

The solubility of fluorite in H₂O and H₂O–NaCl at high pressure and temperature

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Abstract

The solubility of fluorite in H₂O and H₂O–NaCl has been measured at 600–1000 °C, 0.5–2.0 GPa in a piston–cylinder apparatus. Fluorite dissolves congruently at all conditions investigated. The data indicate that the concentration of fluorite dissolved in H₂O is low at 600 °C and 0.5 GPa (0.0014 mol/kg H₂O) but increases strongly with temperature (*T*) and pressure (*P*) to 0.247 mol/kg H₂O at 1000 °C, 2 GPa. The data were fit with the equation $\log m_{\text{CaF}_2} = -6.587 + 2.774P^{1/2} + (2.266 \times 10^{-3} - 4.699 \times 10^{-4}P)T$, where m_{CaF_2} is molality of CaF₂, *T* is in Kelvin, and *P* is in GPa. Fluorite solubility was also measured in H₂O–NaCl fluids at 800 °C and 1.0 GPa. Results indicate a strong increase in dissolved fluorite concentration with increasing NaCl content, from 0.028 mol/kg H₂O at $X_{\text{NaCl}}=0$ to 1.673 mol/kg H₂O at $X_{\text{NaCl}}=0.486$, where X_{NaCl} is the mole fraction of NaCl in the fluid. The data were fit to $m_{\text{CaF}_2} = 0.01035 + 1.141X_{\text{NaCl}} + 4.694X_{\text{NaCl}}^2$. The results indicate that F mobility will be further enhanced by saline brines in high *P*–*T* igneous and metamorphic environments. High F solubility in H₂O and H₂O–NaCl in the deep crust and upper mantle can promote mobilization of high field-strength elements, rare earth elements, U, and Th through transport as F-bearing complexes.

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1. Introduction

Fluorine plays an important role in metal complexing during fluid–rock interaction. Elevated F concentrations in shallow magma–hydrothermal settings are commonly indicated by hydrothermal fluorite-bearing veins (e.g., Richardson and Holland, 1979b; Manning and Bird, 1990; Birkett and Sinclair, 1998; Lentz, 1998; Hill et al.,

2000). Elevated fluorine concentrations are indicated by F-bearing minerals in hydrothermal ore deposits and metamorphic rocks (e.g., Munoz and Luddington, 1974; Valley et al., 1982; Munoz, 1984; Zhu and Sverjensky, 1991). F concentrations may be sufficiently high to reach fluorite saturation in high-grade metamorphic rocks from the lower crust (e.g., Bohlen and Essene, 1978; Markl and Piazzolo, 1998, 1999; Sengupta et al., 2004). Fluorine-rich fluids can strongly influence the solubility and transport of refractory components such as Al₂O₃, high field-strength elements (HFSE), rare earth elements (REE) and U and Th during metamorphism (Stähle et al., 1987; Pan and Fleet, 1996; Rudnick

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et al., 2000; Tagirov and Schott, 2001; Tagirov et al. 2002) and partial melting (Peterson et al., 1991). Although F-rich fluids may occur as immiscible melts (e.g., Klemme, 2004), F transport by an aqueous phase is also important (e.g., Pan and Fleet, 1996).

Despite its importance in the transport of low-solubility cations, little is known about the solubility of F in aqueous fluids at high P and T . Fluorite (CaF_2) is the most common fluorine-rich accessory mineral (e.g., Bohlen and Essene, 1978; Markl and Piazzolo, 1998, 1999; Sengupta et al., 2004), and previous work has therefore focused on its solubility in geologic fluids. However, most experimental investigations have been conducted at low P (<0.2 GPa) and T (<500 °C) (Booth and Bidwell, 1950; Ellis and Mahon, 1964; Strübel, 1965, 1968; Macdonald and North, 1974; Richardson and Holland, 1979a). These experiments show that fluorite is sparingly soluble in H_2O , with a maximum observed solubility of 0.6 mmol/kg H_2O at 500 °C and 0.2 GPa (Strübel, 1965). The addition of chloride salts strongly increases fluorite solubility at $P \leq 0.2$ GPa (Strübel, 1965; Malinin, 1976; Schaefer and Strübel, 1979; Richardson and Holland, 1979a; Malinin and Kurovskaya, 1979a,b; Kurovskaya and Malinin, 1983; Malinin and Kurovskaya, 1992). However, despite its common occurrence in lower crustal metamorphic rocks, and the potential importance of F-complexing on element transport during fluid-rock interaction, the

solubility of fluorite in $\text{H}_2\text{O} \pm \text{NaCl}$ has not previously been measured at high P and T .

We report new measurements of fluorite solubility in H_2O at 600–1000 °C, 0.5–2 GPa, and in H_2O – NaCl at 800 °C and 1.0 GPa. The new data indicate that fluorite has low to moderate solubility in H_2O at T above 600 °C, and extremely high solubility in H_2O – NaCl . These results indicate that in the presence of fluorite, geologic fluids may be strongly enriched in fluorine. Such fluids would have a high capacity to dissolve and transport HFSE and REE at high P and T .

2. Experimental methods

We used chips from a clear, natural fluorite specimen from the mineral collection of the Department of Earth and Space Sciences at the University of California at Los Angeles. Electron microprobe analyses (15 kV accelerating voltage, 15 nA sample current, beam rastered at 10 μm) indicated that the fluorite is nearly pure CaF_2 with minor SrO (0.05–0.09 wt.%), FeO (0.01–0.05 wt.%), and La_2O_3 (<0.01 – 0.04 wt.%). The fluorite was heated to 700 °C for ~ 30 min to decrepitate any natural fluid inclusions. Small fluorite grains (0.5–7 mg) were then placed in an inner, 1.6 mm OD, Pt capsule. To facilitate H_2O penetration during experiments, this capsule was pierced two to four times with a needle and then lightly crimped on both ends to contain the

Table 1
Experimental results

Run	P (GPa)	T (°C)	Time (h)	H_2O in (mg)	H_2O out (mg)	NaCl in (mg)	X_{NaCl}	Fl in (mg)	Fl out (mg)	m_{CaF_2} (mol/kg H_2O)
Fl-17	0.5	600	46	38.206	38.061	0.000	0.000	0.9889	0.9847	0.0014(1)
Fl-19	0.5	700	46	38.586	38.569	0.000	0.000	0.9890	0.9829	0.0020(1)
Fl-18	0.5	800	24	39.036	38.862	0.000	0.000	0.9362	0.9247	0.0038(1)
Fl-8	1.0	600	50	39.857	39.542	0.000	0.000	1.2458	1.2243	0.0070(1)
Fl-9	1.0	700	23	39.865	39.731	0.000	0.000	0.7023	0.6743	0.0090(1)
Fl-22	1.0	800	12	37.550	37.579	0.000	0.000	0.6406	0.6025	0.0130(1)
Fl-1	1.0	800	24	33.585	33.657	0.000	0.000	0.502	0.470	0.0122(15)
Fl-5	1.0	800	12	32.188	32.188	11.571	0.100	4.184	3.762	0.1679(16)
Fl-3	1.0	800	24	32.504	32.474	11.647	0.099	4.002	3.533	0.1850(16)
Fl-4	1.0	800	24	32.128	32.136	44.536	0.299	6.943	5.002	0.7736(16)
Fl-6	1.0	800	24	21.181	21.238	64.899	0.486	7.314	4.540	1.6729(24)
Fl-10	1.0	900	21	38.501	38.528	0.000	0.000	0.4696	0.4026	0.0223(16)
Fl-11	2.0	600	48	38.698	38.755	0.000	0.000	1.3119	1.2236	0.0292(1)
Fl-14	2.0	700	44	40.023	36.902	0.000	0.000	0.4701	0.3599	0.0367(9)
Fl-12	2.0	800	26	38.674	38.679	0.000	0.000	3.1006	2.9445	0.0517(1)
Fl-15	2.0	900	24	39.375	38.285	0.000	0.000	1.1599	0.9260	0.0772(6)
Fl-16	2.0	1000	24	35.637	35.514	0.000	0.000	0.8698	0.5954	0.0989(1)

Explanation: “in” and “out” refer respectively to weights before and after experiment; “Fl” denotes fluorite crystals. Weights given to 3 decimal places were determined using a Mettler M3 microbalance ($1\sigma = 2$ μg), whereas those to 4 decimal places made with a Mettler UMX2 ultramicrobalance ($1\sigma = 0.2$ μg). Fluorite solubility calculated using H_2O -out, except in Fl-14 and Fl-15, which are midpoints between minimum and maximum obtained using H_2O -in and H_2O -out (see text). Parenthetical numbers in solubility entries reflect propagated 1σ weighing errors in last digit(s).

crystal. The inner capsule, appropriate amounts of NaCl, and 21–40 μL H_2O were then sealed by arc welding in an outer 3.5 mm OD Pt capsule with 0.18 mm wall thickness. The double capsule assembly was held at 115 $^\circ\text{C}$ for ≥ 3 h to check for leakage.

All experiments were conducted in an end-loaded piston–cylinder apparatus using 25.4 mm diameter graphite–NaCl furnace assemblies (Bohlen 1984; Manning, 1994; Manning and Boettcher, 1994). Each capsule was placed horizontally in the furnace, packed in NaCl, and covered with a piece of Pt foil to prevent puncture by the thermocouple. Temperature was controlled with Pt/Pt₉₀Rh₁₀ thermocouples (± 3 $^\circ\text{C}$ estimated precision), and pressure was monitored using a Heise gauge (± 0.01 GPa estimated precision). Oxygen fugacity (f_{O_2}) was not buffered in the experiments; however, the furnace assemblies impose f_{O_2} slightly greater than that of the nickel–nickel oxide equilibrium. At these conditions, H_2 loss from capsules is minimal and $f_{\text{HF}} \gg f_{\text{F}_2}$ (e.g., Munoz and Eugster, 1969).

At the end of each experiment, power to the apparatus was cut, causing quench to temperatures < 100 $^\circ\text{C}$ in ≤ 30 s. After quenching, the outer capsule was pierced with a needle, dried for 15 min at 115 $^\circ\text{C}$, and then 15 min at 400 $^\circ\text{C}$. The capsule assembly was then opened and inspected, and the fluorite crystals extracted and weighed. Comparison of water weight before and after experiments (Table 1) indicates H_2O mass balance to within 1%, except in two experiments, FI-14 and FI-15, which respectively show 8% and 3% discrepancies. For these experiments, fluorite solubility is taken to be the midpoint between values determined from minimum and maximum H_2O weights; otherwise, the weight of H_2O after experiment (H_2O -out, Table 1) was used. All run products were examined optically with a binocular microscope; selected run products were examined with a scanning electron microscope.

Reported weights represent three replicate weighings, with uncertainties determined by repeated weighings of a standard. Capsules, H_2O , NaCl and fluorite crystals in early runs (FI-1 through FI-6, Table 1), were weighed with a Mettler M3 microbalance ($1\sigma = 2$ μg). In runs FI-8 through FI-19, a Mettler UMX2 ultramicrobalance ($1\sigma = 0.2$ μg) was used for fluorite crystals.

3. Results

Results are given in Table 1. Run products included partly dissolved starting fluorite crystals and ubiquitous, fine-grained white or colorless quench solids. The original grains displayed rounded edges and, in some cases, significant new subhedral octahedral overgrowths

(Fig. 1a). The absence of any additional residual solid indicates that fluorite dissolves congruently in $\text{H}_2\text{O} \pm \text{NaCl}$ over the range of conditions investigated.

In addition to partly dissolved starting crystals, run products also contained a mixture of minute (< 20 μm), colorless fluorite octahedra and sub-micron sized white powder (Fig. 1b). Together these materials form a prominent, randomly distributed coating on the outer capsule and, to a minor extent, inside the inner capsule. Because of their morphology, high nucleation density, random distribution, and abundance, we interpret the crystals and powder, as quench material. It is likely that the larger fluorite octahedra nucleated and grew during quench from experimental T , whereas the fine powder was precipitated during drying after initial puncturing of the capsule. We observed no evidence for growth of fluorite at nucleation sites other than the original crystal while the experiments were at high P and T , unlike some mineral–fluid systems such as calcite and rutile (e.g., Caciagli and Manning, 2003; Tropper and Manning, 2005).

Run duration necessary to attain equilibrium was determined in two experiments at 800 $^\circ\text{C}$, 1 GPa and $X_{\text{NaCl}} = 0.1$ (FI-3, FI-5) and two experiments at 800 $^\circ\text{C}$, 1 GPa and $X_{\text{NaCl}} = 0$ (FI-1, FI-22). The run times varied in both experiments from 12 h (FI-5, FI-22) to 24 h (FI-3, FI-1). The results in Table 1 show that within uncertainty, constant solubility was reached within 12 h.

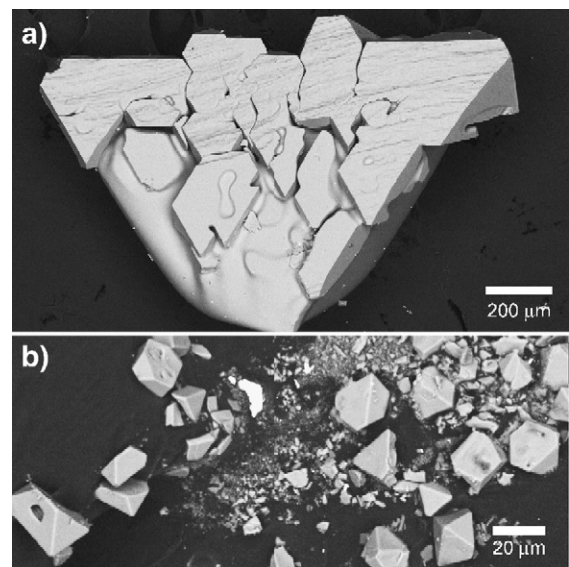


Fig. 1. Backscattered electron images of the reaction products in experiment FI-15. (a) Image of a fluorite chip after the experiment showing recrystallization of fluorite starting crystal at 900 $^\circ\text{C}$, 2 GPa. (b) Ideomorphic quench crystals of fluorite and powder from drying.

3.1. Fluorite–H₂O

The equilibrium solubility of fluorite in H₂O increases strongly with P and T (Table 1, Fig. 2). Total dissolved CaF₂ concentrations ranged from 0.0014 mol/kg H₂O (600 °C, 0.5 GPa) to 0.099 mol/kg H₂O at 1000 °C and 2.0 GPa. The observed increase with P and T continues that observed by previous workers at lower P and T (Ellis and Mahon, 1964; Strübel, 1965; Richardson and Holland, 1979a) and Macdonald and North (1974).

The isobaric increase in fluorite solubility in H₂O is linear with T within uncertainty at 0.5–2 GPa (Fig. 2); however, isothermal increases in solubility are greater between 0.5 and 1 GPa than between 1 and 2 GPa and thus indicate a non-linear behavior with P . These features were incorporated by fitting fluorite solubility in H₂O to the equation

$$\log m_{\text{CaF}_2} = -6.587 + 2.774P^{1/2} + (2.266 \times 10^{-3} - 4.699 \times 10^{-4}P)T \quad (1)$$

where m_{CaF_2} is molality of CaF₂, T is in Kelvin, and P is in GPa. In Eq. (1), the nonlinear increase in solubility with pressure at 0 Kelvin is described by a $P^{1/2}$ dependence, which represents a compromise between functional form and a sparse data set. Average absolute deviation between data and fit is 1.9% relative (maximum absolute deviation is 4.1% relative).

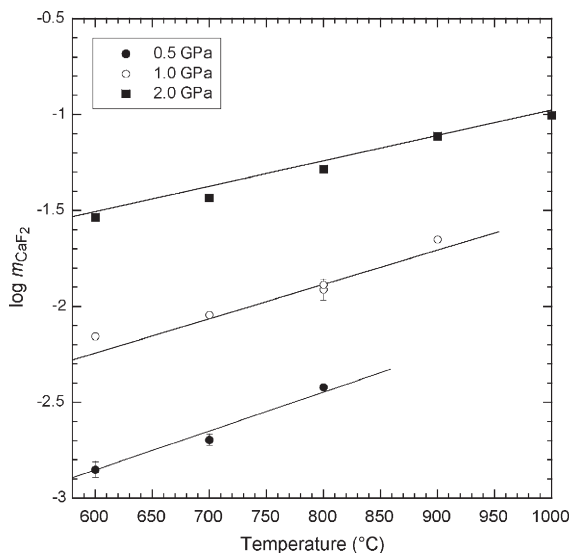


Fig. 2. Logarithm of measured fluorite solubility, as molality of CaF₂, versus temperature at 0.5, 1.0 and 2.0 GPa. Error bars are 1σ (shown only where bigger than symbol size) and represent propagated weighing uncertainties. Solid lines calculated from Eq. (1).

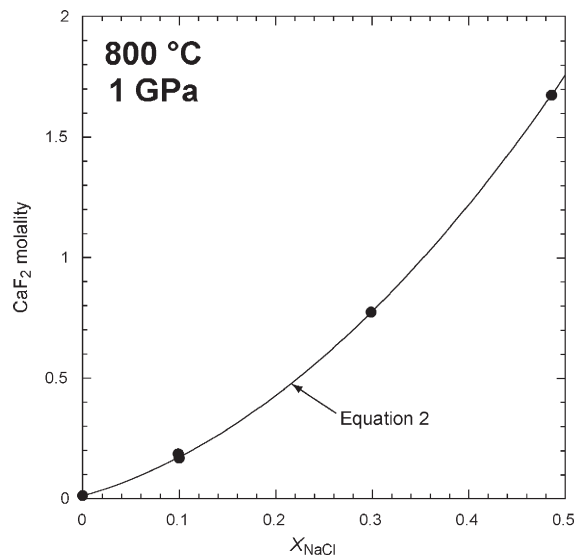


Fig. 3. Measured fluorite solubility, as molality of CaF₂, versus X_{NaCl} at 800 °C and 1 GPa. Errors (1σ) are smaller than the symbols.

3.2. Fluorite–H₂O–NaCl

The solubility of fluorite in H₂O–NaCl fluids at 800 °C, 1 GPa, increases with increasing NaCl from 0.012 mol/kg H₂O ($X_{\text{NaCl}}=0$) to 1.673 mol/kg H₂O ($X_{\text{NaCl}}=0.486$; Fig. 3). This corresponds to an increase

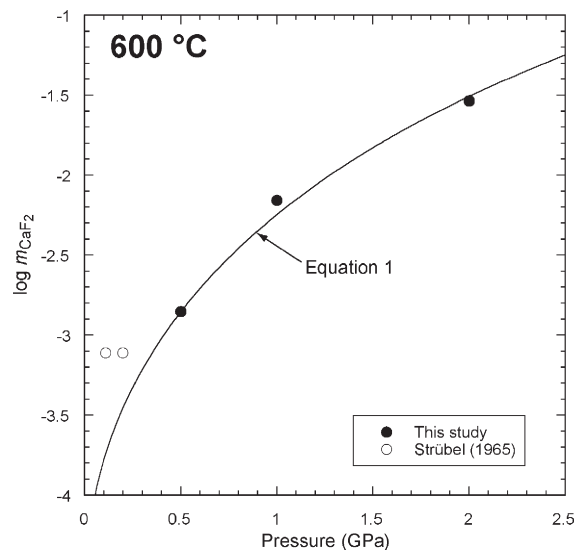


Fig. 4. Comparison of fluorite solubility at 600 °C determined in the present study (filled circles) with results of Strübel (1965, open circles). The solid line was calculated from Eq. (1). Errors (1σ) are smaller than the symbols.

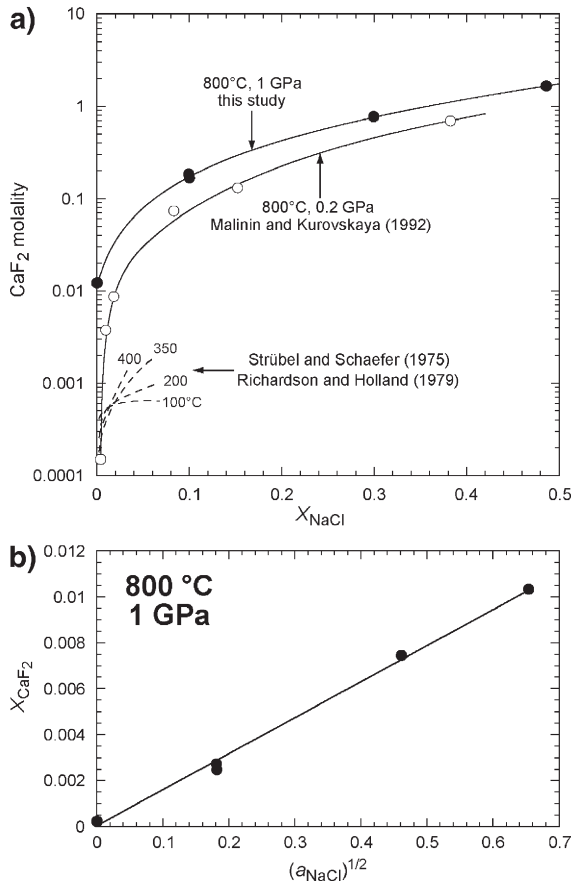


Fig. 5. (a) Comparison of the dependence of fluorite solubility (as CaF₂ molality) on NaCl mole fraction at selected *P* and *T*. Dashed curves show CaF₂ solubility at 100–400 °C at liquid-vapor saturation (Richardson and Holland, 1979a,b; Strübel and Schaefer, 1979); open circles, data at 800 °C, 0.2 GPa (Malinin and Kurovskaya, 1992); filled circles, this study. (b) Fluorite mole as a function of the square root of NaCl activity at 800 °C and 1 GPa (filled circles, this study). Fluorite mole fractions were calculated relative to fully dissociated NaCl, following Newton and Manning, (2006). The ideal activity model of Aranovich and Newton (1996) was used to compute *a*_{NaCl}. The line indicates a linear least-squares fit, corresponding to $X_{CaF_2} = 4.51 \times 10^{-5} + 0.0157(a_{NaCl})^{1/2}$, for which *R*=0.998.

of 140 times over the investigated range. Least-squares regression of the data gives:

$$m_{CaF_2} = 0.01035 \times 10^{-2} + 1.141X_{NaCl} + 4.694X_{NaCl}^2 \quad (2)$$

for which *R*=0.999.

4. Discussion

4.1. Fluorite solubility in H₂O

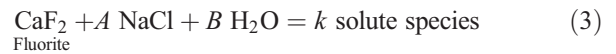
Our results demonstrate that there is a strong increase in fluorite solubility in H₂O with increasing *P* and *T* at

≥ 600 °C. In a previous study, Strübel (1965) found no *P* dependence at 600 °C, 0.1–0.2 GPa (Fig. 4). Extrapolation of our Eq. (1) to the pressure of Strübel’s experiments predicts lower solubility than he reported. However, Strübel (1965) suggested that his results may not reflect equilibrium and for this reason did not report errors. When coupled with estimated uncertainties of up to 83% relative in runs he interpreted to reflect equilibrium, the apparent disagreement between the two studies is probably not significant.

4.2. Fluorite solubility in H₂O–NaCl

The observed increase in fluorite solubility with NaCl concentration at 800 °C and 1 GPa is similar in form to that reported by Malinin and Kurovskaya (1992) at the same *T*, but at 0.2 GPa (Fig. 5a). However, because of the very low solubility in H₂O at 0.2 GPa, the relative enhancement increase is greater at low *P*. It can be seen that, in comparison with 800 °C, CaF₂ solubility increases only slightly with NaCl at *T* ≤ 400 °C, and that at 100 °C, there is a solubility maximum at X_{NaCl} ~ 0.03.

To obtain information on the interaction of fluorite and fluid, a generalized dissolution reaction can be written:



where *A* and *B* are the number of moles of NaCl and H₂O consumed to produce *k* moles of solutes, per mole of

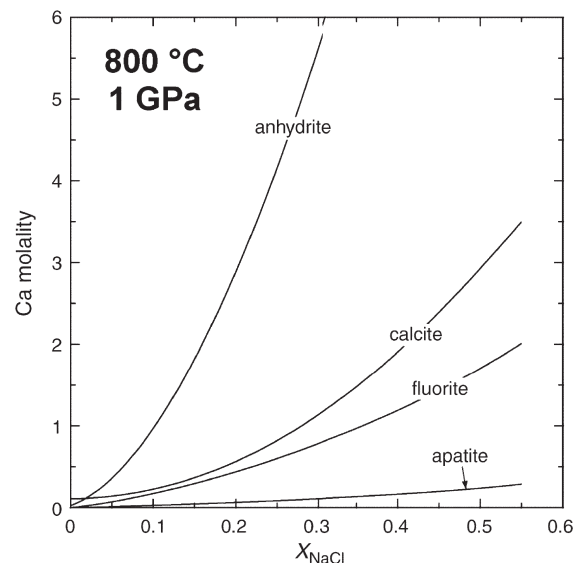


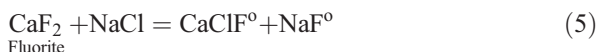
Fig. 6. Comparison of the solubilities of fluorite, calcite, anhydrite, and apatite at 800 °C and 1 GPa. Data sources: calcite, Newton and Manning (2002); anhydrite, Newton and Manning (2005); apatite, Antignano and Manning (2004).

fluorite dissolved. The strong increase of CaF_2 solubility with salinity at constant P and T implies the existence of a solution reaction involving the NaCl component. The accelerating trend indicates that H_2O is not involved in the reaction, since $a_{\text{H}_2\text{O}}$ decreases with increasing X_{NaCl} .

The role of NaCl in controlling fluorite solubility was examined by evaluating correlations with NaCl activity (a_{NaCl}). Following Newton and Manning (2006), NaCl activity was calculated from

$$a_{\text{NaCl}} = \frac{4X_{\text{NaCl}}^2}{(1 + X_{\text{NaCl}})^2} \quad (4)$$

due to the complete dissociation to Na^+ and Cl^- at 800 °C, 1 GPa (Aranovich and Newton, 1996). The minor contribution of dissolved CaF_2 to NaCl mole fraction was neglected. Fig. 5b shows that the mole fraction of fluorite in solution increases linearly as the square root of NaCl activity calculated from Eq. (4) over the investigated compositional range ($R=0.998$). This confirms that $B=0$ in Eq. (3) and implies that ~ 2 mol of solutes are produced per mole of NaCl consumed in the dissolution of fluorite. A simple (but nonunique) equilibrium that could account for this relationship is



A strong increase in solubility with X_{NaCl} has also been observed for calcite (Newton and Manning, 2002), anhydrite (Newton and Manning, 2005) and apatite (Antignano and Manning, 2004). Fig. 6 compares the X_{NaCl} -dependence of the solubility of fluorite with that of other minerals at 800 °C and 1 GPa. Fluorite solubility

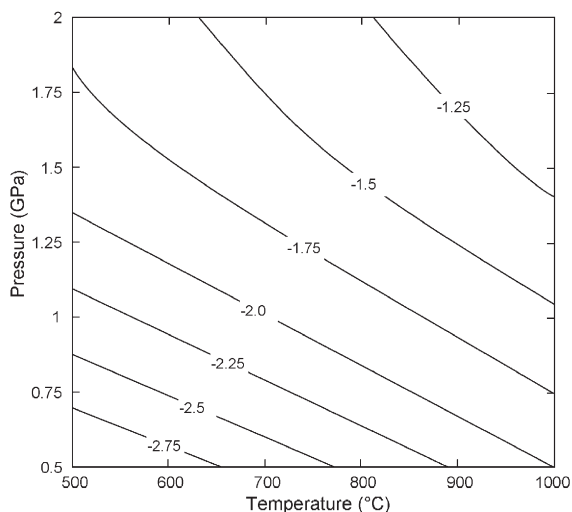


Fig. 7. Fluorite solubility in H_2O as a function of P and T . The numbers on the curves are solubility isopleths ($\log m_{\text{CaF}_2}$), as calculated from Eq. (1).

increases less strongly with X_{NaCl} than anhydrite or calcite, but more strongly than apatite. The similar forms of the curves imply similar dissolution mechanisms involving NaCl , but the different degrees of enhancement with X_{NaCl} suggest that anion complexes involving SO_4^{2-} (Na_2SO_4) and CO_3^{2-} (Na_2CO_3) are more stable and thus lead to higher solubilities when compared to F^- (NaF^0) and PO_4 (Na_3PO_4) complexes.

4.3. Variation in fluorite solubility with fluid flow

Fig. 7 illustrates the variation of $\log m_{\text{CaF}_2}$ with P and T at high pressure. Increasing P and T lead to a rise in solubility. Thus, a clockwise P – T path during a Barrovian-style metamorphic event would lead to greater precipitation of fluorite if the retrograde P – T path is a combination of simultaneous decompression and cooling than if it involves only isothermal decompression or isobaric cooling. Fluorite-saturated fluid accompanying eclogite-facies metamorphism (~ 600 °C, ~ 2 GPa), would also contain large amounts of dissolved F, since CaF_2 solubility increases at 600 °C from 0.0017 m (0.5 GPa) to 0.028 m (2 GPa), a factor of 17 increase. Thus, even fluorite-undersaturated fluids may have high F contents. This could account for the presence of F-rich minerals, such as titanites, in HP and UHP rocks (Franz and Spear, 1985; Sobolev and Shatsky, 1991; Carswell et al., 1996).

4.4. The role of F-bearing fluids in the formation of fluorite-bearing assemblages in the deep crust

High-grade fluorite-bearing mineral assemblages have been described from several granulite-facies terranes (Bohlen and Essene, 1978; Markl and Piazzolo, 1998, 1999; Sengupta et al., 2004). In the Adirondack localities investigated by Bohlen and Essene (1978), fluorite appears to be part of a primary magmatic assemblage; however, in the other occurrences, fluorite forms with retrograde assemblages, which grew either under amphibolite-facies conditions or granulite-facies conditions. Whereas in the samples of Markl and Piazzolo (1998, 1999) no reaction textures involving amphibolite-facies fluorite were described, Sengupta et al. (2004) show that wollastonite is replaced by fluorite and quartz during isothermal (830 °C) decompression to $P < 0.6$ GPa involving a F-rich fluid. Assuming pure H_2O , this is in accordance with Fig. 7, which indicates decreasing fluorite solubility with decreasing T . Fluorite growth on isothermal decompression would also occur if coexisting fluid was predominantly H_2O – NaCl with roughly constant X_{NaCl} (Fig. 5b).

4.5. F-bearing fluids and the implications for REE transport in the deep crust

The data in Figs. 5B and 7 indicate that fluorite solubility is high in deep crustal fluids. This means that F must become quite concentrated before fluorite will saturate. Thus, dissolved F may be large even in the absence of fluorite, as indicated by F-rich minerals associated with granulite-facies metamorphism (e.g. Chacko et al., 1987; Pan and Fleet, 1996; Tsunogae et al., 2003). The presence of F in high-grade metamorphic rocks has been explained by scenarios such as partial melting and removal of granitic magma leaving an F-rich residue, metamorphism of an unusually F-rich rock, and influx of a F-rich fluid from external sources (e.g. Dooley and Patino Douce, 1996; Mouri et al., 1996; Becker et al., 1999). For instance, high activities of F in fluids associated with charnockitization in southern India have been inferred from elevated F contents in allanite, apatite, biotite and hornblende (Chacko et al., 1987). Tsunogae et al. (2003) also attribute the formation of F-rich pargasites in the Napier Complex to be due to infiltration of F-bearing fluids. Consideration of the role of halogen-bearing fluids in granulites has focused chiefly on Cl (e.g. Sisson, 1987), but Markl and Piazzolo (1998) recognized the role of F-bearing fluids around igneous bodies. Several studies have shown that REE are probably unaffected by high-grade metamorphism under fluid-absent conditions (Taylor and McLennan, 1985; Grauch 1989; Valley et al., 1990); however, Pan and Fleet (1996) showed that REE mobility may be induced by F-bearing fluids. This conclusion was based on the presence of REE-bearing F-apatites in granulites from the Superior Province, Ontario, Canada, in rocks that experienced REE mobility under granulite-facies conditions. Pan and Fleet (1996) also observed an increase in the modal abundance of F-apatite in granulite-facies rocks, when compared to their amphibolite-facies precursors. In addition, whole rock data and mass balance calculations also indicated an increase in REE and HFSE during prograde granulite-facies metamorphism.

Our experimental results show that F contents must reach very high values to attain fluorite saturation in H₂O and H₂O–NaCl fluids that approximate those present during lower crustal metamorphism. This supports interpretations that F may be sufficiently concentrated to play an important role in the mobility of REE at high *P* and *T*.

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