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Title: Characterization of Cement-Geomaterial Interfaces for Subsurface Applications

Abstract: Subsurface seals and wellbores are central to oil and gas production, as well as the containment of subsurface fluids (e.g. methane or CO_2 storage). Studying the evolution of cement-geomaterial interfaces of such systems is important to further our understanding of the fundamental physics and chemistry that underpins catastrophic wellbore seal failure. The objective of this study is to characterize cementitious and geomaterials through pore structure analysis and geochemical modeling. A variety of methods exist to characterize the pore structures and mineralogy of porous systems like cements and subsurface host rocks. This study will utilize traditional porosimetry techniques such as BET and IP, as well as more advanced methods using electron image analysis, to gain a more accurate understanding of pore geometries. The results of this study can help further the understanding of how cementitious materials will evolve, and can be used as inputs to field scale models used to predict wellbore behavior over time.

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Table of Contents:

I. Introduction

Carbon Dioxide Capture and Storage in Geologic Materials

Carbon dioxide capture and storage (CCS) offers a promising near-term solution for reducing anthropogenic CO_2 emissions without disrupting existing energy infrastructures. CCS is a technology that captures and compresses CO_2 at industrial locations, transports the supercritical fluid, and stores CO_2 in subsurface geologic deposits. However, for CCS to have a substantial impact, it must be implemented at a large scale, making it crucial to thoroughly understand processes involved with CO_2 transport and storage (Middleton et al., 2012). Due to the immaturity of CCS technologies, there is concern for associated or unintended risks of such systems. It is important to understand CCS on all levels – from pore to regional scale to help mitigate some of this uncertainty. This study will focus on pore-scale evaluations of host rock material of a potential CCS system, as rock-fluid-cement interactions govern the mobility of CO_2 and the stability of wellbores.

Importance of Cement Material and Geomaterial Characterization

Wellbore failure could have a severe negative impact on many aspects of CCS – from environmental protection to economic costs. Studying the evolution of cement-geomaterial interfaces of CCS systems is important to enhance our understanding of the fundamental physics and chemistry that underpins catastrophic wellbore seal failure. Further, one issue facing the implementation of CCS on a large scale is the availability of suitable geologic disposal opportunities. Determining appropriate geologic structures for CCS is a major constraint holding CCS back from becoming a transitional technology (Rübbelke and Vögele, 2013). Suitable geologic sites must be carefully chosen, keeping in mind parameters such as porosity, thickness, and permeability of reservoir and cap rocks.

Primary concern for loss of well integrity comes from possible sources of leakage pathways, through which CO_2 could travel upwards to the surface. Sources of this instability can come through many phases of well construction – from drilling to completion and abandonment. Weakening of cement casing or fractures in geologic structures could occur at various points in the lifespan of a well. Corrosion of casing and cement bears the highest impact on technical and economic feasibility of CCS systems. Portland cement is the most common cement used for well purposes. When CO_2 is dissolved in water, it creates carbonic acid (HCO_3^-), which reacts with Portland cement to form calcium silicate gel (C-S-H) and calcium hydroxide ($Ca(OH)_2$). The formation of these products can severely impact the strength of cement in the well bore (Bai et al., 2016).

To determine appropriate geologic structures and accurate cement-geomaterial interactions, it is important to gather baseline information on all materials involved so that geochemical modeling and preliminary testing can take place. Laboratory testing can give insight to how the cement-

geomaterial system would behave and where possible sources of leakage may occur. Specifically, this characterization will provide input parameters for reactive transport simulations, as well as validation of these simulations.

Scope of Project

The objective of this study is to characterize geomaterials through pore structure analysis and more advanced electron image analysis. This project offers baseline data and basic insights to the chemistry that will affect wellbore stability. It is important to note that this project falls under a larger scope of research taking place across various institutions. While this paper does not offer any grand, large-scale conclusions, it does provide useful information for further work to be conducted and gives valuable parameters for inputs to modeling problems.

II. Materials and Methods

Geomaterials

Five different geologic samples were used in this study. These samples consisted of sedimentary and carbonate rocks from the Mount Scopus formation in the Negev Desert of Israel. The rocks in this formation are characterized by having high levels of organic material. The samples included: Sandstone (SST), chalk (C), marl (M), phosphorite (P), and oil shale (OS).

Two types of rock samples will be referenced in this paper: baseline material that has not undergone any testing and samples that have undergone EPA method 1315 leaching test. EPA method 1315 is described in detail in a following section.

Procedures

i. Nitrogen Gas Adsorption Experiment

The Brunauer Emmett and Teller (BET) theory describes the adsorption of gas molecules on a solid surface and gives a basis for the measurement of specific surface area of materials. Brunauer, Emmett and Teller expanded Langmuir's kinetic theory to multi-layer adsorption, which assumes that the uppermost molecules in adsorbed stacks are in dynamic equilibrium with the vapor (Lowell and Shields, 1987). Typically, and in the case of this paper, the adsorbate used is N_2. Different degas conditions were used, depending on type of material. Degas conditions for the geomaterials are listed in the table below, and were determined through reference to literature (see: Kuila, 2011, Landrot, 2013, Mastalerz et al., 2013, Okhrimenko et al. 2014, and Ruiz et al., 2012).

	Temperature (□C)	Time (minutes)
Chalk	65	180
Marl	130	720
Phosphorite	60	1440
Sandstone	90	1080
Oil Shale	110	840

Table 1: Compilation of BET degas conditions for each rock material.

ii. Mercury Intrusion Porosimetry (MIP)

MIP is a useful method to characterize porous material. With this method, pore sizes from 500 μm to 3.5 nm can be investigated, and a wide range of information can be generated, from pore size distribution, percent porosity, total pore volume, etc. Samples are evacuated to remove air and avoid contamination. Then, the sample cell is filled with mercury as the pressure in the system slowly increases, intruding mercury into smaller and smaller pore spaces (Giesche, 2006). Samples were sent to Micromeritics Instrument Corporation, where the MIP test was performed and an extensive report for each rock type was generated.

iii. Overview of Environmental Protection Agency (EPA) Method 1315

EPA Method 1315 is a mass transfer rate, tank leaching test. The test consists of continuous leaching of water-saturated monolithic or compacted granular material with periodic renewal of the leaching solution at predetermined intervals (US EPA). After the exchanges, the eluate is analyzed for pH, conductivity, E_h, ICP-OES, TOC and other parameters of interest. This test was modified for the inclusion of lithium bromide (LiBr) as an ingress tracer and post-test profile characterization of the geomaterial samples.

iv. Scanning Electron Microscopy

A TESCAN VEGA3 SEM was used for imaging samples and Energy Dispersive Spectroscopy (EDS) software EDAX TEAM was used for elemental analysis. Samples were imaged in low vacuum using backscatter SEM. Regions were examined based on potential ingress profile determination as well as basic characterization of rock composition. Both line scans and point analysis of the samples were conducted. Samples analyzed with backscatter SEM for this paper included marl, phosphorite, and oil shale, which had undergone approximately 200 days of the 1315 leaching test. EPA method 1315 test is being continued for chalk and sandstone samples, which will be processed analyzed at a later date.

v. Petrographic Microscope Imaging

A Leitz Orthoplan microscope with a Leica DFC425 camera and Leica Application Suite software were used at 4x magnification to take images of the marl, phosphorite, and oil shale thin sections. Images were analyzed visually to determine key structures present in the rocks.

III. Results and Discussion

Host Rock Characterization

i. BET and MIP

The following table summarizes data obtained from BET and MIP tests. Marl, oil shale, and phosphorite rocks have the highest BET surface area and percent porosity, while chalk and

sandstone have the lowest BET surface area and percent porosity. Data reported seems reasonable, though the oil shale seems to have a high porosity for a shale. Typical porosity values for shales can be as low as 5% or as high as 20% (Manger, 1964).

Rock	BET Surface Area (m^2/g)	Porosity (%)	Average Pore diameter (um)	Total Pore Area (m2/g)	Total Intrusion Volume (mL/g)	Bulk density (g/mL)	Tortuosity (Calc)	Cumulative Pore Volume (mL/g)
Sandstone	0.4926	8.2597	0.3953	0.345	0.0341	2.4201	26.9447	0.0314
Marl	5.5523	31.6708	0.13764	4.983	0.1715	1.8471	87.5473	0.1318
Chalk	0.6428	6.8169	0.10467	1.056	0.0276	2.4672	67.6575	0.253
Phosphorite	15.0786	34.8568	0.03646	26.415	0.2408	1.4476	4.3768	0.121
Oil Shale	15.9254	32.8374	0.02751	25.318	0.1741	1.8858	64.966	0.1018

Table 2: Summary of porosimetry data from BET and MIP tests.

See Appendix A figures 1-5 for pore size distribution graphs obtained from the Micromeritics Instrument Corporation report. This data indicates that the rocks are comprised mostly of micropores, though sandstone has a slightly greater distribution of transitional pore sizes.

ii. Petrographic Microscope Images

Notable characteristics include fossils (M and OS), dark bands of organic matter (OS), and apatite grains within a calcite matrix (P). (Appendix B, figures 1-3)

iii. Backscatter SEM

Graphs and images from SEM analysis can be found in Appendix C.

When analyzing the thin sections under backscatter SEM, a few obstacles arose. First, detecting LiBr ingress proved a challenge, since the atomic weight of Li is too light for the SEM to detect, and the peak for Br overlaps with Al, creating uncertainty of an accurate Br measurement. The samples also proved to be noisy samples – even for expected elements, such as Ca. However, other factors can be examined to determine an ingress front. One method attempted was to determine a depletion zone of Ca. For data gathered from line scans, exponential smoothing in Microsoft excel was used to determine trends in the elemental composition or possible depletion zones. Marl and Oil Shale samples show a slight decrease in Ca counts less than 100 μm from the edge of the samples, before reaching a somewhat stable reading of Ca (Appendix C, figures 1 and 2). Phosphorite does not show this initial decrease, but Ca counts do start to increase approximately 500 μm from the edge of the sample (Appendix C, figure 3). Backscatter SEM images also offer insight to basic composition of the rocks. Within the phosphorite sample, there are noticeable changes as the line scan moves across one mineral to the next – i.e. moving from an apatite mineral to a carbonate mineral (Appendix C, figure 4).

IV. Conclusions

Lessons Learned

Imaging of the samples – through backscatter SEM and petrographic microscope – offers insight to the structure and composition of the rocks, while more traditional porosimetry analysis such as BET and MIP give valuable information regarding pore size distribution and surface area of materials. The characterization of these materials does not yield any surprises to the composition of the geomaterials. Continuing work with SEM/EDS analysis is important as a potential method to measure an accurate ingress profile.

Future Work

There is extensive work that can be done with SEM analysis of samples. SEM images should be further analyzed using image processing software such as MATLAB or ImageJ to determine porosity percent change and other parameters of interest. Further, there must be additional work done to determine an accurate ingress profile of the leached samples. In the cases of Ca depletion, Mg content should be examined to see what exchange may be taking place. While this work provides a good starting point of analysis of materials, the leaching profile is important to understanding the processes that involve ingress and egress of constituents of concern.

The next phase of this work should also include similar porosimetry studies of cement samples, utilizing BET, MIP, and electron microscopy. While some preliminary work has been conducted on cement samples, there remains a great deal of analysis to be completed.

V. Reflection

In my time at Sandia National Laboratories I have had the opportunity to garner hands on experience with methodologies and technologies that I might not have otherwise had the chance to work with. The work accomplished this summer has given me a better understanding and appreciation for the pace, dedication, and time that proper scientific research requires. While it is difficult to complete experimental, laboratory work in the scope of eight weeks, I believe that strides were taken to contribute to the overall project. Further, the things that I learned while at Sandia – beyond what has been presented in this paper – will offer valuable opportunities for me to utilize my new skill set at my university and beyond. The experience this summer offers a great jumping off place for continued work on the project.

Acknowledgements

It is important to first thank my mentors at SNL, Ed Matteo and Carlos Jove-Colon, without whom I would have been totally lost. Their time and expertise were greatly appreciated as I maneuvered my way through the project and life at Sandia. I would also like to thank the numerous others who helped me with my work this summer– Melissa Mills, Jessica Kruichak, and Carlos Lopez just to name a few.

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Appendix A: MIP Graphs – Pore size distribution

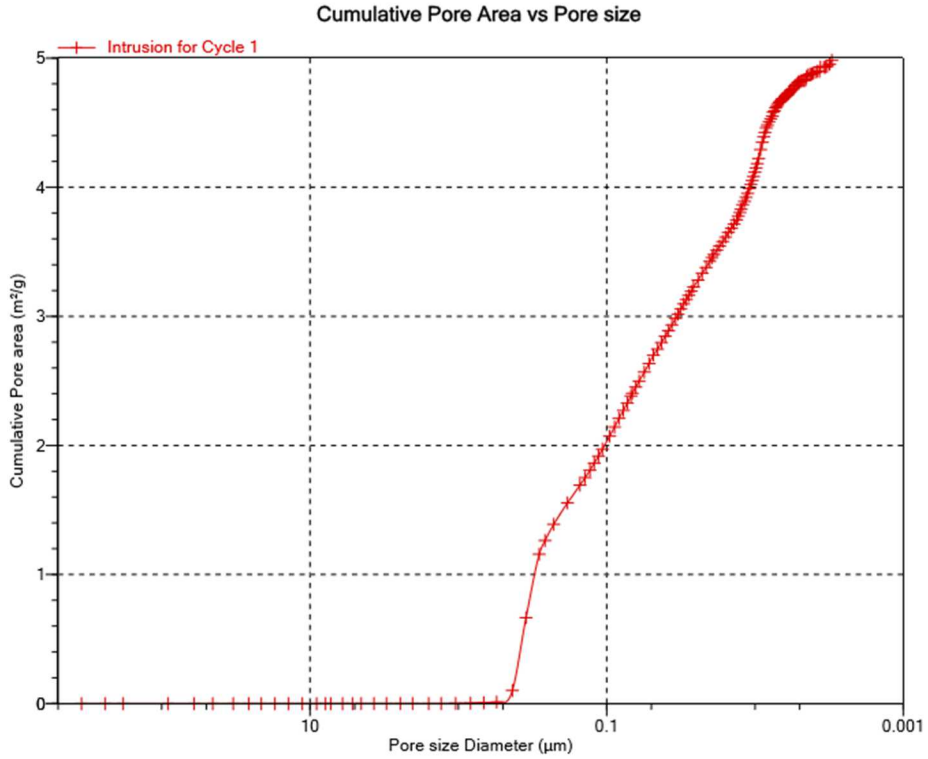


Figure 1: Marl MIP cumulative pore area vs pore size, consists primarily of micropores, with some transitional pore sizes.

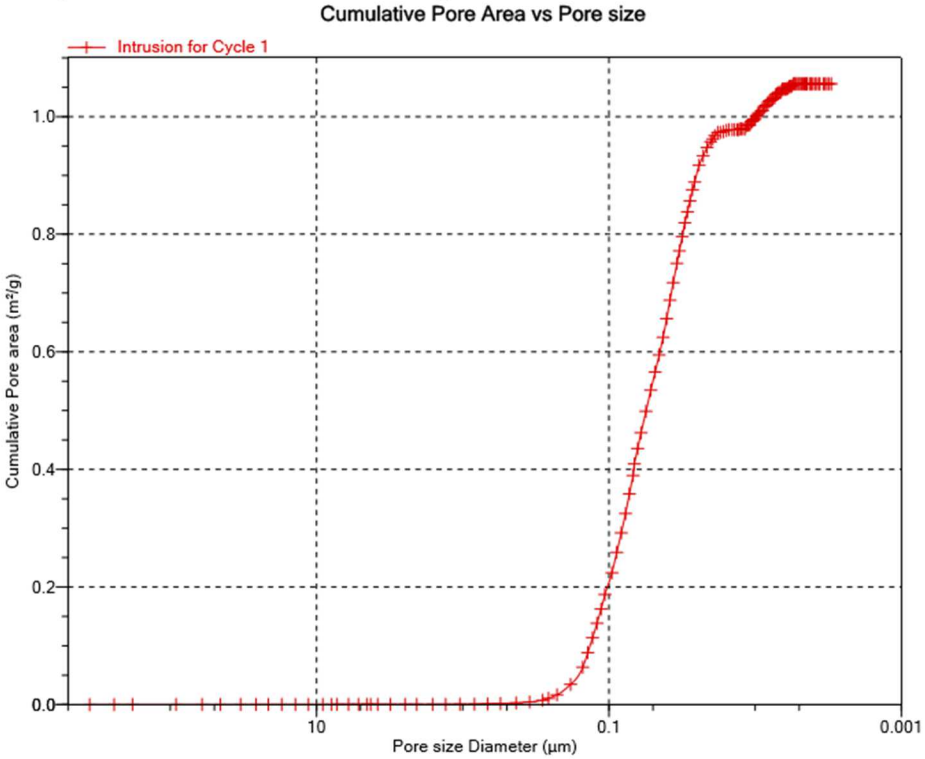


Figure 2: Chalk MIP cumulative pore area vs pore size, consists primarily of micropores.

Appendix A Continued

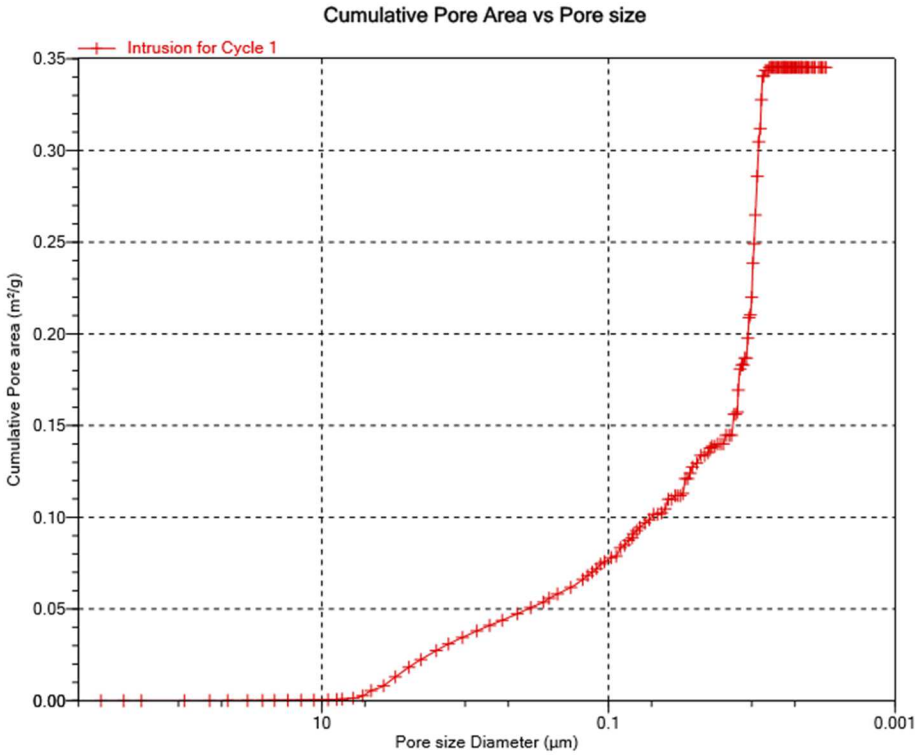


Figure 3: Sandstone MIP cumulative pore area vs pore size, consists of transitional and micropores.

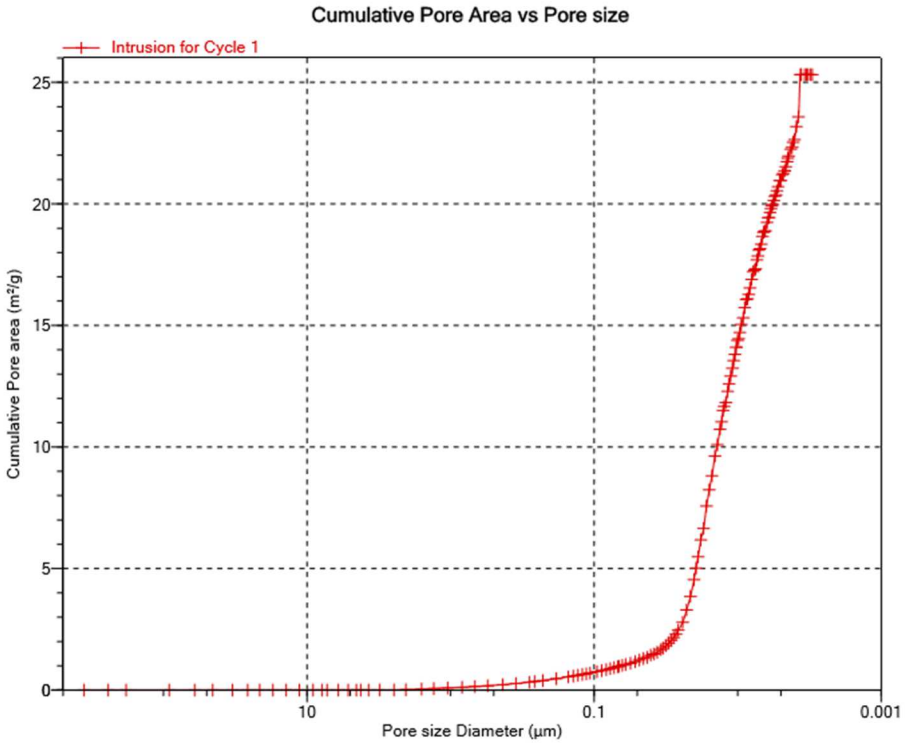


Figure 4: Phosphorite MIP cumulative pore area vs pore size, consists primarily of micropores.

Appendix A Continued

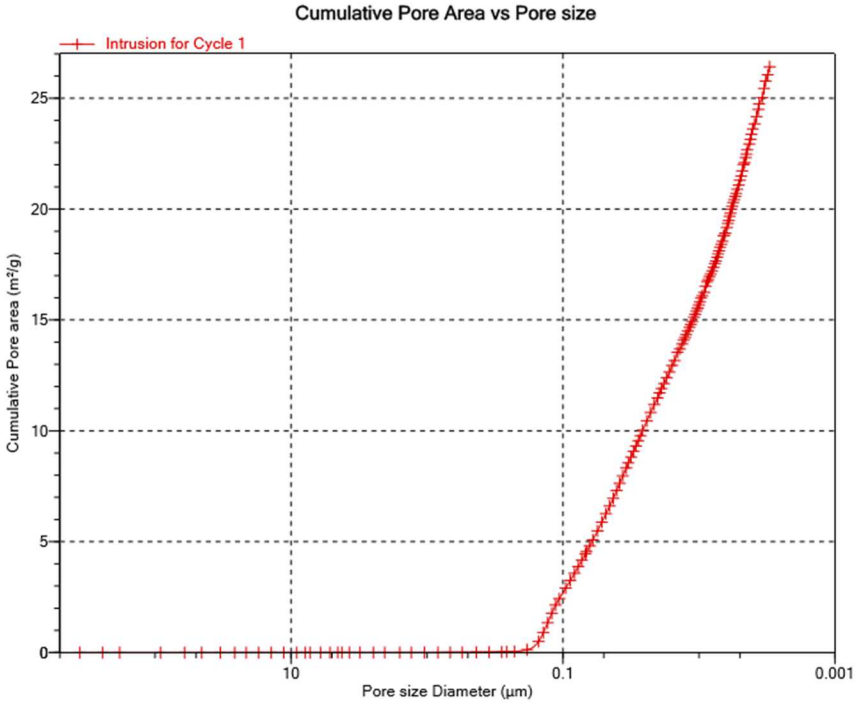


Figure 5: Oil Shale MIP cumulative pore area vs pore size, consists primarily of micropores.

Appendix B: Petrographic Microscope Images

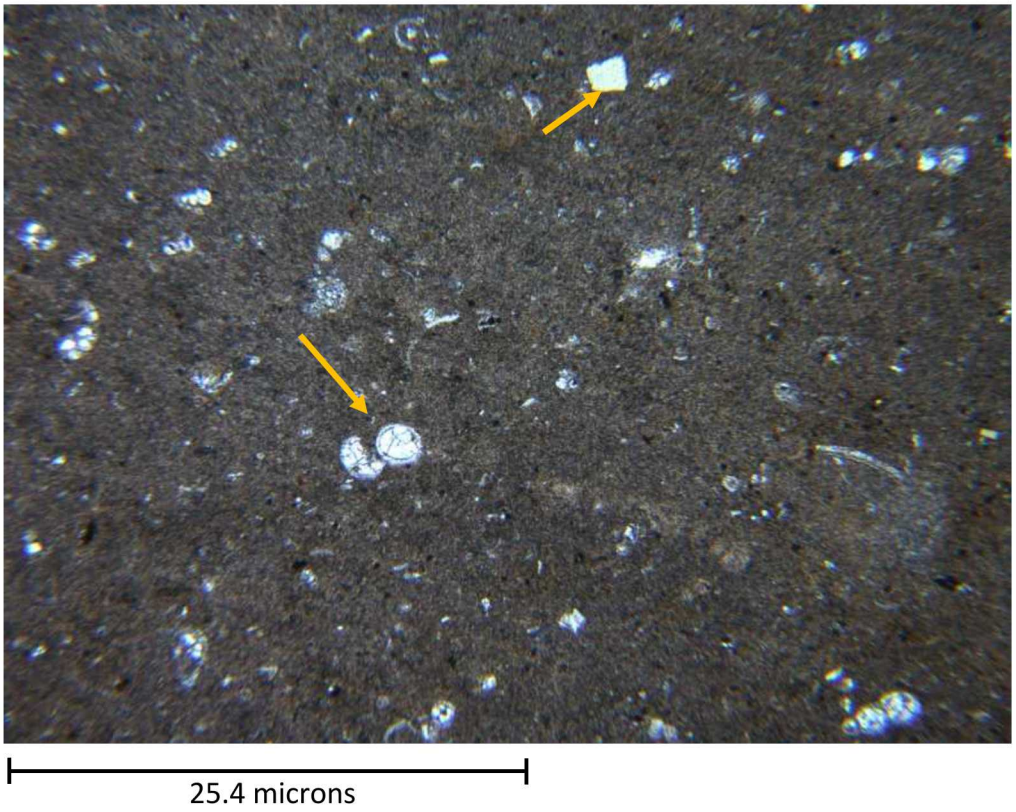


Figure 1: Petrographic image of marl thin section, showing fossils and quarts grain.

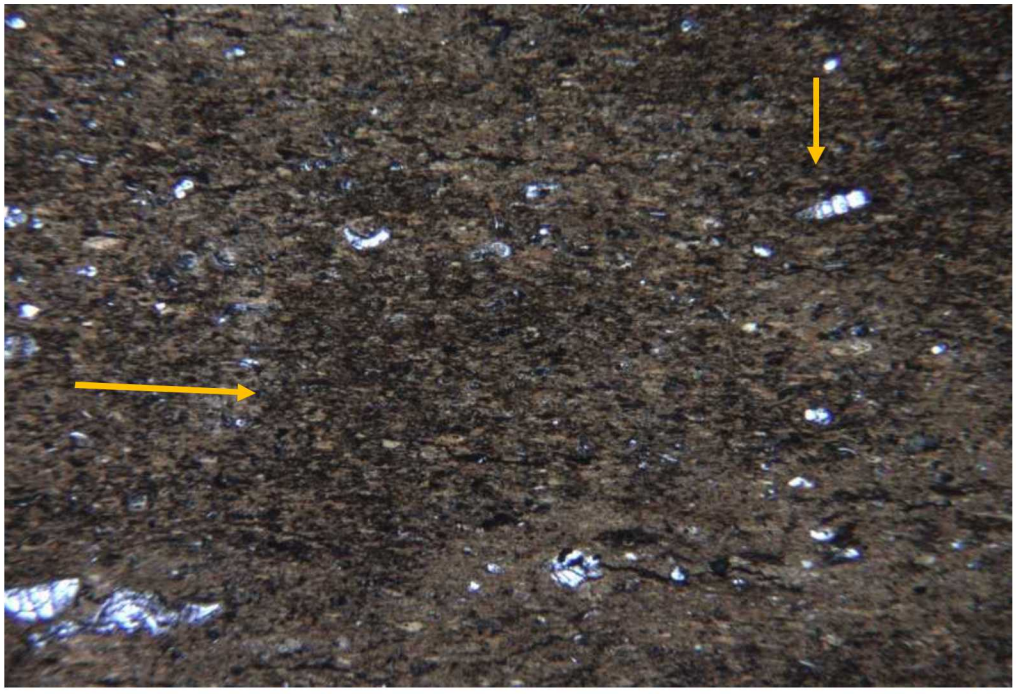


Figure 2: Petrographic image of oil shale thin section, showing fossils and dark banding.

Appendix B Continued

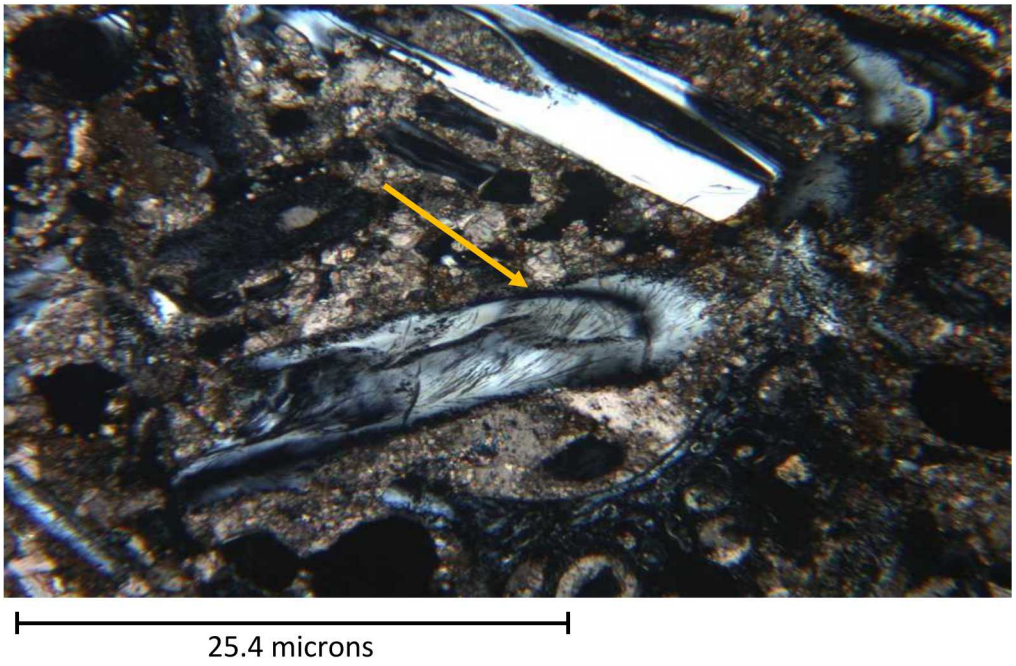
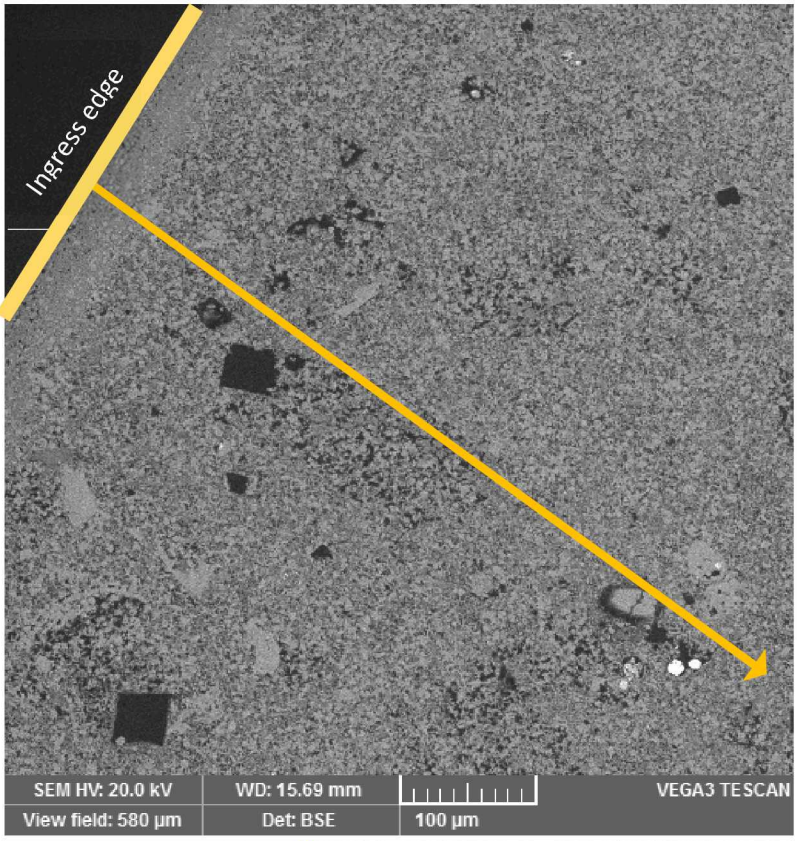


Figure 3: Petrographic image of phosphorite thin section, showing apatite grain within a calcite matrix.

Appendix C: SEM Data

Note: Blue line with arrow indicates line scan and direction of scan.



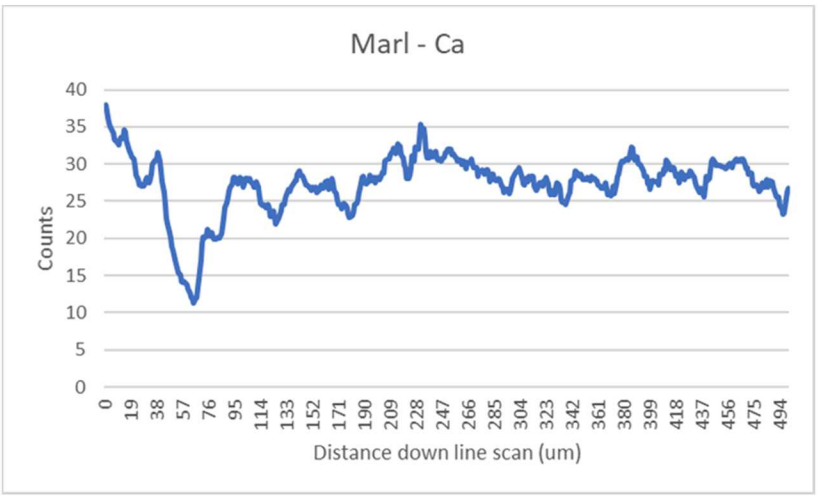
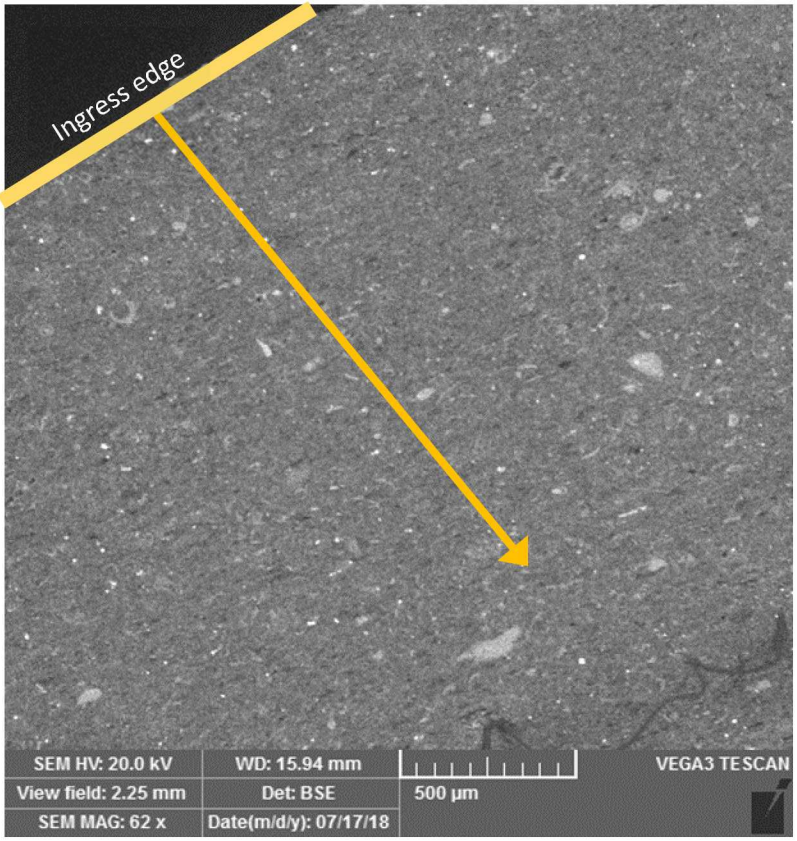


Figure 1: Marl thin section with image and graph of line scan. Shows some initial depletion of calcium



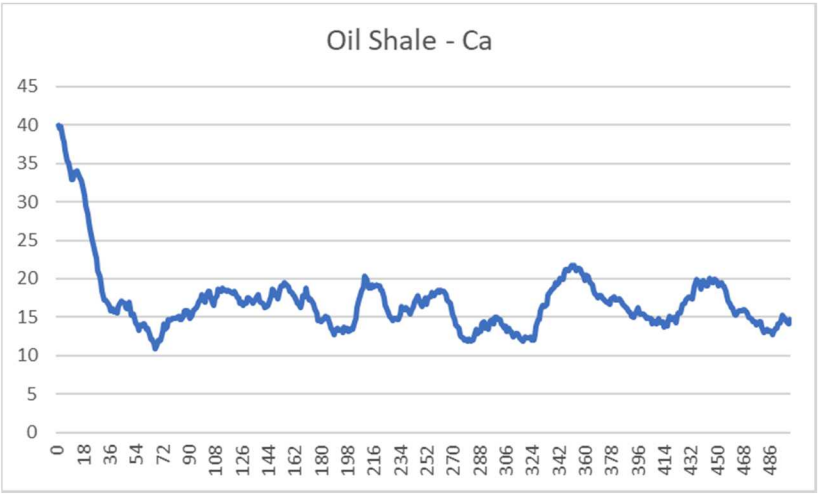
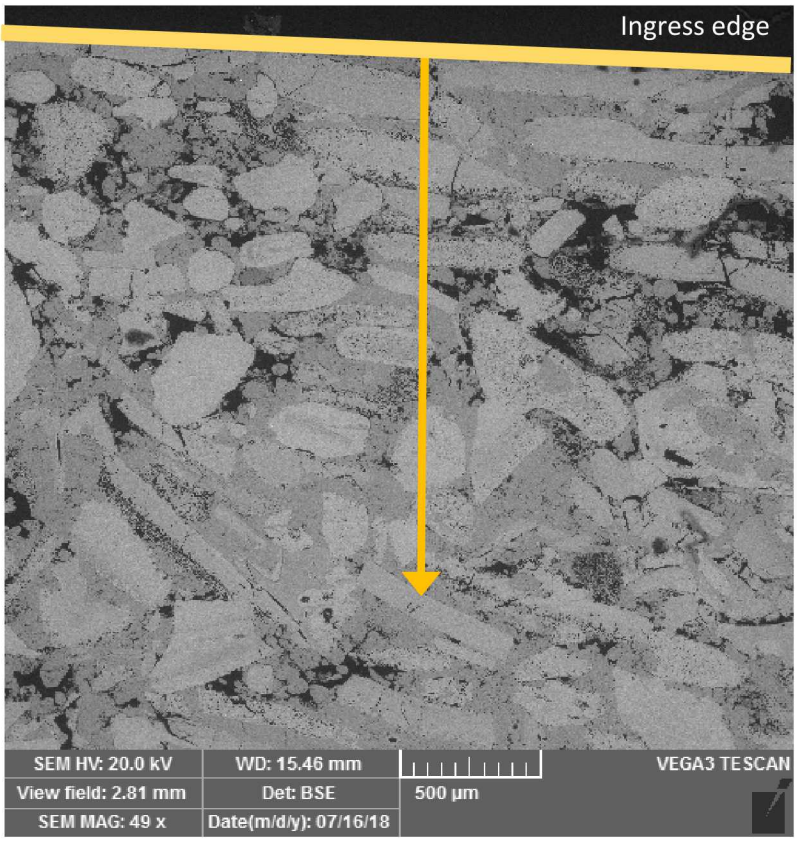


Figure 2: Oil shale thin section with image and graph of line scan. Shows some initial depletion of calcium.

Appendix C Continued



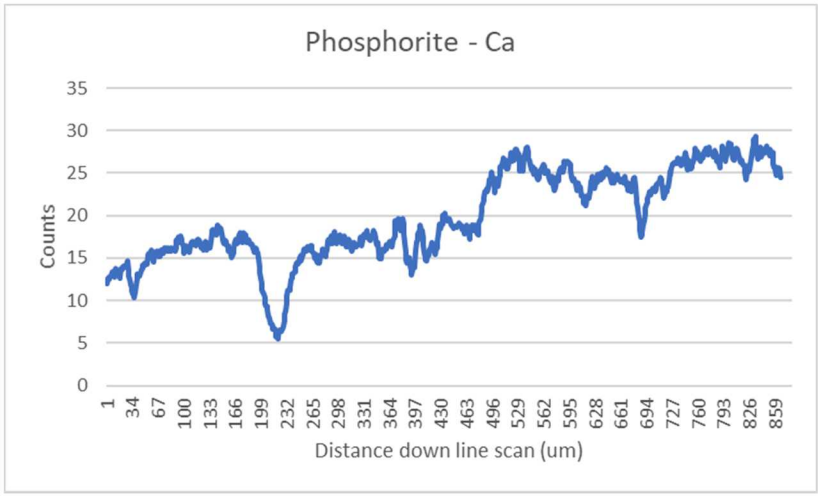
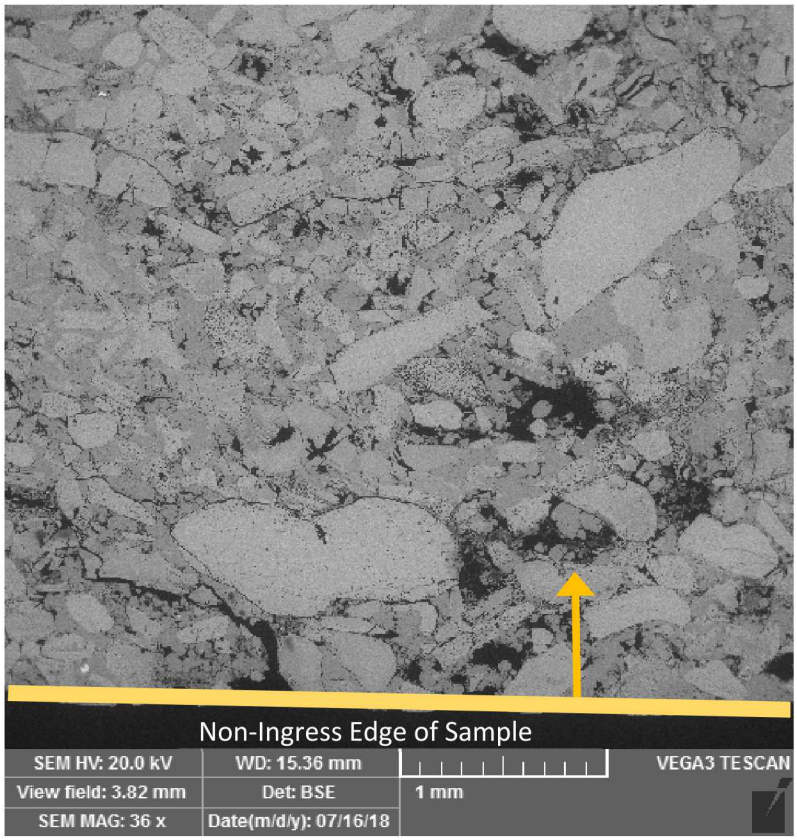


Figure 3: Phosphorite thin section with image and graph of line scan, showing increase of Ca away from the edge of the sample.



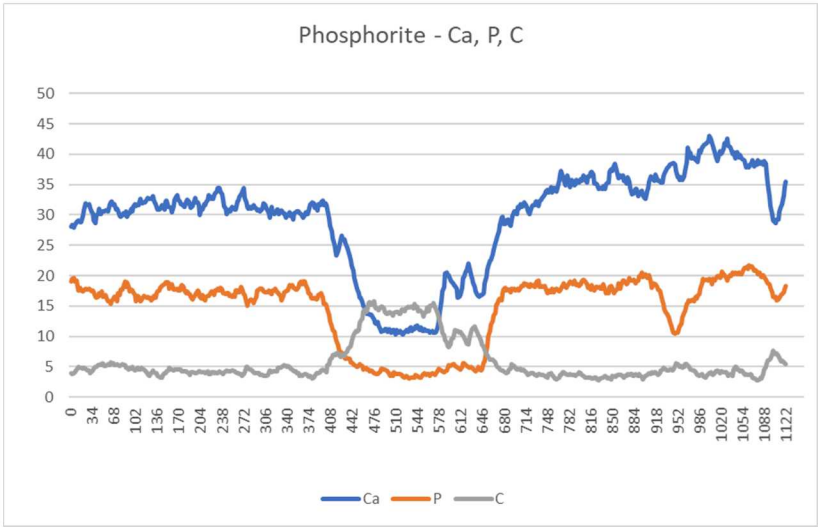


Figure 4: Phosphorite thin section with image and graph of line scan on opposite edge of sample. There are obvious changes in concentration moving from apatite grain to carbonate.