

Common Os in Molybdenite: How negligible is negligible?

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An oft-touted benefit of molybdenite Re-Os geochronology, in addition to ppm level Re, is 'negligible' common Os [1]. As such, Re-Os model ages prove robust and geologically meaningful. But we find, in certain geologic settings, that common Os in molybdenite is far from negligible, and thus, this default assumption should not go unchecked. The question is 'How can we track, quantify, and correct for common Os in molybdenite?' With Re-Os ages for hundreds of molybdenites derived from fully constrained geologic contexts, the AIRIE Program has the sample archive to test for and track common Os in molybdenite.

We have explored several methods for quantifying and correcting for common Os using various spiking techniques, most notably a mixed-double spike (¹⁸⁵Re-¹⁸⁸Os-¹⁹⁰Os [2]). For ¹⁸⁷Re-¹⁸⁷Os age determinations, the impact of common Os in molybdenite is dependent on the Re/Os ratio on crystallization and the sample age. The most serious impact is derived from moderately young molybdenites (e.g. Phanerozoic) with low Re concentrations. Sub-ppm and even ppb level Re combined with low ppb level initial Os yields 'apparent' molybdenite ages that are markedly older than the 'true' age of the sample. That is, the initial ¹⁸⁷Os present will be erroneously counted as radiogenic ¹⁸⁷Os. This situation is far more common than workers realize, and has led to convoluted interpretations by some groups challenging the integrity of this mineral.

Additionally, molybdenites with notable common Os provide insight into geologic settings and unique processes not afforded by high Re molybdenites.

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[1] Stein *et al.* (2001) *Terra Nova* **13**, 479–486. [2] Markey *et al.* (2003) *Chemical Geology* **200**, 395–406.

Plutonium-humic acid stability constant determination and subsequent surface complexation studies

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Plutonium has been released to the environment through a variety of intentional and unintentional mechanisms; including atmospheric testing, disposition from weapons manufacturing processes, and subsurface disposal. Therefore, a thorough understanding of the chemical, physical, and biological processes affecting plutonium transport is imperative. It has been shown that humic acid (HA) (a refractory component of natural organic matter (NOM)) can effectively solubilize plutonium [1]. Increased solubility may result in enhanced subsurface transport, due to the higher concentration of Pu in the aqueous phase. In contrast, the formation of ternary surface complexes may hinder actinide transport. Solution pH is likely to affect the dominance of one species over another. For these reasons, a better understanding of binary Pu-HA and Pu-mineral and ternary Pu-HA-mineral systems is essential for accurately predicting plutonium fate and transport.

The primary objective of this research was to determine the conditional stability constants for Pu-HA complexes using a hybrid ultra-filtration/equilibrium dialysis ligand exchange (EDLE) technique from pH 4 to 6.5. Ethylenediaminetetraacetic acid (EDTA) was used as a reference ligand to allow the aqueous chemistry of the Pu-HA system to be probed at increased pH, without appreciable metal hydrolysis. Partitioning of Pu between HA and EDTA indicated that the Pu-HA complex is favorable. Comparisons with Th (IV), as a chemical analog of tetravalent actinides, indicated that Pu was primarily present in the tetravalent state.

Preliminary sorption studies were also conducted to evaluate the effects of Pu-HA complex formation on Pu sorption behavior. Enhanced Pu sorption was observed in the presence of HA. Notably, enhanced sorption was observed at low pH (pH 4) which is indicative of ligand promoted sorption. Therefore, despite observations of increased solubility of Pu in the presence of HA, the formation of ternary surface complexes may prevent enhanced subsurface transport. The data from these studies will aid in modeling the fate and transport of Pu in the environment and inform the development of conceptual models describing the influence of ternary surface complex formation on Pu sorption.

[1] Santschi *et al.* (2002) *Environ. Sci. Technol.* **36**, 3711–3719.