

What mechanism controls rhenium deposition from euxinic waters?

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Rhenium is often enriched in black shales and euxinic basin sediments by 100 to 1000 times over its crustal abundance. Enrichment previously has been attributed to reduction of ReO_4^- , the principal Re species in natural waters. The product is assumed to be an insoluble Re(IV) oxide or sulfide. So far, the specific biotic or abiotic mechanism of reduction has escaped identification. Pure cultures of sulfate and iron reducing bacterial fail to precipitate Re, but precipitation has been observed in Re-enriched natural sediments under sulfate reducing conditions. In this talk, I explore an alternate, non-reductive mechanism of fixing Re in sediments: sulfidation of ReO_4^- to particle-reactive thioperrhenates ($\text{Re}^{\text{VI}}\text{O}_n\text{S}_{4-n}$) or to Re^{VI} sulfide precipitates or coprecipitates. Using UV-vis spectroscopy, equilibrium constants for formation of ReO_3S^- and ReS_4^- as well as a solubility constant for a colloidal Re_2S_7 polymer have been measured for the first time. From these constants, I conclude that most euxinic environments contain insufficient sulfide to stabilize thioperrhenates as major species. Similarly, Re_2S_7 polymers are too soluble to form in near-neutral pH waters, although they might form in acidic mine waters or during supergene-hypogene enrichment processes. To explain remarkable similarities between Mo and Re vertical profiles in the Black Sea, I propose that both elements become thiolated and coprecipitate at surfaces of the Fe-Mo-S colloidal phase that has previously been proposed to explain Mo deposition from euxinic basins. Coprecipitation implies that the critical step for Re removal from euxinic basins involves neither reduction nor thiolation of ReO_4^- , but instead saturation of sulfidic waters with the Fe-Mo-S phase. Coprecipitation favors removal of Mo more than Re from the aqueous phase, explaining increasing aqueous phase Re/Mo ratios as these elements are depleted from sulfidic waters. This process is well-described by the Raleigh fractionation law. Similar partition coefficients describe the evolution of Re/Mo ratios quantitatively both in sulfidic Black Sea waters and in sulfidic Hingham Bay pore waters. This implies that Re chemistry in sulfidic pore waters does not differ from that in sulfidic water columns in any fundamental way, contrary to some previous views. This mechanism accounts for the remarkable coherence in the profiles of Re and Mo in the Black Sea and for the failure of Re to be precipitated in pure sulfate reduction cultures that lack Mo.

Inter-laboratory Evaluation of $^{40}\text{Ar}/^{39}\text{Ar}$ Data for Sanidines from the Fire Clay Tonstein

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Because the $^{40}\text{Ar}/^{39}\text{Ar}$ method requires age standards, an important step towards improving the overall precision and accuracy of the method is to develop standard materials for inter-laboratory comparisons that span a wide array of age. It has been previously demonstrated that sanidines of the Carboniferous Fire Clay tonstein give analytically indistinguishable plateau ages over a 300 km distance in the Appalachian Basin [1]. Here we show that sanidines from the Carboniferous Fire Clay Tonstein of the Appalachian Basin of the southern United States are homogeneous at the single crystal scale, at least as measurable with single collector approaches, and reasonably reproducible among laboratories.

The reproducibility of the Fire Clay populations for the 8 iterations in the LDEO experiment (including 304 individual grains of Fire Clay sanidine and 137 of Fish Canyon) is 0.03% (1σ , analytical only). Encouraged by these results we distributed aliquots to four other labs for inter-laboratory comparisons.

Preliminary results are promising. All labs find a small range of ages, although the reported estimates are not all overlapping with estimated analytical errors. The agreement in terms of R -values, defined as the $^{40}\text{Ar}^*/^{39}\text{Ar}_K$ of the Fire Clay sanidine relative to the Fish Canyon sanidine standard, is quite reasonable with an interlaboratory average of 12.0799 ± 0.0296 (0.24%), and the small variability of ages suggests the potential for probing interlaboratory biases. This R -value translates to 315.3 ± 0.7 Ma and 314.6 ± 1.1 Ma using the calibrations of [2] and [3,4], respectively, including full systematic uncertainties. The Fire Clay tonstein is a promising natural sample for inter-laboratory comparisons and is a good candidate for producing a Carboniferous sanidine monitor standard.

[1] Kunk and Rice, 1994

[2] Renne et al., 2011, GCA, 75, 5097-5100.

[3] Kuiper et al., 2008, Science, 320, 500-504.

[4] Min et al., 2000, GCA, 64, 73-98.