Validating the use of marine pyrite as a record of trace element concentrations in seawater

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Marine pyrite has proved its mettle as a indicator of redox changes in the atmosphere and oceans throughout Earth's history through its iron and sulfur isotopic compositions. Recently, the trace element contents of authigenic marine pyrite have been used to reconstruct fluctuations in the trace element contents of seawater through time [1,2], which provide additional insight into the causes and consequences of ocean-atmosphere redox change, as well as constraints on biological activity and evolution.

The validity of trace element contents in marine pyrite as redox proxies rests on the processes controlling trace element uptake and retention. The formation in marine pyrite likely proceeds through an initial FeS precipitate that subsequently become oxidized to pyrite. Our objectives are to explore the fate of trace elements during this transition using synchrotron-based micro X-ray fluorescence and spectroscopy, which can map both the distribution and oxidation state of iron and sulfur, and provide information about the coordination environment of sulfur, iron or trace elements with spectroscopy.

We have focused on the fate of cobalt and nickel during formation of mackinawite, and after simulated diagenetic transformation to pyrite, because these elements incorporate into the pyrite structure. We will present data linking the heterogeneities of trace element concentrations to shifts in the coordination environment and oxidation state of sulfur. The consequences of these heterogeneities will be discussed in terms of the variations seen in the sedimentary pyrite record.

[1]Large *et al* (2014) *EPSL,* **389**, 209-220. [2]Swanner *et al*. (2014) *EPSL*, **390**, 253-263.