

Observing iron redox dynamics at the nanosecond scale with time-resolved X-ray spectroscopy

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Redox processes at the surfaces of minerals drive crucial (bio)geochemical cycles. However, electron transport steps, structural rearrangement, and the formation of transition state complexes often occur too quickly for straightforward identification. Progress towards understanding rapid reaction steps will be aided by ultrafast X-ray science, an emerging field that will transform our understanding of molecular-scale processes in diverse disciplines, including geochemistry. This field requires the development of the technology and methodology to capture the molecular-scale steps in reactions of importance to environmental redox cycles.

Our work is focused on the reductive dissolution of iron oxide and oxyhydroxides, a central process in the biogeochemical cycling of iron. In this system, interfacial electron transfer leads to the formation of structural ferrous iron that may be released into solution or further react with adsorbed ions. We will describe the first ultrafast X-ray absorption studies of interfacial electron transfer to two crystal phases of iron oxide – ferrihydrite and maghemite. We have demonstrated that the binding of photoactive dye molecules to iron oxide nanoparticles permits reduction of Fe (III) in the oxide to be initiated by optical excitation of the dye. Iron redox dynamics were followed by time-resolved X-ray absorption spectroscopy (TR-XAS) at the Fe *K*-edge, using the pump-probe approach to observe the rate of formation and evolution of ferrous iron. Transient XAS spectroscopy at specific timepoints after electron transfer provide insight into the electronic structure and coordination of the transient Fe (II) species. This work represents the first studies of the nanosecond dynamics and eventual fate of ferrous iron sites formed in an iron oxide.

The development of a nickel sulphide standard for the *in situ* analysis of platinum group elements and gold by Laser Ablation ICP-MS

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A new LA-ICPMS SRM has been developed, which contains the platinum group elements and Au. The standard NiS3 was made from high purity Ni and S powders which were spiked with a solution containing Ru, Rh, Pd, Os, Ir, Pt and Au, aiming at a concentration of ~25 ppm for each element in the SRM. The mix was dried at 105 °C and subsequently fused with Na₂CO₃ at 1000 °C for 1.75 hours, yielding a 5 g NiS button. The button was cut, and a polished portion was examined by optical microscope and electron microprobe and determined to be a single phase nickel sulphide (Ni₃S₂). Quantification was performed on four, 100 mg powdered portions of the button, which were digested in aqua regia. To retain Os in solution, the portions were digested in closed vessels and the acid was not evaporated. Solutions were then diluted to 1000x immediately prior to analysis on an Agilent 7700x ICP-MS. Matrix effects were corrected for by analysing a pure pyrite sample solution spiked with similar amounts of PGEs and Au. The concentrations of the PGEs and Au were determined to be 21-24 ppm. Homogeneity of NiS3 was assessed on 15 randomly selected, 100 micron diameter LA-ICP-MS spot analyses with a New Wave UP213, yielding 1 sigma %RSDs of <4 % for Ru, Os and Ir; <8 % for Rh and Pt and ~15 % for Pd and Au. NiS3 has also been assessed against a number of other PGE and Au SRMs including 8b [1], PGE-A [2], Lombard meteorite and Po41 [3]. The analyses of these SRMs have been compared and the problems with internal consistency of the reference values will also be discussed.

[1] Wohlgemuth-Ueberwasser *et al.* (2007) *Contrib. Min. Petrol.* **154**, 607–617. [2] Alard *et al.* (2000) *Nature* **407**, 891–894 [3] Sylvester *et al.* (2005) *10th International Pt Symposium*, pp. 16–20.