In situ studies of aqueous fluid properties at high pressures and temperatures using hydrothermal diamond-anvil cells

CHRISTIAN SCHMIDT

GeoForschungsZentrum Potsdam, Telegrafenberg, 14473 Potsdam, Germany (hokie@gfz-potsdam.de)

Aqueous fluids and their interaction with mineral assemblages play a key role for the mobility of elements and, thus, material flux in the lithosphere. The invention of the hydrothermal diamond-anvil cell (HDAC) [1] has extended the *PT* range, in which aqueous fluid properties can be studied *in situ*, up to the conditions of the lower crust and dehydrating slabs.

Modifications of the HDAC design [2,3] permit application of synchrotron-radiation X-ray techniques to investigate the behavior of dissolved heavy elements with X-ray emission energies as low as ~4 keV and absorption edge energies as low as ~5 keV. Time-resolved SR-XRF analyses have been used to study the solubility of minerals containing elements with $Z \geq 22$ in aqueous fluids, the kinetics of fluid-mineral interaction, and trace element partitioning between aqueous fluids and silicate melts [e.g., 4, 5]. A minimum detection limit of about 2 ppm for Ti ($K\alpha$ energy=4.5 keV) was achieved in recent in situ SR-XRF experiments on the solubility and dissolution kinetics of rutile in H_2O+$NaAlSi_3O_8$ and H_2O+$Na_2Si_3O_7$ fluids to 800 °C and 1.3 GPa. Complexation and speciation of heavy elements in aqueous melts and fluids have been investigated in situ by X-ray absorption techniques, e.g., SR-XAFS analyses of the La L_3-edge in a study of the hydration structure of aqueous La^{3+} (0.007 *m*) to 300 °C and 160 MPa [6] or SR-XANES measurements on Fe^{2+} in water-saturated haplogranitic melt up to 700 °C and 500 MPa [7].

Raman spectroscopy and Bassett-type HDACs have been used in a number of studies to obtain information on the behavior of light elements at high *PT*, e.g., on the speciation of silica to 900 °C and 1.4 GPa [8] or the complexation of boron to 600 °C and 2 GPa [9]. However, utilization of Raman spectroscopy as a quanititative tool is still in an early stage. Much remains to be learned about fluids in deeper portions of the lithosphere, and further method developments (e.g., to determine electrical conductance and density of such fluids) are needed.

References

[1] Bassett, W.A. *et al*. (1993), *Rev. Sci. Instrum.* **64** 2340-2345; [2] Bassett, W.A. *et al*. (2000), *Z. Kristallogr.* **215** 711-717; [3] Schmidt, C. and Rickers K. (2003*) Amer. Mineral.* **88** 288-292; [4] Schmidt, C. *et al*. (2007), *Lithos* **95** 87-102; [5] Schmidt, C. *et al*. (2006) *Amer. Mineral.* **91** 1211-1215; [6] Anderson A.J. *et al*. (2002) *Amer. Mineral.* **87** 262-268; [7] Wilke, M. *et al*. (2006) *Chem. Geol.* **229** 144-161; [8] Zotov, N. and Keppler, H. (2002) *Chem. Geol.* **184** 71-82; [9] Schmidt, C. *et al*. (2005) *Geochim. Cosmochim. Acta* **69** 275-281

Trace elements in foraminiferal calcite: New understanding based on *in situ* analysis

D.N. SCHMIDT[1] AND S. A. KASEMANN[2]

[1]Department of Earth Science, University of Bristol, Bristol Uk; (d.schmidt@bristol.ac.uk)
[2]Grant Institute of Earth Science, University of Edinburgh, Edinburgh UK; (simone.kasemann@ed.ac.uk)

Trace element concentrations in foraminiferal carbonates are a widely used as proxy to assess past climates and ocean circulation. Planktic foraminifers strongly discriminate against trace element incorporation, resulting in Me/Ca ratios which are significantly lower than ambient sea water concentrations. Physiological (e.g. photosynthesis, respiration, and calcification) and ecological processes (e.g. depth migration) can modify the trace element uptake into the foraminiferal calcite and thus exert an important influence on Me/Ca ratios. *in situ* analysis of spatially resolved elemental ratios increase our understanding of biological processes influences in incorporation of these proxies in foraminifers. The applicability of the proxy and the precision of palaeoclimate assessment will depend on our understanding of the incorporation of these trace elements into foraminiferal carbonate.

To this end, we have performed trace element analysis using Secondary Ionization Mass Spectrometry and Electron Microprobe on planktic foraminifers from sediment samples and sediment traps. The sediment trap samples from the Canary Islands and the western equatorial Atlantic allow for direct comparison between ambient conditions and Me/Ca ratios. We analysed symbiont bearing *(G. ruber*, *G. sacculifer*) and asymbiotic (*G. truncatulinoides*, *G. tumida*) species which are living in different depth habitats. Mg/Ca, Ba/Ca, Li/Ca and Sr/Ca ratios were analysed in profiles and spot measurements in and across several chambers and specimens. The profiles at a resolution 2.0 µm clearly display the chemical variability within the multi-layered foraminiferal test. Additionally, we document Me/Ca variability during the development of the organism and, using specimens from different seasons with optimal and suboptimal growth rates, assessed the influences of foraminiferal growth rates on element incorporation.

Foraminiferal test displays strong heterogeneity in Mg/Ca, B/Ca, Ba/Ca, and Li/Ca but not in Sr/Ca ratios. B/Ca within one specimen range from 20 to 120 mmol/mol, Ba/Ca from 1.2 to 4.5 mmol/mol, Mg/Ca ratios from 0.6 to 1.2 mmol/mol. The proloculus, the first chamber, displays significantly higher Mg/Ca and B/Ca ratios but not Sr/Ca and Ba/Ca which can not be explained by environmental conditions alone.