DISCERNING BIOGENIC FROM ABIOGENIC PHOSPHATES IN THE FOSSIL RECORD WITH APPLICATIONS FOR THE SEARCH FOR LIFE ON MARS

Prescott Vayda
Shuhai Xiao
Virginia Tech

Abstract

Earth is the only place in the universe currently known to sustain life. The long history of evolution from single celled organisms to the diversity we observe today is preserved in the geological record of our planet. Therefore, it is critical that we can accurately interpret that record to understand the history of life. Here we investigate phosphatic fossils from the early Cambrian (~540-510 Ma) of Yukon, Canada to evaluate how the fossils were preserved and their geochemical make up. The mineral chemistry of these fossils has the potential to record environmental parameters at the time the organisms were buried and preserved. We also discuss the diagenetic processes that may have later affected these records. We collected data on concentrations of major elements (e.g. Al, Si, P) first row transition elements (e.g. Sc, Ti, V), high field strength elements (e.g. Zr, Nb), rare earth elements (e.g. La, Ce, Nd), and U-Pb ratios for geochronology. Results of this work indicate that local diagenetic factors play a key role in the signal that is preserved for many geochemical proxies even on the scale of different spots on the same thin section. This variation was a stronger control than the type of material (e.g. fossil or cement) within the rock. This also suggests that these rocks have been geochemically "reset" later after burial. The most striking evidence of this later alteration is a consistent U-Pb date of ~438±7.3 Ma, which is nearly 100 million years younger than the age of the fossils in the rock. Despite this alteration, some signals may be representative of the original seawater conditions. Together, this data suggests that the record preserved in ancient phosphatic fossils is complex and records the history of not only the depositional conditions but also later diagenetic events. This work has useful applications in the study of phosphorites not only on Earth, but also in the search for extraterrestrial life such as the investigation of phosphatic deposits on Mars.

Introduction

The history of life on Earth spans nearly the entire 4.6 billion years since the planet formed (Schopf, 2006). We know so much about this history through what is preserved in the fossil record. The way that fossils are preserved plays a crucial role in what information is retained (Allison and Briggs, 1991). Our ability to accurately reconstruct the history of life on Earth is dependent on effectively extracting that information from the fossil record. Therefore, we must understand the processes that lead to fossilization in order to enhance our knowledge of how life started and evolved on Earth.

There are many different ways that fossils can be preserved, and each imparts its own biases on what biological or environmental information is preserved (Allison and Briggs, 1991). One of the most enigmatic yet significant taphonomic pathways is phosphatization. Phosphorus is the limiting macronutrient in the oceans on geologic timescales (Schiffbauer et al., 2014), so it is perplexing how there could be times in Earth's past that phosphorus was so abundant as to form meter thick crusts. The source of this phosphorus and its subsequent burial would have had significant impact on biological fluxes at the time (Cook and Shergold, 1984). Further, the phosphatization process has the capability of preserving subcellular detail, such as the oldest known fossil embryos (Xiao et al., 1998). In addition, calcium-phosphate minerals are generally robust and thought to be resistant to diagenetic alteration, making them a useful reservoir for geochemical clues to past environments (e.g. Suarez et al., 2010; Goldhammer et al., 2011). The combination of these characteristics makes phosphatization an important pathway for fossil preservation and a useful tool for reconstructing the past. There are also organisms, such as vertebrates, that use calcium-phosphate to build their skeleton, which means that some phosphatized fossils may be the original biomineralized material while others have been secondarily replaced. Distinguishing these two types can provide useful phylogenetic information for how organisms were building their skeletons and may have implications for what conditions are recorded in the geochemical data within these fossils.

One period in Earth history where we find an abundance of phosphatized fossils is the early Cambrian (~540-510 Ma) (Porter, 2004). This interval, sometimes referred to as the "phosphatization window" coincides with the rapid emergence and diversification of animal life (Zhuravlev and Wood, 2018). Fossils from this period provide insights into the origins of the diversity of animals we observe on Earth today. Many of these fossils do not closely resemble any extant organisms, so their phylogenetic placement remains a mystery. Characteristics such as what material they use to build their shell could help with placing them on the tree of life.

Geological Setting

The rocks and fossils used in this study were collected in the Wernecke Mountains in Yukon Canada (Fig. 1) during summer field seasons in 2022 and 2023. The stratigraphy in northwestern Canada consists of rocks from the Tonian period (~1000 Ma) to the Ordovician (~480 Ma) (Moynihan et al., 2019). This succession preserves the history of the breakup of the supercontinent Rodinia and the formation of a passive continental margin on the paleogeographically northern coast of Laurentia. During this time, northwestern Canada was a shallow ocean basin, which provides us with a near continuous and fossil rich record of this critical time interval (Scott et al., 2022). Our field sites are located approximately 185 km northeast of Mayo. We collected rocks and fossils from two early Cambrian units: the Ingta and Sekwi formations.

Ingta Formation

The Ingta Formation is approximately 250 m thick and consists of a mix of clastic and carbonate units (Aitken, 1989). Most of the unit is made up of green and brown siltstone which is capped by peloidal and micritic beds. At the very top of the unit is a phosphatic crust which contains phosphatic small shelly fossils (Pyle et al., 2006). These fossils indicate the Ingta Formation is earliest Cambrian in age (Conway Morris and Fritz, 1985; Nowlan, Narbonne, and Fritz, 1985).

Figure 1: Map of Yukon, Canada showing location of field site.

The Ingta Formation also contains trace fossils that corroborate this age (MacNoughton and Narbonne, 1999). The Ingta Formation unconformably overlies the dolomitic Risky Formation and is overlain by the quartzitic Backbone Ranges Formation (Aitken, 1989).

Sekwi Formation

The Sekwi Formation ranges in thickness from 500 m to over 1000 m (Handfield, 1968). The unit is made up of gray bedded limestone, orange weathering dolostone, and gray silty limestone (Fritz, 1976). The Sekwi Formation contains abundant fossil material including archaeocyaths, brachiopods, chanceloriids, trilobites, and abundant small shelly fossils (Fritz, 1972; Stelck and Hedinger, 1975; Randell et al., 2005). Based on the trilobite biostratigraphy, the Sekwi Formation is in the *Bonnia-Olenellus* zone, which corresponds to Cambrian Stage 4 (514-509 Ma) (Fritz, 1972). The Sekwi Formation conformably overlies the shaley Vampire Formation and is unconformably overlain by the shaley Hess River Formation (Fritz et al., 1991).

Methods

Sample Collection

Phosphatic material from the Ingta and Sekwi formations was collected over summer field seasons in 2022 and 2023. Carbonate rocks bearing phosphatic grains and visible phosphatic fossils were targeted for collection. Samples were brought back to Virginia Tech and prepared for thin sectioning. Microprobe polished thin sections were produced by an external lab.

Elemental Maps

We produced elemental maps of target areas of thin sections using the JEOL JXA-iHP200F Electron Probe Micro Analyzer (EPMA) in the Electron Microprobe Lab at Virginia Tech. We used a voltage of 15 keV and a nominal beam current of 10 nA. The EDS analysis used a JEOL JED-2300 30-mm dry SDD-EDS detector. The maps were sampled at a resolution of 512 x 384 pixels, a dwell time of 0.2 ms, and 7-10 frames. Elemental maps were used to identify specific materials to target for elemental analysis.

Elemental Analysis

Elemental concentration data was collected in the Laboratory for Isotopes and Metals in the Environment (LIME) at the Penn State University. Concentration data was collected for Mg, Al, Si, P, S, Sc, Ti, V, Mn, Fe, As, Sr, Y, Zr, Nb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb, Th, and U. We used the iCAP-RQ ICP-MS and the New Wave 193 nm excimer laser ablation system (NWR193) with a 50 μm spot size for analysis. In total 295 spots were analyzed across 3 thin sections. U/Pb data was analyzed using IsoplotR. Elemental data was analyzed in R and the REE data was normalized to Post Archean Australian Shale (PAAS). Elemental analysis has only been conducted on Ingta Formation thin sections at this time.

Results

Petrographic Analysis

Ingta Formation

The phosphatic grains, cements, and fossils are found in carbonate grainstones. In addition to the phosphatic material, the rocks also contain rounded quartz grains, carbonate peloids, and calcitic fossils (Fig. 2). Most of the grains are less than 100 μm in diameter except for some fossil grains. Most fossils are simple, conical tubes and can be over 1 mm in length. Phosphatic fossils appear black or dark brown in color. Many of the phosphatized fossils are preserved as phosphatic internal molds, with some retaining a calcitic shell. More rarely, the shell is preserved in phosphate as either original material or a cast of an originally calcitic shell. Fossil abundance varies by layer with some portions containing no fossils and only quartz grains in a carbonate cement. The phosphatic cements appear

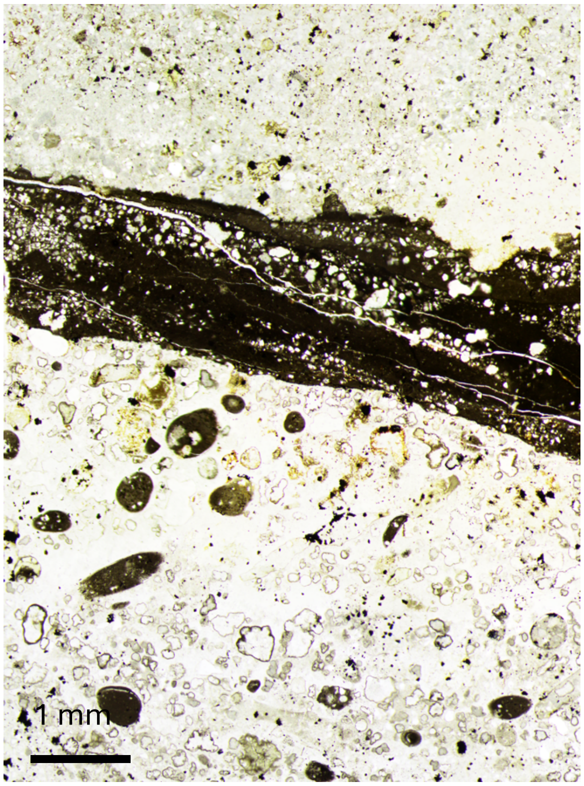

Figure 2: Petrographic micrograph of sample from the Ingta Formation showing calcite matrix (white) with abundant quartz sand grains (also white) and phosphatic crust (black). Note the lack of fossil material above the phosphatic crust and the abundant fossils, often phosphatized, below the crust

black or gray in color (Fig. 2). Often, they occur in planar sheets with parallel laminations. Phosphatized fossils are sometime found within the phosphatic cements, and they appear similar in color. There are also regions of coarse dolomite and pyrite.

Sekwi Formation

The Sekwi Formation rocks consist of carbonate grainstones and wackestones (Fig. 3). Grains include fossils both phosphatized and calcareous, carbonate peloids, and carbonate and phosphatic rip-ups. Identifiable fossils include archaeocyaths and brachiopods. Phosphatized archaeocyaths are internal molds (Fig. 3) whereas brachiopods are originally phosphatic. Phosphatic material is generally gray to black in color. There are no laminated phosphatic cements like those observed in the Ingta Formation. The Sekwi Formation thin sections contain abundant, thin, vertical fractures that have been infilled with calcite cement (Fig. 3).

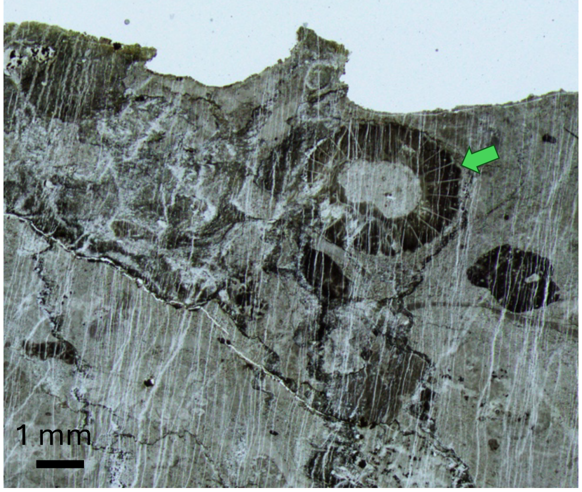

Figure 3: Petrographic micrograph of sample from the Sekwi Formation showing calcite matrix (gray) with phosphatic grains (black), cements (black), and phosphatized archaeocyath (indicated by green arrow). Sub-vertical white lines are fractures infilled with calcite.

<u>U/Pb age dates</u>

When all 295 samples are considered together, the U/Pb data give a concordia age of 438.8±7.3 Ma (Fig. 4). All samples exhibit some degree of lead loss. However, the data are strongly colinear suggesting a single age for all the samples. When only fossil spots (n=84) are analyzed, the U/Pb data give a concordia age of 463.3±7.5 Ma, similar to the overall data.

<u>REE concentrations</u>

The concentrations measured in samples range from 0.3 to 30 PAAS normalized values (Fig. 5). Most of the data show a “dome” or “hat” shape that is common for phosphatic material of this age. This shape is characterized by a relative enrichment of middle rare earth elements. Much of the data is characterized by a positive cerium anomaly, positive, a europium anomaly, and a positive yttrium anomaly. Measurements from the same general location on a thin section tend to be more similar in their pattern and overall concentrations (Fig. 5A).

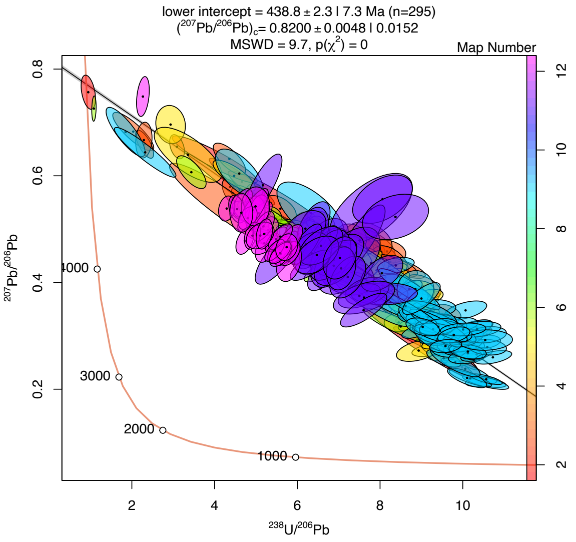

Figure 4: Concordia plot for U/Pb ages for all samples (n=295). Samples are colored by map, which corresponds to each of the twelve target areas across the three thin section.

Samples do not appear to cluster based on material type (e.g. fossil or cement) (Fig. 5B). Samples with higher aluminum concentration tend to have higher concentrations of rare earth elements, but this does not appear to affect the overall shape of the curve (Fig. 5C).

Discussion

Thin Sections

Petrographic analysis allows for the identification of textures and minerals that provide a history of how the rock formed and was altered over time. The formational processes are critical to the preservation of the fossils and the accompanying geochemical signals. Later alteration can impact the biological information preserved in the rock and the environmental conditions recorded in the geochemistry.

The phosphatic material found in both units have likely been transported at least a short distance due to the fragmentary nature of many fossils and the concentration of material. It is unclear whether the phosphatization happened before or after transport. The presence of carbonate fossil material (especially large fragments of archaeocyaths in the Sekwi Formation) are perhaps suggestive that the phosphatization happened after transport as not all material was altered the same.

Laminated phosphatic cements in the Ingta Formation thin sections are suggestive of microbial fabrics (Fig. 2) and may indicate the role that microbes play in the phosphatization process. This mechanism would indicate that the phosphatization happened relatively early after burial. The Sekwi Formation samples did not have any laminated fabrics, which may be suggestive of a different phosphatization mechanism. Additionally, the Sekwi Formation contains more rounded phosphatic clasts that could possibly represent material that was phosphatized before transport (Fig. 3), suggesting the possibility of different or multiple phosphatization mechanisms in this basin during this time interval (Creveling et al., 2014).

The dark color of the phosphatic material in both the Ingta and Sekwi formations is perhaps an indicator of greater thermal alteration, similar to that seen in conodonts (Epstein, Epstein, and Harris, 1977). The presence of dolomite and pyrite in the Ingta samples and the abundant fractures in the Sekwi samples are also likely evidence of later diagenetic fluids moving through the rock (Zhang et al., 2014). This potential for alteration has implications for the geochemical signal preserved in the rocks.

U/Pb Analysis

The U/Pb dates obtained from the material are robust and concordant. The age of ~438 Ma is nearly 100 million years younger than the inferred age of the fossils based on the known occurrence of the *Anabarites trisulcatus* biozone in radiometrically dated rocks at other localities around the globe (Peng, Babcock, and Ahlberg, 2020). This date is relatively consistent between fossil and non-fossil material, suggesting that the entire system was affected by some process later after burial. Other ancient phosphatic deposits have been documented to have U/Pb dates younger than the inferred age based on other techniques, however previous discrepancies have been no greater than ~30 Ma (e.g. Aubineau et al., 2024). While calcium phosphate is highly insoluble and generally considered resilient to geochemical alteration, the large divergence between the actual age and the recorded age in these samples is suggestive of some event that "reset" the geochemical clock. The paleo-northern (now western) margin of Laurentia was still experiencing rifting until the Silurian (Pyle and Barnes, 2001), which would correspond with the ~438 Ma age recorded in the phosphatic materials. The end of rifting, and related thermal activity, could have allowed the geochemistry to stabilize, thus closing the U/Pb system. While these results demonstrate that the geochemistry of the samples has been altered since their deposition, each elemental system behaves independently and may record a signal of different events.

<u>REE Analysis</u>

The samples from the Ingta Formation overall show very similar trends in rare earth element (REE) concentrations across multiple samples and all materials. The distinctive dome shaped enrichment of middle REEs is common in early Paleozoic phosphorites, both abiogenic materials and biomineralized fossil (Lecuyer et al., 1998; Shields and Stille, 2001). When the data is sorted by material type (e.g. fossil or cement) there is no clear distinguishing between the groups, perhaps suggesting that they were formed through the same process, or later altered and homogenized. The greatest tool for grouping the samples is based on which map area the sample came from. Samples from one map are more similar to each other regardless of material than they are to samples from another map of the same material (Fig. 5A). Further, when comparing maps, samples from different maps on the same thin section show just as much variability as samples on different thin sections. This suggests that the heterogeneity that does exist in the samples is incredibly locally variable at the millimeter scale.

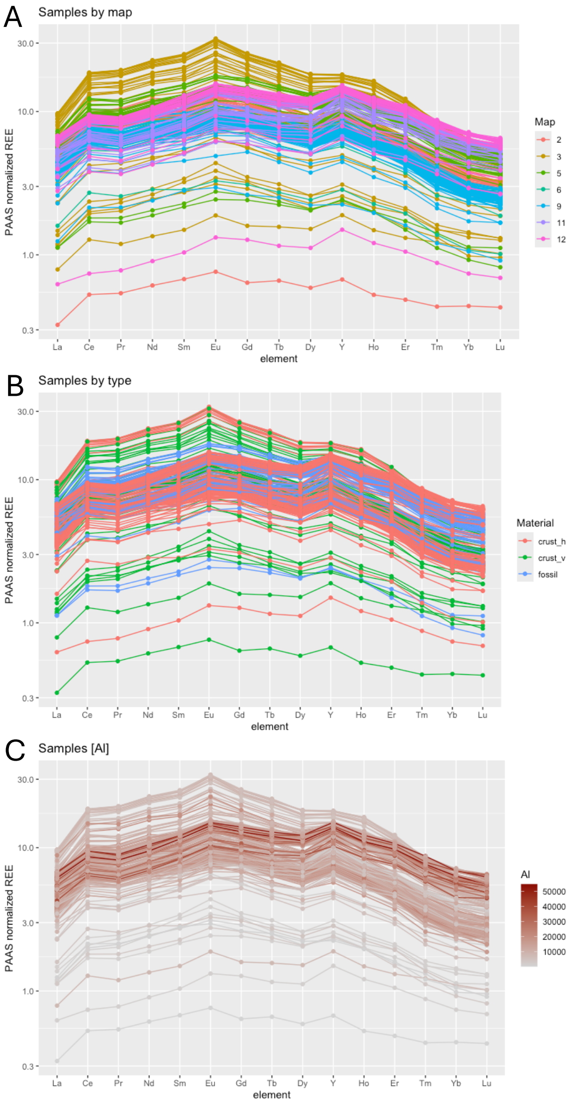

Figure 5: Rare Earth Element concentration plots for all data. 5A, data colored by mapping area. 5B, data colored by material type where crust_h is a horizontal transect through a laminated cement and crust_v is a vertical transect across a laminated cement. 5C, data colored by aluminum concentration.

Particular trends in REE curves have been used as proxies for particular geochemical changes in the environment. The first of these proxies is the cerium anomaly. Cerium is unique among the rare earth elements for being redox sensitive (Tostevin et al., 2016). In oxic conditions, it bonds with oxygen to form a solid, thus pulling cerium out of the water column. As such, well oxygenated water, such as the modern ocean, is characterized by a negative cerium anomaly (having less cerium than expected based on lanthanum and praseodymium concentrations). Most of the samples from this study show a slightly positive cerium anomaly, suggesting anoxic conditions. Depending on when the phosphatic materials formed, this could indicate an anoxic water column, anoxic pore waters, or anoxic diagenetic fluids moving through the rock at a later time. Considering the abundance of fossils in these units, it is unlikely that the water column was largely anoxic, so the phosphatic material must not have formed in equilibrium with seawater. This is important to recognize if these phosphatic materials were to be used for other geochemical proxies such as oxygen isotopes, which are used as a proxy for water temperature. These samples would record the conditions in the sediment sometime after burial, which may vary from the overlying seawater. The samples also show a small positive europium anomaly. Europium is slightly enriched in modern seawater, although greater concentration can occur due to the preferential incorporation of europium by clay minerals or due to alteration from hydrothermal fluids (Tostevin et al., 2016). Aluminum concentration can serve as an estimation of clay content in a sample. There is no apparent strong correlation between aluminum content and the magnitude of the europium anomaly in these samples, suggesting that clay mineral enrichment is not a major cause of the observed anomaly. There is a possibility that this signal is the result of later alteration by diagenetic fluids that moved through the rock, possibly associated with rifting processes throughout the early Paleozoic in the region, however, the magnitude of the europium anomaly is rather small and can be fully explained by recording a seawater like signal. Many samples also exhibit a small positive yttrium anomaly. A positive yttrium anomaly is also recognized as a signal for seawater (Tostevin et al., 2016). A higher value generally corresponds to the open ocean, while a smaller positive value is attributed to more restricted settings. This, in conjunction with the positive europium anomaly might suggest that the signal recorded in these rocks is not too far removed from seawater. Porewater that has been depleted in oxygen due to microbial metabolisms but otherwise is in connection with seawater may be expected to give a signal similar to that observed in these rocks.

The greatest test for these results will be the examination of the Sekwi Formation material which includes phosphatic brachiopods that we know were formed in the water column. Direct comparison between original biomineral in brachiopods and known secondary phosphate in archaeocyaths will help determine the role of diagenetic alteration on the signal that we get from these rocks. Further, we know that there is a time gap between the fossils of the Ingta formation and the Sekwi Formation, so a comparison between the units will give clues to the timing of any alteration that occurred in these rocks.

Applications to Extraterrestrial Systems

Phosphorus is a critical nutrient for all life on Earth. As such, it has been suggested that finding phosphorus on other planets is a key first step in finding evidence of life on other worlds (Weckworth and Shidlowski, 1995; Mojzsis and Arrhenius, 1998). The results from multiple successful rover missions to Mars include the identification of phosphatic minerals on Mars' surface (Maciá et al., 1997; Maurice et al., 2016). These phosphatic phases would not only provide a source of phosphorus for life on Mars, but also serve as an archive of geochemical conditions in the history of the red planet. By better constraining the processes that impact the record of phosphatic minerals on Earth, we will be better equipped to accurately interpret the material that we recover from Mars.

Conclusion

Phosphatic minerals are critical to the existence of life on Earth and the record of their history. By studying phosphatized fossils, we can learn about the biology of ancient organisms and also gain insights into the environments they lived in. Interpreting the record preserved in phosphatic deposits is dependent on our comprehensive understanding of the processes that control the preservation of phosphatized fossils. Here we demonstrate that phosphatic fossils from the early Cambrian of Yukon, Canada preserve a mix of original depositional signals that have been affected by later alteration. Together, this data preserves the history of not only the fossils, but also the conditions in which they were preserved, and the later tectonic history of the region. Phosphatic minerals have already been identified on Mars and will likely prove useful in reconstructing the history of the planet and provide the greatest potential for discovering life beyond Earth.

Acknowledgements

All fossil material comes from land of the First Nation of Na-cho Nyäk Dun and has been collected with their permission. I thank my advisor, Shuhai Xiao, for guidance at every step of this project. I thank Justin Strauss, Scott Evans, and Reina Harding for assistance with collecting fossil material in the field. I thank Kim Lau and Joshua Garber for assistance with collecting geochemical data and subsequent analysis of that data. This research is funded by grants from the National Science Foundation, the Paleontological Society, Virginia Tech Department of Geosciences, and the Virginia Space Grant Consortium.

References

Aitken, J. D. 1989. Uppermost Proterozoic Formations in Central Mackenzie Mountains, Northwest Territories. Geological Survey of Canada, Bulletin 368: 1-26.

Allison, P. A. and D. E. G. Briggs. 1991. Taphonomy: releasing the data locked in the fossil record. Plenum Press.

Aubineau, J., M. Séranne, E. C. Fru, M. Poujol, R. El Bamiki, P. Y. J. Antonio, M. Muñoz, A. Elghali, O. Raji, E.-S. Jourani, J.-L. Bodinier, and F. Parat. 2024. Deciphering the U-Pb dates of sedimentary phosphates: A complex example from the Upper Cretaceous-Lower Paleogene series in northwestern Morocco. Chemical Geology, 661:122178.

Conway Morris, S., and W. H. Fritz. 1980. Shelly microfossils near the Precambrian-Cambrian boundary, Mackenzie Mountains, northwestern Canada. Nature, 286: 381-384.

Creveling, J. R., D. T. Johnston, S. W. Poulton, B. Kotrc, C. März, D. P. Schrag, and A. H. Knoll. 2014. Phosphorus sources for phosphatic Cambrian carbonates. Geological Society of America Bulletin, 126: 145-163.

Cook, P. J. and J. H. Shergold. 1984. Phosphorus, phosphorites and skeletal evolution at the Precambrian-Cambrian boundary. Nature, 308:231-236.

Epstein, A. G., J. B. Epstein, and L. D. Harris. 1977. Conodont color alteration – an index to organic metamorphism. USGS Professional Paper, 995:1-27.

Fritz, W. H. 1976. Lower Cambrian Stratigraphy Mackenzie Mountains, Northwestern Canada. Geological Survey of Canada, Open File 333: 1-20.

Fritz, W. H., M. P. Cecile, B. S. Norford, D. Morrow, and H. H. J. Geldsetzer. 1991. Cambrian to Middle Devonian Assemblages. Geological Survey of Canada, Geology of Canada: 151-218.

Goldhammer, T., B. Brunner, S. M. Bernasconi, T. G. Ferdelman, and M. Zabel. 2011. Phosphate oxygen isotopes: Insights into sedimentary phosphorus cycling form the Benguela upwelling system. Geochimica et Cosmochimica Acta, 75:3741-3756.

Handfield, R. C. 1968. Sekwi Formation, A New Lower Cambrian Formation in the Southern Mackenzie Mountains, District of Mackenzie (95L, 105I, 105P). Geological Survey of Canada, Paper 68-47: 1-23.

Lécuyer, C. P. Grandjean, J.-A. Barrat, J. Nolvak, C. Emig, F. Paris, and M. Robardet. 1998. d18O and REE contents of phosphatic brachiopods: A comparison between modern and lower Paleozoic populations. Geochimica et Cosmochimica Acta, 62(14):2429-2436.

Maciá, E., M. V. Hernández, and J. Oró. 1997. Primary sources of phosphorus and phosphates in chemical evolution. Origins of life and evolution of the biosphere, 27: 459-480.

MacNoughton, R. B., and G. M. narbonne. 1999. Evolution and Ecology of Neoproterozoic-Lower Cambrian Trace Fossils, NW Canada. Palaios, 14: 97-115.

Maurice, S., S. M. Clegg, R. C. Wiens, O. Gasnault, W. Rapin, O. Forni, A. Cousin, V. Sautter, N. Mangold, L. Le Deit, M. Nachon, R. B. Anderson, N. L. Lanza, C. Fabre, V. Payre, J. Lasue, P. Y. Meslin, R. J. Leveille, B. L. Barraclough, P. Beck, S. C. Bender, G. Berger, J. C. Bridges, N. T. Bridges, G. Dromart, M. D. Dyar, R. Francis, J. Frydervang, B. Gondet, B. L. Ehlmann, K. E. Herkenhoi, J. R. Johnson, Y. Langevin, M. B. Madsen, N. Melikechi, J. L. Lacour, S. Le Mouelic, E. Lewin, H. E. Newsom, A. M. Ollila, P. Pinet, S. Schroder, J. B. Sirven, R. L. Tokar, M. J. Toplis, C. d'Uston, D. T. Vaniman, and A. R. Vasavada. 2016. ChemCam activities and discoveries during nominal mission of the Mars Science laboratory in Gale crater, Mars. Journal of Analytical Atomic Spectrometry, 31:863-889.

Mojzsis, S. J., and G. Arrhenius. 1998. Phosphates and carbon on Mars: exobiological implications and sample return considerations. Journal of Geophysical Research, 103: 28495-28511.

Moynihan, D. P., J. V. Strauss, L. L. Nelson, and C. D. Padget. 2019. Upper Windermere Supergroup and the transition from rifting to continent margin sedimentation, Nadaleen River area, northern Canadian Cordillera. Geological Society of America Bulletin, 131: 1673–1701.

Nowlan, G. S., G. M. Narbonne, and W. H. Fritz. 1985. Small shelly fossils and trace fossils near the Precambrian-Cambrian boundary in the Yukon Territory, Canada. Lethaia, 18:233-256.

Peng, S. C., L. E. Babcock, and P. Ahlberg. 2020. Chapter 19: The Cambrian Period. Geologic Timescale 2020, 2:565-629.

Porter, S. M. 2004. Closing the phosphatization window: Testing for the influence of taphonomic megabias on the pattern of small shelly fossil decline. Palaios, 19:178–183.

Pyle, L. J., G. M. Narbonne, G. S. Nowlan, S. Xiao, and N. P. James. 2006. Early Cambrian metazoan eggs, embryos, and phosphatic microfossils from northwestern Canada. Journal of Paleontology, 80:811-825.

Pyle, L. J., and C. R. Barnes. 2001. Ordovician-Silurian stratigraphic framework, Macdonald Platform to Ospika Embayment transect, northeastern British Columbia. Bulletin of Canadian Petroleum Geology, 49(4):513-535.

Randell, R. D., B. S. Lieberman, S. T. Hasiotis, and M. C. Pope. 2005. New Chancelloriids from the Early Cambrian Sekwi Formation with a Comment on Chancelloriid Affinities. Journal of Paleontology, 79:987-996.

Schiffbauer, J. D., A. F. Wallace, J. Broce, and S. Xiao. 2014. Exceptional fossil conservation through phosphatization. in Marc Laflamme, James D. Schiffbauer and Simon A. F. Darroch (eds.), Reading and Writing of the Fossil Record: Preservational Pathways to Exceptional Fossilization (The

Paleontological Society Papers, Volume 20).

Schopf, J. W. 2006. The first billion years: When did life emerge?. Elements, 2:229–233.

Scott, R. W., E. C. Turner, R. B. MacNoughton, and K. M. Fallas. 2022. Biostratigraphic evidence for incremental tectonic development of early Cambrian deep-water environments in the Misty Creek embayment (Selwyn basin, Northwest Territories, Canada). Canadian Journal of Earth Science, 59:216-231.

Shields, G., and P. Stille. 2001. Diagenetic constraints on the use of cerium anomalies as paleoseawater redox proxies: an isotopic and REE study of Cambrian phosphorites. Chemical Geology, 175:29-48.

Stelck, C. R., and A. S. Hedinger. 1975. Archaeocyathids and the Lower Cambrian Continental Shelf of the Canadian Cordillera. Canadian Journal of Earth Science, 12:2014-2020.

Suarez, C. A., G. L. Macpherson, L. A. González, and D. E. Gradnstaff. 2010. Heterogenous rare earth element (REE) patterns and concentrations in a fossil bone: Implications for the use of REE in vertebrate taphonomy and fossilization history. Geochimica et Cosmochimica Acta, 74:2970-2988.

Tostevin, R., G. A. Shields, G. M. Tarbuck, T. He, M. O. Clarkson, and R. A. Wood. 2016. Effective use of cerium anomalies as a redox proxy in carbonate-dominated marine setting. Chemical Geology, 438:146-162.

Weckworth, G., and M. Shidlowski. 1995. Phosphorus as a potential guide in the search for extinct life on Mars. Advances in Space Research, 15:185-191.

Xiao, S., Y. Zhang, and A. H. Knoll. 1998. Three-dimensional preservation of algae and animal embryos in a Neoproterozoic phosphorite. Nature, 391:553-558.

Zhang, W., P. Guan, X. Jian, F. Feng, and C. Zou. 2014. In situ geochemistry of Lower Paleozoic dolomites in the northwestern Tarim basin: Implications for the nature, origin, and evolution of diagenetic fluids. Geochemistry, Geophysics, Geosystems, 15(7):2744-2764.

Zhuravlev, A., Yu., and Rachel A. Wood. 2018. The two phases of the Cambrian Explosion. Scientific Reports, 8:16656.