PHOSPHATES IN BANDED IRON FORMATIONS (BIF). A TOOL FOR EXPLORING ANCIENT OCEANS AND LIFE ON MARS.

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Introduction: Microbial metabolic activity is significant in the cycling of phosphorus in aquatic and sedimentary environments. The requirement of microorganisms to use elemental phosphorous for energy transfer and to bind, concentrate and cause crystallization of phosphates is well established [e.g. 1,2]. The crystallization of phosphates in a sedimentary environment commonly occurs when the proper physical conditions and biological activity coincides [2]. Phosphates and biogenic apatites are used in paleoclimatological and environmental studies to obtain critical information on temperature of formation and environmental conditions under which the phosphate minerals were formed or deposited. Many of these studies have explored the possibility that trace elements and stable isotopes in sedimentary apatite may be used as a proxy for water chemistry. Martian sample return missions will focus upon both the search for life and reconstructing the history of water on the martian surface. Initial missions could center upon iron-rich lithologies on the martian surface. Phosphates could potentially provide a means of exploring the composition of the surface water and the phosphorus cycle on both the ancient Earth and Mars. Here, we report the results of our initial study of phosphates in the very low-grade metamorphic lithologies of the Gunflint BIF. Our focus is to understand the presence and distribution of phosphates in BIFs and to evaluate the possibility that their major and trace element characteristics reflects conditions of BIF deposition or early diagenesis.

Gunflint BIF: The 1.9 billion year old Gunflint BIF is approximately 120 m thick and extends over more than 180 km from the north shore of Lake Superior westward along the Ontario-Minnesota boundary. Stratigraphically, this formation is part of the Animikie Group and consists mainly of clastic and chemical sedimentary rocks. Both the lowermost and the uppermost facies of the Gunflint consist of algal chert that is overlain by tuffaceous shale, which in turn is succeeded by a thick, granular taconite facies that grades into banded chert-carbonate layers. The Gunflint is a virtually unmetamorphosed Precambrian iron-formation in which primary textures have been well preserved. It is estimated that the Gunflint experienced burial temperatures of 100 to 130ºC, [3]. However, areas of higher metamorphic grade are better represented by the pyroxene-hornfel facies [4].

Analytical Approach: Four thin sections of the low-grade metamorphic lithologies of the Gunflint BIF were selected for study. These samples contain primary sedimentary textures (i.e. microspheres and ooliths) and minerals in addition to secondary diagenetic minerals. The thin sections exhibit banded chert-carbonate assemblages. Phosphates were located and imaged with a JEOL JSM-5800 LV SEM. Major and minor elements in the phosphates were analyzed with a JEOL 733 superprobe. Trace element analyses of the apatite were conducted using a Cameca ims 4f ion microprobe. All instruments are located at the University of New Mexico and operated by the Institute of Meteoritics.

Morphology, Distribution and Major Element Chemistry of Apatite: In the four thin sections of the BIF that we studied, the apatite occurs as tabular, euhedral to subhedral grains approximately 10 to 50 μm in size (Fig. 1). The euhedral to subhedral nature of the apatite suggests that they were not detrital, but were either primary precipitates or crystallized from an amorphous, calcium phosphate gel during very early stages of diagenesis. They occur within the cherty layers of the BIF contiguous to carbonate-chert interfaces. Apatite ($\approx 1\mu$m in diameter) also occurs in the cores of some sideritic spheres [5].

The major- and minor-element composition of the phosphate in the Gunflint BIF indicates that they are primarily fluor-apatite with between 2.5 and 4.5% F and less than 0.1% Cl. The concentration of FeO is variable ranging between <0.1 to 0.6 weight %. The concentrations of MgO and MnO are both less than 0.1 weight %. The low concentrations of MgO are particularly important because Mg^{2+} inhibits both the growth of apatite and the transformation of amorphous calcium phosphate to crystalline apatite. The possibility of OH and CO_3 in the apatite structure could not be determined directly with the electron microprobe. However, based on the relationship between PO_4^{3-} and CO_3^{2-} documented by McClellan and Van Kauwenbergh [6] the apatites may have up to 0.6 ions of C per formula unit (on the basis of 26 O, OH, F, Cl).

REE and Sr in Apatite: The REE patterns (Fig. 2) for the apatites are LREE enriched with La ranging from 430 to 12,800 times chondrite and Yb ranging from 50 to 740 times chondrite. These concentration levels are 6 to 10 orders of magnitude greater than current seawater. The REE pattern of the apatite with

lower REE concentrations tends to be slightly concave downward (Nd_N/La_N= 1.2; $La_N/Yb_N \approx 9$), whereas the apatite with significantly higher REE concentrations show a consistent decrease from LREE to HREE (Nd_N/La_N= 0.5) and exhibit greater depletion in HREE ($La_N/Yb_N \approx 17$). Ce anomalies in the apatite are not apparent. The patterns also exhibit a slightly positive to no Eu anomaly. The Sr in the apatite ranges from 800 to 8000 ppm and is positively correlated to the abundance of REE.

Discussion: Based on earlier experimental work, Knudsen and Gunter [2] concluded that apatite precipitates from water at pH levels of 7.5 – 8 at a Ca/Mg ratio above 5.2. For apatite to crystallize at a pH of 7, the Ca/Mg value must decrease to 1.2. Because the Ca/Mg of modern seawater is approximately 0.2, the apatite in the BIF must have crystallized from seawater with low pH (< 7) or unusually high Ca/Mg or from interstitial water in which the Ca/Mg evolved separately. Phosphate precipitation primarily occurs in interstitial water between the sediment-water interface and the oxygen minimum zone [2,7]. Increase in the concentration of phosphate in the interstitial water relative to seawater may be accomplished by microbial breakdown and release of phosphate into the pore waters of the oxygen minimum zone [7]. The occurrence of apatite in the cherty bands in close association with the interface between carbonate and silicate banding implies this horizon was critical for the concentration of phosphorous and precipitation of apatite. Slansky [7] and Sanchez-Navas et al. [8] proposed that instead of direct crystallization of apatite, amorphous calcium phosphate precursor gels formed under rapidly created supersaturated conditions. The precipitation of calcium phosphate from either seawater or interstitial water may have occurred with or without the aid of microbial activity.

The high REE concentration in the apatite is the result of the enrichment of the interstitial water in REE and the mechanism behind trace element incorporation into the apatite. The differences in REE abundance and pattern shape may be a result of duration of apatite exposure to interstitial water and the relative importance of absorption versus direct ion substitution. Provided that the REE in the interstitial water is enriched but not fractionated relative to seawater and that the extent of apatite REE fractionation is negligible or predictable, the characteristics of the interstitial water and seawater may be calculated. This REE data suggests that extensive hydroxide and oxide precipitation in an oxic environment is not recorded by the phosphates. Extensive upwelling of anoxic deep water into a shallow, oxic environment may have diluted a negative Ce anomaly through mixing. Alternatively, the precipitation of the cherty layers occurred during a less

oxic cycle of BIF precipitation. The absence of a negative Eu anomaly may reflect the addition of a small hydrothermal solution component to the local water. The LREE enrichment recorded by the apatite may reflect the proximity of the site of deposition adjacent to the Precambrian coast.

In summary, this preliminary study has identified phosphates in BIF and provided some of the first trace element data on these primary or early diagenetic minerals. If apatite from sedimentary rocks truly records conditions of deposition they will be extremely valuable to our exploration of ancient Mars.

References: [1] O'Brien et al (1981) Nature, 294, 442-444. [2] Knudsen and Gunter (2002) *Reviews in Mineralogy 48, Phosphates.* Mineralogical Society of America, Washington D.C., 363-389. [3] Carrigan and Cameron, E.M., (1991) *Precambrian Research, 52*, 347-380. [4] Floran and Papike (1978) Journal of Petrology, 19, 215-288. [5] Heaney and Veblen (1991) Precambrian Research 49, 355-372.[6] McClellan and van Kauwenbergh (1990) Phosphorite Development and Research, 52, 23-31. Geological Society Special Publication. [7] Slansky (1986) Geology of Sedimentary Phosphates, Kogan Page Ltd. [8] Sanchez-Navas et al. (1998) Sedimentology 45, 519-533.

Figure 1. Backscattered electron images of apatite in finely banded lithologies from the Gunflint Iron Formation. A=apatite, C= carbonate, and Si = chert-rich assemblages.
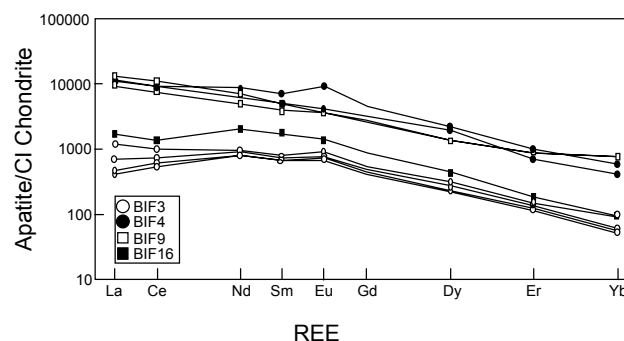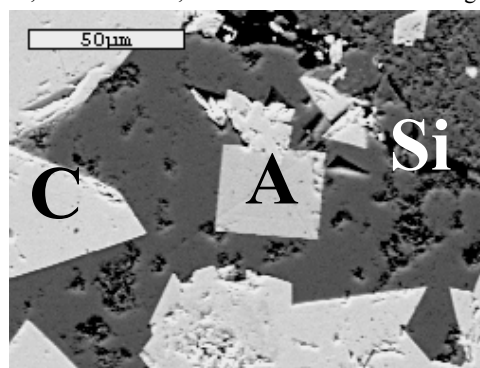

Figure 2. Chondrite normalized REE patterns of apatite from the Gunflint formation.