

Enhanced stability and inhibited dissolution of uraninite by nanoparticulate iron sulfide under oxic conditions

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Redox transition of uranium from dissolved U(VI) species to insoluble U(IV) precipitates can result in successful sequestration of uranium in contaminated soils and sediments. Recent studies have shown that naturally-occurring mackinawite (FeS) can provide an electron source for U(VI) reduction and retard uraninite reoxidation upon oxygen intrusion [1]. However, few studies have provided mechanistic and kinetic information on the interactions of uraninite with FeS solid under oxic conditions. The present study investigated the mechanism(s) and reaction kinetics of inhibited U(IV) reoxidation and transport by nanoparticulate FeS. The oxidative dissolution of uraninite by dissolved oxygen (DO) in FeS-bearing groundwater were conducted using batch and flow-through reactors as a function of pH, FeS content, DO and calcium concentrations, to assess the impact of critical geochemical factors on UO₂ dissolution kinetics. The results indicated that the dissolution rate of UO₂ decreased by an order of magnitude when FeS was present relative to control. The rate decreased rapidly with decreasing DO levels and increasing FeS content. In the presence of Ca²⁺, the rate was even lowered owing to the formation of Ca-containing passivation layer on uraninite surfaces. Until the depletion of FeS, DO concentration remained at significantly low levels, suggesting FeS was an effective oxygen scavenger. During the inhibition period, dissolved Fe(II), Fe(III) hydroxides, and elemental sulfur were produced from FeS oxidation. In contrast, uraninite remained as U(IV) solid as verified by X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). Although dissolved Fe(II) was not shown to reduce U(VI) under oxic conditions, residue FeS particles was responsible for inhibiting UO₂ dissolution by reducing soluble U(VI). This study suggests that naturally-occurring FeS may serve as an oxygen scavenger and a U(VI) reductant for effective uranium sequestration. These findings have direct implications for our understanding of uranium redox transition and long-term stability in the subsurface.

[1] Bargar *et al.* (2013), *PNAS*

The Mesozoic dolomites of the Levant margin - evaluating dolomitization style and mechanism from configuration and stable isotope geochemistry

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The record of the Levantine margin provides a unique window into dolomitization through the Mesozoic [1] and dolomitization in general. Ample carbonate sediments have accumulated through the Triassic, Jurassic and Cretaceous in this region, maintained at relatively shallow burial depth [2], and currently exposed at the surface. We examined the depositional configuration, and the geochemical and stable isotope compositions across several limestone-dolostone transitions, with the intention of inferring the paleoenvironmental trends leading to these transitions and the style of dolomitization in these rocks.

Sequences were selected based on the presence of repeated interchanges between limestone and dolostone, in settings where the occurrence of the dolomite is likely to be derived from early diagenetic processes and interaction with marine or evaporated marine water. Three different settings were targeted: *i*) sub-tidal, open marine, evaporite-free (Cretaceous), *ii*) intertidal, open marine, evaporite-free (Jurassic), and *iii*) restricted lagoon, in association with sulphate evaporites (Triassic). In each case, a cross-section was sampled at a spatial resolution of about 50 cm to evaluate lithological changes and variability in stable isotope ratios. Following the identification of transitions of interest, these were sampled at a spatial resolution of 1-3 cm.

Mineralogy and Ca to Mg ratios in the carbonates were determined by X-ray diffractometry, and the isotopic ratios of carbon and oxygen ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) were measured by mass spectrometry. Sedimentary textures were investigated in hand samples and in some cases by petrographic microscopy. The results of these analyses will be presented and their implications for mechanisms of dolomite genesis discussed. Future work will include analysis of Ca and Mg isotope ratios in the samples to further illuminate dolomitization mechanisms.

[1] Sass & Katz (1982) *American J. Sci.* **282**. 1184-1213. [2] Gvirtzman (2003) *Isr. J. Earth Sci.* **53**. 47-61.