

High Arctic perennial spring activity and associated minerals: their value to Mars analogue studies

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Saline spring discharge in cold environments is of specific relevance to ongoing interest in the search for the presence of water on other planets such as Mars [1]. Inherent to this search is the goal of finding morphological or geochemical evidence that life once existed on these planets. To better understand what these biosignatures may look like, current work aims to understand both how life survives in analogous environments on Earth and how such life interacts with their surroundings to produce biosignatures that may be preserved over geologic timescales.

Saline perennial springs in the Canadian high Arctic are a unique target for such studies. The brines emerge from the subsurface at constant temperatures and flow rates despite extremes in seasonal climate conditions. Mineral precipitates associated with spring discharge include carbonates, sulfates, and chlorides, however the majority of mineral growth occurs during winter months when cold temperatures drive freezing fractionation of salts within the waters to produce large amounts of ice and ice-rich minerals including ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), and hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$). Halotolerant bacteria inhabit springs at several sites including Gypsum Hill Diapir, Colour Peak Diapir, and Wolf Diapir, but they are restricted to spring outlets where chemical energy such as sulfide and methane are present and temperatures remain near 0°C. In contrast, it is hypothesized that a lack of energy source coupled with extremely high measured salinities in waters emanating from Stolz Diapir limits microbial colonization of this habitat.

Examination of mineral precipitates from these sites by microscopy and synchrotron radiation show variations in mineralogies due to differences in source water geochemistry. There is scant evidence of microbial colonization of mineral surfaces or creation of biosignatures at Gypsum Hill and Wolf Diapirs due to low accumulations of mineral precipitates or the soluble nature of minerals at near-freezing temperatures. At Colour Peak, however, bacterial sulfate reduction in the deep subsurface is recorded in carbonate precipitates as interbedded FeS_2 laminations, which may be distantly comparable to mineral precipitation associated with a nearby inactive fossil spring adjacent to the White Glacier that formed ancient deposits. Independent data suggests the fossil spring may have been active for several million years and involved warm brines originating at depth, a habitat that could have provided restricted ecological niches for microbial evolution.

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Lead Incorporation within Biological Apatite May Occur through a Polyphosphate Precursor

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Introduction

Elevated levels of lead in seawater close to a lead and zinc mine in Greenland has been positively correlated to lead levels in seaweed, mussels, prawns, and in the liver and bone of wolf-fish and sculpin [1]. Although environmental lead is known to report to bone, the pathway between lead injection and transport to bone mineral has not been elucidated. A new bone mineral nucleation theory suggests that a precursor to biological apatite is calcium polyphosphate. Polyphosphate chelates strongly to calcium, and other divalent cations such as lead [2]. It is possible that polyphosphate chelation to lead could be one of many biological strategies to immobilize lead and prevent it from reacting with other species. A lead-calcium-polyphosphate complex could also be a precursor to biological apatite.

Alkaline phosphatase has been associated with apatite biomineralization [3]; tissue-nonspecific alkaline phosphatase was shown to break down polyphosphate ions into orthophosphate ions [4]. It is proposed that breaking down a calcium polyphosphate complex into orthophosphates increases the apatite saturation and allows for apatite nucleation.

To determine if a lead-calcium-polyphosphate complex could be transformed into biological apatite containing lead, calcium-lead complexes were formed in neutral pH solutions, and exposed to alkaline phosphatase under basic pH conditions.

Figure 1 shows the powder x-ray diffraction of the reaction products.

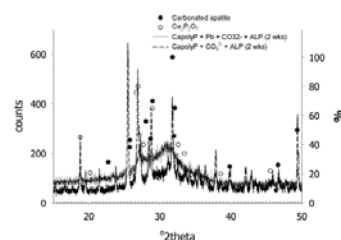


Figure 1: Powder x-ray diffraction of the products of exposing calcium- or lead-calcium polyphosphate to alkaline phosphatase for 2 weeks at 37 °C.

Results and Conclusion

Crystalline materials that have not yet been identified are the product of these in vitro experiments, however, this demonstrates that lead-calcium polyphosphate is a substrate for alkaline phosphatase. With further work on the experimental conditions, lead might be incorporated into biological apatite formed from the degradation products of lead, calcium, and polyphosphate.

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[2] Van Wazer (1950) *Journal of the American Chemical Society* **72**, 655-663.

[3] Robison (1923) *Biochemical Journal* **17**, 286-293.

[4] Omelon (2009) *PLoS ONE* **4**, e5634-49.