

Oxygen isotopy of arsenate/arsenite: A novel approach to constrain the source of As in groundwater

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The isotopic composition of oxygen in As-oxyanions, is an isotope system which has not been investigated until now, but with a strong potential in getting new insights into the circumstances and processes that led to the development of high arsenic groundwaters in many parts of the world.

In general terms, the determination of the isotope composition of oxygen in aqueous As-oxyanions involves the successive pre-concentration, quantitative separation and precipitation of the respective species, followed by the actual measurement of the $\delta^{18}\text{O}$ values by high temperature reduction with graphite and continuous flow mass spectrometry.

Arsenite and arsenate can be readily precipitated with AgNO_3 , but since in natural aquatic systems P is much in excess relative to As, phosphate will also precipitate. Therefore, a key issue in elaboration of an adequate analytical protocol is the development of a procedure for the quantitative separation of arsenite, arsenate and phosphate from low concentration aqueous solutions. The method of Meng *et al.* [1] is widely used for the separation of As (III) and As (V) in the field, but about the behavior of P (V) during this procedure was not reported until now. Our first experiments show that at the recommended pH value not only As (V), but phosphate is also practically completely retained on the sorbent. Phosphate concentrations in effluent increase slightly with decreasing initial $\text{As}_{\text{total}}/\text{P}$ ratios from 5.0% (at a ratio of 1:5), through 5.5% (at 1:10) to 8.0% (at 1:50). Passing the effluent for a second time through the column, total P concentration decreased to 1.2% of the initial value, even when P was 50 times higher than As.

For the applicability of this isotope system the exchange kinetics between water and As-oxyanions is of particular interest. The rate constants for oxygen exchange in arsenite/arsenate seems to be order of magnitude faster than between dissolved phosphate and water [2][3]. This aspect must be taken into account in the interpretation of the isotope data.

[1] Meng, *et al.* (2001) *Water Res.* **35**, 2805–2810.

[2] Lecuyer *et al.* (1999) *Geochim. Cosmochim. Acta* **63**, 855–862. [3] Okumura *et al.* (1995) *Bul. Chem. Soc. Japan* **68**, 1839–1849.

Non-uraninite products for microbial U(VI) reduction

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The microbially-mediated reduction of U (VI) is a potential *in situ* strategy for the remediation of uranium-contaminated sites. The product of this reduction is often thought to be the highly insoluble mineral uraninite (UO_2). While this product is dominant under certain conditions, recent work has shown that other species of U (IV) are likely to be involved in uranium immobilization. Here, we present work investigating the product of U (VI) reduction by three bacteria – *Shewanella oneidensis* MR-1, *Desulfotomaculum reducens* and *Clostridium acetobutylicum*– under various geochemical conditions using X-ray absorption spectroscopy (XAS) and high-resolution transmission electron microscopy (HRTEM). Results for these three organisms show that at higher ionic strength, the product of microbial U (VI) reduction is primarily a U (IV) species sorbed to the bacterial biomass. In contrast, in incubations for which reduction occurs at low ionic strength, the same bacterium yields uraninite. The structure of the sorbed U (IV) species is unknown but Energy Dispersive X-ray (EDS) analysis reveals consistent association of U (IV) with phosphorus, suggesting that phosphato groups may be the associated with U (IV). Additionally, HRTEM suggests the presence of other mineral phases such as a ningyoite-like mineral ($\text{CaU}(\text{PO}_4)_2$) and a U (IV) phosphate phase $\text{U}_2\text{O}(\text{PO}_4)_2$. These two minerals were not detected by XAS, suggesting their presence at lower ratios of total species (<20%). Our study suggests that the products of microbial U (VI) reduction can vary considerably as a function of *in situ* geochemical conditions. The stability of these products with respect to oxidation may also deviate significantly from that expected for uraninite.