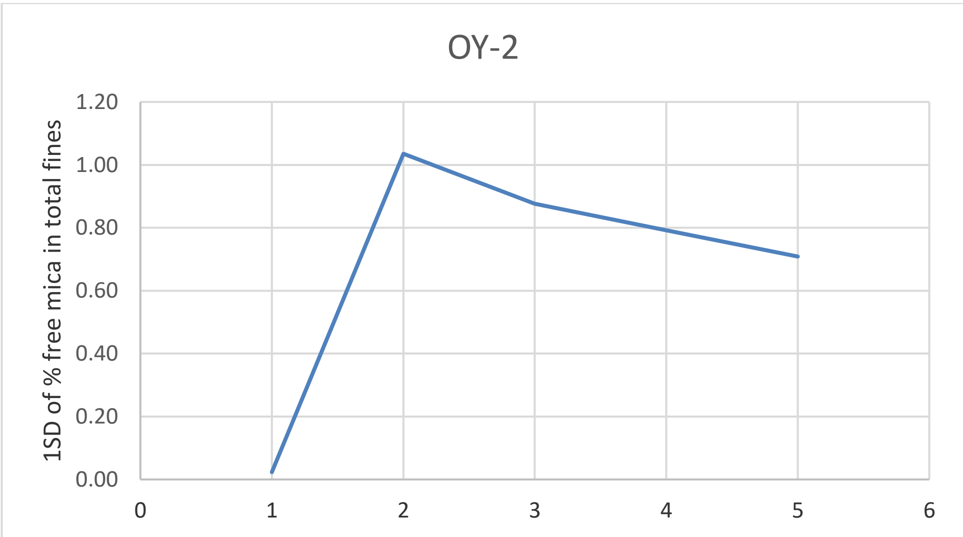


Figure 48: Sand sample OY-2, Co. Offaly. (A); Backscattered electron image of sand, a montage of 9 images at 500x magnification. (B); Free mica fines are identified in red.

Table 32: OY-2, % free mica in total fines by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
OY-2 2a	637000	242000	565	3344	15	0.23	
OY-2 2b	358000	134000	357	2210	15	0.27	0.02
OY-2 2c	229000	79300	1620	1751	8	2.04	1.04
OY-2 2d	229000	86300	329	1809	11	0.38	0.88
OY-2 2e	229000	96300	219	1680	5	0.23	0.79
OY-2 2f	1800000	649000	4120	13675	72	0.63	0.71
MEAN						0.63	
STD DEV						0.71	



Graph 20: 1σ (standard deviation) of free mica in total fines.

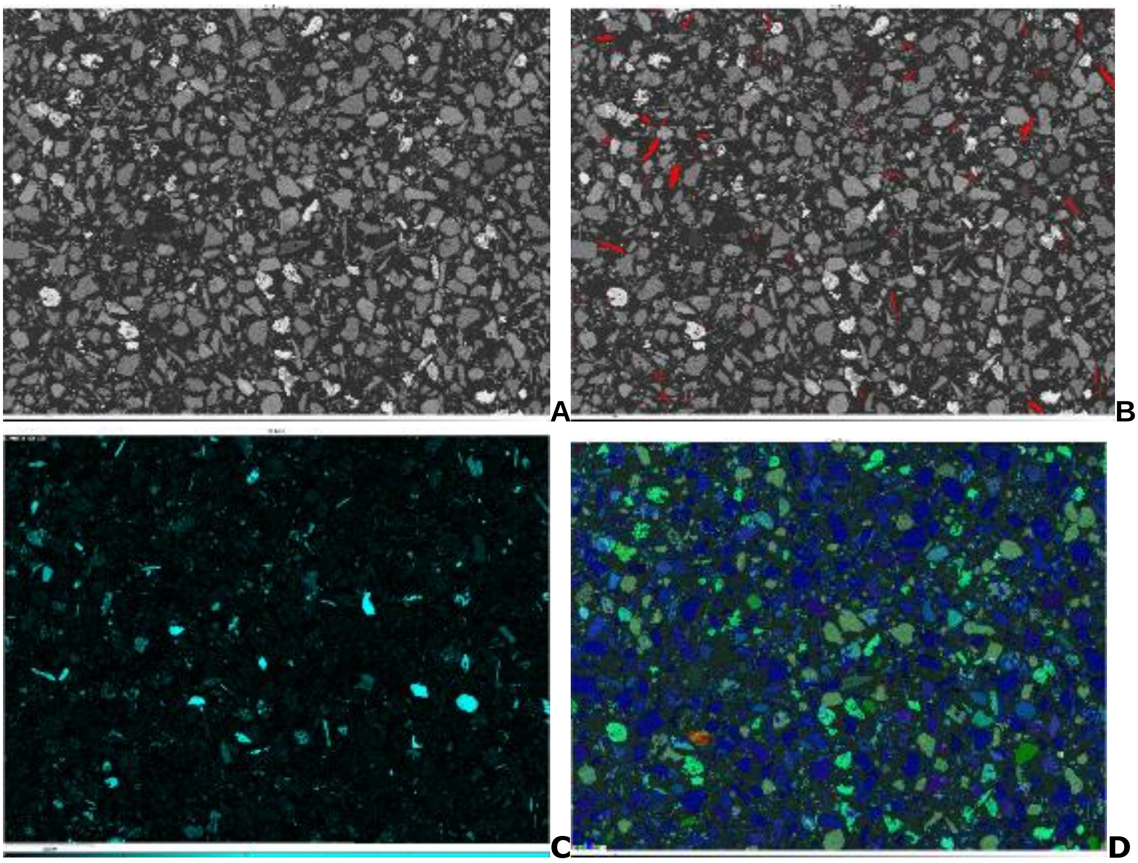
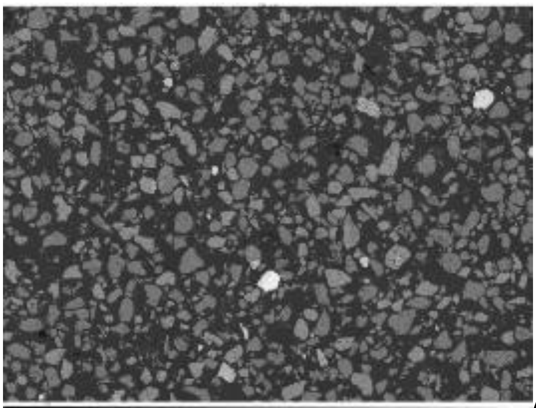


Figure 49: Sand sample OY-3, Co. Offaly. (A); Backscattered electron image of sand, a montage of 9 images at 500x magnification. (B); Free mica is identified in red. (C) Potassium EDS map. (D); Layered multi-element EDS Map.

Table 33: OY-3, % free mica in total sand fines by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
OY-3 1a	637000	227000	4240	3659	31	1.87	
OY-3 1b	358000	124000	537	2762	14	0.43	1.01
OY-3 1c	229000	85800	1240	2099	22	1.45	0.74
OY-3 1d	229000	78900	1060	2017	19	1.34	0.60
OY-3 1e	229000	82000	225	1835	12	0.27	0.69
OY-3 1f	1800000	630000	12800	15627	159	2.03	0.73
MEAN						1.23	
STD DEV						0.73	



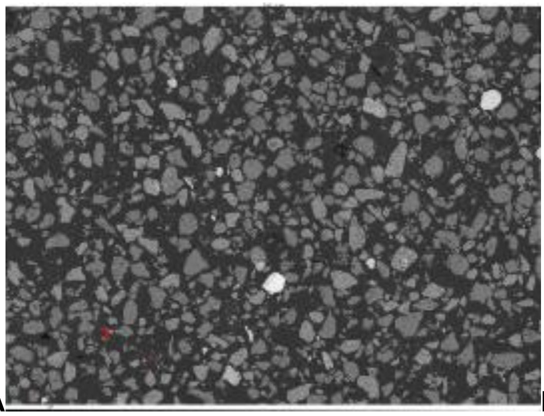
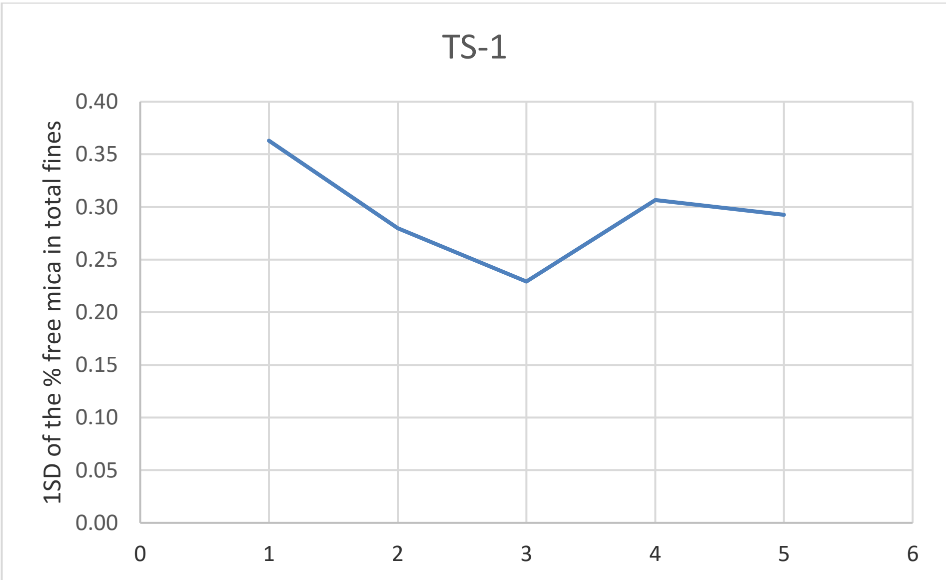


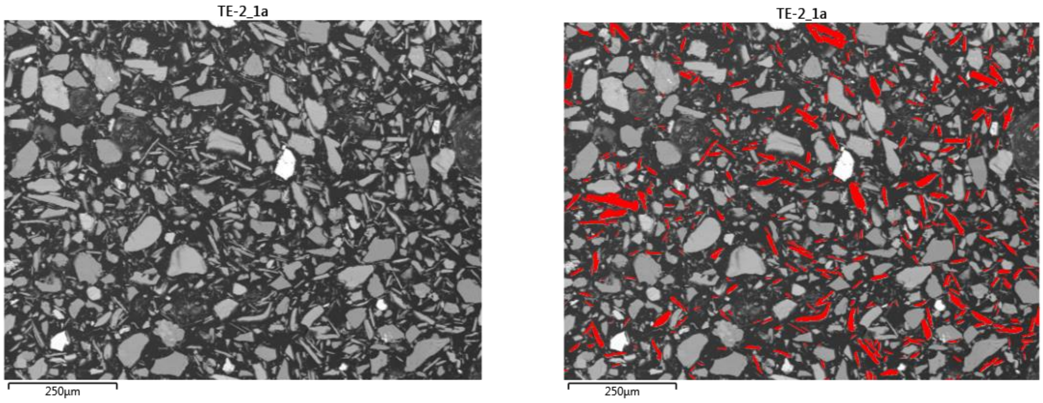
Figure 50: Sand sample TS-1 (2f), Co. Tipperary. (A); Backscattered electron image of sand, a montage of 9 images at 500x magnification. (B) In red free mica is identified by Oxford Instruments Aztec Feature mineral liberation software.

Table 34: TS-1, %free mica in total fines by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
TS-1 2a	637000	230000	73	1728	4	0.03	
TS-1 2b	358000	122000	665	1132	3	0.55	0.36
TS-1 2c	229000	74300	71	906	2	0.10	0.28
TS-1 2d	229000	78700	147	933	5	0.19	0.23
TS-1 2e	229000	73600	543	825	3	0.74	0.31
TS-1 2f	1800000	629000	444	7168	24	0.07	0.29
MEAN						0.28	
STD DEV						0.29	



Graph 21: 1σ (standard deviation) of free mica in total fines.

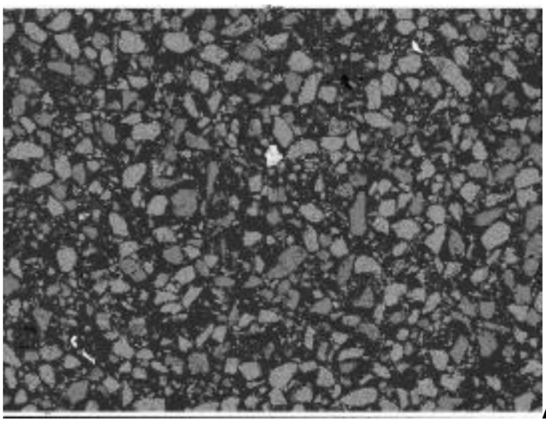


A B

Figure 51: (A) BSE image, sand sample TE-2, Co. Tyrone. (B) BSE image with free mica highlighted in red.

Table 35: TE-2, % free mica in total fines by SEM-EDS.

Code	Total area analysed (sq. μm)	Total fines area (sq. μm)	Free mica fines area (sq. μm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
TE-2 1a	917000	277000	38940	3863	399	14.06	
TE-2 1b	229000	77700	12900	152	167	16.60	1.80
TE-2 1c	229000	74000	10800	1435	156	14.59	1.34
TE-2 1d	229000	62900	10100	1750	157	16.06	1.20
TE-2 1e	229000	73600	14400	1580	215	19.57	2.16
TE-2 1f	1800000	524000	96400	6725	1378	18.40	2.13
MEAN						16.55	
STD DEV						2.13	



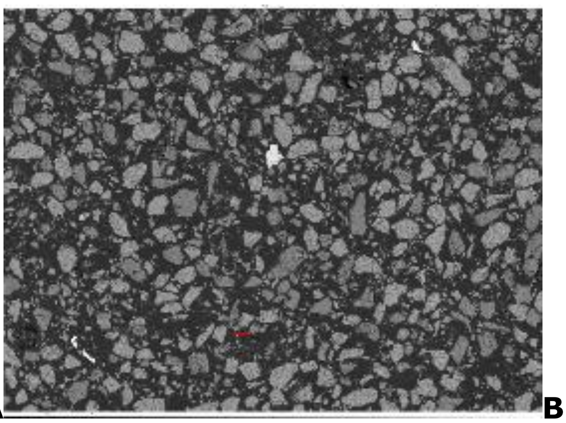
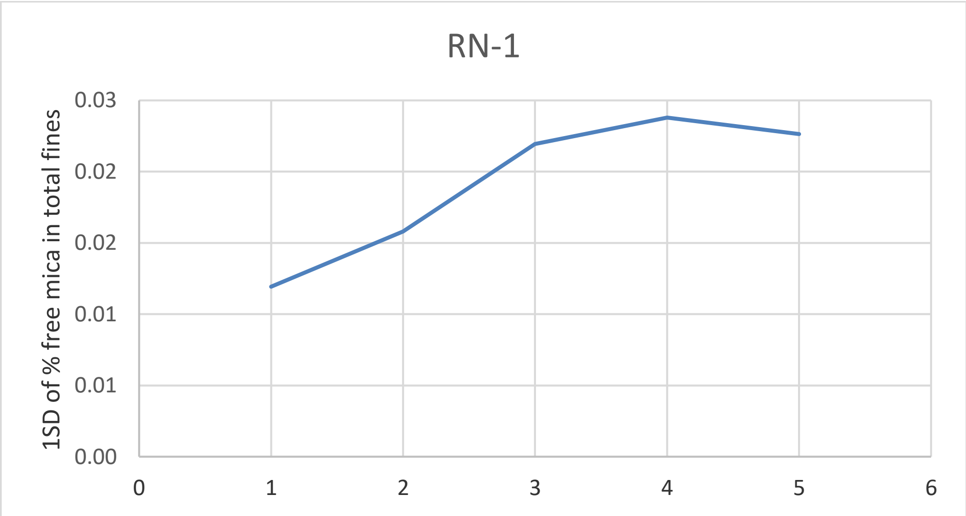


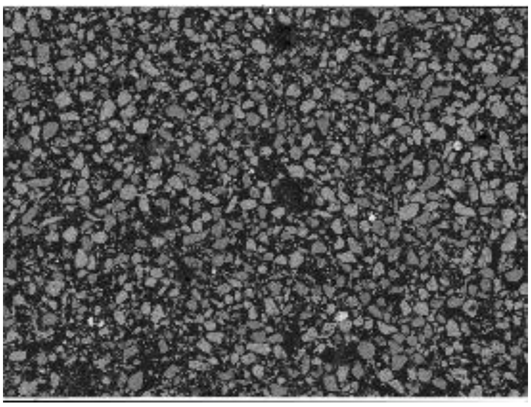
Figure 52: Sand sample RN-1 (2f), Co. Roscommon. (A); Backscattered electron image of sand, a montage of 9 images at 500x magnification. (B); Free mica is identified by Oxford Instruments Aztec Feature mineral liberation software.

Table 36: RN-1, % free mica in total fines by SEM-EDS.

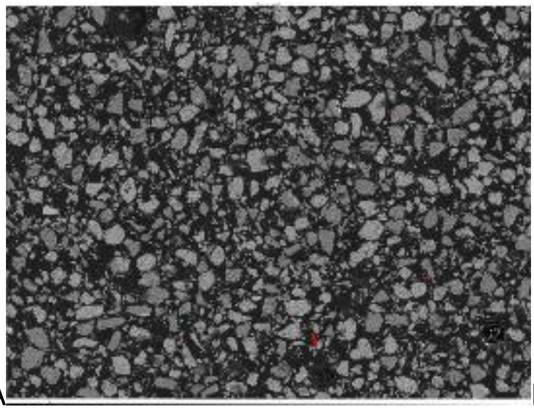
Code	Total area analysed (sq. μm)	Total fines area (sq. μm)	Free mica fines area (sq. μm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
RN-1 2a	637000	237000	27	2556	1	0.01	
RN-1 2b	358000	138000	39	2525	2	0.03	0.01
RN-1 2c	229000	97700	42	1151	2	0.04	0.02
RN-1 2d	229000	85700	54	1483	2	0.06	0.02
RN-1 2e	229000	91400	4	1137	1	0.00	0.02
RN-1 2f	1800000	679000	332	12338	10	0.05	0.02
MEAN						0.03	
STD DEV						0.02	



Graph 22: 1σ (standard deviation) of free mica in total fines.



A

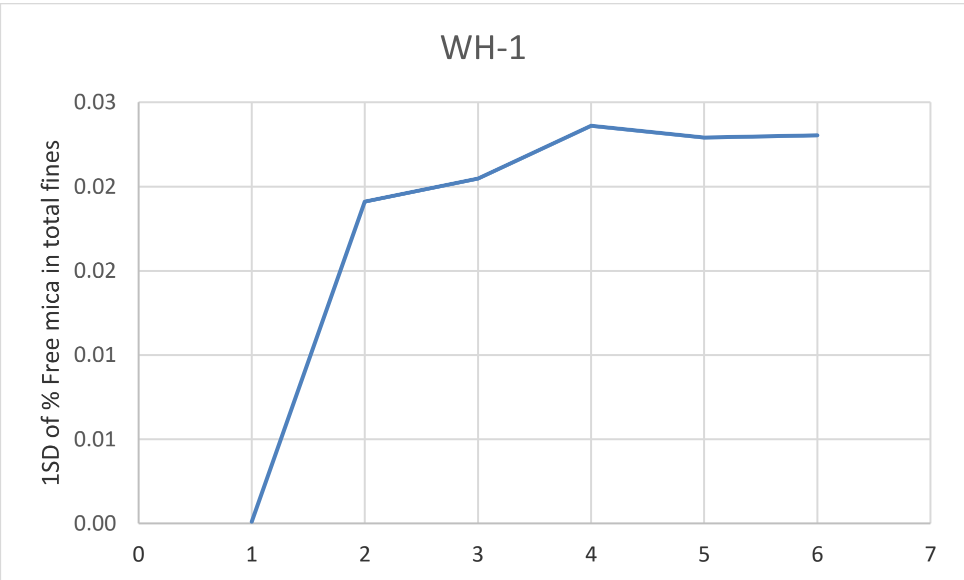


B

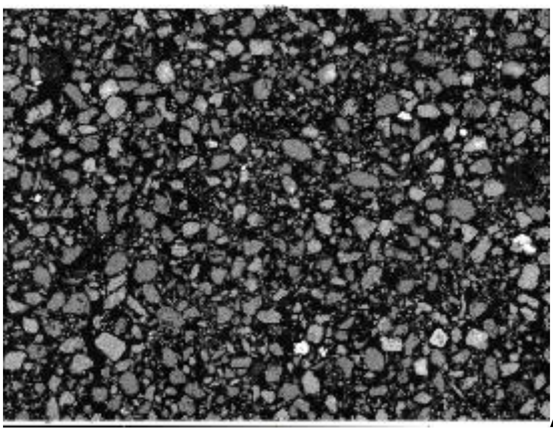
Figure 53: Sand sample WH-1 (1g), Co. Westmeath. (A); Backscattered electron image of sand, a montage of 9 images at 500x magnification. (B) Free mica is identified in red.

Table 37: WH-1, % free mica in total fines by SEM-EDS.

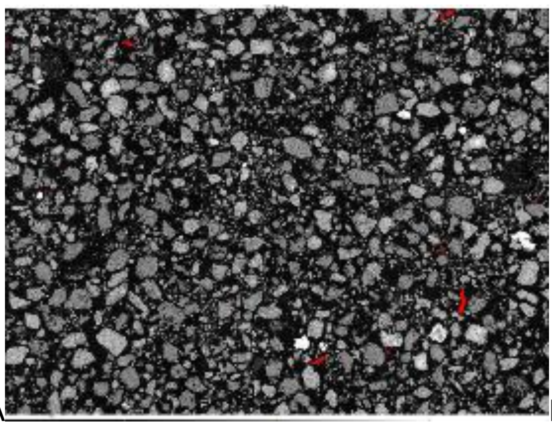
Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
WH-1 1a	637000	234000	147	3577	5	0.06	
WH-1 1b	358000	142000	89	2655	6	0.06	0.00
WH-1 1c	229000	79300	76	1920	6	0.10	0.02
WH-1 1d	229000	86700	41	1528	2	0.05	0.02
WH-1 1e	229000	86700	28	1481	2	0.03	0.02
WH-1 1f	1800000	701000	574	13556	27	0.08	0.02
WH-1 1g	3140000	1320000	1180	23532	50	0.09	0.02
MEAN						0.07	
STD DEV						0.02	



Graph 23: 1σ (standard deviation) of free mica in total fines.



A

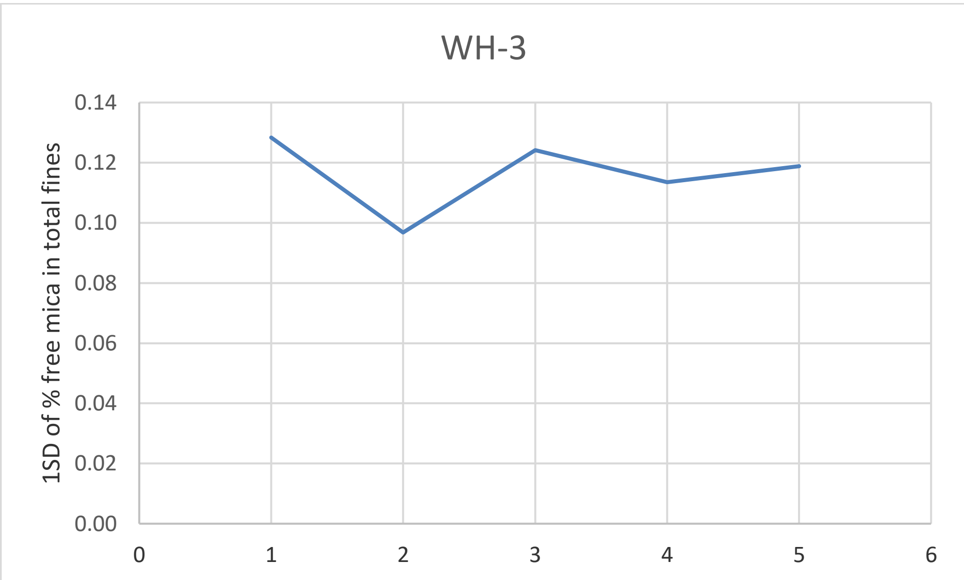


B

Figure 54: Sand sample WH-3 (1f), Co. Westmeath. (A); Backscattered electron image of sand (a montage of 9 images at 500x magnification. (B) Free mica is identified in red by Oxford Instruments Aztec Feature mineral liberation software.

Table 38: WH-3, % free mica in total sand by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
WH-3 1a	637000	245000	794	5202	7	0.32	
WH-3 1b	358000	141000	201	3391	4	0.14	0.13
WH-3 1c	229000	93100	163	2427	6	0.18	0.10
WH-3 1d	229000	88900	20	2624	2	0.02	0.12
WH-3 1e	229000	89700	222	2583	7	0.25	0.11
WH-3 1f	1800000	710000	2370	18052	33	0.33	0.12
MEAN						0.21	
STD DEV						0.12	



Graph 24: 1σ (standard deviation) of free mica in total fines.

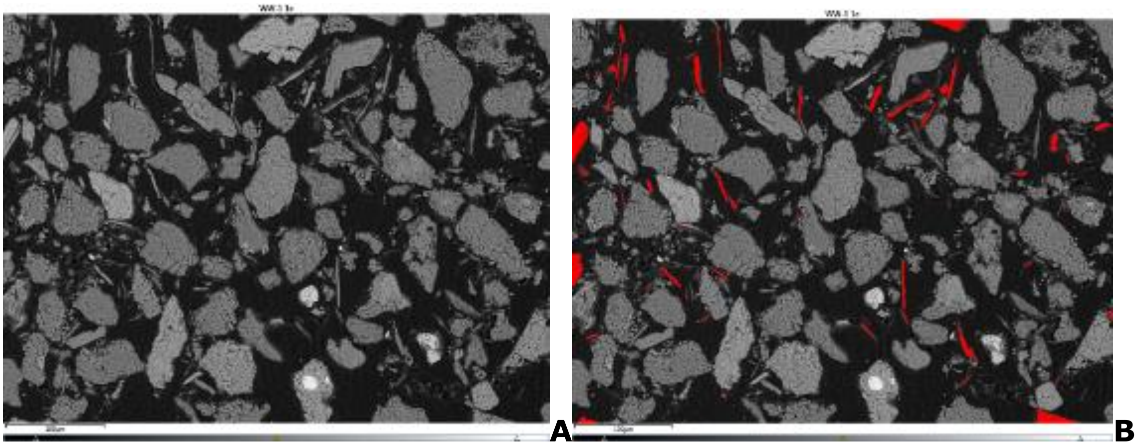
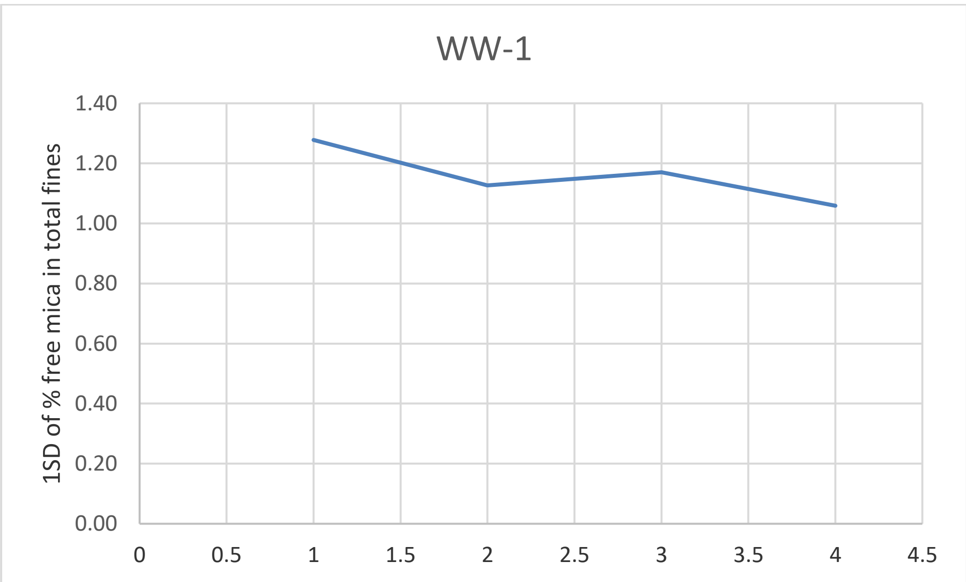


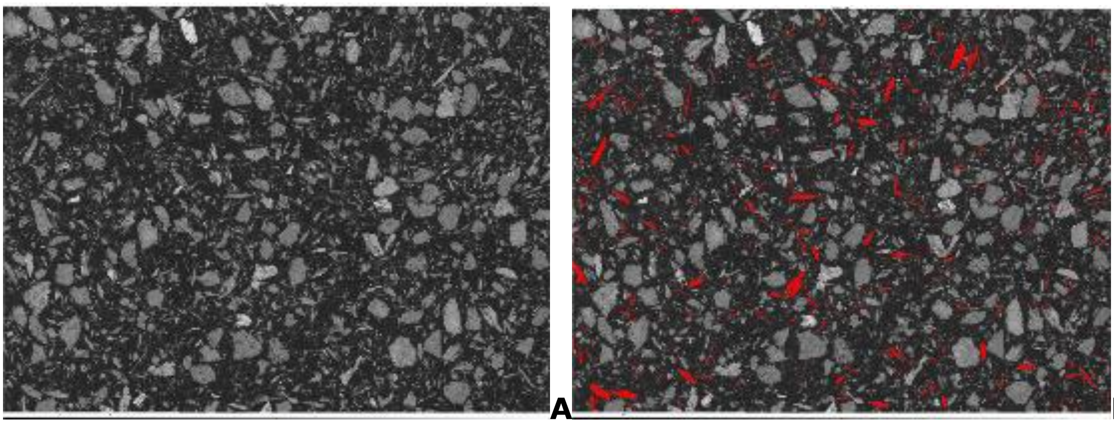
Figure 55: Sand sample WW-1 (1e), Co. Wicklow. (A) Backscattered electron image of sand at 300x magnification. (B) Free mica is identified in red by Oxford Instruments Aztec Feature mineral liberation software.

Table 39: WW-1, % free mica in total fines by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
WW-1 1a	637000	271000	3830	3154	68	1.41	
WW-1 1b	358000	136000	4380	2222	77	3.22	1.28
WW-1 1c	229000	94800	3300	1571	38	3.48	1.13
WW-1 1d	229000	85500	3550	1537	50	4.15	1.17
WW-1 1e	229000	87900	3300	1463	56	3.75	1.06
MEAN						3.20	
STD DEV						1.06	



Graph 25: 1σ (standard deviation) of free mica in total fines.

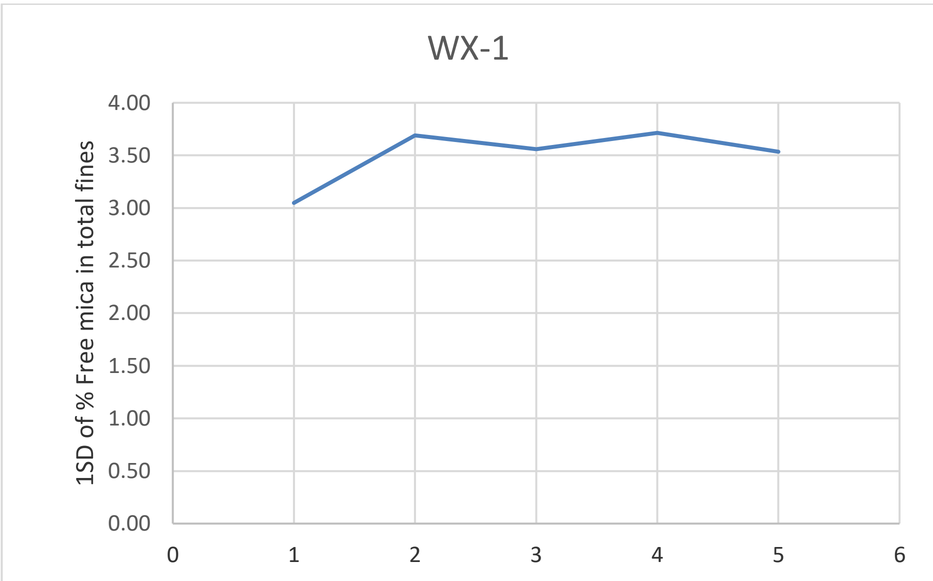


A B

Figure 56: Sand sample WX-1 (1f), Co. Wexford. (A); Backscattered electron image of sand, a montage of nine 500x magnification. (B) Free mica fines are identified in red by Oxford Instruments Aztec Feature mineral liberation software.

Table 40: WX-1, % free mica in total fines by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	SD of the % free mica in total fines
WX-1 1a	637000	123000	14400	3572	210	11.71	
WX-1 1b	358000	66800	10700	2398	167	16.02	3.05
WX-1 1c	229000	56500	4900	2025	138	8.67	3.69
WX-1 1d	117000	29400	4680	1266	90	15.92	3.56
WX-1 1e	159000	38600	3260	2019	120	8.45	3.71
WX-1 1f	1250000	300000	27600	12468	723	9.20	3.53
MEAN						11.66	
STD DEV						3.53	



Graph 26: 1σ (standard deviation) of free mica in total fines.

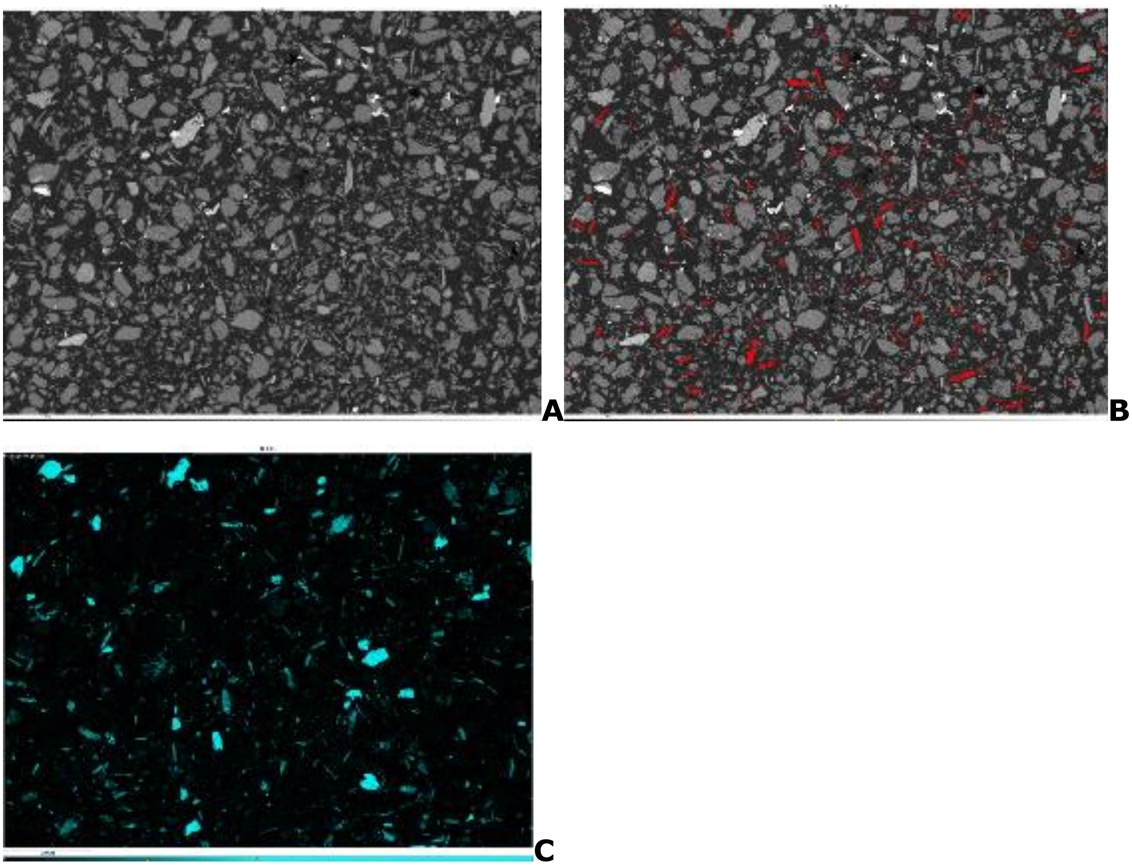


Figure 57: Sand sample WX-2 (1f), Co. Wexford. (A); Backscattered electron image of sand, a montage of nine images at 500x magnification. (B) In red free mica is identified in red. (C) Potassium EDS map.

Table 41: WX-2, % free mica in total fines by SEM-EDS.

Code	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
WX-2 1a	637000	198000	12800	3105	102	6.46	
WX-2 1b	358000	115000	5120	2248	83	4.45	1.42
WX-2 1c	229000	74200	3720	1670	46	5.01	1.04
WX-2 1d	229000	65600	4970	1766	49	7.58	1.42
WX-2 1e	229000	75300	2830	1823	49	3.76	1.55
WX-2 1f	1800000	575000	25500	13908	358	4.43	1.45
MEAN						5.28	
STD DEV						1.45	

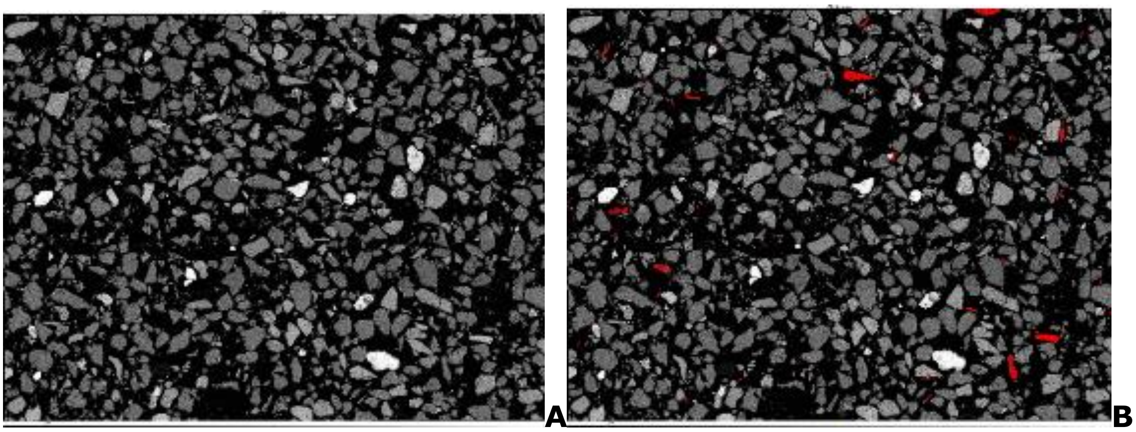
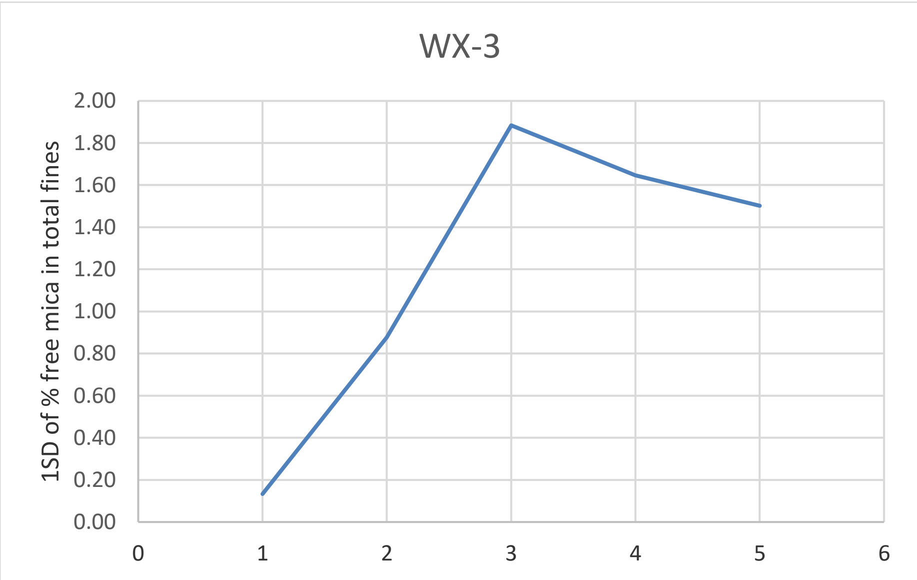


Figure 58: Sand sample WX-3 (1f), Co. Wexford. (A); Backscattered electron image of sand, a montage of nine 500x magnification. (B); in red free mica fines are identified.

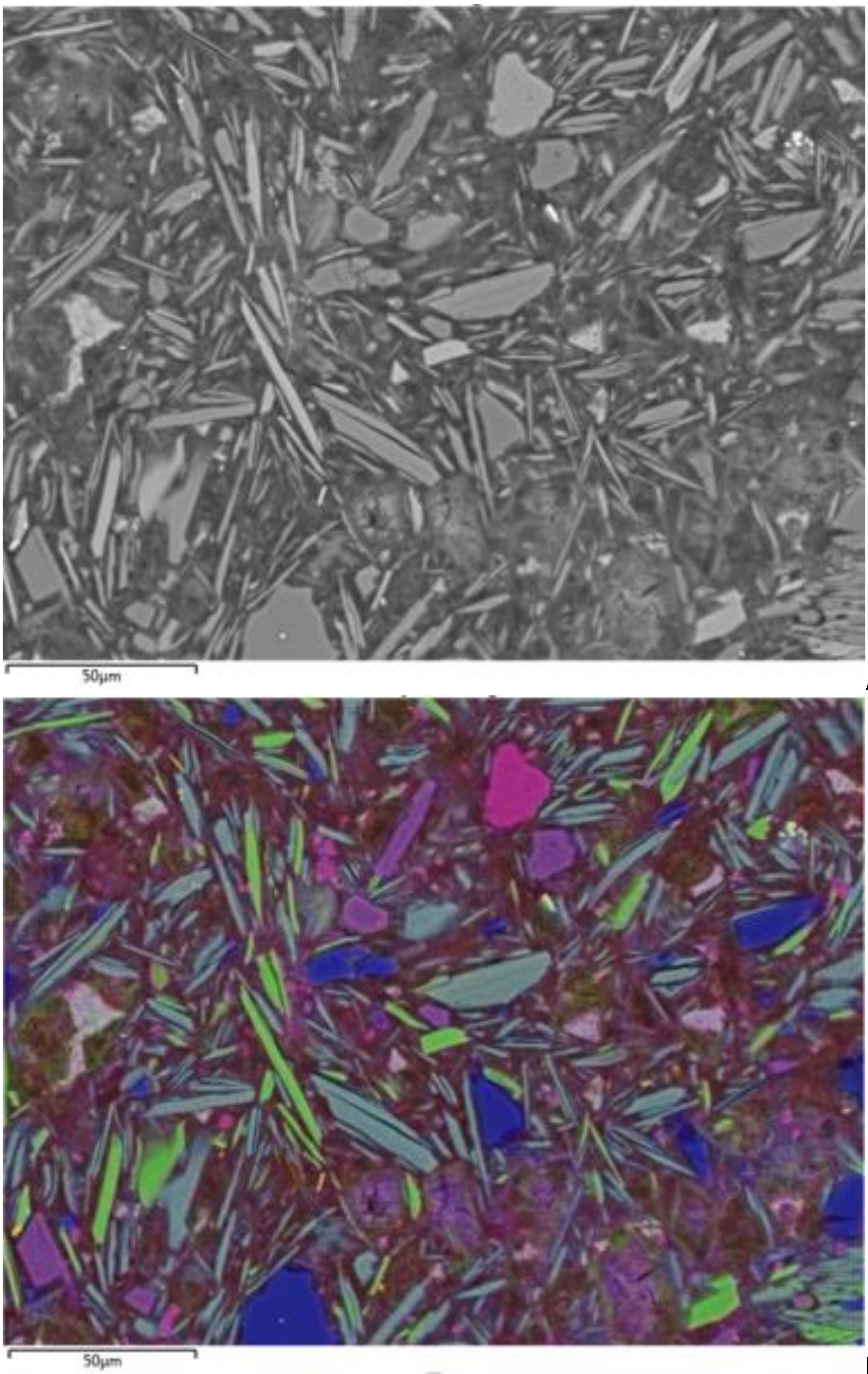
Table 42: WX-3, % free mica in total fines by SEM-EDS.

Cose	Total area analysed (sq. µm)	Total fines area (sq. µm)	Free mica fines area (sq. µm)	Total No. of fines	No. of free mica fines	% area free mica in total fines	1SD of the % free mica in total fines
WX-3 1a	637000	221000	3900	2356	23	1.76	
WX-3 1b	358000	118000	1860	1952	18	1.58	0.13
WX-3 1c	358000	77200	125	1774	4	0.16	0.88
WX-3 1d	229000	73500	3420	1762	14	4.65	1.88
WX-3 1e	229000	73500	1870	1894	19	2.54	1.65
WX-3 1f	1800000	613000	8720	10000	71	1.42	1.50
MEAN						2.02	
STD DEV						1.50	



Graph 27: 1σ (standard deviation) of free mica in total fines.

Appendix B



A

B

Figure 59: Concrete block sample AA63210. (A) BSE image at 1200x mag. (B); Corresponding layered EDS multi-element map with free mica in dark green (quartz in blue).

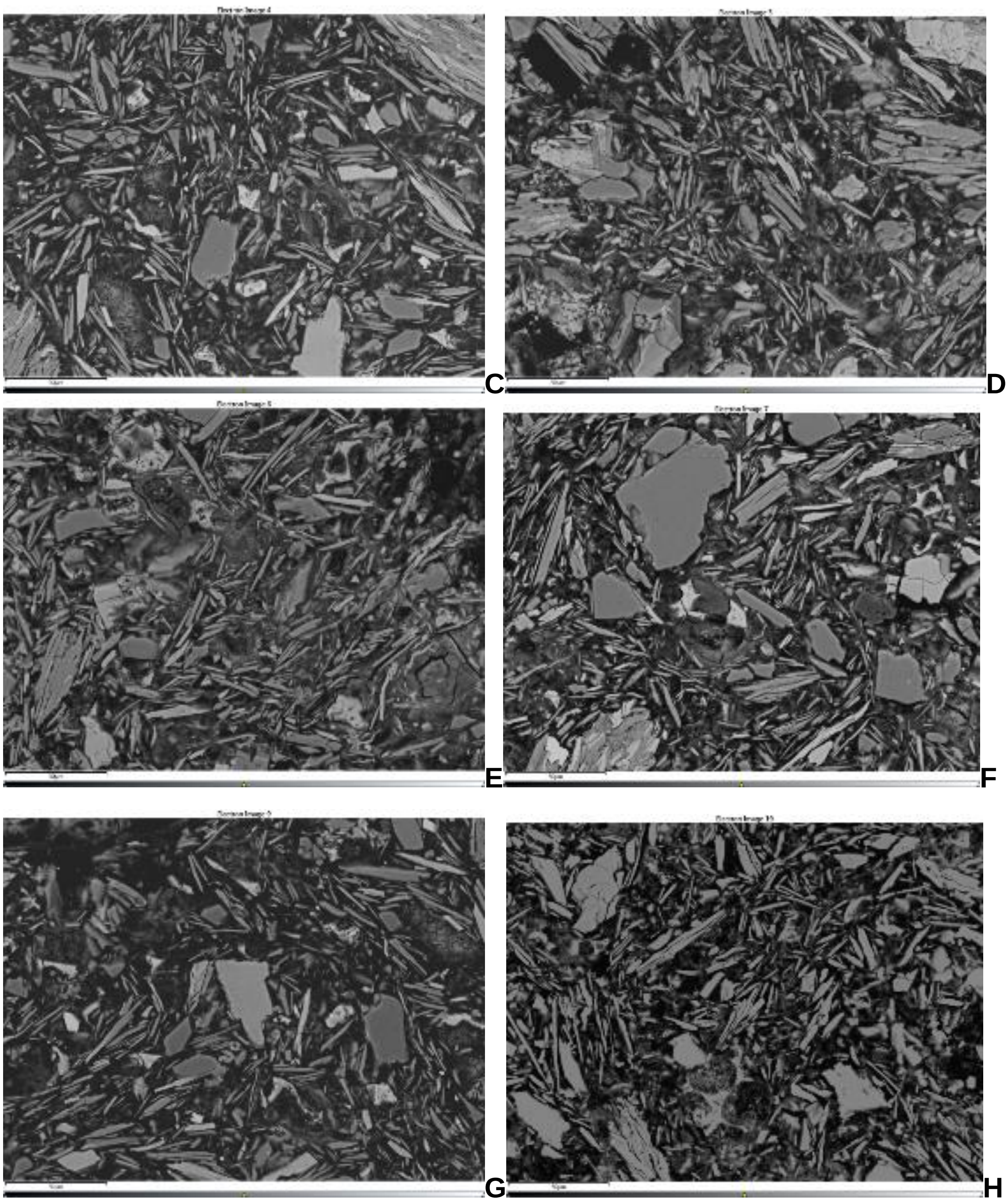
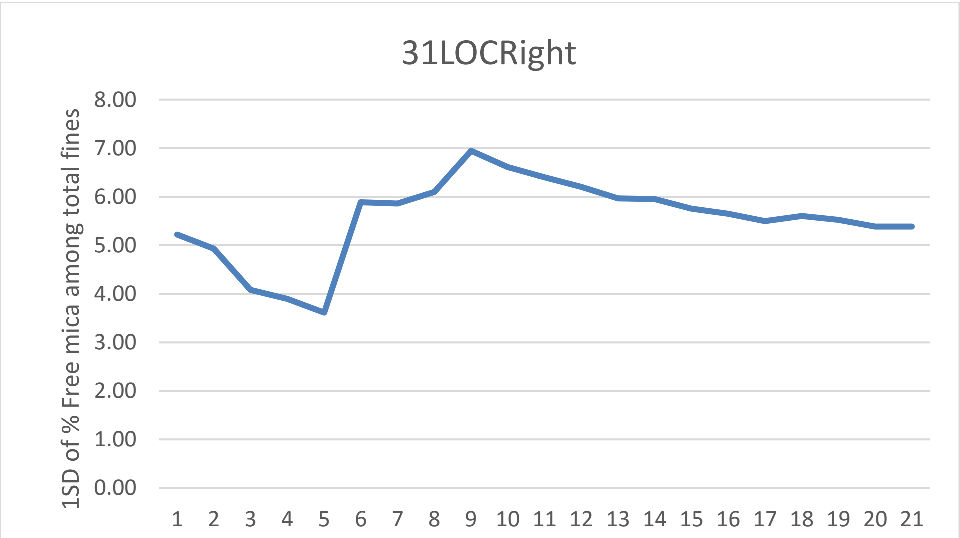


Figure 60: Concrete block sample AA63210. (A–G); Backscattered electron (BSE) images at 1200x magnification of the cement matrix of the hardened concrete block.

Table 43: Concrete block sample 31LOCRight, % free mica by SEM-EDS.

Sample ID	Total image area, µm²	Total fines area, µm²	Free mica fines area, µm²	% Free mica in hardened cement matrix	% Free mica among total fines	1SD of % Free mica among total fines	No. of features classified as free mica	Total No. of features
A	32200	10500	3310	10.28	31.52		272	2093
B	32200	7890	3070	9.53	38.91	5.22	289	2024
C	32200	9370	3830	11.89	40.88	4.93	308	2249
D	32200	8210	2940	9.13	35.81	4.08	258	3070
E	32200	11300	3740	11.61	33.10	3.90	234	1707
F	32200	8720	2940	9.13	33.72	3.61	231	1776
G	32200	13100	2980	9.25	22.75	5.89	194	1725
H	32200	11800	3270	10.16	27.71	5.86	202	1668
I	32200	13400	3360	10.43	25.07	6.09	213	1548
J	32200	11400	2260	7.02	19.82	6.95	191	1902
K	32200	9980	2900	9.01	29.06	6.61	244	1783
L	32200	12400	3340	10.37	26.94	6.40	219	1797
M	66200	20500	5530	8.35	26.98	6.20	324	3600
N	32200	9890	2890	8.98	29.22	5.97	142	2126
O	32200	7230	2610	8.11	36.10	5.95	225	1755
P	32200	12600	3860	11.99	30.63	5.75	216	1842
Q	32200	14100	3750	11.65	26.60	5.65	192	1661
R	32200	10800	3460	10.75	32.04	5.50	210	1782
S	32200	9910	3740	11.61	37.74	5.60	211	2161
T	37200	14000	3760	10.11	26.86	5.52	251	1991
U	32200	9500	2800	8.70	29.47	5.39	217	1928
V	32200	12000	3000	9.32	25.00	5.39	184	2149
MEAN				9.88	30.27			
STD DEV				1.34	5.39			



Graph 28: 1σ (standard deviation) of free mica among the total fines in the cement matrix of a hardened concrete

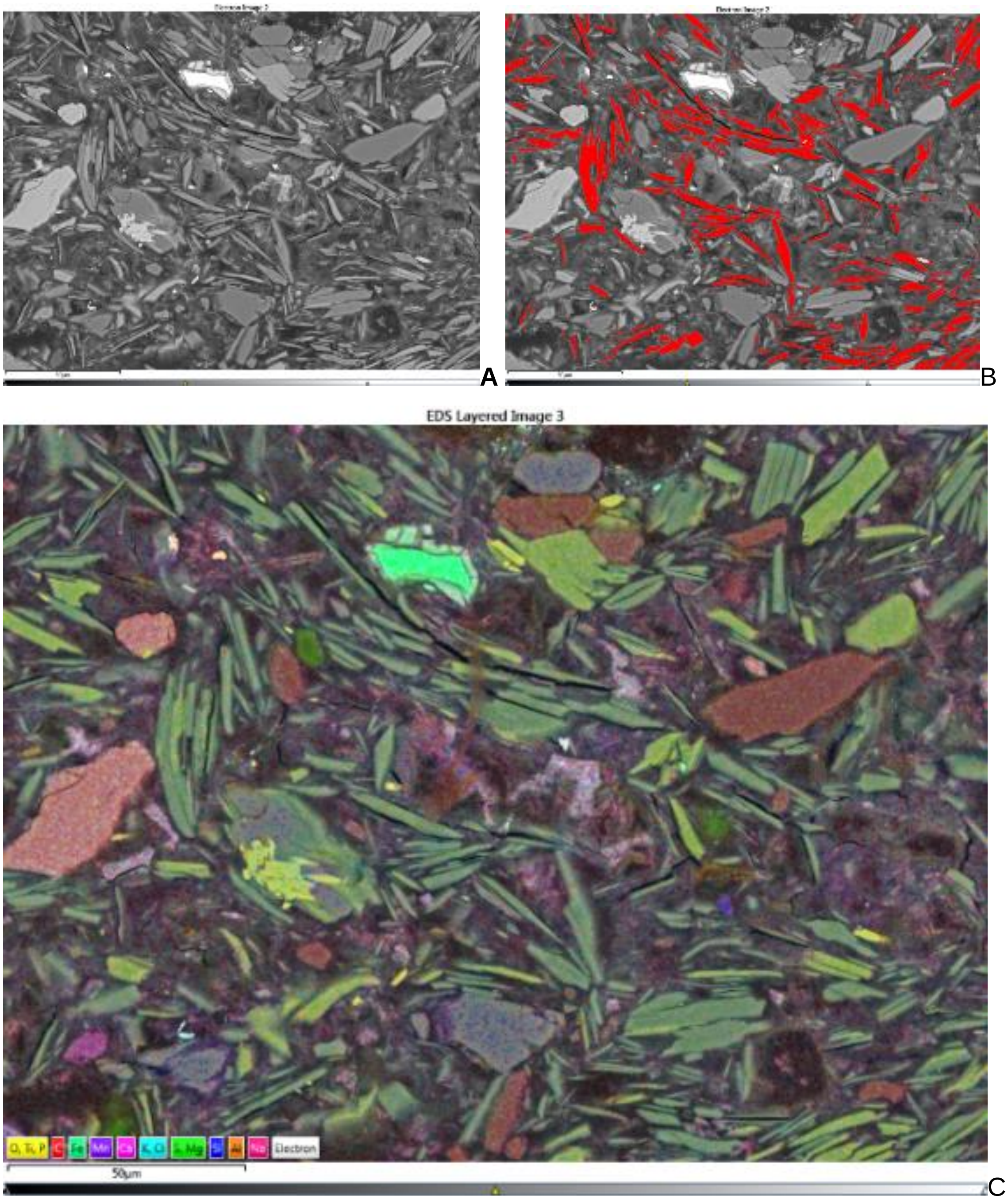


Figure 61: Concrete block sample 31LOCRight (A Site 5 220719). (A); BSE image at 1200x magnification of the cement matrix, avoiding large aggregate. (B); free mica fines highlighted in red over the BSE image. (C); corresponding layered EDS element map.

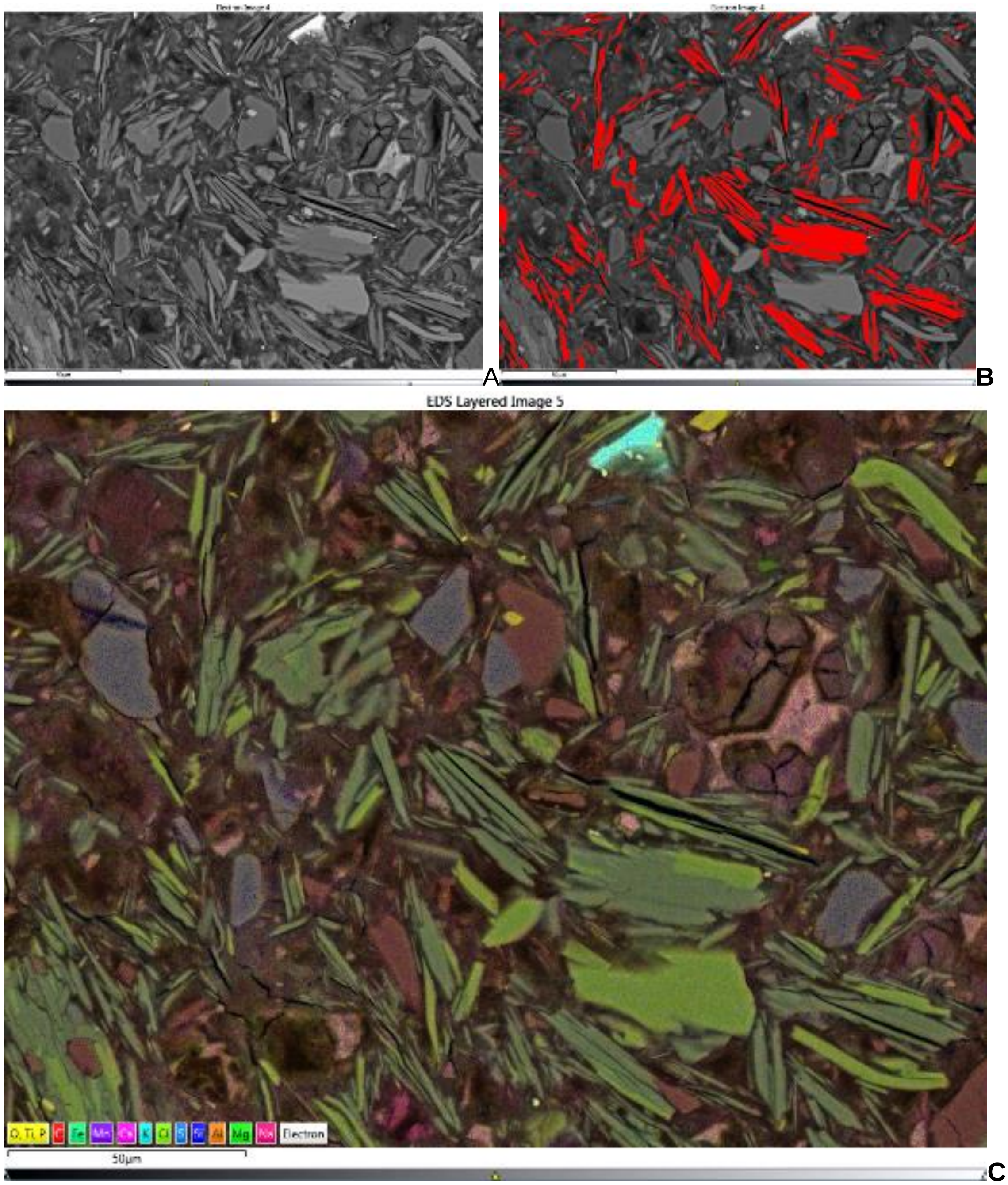


Figure 62: Concrete block sample 31LOCRight (C Site7 220719). (A); BSE image at 1200x magnification of the cement matrix, avoiding large aggregate. (B); free mica fines highlighted in red over the BSE image. (C); corresponding layered EDS element map.

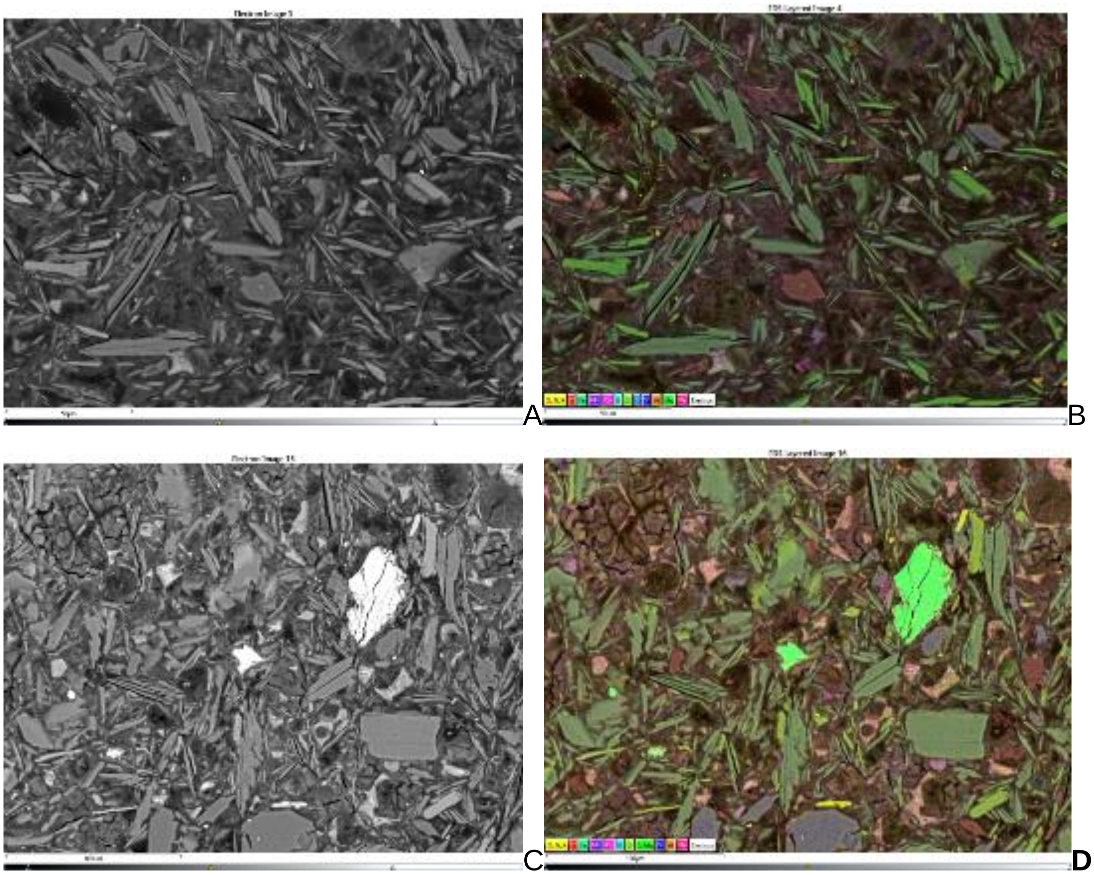
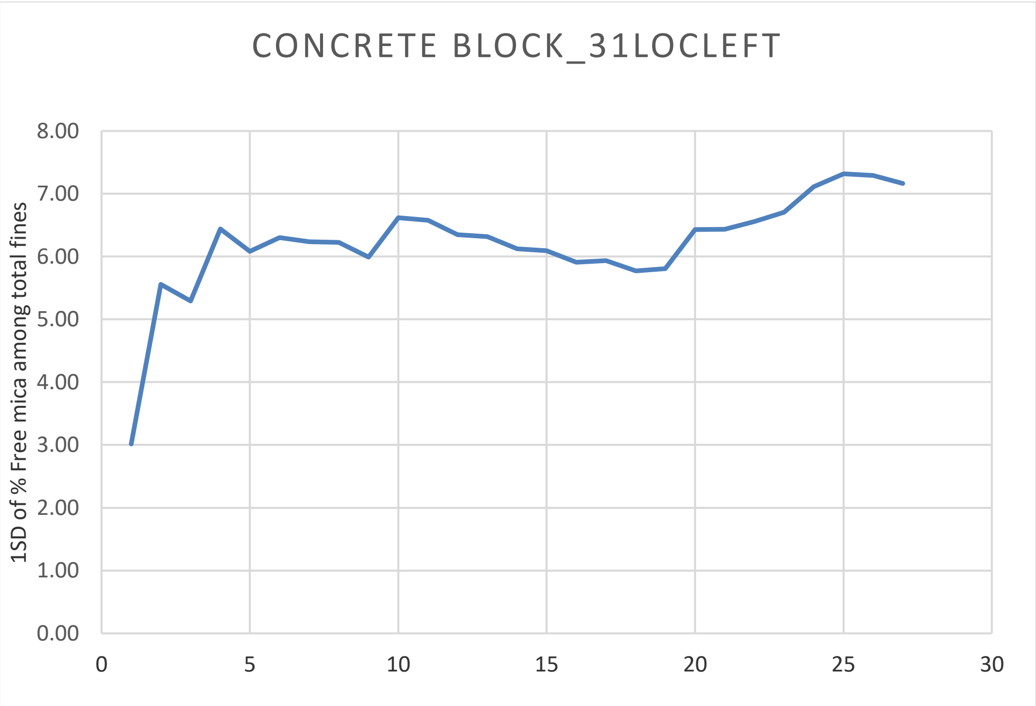


Figure 63: Concrete block sample 31LOCRight. (A, C); BSE Images at 1200x magnification. (B, D); the corresponding layered EDS element maps.

Table 44: Concrete block sample 31LOCLeft, % free mica by SEM-EDS.

Sample ID	Total image area, µm²	Total fines area, µm²	Free mica fines area, µm²	% Free mica in hardened cement matrix	% Free mica among total fines	1SD of % Free mica among total fines	No. of features classified as free mica	Total No. of features
A3	63500	27900	6350	10.00	22.76		319	2339
B3	63500	22600	4180	6.58	18.50	3.02	253	2364
C3	63500	18800	5550	8.74	29.52	5.56	324	2272
D3	63500	21100	3830	6.03	18.15	5.29	290	2029
E3	39800	11100	3590	9.02	32.34	6.44	340	1717
F3	39800	10700	3110	7.81	29.07	6.08	295	1843
G3	39800	13300	4380	11.01	32.93	6.30	285	1762
H3	39800	11700	3790	9.52	32.39	6.23	235	1736
I3	39800	16200	3310	8.32	20.43	6.22	232	2134
J3	39700	16400	3670	9.24	22.38	5.99	218	1789
K3	39900	13100	4860	12.18	37.10	6.62	204	1734
L3	39800	12300	2520	6.33	20.49	6.58	212	1776
M3	39800	13600	3180	7.99	23.38	6.35	192	1938
N3	39800	8610	2780	6.98	32.29	6.32	253	2536
O3	39800	11600	3360	8.44	28.97	6.12	287	2617
P3	39800	9730	2030	5.10	20.86	6.09	228	2526
Q3	39800	11400	3170	7.96	27.81	5.91	229	2024
R3	40100	13000	2593	6.47	19.95	5.93	219	2348
S3	40000	17000	4620	11.55	27.18	5.77	247	2421
T3	39800	12800	4190	10.53	32.73	5.81	377	1880
U3	39800	12000	4850	12.19	40.42	6.43	416	1848
V3	39800	11700	3960	9.95	33.85	6.44	307	2319
W3	39800	13000	2400	6.03	18.46	6.56	205	2156
X3	39800	10200	1780	4.47	17.45	6.71	158	1750
Y3	39800	9580	3860	9.70	40.29	7.11	327	1871
Z3	39800	10700	4130	10.38	38.60	7.32	305	1719
AA3	39800	14500	3020	7.59	20.83	7.29	253	1723
BB3	39800	11900	3460	8.69	29.08	7.16	259	1937
MEAN				8.53	27.44			
STD DEV				2.02	7.16			



Graph 29: 1σ (standard deviation) of free mica among the total fines in the cement matrix of a hardened concrete block.

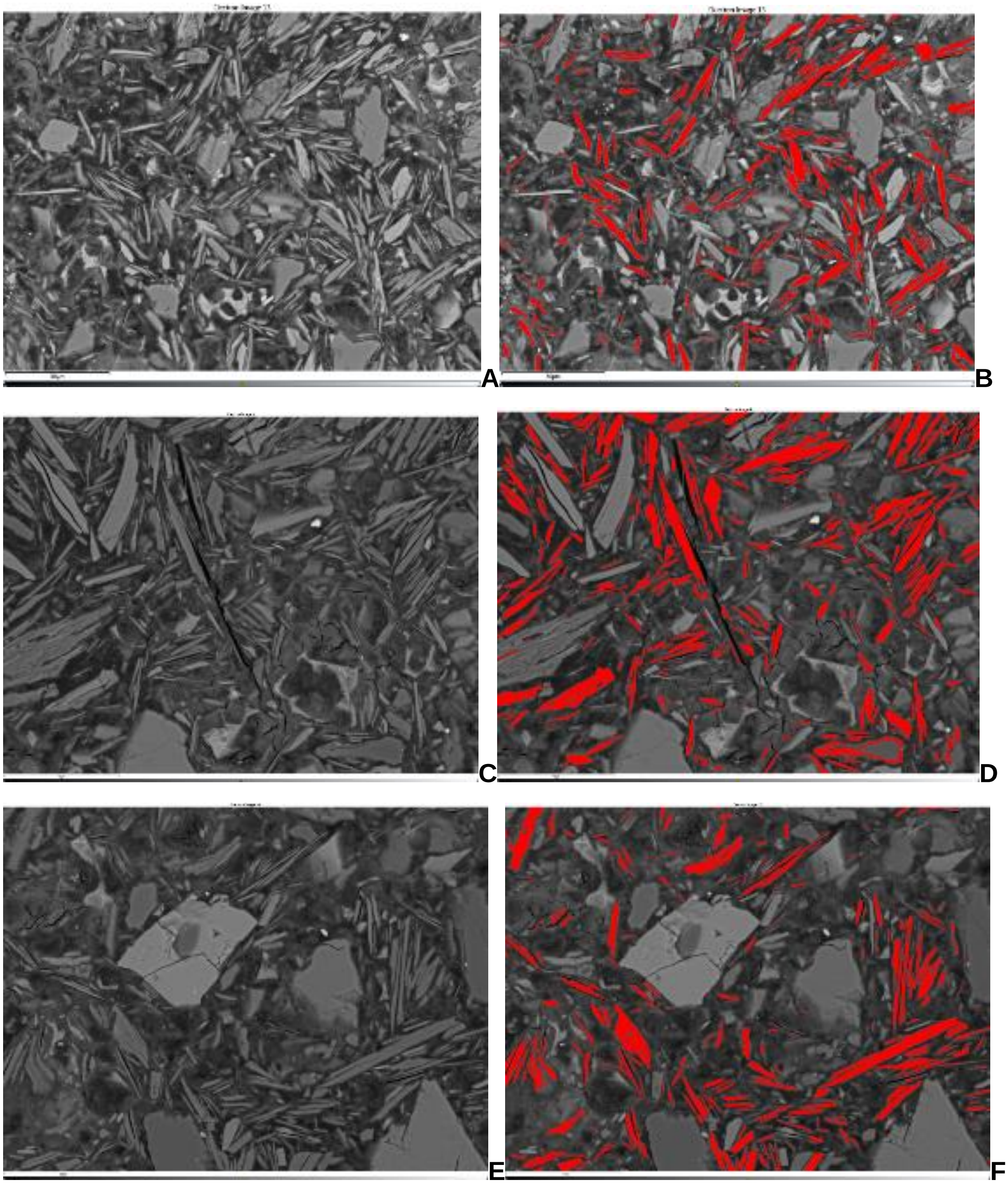


Figure 64: Concrete block sample 31LOCLeft. (A, C & E); BSE images at 1200x magnification of the cement matrix (avoiding large aggregate). (B, D & F); Corresponding BSE images with free mica highlighted in red.

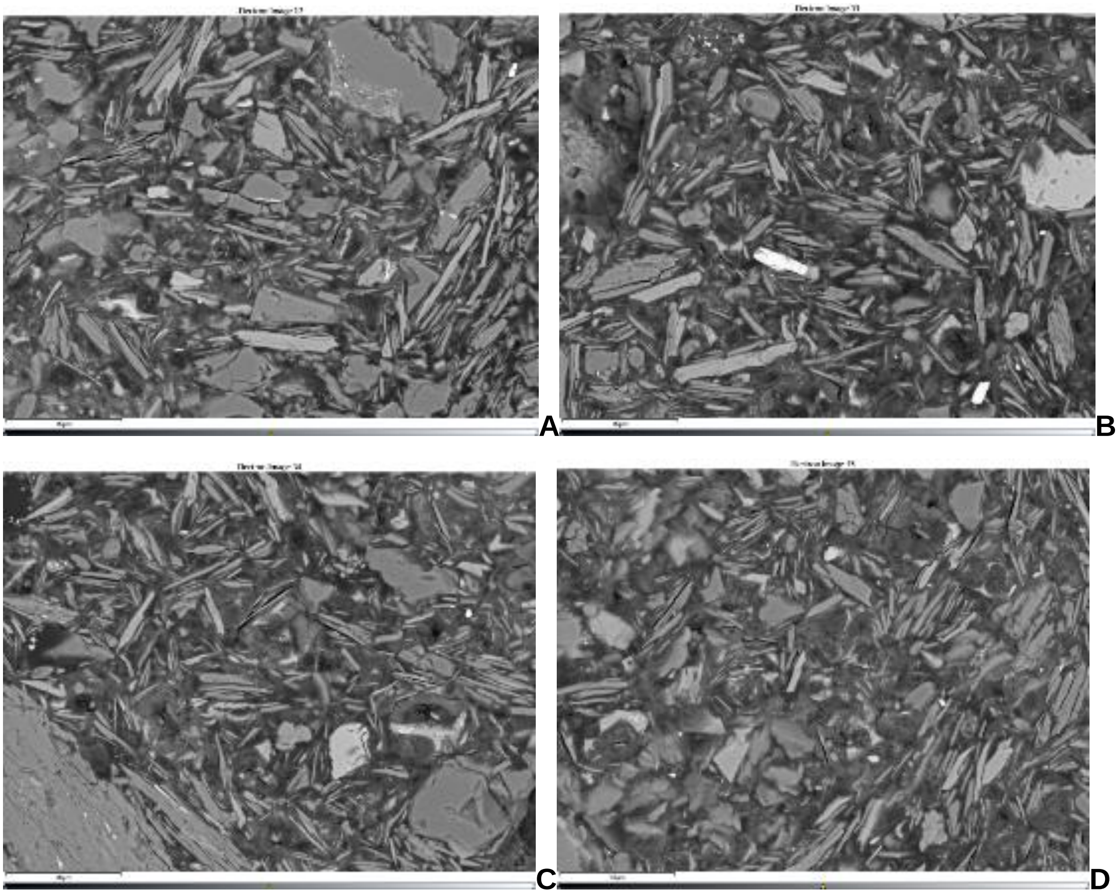
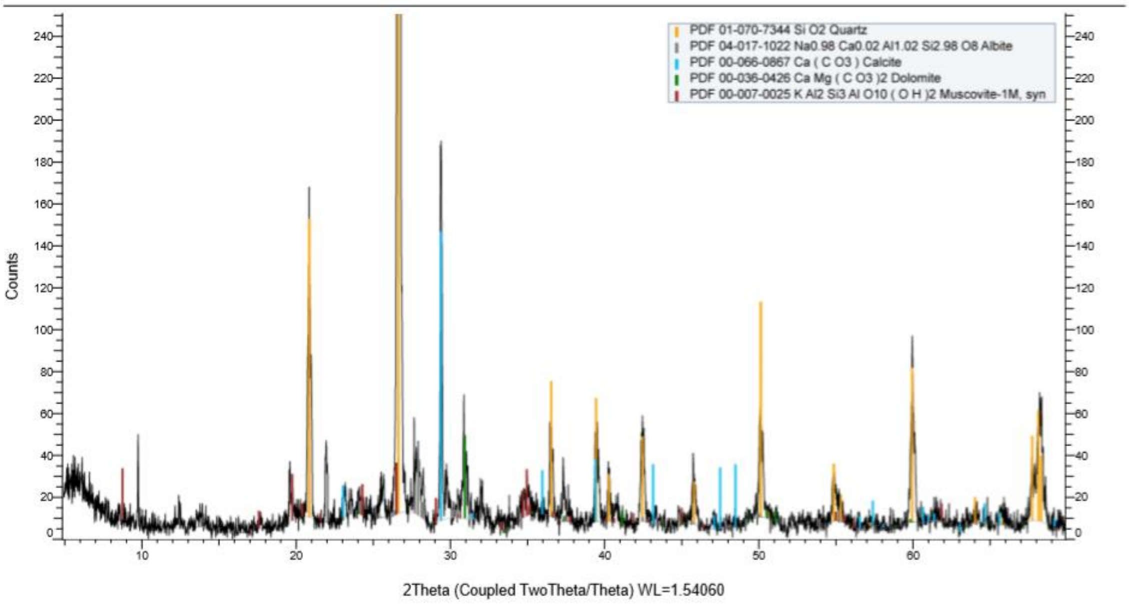


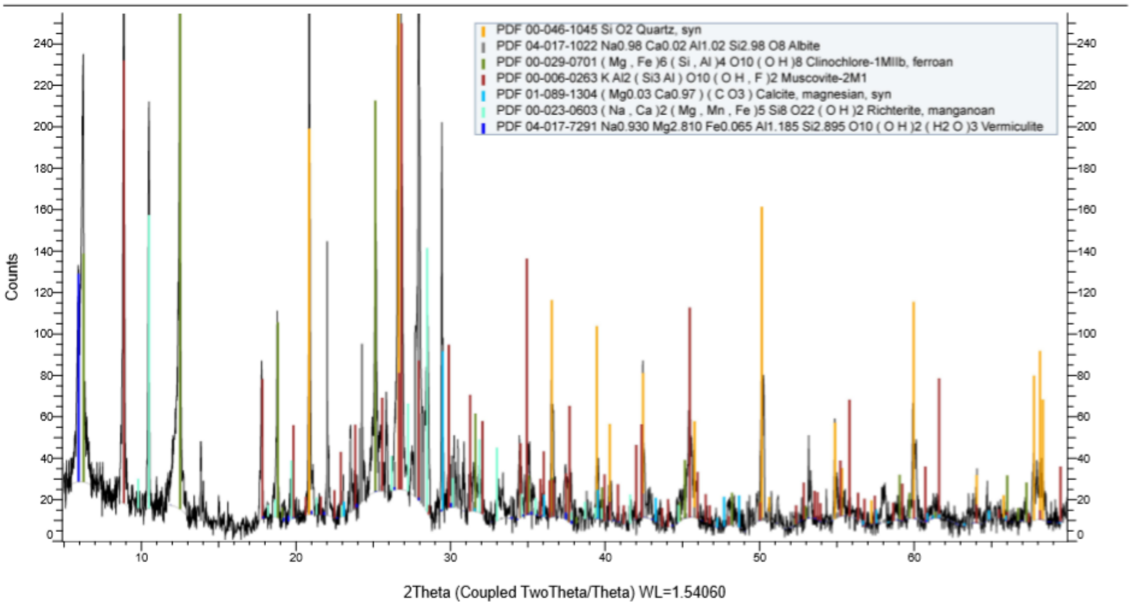
Figure 65: Concrete block sample 31LOCLeft. (A–D); BSE images at 1200x magnification of the cement matrix.

Appendix C XRD raw data for the sand samples.

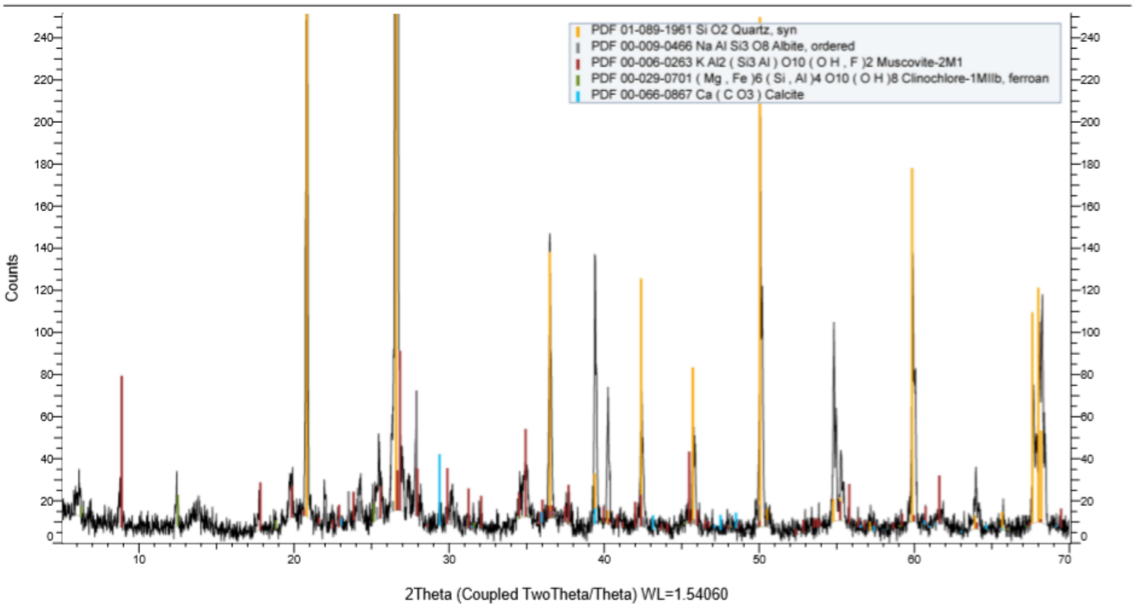
AH-1 <63 um (y-axis zoom)



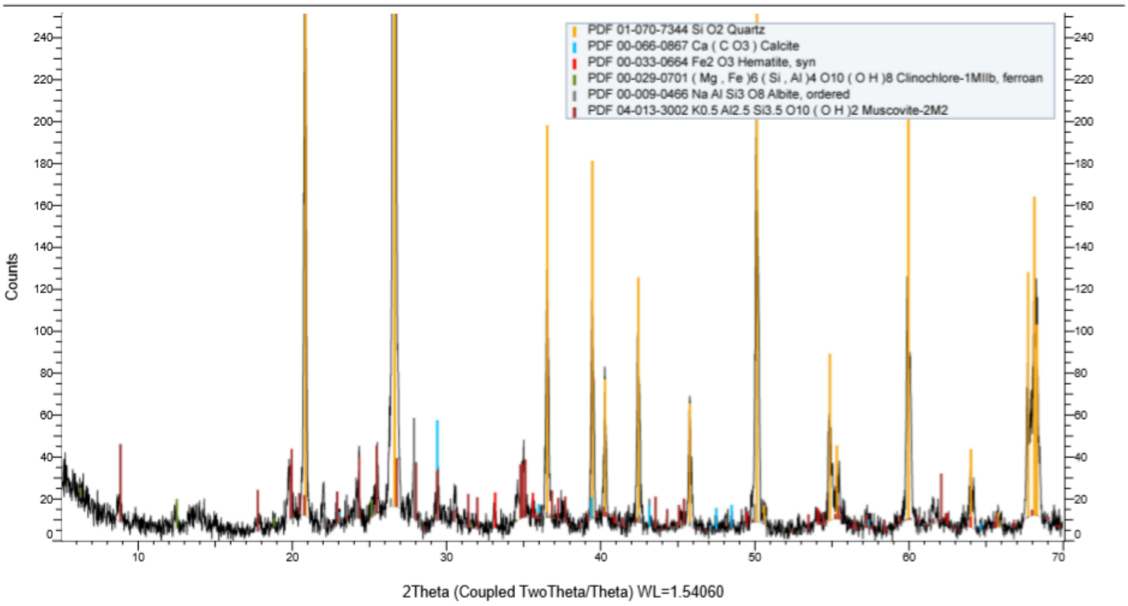
AH-2 <63 um (y-axis zoom)



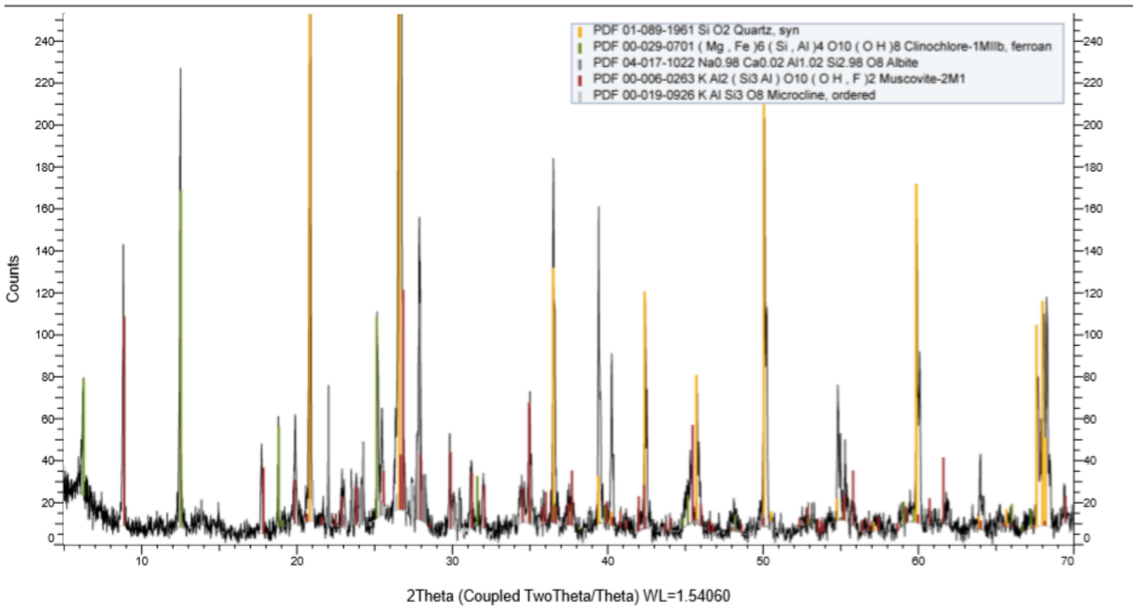
CE-1 <63 um (y-axis zoom)



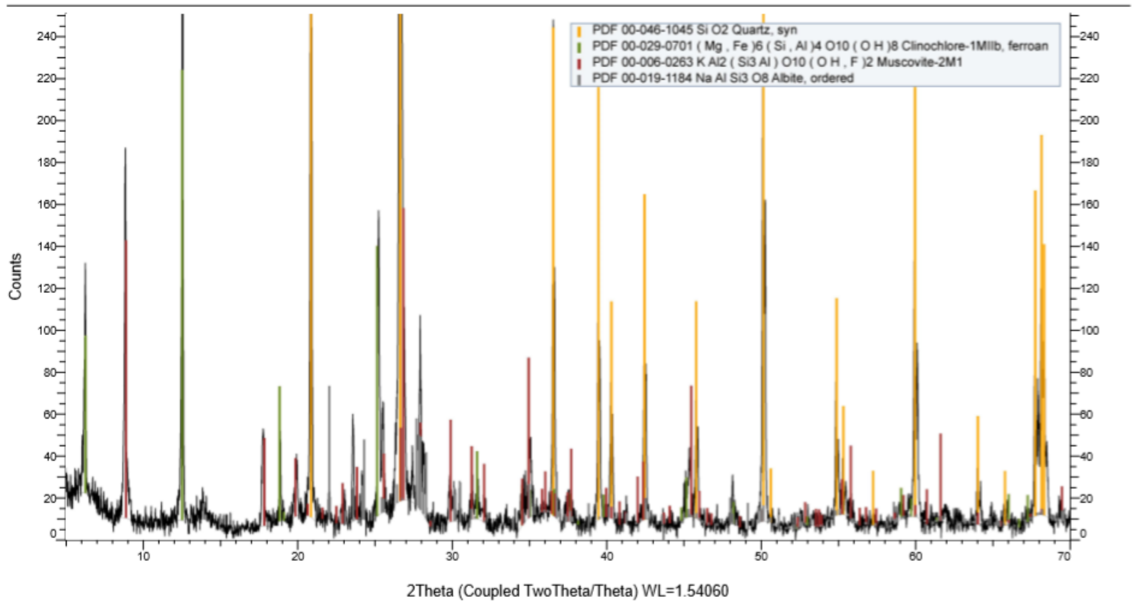
CK-2 <63 um (y-axis zoom)



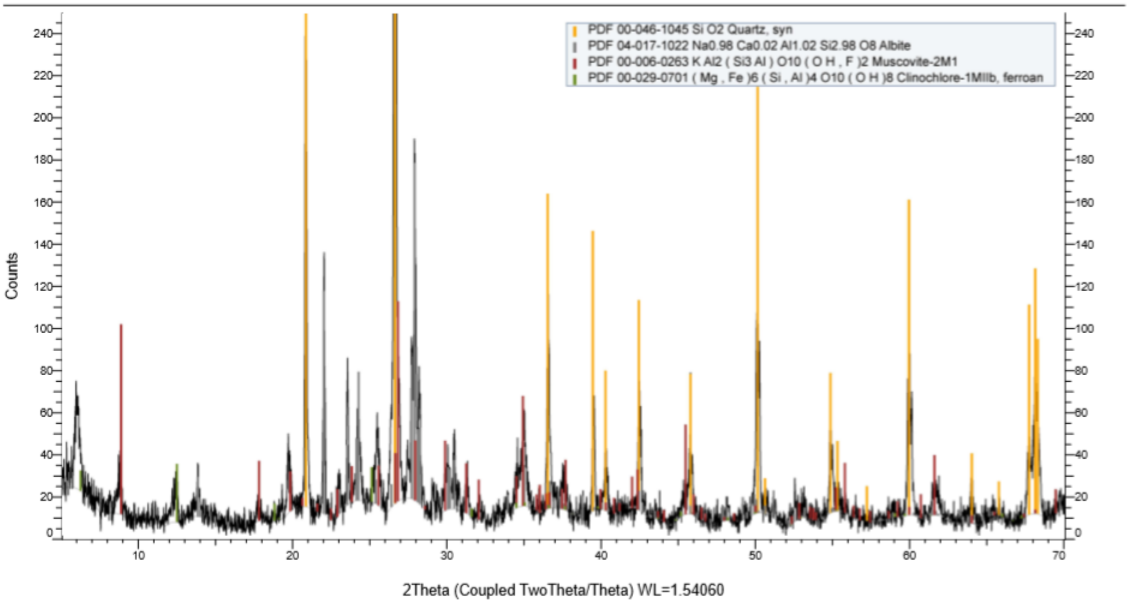
CK-3 <63 um (y-axis zoom)



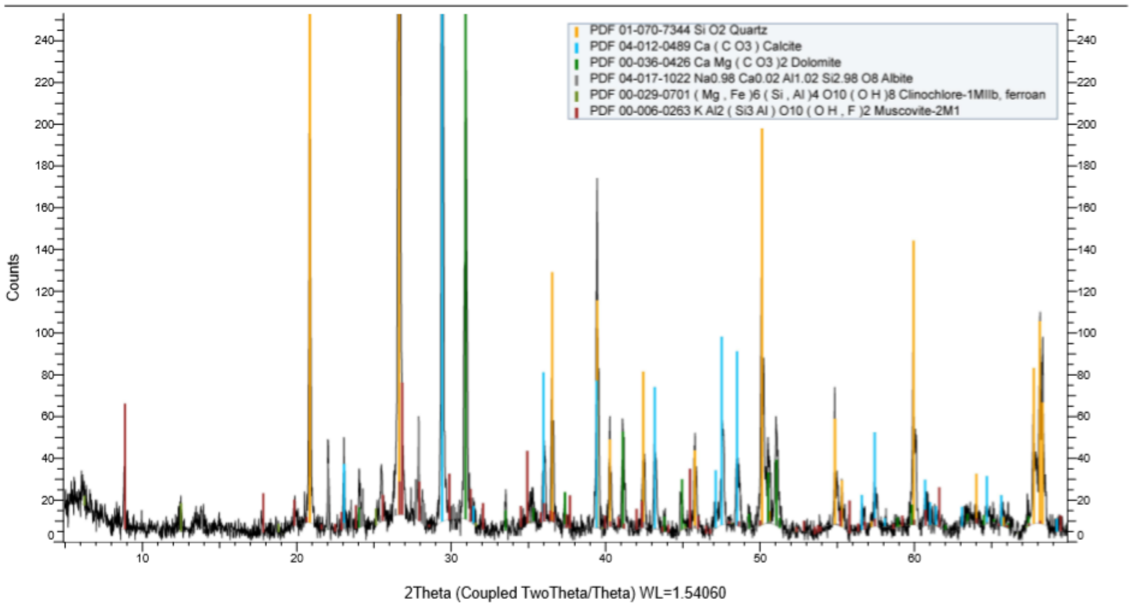
CK-4 <63 um (y-axis zoom)



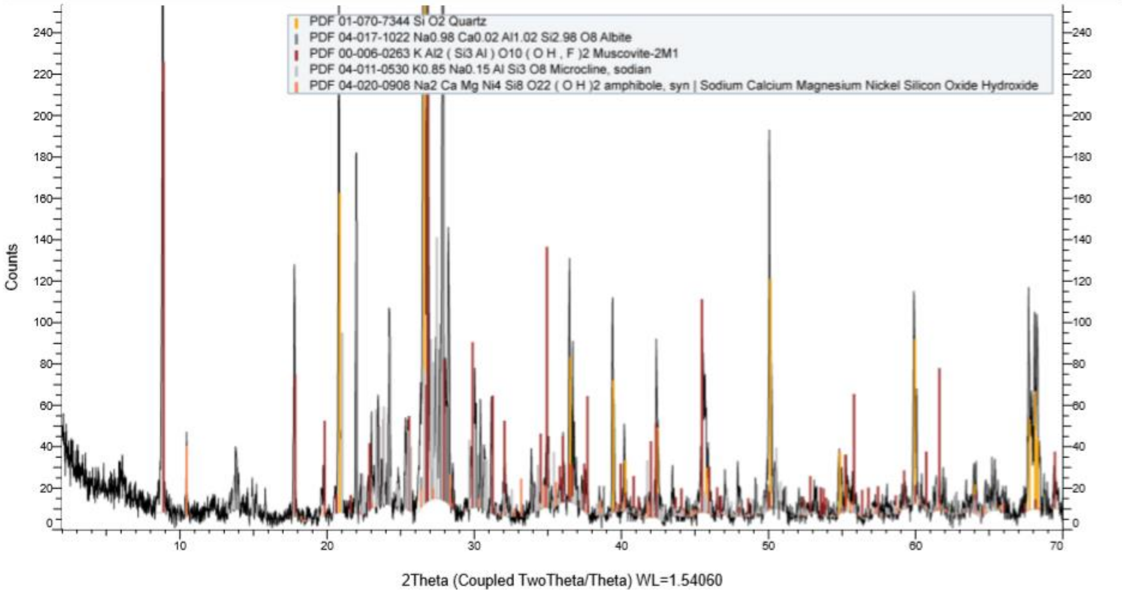
CN-1 <63 um (y-axis zoom)



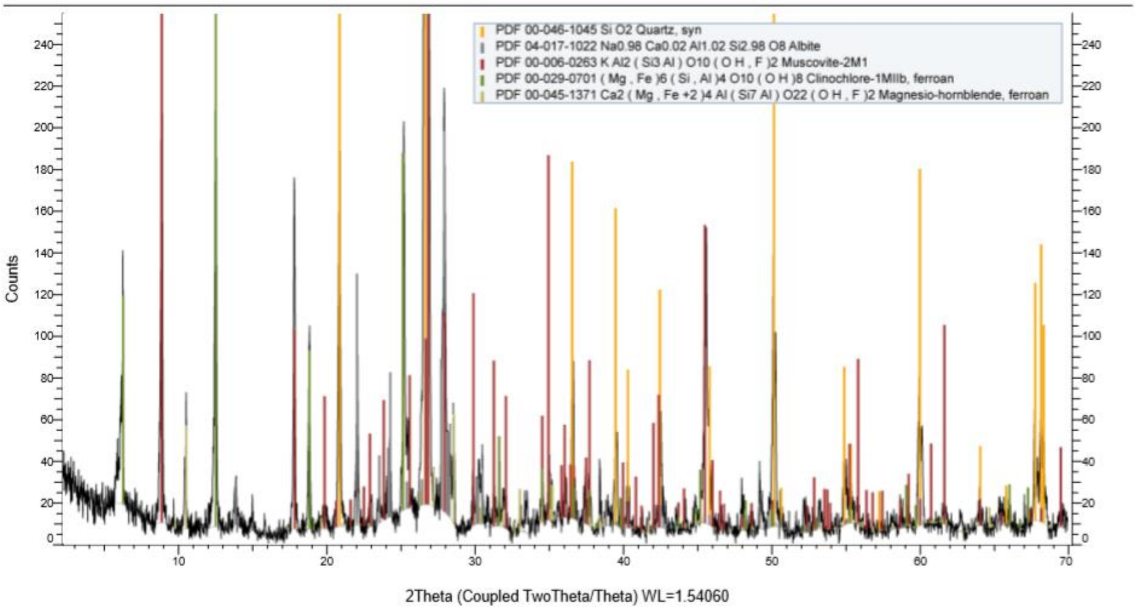
CW-1 <63 um (y-axis zoom)



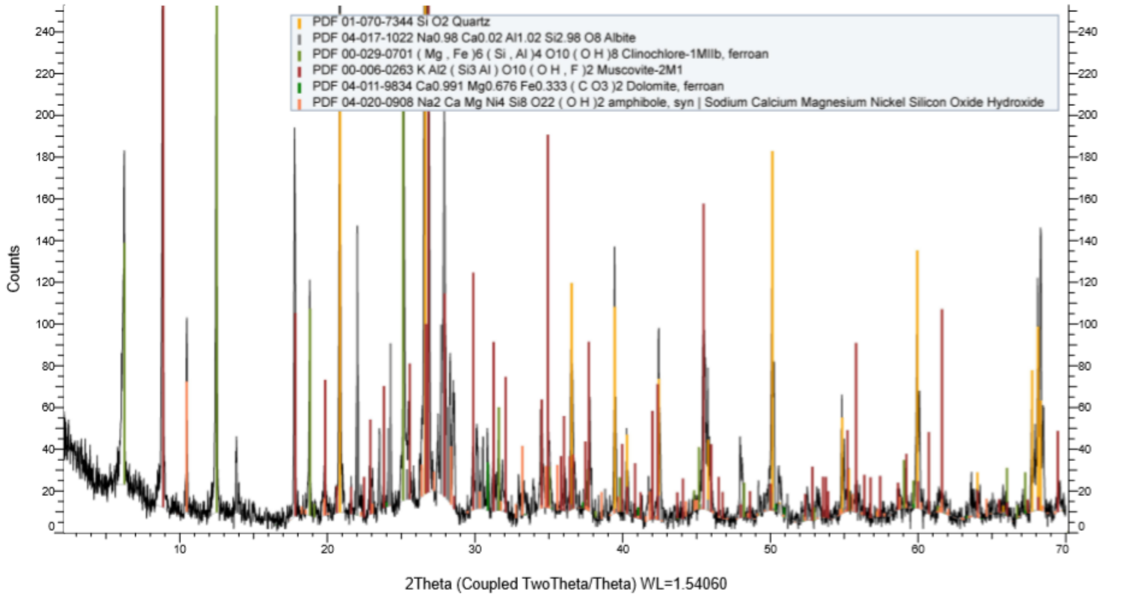
DL-1 <63 um (y-axis zoom)



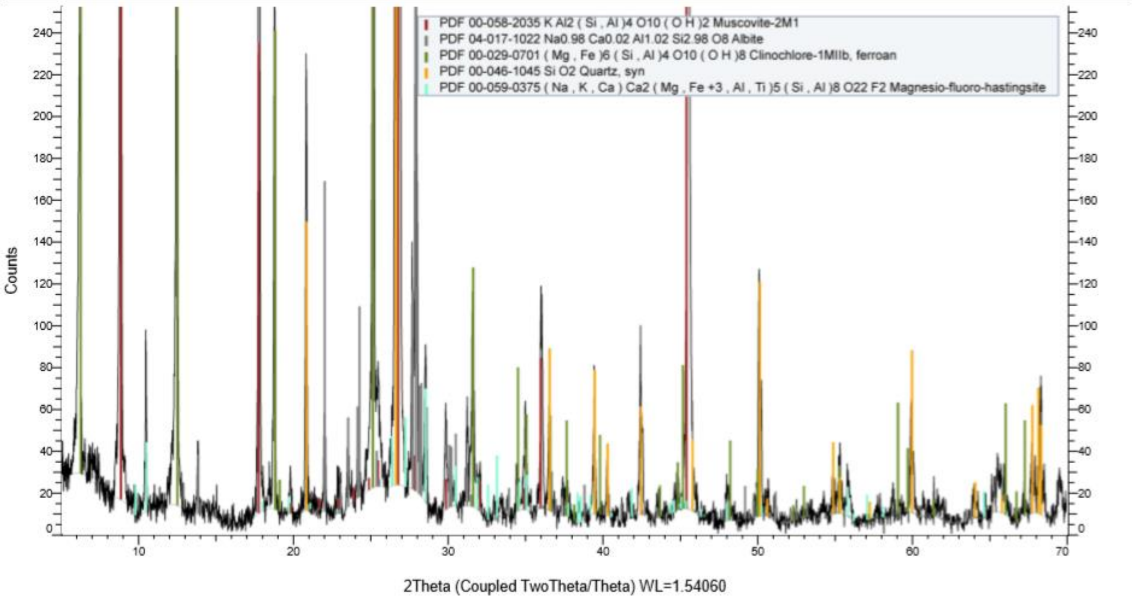
DL-2 <63 um (y-axis zoom)



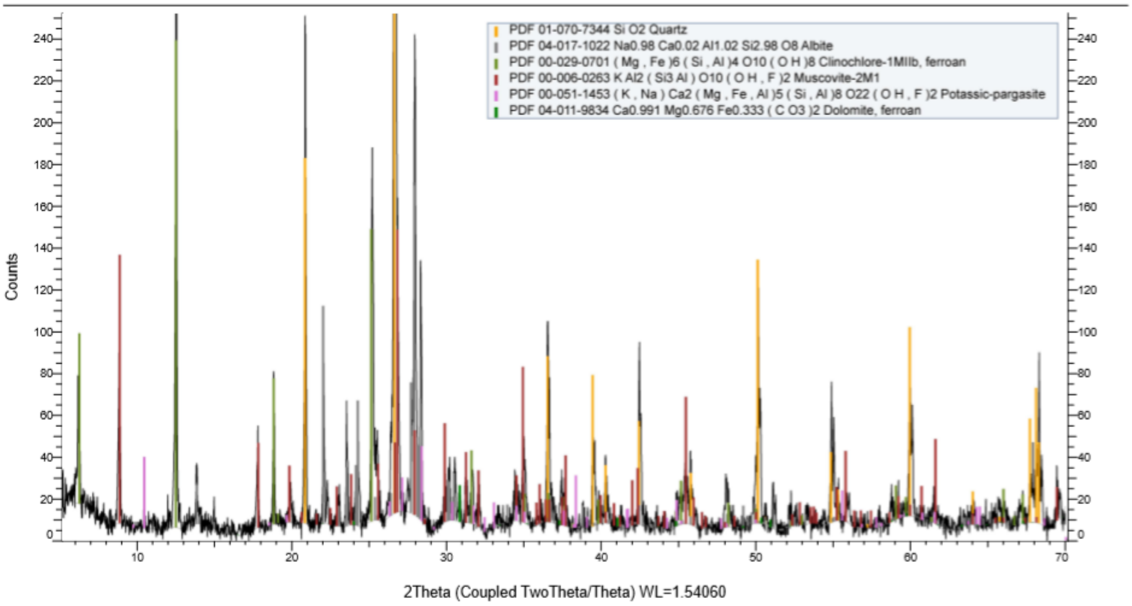
DL-3 <63 um (y-axis zoom)



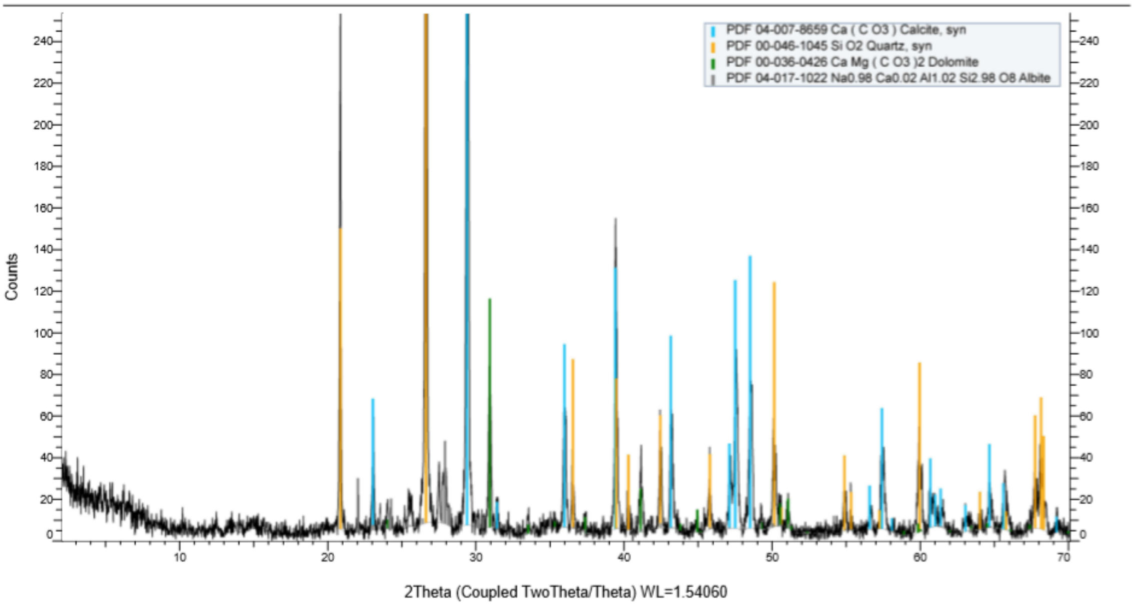
DL-4 <63 um (y-axis zoom)



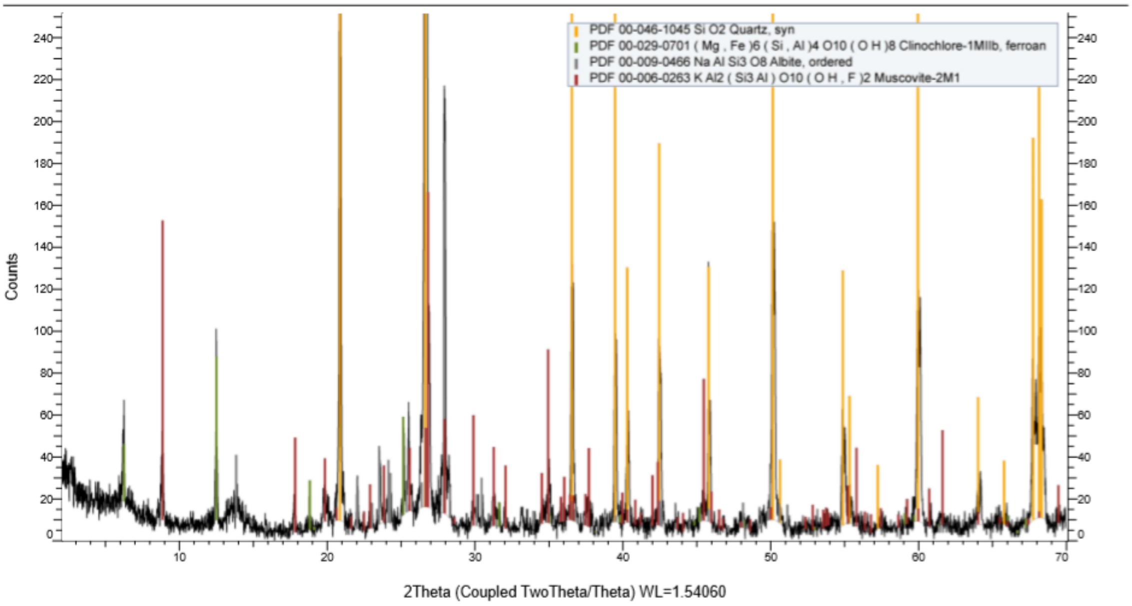
DL-5 <63 um fines (y-axis zoom)



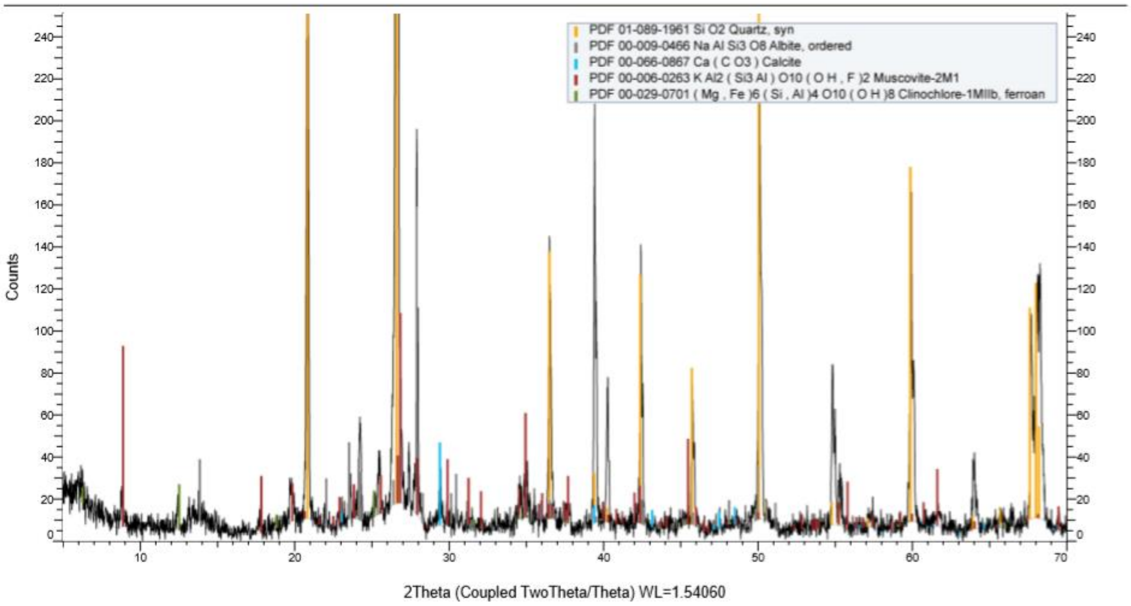
GY-1 <63 um (y-axis zoom)



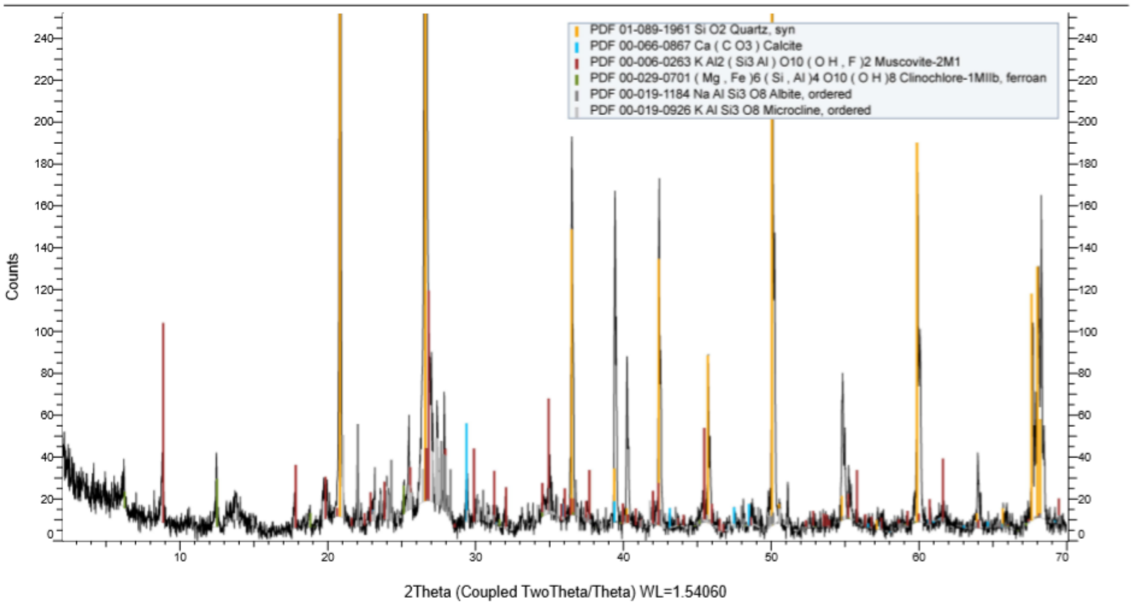
KY-1 <63 um (y-axis zoom)



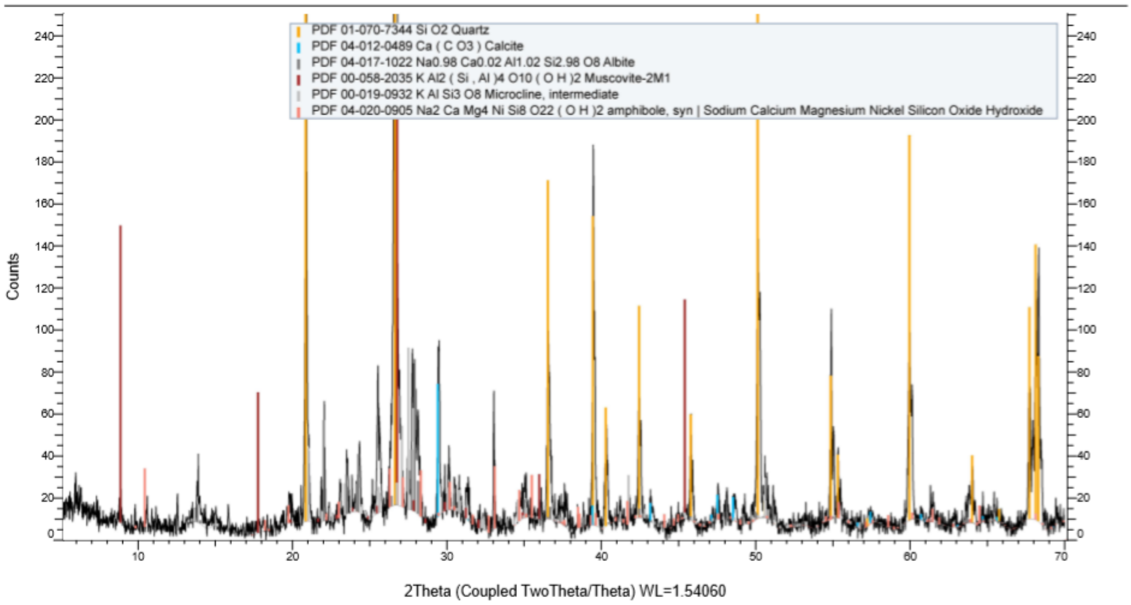
LK-1 <63 um (y-axis zoom)



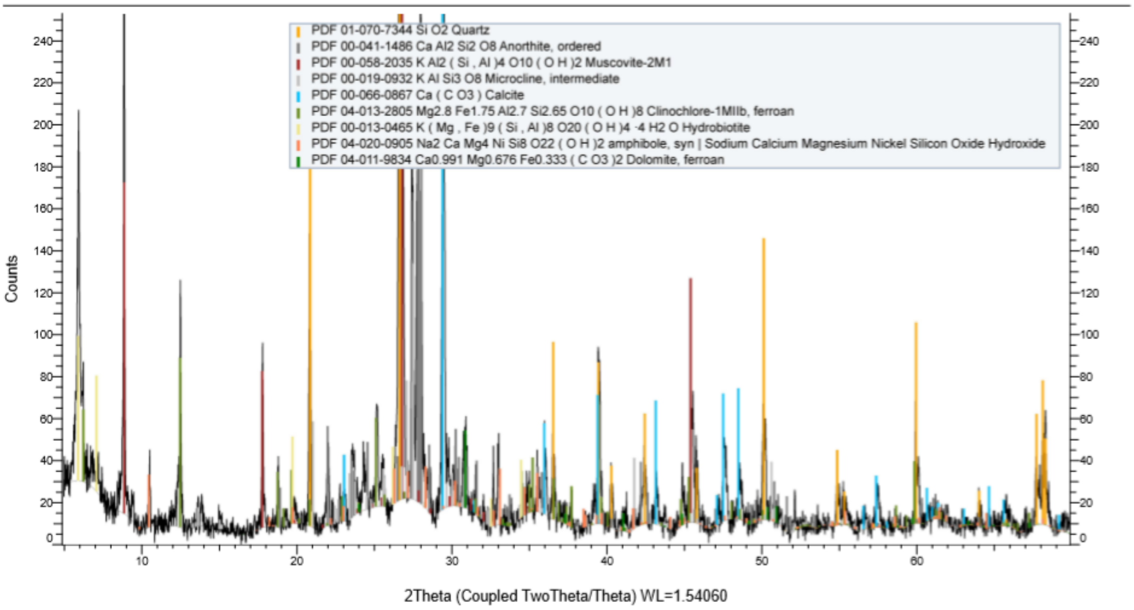
LK-2 <63 um (y-axis zoom)



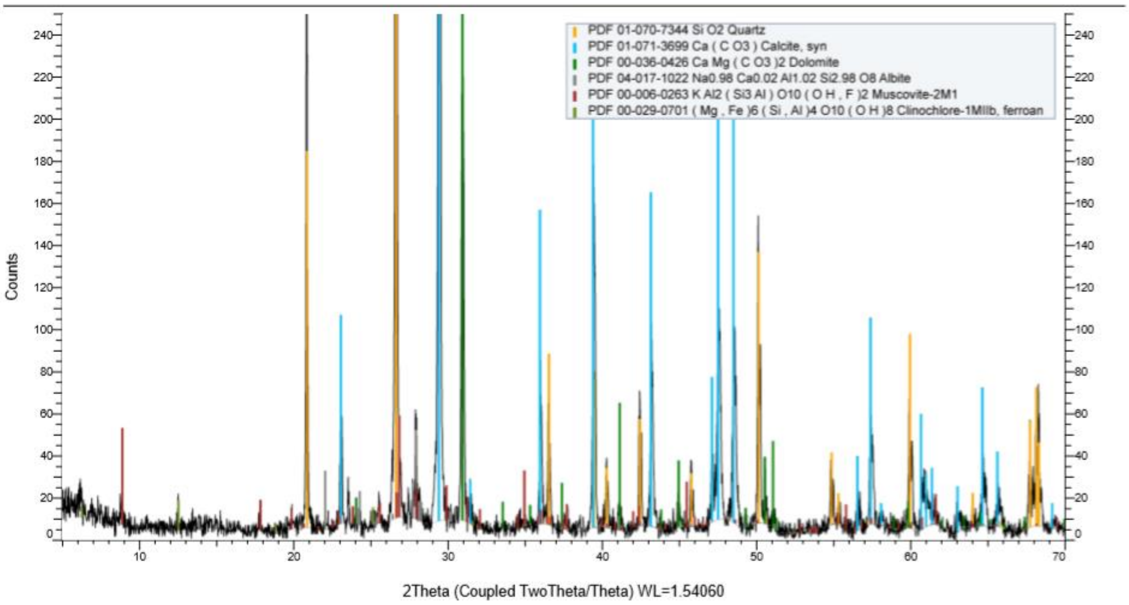
MO-1 <63 um (y-axis zoom)



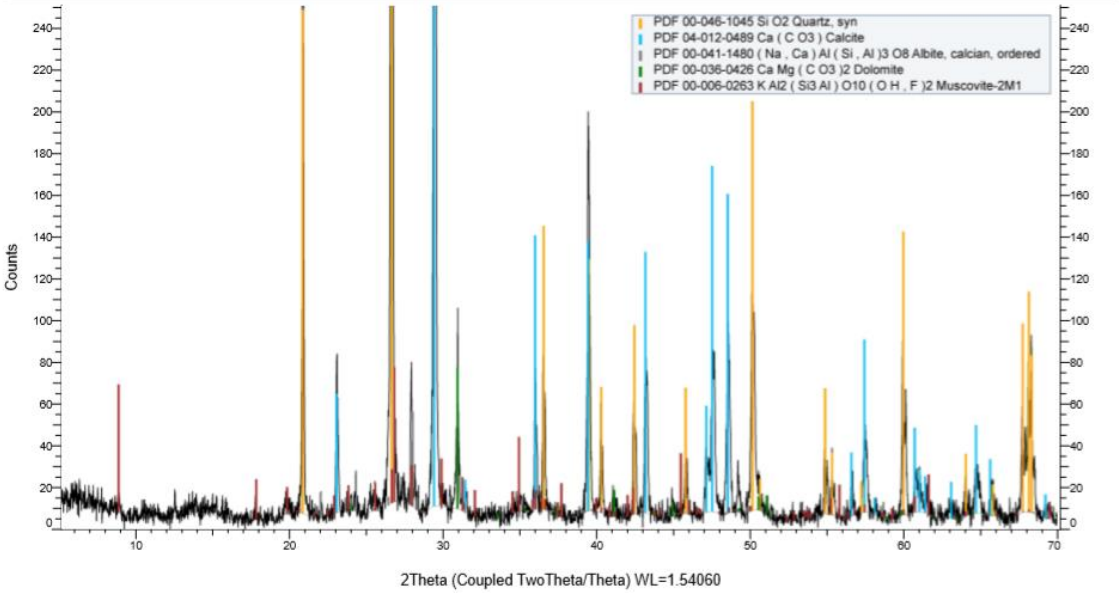
MO-2 <63 um (y-axis zoom)



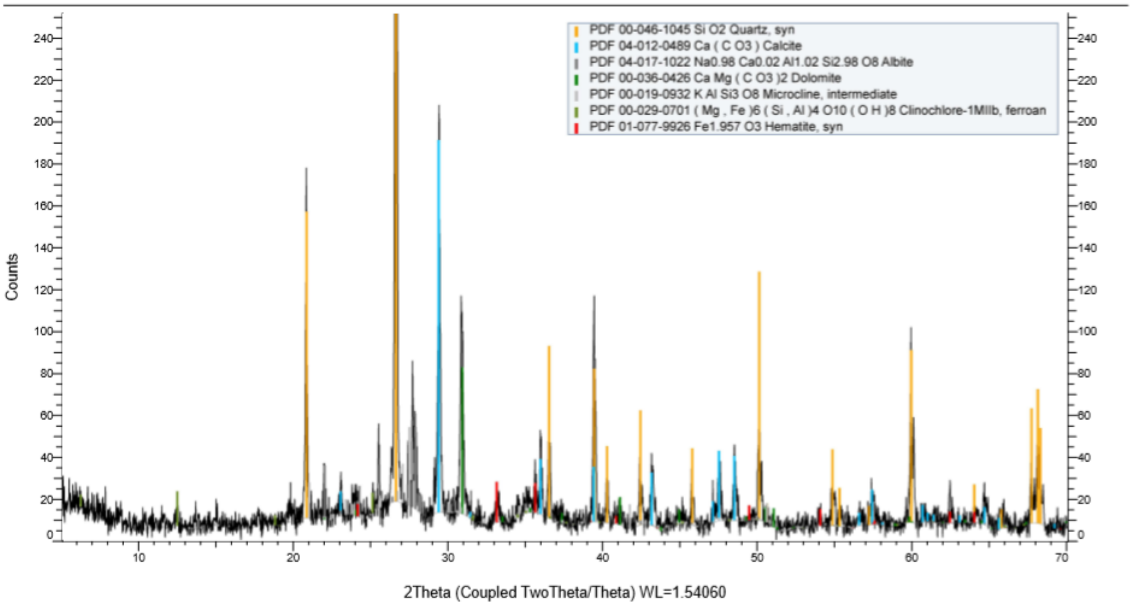
OY-1 <63 um (y-axis zoom)



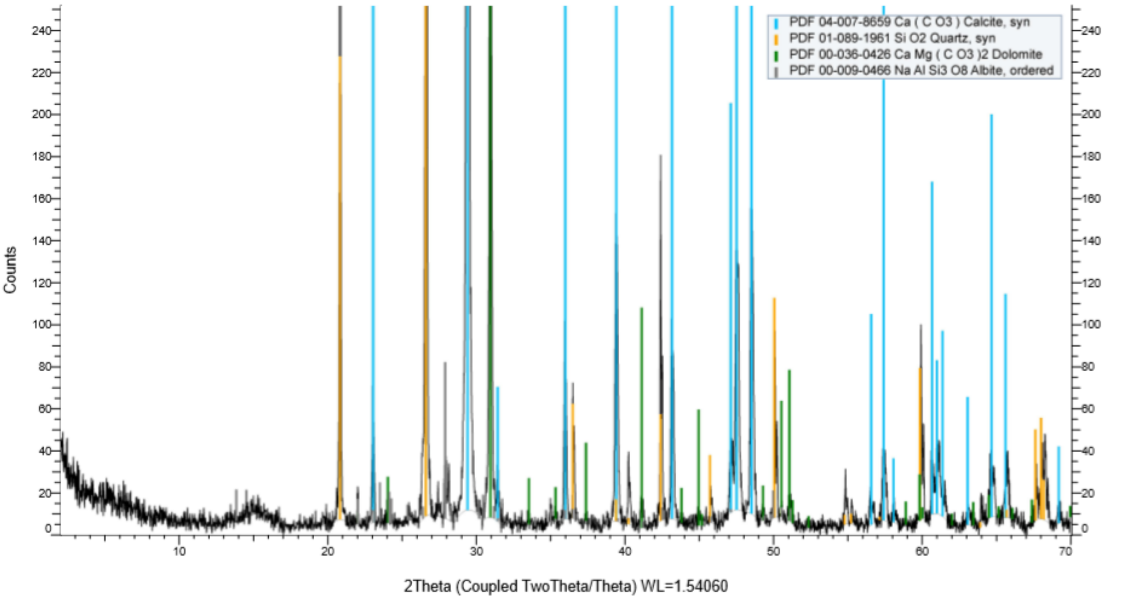
OY-2 <63 um (y-axis zoom)



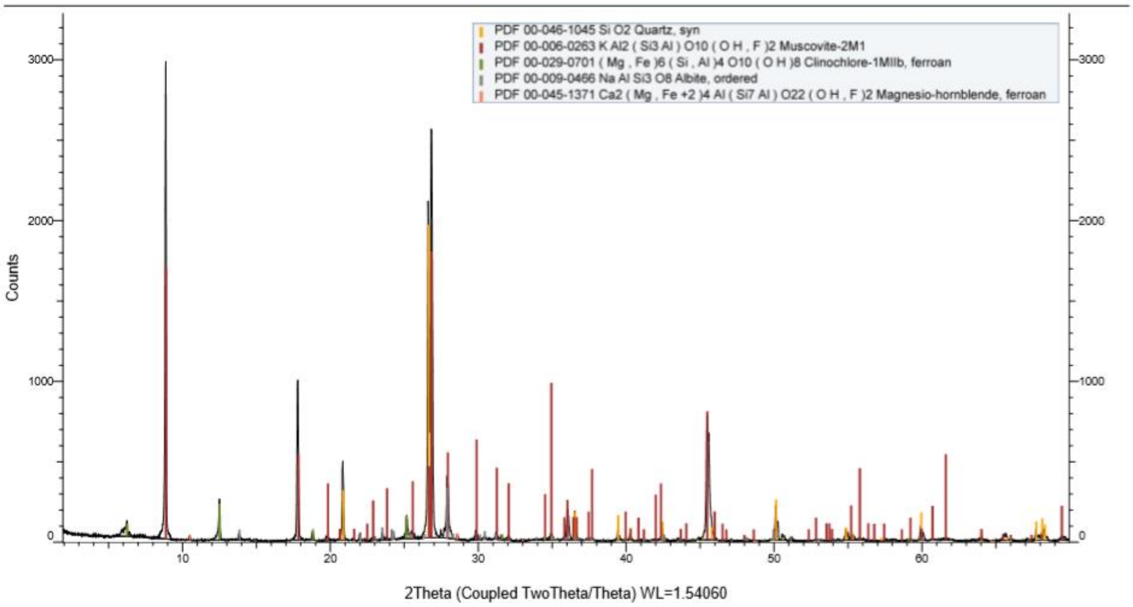
OY-3 <63 um (y-axis zoom)



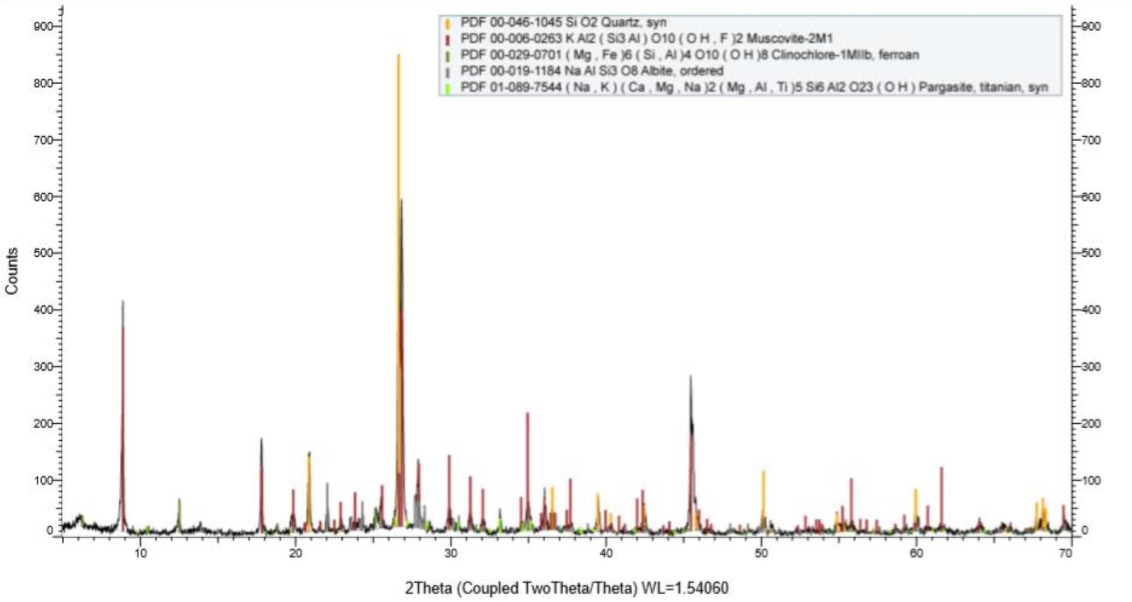
RN-1 <63 um (y-axis zoom)



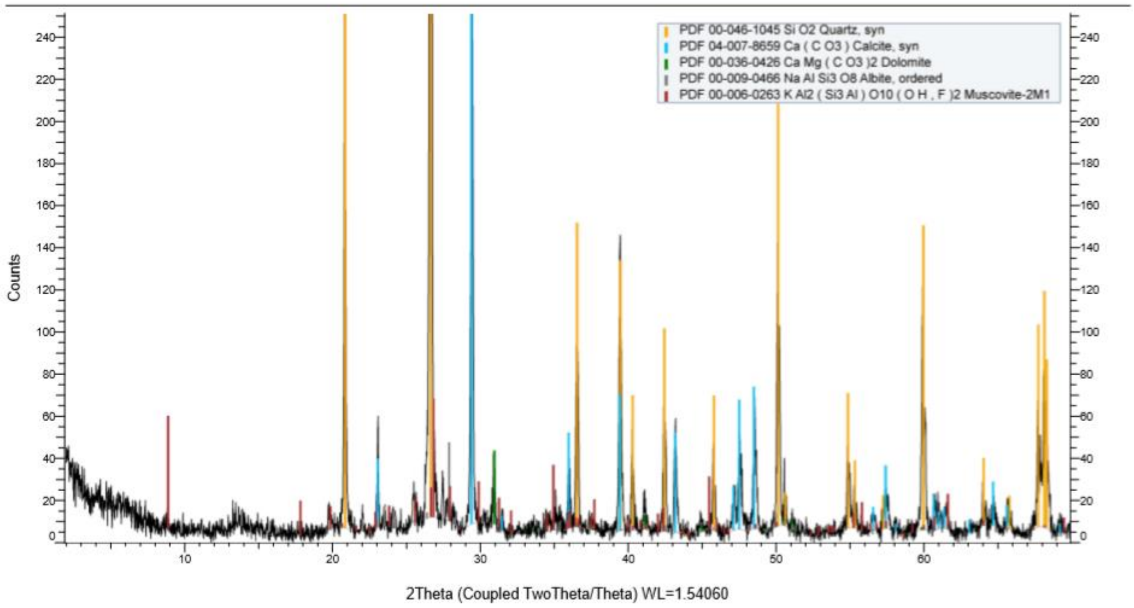
TE-1 <63 um



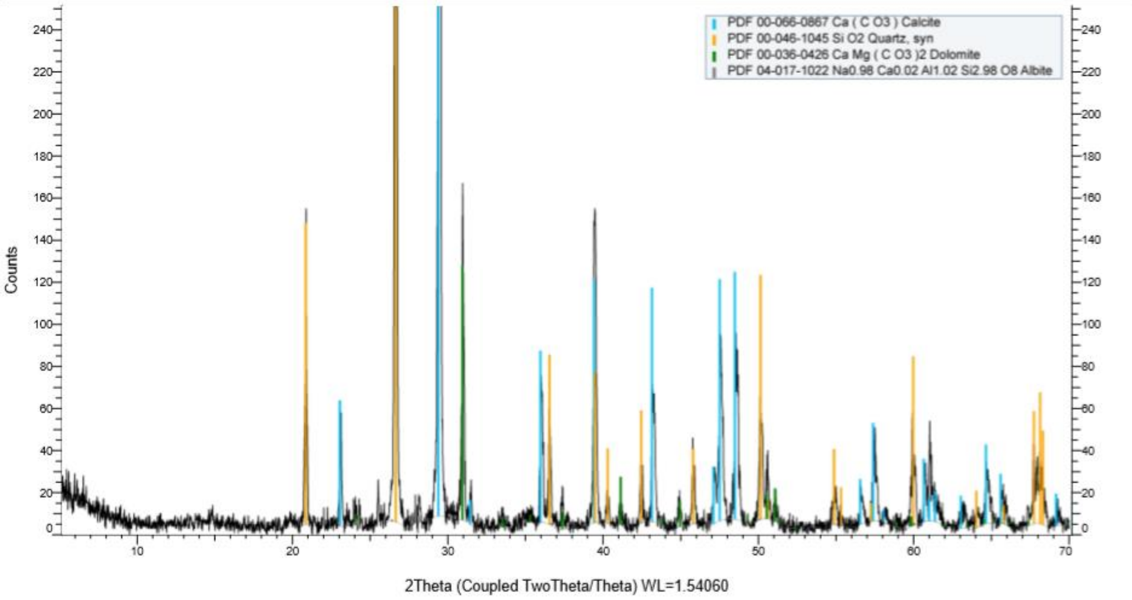
TE-2 <63 um



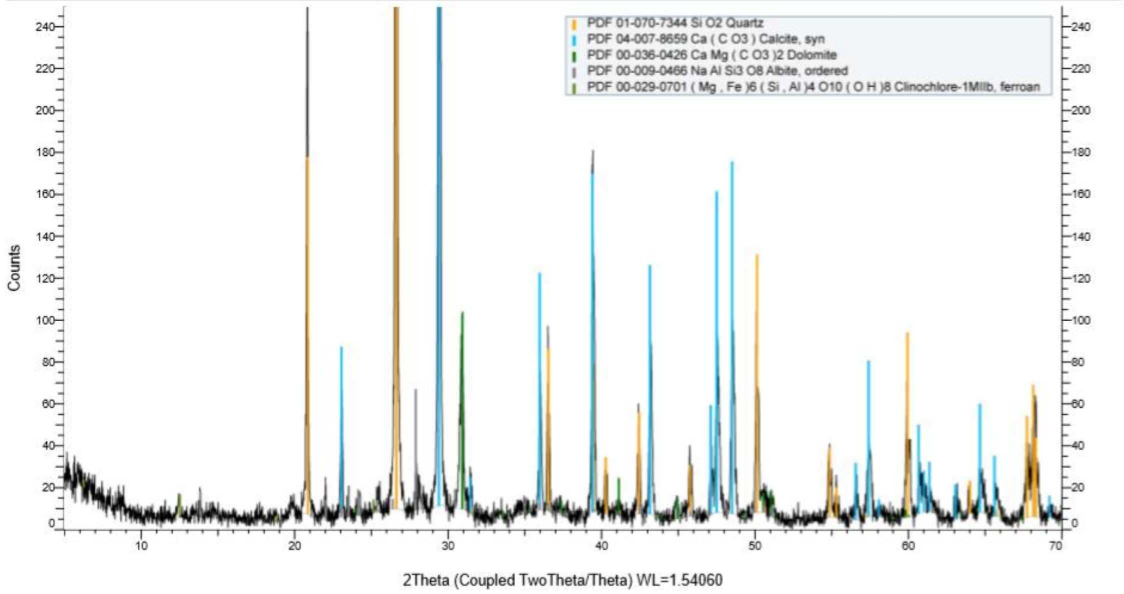
TS-1 <63 um (y-axis zoom)



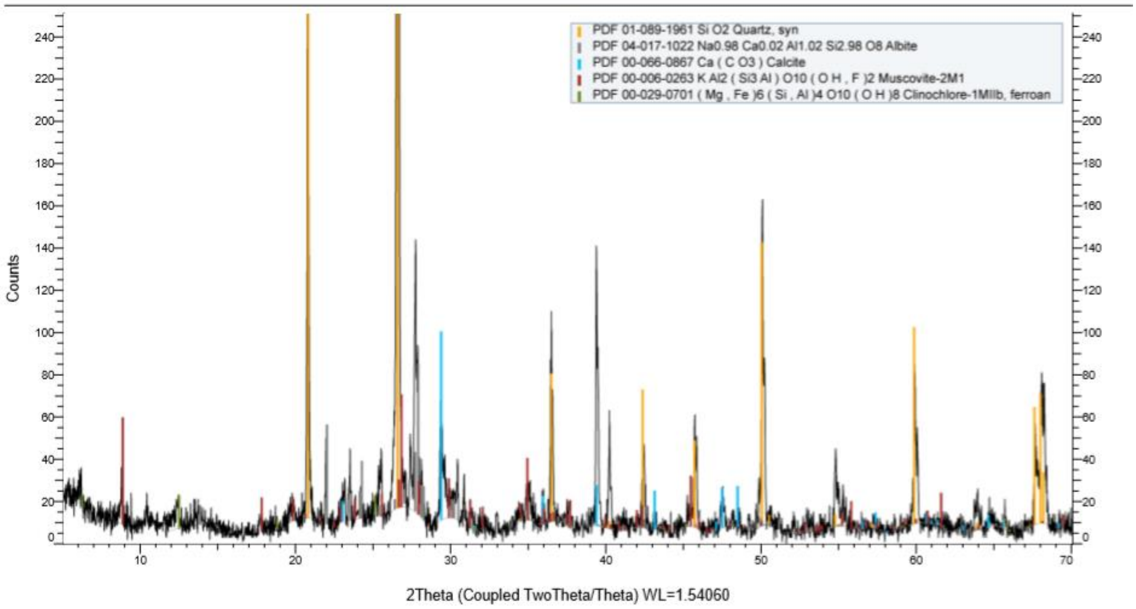
WH-1 <63 um (y-axis zoom)



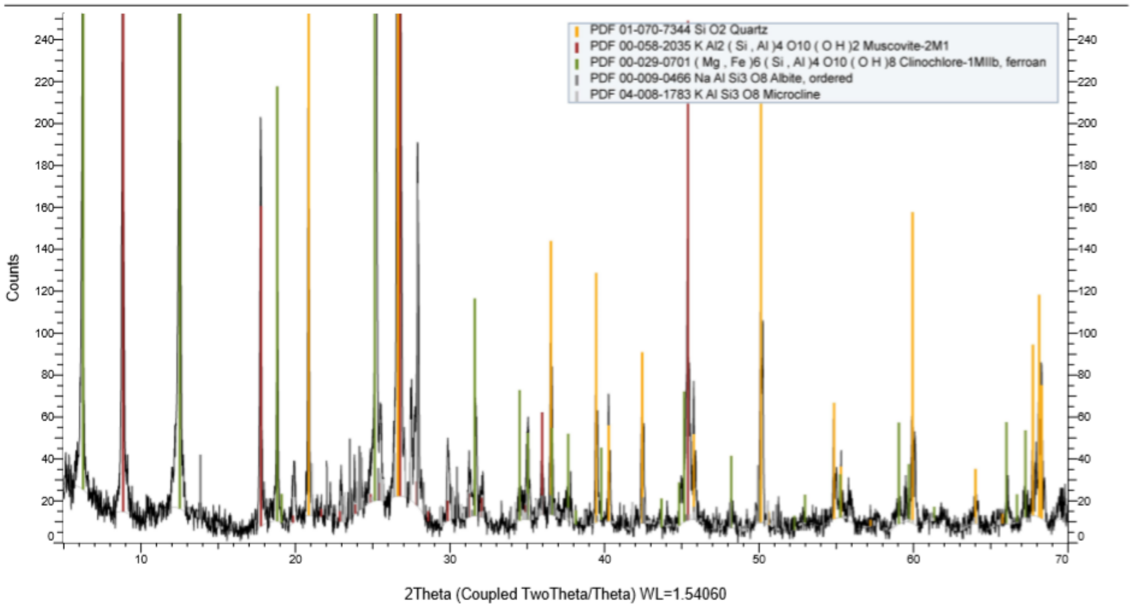
WH-3 <63 um (y-axis zoom)



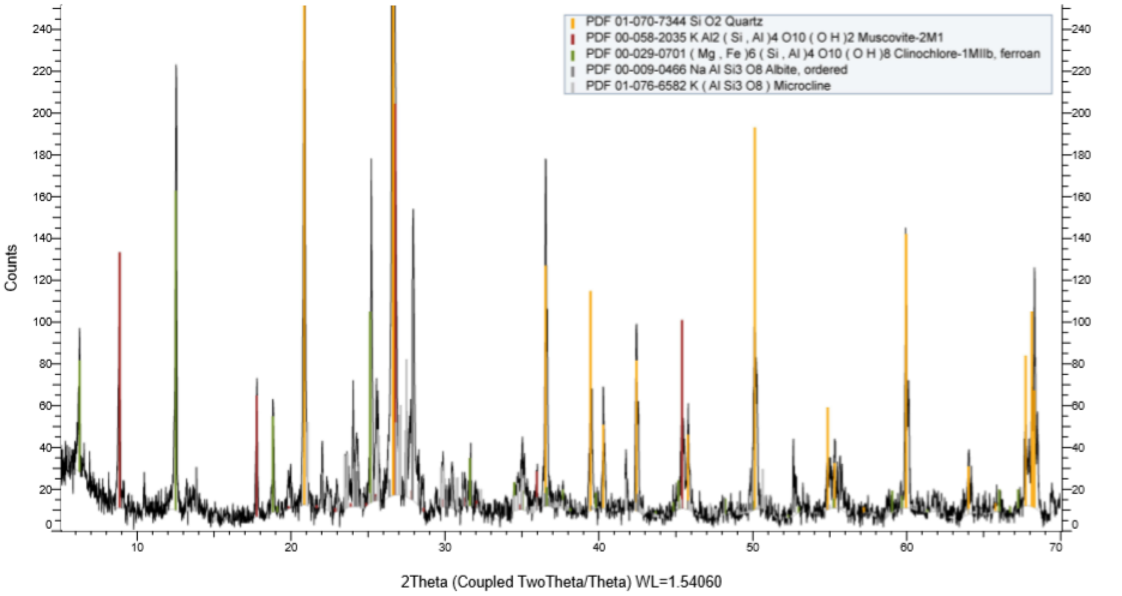
WW-1 <63 um (y-axis zoom)



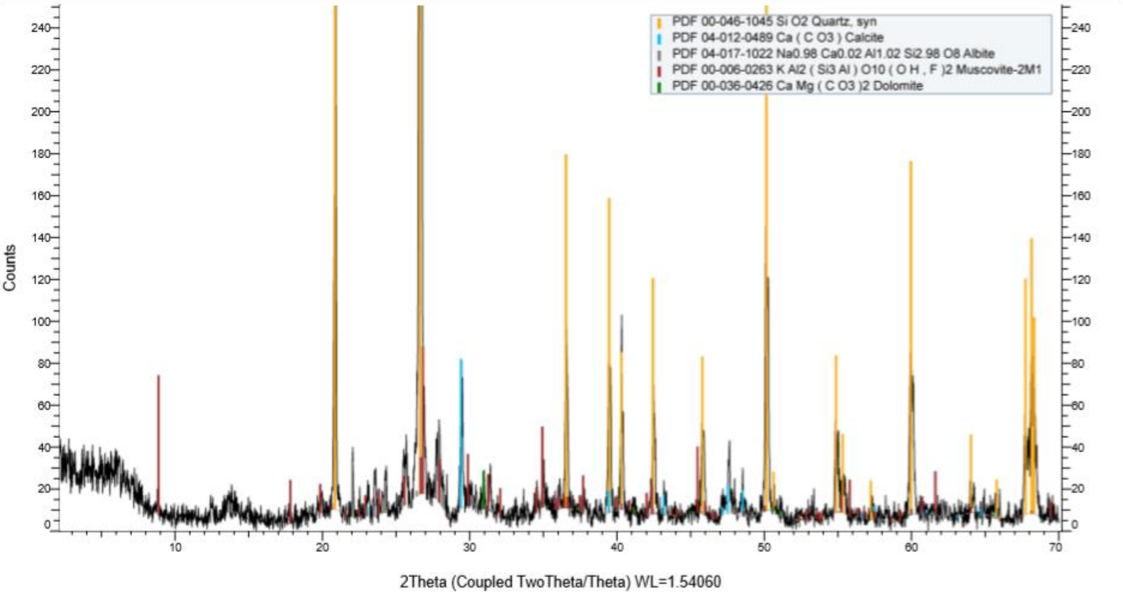
WX-1 <63 um (y-axis zoom)



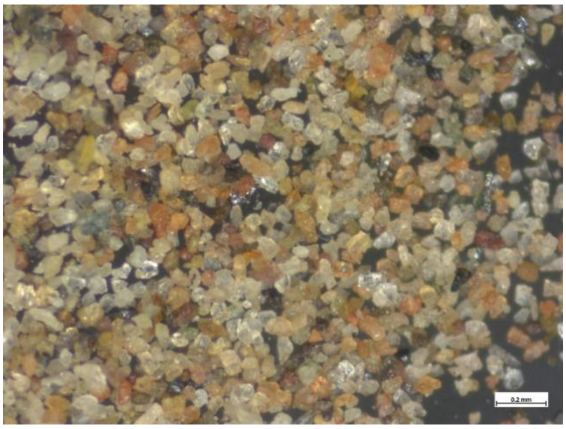
WX-2 <63 um (y-axis zoom)



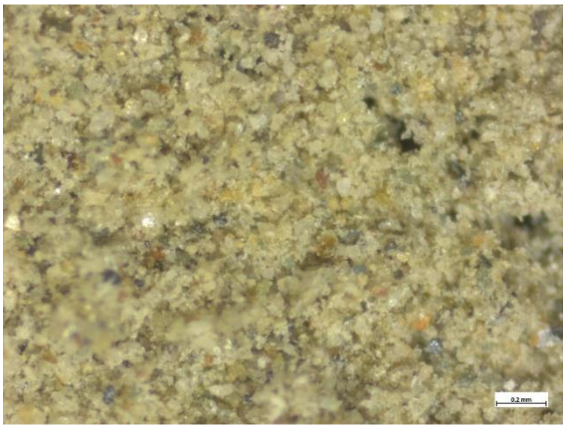
WX-3 <63 um (y-axis zoom)



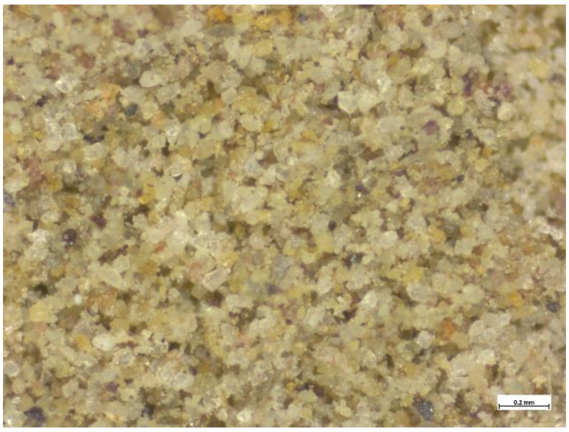
Appendix D Sand photographs



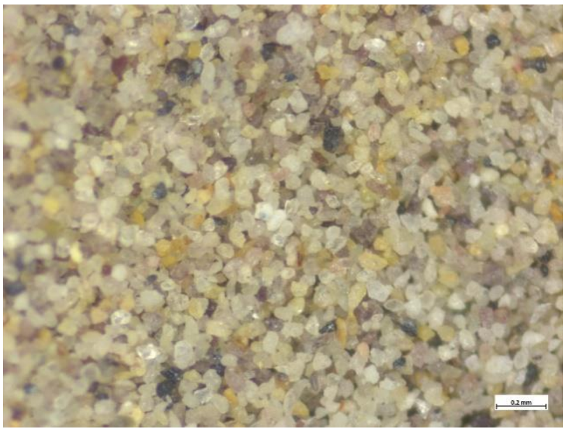
AH-1



AH-2

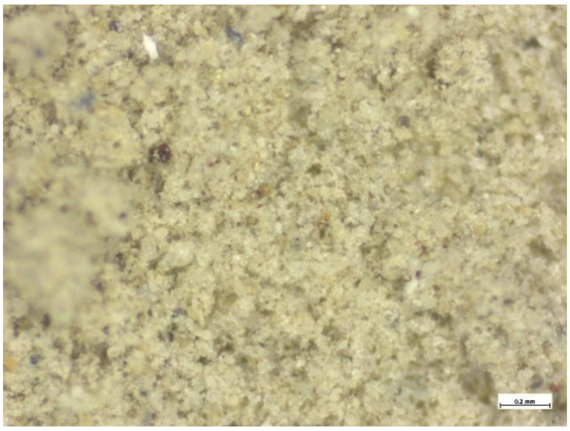


CE-1

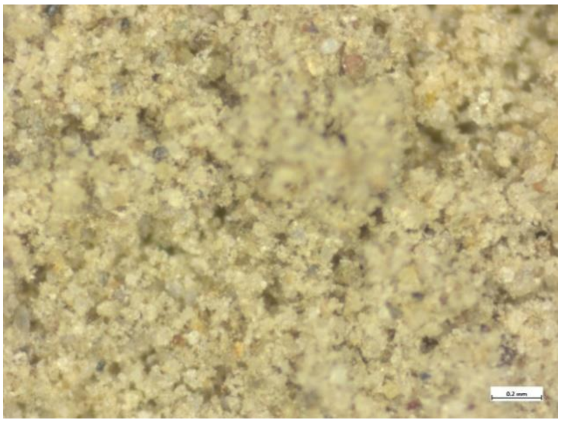


CK-1

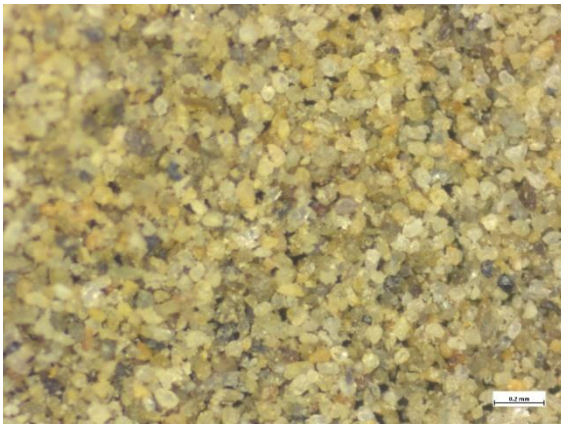
CK-2



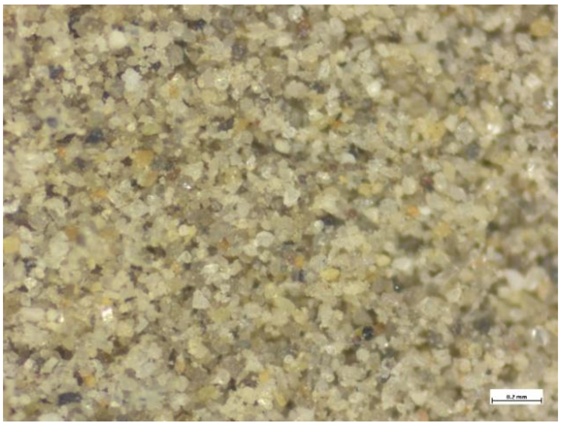
CK-3



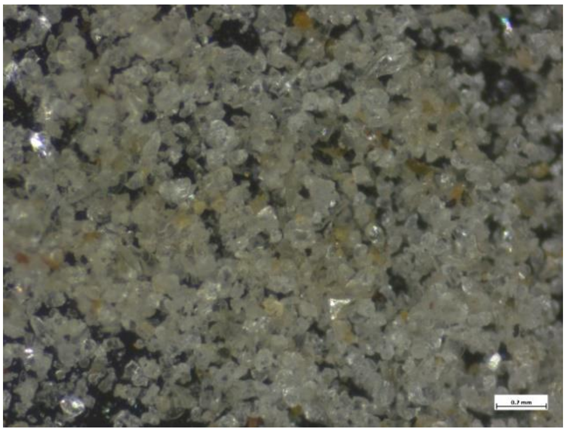
CK-4



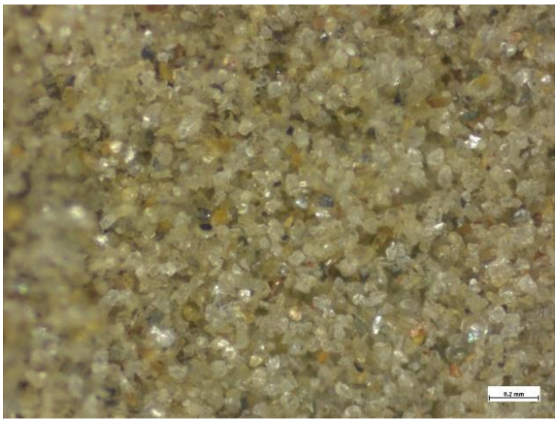
CN-1



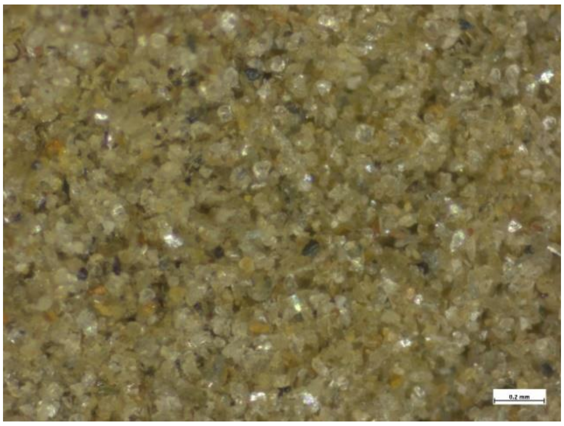
CW-1



DL-1



DL-2



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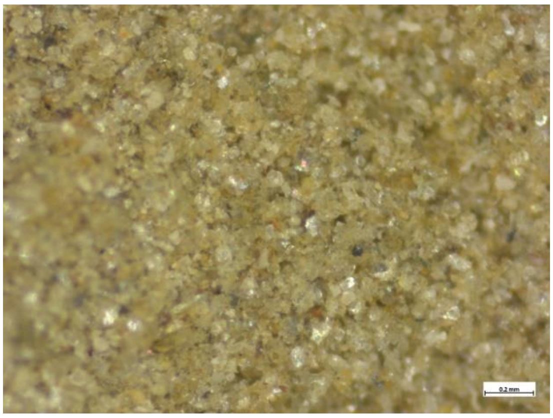
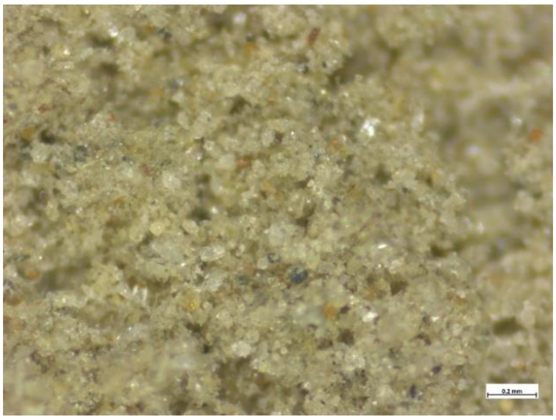
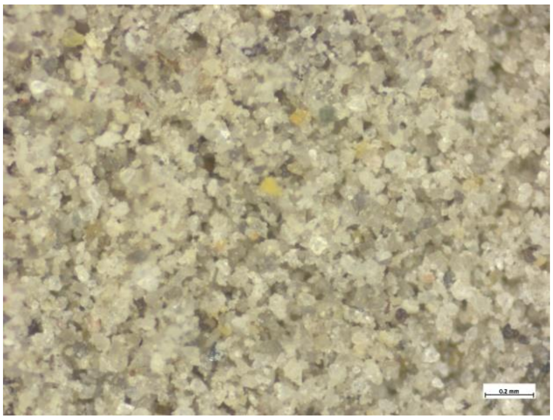


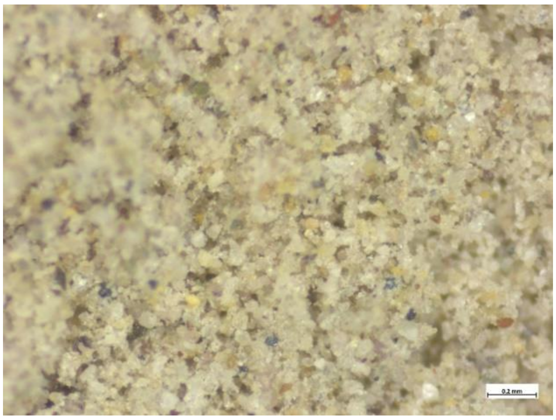
DL-4



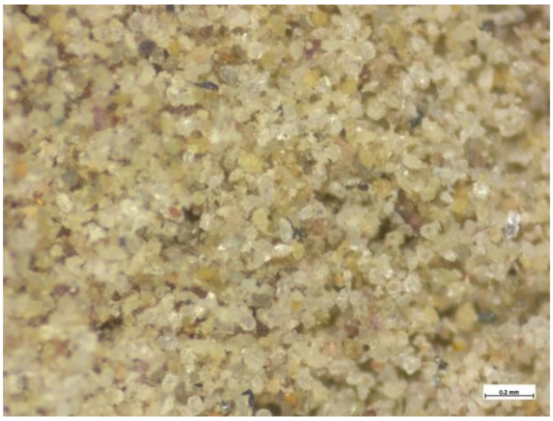
DL-5



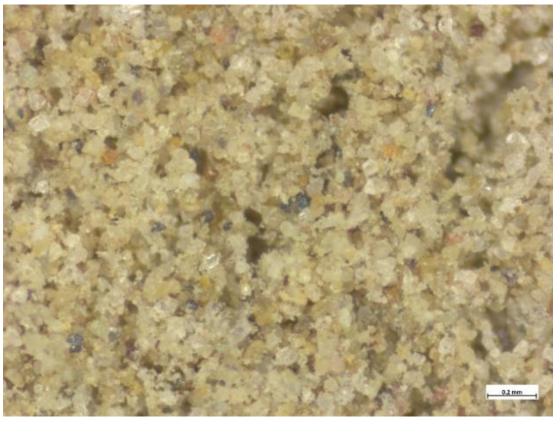
GY-1



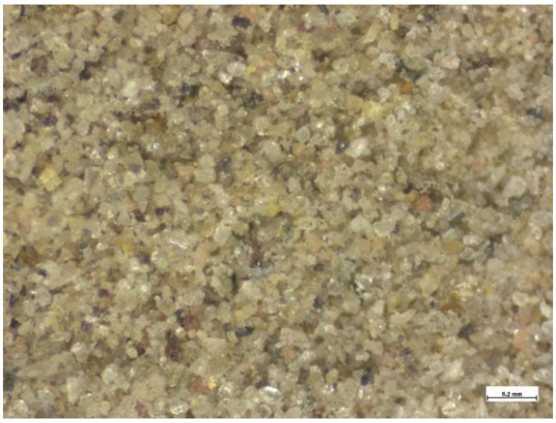
KY-1



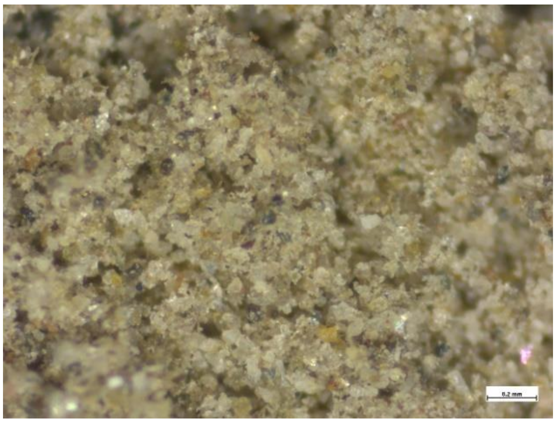
LK-1



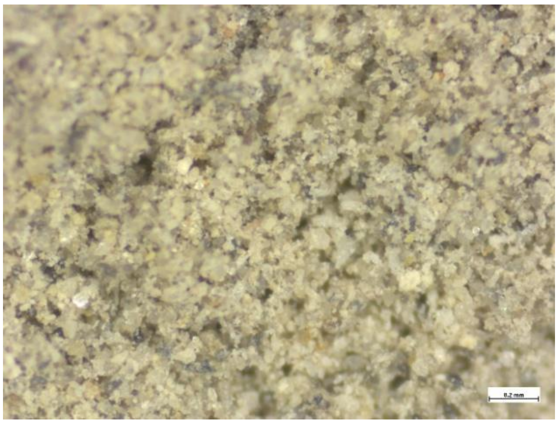
LK-2



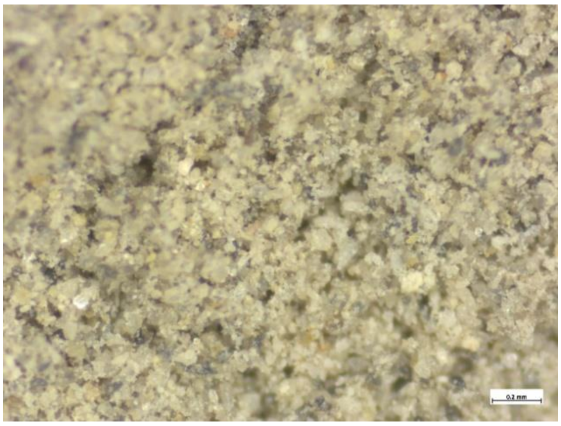
MO-1



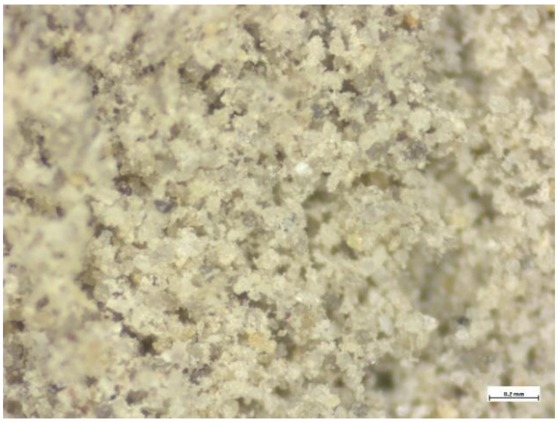
MO-2



OY-2

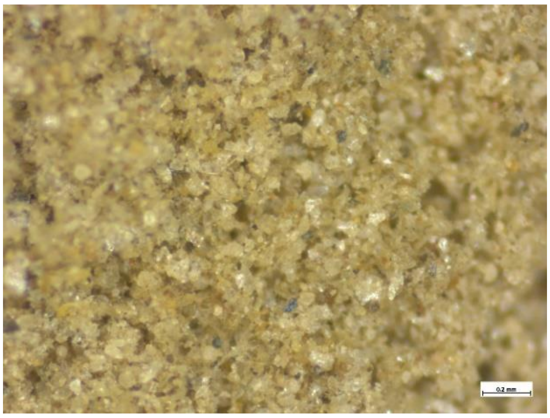


OY-3

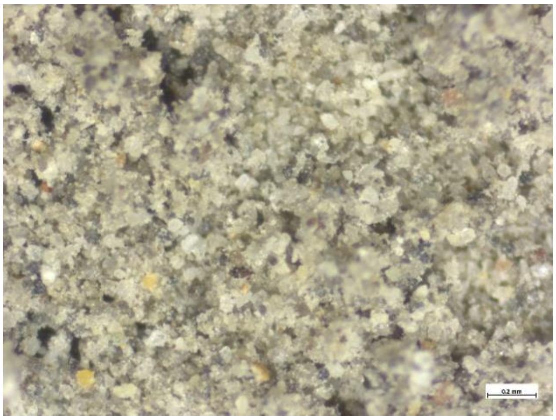


RN-1

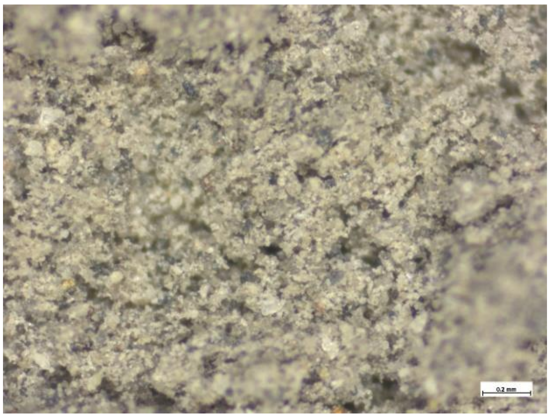
TE-1



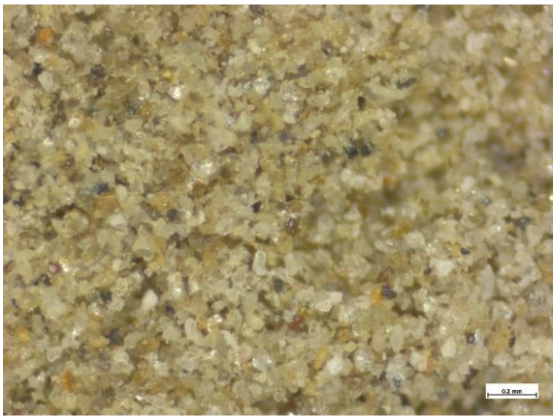
TE-2



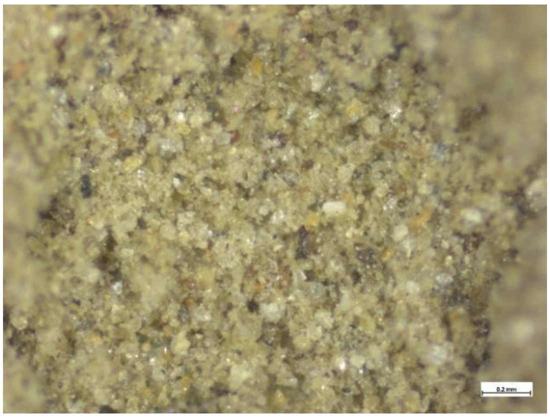
WH-1



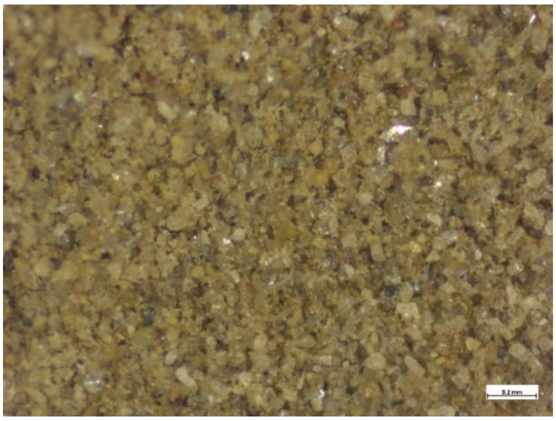
WH-3



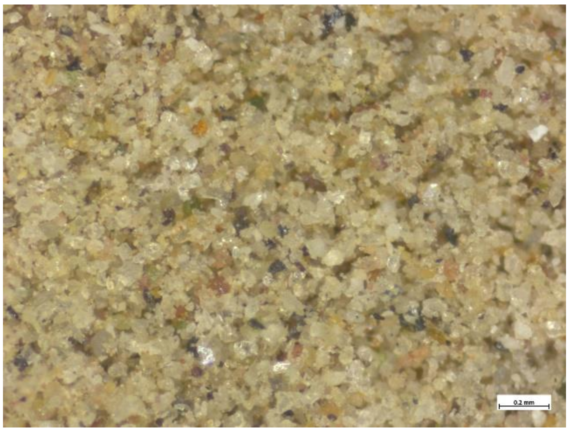
WW-1



WX-1



WX-2



WX-3

Appendix E

Research article

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Methodology for the determination of <63 µm free mica fines in sand and within the cement matrix of hardened concrete blocks using scanning electron microscopy and energy dispersive spectroscopy

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[2] Department of Geology, School of Natural Sciences, Trinity College Dublin, Ireland
*Correspondence: mulveyle@tcd.ie

Abstract: We propose a method for quantification of the percentage of <63 µm muscovite fines (termed free mica) in mixed sand fines and the identification/semi-quantitative analysis of free mica in the cement matrix of hardened concrete blocks. In recent times homeowners in County Donegal, Ireland reported structural problems in their buildings and concern that it is due to high concentrations of free mica within the concrete blocks. Our method requires the generation of high-resolution backscattered electron (BSE) images using field emission scanning electron microscopy (FE-SEM), where the characteristic needle-like morphology of mica can easily be identified. Additional information on the size, shape and chemical composition of the free mica fines, is gathered using energy dispersive spectroscopy (EDS or EDX). The combination of high-magnification images, high-resolution elemental maps, and mineral liberation software allows accurate identification and quantification of free mica within the sand fines and cement matrix.

Supplementary material: Information pertaining to the measurements by SEM-EDX are reported in Supplementary Tables 1 and 2, available at https://doi.org/10.6084/m9.figshare.c.4709390

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The Report of the Expert Panel on Concrete Blocks in counties Donegal and Mayo (2017) (Department of Housing Planning and Local Government 2017, p. 4) observed that

> The presence of muscovite mica in abundant quantities in the aggregate constituent of the concrete blocks was suggested as being one of the main factors contributing to the deterioration of the concrete blocks.

Subsequent analysis commissioned by local action groups in County Donegal, government departments and the National Standards Authority of Ireland (NSAI), during the development of a new standard, Irish Standard 465:2018 ('Assessment, testing and categorisation of damaged buildings incorporating concrete blocks containing certain deleterious materials'), highlights the need for a viable, quantitative, analytical method for the determination of free mica. Irish Standard 465:2018 acknowledges that scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) may be recommended by the professional geologist/petrographer for quantitative mineralogical analysis and their morphology and distribution, but does not make further comment on the technique (Irish Standard 465:2018).

Technical research published in the UK (Lees 1987), Sweden (Novikova 2008), USA (Schmitt 1990) and South Africa (Muller 1971), on the topics surrounding the implications for concrete made with high levels of muscovite-bearing aggregate, provide a plausible concrete block deterioration mechanism. In concrete manufacture, free mica attracts a disproportionate amount of water compared to other lithologies, and is associated with a reduction in workability and strength of the concrete. Once cured, the concrete may be susceptible to loss of integrity in freeze–thaw conditions (Wakizaka *et al.* 2001; Department of Housing Planning and Local Government 2017). Analysis of free mica is complicated by its small particle size, the low concentration of <63 µm fines in concrete aggregate (which is generally <3% by weight), the common abundance of muscovite in coarse aggregate and the inclusion of other non-muscovite mica minerals (Ash & Mellas 1993; Scrivener 2004; Stutzman 2004; Johansson *et al.* 2008; Kondelchuk & Miskovsky 2009). In Irish Standard 465:2018 the suspected safe/dangerous limits for mica are not specified in relation to the risk factor assessment for mica degradation in concrete blocks. A lack of data from quantitative methods exists to support limits and, instead, the risk is subjectively quantified by a professional geologist/petrographer. Thus, SEM-EDS may provide non-subjective quantification of free mica in sand fines and within the cement matrix of hardened concrete.

Experimental procedure

Sample preparation

Samples of <63 µm sieved building sand fines, from quarries and builders' suppliers in Ireland were collected. Two batches of sand were selected for analysis, one batch suspected of being highly micaceous, the second suspected of containing lower levels of free mica. Each sand sample was set in a round one-inch puck, with low-fluorine cold-setting resin, cured and highly polished when hardened.

Sub-samples of concrete blocks were extracted from two semi-detached dwellings in Co. Donegal, exhibiting the characteristic damage patterns associated with concrete blocks containing high concentrations of free mica. The sampling locations were the gable end, external leaf and internal leaf (standard 4 inch blocks used on their edge) and one of the big 12s/load-bearing blocks (larger than the 4 inch standard and laid on their flat, at the base of the foundation). All concrete blocks were sub-sampled horizontally, at mid-block height, with a 100 mm water-lubricated rig and the thin sections were produced in the horizontal plane, orthogonal to the long axis of the block in the Department of Geology, Trinity College Dublin. It is recommended to prepare thin sections from more than one plane, due to the aspect ratio of free mica and the possibility of preferential alignment when concrete blocks are manufactured. The thin section results in this paper are single-plane samples. The concrete samples were dried, impregnated with a low-fluorine cold-setting resin, mounted to a glass slide, trimmed and reduced to a thickness of 30 µm, using a rotating plate polisher. A high quality polished thin section is critical to successful quantitative SEM-EDX analysis.

Carbon coating the thin section

The SEM-EDS analysis is performed under high vacuumat 20 kV; therefore, steps are required to create a conductive sample surface in order to eliminate charging artefacts. The thin section and pucks are cleaned by wiping gently with ethanol, the surface is dusted off using a nitrogen air gun to remove any residual fibres. Carbon tracks are paintedon the sample boundary and edges, then left to dry. Once dried, the samples are placedinto the Cressington 208 carbon coater. When a suitable vacuum is achieved, 12 nm of carbon is applied to the sample surfaces. This step, which creates a conductive sample surface, is imperative for high quality SEM imaging (Ubide *et al.* 2017; Ubide & Kamber 2018).

Backscattered electron imaging on the SEM

A Tescan MIRA3 variable pressure scanning electron microscope (VP-SEM) was used to take the backscattered electron (BSE) images. Elements with a high atomic mass number (heavy elements) appear brighter in the image; the darker areas in the BSEimage are elements with lower atomic mass numbers (light elements). The SEM has a Schottky field emission source and an electron gun maintained at high vacuum; the sample chamber is pressurized once the samples are inserted. The energy range, which spans from 1–30 kV, was set to 20 kV for the cement matrix/sand fines imaging and EDS analysis. At 20 kV, sufficient energy is applied to the samples to excite the atoms in the elements of interest withinthe cement matrix and sand fines to generate the EDS spectrum. With a focused and de-stigmatized, corrected image in resolution/analysis mode and using a WD & Z (working distance and *z* height) of 15 mm, the electron beam is aligned at 20 kV. Beam alignment includes automatic adjustments to the metal apertures and magnetic lenses in the gun and column, which is performed to create a thin, focused and stable electron beam. The image is refocused and degaussed as required during the working day. Due to the variation in fines/aggregate and cement hydration products, no one contrast and brightness setting is found to suit all images, so these settings vary. The image parameters are noted: resolution (width) pixels, resolution (height) pixels, the magnification, pixel dwell time (µs), image width (µm) and image height (µm) in the acquired images. The characteristic needle-like morphology of the free mica can easily be observed in the cement matrix BSE image, taken at ×1200 magnification (see Fig. 1), and is different to the more irregular or rounded shapes of the other mineral fines.

SEM-EDS operating conditions and calibration

The Tescan MIRA3 variable pressure FE-SEM was used with two Oxford X-Max 150 mm^2 energy dispersive X-ray analyser detectors, which were controlled using Oxford Instruments Aztec X-ray microanalysis software (https://nano.oxinst.com/products/aztec/azteclive). The SEM settings included a beam intensity of

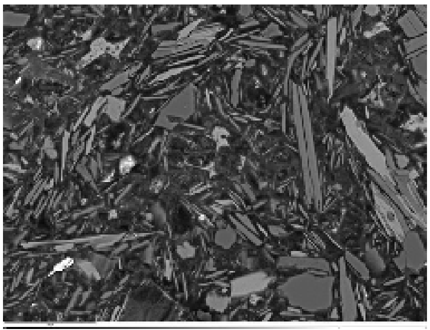

Fig. 1. Cement matrix: backscattered electron SEM image of free mica and other fines in the cement matrix of a hardened concrete block (×1200 magnification).

ten, absorbed current of *c.* 300 pA and a working distance of 15 mm. Cobalt was used to perform a quantitative optimization of the electron beam prior to sample analysis and also at intervals during the day to monitor beam current drift.

Quantitative analysis of free mica within the sand fines was possible after the instrument was calibrated for selected elements, from the reference minerals in a certified Smithsonian mineral puck. The elements of known weight percentage (wt%) in the calibration were Si (in microcline), Al, Ti, Mg and Ca (in augite), Fe and Mn (in pyrope), Na and K (in anorthoclase), and Cr (in synthetic Cr_2O_3) and Ni (in synthetic Ni). Diopside and anorthoclase were subsequently used as quality control checks against this calibration. Precision was <1% for all elements measured with accuracy better than 2%. A calibration using a certified SIRA grid is performed to demonstrate the accuracy of length measurements on the SEM image, with five 10 µm lengths on the grid selected, which resulted in an average measurement of 10.04 µm.

SEM-EDS analysis

Elements are identified by their characteristic X-ray energies (KeV) and quantified by their peak intensities. Using the EDS, element maps are acquired from the same field of viewas the BSE image, with the map function on the Oxford Instruments Aztec software (https://nano.oxinst.com/products/aztec/azteclive). Each element selected for analysis is attributed a colour and theindividual element maps are combined by the software to generate a multi-coloured, layered EDS element map (Fig. 2). The elements selected for EDS mapping are C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn and Fe (examples of K and Mg individual element maps are displayed in Figs 3 and 4); additional or fewer elements may be displayed in the map, as data for the full elemental spectrum are automatically acquired.

Data processing

The histogram of the BSE image is utilized by making adjustment to the upper and lower thresholds. The histogram, from black to white, covers a range from 0 to 32 767. Identifying the threshold range for mica and other fines distinguishes them from the epoxy resin matrix in the sand fines pucks and from the cement matrix in the polished concrete thin sections. By selecting a feature of interest in the BSE image, namely a mica fine, the software identifies its grey-level and

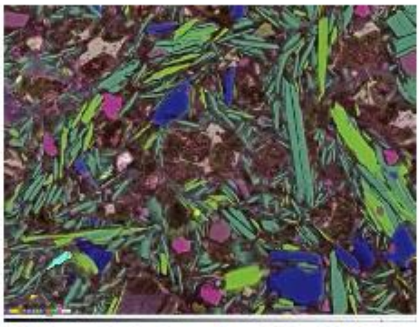

Fig. 2. Cement matrix: layered energy dispersive X-ray (EDX or EDS) analysis map of free mica (darker green) and other fines (e.g. quartz in blue) in fines in the cement matrix of a hardened concrete block (×1200 magnification).

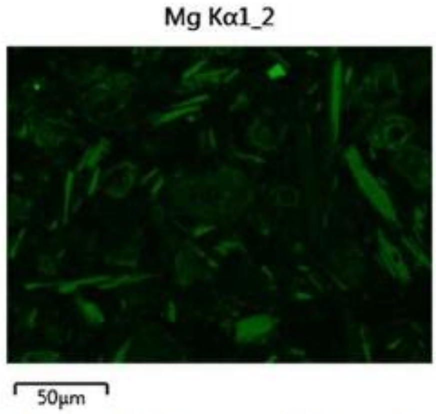

Fig. 4. Cement matrix: magnesium EDS map of fines in the cement matrix of a hardened concrete block (×1200 magnification).

can highlight all similar grey-level features in the image; manual adjustments may also be utilized to adjust threshold limits visually. To facilitate the extraction of the maximum statistical information from the images, the threshold limits are set to also include the non-mica fines within the sand fines and cement matrix. The sieved mixed sand analysis yields the total number and area of fines tested, enabling calculation of the percentage of free mica within the total sand tested. For the concrete thin section, the area percentage of free mica can be expressed in terms of its abundance within the cement matrix in the fields of view tested. By excluding the cement paste, using its greyscale on the histogram and focusing only on the fines, the percentage of free mica among the other fines in the fields of view tested can be determined.

Figure 5 is a high magnification (×1200) BSE image of cement matrix overlaid with features identified by thresholding, with the multi-coloured areas highlighting the unclassified fines. Classification of these features (or fines) follows, depending on the size, shape and chemistry classification criteria set. As free mica has a very characteristic morphology (it appears needle-like in the BSE image), the following measurements are set to identify free mica from the other fines: aspect ratio, breadth, length and shape. Fines with an aspect ratio less than 2.8 and shape factor less than 2 are rejected; length and/or breadth measurements are set to identify fines <63 µm. A circle has a shape value of 1; elongated and irregular features have larger values. Shape is defined as $P^2/4\pi A$, where P is the perimeter and A is the area (Oxford Instruments, https://nano.oxinst.com/products/aztec/azteclive). The chemistry criterion used is potassium must be detected and magnesium may be used to distinguish between muscovite and other mica minerals. Biotite and phlogopite can be distinguished from muscovite by EDS. Biotite and phlogopite consist of Si, Al, K, Mg, Fe and Ti, whereas muscovite contains only a minor amount of Fe and no Mg (Welton 1984). Figure 6 shows the cement matrix result: the <63 µm free mica is highlighted in red over the SEM image; the area of the fines is measured, enabling the calculation of the free mica percentage in the field of view of the cement matrix tested. It must

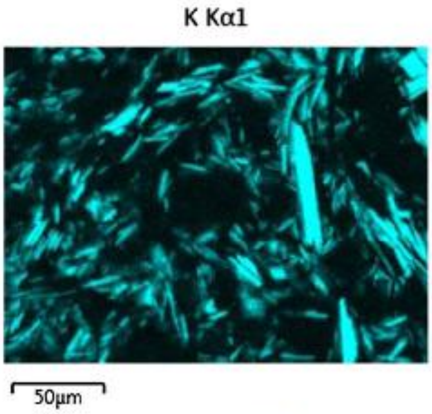

Fig. 3. Cement matrix: potassium EDS map of fines in the cement paste of a hardened concrete block (×1200 magnification).

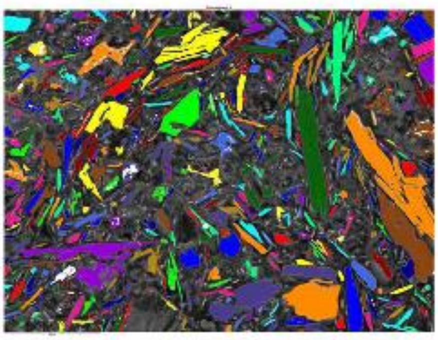

Fig. 5. Cement matrix: backscattered electron SEM image, with fines – highlighted (multi-coloured) using grey-level threshold adjustments – in the cement matrix of a hardened concrete block (×1200 magnification).

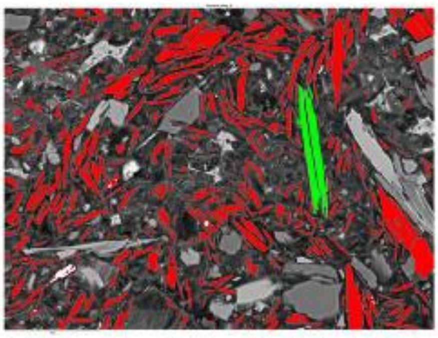

Fig. 6. Cement matrix result: BSE image with <63 µm free mica in red and >63 µm free mica in green. Based on one field of view, the percentage of free mica within the <63 µm fines is 57.22% and the percentage of free mica within the cement matrix is 15.70% (×1200 magnification).

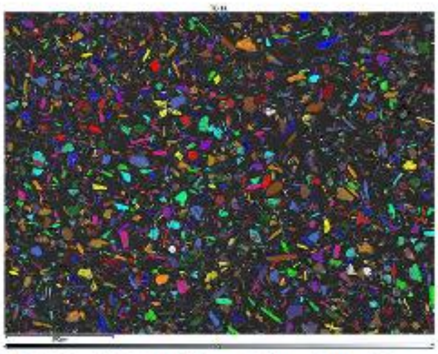

Fig. 8. Sand analysis TE-1a: BSE image of <63 µm sieved sand fines, with all fines highlighted in multi-colour using grey-level thresholding (×138 magnification).

be noted that the 63 µm is a sieve mesh size, so some elongate grains >63 µm in diameter could have passed through into the sand batches used in manufacturing; such a feature is highlighted in green (Fig. 6) and such features are included in the <63 µm free mica calculation. Twelve or excess fields of view of the cement matrix (at ×1200 magnification) per thin section were chosen for analysis, avoiding large aggregate and focusing on the cement paste in between the aggregate. Lange *et al.* (1994) worked on 12 BSE images per block for porosity determination in concrete. ASTMC457 provides information on the minimum area of finished surfaces for microscopical measurements in other applications. The 1 standard deviation (SD) graphs of the free mica results in the cement matrix and sand assisted determining the optimum number of fields of view for analysis.

The sand tested was sieved so that only the <63 µm fraction remained. A sand fines BSE image (Fig. 7) and matching EDS element map were acquired at ×500 magnification. Images from a range of magnifications (×138–700) were acquired. The BSE and EDS pixel dwell times were set at 200 and 5000 µs and the BSE and EDS resolution was set to 1024 and 512, giving an EDS live frame time of *c.* 16 min. Figure 8 shows all the sand feature identified by grey-level thresholding. The results of the size, shape and chemistry criteria applied to the fines tested are then calculated (Fig. 9); the <63 µm area fines are displayed in red, with green representing all other fines. Additional random single fields of view were tested and a montage of multiple fields of view were stitched together, creating large-area BSE and EDS maps; one such montage map is shown in Figure 10. The results of this and an additional sand sample tested are displayed in Supplementary Tables 1a, 1b and 1c.

Results

Sand fines results

A BSE image of the sieved sand sample (Fig. 7) was acquired at ×138 magnification. Grey-level thresholding identified 6832 fines (Fig. 8), with a total fines area measurement of 473 000 µm^2 in the field of view tested (2 mm image height × 1.5 mm image width).

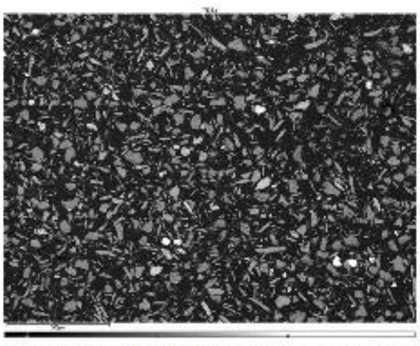

Fig. 7. Sand analysis TE-1a: BSE SEM image of <63 µm sieved sand set in a low fluorine resin polished puck. The needle-like morphology of free mica can easily be observed in this image (×138 magnification).

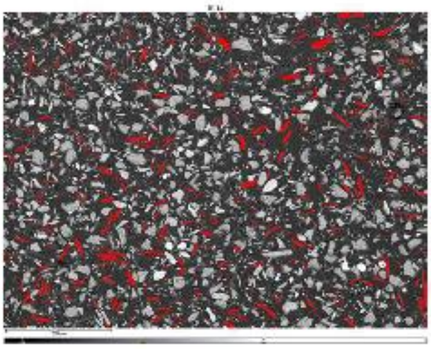

Fig. 9. Sand analysis results for TE-1a: BSE image of <63 µm sieved sand fines, with free mica fines identified in red, using potassium, shape and aspect ratio criteria. 6832 fines are tested in this single field of view and the percentage area of free mica is 20.04% (image length 2000 µm × breadth 1500 µm; ×138 magnification).

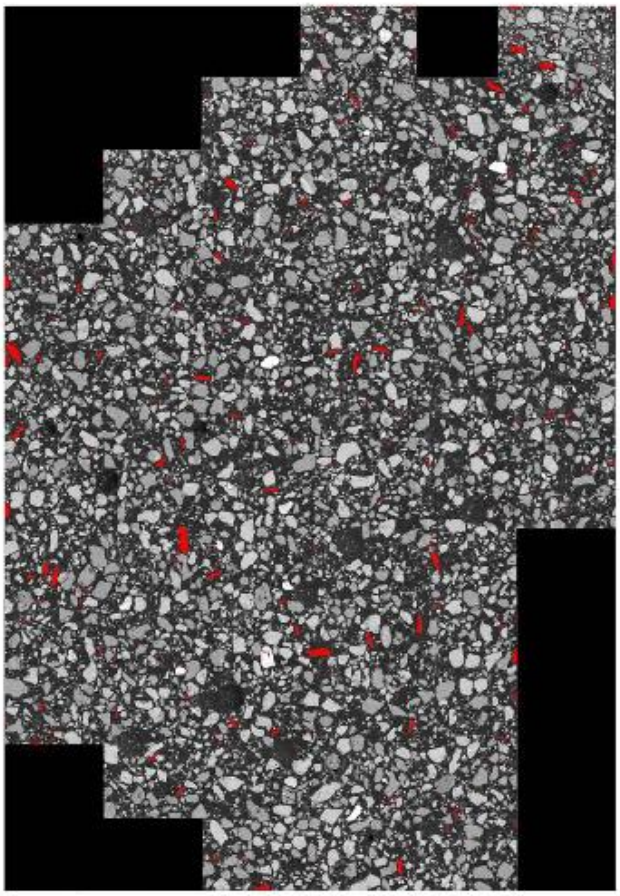

Fig. 10. Sand analysis result for OY-1X11: montaged large-area BSE SEM map of <63 µm sieved sand, comprising 55 fields of view, each field imaged at ×700 magnification (with individual field image dimensions of 395 µm length × 296 µm breadth). 43 147 fines are tested in this montage and the area percentage of free mica is 2.21%.

The free mica classification criteria (potassium, shape and aspect ratio) identified 400 fines (Fig. 9), with an area measurement of 94 800 µm^2. The area percentage of free mica in the sand fines may be calculated as follows:

$$\frac{94\,800\ \mu m^2}{473\,000\ \mu m^2} \times 100 = 20.04\% \qquad (1)$$

Additional random single fields of view from the same sieved sand, at ×300 and ×400 magnification, measured free mica concentrations at 16.45, 20.56 and 20.29%. The total number of fines tested from the four measurements totalled 12 969 fines. The method would incline towards under-estimating rather than over-estimating the free mica fines, as a free mica fine physically overlapping another fine may be excluded by the software. The software allows features to be manually added, removed or erosionfilters appliedto separate features, if required. The magnification selected may require increasing or decreasing, depending on how closely packed are the fines. Large-area maps may be acquired, montaging multiple fields of view together to increase the area of fines tested; the analysis time is increased significantly depending on analysis settings. The maximum number of fines the software will currently process is 60 000 features per map.

The result of the second sand sample tested (Fig. 10) is a large-area montaged map of fines, with free mica highlighted in red. This is a montage of 55 fields, each field 395 µm (image length) × 296 µm (image breadth), at ×700 magnification. The area percentage of free mica among the total fines in this montage is 2.21%.

Cement matrix results

In the first field of view of the cement matrix tested, 950 features were identified using grey-level thresholding, with a total measured area of 10 644.41 µm^2 (Fig. 5). The total area for this field of view was 172 µm (image height) × 230 µm (image width) = 39 790 µm².

The (area) percentage <63 µm fines may be calculated as follows:

$$\frac{10\,644.41\ \mu\text{m}^2}{39\,790\ \mu\text{m}^2} \times 100 = 26.75\% \tag{2}$$

From the same field of view in the cement matrix, 478 features met the morphological and chemical criteria for free mica, with a total measured area of 6090.31 µm^2 (Fig. 6). The percentage of free mica within the <63 µm fines may be calculated as follows:

$$\frac{6090.31\ \mu\text{m}^2}{10\,644.41\ \mu\text{m}^2} \times 100 = 57.22\% \tag{3}$$

Finally, the percentage of free mica within the cement matrix (based on a single field of view, Fig. 6) is calculated as follows:

$$\frac{6090.31\ \mu\text{m}^2}{39\,790\ \mu\text{m}^2} \times 100 = 15.70\% \tag{4}$$

Avoiding coarse aggregate (>4 mm) and using the same analysis conditions, analysis was completed on an additional 13 random fields of view of cement matrix from the same thin section, i.e. from the same concrete block; the results are displayed in Supplementary Table 2a. A 1 SD graph of the results assists in determining the number of fields of view suitable for representative analysis of the sample. The average percentage of free mica within the <63 µm fines is 64.13 ±9.04%. Concrete is a very heterogeneous material, and the concrete block is large in comparison to the fields of view tested; therefore, the average percentage of free mica fines in the tested cement matrix of the hardened concrete block (14.06 ±2.10%) gives a semi-quantitative measurement value. Supplementary Tables 2b, 2c and2d give the analysis results from three additional concrete blocks from the same dwelling.

Conclusions

Compliance with quality control practices in manufacturing gives confidence to the manufacturer that the product they are selling meets regulatory requirements and to the consumer that the product they are purchasing is fit for purpose. The SEM-EDS method for the analysis of the sand fines to identify and quantify the percentage of <63 µm free mica fines demonstrates its potential as a viable analytical technique for this purpose. Batches of sieved sand fines, intended for use in construction, can be examined and classified for deleterious material. This method demonstrates the power of utilizing the latest technology and software in scanning electron microscopy coupled with energy dispersive X-ray microanalysis to extract quantitative information on free mica. Current analytical approaches to quantifying free mica content are limited; they include an experienced petrographer's opinion based on optical microscope imaging, with reflected light offering the best approach. The useof this application to examine the cement matrix of hardened concrete blocks provides a useful technique for identification and semi-quantitative analysis where failure in a structure has occurred.

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Author contributions LMO: Data curation (Lead), Formal analysis (Lead), Funding acquisition (Equal), Investigation (Equal), Methodology (Lead), Project administration (Lead), Resources (Equal), Software (Lead), Supervision (Lead), Validation (Lead), Visualization (Equal), Writing – Original Draft (Lead), Writing – Review & Editing (Equal); RG: Conceptualization (Lead), Funding acquisition (Lead), Resources (Equal), Supervision (Lead), Writing – Review & Editing (Equal)

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