

## MOLYBDENUM SEQUESTRATION IN SULFIDIC SEDIMENTS: XAFS EVIDENCE FOR MO REDUCTION

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Molybdenum (Mo) has attracted attention as a paleoredox proxy particular because of its isotopic behavior and concentration relationships in sediments [1,2]. Much of this strength lies with the specifics of Mo redox behavior. In oxygenated water, Mo occurs dominantly as unreactive molybdate ( $\text{Mo}^{\text{VI}}\text{O}_4^{2-}$ ). When sulfide appears under in the sediments or water column, sulfur substitutes progressively for oxygen in  $\text{MoO}_4^{2-}$ , leading to reactive tetrathiomolybdate ( $\text{Mo}^{\text{VI}}\text{S}_4^{2-}$ ) by way of transient intermediates ( $\text{Mo}^{\text{VI}}\text{O}_x\text{S}_{4-x}^{2-}$ ) [3]. However, the post-thiomolybdate steps and the ultimate Mo host in sulfidic sediments remain unclear and thus compromise its strength as a redox proxy.

We used x-ray absorption fine structure spectroscopy (XAFS) to determine the oxidation state and molecular coordination environment of solid phase Mo in sediments deposited under a permanently sulfidic (euxinic) water column. Samples were taken from a 9 meter drill core from Lake Cadagno representing the last ten thousand years of deposition.

Our data provide unequivocal evidence for Mo reduction in the sulfidic water column and/or in the sediments. We identified two types of spectral patterns. Type 1 samples contain primarily  $\text{Mo}^{\text{IV}}$  bonded exclusively to sulfur atoms; Type 2 samples contain mainly  $\text{Mo}^{\text{VI}}$  bonded to both oxygen and sulfur atoms.

Based on experiments, we argue that  $\text{Mo}^{\text{VI}}$ -O-S compounds have been oxidized after collection. These Type 2 compounds compare to spectra previously reported for black shales and thiomolybdate adsorption experiments on Fe-sulfides [4,5] and suggest that oxygen exposure might have altered these samples too.

$\text{Mo}^{\text{IV}}$ -S compounds are found in both modern and ancient sediments indicating that Mo has not experienced diagenetic alteration over the last ~10,000 years. These Type 1 compounds show many similarities with the Mo-Fe-S cubane structure. Finally, our results support a model involving post-thiomolybdate reactions wherein the  $\text{Mo}^{\text{VI}}$  reduction proceeds via reactions with with zero-valent sulfur ( $\text{S}_8$ ) [6].

We conclude that Mo-XAFS is a powerful way to study the geochemical details of the Mo burial pathway and enhance our ability to infer ancient environmental conditions from the sedimentary rock record. Further, the post-thiomolybdate reduction may exert isotope fractionation that could affect the Mo isotope composition in euxinic sediments.

[1] Scott et al. (2008) *Nature* **452** 456-459 [2] Dahl et al. (2011) *EPSL*, **311** 264-274 [3] Ericksson & Helz (2000) *GCA* **64** 1149-1158, [4] Helz et al. (1996) *GCA* **60** 3631-3662, [5] Bostick et al. (2003) *ES&T* **37** 285-291 [6] Vorlicek et al. (2004) *GCA* **68** 547-556.

## Number density considerations in the dispersion-dissolution behavior of engineered silver nanomaterials

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### Background

With the acquisition of new technologies, the U.S. Army is now required to consider the environmental implications of fielding new nanomaterial-based technologies in theater and as part of warfighter training. To this end, the U.S. Army Engineer Research & Development Center (ERDC) has expended considerable effort and resources into quantifying the environmental fate of nanomaterials. Here is presented our work on the dispersion-dissolution processes associated with silver nanoparticle dispersions under simulated environmental conditions.

### Methods

Long-term dispersion studies were conducted either by shaking or stirring nanomaterial suspensions under laboratory-controlled conditions. Systems were sampled periodically with time and analyzed for multiple dispersion and dissolution endpoints.

### Results & Discussion

Our results demonstrate that the dissolution processes were coupled to the solid-phase dispersion characteristics. We note that such linkages are often apparent in the scientific literature yet not explicitly explained because this behavior is almost invariably considered in terms of particle mass concentrations. Instead, these relationships are preferably viewed through considering the change in the suspension number density. The number density parameter is (i) inversely related to the size distribution of the dispersion and (ii) shifts by several orders of magnitude with small changes in particle size at the nano-scale. Experimental results show that an increase in dissolved Ag concentration observed over a two-week period correlated with the increase in the number density of silver nanoparticle dispersions. This relationship was only apparent as long as the suspension remained in a sub-saturation mode. This latter observation is important as at the nanoscale, where the nearly two-order magnitude length difference in our current analytical technologies blurs the classical definitions between particles and dissolved solutes. We reason that the relationship to nanoparticle dissolution and particle surface area commonly portrayed in the scientific literature is mathematically fortuitous but mechanistically inaccurate. Here, we discuss number density in terms of implications for ecosystem effects described in eco-toxicology literature.