Solubility of corundum in aqueous KOH solutions at 700 °C and 1 GPa

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ABSTRACT

The solubility of corundum in aqueous KOH solutions was measured at 700 °C and 1 GPa, using a piston-cylinder apparatus and a weight-loss method. Total potassium molality (m_K) ranged from 0.0011 to 3.9. At the lowest m_K, corundum solubility (m_{Al}) was 0.0016 ± 0.0004 molal, which is slightly higher than that in pure H_2O at the same conditions (0.0011 molal). Corundum solubility increased with added KOH to a maximum of $m_{Al} = 2.66$ at the highest m_K. At $m_K \geq 0.03$, m_{Al} increased linearly with m_K, with $dm_{Al}/dm_K = 1$. The results were combined with previous work to evaluate the stability of the neutral ion-pair $KAlO_{2,aq}$ at 700 °C and 1 GPa. We obtained an optimal fit to the experimental data with an equilibrium constant (K) for the reaction $KOH_{aq} = K^+ + OH^-$ of $10^{-1.206}$, which was extrapolated from the data of Ho and Palmer [Ho, P.C. and Palmer, D.A., 1997. Ion association of a dilute aqueous potassium chloride and potassium hydroxide solutions to 600 °C and 300 MPa determined by electrical conductance measurements. Geochimica et Cosmochimica Acta, 61, 15, 3027–3040.] using linear isothermal correlations between the logarithms of H_2O density and K. This gave an equilibrium constant for the reaction $KAlO_{2,aq} = K^+ + AlO_2^-$ of $10^{-0.299}$. The results permit assessment of the dominant aqueous species in K–Al–O–H fluids at high pressure and temperature. We find that the dominant Al-bearing species in such fluids is predicted to be the neutral hydrate ($HAlO_{2,aq}$) at $m_K < 0.01$ (pH < 4.8), whereas AlO_2^- predominates to higher m_K and pH, over most geologically realistic conditions. The $KAlO_{2,aq}$ ion pair will only be the most abundant Al-bearing species at very high pH (>8), which corresponds to KOH molality of >10 at 700 °C and 1 GPa. Thus, $KAlO_{2,aq}$ is not a major reservoir for dissolved aluminum in low-chloride crustal and mantle aqueous fluids.

1. Introduction

Aluminum is generally assumed to be immobile during crustal metamorphic and metasomatic processes (e.g., Carmichael, 1969). This is supported by the relatively low solubility of corundum (Al_2O_3) in H_2O at high pressure (P) and temperature (T) (Becker et al., 1983; Ragnasdottir and Walther, 1985; Walther, 1997; Tropper and Manning, 2007). However, the amphoteric nature of the aqueous Al hydroxides dictates that corundum solubility is enhanced by raising or lowering pH. Hemley and Jones (1964) suggested that Al mobility was promoted by acid leaching by magmatic fluids, and this approach has been widely applied to explain Al-rich veins and segregations in metamorphic rocks (e.g., Yardley, 1977; Kerrick, 1988; Nabelek, 1997; McLelland et al., 2002). High corundum solubility will also be associated with high-pH fluids, as illustrated in the experimental investigations of corundum solubility in KOH solutions reported by Barns et al. (1963), Anderson and Burnham (1967), Pascal and Anderson (1989) and Azaroual et al. (1996). Characterization of Al solubility at high pH is important because model crustal mineral assemblages, such as feldspar + mica +

quartz, in equilibrium with an internally derived H_2O-rich pore fluid, will buffer pH at values more alkaline than neutrality (e.g., Walther and Woodland, 1993).

A key problem that has arisen in the study of Al solubility in alkaline solutions at metamorphic pressures and temperatures is the extent of complexing between alkalis and Al. Experimental investigations of Anderson and Burnham (1967, 1983), Woodland and Walther (1987), Pascal and Anderson (1989), Castet et al. (1992), Diakonov et al. (1996), and Azaroual et al. (1996) argue for alkali–aluminate complexing to explain the high concentration of aluminum in solution. In contrast, Walther and Woodland (1993) presented data on the solubility of the assemblage microcline + muscovite + quartz in H_2O at 0.2 GPa between 400 and 600 °C, and showed that an explanation was possible without including an alkali–aluminate complex, and that the aluminum concentration can be interpreted by the increasing solubility of the aluminate ion with pH. The different interpretations could be due in part to uncertainties in extrapolated equilibrium constants (Anderson, 1995; Azaroual et al., 1996).

The experimental studies described above were limited to low to moderate pressures (≤0.6 GPa) and therefore do not give insight into the role of pH and alkalis at high pressure and temperature, where Al mobility can be substantial (e.g., Kerrick, 1988; Ague, 1995; Widmer and Thompson, 2001; Beitter et al., 2008). To address this, we measured corundum solubility in aqueous KOH solutions at 1 GPa at 700 °C. The results are the first experimental measurements of Al

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Table 1
Experimental results at 700 °C and 1 GPa.

Exp. no	Duration (h)	Type	KOH solution in (mg)	Cor in (mg)	Cor out (mg)	m_k (mol/kg H$_2$O)	m_{Al} (mol/kgH$_2$O)
KOH 2	45.5	b,s	35.314	32.6999	32.6975	0.0011	0.0013(2)
KOH 1	46	b,c	39.271	6.5800	6.5760	0.0011	0.0020(1)
KOH 10	45.5	a,s	34.272	32.9015	32.8965	0.0012	0.0028(2)
KOH 9	48.5	a,s	30.670	33.0540	33.0485	0.0020	0.0036(2)
KOH 7	42.5	b,s	34.994	32.9098	32.8968	0.0079	0.0073(2)
KOH 8	46.5	a,s	30.801	32.6494	32.6239	0.0277	0.0187(2)
KOH 3	48	b,s	35.147	32.6826	32.5616	0.1017	0.0685(2)
KOH 5	44	b,c	34.416	1.2862	0.6941	0.5085	0.3421(2)
KOH 4	46	b,s	34.690	32.6500	31.4653	1.0099	0.7107(2)
KOH 6	46	b,s	36.296	32.9821	28.9439	3.9206	2.6623(3)

Run type: a, diluted 10% W/V KOH solution; b, KOH chip; c, Corundum chip; s, corundum sphere. Parenthetical numbers in solubility entries reflect propagated weighing errors (1σ).

solubility in aqueous KOH solutions above 0.6 GPa. They provide a foundation for investigations of Al solubility, assessment of the stability of the KAlO$_{2,aq}$ ion pair, and quantifying species abundance in aqueous fluids of the deep crust and upper mantle.

2. Experimental methods

Two types of corundum starting material were used. Most experiments utilized high-purity spheres of synthetic corundum (Tropper and Manning, 2007). The spheres were ~33 mg in weight, ~2.5 mm in diameter, and contained no constituents detectable by electron microprobe analysis other than Al$_2$O$_3$. For two experiments, we used small chips from a synthetic corundum boule (~0.5–1 mm), also pure Al$_2$O$_3$ at the limits of detection. Before loading, the chips were smoothed using sandpaper (Newton and Manning, 2006, 2007, 2008).

The KOH solutions were prepared in two ways. In the first, a reagent-grade KOH chip was dried at 110 °C, weighed, and then added immediately to a precisely determined mass of nanopure H$_2$O. All such solutions were subsequently reweighed to check mass balance. In the second method, a reagent-grade 10% W/V aqueous KOH solution (Ricca Chemicals) was diluted to the desired concentration using density data from Akerlof and Bender (1941).

For each experiment, a single corundum sphere or chip was loaded into a 1.8 cm long Pt capsule of 3.5 mm diameter and 0.2 mm wall thickness, which had been welded on one side. After addition of aqueous KOH solution, the capsule was sealed by arc welding. Welded seams of each capsule were inspected for holes using a binocular microscope then held at 110 °C for at least 2 h and reweighed to ensure that the capsules did not leak. As in the investigation of Newton and Manning (2008), the corundum crystals proved to be mechanically coherent, which obviated the need for the inner capsules used in some solubility studies in our laboratory (e.g., Antignano and Manning, 2008a,b).

Run conditions were 700 °C and 1 GPa. All experiments were conducted with a 2.54 cm diameter end-loaded piston-cylinder apparatus with sodium chloride pressure media and 1.25 cm diameter graphite heater-sleeves (Manning and Boettcher, 1994). Flattened and folded capsules were placed horizontally in the center of the furnace, packed in NaCl, and covered with a 0.1 mm thick Pt foil to prevent thermocouple puncture. Experiments were pressurized to 0.8 GPa at room temperature and then heated to 700 °C. Heating brought the final pressure to ~1 GPa; only small pressure adjustments were necessary to prevent overshooting. Temperature was maintained to within ±1 °C using Pt–Pt$_{90}$Rh$_{10}$ thermocouples, considered accurate
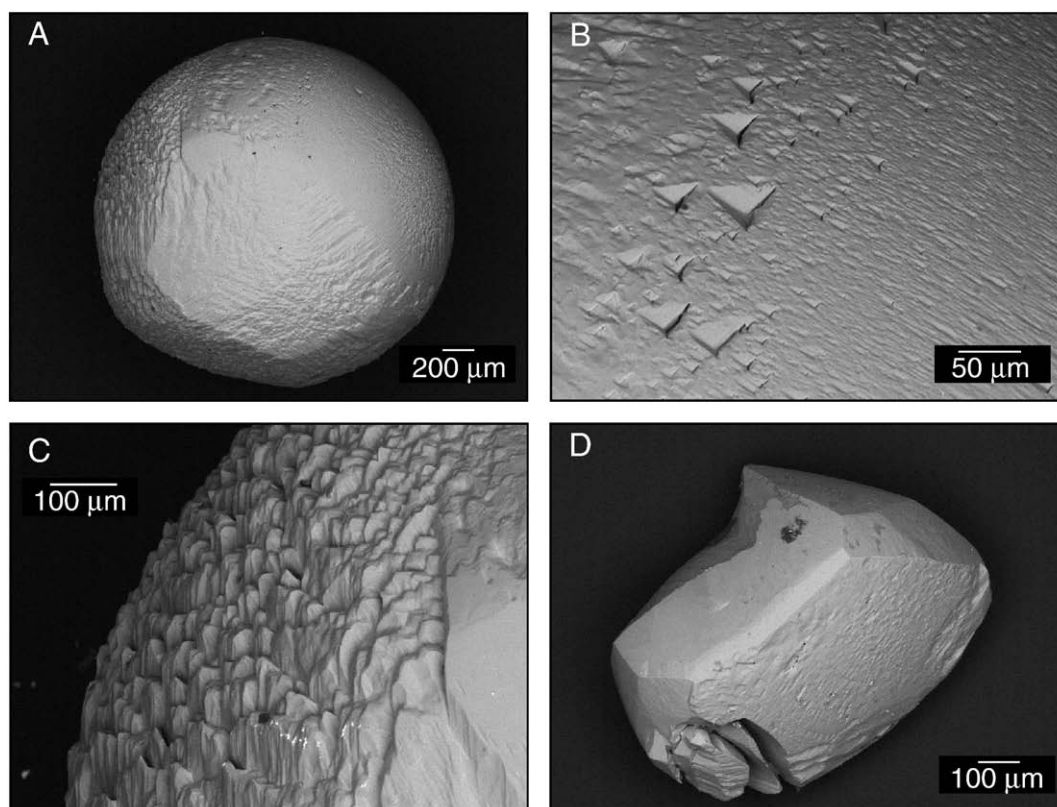
Fig. 1. Backscattered-electron (BSE) photomicrographs of representative corundum textures after experiments. (A) Initially spherical corundum crystal showing etch pits and crude facets that probably developed due to crystallographically controlled dissolution and reprecipitation (KOH 6) (Table 1). (B) Enlargement of sphere shown in (A) illustrating etch pits created by partial dissolution (KOH 6) (Table 1). (C) Irregular corundum terminations suggesting dissolution and reprecipitation. (D) Corundum chip showing smooth, newly grown facets exposed to the solution, and etch-pitted face interpreted to be the base of the crystal, which was in contact with the Pt capsule.