

Element Partitioning between Fluids and Melts and between Fluids and Solids by XRF Analyses in a Hydrothermal Diamond Anvil Cell Modified for Low-energy Spectroscopy

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Introduction

The development of x-ray microprobes, reliable hydrothermal diamond anvil cells (HDACs) [1], and pioneering *in situ* work on hydrothermal solutions [2-4] now permits controlled pressure- and temperature-dependent x-ray fluorescence and x-ray fine structure (XAFS) studies in solutions at high temperatures and pressures. These techniques and cells have been used for studies of water-solid reactions [5], melting of water-silicate systems [6], and speciation of Sr, Rb, La, Cu, and Zn ions in solution by XAFS [3, 7].

An HDAC [1] was used to subject samples consisting of coexisting silicate melts and aqueous solutions to pressures up to 5 GPa and temperatures up to 800°C. Our principal objective is to obtain the first *in situ* quantitative measurements of element partitioning between melts and aqueous fluids and between solids and aqueous fluids at elevated temperatures and pressures. In addition, we hope to be able to directly determine the speciation of selected metals in the aqueous fluid coexisting with a silicate melt or solid in both subcritical and supercritical fluids.

Methods and Materials

In a modified version of the HDAC, the amount of diamond in the x-ray path has been reduced to only 80 μm for the entering beam and 80 μm for the fluorescence emission. This modification makes it possible to analyze samples for elements having absorption-edge energies below 10 keV [8]. This includes the K-absorption for first-row transition elements and the L_3 -absorption for lanthanides. Half of the sample resides in a laser-drilled recess (50 μm deep) in the face of one of the diamond anvils. The other half resides inside a 300- μm -diameter hole in the center of a rhenium gasket that is 50- μm thick. This design enables us to analyze by x-ray fluorescence (XRF) only the portion of sample in the diamond recess. It is possible, for instance, to analyze only the fluid portion of a mixture while keeping the solid or melted portion in the shadow of the gasket. With this capability, we obtain quantitative analyses of the fluid in equilibrium with a solid or melt at pressures up to 5 GPa and temperatures up to 800°C while visually observing the sample for changes. This approach allows us to calculate

the partitioning of elements between the phases. We have carried out experiments in which we were able to observe strong signals from copper and lanthanum in solution at ppm concentrations [9] and expect that we will be able to analyze for elements as light as potassium.

Results

For the first set of runs at GSECARS in July 2001, we prepared a sample consisting of rhyolite glass and water. We then analyzed the aqueous phase in equilibrium with the rhyolite melt at temperatures up to 800°C. The resulting analyses successfully showed variations in the concentration of Rb and Fe in the aqueous fluid as a function of temperature. In addition, we were able to collect Rb K-edge XAFS spectra from the aqueous fluid. The results were preliminary but indicated that the method has considerable promise.

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