

## A multi-scale investigation of the kinetics and mechanisms of As(III) oxidation on hydrous manganese oxide

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Arsenite (As(III)) oxidation to arsenate (As(V)) by manganese(IV) oxide is an important reaction impacting the natural cycling of As. The As(III) species is substantially more toxic and tends to bind more weakly to soils than As(V) does. Heterogeneous oxidation of As(III) on the surface of manganese oxides has previously been studied; however, detailed studies on the kinetics and mechanisms of the oxidation reaction are still needed. We have employed a multi-scale approach, involving stirred-flow kinetic investigations, quick-scanning and traditional X-ray absorption spectroscopy (Q-XAS & XAS), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and high resolution transmission electron microscopy to study the As(III) oxidation mechanism.

Using Q-XAS, at a time resolution of 1 s, we determined the rate of As(III) oxidation in the first 30 s of reaction, and found that it was a factor of 2 faster than the rate observed using traditional batch techniques. A similar trend in As(V) production was observed using *in situ*, real-time ATR-FTIR. In stirred-flow experiments we observed complete As(III) oxidation and sorption during early time-points. As(V) is then observed in the reactor effluent, followed by As(III) and Mn(II). Column experiments, where Q-XAS was used to monitor As speciation at the HMO-water interface, revealed that as As(III) is introduced, first As(V) is retained followed by As(III) retention. HR-TEM analysis of the solids from column experiments revealed the presence of an amorphous layer at the HMO mineral surface.

## Delaminated North China Craton lithosphere preserved in Xugou massif peridotite, E China

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Massif peridotite at Xugou, Su-Lu metamorphic belt, E China, is dominantly, serpentinized (60-90%) and compositionally layered, Chr and Phl bearing Grt harzburgite that contains minor lenses and layers of Grt clinopyroxenite and eclogite [1]. Peridotite (mm to sub-mm scale in grain size) has porphyroclastic Pyx (cm-scale) that records at least two stages of lamellae type exsolution involving Al, Cr and Ca phases. Steep Ca isopleths and Cr-Al systematics constrain two generations of exsolution in Opx occurred during near isobaric cooling. Image quantification data suggests Opx exsolved 3.0 vol% Cpx and 1.4-3.6 vol% Grt implying precursor Pyx was stable at >1200°C and c. 5 GPa (UHP-HT). Low Al<sub>2</sub>O<sub>3</sub> content (0.20 wt%) in Opx, major element partitioning and REE partitioning ( $D^{Cpx/Grt}(Ce) > 300$ ) of the exsolved phases show chemical equilibration after exsolution at 5.6 GPa and 760°C, i.e. at greater depth than the North China Craton lithosphere after late Mesozoic delamination [2]. In contrast, the recrystallized matrix mineral assemblage has grain shape preferred orientation, replaces porphyroclasts, lacks lamellae type exsolution and has Opx with lower Al<sub>2</sub>O<sub>3</sub> content (0.12 wt%) implying strain-induced recrystallization during prograde metamorphism destroyed the Grt-Pyx exsolution microstructure until the peak at 6.3 GPa and 840°C (UHP-LT).

In conclusion, the record of Grt-Pyx mineral microstructures in mantle fragments from Xugou exceeds that of the mineral chemistry and predates local tectonic UHP metamorphism. Similar results are reported from massif peridotite in the Scandinavian Caledonides [3]. Increasing recognition that Grt-Pyx microstructures in mantle fragments (peridotite massifs and xenoliths) both are of mantle origin and occurring in global Archaean areas [2-5] requires their uptake into current models for formation and evolution of the sub-continental lithospheric mantle of the early Earth.

[1] Zhang *et al.* (2003) *JoMG* **21** 539-550. [2] Griffin *et al.* (1998) AGU Geodynamics Series **27** 107-126. [3] Spengler *et al.* (2009) *EPSL*. **281** 27-35 [4] Haggerty & Sautter (1990) *Science* **248** 993-996. [5] Spengler *et al.* (2006) *Nature* **440** 913-917.