

## Is there a link between Fe(III) oxide reactivity, Fe(II)-catalysed crystallisation and U(VI) reduction?

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The discovery that Fe (II) catalyses the crystallisation of highly disordered Fe (III) oxides from years to hours has dramatically changed our perception of the time-scales that may be involved in the iron redox cycle with far-reaching ramifications to the kinetics of other globally important biogeochemical cycles such as carbon and sulfur [1] as well as that of redox sensitive elements such as uranium [2].

While we still explore the mechanisms of this potentially exciting new pathway in the iron redox cycle, in very simplified systems, one must ask of the relevance of such studies when these conditions are typically far-removed from those experienced in the natural environment. Indeed, when done so, it is observed that the Fe (II)-catalysed crystallisation process may not have global applicability [3, 4]. However, obtaining information on why a process does not work is often as enlightening as direct observation of the process in motion.

Here we report on experiments which demonstrate that no relationship exists between Fe (III) oxide reactivity and its propensity for Fe (II)-catalysed crystallisation when the intrinsic reactivity of the Fe (III) oxide is induced by the presence of the sulfur tetrahedral oxyanion - SO<sub>4</sub>. We further demonstrate that Fe (III) oxide crystallinity is key for the Fe (II) reduction of U (VI) and, moreover, that (FeII)-U (VI) electron transfer is related to the redox potential of the Fe (II)-Fe (III) couple. In other words, U (VI) will not be reduced by Fe (II) when both are sorbed to highly disordered Fe (III) oxides such as ferrihydrite and/or schwertmannite.

[1] Burton *et al.* (2008) *GCA* **72**, 4551–4564. [2] Nico *et al.* (2009) *Environ. Sci. Technol.* **43**, 7391–7396. [3] Jones *et al.* (2009) *GCA* **73**, 4409–4422. [4] Collins *et al.* (2010) *GCA* **74**, 482–496.

## Relative Greenland and Antarctic ice sheet contributions to sea level during Marine Isotope Stage 5e

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In response to the predicted ~4°C warming by 2100, sea level is expected to rise ~0.2-0.6 m. The most recent time period with boreal summer temperatures similar to those projected is Marine Isotope Stage (MIS) 5e. During MIS 5e, sea level was at least +4-6 m above present indicating a significantly diminished Greenland (GIS) and/or Antarctic (AIS) Sheet. To estimate the GIS contribution to the MIS 5e high stand, we determine its southern margin extent using Nd-Sr-Pb isotopes from the silt fraction of sediment core MD99-2227 (58°12.64'N, 48°22.38'W, 3460 m of water depth) located on the Eirik Drift, off the coast of southern Greenland. We compare the geochemical signatures of the silt fraction of MD99-2227 to that of newly established geochemical end members of the four main southern Greenland geologic terranes: Ketilidian Mobile Belt (KMB), Archean Block (AB), Nagssugtoqidian Mobile Belt (NMB), and Tertiary Basalt (TB). End-member mixing calculations show that the silt was sourced from all four terranes during MIS 5e, indicating that no single southern Greenland terrane was completely deglaciated during MIS-5e, similar to our observations from the Holocene portion of MD99-2227. However, low <sup>87</sup>Sr/<sup>86</sup>Sr with more negative ε<sub>Nd</sub> values indicate a greater NMB provenance component during MIS-5e relative to the Holocene, which has a larger AB component as evidenced by the higher <sup>207</sup>Pb/<sup>206</sup>Pb and more negative ε<sub>Nd</sub>. The enhanced input from the NMB at the expense of the AB implies greater southern GIS retreat during MIS-5e. A comparison of these results to published MIS 5e ice sheet model extents indicate a MIS 5e sea-level high stand contribution from the GIS of 1.6-2.5 m, requiring that the AIS supplied >1.5 m of the +4-6 m sea-level high stand. These results indicate that both the GIS and AIS are sensitive to climates warmer than present and will equally contribute to future sea level rise.