In-situ determination of mineral solubilities in fluids using a hydrothermal diamond-anvil cell and SR-XRF: Solubility of AgCl in water

CHRISTIAN SCHMIDT1,* AND KAREN RICKERS2,1

1GeoForschungsZentrum Potsdam, Telegrafenberg, Potsdam 14473, Germany
2Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronensynchrotron DESY, Notkestrasse 85, Hamburg 22603, Germany

ABSTRACT
A hydrothermal diamond-anvil cell has been designed for the in situ analysis of the concentration of elements in fluids and melts using synchrotron radiation X-ray fluorescence. This technique permits determination of the solubility of minerals in fluids at high pressures and temperatures (tested to 1.1 GPa and 800 °C). Further advantages include multi-element analytical capability and applicability for sparingly soluble compounds, for congruent or incongruent dissolution, and for studies of dissolution kinetics.

The solubility of AgCl(s) in water was determined at 300 to 450 °C and pressures to 760 MPa. The molality of silver in the fluid was obtained from density corrected Kα peak areas by calibration to the known solubility at 300 °C and vapor pressure and, standardless, by comparison with Monte-Carlo simulated spectra. The results from both methods were internally consistent and in good agreement with literature data for comparable P-T conditions.

INTRODUCTION
Fluid-mineral equilibria control the mobility of elements during geologic processes. Consequently, quantitative information about the solubility of minerals in fluids at the pressure-temperature conditions of the Earth’s crust and upper mantle is of great importance in geochemistry, petrology, and ore deposit geology. Various experimental techniques have been designed for such studies. Most of these methods rely on indirect observation, i.e., the solubility is determined after quenching based on weight loss (e.g., Anderson and Burnham 1965) or from analysis of the fluid composition (e.g., Walther and Orville 1983; Manning and Boettcher 1994). A number of experimental problems are associated with indirect techniques for hydrothermal solubility studies under high P-T conditions. Back reactions between fluid and minerals on quenching cause uncertainties in the determined absolute solute concentration (Walther and Orville 1983; Manning and Boettcher 1994). Use of a large fluid volume limits the attainable experimental pressure. Measurement of the weight loss of single crystals after equilibration with a fluid is not sufficient to derive the fluid composition if the mineral dissolves incongruently (Manning and Boettcher 1994).

Quenching and fluid sampling problems are avoided if the concentration in the fluid is determined directly at high pressures and temperatures. So far, such data are scarce. Zotov and Kepller (2002) determined the solubility of quartz in water at 700 to 900 °C and 0.56 to 1.4 GPa from in situ Raman spectra of the aqueous fluid using a hydrothermal diamond-anvil cell. Mavrogenes et al. (2001) described how the solubility of ore metals in aqueous fluids can be determined with detection limits in the ppm range using synchrotron radiation X-ray fluorescence (SR-XRF) analyses of heated synthetic fluid inclusions. However, this technique is limited to relatively low pressures because of inclusion decrepitation. Other in situ techniques have been successfully applied to highly soluble substances such as salts. In such cases, the liquidus temperature can be obtained directly for a known bulk composition, either by optical observation of the dissolution of a phase in synthetic fluid inclusions (e.g., Bodnar 1994) or by using differential thermal analysis (e.g., Gunther et al. 1983).

In this paper, we describe an in situ technique to determine the solubility of solid phases in fluids based on SR-XRF analysis of the concentration of dissolved elements in a fluid through the windows of a hydrothermal diamond-anvil cell (HDAC). We show that this method is applicable at relatively low solubilities, pressures to at least 1.1 GPa, and temperatures to 800 °C. Furthermore, we present the results of an in situ determination of the solubility of chlorargyrite in water to 450 °C and 760 MPa. This system was selected to test this technique because of the availability in the literature of data for the solubility of chlorargyrite to 450 °C.

EXPERIMENTAL METHODS
The experiments were conducted using a Bassett-type HDAC (Bassett et al. 1993). We adapted the cell design for the purpose of solubility experiments and SR-XRF analyses at temperatures to 900 °C and pressures to approximately 2 GPa (Fig. 1a). The cell is heated externally by NiCr coils around the tungsten carbide seats supporting the diamond anvils. The power input to the two resistive heaters was controlled with Eurotherm® 2408 temperature controllers, which kept the temperature to within ±0.5 °C of the desired value. The temperature was measured using K-type (NiCr/NiAl) thermocouples attached to the diamonds. The actual temperature in the sample chamber was determined to ±1.5 °C by calibration before or