Primary origin *vs.* redistribution of trace elements by fluid flow in slope facies Ediacaran carbonate rocks from the Yangtze Platform (South China)

HARRY BECKER[1*], WIEBKE BAERO[1], MANUEL QUIRING[1], KONRAD HAMMERSCHMIDT[1], UWE WIECHERT[1] AND DOROTHEE HIPPLER[2]

[1]Freie Universitaet Berlin, Institut fuer Geologische Wissenschaften, Germany, hbecker@zedat.fu-berlin.de (* presenting author)

[2]Technische Universitaet Berlin, Institut fuer Angewandte Geowissenschaften, Germany

A major problem for the interpretation of the composition of ancient marine carbonates is the variable response of different elements to diagenesis and post-depositional fluid flow. We have studied this issue in Ediacaran dolostones, limestones and marlstones from members D1, D3 and D4 of the Doushantuo Formation (635-551 Ma) from the slope facies Panmen section (Songtao, Guizhou) on the Yangtze Platform. The carbonate rocks display a strong, but variable influence of secondary processes as indicated by $\delta^{18}O$ (-5 to -14) and $^{87}Sr/^{86}Sr$ (0.723 to 0.710) data in comparison to data of stratigraphically correlated samples from shallow platform settings [1]. Decreasing $^{87}Sr/^{86}Sr$ from bottom to top of the section and very low abundances of feldspar, illite and chlorite in some of these samples suggest that the radiogenic Sr in the carbonates was not introduced by closed-system diagenetic redistribution from silicates within the rock, but by open-system fluid flow and associated recrystallization of carbonates. In the D3 member, the overprint by fluid flow is indicated by a weak correlation of $\delta^{18}O$ with $^{87}Sr/^{86}Sr$ and correlation of $\delta^{18}O$ with $\delta^{13}C_{carb}$. Modeling of fluid-rock interaction shows that high and variable Sr abundances in water rich fluids (low-C/O) are consistent with the data trends in the D3 member, and may account for 1 to 2 ‰ of the variation in $\delta^{13}C_{carb}$. In spite of these secondary modifications, some carbonate rocks at different positions in the section display seawater signals in their acetic acid leachates, such as high Y/Ho and positive or negative Ce anomalies. Relatively high abundances of Th, REE and Pb in the acetic acid leachates and correlations of Th with Fe abundances, suggest that these elements were redistributed by fluid flow. They may have been originally hosted in Fe oxyhydroxide phases in the rock, released upon reduction and dissolution of Fe phases and incorporated into recrystallized carbonates. Further constraints were obtained from leaching experiments on cap dolostones of the section using stepwise digestion in 10% HAc, 6 M HCl and conc. HF-HNO₃. These results indicate the presence of HCl soluble Fe rich phases, presumably oxides or oxyhydroxides. The REE patterns of the HCl fraction are bell shaped and differ considerably from the patterns of acetic acid leachates. The data suggest that in many samples, fluid mobile elements, but also REE, Th and Fe have been redistributed into recrystallized carbonates. This is raising questions about the scale of postdepositional element redistribution in such sections.

[1] Sawaki *et al.* (2010) *Precambrian Research* **176**, 46-64.

Quantum-mechanical calculations on actinide sorption and reduction of sulfides and oxides

U. BECKER[1*] AND D. RENOCK[2]

[1] Dept. of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI., USA, ubecker@umich.edu (* presenting author)

[2] Dept. of Earth Sciences, Dartmouth College, Hanover, NH., USA, Devon.J.Renock@Dartmouth.edu

The results of several recent studies are challenging the way actinide geochemists consider redox processes in the near surface environment. Such studies include: the complex chemistry of electron and spin transitions between $U^{6+} \leftrightarrow U^{5+} \leftrightarrow U^{4+}$ aqueous complexes and solids, spatially separated redox processes linked over millimeter distances by complex networks of bacterial nanowires combined with pyrite, simultaneous oxidative growth and reductive dissolution on a single hematite crystal driven by potential differences between crystal faces, sulfide oxidation mechanisms that are rate-limited by the transition from high spin O_2 to low spin O.

In order to shed light on the electron transfer between reductants (*e.g.*, hydrogen sulfides, Fe^{2+}, hydroquinones as an organic/microbial analogue), oxidants (different actinyl complexes), catalytic mineral surfaces (periodic slabs and nano-clusters of hematite, pyrite, and mackinawite, and galena), and polarizing anions (*e.g.*, carbonate, sulfate).

An example calculation is the co-adsorption of a uranyl cation and a hydroquinone on the opposite sides of a pyrite nano-cube. The interaction of the hydroquinone with the uranyl complex through the pyrite nanoparticle can be quantified/visualized in different ways: (i) by the synergistic energy of the co-adsorption of uranyl and hydroquinone on pyrite, (ii) by the amount of electron transfer to the uranyl, and (iii) by visualization of the charge distribution in different adsorbate configurations.

During the co-adsorption/reduction process, the hydroquinone becomes positive (sum of Mulliken charges = 1.12) and the uranyl with an initial charge of +2 becomes almost neutral (+0.08), indicating electron transfer of about two elemental charges towards the uranyl. This is an indication that a neutral UO_2 unit is formed, which can serve as a nucleus of UO_2 formation. In contrast, if no hydroquinone is present, only about half an elemental charge is transferred from the pyrite nanoparticle. This is an example how the hydroquinone can be used as an analogue for electron shuttling by metal-reducing bacteria through the pyrite towards the uranyl.

Another example is the co-adsorption of hydroquinone and uranyl on a mackinawite nanoparticle. While the π orbitals of the quinone interact with the postitive Fe cations, the uranyl-O comes within bond distance with the Fe on the right. Electrons can be transferred within the same orbital of the entire system (e.g, the HOMO stretches over the entire system). Interestingly, even though mackinawite is a low-spin system as a bulk mineral, the co-attack by quinone and uranyl spin-polarizes the Fe atoms along the path in a down-up-up-down pattern. This is kinetically important to accommodate the spin transition on the right from U^{6+} (no spin) to U^{4+} (two unpaired spins).