

IN SITU DETERMINATION OF THE PARTITIONING OF LEAD, STRONTIUM AND RUBIDIUM BETWEEN HYDROUS MELTS AND AQUEOUS FLUIDS AT HIGH PRESSURE AND TEMPERATURE

H. Bureau¹, B. Ménez², V. Malavergne^{3 and 4}, A. Somogyi⁵, M. Munoz⁶, A. Simionovici⁷, D. Massare¹, M. Burchard⁸, S. Kubsy⁹, C. Shaw¹⁰. ¹LPS – CEA-CNRS, CE Saclay, 91191 Gif s/Yvette, France, hbureau@drecam.cea.fr ²LGM, IPGP, 4 place Jussieu, Paris, France ³Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, USA. ⁴Lab. Géomatériaux, IFG, Marne la Vallée, France ⁵ESRF, BP220, Grenoble, France ⁶LGCA, Grenoble France ⁷ENS Lyon, Lyon, France ⁸Ruhr Universität Bochum, Bochum, Germany ⁹Ruhr-Uni-Bochum, Lehrstuhl für Experimentalphysik III, Germany ¹⁰University of New Brunswick, Fredericton, New Brunswick, Canada

Introduction: Subduction zones are the locations where the oceanic crust, which experienced intense interaction with seawater, is buried back into the Earth's mantle. These environments play a critical role in the global geochemical cycle of Earth, being the location at which chemical components are both recycled into the mantle and returned to the atmosphere through volcanism. It is now generally admitted that magma genesis at subduction zones is mainly induced by the presence and movement of fluids (aqueous fluids and/or silicate melts) released continuously in large amounts due to dehydration reactions in the subducted slab. It is also believed that these fluids may be responsible of the atypical trace-element signature of the Island Arc Basalts (IAB), which are enriched in Large Ion Lithophile Element (LILE= Sr, Rb, Ba, Pb) and depleted in High-Field Strength Element (HFSE= Zr, Ti, Hf, Nb, Ta) compared to Mid-Ocean Ridge Basalts (MORB).

The present study combined diamond anvil cells experiments with the high-brilliance third-generation synchrotron light source of the European Synchrotron Radiation Facility (ESRF Grenoble, France), to study *in situ* the partitioning of key elements (Pb, Rb, Sr) between aqueous fluids and silicate melts, under subduction zones pressure and temperature conditions. We performed experiments with and without chlorine to evaluate the effect of chlorine on partition coefficients of key elements as function of pressure and temperature.

Experimental conditions: Synchrotron Radiation Induced μ -X-Ray Fluorescence (SR-XRF) experiments were performed using Bassett-modified diamond anvil cells as our experimental tool [1]. We used iron-free silica-rich and water-rich (up to 5 wt.%) starting glasses of two different compositions, albite (Ab: NaAlSi₃O₈) and haplogranite (Si_{0.35}Ab_{0.4}Or_{0.25}; Pb-free or with 1360 ppm Pb) respectively. Aqueous fluids of various compositions were equilibrated with these glasses (melts) at high pressures (up to 2 GPa) and temperature (up to 850°C). They were pure water, pure water+NaCl, and standard solutions of Pb (600, 9000 ppm), Rb and Sr (1000 ppm), with and without NaCl.

We used the X-ray microprobe of the ID22 ESRF beamline delivering a monochromatic X-ray beam of 18 keV, focused by means of KB mirrors to a beam-spot size of 2 x 4 μ m², with an associated flux of 10¹¹ ph/second. We measured the Pb, Sr and Rb contents of aqueous fluids and hydrous silicate melts in equilibrium with for the same pressure and temperature conditions, before, and/or after their complete miscibility was reached [2]. The calculation of partition coefficients for the studied element ($i = \text{Pb, Rb, Sr}$) followed the equation: $D^i_{\text{fluid/melt}} = C^i_{\text{fluid}}/C^i_{\text{melt}}$, using the concentrations (C) obtained from *in situ* measurements after the procedure described in [3].

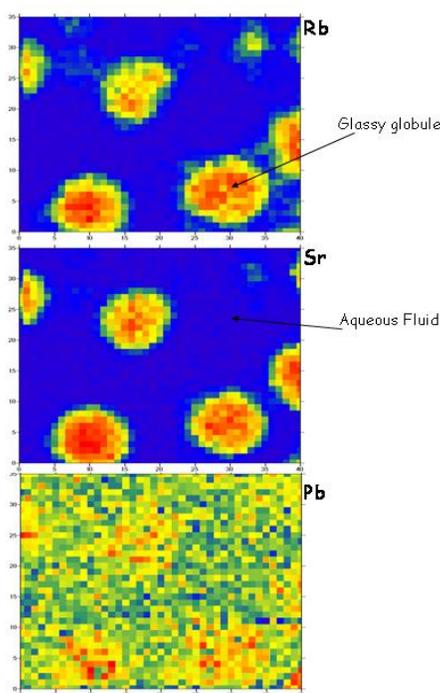


Figure 1: *in situ* SXRF mapping at 25°C of a diamond anvil cell experiments performed with Pb-bearing haplogranite as the starting glass composition and a standard aqueous solution containing Sr, Rb, NaCl. Size is 80 μ m x 70 μ m, step 2 x 2 μ m², 10 sec/point. After the quench, Rb and Sr are enriched in the glassy globules whereas Pb is present in both phases: quench melt as a glass, and aqueous solution.

A *post mortem* study was performed on the quenched samples (glassy ships or “globules” extracted from the cell after the experiments) using μ PIXE mapping (Proton Induced X-ray Emission, at LPS Laboratory, CEA Saclay, France). Operating conditions were a 3 MeV incident Energy beam of 400 pA intensity of a $2 \times 2 \mu\text{m}^2$ size using a scanning mode.

Results and discussion: The presence of Cl in the starting aqueous solution favours a significant affinity of Pb, Rb, Sr for the melt phase in haplogranitic melt compositions (presence of potassium). In Cl free runs Pb shows in contrast to Rb and Sr no partitioning into either the aqueous or the hydrous silicate phase. In the case of experiments performed with albite ($\text{NaAlSi}_3\text{O}_8$) starting compositions, Cl seems to have no partitioning effect on Rb and Sr, that are always enriched into the melt. The elemental distribution maps obtained on quench products inside the cell by SR-XRF (Fig 1), or after the experiments using μ PIXE, both confirm the strong enrichment of Rb and Sr in the glassy globules for experiments performed with or without Cl. However, on quench products, Pb is also concentrated into the fluid (Fig 1). Particularly, μ PIXE maps show that Pb is concentrated in the water-rich fluid inclusions resulting from water exsolution from the melt during the quench. This is due to the strong degassing of Pb with decompression. Therefore any calculation of the partition coefficients based on mass balance and using the concentrations obtained on quench products are strongly compromised.

We found that with haplogranite as the starting glass composition in the presence of chlorine: $D_{f/m}^{\text{Pb}} < 0.2$, in the absence of chlorine $0.8 < D_{f/m}^{\text{Pb}} < 0.9$. Calculations are still under progress for Rb and Sr.

Conclusions: The combination of the high pressures and temperatures attainable in diamond anvil cells together with *in situ* synchrotron light source measurements makes possible the characterisation of chemical equilibrium between “high pressure fluids” at pressure and temperature conditions corresponding to the mantle wedge beneath subduction volcanism. Results demonstrate that a potassium-bearing silica-rich hydrous fluid, enriched in chlorine, is likely the contaminating agent responsible for the Pb, Sr, Rb geochemical fingerprint of the subduction-related magmas. This is in good agreement with recent experimental results after [3] suggesting that, in subduction zones, transport processes may be accomplished by silica-rich hydrous fluids. Results obtained *post mortem* demonstrate that the experimental quench may drastically modify the chemistry of the resulting samples, and consequently may affect our understanding of high pressure fluids equilibrium processes.

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