

The solubility of corundum in (K,Na)OH-H₂O solutions under hydrothermal conditions

Florian Mittermayr¹, Edgar Dachs², Jürgen Konzett¹ & Peter Tropper¹

1 Institut für Mineralogie und Petrographie, Universität Innsbruck, Innrain 52, 6020 Innsbruck, Austria
(Florian.Mittermayr@student.uibk.ac.at, Juergen.Konzett@uibk.ac.at, Peter.Tropper@uibk.ac.at)

2 Institut für Mineralogie and Materialwissenschaften, Universität Salzburg, Hellbrunnerstraße 34,
5020 Salzburg, Austria

The solubility of corundum in supercritical aqueous solutions was studied to contribute to a better understanding of geological transport processes and crystal growth and corrosion mechanisms: In natural rocks supercritical fluids dissolve the surrounding minerals under crustal P-T conditions to form aqueous complexes. It has long been known that SiO₂ is highly soluble in these fluids (e.g. Manning 1994) thus enabling the transport of large amounts of SiO₂. Corundum (α-Al₂O₃), in contrast, is much less soluble than quartz and is transported in pure supercritical water in trace amounts only. Nevertheless, there is clear evidence for significant aluminium transport in natural hydrothermal systems exemplified by feldspathized zones in granites, garnet zones in skarns or muscovite- and quartz-kyanite veins in metamorphic rocks (Pascal und Anderson, 1989). In geochemical systems aqueous solutions are often characterized by significant electrolyte concentrations (e.g. NaCl, KCl, HCl) which can be the origin for ligands to form stable aluminium complexes. The results of high temperature experiments (Anderson und Burnham, 1967, 1983; Pascal und Anderson, 1989; Diakonov et al., 1996) suggest that alkali-aluminium complexes are formed in significant quantities under crustal P-T conditions in the presence of these electrolytes. These may explain the natural evidence for Al-transport in hydrothermal and metamorphic systems. (Pokrovskii und Helgeson, 1994, 1995). The study of corundum-solubility is also of interest for economic reasons and the results may be applied to crystal growing and fracture healing.

The solubility of corundum (α-Al₂O₃) in basic aqueous solutions containing KOH and NaOH was determined by a series of hydrothermal experiments at temperatures from 500 to 700°C and a pressure of 2.0 kbar using cold-seal pressure vessels. The values were acquired by using the classic weight loss method (after e.g. Anderson and Burnham, 1967). For the experiments synthetic mirror finish single crystal white sapphire spheres with approximately 330mg and about 200ml of solution were sealed in gold capsules. The weight loss yielded from 0.67mg for low concentrated to 26.30mg for high concentrated bases. The used bases show concentrations of 0.0757–2.5024 mol/kg H₂O for NaOH and 0.0910–2.3753 mol/kg H₂O for KOH. The aluminium molality increases linearly at 500 °C, 600 °C and 700 °C with increasing concentrations of the solution up to values of

2.3541 mol Al/kg H₂O for KOH at 700°C and 2.3784 mol Al/kg H₂O for NaOH at 600°C. It is presumed that the measured solubility is a result of the formation of neutral (K, Na)Al(OH)₄⁰ complexes (e.g. Anderson and Burnham, 1967, 1983; Azaroual et al., 1996; Barns et al., 1963; Pascal und Anderson, 1989). The ratios (m(Al)/m(K, Na); (mol Al/kg H₂O)/(mol (K, Na)/kg H₂O) increase with increasing concentrations of the solution and temperatures. With (K, Na)OH concentrations > 1.5 mol/kg H₂O and temperatures > 600 °C the m(Al)/m(K, Na) ratios approach a value of 1.0.

- Anderson G.M. and Burnham C.W. (1967). Reactions of quartz and corundum with aqueous chloride and hydroxide solutions at high temperatures and pressures. *Amer. J. Sci.* 265, 12-27.
- Anderson G.M. and Burnham C.W. (1983). Feldspar solubility and the transport of aluminium under metamorphic conditions. *Amer. J. Sci.* 283-A, 283-297.
- Azaroual M., Pascal M.L., and Roux J. (1996). Corundum solubility and aluminium speciation in KOH aqueous solutions at 400°C from 0.5 to 2.0 kbar. *Geochim. Cosmochim. Acta* 60, 4601-4614.
- Barns R.L., Laudise R.A. and Shields R.M. (1963) The solubility of corundum in basic hydrothermal solvents. *J. Phys. Chem.* 67, 835-839.
- Diakonov I., Pokrovskii G., Schott J., Castet S., and Gout R. (1996) An experimental and computational study of sodium-aluminium complexing in crustal fluids. *Geochim. Cosmochim. Acta* 60, 197-211.
- Manning C.E. (1994) The solubility of quartz in H₂O in the lower crust and upper mantle. *Geochim. Cosmochim. Acta* 58, 4831-4839.
- Pascal M.L. and Anderson G.M. (1989) Speciation of aluminium, silicon and potassium in supercritical solutions: Experimental study and interpretation. *Geochim. Cosmochim. Acta* 53, 1843-1855.
- Pokrovskii V.A. and Helgeson H.C. (1994) Calculations of the effect of KAl(OH)₄⁰ formation on the solubility of corundum at high pressures and temperatures. *Goldschmidt Conf. Edinburgh-1994, Min. Mag.* 58A, 736-737.
- Pokrovskii V. A. and Helgeson H. C. (1995) Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: the system Al₂O₃- H₂O -NaCl. *Amer. J. Sci.* 295, 1255-1342.