

How geochemical proxies provide quantifiable evidence of climate shifts over the last 25,000 years

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Some of the best, but still limited, evidence for large climate shifts, including the end of the Last Ice Age, comes in the form of geochemical proxies preserved in seafloor sediments. The proxy data is actually recording oceanic tracer distributions, which in turn, depend upon the sea surface and the atmosphere in a complicated way. In the terminology of inverse methods, the “observation step” must be modelled as well; that is, the process that translates the physical variables of the ocean into a proxy signal must be explicitly (i.e., mathematically) stated. In many cases, this process is calcification in foraminifera, and empirical relationships are used here as the model of this step. In cases where the observation or proxy step is oversimplified in the model, a whole range of plausible solutions can be excluded without good reason.

While it is clearly of interest to estimate past rates of ocean circulation from geochemical proxies, an inverse method is used to show that the seafloor proxies from the Last Glacial Maximum inform us primarily about shifts in the water-mass configuration. In this particular example, I show that the geochemical proxies, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Cd/Ca ratio, give quantifiable evidence for a shift in the pathways of the interior ocean, not just changes in surface boundary conditions. Given this information, estimates of the rate of overturning circulation in the Atlantic are revisited, but significant uncertainties remain in the inverse estimate of this particular quantity.

Selenium reduction by pyrite: pH effect and Mossbauer study

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The radioactive isotope ⁷⁹Se is presently considered as the key mobile fission product for the disposal of spent fuel (SF) and high-level radioactive waste (HLW). Its solubility is largely controlled by oxidation state. Due to the weak adsorption of Se(IV) and Se(VI) on natural minerals, specially on granite and clay minerals, chemical reduction is considered to be the most effective way to immobilize ⁷⁹Se [1,2].

On the other hand, pyrite is the most frequent sulfide mineral and is also present in geological barriers of nuclear waste repositories [3].

Therefore, we investigate the interaction between pyrite and Se(IV) from pH 5.05 to 8.5. After 1 month, solution analyses show that Se(IV) concentration decreases under the detection limit and suggest that Se(IV) is involved in redox reactions with FeS₂.

We focus specially on the behavior of iron species in the immobilization of Selenium. Mossbauer spectroscopy performed on the solid at different pH shows clearly significant iron environment modifications, and thus it suggests particularly the precipitation of new solid phases included Fe and Se, like FeSe or FeSe₂.

These results are confirmed by XAFS spectroscopy used to unravel the selenium speciation, and microscopy analysis (SEM and TEM).

[1] Chen *et al.* (1999) *J. Nucl. Mater.* **275**, 81-94. [2]

Scheinost *et al.* (2008) *Environ Sci & Technol.* **42**, 1984-1989.

[3] Beaucaire *et al.* (2000) *Appl Geochem.* **15**: 667-686.