

Mobilizing aluminum in crustal and mantle fluids

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Received 21 November 2005; accepted 14 December 2005

Available online 9 March 2006

Abstract

Aluminum is a major rock-forming element, but its low solubility in H₂O at upper crustal conditions has led to the assumption that it is effectively immobile during fluid–rock interaction in the deep crust and upper mantle. However, new experimental results on Al solubility in H₂O–SiO₂–NaCl fluids at high pressure and temperature challenge this view. The combined effects of temperature, pressure, dissolved SiO₂ and NaCl yield increases in corundum (Al₂O₃) solubility at 800 °C, 1 GPa of >10³ or 10⁴ relative to that at <0.3 GPa in pure H₂O. Enhancement of Al solubility is best explained by formation of polynuclear Na–Al–Si–O clusters and/or polymers. Aluminum should not be assumed to be immobile during fluid–rock interaction in deep environments. © 2006 Elsevier B.V. All rights reserved.

Keywords: Crustal fluids; Mantle fluids; Aluminum solubility

1. Introduction

Aluminum has long been regarded as one of the least soluble major elements in fluids associated with metamorphic and metasomatic processes. This is based largely on experiments carried out at relatively low pressures (<0.3 GPa), where corundum solubility in H₂O is <0.001 mol/kg H₂O to at least 700 °C (Ragnarsdóttir and Walther, 1985; Walther, 1997).

However, there is abundant geological evidence for significant Al solubility in fluids in medium- to high-pressure geologic environments, chiefly in the form of aluminosilicate vein minerals that formed from aqueous solutions during metamorphism (e.g., Kerrick, 1988; Ague, 1997; Widmer and Thompson, 2001). In the absence of unusually high fluid fluxes, such observations imply high Al concentrations in the fluids.

To address this apparent contradiction, experiments have been conducted on the solubility of corundum (Al₂O₃) and kyanite (Al₂SiO₅) in H₂O±NaCl±SiO₂ solutions from 700–1100 °C and 0.5–2.0 GPa.

2. Methods

All experiments were conducted in a piston-cylinder apparatus using NaCl-graphite furnace assemblies and rapid-quench methods. At high solubility, we employed a double capsule technique, in which starting crystals are placed in a crimped inner Pt capsule, and then added with solvent to a larger outer Pt capsule. This approach largely isolates the crystals of interest from quench solutes, permitting quantitative determination of solubility from the crystal's weight change. All experiments employed ultrapure H₂O, reagent-grade NaCl, synthetic corundum powder or spheres, and natural, high-purity quartz and kyanite.

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3. Results

3.1. Corundum in H_2O

The solubility of corundum in H_2O has been measured at 0.5–2.0 GPa and 700–1100 °C (Becker et al., 1983; Tropper and Manning, 2005a). At 1.0 GPa, corundum solubility increases from 1 millimolal at 700 °C to 20 millimolal at 1100 °C. At all T , Al solubility in H_2O in equilibrium with corundum at 1.0 GPa is at least ten times that at 0.1 GPa. This demonstrates that increasing P enhances the stability of aqueous aluminum.

3.2. Corundum in H_2O –NaCl fluids

The solubility of corundum was also measured at 800 °C, 1.0 GPa, in H_2O –NaCl fluids to $X_{NaCl}=0.5$ (Newton and Manning, 2004, 2005). The dissolved Al content increases with NaCl concentration, rising rapidly from 0.00262(4) molal in pure H_2O to a ~0.02 molal at $X_{NaCl} \approx 0.1$, and then increasing more gently to ~0.03 molal near halite saturation ($X_{NaCl} \approx 0.6$). The large dependence of Al solubility on X_{NaCl} in the dilute range suggests formation of Na–Al complexes.

3.3. Corundum and/or kyanite in H_2O – SiO_2 fluids

Studies in the system Al_2O_3 – $H_2O \pm NaCl$ fail to account for the fact that crustal and mantle fluids will contain significant concentrations of other components with which Al may form complexes, chiefly SiO_2 . Two groups of experiments were undertaken to examine the possible role of complexing between Al and Si (Newton and Manning, 2004; Tropper and Manning, 2005b). First, we determined the solubility of the assemblage corundum+kyanite (Al_2SiO_5) in H_2O – SiO_2 fluids at 700 °C and 1.0 GPa by using natural kyanite crystals with pure H_2O . The higher solubility of Si relative to Al caused growth of a sheath of hexagonal corundum crystals on kyanite surfaces, fixing equilibrium aqueous Al and Si concentrations at corundum+kyanite saturation. The equilibrium Al concentration was 0.0062(6) molal, significantly higher than in pure H_2O and suggesting strong Al–Si interaction in the fluid.

We also measured the solubility of corundum or kyanite in H_2O – SiO_2 fluids at initial $SiO_{2,aq}$ concentrations ranging up to quartz saturation by adding small quartz crystals, which dissolve rapidly relative to corundum to produce the desired initial SiO_2/H_2O ratio. Experiments were conducted at 800 °C and 1.0 GPa. Although kyanite and sillimanite are slightly

more stable than corundum+quartz at these P – T conditions, aluminum silicates did not appear in any of the corundum experiments. At quartz saturation, Al concentration in equilibrium with corundum was 0.013(3) molal, a factor of five increase relative to that in pure H_2O . The solubility of kyanite at the same conditions and at initial $SiO_{2,aq}$ concentrations between corundum and quartz saturation yielded Al solubility enhancements that were identical to the runs on corundum.

3.4. Corundum in H_2O – SiO_2 –NaCl fluids

A final set of experiments was carried out at 800 °C and 1.0 GPa, in H_2O – SiO_2 –NaCl fluids at X_{SiO_2} to quartz saturation over the range $X_{NaCl}=0$ –0.5. Addition of SiO_2 to NaCl– H_2O fluids yields a significant increase in corundum solubility. The greatest enhancement occurs at quartz saturation, where Al molality increases rapidly with NaCl concentration to 0.076 molal at $X_{NaCl}=0.1$ and then rises more slowly to 0.104 molal at halite saturation.

4. Discussion and conclusions

The results show that Al concentration in H_2O in equilibrium with corundum increases strongly with P , such that along any given isotherm from 700 to 1100 °C, raising P from 0.1 to 2.0 GPa yields an increase in Al solubility of ≥ 100 times. Addition of NaCl or SiO_2 at any given P and T further increases Al solubility at corundum saturation by roughly a factor of ten relative to pure H_2O . Even greater enhancements were observed in H_2O – SiO_2 –NaCl brines at quartz and halite saturation, where solubility of corundum at 800 °C, 1.0 GPa, and SiO_2 concentrations near quartz and halite saturation yield Al concentrations ~100 times greater than in pure H_2O at the same P and T .

The mechanisms for enhancement in Al solubility with P , SiO_2 , and NaCl likely involve polymeric complexes not anticipated from low- P studies of aqueous Al. For example, the strong increase in corundum solubility in H_2O with P could be a consequence of increasing stability of multimeric Al clusters. Al clusters have been observed in concentrated solutions at low P and T (e.g., Öhman and Sjöberg, 1981; Bottero et al., 1987; Furrer et al., 1992; Boudot et al., 1996; Gérard et al., 2001). Though no direct observation has yet been made at elevated P and T , it is possible that, as with silica (e.g., Zotov and Keppler, 2002; Newton and Manning, 2003), the enhanced solubility of Al arises in part from increased stability of multinuclear Al clusters. Similarly,

Al–Si complexes involving a bridging O may form in a wide variety of stoichiometries (e.g., Mueller et al., 1981). Pokrovski et al. (1996) and Salvi et al. (1998) showed that $\text{AlOSi}(\text{OH})_3^{2+}$ and other Al–Si complexes become progressively more stable with increasing T along the vapor–saturation curve, and may predominate in high- T environments such as hydrothermal systems. Combination of these observations with the new results on corundum and/or kyanite solubility suggests that enhanced stability of Al–Si complexes persists to the highest P and T yet studied, which represent deep crustal and mantle metasomatic environments. The results in H_2O – SiO_2 – NaCl fluids point to the formation of Na-aluminosilicate complexes with albite-like stoichiometry ($\text{Na}:\text{Al}:\text{Si}=1:1:3$; Newton and Manning, 2004).

The results of this work show that Al is readily dissolved in the SiO_2 -bearing H_2O – NaCl fluids that can be expected to accompany fluid–rock interaction in metamorphic and magmatic environments of the crust and mantle. The elevation of Al solubility is likely a consequence of the greater stability of multimeric complexes at high P . Calculations based on these results and extrapolated thermodynamic data for other aqueous species suggest that Al may be more soluble than Mg and Fe in low-salinity fluids equilibrated with mafic and felsic bulk compositions along typical metamorphic geothermal gradients. There can be little doubt that it would be inadvisable to assume Al immobility in fluids associated with metasomatism in the mid- to lower crust and upper mantle.

Acknowledgements

Supported by NSF EAR-0337170. I thank Bob Newton, Angelo Antignano, and Peter Tropper for discussions and insights.

References

- Ague, J.J., 1997. Crustal mass transfer and index mineral growth in Barrow's garnet zone, northeast Scotland. *Geology* 25, 73–76.
- Becker, K.H., Cemic, L., Langer, K.E.O., 1983. Solubility of corundum in supercritical water. *Geochim. Cosmochim. Acta* 47, 1573–1578.
- Bottero, J.-Y., Axelos, M., Tschoubar, D., Cases, J.-M., Fripiat, J.-J., Fiessinger, F., 1987. Mechanism of formation of aluminum trihydroxide from Keggin Al_{13} polymers. *J. Colloid Interface Sci.* 117, 47–57.
- Boudot, J.-P., Maitat, O., Merlet, D., Rouiller, J., 1996. Occurrence of non-monomeric species of aluminium in undersaturated soil and surface waters, consequences for the determination of mineral saturation indices. *J. Hydrol.* 177, 47–63.
- Furrer, G., Trusch, B., Müller, C., 1992. The formation of polynuclear Al_{13} under simulated natural conditions. *Geochim. Cosmochim. Acta* 56, 3831–3838.
- Gérard, F., Boudot, J.P., Ranger, J., 2001. Consideration on the occurrence of the Al_{13} polycation in natural soil solutions and surface waters. *Appl. Geochem.* 16, 513–529.
- Kerrick, D.M., 1988. Al_2SiO_5 -bearing segregations in the Lepontine Alps, Switzerland, Aluminum mobility in metapelites. *Geology* 16, 636–640.
- Mueller, D., Hoebbel, D., Gessner, W., 1981. ^{27}Al NMR studies of aluminosilicate solutions. Influences of the second coordination sphere on the shielding of aluminum. *Chem. Phys. Lett.* 84, 25–29.
- Newton, R.C., Manning, C.E., 2003. Activity coefficient and polymerization of aqueous silica at 800 °C, 12 kbar, from solubility measurements on SiO_2 -buffering mineral assemblages. *Contrib. Mineral. Petrol.* 146, 135–143.
- Newton, R.C., Manning, C.E., 2004. Solubility of corundum and quartz in the system Al_2O_3 – SiO_2 – NaCl – H_2O at deep-crustal metamorphic conditions, 800 °C and 10 kbar. *Eos Trans. AGU* 85 (47) (Fall Meet. Suppl., Abstract V31A-1406).
- Newton, R.C., Manning, C.E., 2005. Interaction of corundum, wollastonite and quartz with H_2O – NaCl solutions at 800 °C and 10 kbar. *Eos Trans. AGU* 86 (52) (Fall Meet. Suppl., Abstract V31C-0618).
- Öhman, L.-O., Sjöberg, S., 1981. Equilibrium and structural studies of silicon(IV) and aluminum(III) in aqueous-solution. 1. The formation of ternary mononuclear and polynuclear complexes in the system Al^{3+} -gallic acid- OH^- —a potentiometric study in 0.6M NaCl. *Acta Chem. Scand., Ser. A* 201–212.
- Pokrovski, G.S., Schott, J., Harrichoury, J.-C., Sergeev, A.S., 1996. The stability of aluminum silicate complexes in acidic solutions from 25 to 150 °C. *Geochim. Cosmochim. Acta* 60, 2495–2501.
- Ragnarsdóttir, K.V., Walther, J.V., 1985. Experimental determination of corundum solubilities in pure water between 400–700 °C and 1–3 kbar. *Geochim. Cosmochim. Acta* 49, 2109–2115.
- Salvi, S., Pokrovski, G.S., Schott, J., 1998. Experimental investigation of aluminum–silica aqueous complexing at 300 °C. *Chem. Geol.* 151, 51–67.
- Tropper, P., Manning, C.E., 2005a. The solubility of corundum in H_2O at high pressure and temperature, and its consequences for al mobility in subduction zone environments. *Geophys. Res. Abstr.* 7, 03991.
- Tropper, P., Manning, C.E., 2005b. The solubility of kyanite in H_2O – SiO_2 fluids at 800 °C and 1 GPa: implications for Al–Si complexing in subduction-zone fluids. *Eos Trans. AGU* 86 (52) (Fall Meet. Suppl., Abstract V31C-0621).
- Walther, J.V., 1997. Experimental determination and interpretation of the solubility of corundum in H_2O between 350 and 600 °C from 0.5 to 2.2 kbar. *Geochim. Cosmochim. Acta* 61, 4955–4964.
- Widmer, T., Thompson, A.B., 2001. Local origin of high pressure vein material in eclogite facies rocks of the Zermatt-Saas zone, Switzerland. *Am. J. Sci.* 301, 627–656.
- Zotov, N., Keppler, H., 2002. Silica speciation in aqueous fluids at high pressures and high temperatures. *Chem. Geol.* 184, 71–82.