Zr speciation and partitioning in SiO_2-rich aqueous fluids and silicate melts

M. LOUVEL[1]*, C. SANCHEZ-VALLE[1], S. PETITGIRARD[2,4], H. CARDON[2], I. DANIEL[2] AND J. CAUZID[3,4]

[1]Institute for Mineralogy and Petrology, ETH Zurich, CH-8092, Zurich (*correspondence: marion.louvel@erdw.ethz.ch)
[2]Laboratoire de Sciences de la Terre, UMR 5570 CNRS-ENS-UCB Lyon1, F-69364 Lyon Cedex 07, France
[3]Departement des Sciences de la Terre, Nancy-Universite, G2R, 54506 Vandoeuvre-les-Nancy, France
[4]European Synchrotron Radiation Facility, F-38043 Grenoble Cedex 9, France

In the last years, the influence of fluid composition on the mobility of HFSE elements in subduction zones has been a matter of debate [1,2]. Although HFSE are considered as incompatible elements, zircon and rutile-rich veins found in UHP rocks suggest they can be efficiently mobilized under specific conditions [3]. For instance, Manning *et al.* [4] recently reported that the solubility of TiO_2-rutile is strongly enhance in alkali SiO_2-rich fluid. However, there is not experimental constrains on the behavior and mobilization conditions of Zr in high-pressure subuction fluids.

Here we report the results of *in situ* X-ray Absorption Fine Structure (XAFS) and Synchrotron X-ray fluorescence (XRF) experiments designed to investigate the speciation and partitioning of Zr in high P-T SiO_2-rich aqueous fluids and alkali silicate melts up to 600°C and 2.5 GPa. XRF and XAFS data were collected at the ID22 μ-fluorescence beamline of the ESRF (Grenoble, France) using an hydrothermal diamond-anvil cell (HDAC) [5]. For the experiments, either single-crystal of quartz or pieces of $Na_2Si_2O_5$ synthetic glass were loaded in the cell together with standard Zr-bearing aqueous solutions (4 wt% Zr). Pressure in the sample chamber was monitored from the PVT equation of state of a chip of gold added to the experimental volume.

The results of the XRF and XAFS experiments provide valuable information on the partitioning behavior and structural envirommment of Zr in high P-T fluids. The XRF data suggest that Zr preferentially partitions into the silicate melt at the P-T conditions of the experiments. XAFS data are interpreted in terms of Zr speciation and preliminary results suggest that there is no significant change in the structural environment of Zr up to 600°C-2.5 GPa.

[1] Ayers *et al.* (1993) *Contrib. Mineral. Petrol.* **114**, 321-330. [2] Antignano & Manning (2008) *Chem. Geol.* **255**, 283-293. [3] Rubatto & Hermann (2003) *Geoch. Cosmo. Act.* **67**, 2173-2187. [4] Manning *et al.* (2008) *Earth Planet. Sci. Lett.* **272**, 730-737. [5] Bassett *et al.* (1993) *Rev. Sci. Inst.* **64**, 2340-2345.

Molecular biomarker records from mid-Proterozoic sedimentary rocks and kerogens

GORDON D. LOVE[1]*, CHAO LI[1], STEPHEN A. BOWDEN[2], CHARLOTTE STALVIES[3] AND ROGER E. SUMMONS[4]

[1]Department of Earth Sciences, University of California, Riverside, CA 92521, USA (*correspondence: glove@ucr.edu, chaoli@ucr.edu)
[2]Department of Geology and Petroleum Geology, University of Aberdeen, AB24 3UE, UK (s.a.bowden@abdn.ac.uk)
[3]School of Civil Engineering and Geosciences, University of Newcastle , NE1 7RU, UK (farliec@lhotmail.com)
[4]MIT-EAPS, MA 02139, USA (rsummons@.igcas.ac.cn)

It has been proposed that sulfidic ocean conditions [1] could have been prevalent through most of the Proterozoic (~1.8 Gyr to ~0.8 Gyr) and this could have severely impeded the evolution and expansion of eukaryotic life [2]. Previously reported solvent-extractable biomarker data from 1.64 Barney Formation rocks from the McArthur Basin, Australia [3] provided supporting evidence for a highly stratified and euxinic ocean structure with abundant green and purple sulfur bacterial communities thriving in the photic zone but with only trace amounts of regular eukaryotic (4-desmethyl) sterane signal. Yet the extent of sulfidic conditions during the Proterozoic is increasingly questioned and recent multiple S isotope records [4] from a Barney Creek Fm. core point to deposition of these rocks in a restriced marine environment which may not be representative of widespread oceanic conditions at this time.

Here we show biomarker evidence for at least 2 distinct sedimentary organic facies within the B. Creek Fm., representing different depositional environments and associated microbial communities, from a rock core drilled through thermally well-preserved strata. The parallel analyses of free (solvent-extractable) and kerogen-bound biomarkers affords more confidence that we have correctly identified syngenetic compounds. We compare the Barney Creek Fm. biomarker assemblages with those obtained from 1.7-0.85 Gyr rocks from the Jixian section, Yanshan Basin, China, for which putative eukaryotic fossil remains have been previously reported [5].

[1] Canfield (1998) *Nature* **396**, 450-453. [2] Anbar & Knoll (2002) *Science* **297**, 1137-1142. [3] Brocks *et al*. (2005) *Nature* **437**, 866-870. [4] Johnston *et al*. (2008) *GCA* **72**, 4278-4290. [5] Zhu *et al*. (1995) *Science* **270**, 620-622.