Thermodynamic properties of aqueous phenanthrene and isomers of methylphenanthrene at high temperature

JEFFREY DICK[1*], KATY EVANS[2], ALEX HOLMAN[1], CAROLINE JARAULA[1] AND KLITI GRICE[1]

[1]WA Organic and Isotope Geochemistry Centre, Department of Chemistry, and [2]Department of Applied Geology, Curtin University, Bentley WA, Australia, Jeffrey.Dick@curtin.edu.au (* presenting author)

Polycyclic aromatic hydrocarbons, including monomethylated phenanthrenes (MP), are common components of bitumen associated with sediment-hosted ore deposits. Their relative abundances are often interpreted as indicators of thermal maturity and hence may help constrain models for the transport and deposition of metals sharing a genetic history with the organic compounds. A high degree of thermal maturation yields products in chemical equilibrium [1], but a lack of thermodynamic data for aqueous MP at high temperature has precluded a quantitative interpretation of their origin in hydrothermal settings. Values for the standard molal Gibbs energy and enthalpy, entropy, and heat capacity were generated for aqueous phenanthrene and the MP isomers methylated at the 1-, 2-, 3-, 4- and 9-positions on the phenanthrene structure. These values were derived from reported thermodynamic properties of the crystalline compounds [2], their solubilities and enthalpies of solution, and relative properties of the MP isomers from quantum chemical simulations [3] at 25 °C. Preliminary extrapolations to higher temperature were carried out using a constant heat capacity difference between the isomers. At 25 °C, 2-MP is highly favored over 1-MP. With increasing temperature, however, the difference in stability between the two diminishes, eventually crossing over to higher stability of 1-MP at temperatures greater than ~400 °C. The calculated equilibrium ratios of 2-MP to 1-MP (MPR) are consistent with two independent constraints: (1) maximum reported values for mature source rocks (~160 °C), and (2) MPR observed in Archaean rocks exposed to temperatures of 200–300 °C [4].

These comparisons indicate that relative abundances of methylphenanthrenes can be used to infer thermal conditions and sources of bitumen found in ores and host rock. At the Here's Your Chance (HYC) Pb-Zn-Ag deposit (McArthur River, Northern Territory, Australia) bitumen in the ore zones has a lower MPR than unmineralized shale samples. The range of values in the bitumen associated with the ore is consistent with temperatures of isomeric equilibration of ~350–400 °C. The source of MP, therefore, could reasonably have been a hot brine that cooled as it reached the ore zone. The offset in the relative abundances of MP between the ore and shale layers suggests a different degree of interaction of the brine with these layers. Since phenanthrene has a higher average oxidation state of carbon than its methylated counterparts, consideration of their relative abundances in a thermodynamic framework could place constraints on redox conditions in the ore-forming system.

[1] Mackenzie, A. S. (1984) *Advances in Petroleum Geochemistry* **2**, 115-214. [2] Richard, L. and Helgeson, H. C. (1998) *Geochim. Cosmochim. Acta* **62**, 3591-3636. [3] Szczerba, M. and Rospondek, M. J. (2010) *Org. Geochem.* **41**, 1297-1311. [4] Brocks, J. J. et al. (2003) *Geochim. Cosmochim. Acta* **67**, 4289-4319.

The possible role of crystal conduction and inter-particle electron transfer in Fe-oxide phase transformation and growth

K. DIDERIKSEN[1*], B. GILBERT[2], C. FRANDSEN[3], M. ZHU[2], S.L.S. STIPP[1], J.F. BANFIELD[4]

[1]University of Copenhagen, Nano-Science Center, Dept. of Chemistry, knud@nano.ku.dk (*presenting author); stipp@nano.ku.dk
[2]Lawrence Berkeley National Laboratory, Earth Science Division, BGilbert@lbl.gov; mzhu@lbl.gov
[3]Technical University of Denmark, Dept. of Physics, fraca@fysik.dtu.dk
[4]University of California, Berkeley, Dept. of Earth & Planetary Science, jbanfield@berkeley.edu

A series of anerobic experiments have been conducted to study the mechanism of Fe^{2+}-mediated ferrihydrite transformation. At pH 6.5 and 7 and in the presence of 5 mM dissolved $Fe(II)Cl_2$, freshly formed, 2-line ferrihydrite rapidly exchanges isotopes with Fe^{2+} in solution (75% equilibration within 10 minutes). During the first 2-3 hours of reaction, X-ray pair distribution function (PDF) analysis and transmission electron microscopy shows evidence of increasing size of ferrihydrite particles and coherent scattering domains, but minor or no mineral transformation. After this lag phase, more rapid transformation commences to major end-phases lepidocrocite (pH 6.5) and magnetite (pH 7).

Extensive isotope exchange for ferrihydrite without significant phase transformation indicates that interfacial electron transfer and crystal conduction leads to oxidation of adsorbed Fe(II), resulting in Fe(III)-oxide growth, and reductive dissolution of Fe(III) at a different site, similar to what was initially observed for hematite [1]. In contrast to the lag phase observed for 2-line ferrihydrite, transformation of 6-line ferrihydrite to magnetite commences immediately at pH 7. More rapid conversion of larger and presumably less soluble ferrihydrite is inconsistent with recrystallisation by classical dissolution/reprecipitation. Rather, it suggests solid state transformation with magnetite nuclei forming either inside the ferrihydrite or at its surface.

With X-ray diffraction, materials subjected to ultrasonification during reaction display much weaker Bragg peaks from goethite, lepidocrocite and magnetite than those observed from material synthesised in regular experiments and the coherent scattering domains of the phases are smaller in PDF. This indicates that particle contact enhances crystal growth. Such a feature could reflect growth by 1) oriented attachment, which has been observed for ferrihydrite conversion to goethite [e.g. 2], or 2) electronic coupling between crystals, leading to Fe^{2+} electron donation and crystal growth on one particle, then transfer of the electron to an adjacent particle where interfacial reduction and dissolution occur.

[1] Yanina et al. (2008) *Science* **320**, 218-220. [2] Banfield et al. (2000) *Science* **289**, 751-754.