The effect of molybdenum on the transformation kinetics of ferrihydrite to hematite: An *in situ* ED-XRD approach

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Ferrihydrite (FH) is a metastable poorly-ordered phase that has a high affinity for trace metals. During its transformation to stable iron oxide phases (i.e., goethite, GT or hematite, HM), any coprecipitated or adsorbed metals will be either released back into solution or sequestered by the newly formed phases. However, the kinetics and mechanisms of the FH to GT/HM transformation in the presence of coprecipitated ions (in this study Mo), as well as the fate of the metals during this process are poorly understood.

Synchrotron-based Energy Dispersive X-Ray Diffraction (ED-XRD) was used to collect *in situ* and realtime data on the transformation of FH (± Mo) to GT and HM. Experiments were designed to mimic the geochemistry of Mo-iron nanoparticle crystallisation in deep sea hydrothermal plumes (IS = 0.7, pH = 8). Isothermal transformation experiments were perfomed at temperatures ranging from 140 to 240ºC.

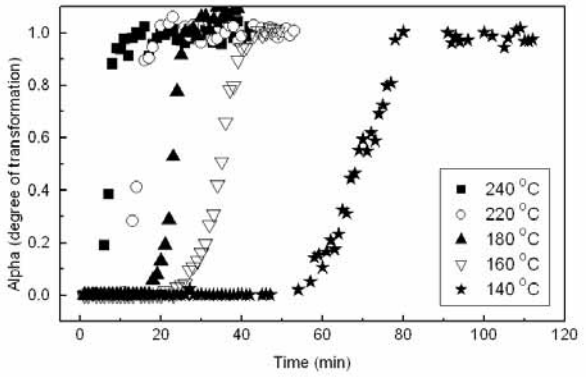

Figure 1: Reaction progress for the HM (110) ED-XRD peak.

The reaction product in all experiments was HM, but a minor amount of GT formed as an intermediate phase. The presence of Mo (1% molar ratio) in the initial FH retarded the transformation to HM by ~ 10%, when compared with the pure FH system. In addition, complementary X-Ray Absorption Spectroscopic (XAS) data showed that most of the Mo in the final product (HM) was structurally incorporated.

The temperature dependence of global rainfall patterns

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Based on computer modeling, Held and Soden predict that the coming global warming will dry out the extratropics and bring extra rainfall to the tropics. We test this prediction against the situation for the last glacial period and find that indeed there was a large increase in rainfall at temperate latitudes and a suggestion of a reduction in rainfall in the tropics. As the decrease in ice cover from glacial to Holocene was far less than that which will be generated by global warming, we use the difference in response between the LGM (26 to 18 kyrs) and the Mystery Interval (17.5 to 14.5 kyrs) as a means of separating the impacts of cooling and ice cover. Our conclusion is that the glacial record supports the Held – Soden hypothesis.