

Atomistic simulation of oxygen transport in actinide oxides and at their interfaces

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Actinides such as uranium and its oxides are receiving increasing attention because of the interest in nuclear fuels not least because of awareness of issues associated with CO₂ emissions, security of energy supply and waning fossil fuel reserves. This also has implications on the storage of these materials in both the long and short term. Computational methods provide a complementary route for studying the corrosion of nuclear fuels and transport through the environment.

We used computer simulation techniques, using both potential-based and electronic structure methodologies to investigate the structure and stability of the surfaces and interfaces, primarily of uranium dioxide as well as the factors controlling oxygen transport through the materials. The electronic structure simulations used the VASP code [1] using GGA+U method, but are further complicated by the magnetic contribution of the 5f electrons. The correct ground state and properties are obtained by correctly controlling the orbital occupation matrices [2]. The interatomic potentials were derived to reproduce the calculated and experimental properties and used to evaluate the grain boundary structures as a function of temperature using molecular dynamics with the DL_POLY code [3].

A number of grain boundary structures were investigated we found that at high temperatures but below the melting point that UO₂ undergoes a fast ion transition where oxygen becomes highly mobile. The grain boundaries showed enhanced diffusivity, displaying fast ionic conduction at significantly lower temperatures than observed in the bulk crystal.

In summary a number of computational techniques have been utilised to investigate actinides such as uranium and their oxides. Increased understanding of the intrinsic disorder present in these oxides and its effect on corrosion offers significant benefits for the safe storage and handling of nuclear fuel materials.

[1] Kresse & Furthmuller (1996), *Phys. Rev. B*, **54**, 11169-11186. [2] Devey (2011) *J. Nucl. Mater* doi:10.1016/j.jnucmat.2011.03.012 [3] Smith and Forester (1996) *J. Mol Graph* **14**, 136-141

Transitional oxygenation recorded in the Paleoproterozoic Turee Creek Group, Western Australia

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In situ, multiple sulfur isotope data from pyrite in the glaciomarine Meteorite Bore Member of the Paleoproterozoic Turee Creek Group, Western Australia, indicate deposition during a transitional stage in the rise of atmospheric oxygen. Abundant detrital pyrite in one diamictite layer exhibits a range of $\Delta^{33}\text{S}$ (-3.6 to 11.6‰) encompassing the entire known range for the Archean. Small, but significant, S-MIF ($\Delta^{33}\text{S}$ from -0.8 to 1.0‰) is preserved in authigenic pyrite throughout the section. A >90‰ range in $\delta^{34}\text{S}(\text{Py})$ (-45.5 to 46.4‰ VCDT) is strong evidence for vigorous microbial sulfate reduction under non-sulfate limited conditions, an indication that oxidative continental weathering of sulfides was sufficient before and during deposition to deliver a large quantity of sulfate to the ocean. Multiple generations of pyrite were observed, distinguished by their isotopic and minor element compositions. Sharp gradients in $\delta^{34}\text{S}$ (30‰ over <4 μm ; defined by 3 μm spots) constrain the degree of sulfur diffusion during metamorphism and thus the time-temperature history of the unit. This is the first observation of such a large range in $\delta^{34}\text{S}$ together with significant S-MIF, and it reveals a chapter in the history of atmospheric oxygenation heretofore unknown from similarly age-constrained glacial deposits in North America [1] and South Africa [2]. The new data highlight the critical role of microbial sulfate reduction in the oxidative transition and are consistent with the proposal by Zahnle *et al.* [3] that increasing seawater sulfate led to the shutdown of the Archean methane greenhouse, curtailing the preservation of S-MIF. However, the suggestion that S-MIF disappears completely before continental glaciation [3] is not supported by our data or those from North America [1] and South Africa [2], and details of the Great Oxidation Event remain to be elucidated.

[1] Papineau *et al.* (2007) *EPSL* **255**, 188-212. [2] Guo *et al.* (2009) *Geology* **37**, 399-402. [3] Zahnle *et al.* (2006) *Geobiology* **4**, 271-283.