Modelling infiltration driven reactions using experiments: Coupled dissolution-precipitation and exchange reaction between spinel grains in the presence of water

T. MÜLLER, R. DOHMEN AND S. CHAKRABORTY

Inst. für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Germany
(Thomas.H.Mueller@rub.de)

Infiltration of fluids (aqueous, carbonaceous or silicate melts) are known to cause reactions that drive processes ranging from diamond formation in the mantle, through melting in subduction zones, metasomatic alteration and ore deposit formation in the crust, to volcanic eruptions closer to the surface. While the thermodynamics of such infiltration driven systems have been the topic of many classical studies [1], the kinetic response of systems to such large, sudden shifts in chemical affinities of a reaction remain poorly studied. We have developed an experimental set up to study the kinetic behavior of such systems that are initially far from equilibrium [2]. It is particularly important to study the response of solid solutions to such perturbations if the results are to be applicable to natural systems.

In our experimental system, pure distilled water that is out of equilibrium with spinel solid solutions of different compositions are brought into contact with these at a defined pressure and temperature (2 kbar, 750°C). At equilibrium, the spinel grains should have the same composition that is in equilibrium with the coexisting aqueous fluid containing dissolved ions. The approach to this state requires the simultaneous operation of net transfer reaction between spinel and water and element exchange reactions between spinels. We track the course of this evolution through time series experiments. We find that texturally as well as chemically the different spinel compositions respond differently to the peturbation (Mg-rich spinel: etch pits on the surface, continuous volume diffusion; Fe-rich spinel: terraces on the surface, surface controlled reaction). Broad aspects of this evolution can be quantified using a model and reaction mechanism map that has been recently proposed by Dohmen and Chakraborty [3].

[1] Korzhinskii, D.S. (1965), *AmJSci*, 193-205. [2] Müller, T., Dohmen R., Chakroborty S. (2008), *EOS Trans*. AGU, V24C-01. [3] Dohmen R. and Chakraborty S. (2003), *AmMin,* 1251-1270.

Direct analysis of ice cores by UV-laser ablation ICPMS

W. MÜLLER[1], J.M.G. SHELLEY[2]
AND S.O. RASMUSSEN[3]

[1]Department of Earth Sciences, Royal Holloway University of London, Egham, Surrey, UK (w.muller@es.rhul.ac.uk)
[2]Laurin Technic P/L, Canberra, ACT 2604, Australia
[3]Centre for Ice and Climate, Niels Bohr Institute, DK-2100 Copenhagen

Polar ice cores as key palaeoclimate archives are crucial for our understanding of the extent and time-scale of past natural climate variability [1]. Accurate dating of ice cores is paramount for comparison with other palaeoarchives, ultimately leading to an assessment of leads and lags between archives and the establishment of cause and effect. Whenever possible, dating of ice cores is achieved by layer counting, which for the Greenland ice cores recently furnished a new time scale (GICC05) based on sub-annual multi-proxy data [2]. These include physical (optical) and chemical properties such as seasonally varying cation (e.g. Ca, Na) and anion (e.g. NO_3, SO_4) concentrations measured by continuous flow analysis (CFA) of melted ice with an effective resolution of >10 mm.

In order to improve the spatial and hence time resolution of ice core analysis, we present data utilizing a new custom-built cryogenic sample holder that facilitates direct chemical analysis of ice from Greenland ice cores at unprecedented time resolution. The new sample holder is fully compatible with a Laurin LA cell (two-volume LA cell), in turn coupled to a RESOlution M-50 excimer (193 nm) LA-system and an Agilent 7500ce/cs ICPMS with collision cell [3]. Three 50 mm strips of ice core ice can be mounted simultaneously and are kept below minus 15°C using water-cooled Peltier elements. This setup facilitates continuous profiling using a rectangular laser spot with large aspect ratio (e.g. 500 x 50 µm) to both maximize time resolution as well as chemical signals, crucial in view of the low cation-concentrations in glacial ice (≤few 100s ppb). UV-LA at 193 nm couples well to glacial ice despite the strongly decreasing absorption between 160 and 200 nm [4] and produces well-defined LA tracks and reproducible ICPMS signals. System setup, pre-cleaning and calibration strategies as well as comparisons to CFA data will be presented.

[1] Steffensen *et al.* (2008) *Science* **321,** 680-684. [2] Rasmussen *et al.* (2006) *J Geophys Res* **111,** D06102. [3] Müller *et al.* (2009) *JAAS* **24,** 209-214. [4] Warren & Brandt (2008) *J Geophys Res* **113,** D14220.