Partitioning of Rb and Sr between haplogranitic melts and aqueous fluids: Information from *in situ* experiments using SR-XRF

M. BORCHERT¹, M. WILKE¹, C. SCHMIDT², K. RICKERS-APPEL³ AND J. KOEPKE⁴

 ¹Universität Potsdam, Karl-Liebknecht-Str. 24, 14476 Potsdam-Golm (manu@geo.uni-potsdam.de)
²GFZ Potsdam, Telegrafenberg, 14473 Potsdam
³HASYLAB/DESY, Notkestr. 85, 22607 Hamburg
⁴Universität Hannover, Callinstr. 3, 30167 Hannover

Knowledge of the partitioning of trace elements between silicate melts and coexisting aqueous fluids is essential for the understanding of mass transfer during late stage magmatic processes. Fluid-melt partitioning depends on numerous parameters such as temperature, pressure, chlorinity and pH of the fluid, and the composition of the melt. Although there are several experimental studies on trace element partitioning in various fluid-melt systems [e.g. 1, 2, 3], the effect of many compositional parameters is still insufficiently known.

We investigated the partitioning of Rb and Sr between synthetic haplogranitic melts and an aqueous NaCl fluid at 750°C and 200 MPa using cold-seal pressure vessels. The resulting partitioning coefficients $(D^{f/m}_{X}=C^{f}_{X}/C^{m}_{X})$ scatter up to a factor of 5. This scatter may be caused by 1) changes in the fluid composition during quenching, 2) fluid loss during extraction from the capsules or 3) feldspar formation during the runs. Therefore, we determined the concentrations of Rb and Sr in the aqueous fluid coexisting with the melt directly at high P and T using a hydrothermal diamond-anvil cell (HDAC) and SR-XRF analyses [4]. The in-situ experiments were done at the SR-XRF microprobe at beamline L of DORIS III at HASYLAB/DESY. A glass chip doped with 2500 ppm Rb and Sr and an aqueous solution were loaded into the sample chamber of the HDAC, which was then heated to 750 °C. Equilibrium was attained in less than 20 min, as indicated by consecutive XRF spectra of the fluid. Because it was not possible to analyse the melt droplets without a contribution from the aqueous phase to the XRF signal, the Rb and Sr concentrations in the melts were measured on the quenched glass using EMP. For pure water as starting fluid, a Rb concentration of 322 ± 23 ppm was obtained in situ at 750°C and 700 MPa in the aqueous phase, which resulted in a $D_{Rb}^{f/m}$ of 0.129 ± 0.013. This is much higher than a $D_{Rb}^{f/m}$ of 0.006 at 750°C and 200 MPa reported in the literature [5] obtained from analyses of quench fluid and glass.

References

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Mechanistic study of the photodissolution of lepidocrocite (γ-FeOOH) by model siderophores

PAUL BORER^{1,2}, STEPHAN J. HUG¹, BARBARA SULZBERGER¹, STEPHAN M. KRAEMER³ AND RUBEN KRETZSCHMAR²

- ¹Swiss Federal Institute of Aquatic Science and Technology (Eawag), Switzerland
- ²Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, Switzerland
- ³Department of Environmental Geosciences, University of Vienna, Austria (paul.borer@env.ethz.ch)

Dissolution of iron (hydr)oxides by siderophores is a process that potentially contributes to the generation of bioavailable iron in marine waters. We have recently shown that the ligand-promoted dissolution of lepidocrocite (\gamma-FeOOH) by model siderophores (aerobactin and desferrioxamine B) is enhanced at pH 6 under simulated sunlight [1]. Based on that study we hypothesized that the photoreactive α -hydroxycarboxylic acid moiety within aerobactin is not involved in the inner-sphere coordination at the surface of lepidocrocite. The enhanced dissolution of lepidocrocite was explained in terms of the intrinsic photoreactivity of the oxide phase itself and not by a lightinduced photolysis reaction of adsorbed aerobactin. To verify the above hypothesis, extensive batch dissolution experiments with aerobactin and the non-photoreactive desferrioxamine B were conducted between pH 3 and pH 8 in the dark as well as under irradiation. Adsorption isotherms were determined and the potential readsorption of Fe(III)-siderophore complexes was evaluated. Based on these results a kinetic rate law for the dissolution of lepidocrocite was formulated for both desferrioxamine B and aerobactin. The calculated dissolution rate constants for the two model siderophores between pH 5 and pH 8 were very similar. This is a strong indication that aerobactin forms inner-sphere surface complexes by the coordination of the terminal hydroxamic acid moieties (as is the case for desferrioxamine B) and not by the photoreactive α -hydroxycarboxylic acid moiety.

References

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