

The solubility of corundum in H₂O at high pressure and temperature and its implications for Al mobility in the deep crust and upper mantle

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Abstract

The solubility of corundum in H₂O was measured at 700–1100 °C and 0.5–2.0 GPa using a piston–cylinder apparatus and weight-loss methods. At 700 °C, 0.5 GPa, Al concentration is 0.41±0.15 millimolal (1σ analytical error). Corundum solubility increases strongly with pressure (*P*) and temperature (*T*), reaching 2.57±0.15 millimolal at 700 °C, 2.0 GPa, and 27.3±1.5 millimolal at 1100 °C, 2.0 GPa. The results were fitted with the equation $\log m_{\text{Al}} = 1.131 + 3827/T - (2.277 - 7336/T)\log\rho_{\text{H}_2\text{O}}$, where m_{Al} is molality of Al, $\rho_{\text{H}_2\text{O}}$ is the density of H₂O in g/cm³, and *T* is in Kelvin. The data indicate that Al can have significant solubility in H₂O during metamorphic and metasomatic processes in the deep crustal and upper mantle.

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1. Introduction

Aluminum has long been regarded as one of the least soluble elements during metamorphic and metasomatic processes (e.g., Carmichael, 1969). However, at least local Al mobility is indicated by hydrothermally deposited aluminosilicate-bearing veins in many regional metamorphic complexes (e.g. Stout et al., 1986; Kerrick, 1990; Cesare, 1994; Ague, 1995; Whitney and Dilek, 2000; McLelland et al., 2002; Sepahi et al., 2004). In the

absence of evidence for unusually high fluid fluxes, such observations imply significant Al solubility in metamorphic fluids.

A necessary foundation for evaluating the possibility of elevated Al concentrations in geologic fluids is the determination of corundum (Al₂O₃) solubility in pure H₂O. Most previous experimental investigations of corundum solubility in H₂O at metamorphic temperatures have been limited to low pressures (≤0.3 GPa). Because these studies generally yielded very low Al solubility and only little change in solubility with temperature (Morey and Hesselgesser, 1951; Morey, 1957; Anderson and Burnham, 1967; Burnham et al., 1973; Ragnarsdottir and Walther, 1985; Walther, 1997), they support the

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assumption of low Al mobility during metamorphism. However, a preliminary investigation by Becker et al. (1983) suggested a strong increase in Al solubility with P at 700 °C. Therefore, the assumption of low Al mobility may break down at moderate to high P .

Here, we report new measurements of corundum solubility in H_2O from 0.5–2.0 GPa and 700–1100 °C. The results significantly increase the P – T range over which corundum solubility has been determined, and demonstrate strong increases in Al solubility in H_2O with both P and T . These observations suggest that Al mobility should be expected in H_2O -rich solutions in high- PT metamorphic and igneous environments.

2. Experimental methods

All experiments were conducted in an end-loaded piston–cylinder apparatus with 25.4 mm diameter furnace assemblies (Boyd and England, 1960). The

furnace assembly for experiments conducted at temperatures lower than NaCl melting was made of graphite, NaCl and MgO (Bohlen, 1984; Manning and Boettcher, 1994; Tropper and Manning, 2005). The furnace design in experiments at 1000–1100 °C, 1 GPa, was modified slightly, in that a Pyrex sleeve was used to prevent penetration of any molten salt into the graphite furnace, and the 3–5 mm long portion of the NaCl interior containing the capsule was replaced by boron nitride (BN). The Pyrex sleeves were cracked before experiments by heating to 800 °C for 5 min and then quenching in cold water. This reduced their strength, thereby preventing capsule rupture during approach to run conditions. Because of the frictionless behavior of furnace assemblies of these types at the run conditions (e.g., Bohlen, 1984), no pressure correction was applied to the experiments.

Three types of starting corundum crystals were used. The first was single-crystal chips from a high-purity boule

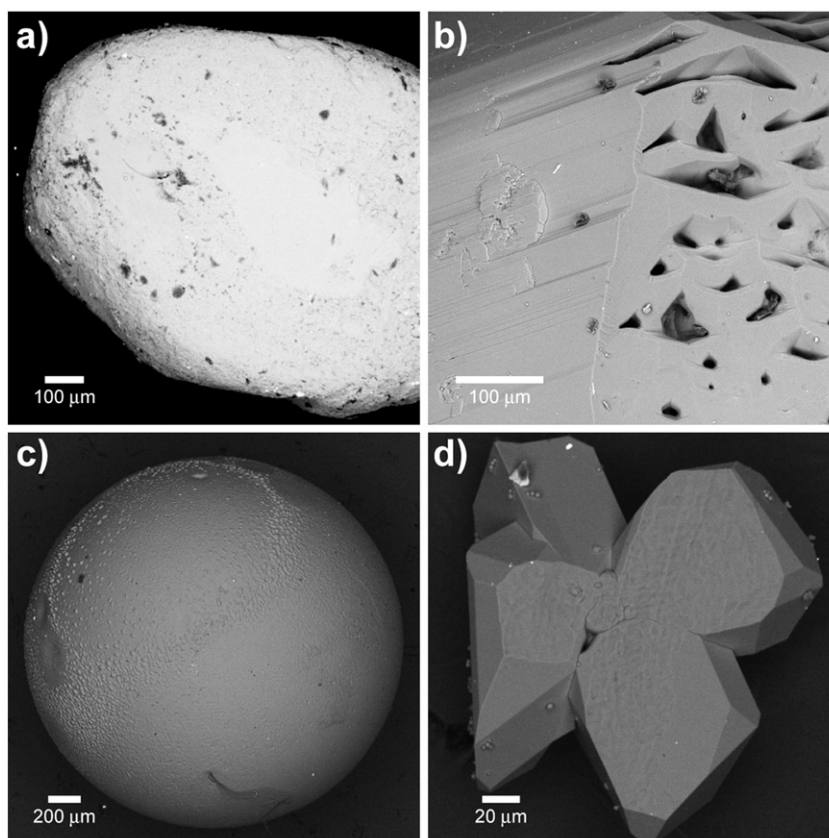


Fig. 1. Backscattered electron images of selected starting materials and run products. (a) Sanded corundum crystal derived from boule chip. (b) Close-up of recrystallized corundum grain after experiment (CB-7). The areas of recrystallization are clearly visible and newly grown crystal faces with striations on the surface of the starting crystal can also be seen. (c) Corundum sphere after the experiment Cor-16, showing minute, newly formed crystal terminations decorating the surface. (d) Newly formed aggregate of vapor-transport crystals in experiment Cor-16.

of synthetic corundum (Newton and Manning, 2006). We also used small ~ 2.5 mm diameter spheres generated from highly polished single crystals of synthetic white sapphire. Electron microprobe analyses of both of these materials (15 kV accelerating voltage, 15 nA sample current) showed Si, Ti, Cr, Fe, Mg, Ca, Na and K to be below detection limits (≤ 0.02 – 0.04 wt.% oxide). The third type of starting corundum was α -Al₂O₃ powder of high purity (certified 99.997%, Alfa Aesar).

Prior to loading, the corundum chips (0.5–2.8 mg) were sanded to remove sharp edges that could break off during experiments (Fig. 1a). A sanded chip or α -Al₂O₃ powder was loaded into a 5 mm long, 1.5 mm O.D. Pt tube, which was crimped at the ends to allow H₂O penetration during runs. Due to their large size, no inner Pt tube was used for the corundum spheres. In each experiment, the crimped capsule or sphere was sealed by arc welding with 35–41 μ L ultra-pure H₂O in an outer Pt capsule (3.5 mm O.D., 0.18 mm wall thickness). The capsule was then heated to 115 °C for ≥ 3 h to check for leakage. The capsule was placed horizontally in the graphite furnace and packed in NaCl (low-*T* runs) or BN (high-*T* runs). A piece of Pt foil was placed on top of the capsule to prevent puncture by the thermocouple.

Run conditions were attained in low-*T* runs by increasing *P* to 0.7 GPa and then raising *T* to 100 °C to prevent freezing of H₂O at higher pressures. Subsequently *P* was increased to ~ 0.3 GPa below the desired final value to allow for expansion of the salt, and then *T* was raised to its final value. In the high-*T* runs (1100 °C), conditions of 0.7 GPa and 100 °C were first generated as above, but then *P* was raised to the final value, due to lower expansivity of the BN-bearing assembly. Temperature was measured with Pt/Pt₉₀Rh₁₀ thermocouples, with an estimated precision of ± 3 °C; *P* was monitored using a Heise gauge to within 0.01 GPa of the reported value.

At the end of an experiment, runs were quenched by cutting power to the apparatus, resulting in *T* drops to < 100 °C in < 30 s. Capsules were extracted, cleaned, pierced with a needle and dried for 15 min at 115 °C and then for 15 min at 400 °C. H₂O mass balance was obtained to ± 0.7 wt.%. The capsules were then opened, and the crystals extracted and weighed. Experimental run products were examined using binocular optical and scanning electron microscopes. Weighings were made with Mettler M3 and Mettler UMX2 microbalances. Repeated weighings of a standard yielded $1\sigma = 2$ μ g on the Mettler M3 and $1\sigma = 0.2$ μ g on the Mettler UMX2, which were propagated to error in Al molality (Table 1).

Table 1
Experimental results

Run	Type	<i>P</i> GPa	<i>T</i> °C	Time h	H ₂ O in mg	H ₂ O out mg	Cor in mg	Cor out mg	log <i>m</i> _{Al} mol/kg H ₂ O
Cor-14	s,1	0.5	700	46	38.683	38.542	32.7553	32.7545	-3.39(15)
Cor-12	s,1	0.5	800	24	41.130	41.209	32.8940	32.8928	-3.24(10)
Cor-11	s,1	1.0	700	23	39.444	39.433	32.6682	32.6658	-2.92(05)
Cor-9	c,1	1.0	800	12	37.007	37.031	5.237	5.231	-2.50(20)
Cor-18	p,1	1.0	800	22	38.222	38.291	86.4959	86.4900	-2.52(02)
CB-19	s,1	1.0	800	161	36.791	36.791	32.6285	32.6236	-2.58(03)
CB-16	c,1	1.0	800	192	35.722	35.776	0.466	0.461	-2.56(25)
Cor-15	s,1	1.0	900	20	39.280	39.477	32.8078	32.7988	-2.34(01)
Cor-8	c,1	1.0	900	48	38.380	38.098	0.735	0.727	-2.39(15)
Cor-4	c,2	1.0	1000	24	38.226	—*	2.846	2.829**	<-2.06(17)
Cor-6	c,2	1.0	1000	24	36.883	36.955	1.028	1.009**	<-2.00(15)
Cor-16	s,2	1.0	1000	12	38.170	38.190	32.8742	32.8609**	-2.17(01)
Cor-7	c,2	1.0	1100	12	34.598	34.644	1.211	1.176**	<-1.70(08)
Cor-10	c,1	2.0	700	23	37.322	37.389	0.9941	0.9892	-2.59(03)
Cor-5	c,1	2.0	800	96	36.402	36.416	2.828	2.818	-2.27(12)
Cor-13	s,1	2.0	900	26	38.730	38.683	32.5976	32.5802	-2.05(01)
Cor-3	c,1	2.0	900	48	35.525	35.582	0.749	0.736**	<-2.14(22)
Cor-1	c,1	2.0	1000	24	35.796	32.256*	1.239	1.212	-1.83(05)
Cor-2	c,1	2.0	1100	12	36.631	36.625	1.136	1.085	-1.56(02)

Run types: s, sphere; c, boule chips; p, α -Al₂O₃ powder; 1, low-*T* furnace; 2, high-*T* furnace. Weights given to 3 decimal places were determined using a Mettler M3 microbalance ($1\sigma = 2$ μ g), whereas those to 4 decimal places were made with a Mettler UMX2 ultramicrobalance ($1\sigma = 0.2$ μ g). Parenthetical numbers in solubility entries reflect propagated weighing errors. * indicates that some, or all H₂O was lost during decompression upon quenching after the experiment; **, vapor-transport crystals lead to maximum solubility only, except Cor-16, in which crystals were collected and weighed (see text).

3. Results

The surfaces of run-product corundum crystals showed minor to strong growth of new crystal faces, indicating significant reaction with H₂O (Fig. 1b,c). In four experiments (Cor-4, 6, 7 and 16; Table 1), blocky crystals occur adjacent to the starting crystal (Fig. 1d). Following Caciagli and Manning (2003) and Tropper and Manning (2005), these crystals are interpreted as having grown during the experiments by convective transport of Al due to minute *T* gradients in the capsules, and are termed “vapor-transport crystals.” It was only possible to quantitatively retrieve and weigh these crystals in one experiment (Cor-16). The remaining experiments in which vapor-transport crystals were identified yield maximum solubilities only, and were not included in the fitting (see below). In two experiments (Cor-4, Cor-1), H₂O was completely or partially lost during decompression upon quenching, but corundum crystals could nevertheless be extracted and weighed to give a meaningful solubility measurement.

Run duration necessary to attain equilibrium was determined in six experiments at 800 °C and 900 °C. We conducted four experiments at 800 °C, 1.0 GPa, for 12–192 h, which yielded constant solubility (Fig. 2). Two experiments were also performed at 900 °C, 1.0 GPa, for 20 and 48 h; these runs also gave indistinguishable solubilities within uncertainty (Table 1). These results indicate that, within uncertainty, constant solubility of

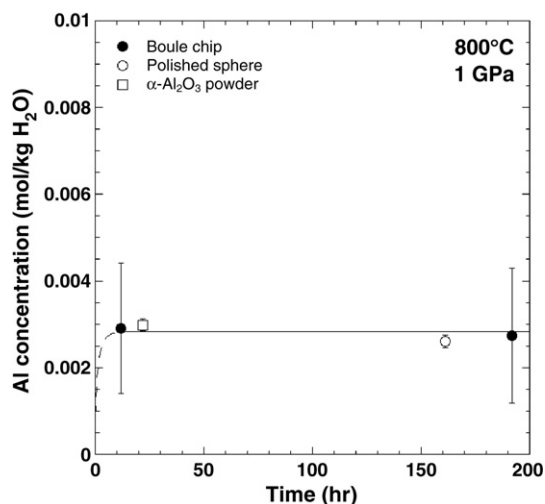


Fig. 2. Corundum solubility vs. experiment duration at 800 °C, 1 GPa. Four experiments (1σ propagated weighing errors) conducted on three different starting materials give a weighted mean (solid line) of 2.83 mm; dashed line shows schematic approach to equilibrium. A constant value is reached in 12 h, supporting the interpretation that equilibrium was attained.

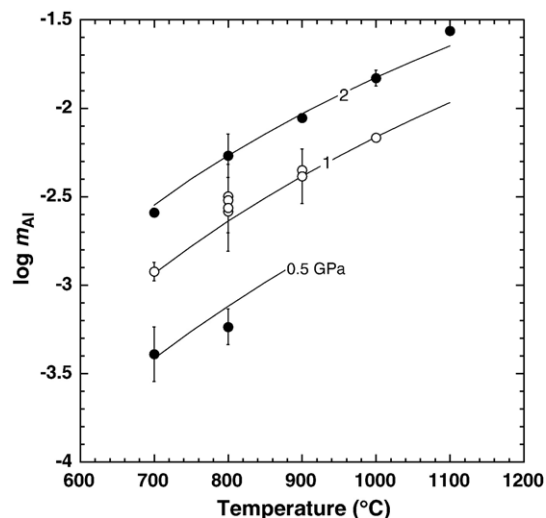


Fig. 3. Variation in corundum solubility, expressed as the logarithm of Al molality, with temperature at 0.5, 1.0 and 2.0 GPa. Filled and open circles show equilibrium solubility measurements (Table 1). Error bars are 1σ propagated weighing uncertainties. Solid curves show isobaric solubility variations at 0.5, 1.0 and 2.0 GPa, as calculated from Eq. (1).

corundum in H₂O is reached within 12 h, which is consistent with other solubility measurements at high *P* and *T* (e.g. Caciagli and Manning, 2003; Tropper and Manning, 2004, 2005). The combination of run times longer than 12 h and textural evidence for new mineral growth (Fig. 1b,c) supports the interpretation of attainment of equilibrium.

Fig. 2 allows comparison of results using different starting materials. It can be seen that no significant differences are indicated between α -Al₂O₃ powder, corundum spheres, and boule chips.

Under the *P*–*T* conditions of the investigation, the solubility of corundum increases with both *T* and *P* (Table 1; Fig. 3). Molality ranges from 0.00041 (700 °C, 0.5 GPa) to 0.0273 (1100 °C, 2.0 GPa). Thus, solubility varies by nearly two orders of magnitude over the range of investigation.

4. Discussion

4.1. Equation for corundum solubility at high *P* and *T*

Manning (1994) showed that, over a wide *P*–*T* range, quartz solubility displays a simple linear dependence on the logarithm of H₂O density at constant *T*. Equations of this form permit reasonable extrapolation to high *P* and possess a simple relationship to thermodynamic properties of the dissolution reaction. Preliminary investigation revealed that corundum solubility also has a linear dependence on isothermal H₂O

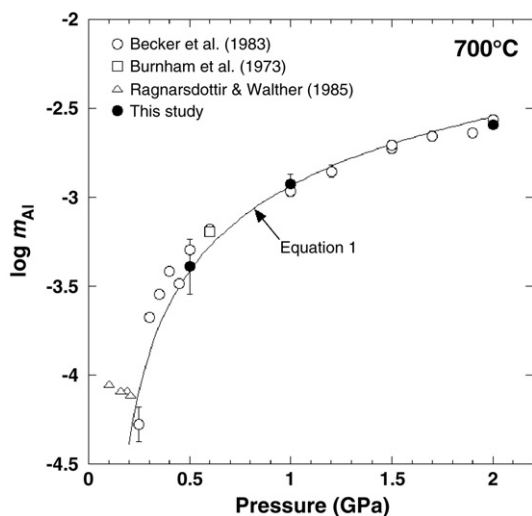


Fig. 4. Comparison of results of this study with previous experiments at 700 °C. Data of Becker et al. (1983) at ≤ 0.6 GPa are ~ 670 °C; data of Ragnarsdottir and Walther (1985) are 685–700 °C. Error bars are 1σ (except for Ragnarsdottir and Walther (1985), who do not report uncertainty). The solid line shows solubility calculated from Eq. (1).

density. We therefore used this approach in fitting the equilibrium solubility data (excluding runs with unweighable vapor-transport crystals), which led to the expression:

$$\log m_{\text{Al}} = 1.131 + 3827/T - (2.277 - 7336/T) \log \rho_{\text{H}_2\text{O}} \quad (1)$$

where m_{Al} is Al molality and T is in Kelvin. Density of H_2O ($\rho_{\text{H}_2\text{O}}$, in g/cm^3) was calculated from the CORK equation of state (Holland and Powell, 1991). Eq. (1) is simpler than the analogous equation for quartz solubility (Manning, 1994) in that it involves only four fit parameters. Although additional parameters would improve the fit somewhat, they were judged to be unjustified because there are fewer experimental data in the present study. Nevertheless, Eq. (1) reproduces all experimental data to within 6% (Fig. 3).

4.2. Comparison to previous results

The conditions investigated in the present study overlap with previous work, chiefly at 700 °C (Fig. 4). Anderson and Burnham (1967) obtained only a maximum solubility of 35.6 mm at 700 °C and 0.6 GPa, which is substantially higher than given by Eq. (1). Burnham et al. (1973) measured corundum solubility at 500–800 °C and 0.6 GPa. Their results at 700 and 800 °C (0.64 ± 0.29 and 0.89 ± 0.48 millimolal, respectively) agree well with values of 0.53 and 1.06 m predicted by Eq. (1). The

most complete previous high- P study is that of Becker et al. (1983). Fig. 4 combines their data at > 0.6 GPa, 700 °C, and at ≤ 0.6 GPa, 670 °C. Corundum solubilities measured in the present study agree closely with the results of Becker et al. (1983). In addition, extrapolation of Eq. (1) to 0.2 GPa reproduces the Becker et al. (1983) data quite well, though they were not included in the derivation of the fit; however, data of Ragnarsdottir and Walther at 0.1–0.21 GPa, 685–700 °C, give slightly higher solubilities than predicted.

Walther (1997) measured the solubility of corundum in H_2O to 600 °C and 0.2 GPa, and concluded that solubilities determined by Ragnarsdottir and Walther (1985) were erroneously low. He speculated that the discrepancy was caused either by stabilization of a low-solubility mineral due to Na in starting materials or by mineral precipitation prior to analysis in the earlier study. However, extrapolation of Walther's (1997) 0.2 GPa results to 700 °C predicts that $\log m_{\text{Al}} = -3.21$ in equilibrium with corundum, which is roughly one order of magnitude higher than the values suggested by Becker et al. (1983) and Eq. (1). Our experiment (Cor-18) using a similar starting $\alpha\text{-Al}_2\text{O}_3$ powder as described by Walther (1997) yielded a corundum solubility at 800 °C, 1 GPa, that was in excellent agreement with that obtained from other starting materials (Table 1; Fig. 2). Thus, our data and those of Becker et al. (1983) appear support the accuracy of the original results of Ragnarsdottir and Walther (1985), rather than those of Walther (1997).

Pokrovskii and Helgeson (1995) obtained the standard Gibbs energies of the aqueous Al species $\text{Al}(\text{OH})_3^\circ$

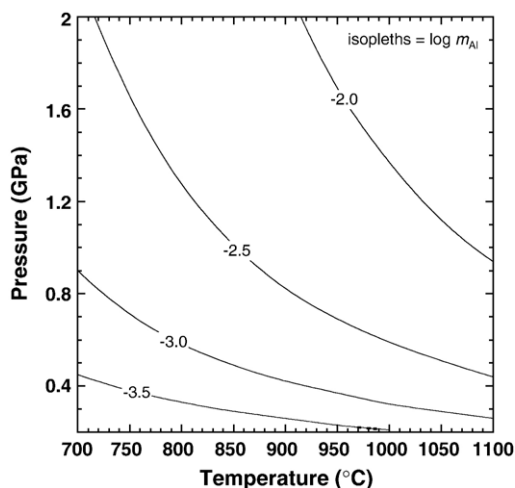


Fig. 5. P - T diagram showing isopleths of predicted Al concentration in H_2O in equilibrium with corundum (in $\log m_{\text{Al}}$), as calculated from Eq. (1).

and $\text{Al}(\text{OH})_4^-$ in equilibrium with corundum in the system Al–O–H based on the data of Becker et al. (1983) and Ragnarsdottir and Walther (1985). This allowed calculation of corundum solubility values at 0.5 GPa and 700 °C which are in very good agreement with our results.

4.3. Implications for Al-mobility in the deep crust and upper mantle

Fig. 5 shows isopleths of corundum solubility in H_2O as a function of P and T , as calculated from Eq. (1). Model fluids in the system $\text{Al}_2\text{O}_3\text{--H}_2\text{O}$ at near-neutral pH and in equilibrium with corundum will show strong isothermal increase in Al concentration with increasing P up to ~ 0.5 GPa. In addition, corundum solubility increases with T at constant P at all T investigated, which contrasts with the behavior at lower P and T (e.g., Ragnarsdottir and Walther, 1985). Fig. 5 illustrates that there is a strong potential for precipitation of corundum (or by analogy, Al-rich silicates) upon both decompression and cooling segments of metamorphic $P\text{--}T$ paths.

The mechanism for the enhancement of corundum solubility at the experimental conditions could be greater stability of the aqueous $\text{Al}(\text{OH})_3^\circ$ species with increasing P and T (Pokrovskii and Helgeson, 1995); however, it is also possible that, as with aqueous SiO_2 , multimeric Al clusters become increasingly stable at high P (Manning, 2006). If pH shifts away from neutrality, corundum solubility will increase (e.g., Pokrovskii and Helgeson, 1995). Moreover, corundum solubility in H_2O increases significantly in the presence of SiO_2 (Manning, in press), probably due to formation of H_5AlSiO_6 dimers and/or other polymeric complexes involving SiO_2 , as has been suggested in acid solutions at lower P and T (Pokrovski et al., 1996; Salvi et al., 1998). Addition of alkalis increases corundum solubility yet further (Manning, 2004b; Wohlers and Manning, 2006). Thus, the elevated Al solubilities in pure H_2O which we observe in this study can be viewed as minimum values in the presence of aluminous minerals at any given P and T , supporting the inference that Al solubility in geologic fluids is likely to be significantly greater than at shallow-crustal metamorphic conditions.

The most obvious geological manifestation of fluid-mediated Al mobility is the formation of quartz veins containing Al_2SiO_5 polymorphs, which are common in high-grade regional metamorphic terranes (e.g., Stout et al., 1986; Ague, 1995; Whitney and Dilek, 2000; McLelland et al., 2002; Sepahi et al., 2004). In addition, Feenstra and Wunder (2002) describe nearly monomineralic corundum-filled hydrofractures by the Naxos

metabauxites, which formed from precipitation of corundum from a water-rich fluid. Our experiments suggest that a simple explanation for such features is retrograde cooling and decompression, consistent with the kinematically late textures of these features. At even higher P (>2 GPa), such as subduction-zone environments, Al concentration in H_2O -rich fluids is at least 3×10^{-3} m at 700 °C. Manning (1998, 2004a) showed that subduction-zone fluids change their major element composition with depth, and have elevated Al concentrations, which may be higher than Ca, Fe and Mg. Since corundum solubility in H_2O is significantly higher at 1000–1100 °C and 2 GPa than at lower P and T , it is likely that interaction of H_2O -rich fluids with Al-rich phases (e.g., spinel) in peridotites in the mantle wedge will result in considerable Al mobility, as has been shown experimentally (e.g., Schneider and Eggler, 1986; Ayers et al., 1997). Geological evidence also points towards Na–Ca–Al–Si-rich fluids leaving the slab, since Al-bearing minerals such as jadeite, paragonite and clinozoisite/zoisite are common as vein minerals in blueschists and eclogites (Becker et al., 1999; Gao and Klemd, 2001; Tropper and Essene, 2002). Thus, the results of this study help explain the common observation of Al-bearing minerals precipitated from fluids at high P and T . There can be little doubt that Al should not be assumed to be immobile during fluid–rock interaction in the mid to lower crust and upper mantle.

Acknowledgments

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