



# The solubility of fluorite in Na-K-Cl solutions at temperatures up to 260 °C and ionic strengths up to 4 mol/kg H<sub>2</sub>O



Wei Zhang <sup>a, b</sup>, Li Zhou <sup>b, \*</sup>, Hongfeng Tang <sup>b</sup>, Heping Li <sup>b</sup>, Wenlei Song <sup>c, d</sup>, Gang Xie <sup>b, e</sup>

<sup>a</sup> Institute for Ecological Civilization of Karst Area, Guizhou Normal University, Guiyang 550001, China

<sup>b</sup> Key Laboratory of High-temperature and High-pressure Study of the Earth's Interior, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

<sup>c</sup> Department of Geology and Pedology, Mendel University in Brno, Brno 61300, Czech Republic

<sup>d</sup> Central European Institute of Technology, Brno University of Technology, Brno 61200, Czech Republic

<sup>e</sup> University of Chinese Academy of Sciences, Beijing 100039, China

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## ABSTRACT

The solubility of fluorite in hydrothermal conditions is important in ore forming and geothermal processes and groundwater utilization. However, a quantitative description of the geochemical behavior of fluorite under hydrothermal conditions has not been previously reported. In this work, the solubility of fluorite in Na-K-Cl solutions at temperatures up to 260 °C and ionic strengths up to 4 M was determined by experiments and modeling. The solubility products obtained in this work at 30 and 50 °C under ambient pressure and those from literature were used to regress the density model parameters for fluorite solubility product calculation at high temperature. The Pitzer interaction model was adopted to calculate the activity coefficient. The fluorite solubility determined in KCl solution at 250 °C under vapor saturated pressure and that from the literature were combined with the low-temperature thermodynamic properties of heat capacity and osmotic coefficient to obtain the binary parameters of NaF and KF at temperatures up to 260 °C. A thermodynamic model was then developed for calculating the fluorite solubility in Na-K-Cl solution at temperatures up to 260 °C, under vapor saturated pressure and ionic strengths up to 4 M. As calculated from this model, fluorite solubility measured at 200 °C and 0.1 M NaCl was well predicted. Both temperature and ionic strength had significant effects on fluorite solubility, and fluorite exhibited a similar dissolution pattern in both NaCl and KCl solution. When the concentration was lower than 2 M, the solubility of fluorite first increased with temperature, reached a maximum at approximately 100 °C, and then decreased. When the concentration was higher than 2 M, the solubility of fluorite increased monotonically with temperature.

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## 1. Introduction

Accurate knowledge of the geochemical behavior of fluorite in high ionic strength solutions at elevated temperatures is important to numerous scientific fields. In ore forming processes, it occurs independently a hydrothermal ore deposit and as an accessory and gangue mineral (Cunningham et al., 1998; Sheard et al., 2012). It controls the concentration of fluoride in the ore formation fluid, where fluoride plays an important role in metal element hydrothermal mobilization and transportation by the formation of fluoride complexes (Timofeev et al., 2015). In geothermal water and

groundwater utilization, the dissolution of fluorite is the mainly source for the origin of fluoride in geothermal water and groundwater which is highly related with human health (Edmunds and Smedley, 2013). It has also been recognized to control the concentration of fluoride, since it is the predominant and least soluble fluorine-bearing mineral. The solubility of fluorite is thought to control the upper limit of the fluoride concentration in calcium-bearing geothermal water and groundwater (Guo, 2012). The dissolution of fluorite is influenced by temperature, complex ions, and ionic strength. It has been reported that SO<sub>4</sub> and HCO<sub>3</sub> have a positive relationship with fluoride (Chae et al., 2007).

Investigation of fluorite solubility is thus significant for understanding the physicochemical mechanism of fluorite deposition, which may be useful in locating new fluorite deposits and an

\* Corresponding author.

E-mail address: [zhouli\\_prc@hotmail.com](mailto:zhouli_prc@hotmail.com) (L. Zhou).

important clue to the processes that controls the deposition of ore minerals, where fluorite is a gangue or accessory mineral (Sallet et al., 2005). The solubility of fluorite can also provide the basics to analyze and evaluate the origin and enrichment of fluoride in geothermal water and groundwater. However, to our knowledge, a quantitative description of the geochemical behavior of fluorite under hydrothermal conditions has not been reported.

### 1.1. Theoretical background

The control of fluorite solubility in hydrothermal fluid by an equilibrium with solid fluorite can be addressed by calculating the activity coefficient of aqueous  $\text{CaF}_2(\text{aq})$  and the fluorite solubility product in hydrothermal conditions:



$$K_{\text{sp}} = \frac{(a_{\text{Ca}^{2+}})(a_{\text{F}^{-}})^2}{a_{\text{CaF}_2(\text{s})}} \quad (2)$$

The activity of a pure solid, by definition, is unity, and the equation is reduced to:

$$K_{\text{sp}} = (m_{\text{Ca}^{2+}})(m_{\text{F}^{-}})^2 \left[ (\gamma_{\text{Ca}^{2+}})(\gamma_{\text{F}^{-}})^2 \right] = Q_S \left[ (\gamma_{\text{Ca}^{2+}})(\gamma_{\text{F}^{-}})^2 \right] \quad (3)$$

where  $K_{\text{sp}}$  is the solubility product of fluorite,  $Q_S$  is the apparent equilibrium constant,  $m$  and  $\gamma$  are the molality and the activity coefficient of calcium and fluoride. To accurately calculate and assess fluorite solubility, the solubility product ( $K_{\text{sp}}$ ) and activity coefficient ( $\gamma_i$ ) of involved species are required.

Numerous studies have been conducted regarding the solubility of fluorite (Garand and Mucci, 2004; Kurovskaya and Malinin, 1983; Malinin, 1976; Malinin and Kurovskaya, 1979a, 1979b; Nordstrom and Jenne, 1977; Richardson and Holland, 1979; Strübel, 1965). In our previous work, we showed that the solubility products of fluorite provided by different authors are widely scattered (Zhang et al., 2015). At 25 °C and 1 bar, the difference can be nearly three orders of magnitude. To assess and avoid those scatter, Garand and Mucci (2004) measured the solubility of fluorite at 25 °C and 1 bar for 32 weeks. However, their result is quite different from that calculated with the most widely accepted solubility product ( $K_{\text{sp}}$ ) calculation equation proposed by Nordstrom and Jenne (1977). The solubility products of Richardson and Holland (1979) at high temperatures are widely accepted for their reproducibility (Table 1 in SI). The discrepancy zone of fluorite solubility products provided by different authors is mainly at temperatures under 100 °C.

The Pitzer interaction model (Pitzer, 1973) is successfully used in calculating mineral solubility at high temperature (Li and Duan, 2011; Monnin, 1999; Shi et al., 2012). When applied to calculate fluorite solubility in NaCl or KCl solution, for the comparatively negligible concentrations of  $\text{Ca}^{2+}$  and  $\text{F}^{-}$ , the standard Pitzer equations can be reduced to the following forms for the activity coefficients of  $\text{Ca}^{2+}$  and  $\text{F}^{-}$ , respectively:

$$\ln \gamma_{\text{Ca}} = Z_{\text{Ca}}^2 F + m_{\text{Cl}}(2B_{\text{CaCl}} + Z_{\text{CaCl}}) + m_{\text{Na}}(2\phi_{\text{Na,Ca}} + m_{\text{Cl}}\psi_{\text{Ca,Na,Cl}}) + |Z_{\text{Ca}}|m_{\text{Na}}m_{\text{Cl}}C_{\text{NaCl}} \quad (4)$$

$$\ln \gamma_{\text{F}} = Z_{\text{F}}^2 F + m_{\text{Na}}(2B_{\text{NaF}} + Z_{\text{NaF}}) + m_{\text{Cl}}(2\phi_{\text{Cl,F}} + m_{\text{Na}}\psi_{\text{Na,Cl,F}}) + |Z_{\text{F}}|m_{\text{Na}}m_{\text{Cl}}C_{\text{NaCl}} \quad (5)$$

where  $\gamma_{\text{Ca}}$ ,  $Z_{\text{Ca}}$  and  $\gamma_{\text{F}}$ ,  $Z_{\text{F}}$  are the activity coefficient and charge of  $\text{Ca}^{2+}$  and  $\text{F}^{-}$ , respectively.  $B$  and  $C$  are coefficients that denote the interactions between two oppositely charged ions.  $\phi$  stands for the interaction between two like-charged ions, and  $\psi$  represents the ternary interactions among three ions.

The calcium ion related binary parameters of  $\beta_{\text{CaCl}}^{(0)}$ ,  $\beta_{\text{CaCl}}^{(1)}$ ,  $C_{\text{CaCl}}^{\phi}$  and ternary parameters of  $\theta_{\text{Na,Ca}}$ ,  $\psi_{\text{Ca,Na,Cl}}$  are comprehensively and accurately studied (Christov and Møller, 2004; Greenberg and Møller, 1989; Møller, 1988). Therefore, the activity of  $\text{CaF}_2$  is heavily dependent on fluoride related parameters, mainly the binary parameters of NaF or KF.

Thermodynamic data on heat capacity, enthalpy, osmotic data, and vapor pressure can be directly used to obtain the activity coefficient (Königsberger et al., 2005). With those fluoride related thermodynamic data, limited up to 100 °C, Weber et al. (2000) obtained the binary Pitzer parameters  $\beta_{\text{NaF}}^{(0)}$ ,  $\beta_{\text{NaF}}^{(1)}$ ,  $C_{\text{NaF}}^{\phi}$  and the ternary parameters of  $\theta_{\text{F,Cl}}$  and  $\psi_{\text{Na,Cl,F}}$ , and the solubility of fluorite up to 100 °C can be accurately expressed with these parameters (Zhang et al., 2015). However, we found these parameters cannot be directly applied to describe the 200 and 260 °C fluorite solubility data of Richardson (1977).

Solubility data have been used to obtain the activity coefficient at high temperatures (Christov, 2007; Shi et al., 2012). Shi et al. (2012) used the barite solubility data in NaCl solution to obtain the Pitzer binary coefficient of Ba-Cl and Na-SO<sub>4</sub> at high temperatures and pressures. This method can be adopted in this work to evaluate parameters for NaF and KF at high temperatures.

Measurement of stoichiometric solubility products ( $Q_S$ ) for a series of fixed ionic strengths can be used to calculate the solubility product constant  $K_{\text{sp}}$  by using an empirical method of extrapolation to infinite dilution. In this work, we experimentally measured the solubility of fluorite in NaCl solution at 30 and 50 °C. Combining the determined solubility products of this work with those obtained from the literature, fluorite solubility products at high temperatures can be calculated by using the density model. The fluoride related Pitzer binary parameters were regressed using low-temperature thermodynamic data and high-temperature experimental solubility data from this work and the literature. With all that, a thermodynamic model for calculating fluorite solubility at temperatures up to 260 °C in Na-K-Cl solution was established.

## 2. Experimental section

### 2.1. Reagents

The fluorite powder ( $\text{CaF}_2 > 99.5\%$ ), sodium chloride ( $\text{NaCl} > 99.99\%$ ) and potassium chloride ( $\text{KCl} > 99.5\%$ ) used for experiments were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd and used without further purification. They were heated at 110 °C for 8 h prior to use. The fluorite mineral crystals were collected from Maoniuping REE deposit, China. The X-ray diffraction pattern of fluorite powder and crystals were a perfect match to the JCPDS reference pattern 35–0816. Their chemical composition as analyzed by X-ray fluorescence (XRF) (Germany, Bruker S8 Tiger) were given in Table 1. Few impurities were

**Table 1**  
The chemical composition of fluorite (XRF, in mass diffraction %).

	CaO	SrO	MgO	Fe <sub>2</sub> O <sub>3</sub>	ZnO	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	LOI
Fluorite powder	61.75	0.01	0.93	0.03	0.03	—	—	37.25
Fluorite crystal	59.58	0.27	0.18	—	—	0.04	<0.01	39.93

\*- undetected.

contained. The PF-01 fluoride electrode and 232-01 calomel reference electrode were purchased from Leici Precision Scientific Instrument Co., Ltd. The fluoride electrode is made of a single crystal of lanthanide fluoride. The 0.1 mol/L NaF and 0.1 mol/L NaCl solution are contained in the electrode tube contains, Ag-AgCl electrode is the internal reference electrode. The 232-01 calomel reference electrode is a double-junction saturated calomel electrode with the salt bridge filled with G.R. grade saturated solution of potassium chloride and the outer salt bridge filled with 0.1 mol/L lithium acetate solution. All solutions were prepared by weight, employing  $18 \text{ m}\Omega \text{ cm}^{-1}$  cm deionized and boiled water.

## 2.2. Low temperature experiments

The isothermal dissolution method, successfully used by Cetiner et al. (2005) and Garand and Mucci (2004), was applied for experiments performed at low temperature. Experiments were carried out in 125 mL capacity high-density polyethylene Nalgene™ bottles. 100 mL the experimental solution was transferred to the bottle with 150–200 mg fluorite powder. The bottles were then sealed and immersed in the THZ-82 type thermostatic shaker with a temperature variation of 0.5 °C, rotating at 135 rpm and a temperature of 50 °C.

The time taken to reach chemical equilibrium was determined from a series of kinetic experiments with durations from 1 to 60 days (Fig. 1). Equilibrium was achieved in 30 days. After equilibrium was attained, the thermostatic shaker was stopped and kept at the constant temperature for 4 h, and 2 mL of the supernatant solution was then withdrawn by a syringe filtrate with 0.45  $\mu\text{m}$  filters. An aliquot of 0.002 M EDTA solution was preloaded into the syringe to avoid fluorite precipitation when the temperature decreased. Each sample was collected three times. After the experiments at 50 °C were completed, the temperature of the thermostatic shaker was set down to 30 °C and shaken for another month, which was sufficient to reach equilibrium. The collected sample was gravimetrically diluted for concentration determination.

## 2.3. High temperature experiments

The weight-loss method was adopted for experiments at high temperature. The experiments were performed in Teflon reactors. Before each experiment, the autoclave and Teflon reactor were

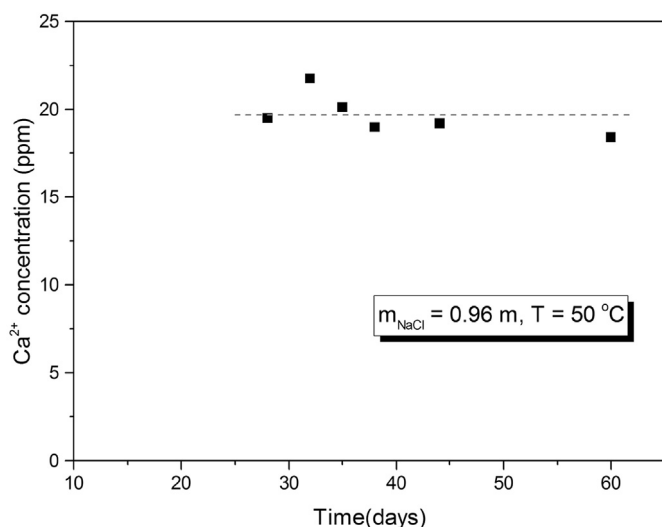


Fig. 1. Fluorite solubilities in 0.96 M NaCl solution at 50 °C as a function of time.

purged of atmospheric air with a stream of nitrogen. A single fluorite crystal, mass of 10–20 mg, free of internal cracks and with a smooth surface, was fixed at the end of a Teflon tube and immersed in a solution of known mass and concentration; the reactors were then sealed with Teflon stoppers and heated to temperatures of 200 and 250 °C in titanium autoclaves. An aliquot of distilled water was placed in the autoclave to balance the pressure that developed inside the reactors during the experiments with the pressure in the autoclaves. After 7–10 days, the oven and autoclave were inverted to separate the fluorite crystal from solution; then, the oven was opened, and the autoclave was air cooled.

## 2.4. Analytical methods

The concentration of fluoride was determined by an ion-selective electrode method using a cell consisting of a fluoride electrode and a calomel reference electrode. The potential was measured by an Agilent 34410A multimeter and automatically acquired by a Microsoft Excel plug-in. The calibration line was obtained using aqueous solutions of  $\text{F}^-$  from 0.38 to 1.9 ppm. The  $R^2$  values of the calibration curves were always above 0.995. The electrode cell was sustained in the diluted solution for at least 10 min for potentials that varied within 0.5 mV. The RSD on three replicate measurements was below 5%. The concentration of calcium was determined by flame atomic absorption spectrophotometry (FAAS) using a PinAAcle 900F spectrophotometer. The calibration line was from 0.5 to 2.0 ppm, and the RSD on three replicate measurements was below 5%. Four calibration lines were established for both the fluoride and calcium concentration measurements to eliminate the ionic strength effect.

As for high temperature weight-loss experiments, after the experiments the fluorite crystals were washed in warm water and dried to a constant weight. The fluorite crystal was weighed on a microbalance (Mettler Toledo XP2U), before and after each experiment. The morphology and composition was analyzed by scanning electron microscopy and energy-dispersive X-ray (SEM-EDX).

## 3. Results

The result of the fluorite solubility experiment at low temperature is summarized in Table 2. It should be noted that the molar concentration ratio of fluoride and 2 times calcium was not equal to its stoichiometric coefficient. Similar phenomena were also noted by Cetiner et al. (2005), in the solubility experiments of rare earth element phosphates. They thought a small amount of undetected, more soluble phosphate impurity contained in the starting material and incongruent dissolution of the REE phosphate were the possible explanations.

From the XRF result of the fluorite powder chemical composition, we can see that some magnesium was contained in the original fluorite powder, which may make some contribution to the “missing” calcium, because  $\text{MgF}_2$  is more soluble than fluorite (Elrashidi and Lindsay, 1986). In addition, incongruent dissolution has also been found in the dissolution of fluorite (Zhang et al., 2006). In their experiment, the concentration ratio of fluoride and calcium was related to the flow rate. At a high flow rate, the concentration of fluoride was more than twice that of calcium, due to the adsorption of Cl onto the surface of fluorite with the formation of the surface complex  $\text{Ca}(\text{F},\text{Cl})_2$ . Our experiments were performed in a high-speed thermostatic shaker. The high flow rate on the surface of fluorite caused by the shaker would also affect the concentration ratio.

Fluorite solubility measurements in NaCl and KCl solution were performed at 200 and 250 °C for 3–20 days in concentrations ranging from 0.1 to 4 M (Table 3). The time needed to reach

**Table 2**  
Fluorite solubility at low temperature in NaCl solution.

Temperature (°C)	Solution (NaCl mol/kg)	Fluoride concentration (mol/kg × 10 <sup>-4</sup> )	Calcium concentration (mol/kg × 10 <sup>-4</sup> )	The ratio of F/(2·Ca)
30	0.10	8.15 ± 0.23	3.05 ± 0.08	1.33
	0.96	10.99 ± 0.14	3.99 ± 0.04	1.38
	2.85	10.21 ± 0.45	3.66 ± 0.29	1.39
	4.50	8.98 ± 0.18	2.99 ± 0.18	1.50
50	0.10	8.57 ± 0.04	3.81 ± 0.20	1.13
	0.96	12.05 ± 0.22	5.22 ± 0.35	1.15
	2.85	11.10 ± 0.15	4.94 ± 0.21	1.12
	4.50	9.71 ± 0.18	3.95 ± 0.12	1.23

**Table 3**  
Fluorite solubility in NaCl and KCl solution at 200 and 250 °C.

Num	Time (days)	T (°C)	Solution	m (mol/kg)	Mass of solution (g)	Weight loss of CaF <sub>2</sub> (mg)	Molality of CaF <sub>2</sub> (mol/kg)
F39	20	200	NaCl	0.4	3.6962	0.123	0.00044
F40	20	200	NaCl	0.1	4.0459	0.122	0.00039
F41	20	200	NaCl	0.1	4.8665	0.141	0.00037
F42	3	250	NaCl	1	7.3781	0.239	0.00044
F43	7	250	NaCl	1	7.4092	0.316	0.00058
F44	7	250	KCl	0.1	7.3131	0.137	0.00024
F45	7	250	KCl	0.4	7.1729	0.192	0.00035
F46	7	250	KCl	1	7.8651	0.260	0.00046
F47	10	250	KCl	2	8.0499	0.377	0.00069
F48	9	250	KCl	4	8.1147	0.364	0.00075
F49	10	250	KCl	4	8.1075	0.362	0.00074

equilibrium was about 7 and 18 days for experiments at 260 °C and 200 °C, respectively (Richardson, 1977). We measured fluorite solubility in 1 M NaCl solution for 3 and 7 days, and the result for 7 days (0.00058 mol/kg) was in very good agreement with the previous result (0.00056 mol/kg, Table 1 in SI). Fluorite solubility in 0.4 M NaCl solution at 200 °C also agreed very well that of Richardson's. The reproducibility between the fluorite solubility measured in 4 M KCl solution for 9 and 10 days was excellent.

## 4. Discussion

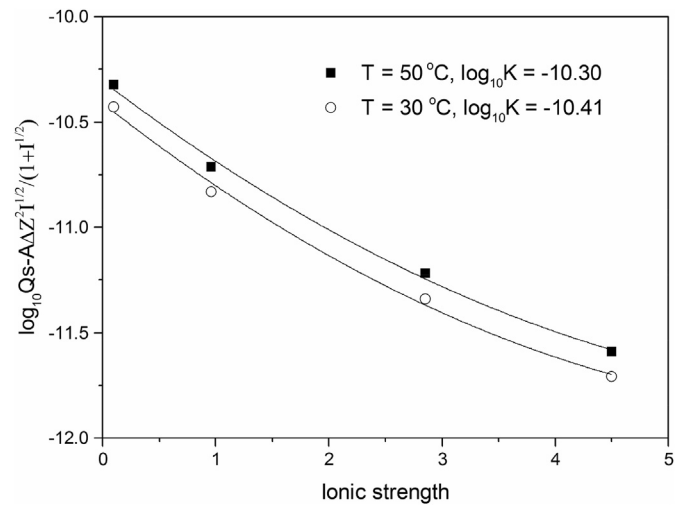
### 4.1. Solubility product of fluorite

The fluorite solubility products at 30 and 50 °C were extrapolated from the stoichiometric solubility products ( $Q_s$ ) at a series of fixed ionic strengths. This extrapolation was accomplished using the following relationship (Cetiner et al., 2005):

$$\log_{10}Q_s(I) = \log_{10}K_{sp} + \frac{A\Delta Z^2\sqrt{I}}{1 + \sqrt{I}} + CI + DI^2 + \dots \quad (6)$$

where  $K_{sp}$  is the equilibrium constant at infinite dilution,  $Q_s(I)$  is the apparent equilibrium constant at the ionic strength  $I$ ;  $\Delta Z^2$  is the change in charges squared for fluorite solution reaction ( $\Delta Z^2 = 6$ ),  $A$  is the Debye–Hückel parameter obtained from (Helgeson et al., 1981), and  $C$ ,  $D$  are adjustable parameters. The values of  $\log_{10}K_{sp}$  were determined via a regression analysis of the experimental data, in which  $\log_{10}Q_s(I) - \frac{A\Delta Z^2\sqrt{I}}{1 + \sqrt{I}}$  was the dependent variable and  $I$  was the independent variable. The results of the regression are shown in Fig. 2.

The density model proposed by Anderson et al. (1991) is widely accepted for the calculation of the solubility products (Bénézech et al., 2009; Dolejš, 2013; Xiong, 2003). The expression is



**Fig. 2.** Values of  $\log_{10}Q_s(I) - \frac{A\Delta Z^2\sqrt{I}}{1 + \sqrt{I}}$  as a function of ionic strength.

$$\begin{aligned} \ln K = & \ln K_r - \frac{\Delta H_r^0}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) + \frac{\Delta a}{R} \left( \ln \frac{T}{T_r} + \frac{T_r}{T} - 1 \right) + \frac{\Delta b}{2R} \left( T + \frac{T_r^2}{T} \right. \\ & \left. - 2T_r \right) + \frac{\Delta c}{R} \frac{(-T^2 - T_r^2 + 2TT_r)}{2T^2T_r^2} \\ & + \frac{\Delta C_{pr}^0}{RT_r(\partial\alpha/\partial T)_{pr,Tr}} \left[ \frac{1}{T} \ln \frac{\rho_r}{\rho} - \frac{\alpha_r}{T} (T - T_r) \right] \end{aligned} \quad (7)$$

$$\log_{10}K = \frac{\ln K}{2.303} \quad (8)$$

where  $\ln K$  is the equilibrium constant at the temperature of interest;  $\ln K_r$  is the equilibrium constant at the reference temperature;  $\rho$  is the density of water ( $\rho_r$  is  $0.9998 \text{ g cm}^{-3}$ );  $\alpha_r(2.593 \times 10^{-4} \text{ K}^{-1})$  and  $(\partial\alpha/\partial T)_{pr}(9.5714 \times 10^{-6} \text{ K}^{-2})$  are the thermal expansion and isobaric temperature derivative for the thermal expansion of water at the reference condition of  $T_r = 298.15 \text{ K}$  and  $1 \text{ bar}$ .  $\Delta a$ ,  $\Delta b$  and  $\Delta c$  are the heat capacity parameters of the solid mineral in the Maier–Kelley equation, and for fluorite, these are  $14.3$ ,  $7.28 \times 10^{-3}$  and  $-0.47 \times 10^{-5}$  (Naylor, 1945), respectively.  $\Delta C_{pr}^o$  refers to solute species only, and  $R$  stands for the gas constant. The only needed parameters are  $\ln K_r$ ,  $\Delta H_r^o$  and  $\Delta C_{pr}^o$  at the reference state of  $25 \text{ }^\circ\text{C}$  and  $1 \text{ bar}$ .

The solubility products at  $25 \text{ }^\circ\text{C}$  from Garand and Mucci (2004), at  $30$ ,  $50 \text{ }^\circ\text{C}$  from our study, and at  $100$ ,  $200$ ,  $260 \text{ }^\circ\text{C}$  from Richardson and Holland (1979) are applied to regress the density model parameters for the fluorite solubility product calculation in the temperature range of  $25$ – $260 \text{ }^\circ\text{C}$  (Table 4). The regressed parameters are listed in Table 5. Fig. 3 gives the solubility products of fluorite calculated using the density model and those from the literature. As we can see, fluorite solubility products calculated by the density model were quite different with those calculated from Nordstrom and Jenne (1977)'s model, and the convergence zone of the discrepancies was at temperature under  $100 \text{ }^\circ\text{C}$ .

## 4.2. Determination of Pitzer model parameters

### 4.2.1. Binary interaction parameters for aqueous Na-F at high temperature

The experimental thermodynamic heat capacity data (Fortier et al. (1974), Saluja et al. (1992), Ziemer et al. (2004),  $278.15$ – $373.15 \text{ K}$ ), enthalpies (Fortier et al. (1974),  $298.15 \text{ K}$ ) and raw solubility data from Richardson (1977) were used to obtain the temperature dependence of binary parameters of NaF.

To avoid the complex temperature behavior of NaF standard partial heat capacity, an indirect fitting method using a reference heat capacity was adopted. Details can be found in Archer (1992). The equation used to calculate the apparent partial heat capacity at the reference concentration is

$$Cp(m_r) = a_1 + a_2T + a_3T^2 \quad (9)$$

The equation for calculating the Pitzer binary parameters is

$$\beta^{(0)} = b_1 + a_4(T - T_r) + a_5\left(\frac{1}{T} - \frac{1}{T_r}\right) + a_6 \ln\left(\frac{T}{T_r}\right) + a_7(T^2 - T_r^2) \quad (10)$$

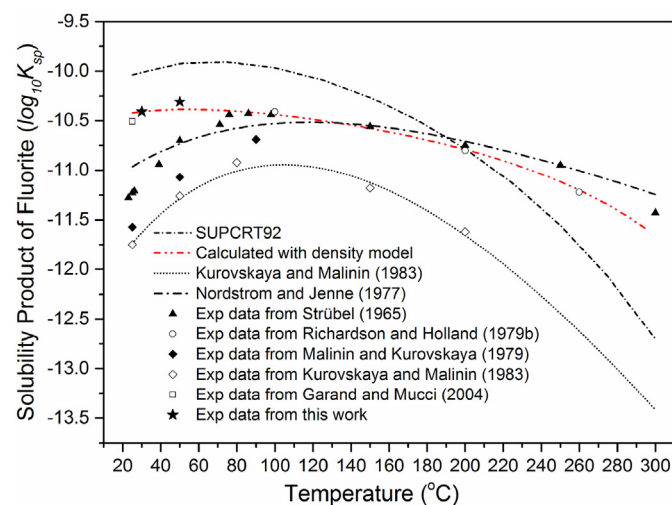
where  $a_1$ – $a_7$  are the parameters;  $b_1$ – $b_3$  are Pitzer binary parameters at  $298.15 \text{ K}$  and  $1 \text{ bar}$ , which were taken from Weber et al. (2000);  $m_r$  is the reference concentration ( $1.0 \text{ mol/kg H}_2\text{O}$  for NaF);  $T$  is the

**Table 4**  
Fluorite solubility products.

Temperature ( $^\circ\text{C}$ )	$\log_{10}K_{sp}$	Reference
25	–10.51	Garand and Mucci (2004)
30	–10.41	This study
50	–10.30	
100	–10.41	Richardson and Holland (1979)
200	–10.80	
260	–11.22	

**Table 5**  
Parameters of density model for fluorite solubility product calculation.

$\ln K_r$	$\Delta H \text{ J/mol/K}$	$\Delta C_{pr}^o \text{ J/mol}$
–24.00	11867.60	–270.08



**Fig. 3.** Fluorite solubility products calculated with the density model and those from the literature.

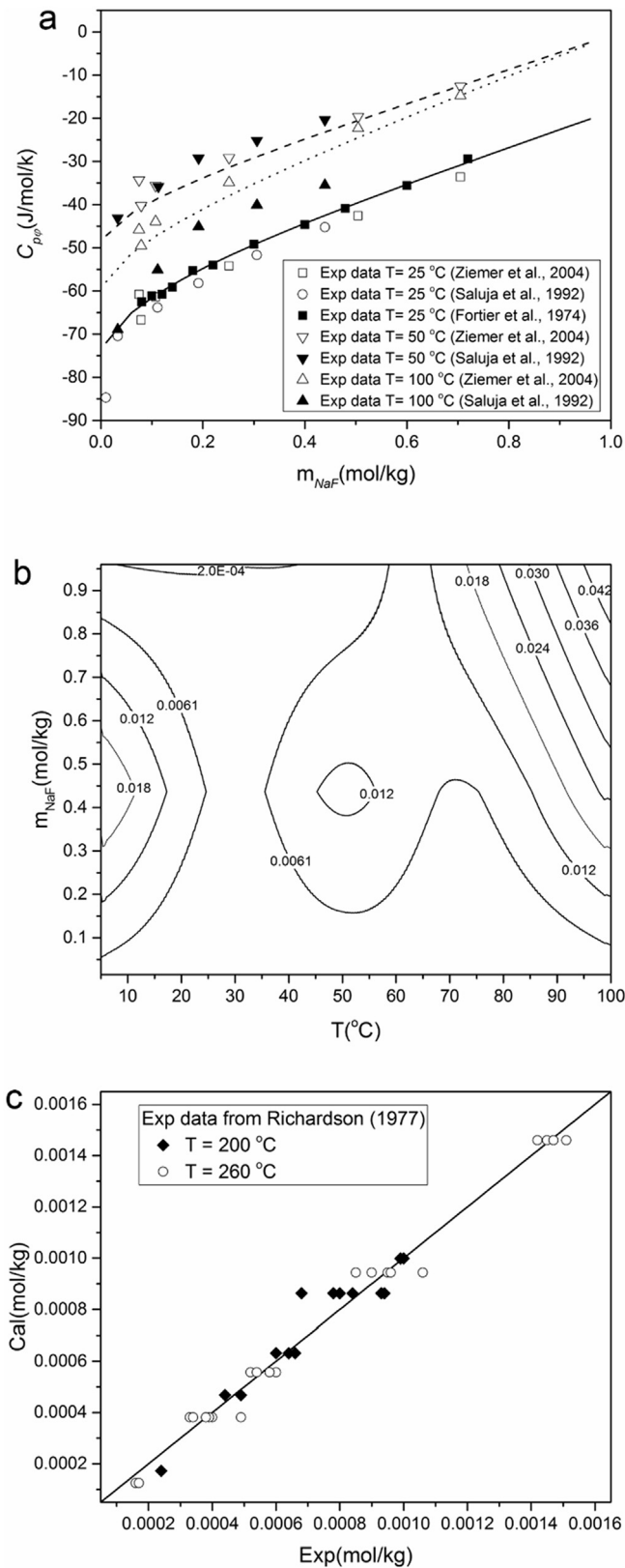
temperature in Kelvin and  $T_r$  is the reference temperature  $298.15 \text{ K}$ . The equation format is the same for  $\beta^{(1)}$  and  $C^\phi$ . The parameters were determined by non-least squares regression, simultaneously obtained by minimizing the residuals between calculated and measured data. It was performed on a MATLAB<sup>®</sup> platform using a simplex algorithm. The parameters are listed in Table 6.

Fig. 4a compares the experimental apparent molar heat capacity of NaF with those calculated from our model. The apparent heat capacity was well predicted by our model. Fig. 4b shows that the NaF mean activity calculated with our parameters are in good agreement with that calculated with Weber's parameters at temperature up to  $100 \text{ }^\circ\text{C}$ . Fluorite solubilities were also well predicted by our model (Fig. 4c).

Malinin and his co-worker have measured the solubility of fluorite from  $25$  to  $260 \text{ }^\circ\text{C}$  (Kurovskaya and Malinin, 1983; Malinin,

**Table 6**  
Parameters for NaF and KF Pitzer binary parameters calculation.

Parameters	NaF	KF
$m_r$	1.0	2.0
$a_1$	–1.13556870 E+03	–1.45787454 E+03
$a_2$	6.57797185 E+00	8.08646894 E+00
$a_3$	–9.44877812E-03	–1.16224527E-02
$a_4$	8.21533471E-03	4.83668820E-03
$a_5$	–1.46561435 E+03	–1.19781943E+03
$a_6$	–5.01546192 E+00	–3.69472318 E+00
$a_7$	–9.54754860E-06	–7.04817208E-06
$a_8$	5.65076178E-02	6.48387572E-02
$a_9$	–5.36120338 E+03	–5.94417870 E+03
$a_{10}$	–4.35961140 E+01	–4.78741160 E+01
$a_{11}$	3.63735532E-05	3.47267092E-05
$a_{12}$	–1.86029297E-03	1.91766580E-04
$a_{13}$	–2.38848808E-04	–2.59935492E-04
$a_{14}$	2.51923105E-02	–5.06717796E-01
$a_{15}$	3.10152119E-06	2.06679763E-06
$b_1$	0.0330	0.08089
$b_2$	0.2456	0.2021
$b_3$	0.00281	0.00093



**Fig. 4.** (a) Comparison of apparent molar heat capacity of NaF solution with that calculated by our model. (b) Contour map of the difference between the mean activity of NaF calculated by our model and that calculated from the model of Weber et al. (2000) from 0 to 100 °C and 0–1 M. (c) Comparison of experimental and model calculated fluorite solubility in NaCl solution.

1976; Malinin and Kurovskaya, 1979a, b). Although their solubility product calculating equation is quite different from ours, their experimental data could be used to test the activity of fluoride, in other words, the Pitzer binary parameters of NaF. It can be seen from Fig. 5, that combining the binary parameters regressed from Richardson (1977)'s solubility data with Malinin's solubility product, the experimental data of Malinin was in good agreement with the model prediction. The fluorite solubility in 0.1 M NaCl solution at 200 °C is excellently predicted with these parameters.

#### 4.2.2. Binary interaction parameters for aqueous K-F at high temperature

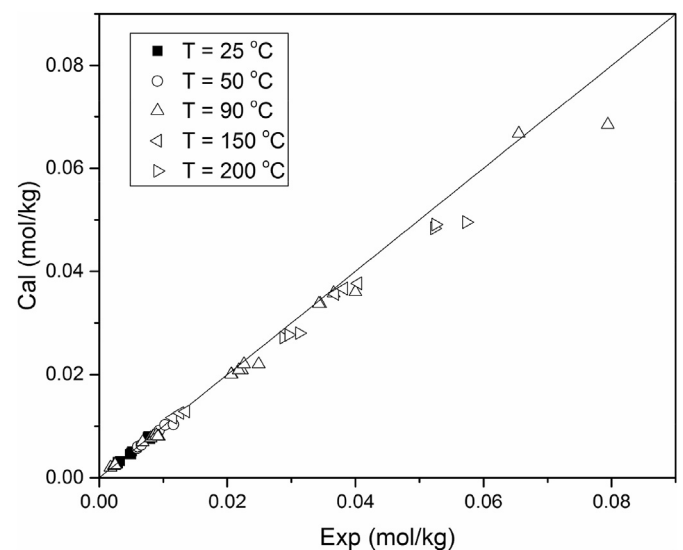
For the KCl solution, the fluorite solubility is heavily dependent on the Pitzer binary parameters of KF. Similar procedures as applied in NaCl solution can also be used in KCl solution. The low-temperature thermodynamic data of the KF solution, such as the osmotic coefficient (Jakli and Van Hook (1972), 276–357 K), and heat capacity (Fortier et al. (1974), Rueterjans et al. (1969), Saluja et al. (1992), 303.15–403.15 K), can be used with the high-temperature solubility data. The Pitzer binary parameters of KF at 25 °C were taken from Pitzer and Mayorga (1973), which were regressed from the isopiestic measurements of Robinson (1941).

Richardson had only conducted a few experiments to measure the solubility of fluorite in KCl solution, and the results were a bit of a scatter with each other (Table 1 in SI). In this work, the fluorite solubility measurement in the KCl solution was performed at 250 °C for 7–10 days in concentrations ranging from 0.1 to 4 M (Table 3). Combining Richardson's experimental data and our own measured solubility data with the low-temperature thermodynamic data, the Pitzer parameters of KF at elevated temperatures were obtained. The equations are the same as equations (4) and (5), and the results are listed in Table 6.

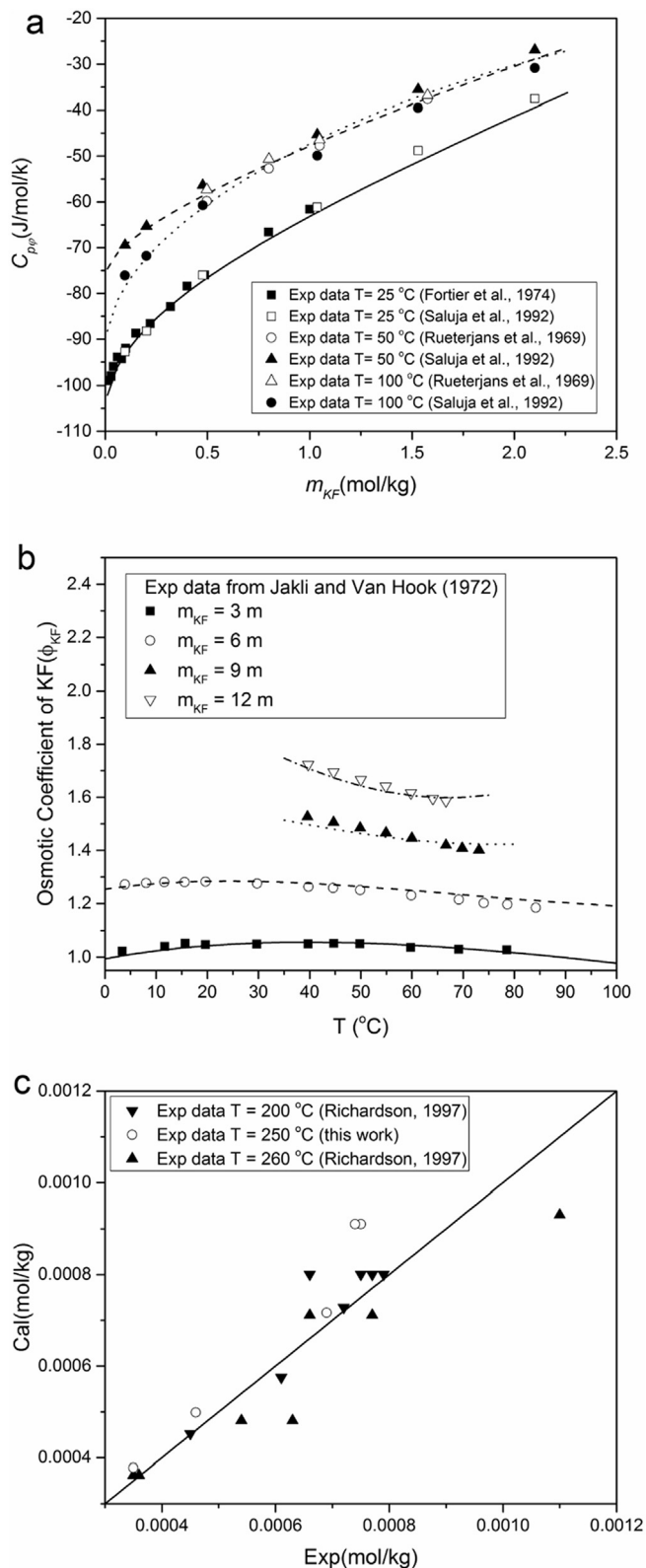
Fig. 6a and b compares the apparent molar heat capacity and osmotic coefficient of KF solution with those calculated from this model. As shown, the thermodynamic properties of KF at low temperature are perfectly predicted by the model. Fluorite solubilities were also well predicted by our model (Fig. 6c).

#### 4.3. Fluorite solubility in Na-K-Cl solution at elevated temperature

The revised EQBRM code (Anderson, 2008) was used to calculate the concentrations of all of the aqueous species in the equilibrium



**Fig. 5.** Comparison of the calculated and experimental solubility data of fluorite.



**Fig. 6.** Comparison of experimental and model calculated thermodynamic data. (a) Apparent heat capacity of KF solution, (b) Osmotic coefficient of KF solution, (c) Fluorite solubility data in KCl solution.

system, and the calculations were conducted on the MATLAB® platform.

The solubility product of fluorite and the Pitzer binary parameters of Na-F and K-F were obtained above. Other Pitzer parameters

(the binary parameters of Na-Cl, K-Cl, Ca-Cl; and the ternary parameters in the Na-K-Ca-Cl system) were taken from the literature (Christov and Møller, 2004; Greenberg and Møller, 1989; Møller, 1988). Fluoride related ternary parameters were taken from Weber et al. (2000), and their temperature dependence was ignored due to a lack of data. In addition, other researchers reported constant values of the ternary parameters giving an adequate representation of mineral solubility (e.g., Pabalan and Pitzer, 1987a).

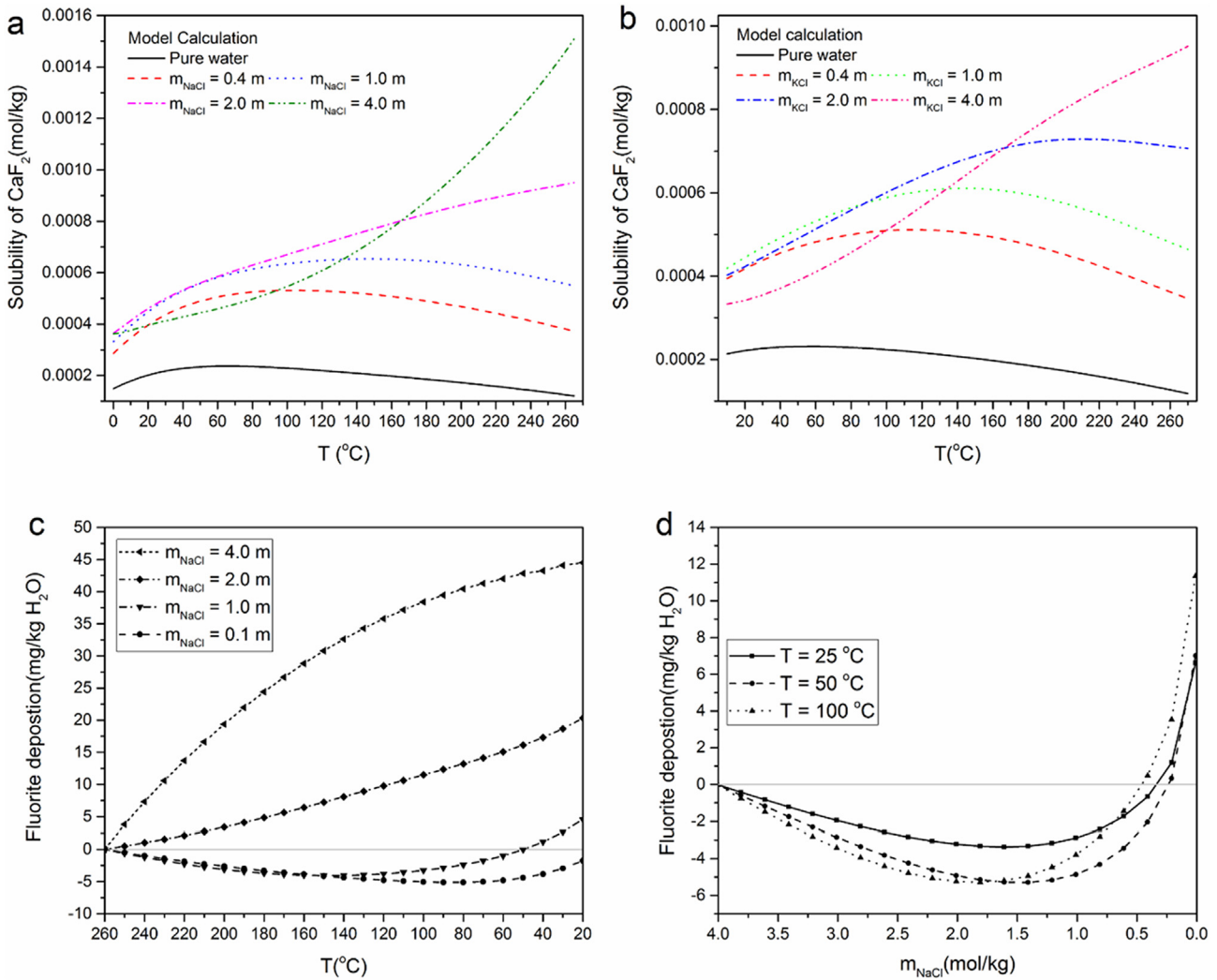
Fluorite solubility in NaCl and KCl solution at temperatures up to 260 °C and ionic strengths up to 4 M was calculated (Fig. 7). As we can see, the fluorite dissolution behavior is similar in NaCl and KCl solution. When the concentration was lower than 2 M, fluorite solubility reached a maximum at about 100 °C and decreased with increasing concentration. While, for concentrations higher than 2 M, fluorite solubility increased monotonically with temperature.

As shown, temperature and ionic strength have a significant effect on the solubility of fluorite, which means that it could precipitate as a consequence of changes in temperature and salinity. Fig. 7 shows the precipitation of fluorite with decreasing temperature (Fig. 7c) and NaCl concentration (Fig. 7d). It was believed that cooling of a hydrothermal fluid has made a large contribution for fluorite deposition but that contribution depends on fluid concentration. For concentrations  $\geq 2$  M, fluorite tends to precipitate with decreasing temperature monotonically. However, dilute ( $<1.0$  M) NaCl solutions do not obey this rule. In such dilute solutions, fluorite became more soluble as solutions cooled from 260 °C. For fluorite solubility at temperatures below 100 °C, the solubility of fluorite reaches a maximum at approximately 1.5 M and decreases with increasing concentration. Therefore, as the concentration decreased from 4.0 M to 0, it first became unsaturated with respect to fluorite and did not begin to precipitate until the concentration was below 0.5 M.

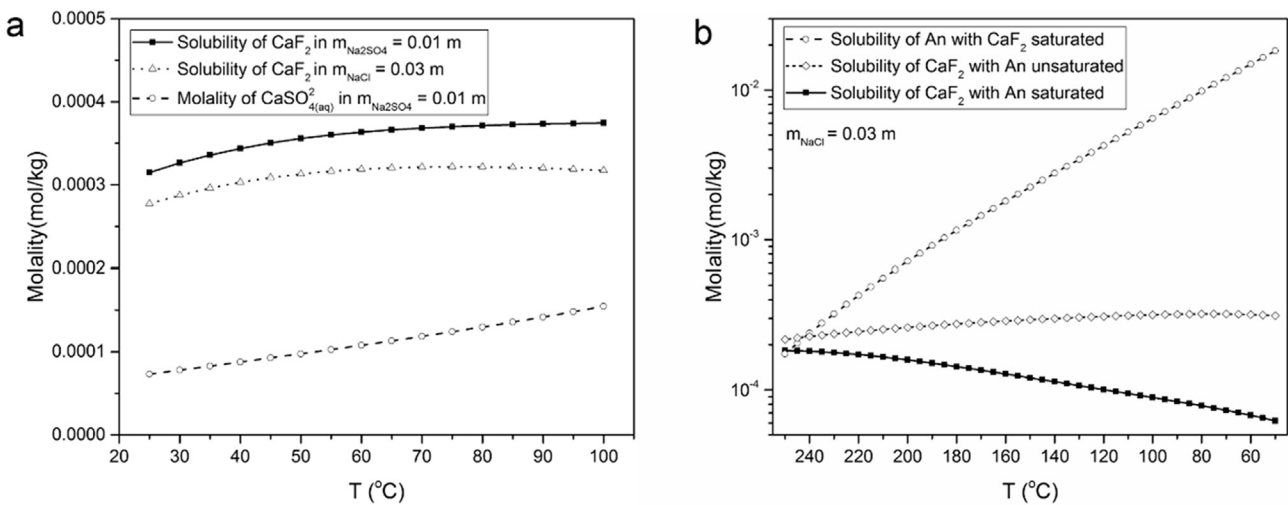
#### 4.4. Fluorite solubility in $\text{Na}_2\text{SO}_4$ solution at elevated temperature

Those parameters obtained above could also be used to assess the effect of  $\text{SO}_4$  on fluorite solubility. As we can see from Fig. 8a, because of the formation of  $\text{CaSO}_{4(aq)}$ , the solubility of  $\text{CaF}_2$  in  $\text{Na}_2\text{SO}_4$  solution is higher than that in NaCl solution with the same ionic strength. However, fluorite solubility under Anhydrite (An) saturated conditions is lower than that under anhydrite unsaturated conditions (Fig. 8b). The solubility of anhydrite increases with temperature decreasing. The released calcium suppresses the dissolution of fluorite and causes precipitation of fluorite. This is probably the reason that fluorite-barite is the common mineral assemblage in hydrothermal deposit.

During the NaF Pitzer binary parameters regression process and fluorite solubility calculation in NaCl and  $\text{Na}_2\text{SO}_4$  solution, we did not consider the complex of  $\text{NaF}_{(aq)}^{(0)}$ , which was thought to make some contribution to fluoride speciation (Majer et al., 1997; Richardson and Holland, 1979) at high temperature. However, the NaF ion-pairing constant at 25 °C has an order of magnitude discrepancy (Chan et al., 1984), and the thermodynamic properties of the NaF solution were scarce at elevated temperature, which made it difficult to accurately evaluate its ion-pairing constant. It can be expected that the  $K_{ip}$  of NaF should be close to that of  $\text{NaOH}_{(aq)}^{(0)}$ , considering the similarity of  $\text{F}^-$  and  $\text{OH}^-$  ions (Majer et al., 1997). The activity and osmotic coefficient of NaOH can be perfectly predicted using the Pitzer model without considering ion-pairing under 300 °C (Pabalan and Pitzer, 1987b), and the additional term of  $\text{NaOH}_{(aq)}^{(0)}$  does not have a large effect on the activity or osmotic coefficients for concentrations as high as 6.3 mol/kg



**Fig. 7.** Prediction of fluorite solubility as a function of temperature in various ionic strengths of NaCl (a) and KCl (b) solution. The quantity of fluorite precipitation with decreasing temperature from 260 to 20  $^{\circ}\text{C}$  (c) and NaCl concentration from 4.0 M to 0 (d). Negative amounts of fluorite deposition indicate fluorite dissolution.



**Fig. 8.** (a) The solubility of fluorite in NaCl and  $\text{Na}_2\text{SO}_4$  solution with the same ionic strength as function of temperature; (b) fluorite solubility under anhydrite saturated and unsaturated conditions and anhydrite solubility under fluorite saturated conditions in a 0.03 m NaCl solution as function of temperature.



(Simonson et al., 1989). Therefore, in this work, the ion-pairing of NaF was not considered. For KF(aq), there is virtually no ion-association data at high temperatures relevant to the present work because of the larger size of the potassium ion. For simplicity, we also do not consider the hydrolysis of the F<sup>-</sup> ion and the complex of CaF<sup>+</sup>, although we are aware that these reactions may contribute to the speciation in fluoride solutions at low pH and high calcium concentration, which we will consider in our future work.

## 5. Conclusion

We have experimentally determined fluorite solubility in NaCl solution at 30 and 50 °C under ambient pressure, in NaCl solution at 200 °C and in KCl solution at 250 °C under vapor saturated pressure. Combining the solubility products obtained from our experimental data with those from the literature, the solubility product of fluorite at temperatures up to 260 °C, under saturated vapor pressure, could be calculated by the density model. The Pitzer binary parameters of NaF and KF at elevated temperatures up to 260 °C were obtained by combining the low-temperature thermodynamic properties of heat capacity and osmotic coefficient with fluorite solubility data at high temperature. With all that, a thermodynamic model for fluorite solubility calculation in Na-K-Cl solution up to 260 °C and under vapor saturated pressure was established. As calculated using this model, fluorite solubility measured at 200 °C and 0.1 M NaCl agreed well with model calculation. Temperature and ionic strength have a significant effect on the solubility of fluorite which indicates fluorite can precipitate as a consequence of changes in temperature and salinity. Fluorite solubility had a similar pattern in both NaCl and KCl solution. When the concentration was lower than 2 M, the solubility of fluorite first increased with temperature, reached a maximum at 100 °C, and then decreased. When the concentration was higher than 2 M, the solubility of fluorite increased monotonically with temperature. Fluorite solubility in Na<sub>2</sub>SO<sub>4</sub> solution is larger than that in NaCl solution with the same ionic strength for the formation of CaSO<sub>4</sub>(aq).

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## Appendix A. Supplementary data

Supplementary data related to this chapter can be found at <http://dx.doi.org/10.1016/j.apgeochem.2017.04.017>.

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