

Partitioning of Si, P, V, Mo, and Ni during the experimental precipitation of ferric oxyhydroxides and their use as paleo-proxies in banded iron formation

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During the Archean and Paleoproterozoic, large amounts of iron precipitated from seawater to yield banded iron formation (BIF). It has been argued that during this time, the presence of abundant and highly reactive iron oxyhydroxides may have limited critical nutrients as a consequence of various adsorption and co-precipitation processes. More recently, the idea that these iron oxyhydroxides acted as important nutrient sinks appears to be giving way to the idea that BIF simply serve as paleo-proxies for the composition of seawater by the predictable nature of iron oxyhydroxide sorption reactions. We add to the debate regarding the composition of ancient seawater throughout BIF deposition by evaluating the degree to which ferric oxyhydroxides sequester aqueous Si, P, Mo, Ni, and V. Mo, Ni, and V act as enzymatic co-factors that are critical, and at times limiting, for specific biological functions in modern microbes, while P is a major nutrient controlling oceanic productivity today. Dissolved silica was more abundant at the time of BIF deposition and likely influenced elemental partitioning to iron oxides through a combination of competitive surface adsorption and co-precipitation processes. Accordingly, we examine its role in the sequestration of these nutrients into iron oxyhydroxides, and the fate of silica itself in terms of the Si/Fe compositions of the resulting particles. Finally, we evaluate our experimental data in light of the concentrations in which these elements are found in BIF, and make preliminary estimates of their availability in ocean water at the time of BIF deposition.

Kinetics of production and dissolution of earthworm excreted calcite

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Earthworms excrete exquisite granules of calcium carbonate comprising aggregates of rhombohedral calcite grains. If one looks closely the granules also contain significant amounts of amorphous calcium carbonate [1]. The function of the granules is not known.

This presentation relates to the kinetics of granule production and dissolution. The granules can't last forever or we would be knee-deep in granules. However, under favourable conditions they can last for significant periods of time and are routinely recorded in Quaternary soils and sediments during archaeological investigations. The question of how rapidly granules are produced and how long they last is of relevance to the terrestrial C cycle, but also to possibilities of palaeo-environmental interpretation and dating through analysis of C and O isotopes in the granules.

To investigate granule production rates earthworms of the species *Lumbricus terrestris* were cultured for 28 days in a variety of soils from which we had removed existing earthworm calcite granules. After 28 days freshly produced granules were extracted and weighed. Masses of granules produced varied from 0 to 4.3 milligrams of calcite per earthworm per day. A good correlation ($r = 0.8$, $p \leq 0.05$) was seen between soil pH and mass of granules recovered, but it is highly possible that rather than reflecting different production rates this reflects more rapid dissolution of granules in the acid soils. In a parallel experiment mass of granules produced by individuals over time has been monitored. To date the experiment has lasted 219 days. Over time the earthworms have lost mass and the mass of granules produced has shown a proportional decrease.

Kinetics of granule dissolution are being addressed through two approaches. 1: Granules are being dissolved in flow-through reactor vessels and calculated dissolution constants compared to those generated for inorganic calcite (Iceland spar). 2: Granules have been added to granule-free soil and soil leaching columns established. Changes in leachate chemistry are being used to assess granule dissolution rates and granules are being recovered after fixed periods of time to assess dissolution via mass loss.

Results will be discussed with reference to granule longevity and implications for soil C cycling.

[1] Lee, Hodson & Langworthy (2008) *Geology* **36**, 943–946.