Trace element patterns in pyrite nodules as a window to bioessential metal availability in Archean marine sediments

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Trace element contents of whole rock [1] and pyrite [2] samples can be used in the reconstruction of geochemical conditions of the oceans through geologic time. However, currently the compostion of ancient pore waters and how they might have evolved over time is unknown. This is important because processes that occur deep within sediments can be essential in controlling paleoclimate and biospheric redox, as well as the early evolution of life. Pyrite nodules can form over a protracted period during diagenesis. We propose that trace element content and S isotope variation within nodules can give a qualitative understanding of changes in pore water trace element content during diagenesis.

Here we report LA-ICPMS analyses across pyrite nodules from the 2629 ±5 Ma Jeerinah Formation, Western Australia. The data show distinctly lower trace element contents in the rims of the pyrite nodule. The coarser grained pyrite in the rims suggest they formed later, and a lack of alteration in the sample area precludes the possibility that the rims are from high T fluids/processes. Therefore, we suggest that a significant decrease in trace elements in the pore waters occurred during diagensis and that we can track those trends and their biogeochemical implicatons through time. Of particular interest is the two orders of magnitude drop in Ni content. Nickel is an important enzymatic cofactor for methanogenic bacteria, and a decrease in Ni via diagenetic uptake during burial, such as that suggested by the pyrite data, could significantly limit the depth at which methanogenesis could proceed. This subsurface deficiency might have reduced methane availability in the Neoarchean biosphere—despite suggestions of high seawater Ni and low sulfate that would otherwise favor methane production [3]. More generally, this technique may provide novel perspectives on factors controlling life in the deep biosphere.

[1] Tribovillard *et al.*(2004) *Chem. Geol.* **213**, 385-401. [2] Gregory *et al.* (2015) *GCA* **149**, 223-250 [3] Konhauser et al. (2009) *Nature* **458**, 750-753.