

COVARIATION OF FE & B IN PALEOPROTEROZOIC FE-CARBONATES: INSIGHTS INTO THE PRECAMBRIAN OCEAN AND MARTIAN HABITABILITY. E.A. Holme¹, J.A. Hurowitz¹, G.A. Henkes¹, E.T. Rasbury¹, ¹Stony Brook University, Department of Geosciences, Stony Brook, NY 11794 (e-la.holme@stonybrook.edu)

Introduction: An understanding of fluid chemistry in the early Earth is essential when characterizing how habitable environments are created and maintained on geologic timescales and in determining what signatures of habitability might look like on other planetary bodies, such as Mars. The study of carbonates as paleoclimatic records using stable isotopes is well-established due to the ability of this mineral family to preserve signatures of parent fluid chemistry. It has been shown that the preferential incorporation of borate ions ($\text{B}(\text{OH})_4^-$) into the carbonate mineral lattice can provide insight into the pH of precipitation because the speciation of boron in seawater is strongly pH-dependent [1]. The B-isotopic depletion of $\text{B}(\text{OH})_4^-$ relative to $\text{B}(\text{OH})_3$ is reflected in the $\delta^{11}\text{B}$ of marine carbonates, and trends in seawater pH can thus be determined by measuring their B-isotopic composition [1].

Previous studies of B-isotopes in carbonate have focused on calcium carbonates due to their abundance in both modern systems and the geologic record as well as the relative ease with which they can be analyzed. However, investigation into B-isotope systematics in ferromagnesian carbonates has the potential to reveal information about water bodies whose fluid chemistry remains relatively unconstrained. In order for such a study to be successful, it is imperative to first characterize the systematics of B-inclusion in the lattice of Fe-Mg carbonates, and particularly to demonstrate that such phases could retain primary signatures.

The Paleoproterozoic Gunflint Iron Formation, located along the northern shore of Lake Superior, presents an excellent opportunity for study of B in Fe-Mg carbonates, as it is host to minimally-altered carbonate ranging from siderite to ankerite with dolomite/calcite becoming more common as metamorphic grade increases [2]. In this study, we show that B is preferentially incorporated into Gunflint siderite above other carbonate phases; if (a) siderite is precipitated from native seawater and (b) B is unaffected by earliest carbonate diagenesis, this observation could have important implications for future studies of pH in the Precambrian ocean and water bodies on early Mars in which carbonates were formed [3, 4, 5].

Samples: Samples were selected from Zones 1 & 2 of the Gunflint, where maximum burial temperature is thought to be $< 160^\circ\text{C}$ [6], with emphasis placed on samples showing the least visual and petrographic evi-

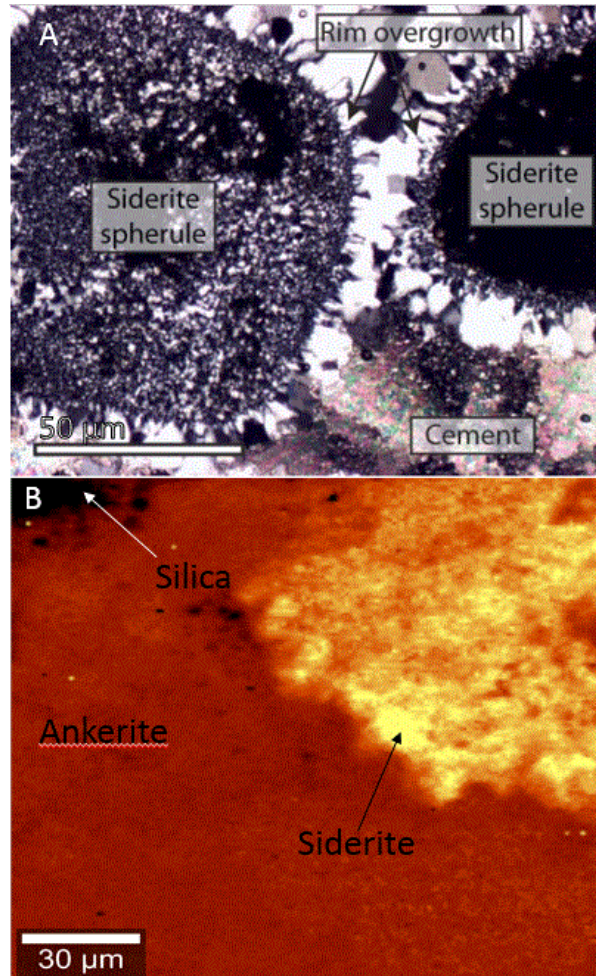


Figure 1. (A) Photomicrograph of Gunflint sample 726-5, taken from Zone 2. Ankeritic rims are interpreted as diagenetic products. (B) Raman peak intensity map of siderite nodules from 726-5. Yellow regions show highest peak intensity.

dence of alteration. Targeted facies are the banded chert-carbonate facies, which contain both fine-grained carbonate matrix interbanded with chert and Fe-carbonate nodules with ankeritic rims encased in a silicic matrix.

Methods: Samples were analyzed using a combination of petrographic microscopy, Raman spectroscopy and LA-ICP-MS. Thin sections were prepared from cut samples for petrographic and spectral analysis (Figure 1). Raman spectra were collected using a WiTEC alpha300R confocal Raman imaging system

coupled with a 532 nm green NdYAG excitation laser using an integration time of 0.05-0.1 s. Elemental analysis was conducted using an Agilent Technologies 7500 Series ICP-MS equipped with a New Wave UP-213 Laser Ablation System utilizing a Tempest 213 nm 20 Hz laser at a spot size of 120 μm .

Results & Discussion: Siderite nodules are primarily micritic and are surrounded by isopachous silica cement, with ankeritic rims forming as a result of early diagenesis. Within the nodules, B is highly correlated with Fe and shows no association with Ca or Mg (Figure 2). This correlation was observed in most samples analyzed, with exceptions in samples in which Fe, Ca, Mg are intimately comingled; in these high-Fe ankeritic occurrences, B is associated with areas of high Fe, Ca, & Mg concentration. Generally, our observations indicate that B incorporation increases as carbonate compositions move towards siderite.

The sample shown in Figure 2 is of particular interest due to the unusually high B concentration exhibited. In this sample, average B concentration within the siderite nodule is ~ 450 ppm, while modern marine carbonates are well under 100 ppm B [1]. We hypothesize that these anomalously high B concentrations demonstrate the high pH of Gunflint seawater, and that this signature is preserved due to sample silicification. Because silicification occurred early in the sample's burial history [7], diagenetic alteration of carbonate nodules would have been limited later in its burial history. In contrast, the significantly lower B concentrations found in banded carbonate samples from the Gunflint that were not silicified. We hypothesize that silicification of the siderite nodules in this sample enabled the preservation of primary seawater chemical signatures. If true, a significantly higher pH than observed in the modern ocean could be indicated, as borate is the dominant species above a pH of 8.5. B-isotopic composi-

tion measurements will be taken before the time of presentation to confirm this hypothesis.

Conclusions: In this preliminary study, we have shown that B and Fe are highly correlated in Gunflint carbonate, indicating a preference for B incorporation with increasing Fe content. Further studies will use the same approach to investigate samples from different localities. Additionally, we plan to experimentally precipitate siderites with a range of conditions and B concentrations to further consider the applicability of seawater for archiving seawater chemistry.

The connection between Fe-redox conditions and pH strongly influenced the geochemistry and habitability of Fe-rich water bodies on early Mars [8], and understanding the evolution of analogue environments on early Earth could place key constraints on past martian fluid chemistry and biological potential. Determining the processes of boron incorporation into ferromagnesian carbonates is an important step toward understanding the aquatic conditions that fostered the earliest life on Earth and how such processes could have operated on Mars.

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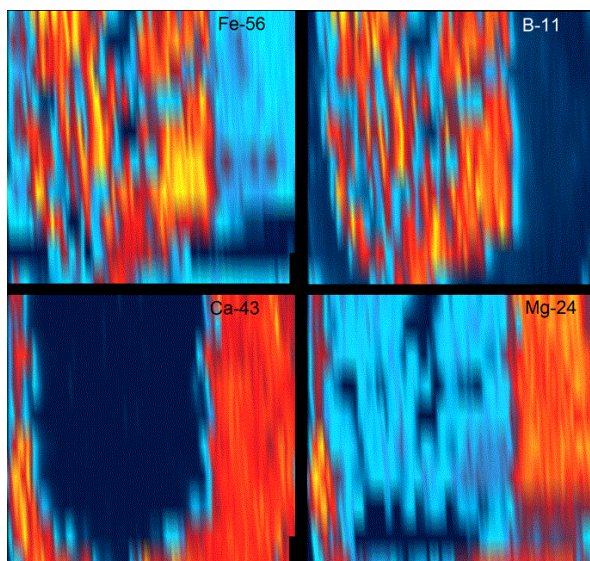


Figure 2. LA-ICP-MS maps of Fe, B, Ca, & Mg concentration in a siderite nodule of sample 726-5. Note the correlation between Fe/B as well as between Ca/Mg.