

The energetic and kinetics of uranyl reduction on pyrite, hematite, and magnetite surfaces: a powder microelectrode study

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There are many studies describing the influence of parameters such as pH, pCO₂, and complexing ligands on the sorption of aqueous uranyl ions on mineral surfaces. However, few of these studies describe the reduction reaction mechanisms and the factors that influence the rate of reduction, despite the fact that the oxidation state of uranium is the most important factor controlling the mobility of uranium. In this study, the energetics and kinetics of the U(VI) reduction half-reaction on pyrite, hematite, and magnetite were investigated by electrochemical methods using a powder microelectrode (PME) as the working electrode. Anodic and cathodic peaks corresponding to the 1 e⁻ reaction redox couple, U(VI)/U(V), were identified in cyclic voltammograms of pyrite, hematite, and magnetite at pH 4.5. A second oxidation peak, corresponding to the oxidation of U(IV), was identified and provides evidence for the formation of reduced uranium phases on the mineral surfaces. In addition, uranium-containing precipitates were identified on pyrite surfaces after polarization in a PME. High Tafel slopes (> 220 mV/dec on all minerals evaluated) suggest that uranyl reduction is mediated by insulating oxide layers that are present on the semiconducting mineral surfaces. The onset potential for uranyl reduction was determined for pyrite (>0.1 V vs. Ag/AgCl), and hematite and magnetite (between -0.02 and -0.1 V vs. Ag/AgCl). The onset potential values establish a baseline kinetic parameter that can be used to evaluate how solution conditions (*e.g.*, dissolved reductants, complexing ligands, and polarizing ions) affect the kinetics of uranyl reduction.

In addition, this is the first study that uses a PME, instead of a conventional mineral electrode, to evaluate redox processes on mineral surfaces. Stable and reproducible voltammograms obtained for pyrite, hematite, and magnetite were obtained with minimal electrode preparation. The results of this study demonstrate the feasibility of using PME's to evaluate redox energetics, kinetics, and mechanisms for other environmentally-relevant, mineral-analyte systems.

²³⁸U-²³⁰Th equilibrium in arc magmas: Implications for the time scales of fluid transfer in subduction zones.

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The transfer of fluids in subduction zone can be fingerprinted in the chemistry of erupted magmas. However, there remain uncertainties regarding the processes and location of material transport from the subducting plate to the mantle wedge. Constraints on the timing of transfer relative to mantle melting are essential to understand the processes at play and the volatile cycles. Large excesses in ²³⁸U and ²²⁶Ra measured in some arc magmas are taken as indicating short time scales (hundreds to thousands of years) and, therefore, direct causality between slab fluid fluxes and mantle melting. A large proportion of arc magmas are, however, in or close to ²³⁸U-²³⁰Th equilibrium. This is generally interpreted as resulting from “buffering” of the young slab-fluid U-series signal by an older sediment component in secular equilibrium (*i.e.* >400 kyr).

Samples from Volcan de Colima, Mexico demonstrate that magmas in ²³⁸U-²³⁰Th equilibrium can have significant ²³¹Pa and ²²⁶Ra excesses. Chemical modelling indicates that, in this case, the U-Th contribution from the sediments is not sufficient to offset the ²³⁸U excesses produced by slab fluids. Melting of a mantle source that returned to secular equilibrium after addition of the slab components (time interval >400 kyr) and production of ²³¹Pa and ²²⁶Ra excesses during melting is the most likely scenario at Colima. Compilation of U-series data suggests that this scenario is common in arc settings, implying that the time span and consequently the causal relationship between slab-fluid addition and mantle melting are variable at regional and global scales.