

## Hydrothermal Fe(II) oxidation during phase separation: Relevance to the origin of Algoma-type BIFs

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Precipitation of Fe-oxide resulting in deposition of Archean banded iron formations (BIFs) has been mainly linked to UV-induced photochemical and/or enzymatic Fe(II) oxidation by photoferrothrophic bacteria. Hydrothermal plumes are thought to be the main source of Fe for BIFs; however, their deposition in deep anoxic settings in close association with submarine volcanism in Archean basins imposes significant limitations for both processes for ferrous iron oxidation during hydrothermal discharge onto the seafloor. Accordingly, the physical and chemical conditions that enhanced oxidation and formation of insoluble ferric Fe phases in deep-sea hydrothermal environments remain enigmatic.

In modern submarine hydrothermal systems, the combined effect of high temperature and relatively shallow hydrothermal circulation results in phase separation and boiling phenomena intrinsic to the NaCl-H<sub>2</sub>O system. During vapor-liquid separation, distinctly different partition coefficients for alkalis, transition metals, and volatiles are anticipated, closely controlled by the extent of phase separation. Experimental studies have shown the tendency for vapor to be enriched in volatile and neutral species (e.g. H<sub>2</sub>, HCl), while hypersaline liquid develops oxidizing and alkaline conditions combined with metal-enrichment due to the strong affinity of transition metals for chloro-complexes. Theoretical models allow to assess the effect of phase separation on Fe(II) oxidation deep in the reaction zone. Experimentally-derived H<sub>2(aq)</sub>, HCl<sub>(aq)</sub> and Fe vapor-liquid partition coefficients, combined with thermodynamic data on OH- and Cl-bearing Fe(III) aqueous species suggest that iron oxidation is plausible for the Fe-enriched but H<sub>2</sub>-depleted liquid formed by phase separation. Iron speciation appears to be dominated by chloro-complexes, however, under strongly alkaline conditions Fe(III) hydroxides might form. Fe(III)-enriched liquids could reside as brine pools within the crust, until mixing with seawater facilitates their discharge onto seafloor. Phase separation might have contributed to Fe-oxide deposition in deep anoxic Archean basins in close association with submarine volcanism, especially considering shallow-water setting and higher heatflow conditions of Precambrian hydrothermal systems relative to modern analogues.

## Geochemistry of Paleoproterozoic Gunflint Formation carbonate: Implications for early hydrosphere-atmosphere evolution

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Rock comprising the 1.878 Ga Gunflint Formation lies on the southern Canadian Shield and primarily consists of an assemblage of chemical sediments including chert, iron oxides and carbonates. The sediments were deposited on a wave and tide influenced broad shelf deepening to the south [1]. In this study we examine the limestone unit at the top of the Gunflint Formation and compare its petrology and geochemistry to ferronian dolomitic (ankeritic) grainstones common in the shore-proximal exposures near Thunder Bay. The limestone consists of very coarse sand to granule grainstone layers overlain by cabbage sized stromatolites and a boulder conglomeratic tsunami deposit produced by a large asteroid impact event [2]. The ankeritic grainstones represent neomorphically altered shallow water sand sheets. The carbonate was precipitated from seawater. These ankerites have high concentrations of Ca, Fe, Mg and Mn with relatively low abundances of most other elements. Their REE curves have positive La and, to a lesser extent, Ce anomalies. Eu is flat to positively enriched. The carbonate in the limestones forms the cement surrounding chloritic clasts. Stratigraphic evidence shows it formed between withdrawal of the Gunflint sea from this area and the 1850 Ma asteroid impact event. The calcite cement in the limestones has higher values of most elements, but especially U (5 to 10 times more abundant), REE's (10 to 100 times more abundant) and V (100 times more abundant). Their REE curves show distinct Ce and Eu depletion. The extreme V-U enrichments of these calcite meteoric cements indicate oxidized fluids leached V and U from the subaerial environment and precipitated these redox sensitive elements upon encountering the organic-rich sediments. The negative Ce anomalies of the REE curves for the calcite cements agree with this interpretation. The ankeritic sediments deposited in the marine environment have REE abundances typical of precipitation from oxygen deficient water with abundant dissolved Fe and Mn. This data points to an imbalance in oxygen levels at this time with a relatively oxic atmosphere and anoxic oceans.

[1] Pufahl & Fralick (2004) *Sedimentology* **54**, 791-808.

[2] Addison *et al.* (2005) *Geology* **33**.