

Experimental determination of the solubilities of quartz, kyanite, and corundum in H₂O in the lower crust and upper mantle

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Introduction

The dissolution, transport, and precipitation of mass by aqueous fluids plays an important role in petrologic processes. Quartz and kyanite are common vein-filling minerals in intermediate- to high-pressure metamorphic environments (e.g., Kerrick, 1990), suggesting that solubilities of Si and Al are large in water-rich solutions at these conditions. However, quantitative models of Si and Al metasomatism are limited by the lack of data on high-pressure mineral solubility. To address this problem, I measured solubilities of quartz, kyanite, and corundum in H₂O from 5 to 20 kb and from 500 to 900°C. Results of this research provide the first experimental constraints on Si and Al mass transport in high-pressure environments.

Measurement of mineral solubilities requires rapid quenching and accurate and precise analysis of fluid compositions. Recent advances in experimental methods allow such experiments using the piston-cylinder apparatus (e.g., Manning, 1994; Manning and Boettcher, 1994). These techniques enable encapsulation and preservation of large crystals, as well as extraction and analysis of coexisting fluids. In the present study, quartz solubilities were determined by weight-loss methods using both crushed grains and single crystals. The solubilities of kyanite ± corundum were determined by extraction, dilution, and ICP analysis of the experimental fluid. Optical and scanning electron microscopy of product grains established the absence of quench phases. Experiments involving kyanite approached equilibrium from both undersaturation and supersaturation; experiments on quartz solubility approached equilibrium from undersaturation.

The solubility of quartz in H₂O at high pressures

The solubility of quartz in H₂O was measured from 500 to 900°C and from 5 to 20 kb (Manning, 1994). These experiments double the pressure range over which quartz solubility has been

determined and provide a basis for predicting Si concentrations in aqueous solutions at high pressures. Uncertainties in solubility determinations are ±0.020 molal (1σ), as constrained by pooled results of repeated experiments. The molality of aqueous silica, $m_{\text{SiO}_2(\text{aq})}$, increases with increasing pressure and temperature. Values of $\log m_{\text{SiO}_2(\text{aq})}$ increase from -0.883 at 500°C, 5 kb to -0.644 at 500°C, 20 kb and to -0.180 at 800°C, 5 kb. Measured solubilities increase more strongly with pressure at successively greater temperatures and $(\partial \log m_{\text{SiO}_2(\text{aq})} / \partial P)_T$ decreases with increasing pressure. The new results are systematically higher than those of Anderson and Burnham (1965) by up to 10%. This is probably because of the faster quench rates in the present study (Manning, 1994).

Values of $\log m_{\text{SiO}_2(\text{aq})}$ in equilibrium with quartz are linear functions of $\log \rho_{\text{H}_2\text{O}}$ at constant temperature. I combined the new, high pressure solubility measurements with the data of Hemley *et al.* (1980) and Walther and Orville (1982) to obtain the following equation for quartz solubility as a function of temperature and the density, ρ , of H₂O (Halbach and Chatterjee, 1982): $\log m_{\text{SiO}_2(\text{aq})} = 4.2620 - 5764.2T^{-1} + 1.7513 \times 10^6 T^{-2} - 2.2869 \times 10^8 T^{-3} + [2.8454 - 1006.9T^{-1} + 3.5689 \times 10^3 T^{-2}] \log \rho_{\text{H}_2\text{O}}$. This equation is similar to those describing the dissociation of H₂O and geologically important salts (e.g., Marshall and Franck, 1981; Eugster and Baumgartner, 1987; Anderson *et al.*, 1991). It reproduces the experimental measurements from 5–20 kb. Moreover, it accurately represents quartz solubility in H₂O at low pressures and provides a sound basis for extrapolation to pressures beyond 20 kb (Manning, 1994).

The solubility of kyanite in H₂O at high pressures

Initial studies of aqueous Al transport at high pressures focused on the solubility of the assemblage kyanite + corundum in H₂O at 700°C and 10 kb. Eight experiments approaching equilibrium from both undersaturation and super-

saturation gave reversed fluid compositions of $\log m_{\text{Si}} = -0.520 \pm 0.048$ and $\log m_{\text{Al}} = -2.273 \pm 0.133$ (1σ uncertainties). Becker *et al.* (1983) found that $\log m_{\text{Al}} = -2.39$ in H_2O in equilibrium with corundum at the same pressure and temperature. The Al concentrations measured in the present study in Si-bearing aqueous solutions are thus in agreement with the results of Becker *et al.* (1983) within uncertainties, suggesting that the presence of Si in solution does not influence the Al concentrations at these conditions. Solutions equilibrated with kyanite alone had higher $\log m_{\text{Si}}$ (-0.420 to -0.250) and similar $\log m_{\text{Al}}$ (-2.432 to -2.129), consistent with the geometry of the kyanite phase boundary in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. Additional experiments at 700°C and 15 kb gave $\log m_{\text{Al}} = -2.090 \pm 0.143$, also in agreement with Becker *et al.* (1983). When compared to corundum solubilities in H_2O below 5 kb ($\log m_{\text{Al}} < -3$), these results illustrate that Al solubility in H_2O in equilibrium with corundum increases dramatically with increasing pressure at constant temperature.

Conclusions

The large isothermal increases in Al solubility in H_2O inferred from this study help to explain the common observation of kyanite-bearing hydrothermal veins in high-pressure metamorphic environments. Also, results of this work allow comparison of the capacity of H_2O to transport Si and Al in different high-pressure environments. For example, quartz-saturated H_2O liberated from subducting slabs at 12–15 kb and 500–600°C will

contain 0.3 to 0.6 mol/kg Si. Similar concentrations would be found in H_2O in equilibrium with quartz at the peak conditions experienced in many Barrovian metamorphic belts (6–8 kb and 600–700°C). Moreover, the experiments provide the basis for evaluating Si and Al metasomatism of the mantle wedge above subducting slabs, where transport of these elements may strongly influence the production of arc magmas.

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