

Chances and challenges in applying sulfur-oxygen isotope relationships of sulfate to studying sulfur cycling in engineered environments

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In recent years, our understanding of the mechanics of sulfur and oxygen isotope fractionation by sulfate reducing microorganisms has drastically improved. Based on multi-step sulfate reduction models, we are not only able to answer the question of why there is a large range of sulfur and oxygen isotope fractionations related to this process, but can also predict sulfur-oxygen isotope fractionation relationships (Brunner *et al.* 2012 [1]).

While this progress is exciting, it does not automatically provide new insight into sulfur cycling in perturbed ecosystems, such as polluted soils and aquifers, sites where sulfate reduction can be anthropogenically stimulated as a means to remove or sequester organic and inorganic contaminants.

Such systems are often highly complex because they are affected by different modes of microbial and abiotic sulfur cycling (i.e., reductive and oxidative processes), non-steady state conditions, and by mixing of waters from different sources. Additional challenges arise from the fact that monitoring of such systems is typically restricted to a few sampling points and cannot be carried out continuously.

Despite these complications, by comparing the combined sulfur and oxygen isotope signature of sulfate to the predicted sulfur-oxygen isotope relationship for sulfate reduction, it should be possible to tease out crucial information about sulfur cycling in engineered ecosystems, such as the extent to which sulfate is reduced, and the extent to which reduced sulfur is re-oxidized to sulfate.

Approaches where natural abundance sulfur and oxygen isotope signatures are combined with the outcome of stable isotope tracer experiments and evaluated by comparison to numerical models yield promising results. However, such modeling efforts can only yield meaningful conclusions when appropriate model assumptions are chosen. The evaluation and definition of these assumptions may prove to be the biggest challenge in deciphering sulfur cycling in engineered environments.

[1] Brunner *et al.* (2012) Isotopes in Environmental and Health Studies **48**, 33–54.

The stability of uraninite in anaerobic conditions: Revisiting Cigar Lake and Oklo Natural Analogues

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Recent experimental work indicates that the UO₂ matrix of the spent nuclear fuel is stable under the reducing conditions imposed by hydrogen evolution as the result of the anaerobic corrosion of the steel components.

There are a number of hypothesis concerning the mechanisms and processes that activate the hydrogen molecule on the UO₂ surface. They basically imply the catalytic effect of some of the metallic particles in the fuel, as well as the potential activation by alpha and gamma radiation.

One of the key remaining issues is to which extent the proposed mechanisms operate in the long-term of a spent fuel repository.

In this context, it is interesting to discuss to which extent the extensive information generated in previous natural analogue projects can be used to verify or falsify some of the mechanistic hypotheses. In particular, what concerns to the long-term validity of the proposed mechanisms.

Among the various natural analogue studies of uranium deposits, the Cigar Lake ore deposit in Canada and the Oklo fission reactors in Gabon, provide some interesting observations and data under anaerobic conditions that may illustrate some of the key stabilisation processes under hydrogen conditions.

The objective of this presentation will be to discuss the findings of the Cigar Lake and Oklo natural analogue projects which may contribute to enlighten some of the open questions regarding the long-term validity of the so-called hydrogen effect in the stability of the UO₂ spent nuclear fuel matrix.