

# Role of saline fluids in deep-crustal and upper-mantle metasomatism: insights from experimental studies

R. C. NEWTON AND C. E. MANNING

*Department of Earth and Space Sciences, University of California, Los Angeles, CA, USA*

## ABSTRACT

Chloride-rich brines are increasingly recognized as playing an important role in high pressure and temperature metamorphic and magmatic systems. The origins of these saline multicomponent fluids are debated, but experimental evidence suggests that regardless of their origin they must be important agents of rock alteration and mass transfer wherever they occur. Studies of the solubility of quartz in H<sub>2</sub>O, CO<sub>2</sub>–H<sub>2</sub>O and salt–H<sub>2</sub>O solutions provide a framework for understanding the role of brines in the deep crust and upper mantle. While quartz solubility in the system SiO<sub>2</sub>–H<sub>2</sub>O–NaCl–CO<sub>2</sub> is maximal at a given high pressure and temperature if the solvent is pure H<sub>2</sub>O, the decline in quartz solubility with NaCl content (salting-out) is less severe than in CO<sub>2</sub>–H<sub>2</sub>O fluids at comparable H<sub>2</sub>O activities. Moreover, at lower pressures, quartz solubility initially salts in at low salt contents, before reaching a maximum and then declining. The behavior of quartz solubility in salt–H<sub>2</sub>O solutions has not yet been fully explained and is the subject of active debate. Experimental investigations of the solubility of some other rock-forming oxides and silicates show enhancements due to NaCl addition. As illustrated by the well-studied CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–NaCl–H<sub>2</sub>O system, enhancements initially increase to maxima, and then decline. This behavior can be explained by formation of a range of hydrated aqueous complexes and clusters with specific NaCl:H<sub>2</sub>O stoichiometries. In contrast, solubilities of calcium salts, including calcite, fluorite, fluorapatite and anhydrite, rise monotonically with increasing NaCl, implying complexing to form anhydrous ionic solutes and/or ion pairs. The experimental studies offer new insights into fluid-rock interaction in a range of settings, including carbonatite–fenite complexes, granulite-facies metamorphism, porphyry ore deposits and aluminum-silicate vein complexes in high-grade metamorphic terranes.

Key words: experimental petrology, metamorphic fluids, mineral solubility, salt effects

Received 21 August 2009; accepted 30 November 2009

Corresponding author: C. E. Manning, Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095-1567, USA.

Email: [manning@ess.ucla.edu](mailto:manning@ess.ucla.edu). Tel: +1 310 206 3290. Fax: +1 310 825 2779.

*Geofluids* (2010) 10, 58–72

## INTRODUCTION

The generation and migration of chloride-rich brines is an important geologic process in the lower crust and upper mantle (e.g. Touret 1985; Newton *et al.* 1998; Yardley & Graham 2002). Fluid inclusions containing chloride brines with >10 wt% NaCl equivalent have been reported from granulites (Touret 1985; Crawford & Hollister 1986; Smit & Van Reenan 1997; Touret & Huizenga 1999; Van den Berg & Huizenga 2001), eclogites (e.g. Philippot & Selverstone 1991; Fu *et al.* 2001), and mantle diamonds (e.g. Izraeli *et al.* 2001, 2004; Klein-BenDavid *et al.* 2007). In addition, crystalline salts have been observed in high-grade

metamorphic rocks (Markl & Bucher 1998). Calcium-rich silicates record equilibration of minerals with saline brines in a range of metamorphic settings (e.g. Munoz 1981; Mora & Valley 1989; Nijland 1993; Kullerud 1996; Markl *et al.* 1998). Finally, magnetotelluric observations suggest the presence of conductive, saline fluids in deep-crustal fault zones (e.g. Wannamaker *et al.* 2004).

Saline fluids can be produced or concentrated in deep fluid-flow systems by a variety of mechanisms (Newton *et al.* 1998; Yardley & Graham 2002), including inheritance of an originally saline connate fluid, dissolution of salts of sedimentary origin, H<sub>2</sub>O loss by preferential partitioning into hydrous minerals during retrograde

metamorphism or into hydrous silicate liquids during melting and infiltration of externally derived magmatic fluids. Regardless of origin, a fundamentally important factor in the evolution of brines in the deep crust and upper mantle is their immiscibility with CO<sub>2</sub>-rich aqueous fluid over a wide range of pressure (*P*) and temperature (*T*) (Bowers & Helgeson 1983; Johnson 1991; Duan *et al.* 1995; Heinrich 2007). Fluid inclusion evidence suggests that, in many instances, saline fluids of the lower crust and upper mantle may coexist across a miscibility gap with CO<sub>2</sub>-rich fluids (e.g. Touret 1985; Gibert *et al.* 1998). The CO<sub>2</sub>-rich fluids are more commonly observed as inclusions in minerals because they are trapped more efficiently due to their relatively low ability to wet grain boundaries (Watson & Brennan 1987). Also, postentrapment modification of fluid inclusions due to diffusion (Sterner & Bodnar 1989) or deformation (Barker 2007) is more likely for salty inclusions than for CO<sub>2</sub>-rich inclusions because of higher mineral solubility and reactivity. However, in spite of their volumetrically minor representation as fluid inclusions, it is likely that the saline components play a more important role than CO<sub>2</sub> in metasomatic mass transfer in the deep crust and upper mantle.

The potential role of saline fluids in mass transfer has only recently gained experimental attention, but a growing body of data offers important and surprising insights into interactions among salty fluids and minerals at moderate to high *P* and high *T*. Here, we review experimental results on mineral solubility in saline fluids at conditions relevant to the lower crust and upper mantle. The data point to the conclusion that alkali halide brine components of deep-crustal and upper-mantle fluids represent powerful solvents capable of significant mass transfer – not just of metals, but of nearly all major rock forming oxides. This behavior helps explain petrologic observations from a wide range of deep geologic environments.

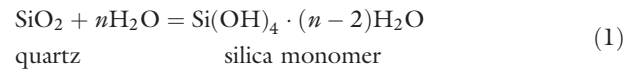
## SILICA IN HIGH-GRADE FLUIDS

Silica is among the most abundant solutes in H<sub>2</sub>O-bearing fluids of the deep crust and upper mantle, even when diluted by significant CO<sub>2</sub> or salts, or when fluids coexist with bulk compositions possessing low silica activity (Anderson & Burnham 1965; Manning 1994; Newton & Manning 2000, 2002). Thus, investigation of the interactions between fluids and minerals in the lower crust and upper mantle most conveniently begins by consideration of SiO<sub>2</sub>.

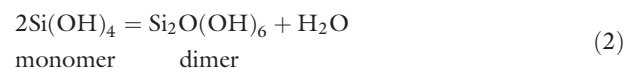
### Quartz solubility in H<sub>2</sub>O

The dissolution of quartz into H<sub>2</sub>O at deep-crustal and upper-mantle conditions is strongly dependent on *P* and *T*, and on the polymerization of solute silica (Manning

1994; Zotov & Keppler 2000, 2002; Newton & Manning 2003, 2008a). Equilibrium between quartz, H<sub>2</sub>O and neutral monomeric silica, can be described by the reaction



Equation 1 includes two forms of interaction between solvent H<sub>2</sub>O and solute SiO<sub>2</sub>: for each mole of SiO<sub>2</sub>, two moles of H<sub>2</sub>O form hydroxyls, and *n* – 2 moles of molecular H<sub>2</sub>O form a hydration shell (e.g. Weill & Fyfe 1964; Sommerfeld 1967). Polymerization of solute silica is an additional interaction. Taking the H<sub>2</sub>O of hydration as implicit, homogeneous equilibrium in an H<sub>2</sub>O–SiO<sub>2</sub> fluid can be written



(Newton & Manning 2002a, 2003; Zotov & Keppler 2002). Newton & Manning (2002a, 2003) showed that a simple mixing model which assumes only monomers and dimers adequately describes phase relations in SiO<sub>2</sub>–H<sub>2</sub>O fluids to ≥20 kbar and approximately 900°C. By equating activities (*a<sub>i</sub>*) of the monomer (*m*) and dimer (*d*) to their mole fractions (*X<sub>i</sub>*), the equilibrium constant for Equation 2 (*K<sub>md</sub>*) is

$$K_{md} = \frac{X_d a_{\text{H}_2\text{O}}}{X_m^2} \quad (3)$$

When H<sub>2</sub>O is the only solvent component, *a<sub>H<sub>2</sub>O</sub>* ≈ 1 over a wide range of crustal and mantle conditions, and *K<sub>md</sub>* values can be described by

$$\log K_{md} = 1.480 + 0.0012T + (0.000119T - 0.1685)P \quad (4)$$

where *T* is in Kelvins and *P* is in kbar (Newton & Manning 2002a, 2009).

This description of quartz solubility fails as temperatures rise above 900°C and pressures approach 10 kbar. Along the quartz hydrothermal melting curve, there are increases with rising *P* in SiO<sub>2</sub> solubility in H<sub>2</sub>O, and in H<sub>2</sub>O solubility in coexisting melt. These factors lead to critical mixing of SiO<sub>2</sub>-rich aqueous fluid and hydrous silica melts at a critical end point on the hydrothermal melting curve of quartz near 10 kbar and 1080°C (Kennedy *et al.* 1962; Newton & Manning 2008a). Under these *P*–*T* conditions, SiO<sub>2</sub>-rich fluids and liquids must be highly polymerized, with constitutions similar to pegmatitic rock melts; it is of some interest to inquire what effect saline and carbonic components have on critical mixing of fluids in the system SiO<sub>2</sub>–H<sub>2</sub>O at high *P* and *T*.

Figure 1 shows log *K<sub>md</sub>* isobars at deep-crustal and upper-mantle temperatures. With rising *T*, log *K<sub>md</sub>*

increases isobarically, indicating increasing fraction of dissolved silica in dimers relative to monomers. In contrast, isothermal increases in pressure yield depolymerization of aqueous silica. Higher oligomers such as the ring trimer become increasingly abundant at 10 kbar within approximately 150°C of the critical end point at 1080°C in the system SiO<sub>2</sub>-H<sub>2</sub>O (Newton & Manning 2008a), but at lower temperatures appear to have negligible concentration in SiO<sub>2</sub>-H<sub>2</sub>O fluids.

**Quartz solubility in CO<sub>2</sub>-H<sub>2</sub>O fluids**

The solubility of quartz in CO<sub>2</sub>-H<sub>2</sub>O fluids at high *P* and *T* declines steadily with increasing CO<sub>2</sub> content. This is illustrated in Fig. 2A, using data from Newton & Manning (2009) at 800°C, 10 kbar. The data indicate that quartz is effectively insoluble in pure CO<sub>2</sub>, consistent with the absence of interaction or complexing between CO<sub>2</sub> and SiO<sub>2</sub> in the fluid phase. Thus, CO<sub>2</sub>-rich solutions are very poor solvents for silica.

Data on mixed solvents in which one component does not interact with dissolved silica can be utilized to gain insight into the interactions between the silica and solvent H<sub>2</sub>O. *A priori*, it is uncertain whether the number of H<sub>2</sub>O molecules that hydroxylate and hydrate dissolved SiO<sub>2</sub> are fixed or variable, or whether they change with *T*, *P* or H<sub>2</sub>O activity. In the absence of direct *in situ* observation, the value of *n* in Equation 1 can be derived from quartz solubility measurements in CO<sub>2</sub>-H<sub>2</sub>O fluids because CO<sub>2</sub> does not interact detectibly with solute silica. Following

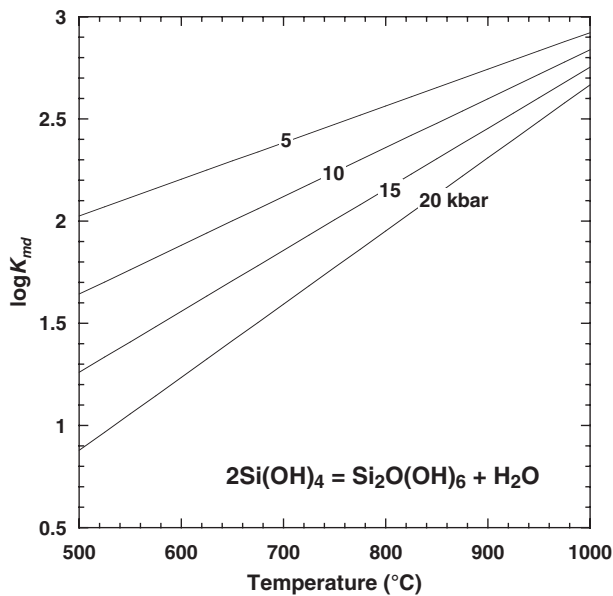


Fig. 1. Variation in the equilibrium constant (*K<sub>md</sub>*) for homogeneous equilibrium between silica monomers and dimers (Equation 2) as a function of *P* and *T*, as calculated from Equation 4 (Newton & Manning 2002a, 2009).

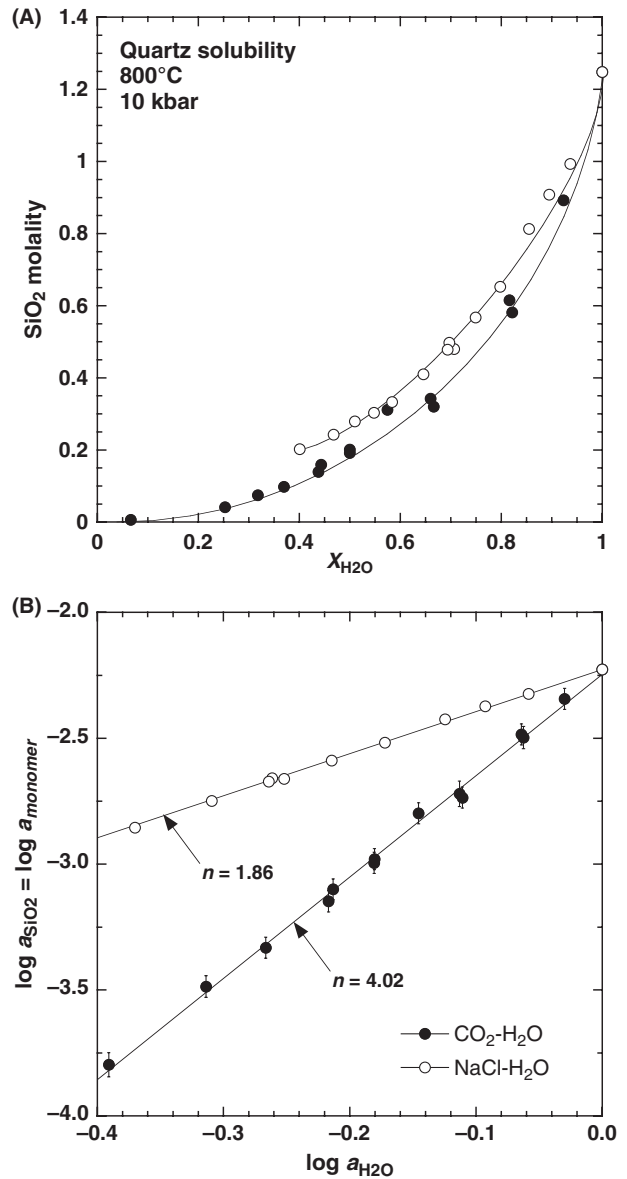


Fig. 2. (A) Variation in the molality of SiO<sub>2</sub> at quartz saturation with CO<sub>2</sub> (filled circles) and NaCl (open circles) at 800°C, 10 kbar. Data from Newton & Manning (2000, 2009). (B) Variation in calculated activity of the aqueous silica monomer with H<sub>2</sub>O activity for same data as in (A). Activity models from Aranovich & Newton (1996, 1999). Slopes from linear fits to data correspond to *n*, the total hydration number; *n* in CO<sub>2</sub>-H<sub>2</sub>O of 4 indicates 2 molecular H<sub>2</sub>O of solvation; the lower *n* and higher solubility of quartz in NaCl-H<sub>2</sub>O at a given H<sub>2</sub>O activity implies solubility enhancement; however, the mechanism is debated (see text).

Walther & Orville (1983), the hydration state of solute silica can be derived from the equilibrium constant (*K*<sub>1</sub>) for Equation 1 at fixed *T* and *P*,

$$K_1 = \frac{a_m}{a_{H_2O}^n} \tag{5}$$

where the activity of quartz is assumed to be unity,  $a_m$  is the activity of the monomeric species, and  $a_{\text{H}_2\text{O}}$  is the activity of  $\text{H}_2\text{O}$ . Taking logarithms and rearranging leads to

$$\log a_m = n \log a_{\text{H}_2\text{O}} + \log K_1 \quad (6)$$

from which it can be seen that  $n$  is given by the variation in monomer activity with  $\text{H}_2\text{O}$  activity.

Walther & Orville (1983) proposed that the number of  $\text{H}_2\text{O}$  molecules per silica unit is two (i.e.  $n = 4$ ) based on their quartz solubility measurements in  $\text{CO}_2$ - $\text{H}_2\text{O}$ . However, they had to assume that  $\text{H}_2\text{O}$  and  $\text{CO}_2$  form ideal mixtures at their experimental conditions (2 kbar and  $600^\circ\text{C}$ ) and that  $\text{SiO}_2$  solubility was low enough that total molality could proxy for monomer activity. Subsequent studies gave  $n = 3.5$  or 2, or suggested that  $n$  varies with  $X_{\text{CO}_2}$  (Newton & Manning 2000; Shmulovich *et al.* 2006; Akiniev & Diamond 2009).

With the advent of accurate and precise solution models for  $\text{CO}_2$ - $\text{H}_2\text{O}$  (Aranovich & Newton 1999) and aqueous silica (Newton & Manning 2002a, 2003), it is now possible to evaluate  $n$  more rigorously. As shown in Fig. 2B, results on quartz solubility in  $\text{CO}_2$ - $\text{H}_2\text{O}$  over a wide range of  $\text{CO}_2$  contents at 10 kbar,  $800^\circ\text{C}$ , show that  $n = 4$  (Newton & Manning 2009). The same analysis for the dimer yields  $n = 7$ . Other high-quality data on quartz solubility in  $\text{CO}_2$ - $\text{H}_2\text{O}$  at lower  $P$  and  $T$  yield the same values for  $n$  when  $\text{SiO}_2$  and  $\text{H}_2\text{O}$  activities are calculated with the same models. Evidently, the aqueous silica monomer and dimer possess fixed stoichiometry of  $\text{Si}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Si}_2\text{O}(\text{OH})_6 \cdot 4\text{H}_2\text{O}$  – i.e. two solvating  $\text{H}_2\text{O}$  molecules per Si – in  $\text{H}_2\text{O}$ - $\text{CO}_2$  fluids for a large range of crustal and mantle conditions. To the extent that  $\text{CH}_4$  and  $\text{CO}$  are also unreactive with  $\text{SiO}_2$ , the simple model for quartz solubility in  $\text{CO}_2$ - $\text{H}_2\text{O}$  should apply generally to quartz solubility in  $\text{COH}$  fluids over a wide range of oxygen fugacities.

### Quartz solubility in alkali-halide salt solutions

#### Comparison with $\text{CO}_2$ - $\text{H}_2\text{O}$

At high  $P$  and  $T$ , quartz solubility in  $\text{NaCl}$ - $\text{H}_2\text{O}$  solutions behaves as in  $\text{CO}_2$ - $\text{H}_2\text{O}$  solutions: it declines systematically with increasing  $\text{NaCl}$  (Fig. 2A, Newton & Manning 2000; Shmulovich *et al.* 2001). Quartz solubility is not greatly different in the two solvent media on an  $\text{H}_2\text{O}$  mole fraction basis. More importantly, however, at the same  $\text{H}_2\text{O}$  activity, quartz solubility is much higher in the salt solutions (Fig. 2B). Because the difference grows larger with decreasing  $X_{\text{H}_2\text{O}}$ ,  $\text{NaCl}$  brines will be more effective solvents than  $\text{CO}_2$ - $\text{H}_2\text{O}$  fluids – not just for metals, but also for  $\text{SiO}_2$ , the major rock forming oxide.

The more subdued decline in solubility with decreasing  $X_{\text{H}_2\text{O}}$  is not the only way in which quartz interacts differ-

ently with  $\text{NaCl}$  solutions than with  $\text{CO}_2$  solutions. Quartz solubility in  $\text{H}_2\text{O}$ - $\text{NaCl}$  solutions at low but constant  $P$  and  $T$  displays the interesting behavior of initially increasing with added salt (Fig. 3); i.e. it ‘salts in’. At 1 kbar, quartz solubility increases substantially with increasing  $\text{NaCl}$  concentration (Novgorodov 1977; Xie & Walther 1993). At 2 kbar and  $700^\circ\text{C}$ , the solubility first increases, but reaches a maximum at about 10 mol %  $\text{NaCl}$  and then decreases with further increase in salinity (Fig. 3). This transition from salting-in to salting-out behavior probably has to do with ionization of  $\text{NaCl}$ , considering that solute  $\text{NaCl}$  at low pressures, high temperatures is strongly associated (e.g. Quist & Marshall 1968), but at pressures higher than about 4 kbar at  $700^\circ\text{C}$  becomes progressively ionized at all temperatures and concentrations (Aranovich & Newton 1996; Tropper and Manning 2004). This is supported by the solubility behavior at 4.35 kbar,  $700^\circ\text{C}$  (Fig. 3).

In addition, dissolved silica appears to interact differently with different salts. Shmulovich *et al.* (2006) investigated quartz solubility in a variety of salt solutions to 9 kbar and  $800^\circ\text{C}$ . Large-ion alkali halides (with  $\text{Cs}^+$ ,  $\text{I}^-$ , etc.) have a greater tendency toward salting-in of silica, such that the enhancement persists to high pressures. In contrast, these authors found that  $\text{CaCl}_2$  produces no enhancement, even at low pressure (Fig. 4). The unique behavior of quartz

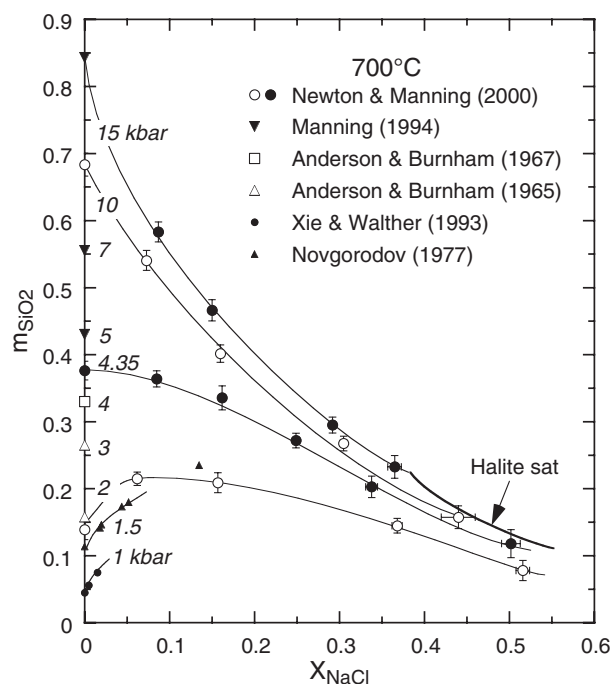


Fig. 3. Variation in quartz solubility with  $\text{NaCl}$  mole fraction and pressure at  $700^\circ\text{C}$  (Newton & Manning 2000). At low pressures, quartz solubility initially rises ('salts-in') with increasing  $\text{NaCl}$  concentration. The behavior disappears above approximately 5 kbar, so that quartz salts out at all  $\text{NaCl}$  concentrations (with permission from Elsevier).

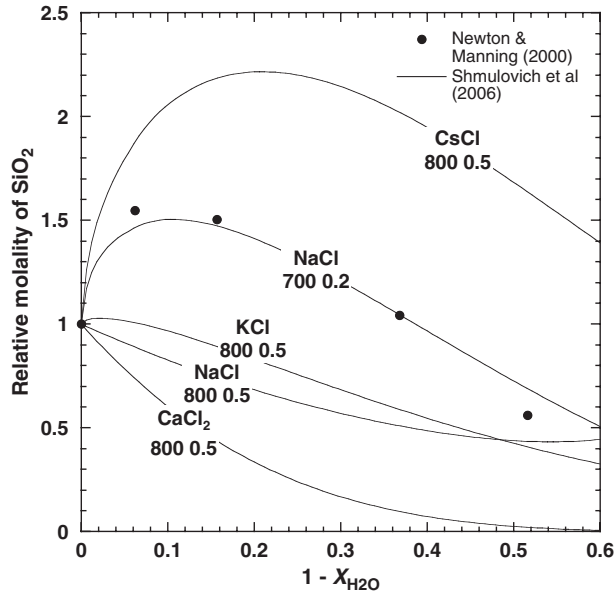


Fig. 4. Variation in quartz solubility in salt solutions at various  $T$  and  $P$ . Lines showing Si molality relative to that in pure  $\text{H}_2\text{O}$  are from Shmulovich *et al.* (2006), with labels identifying salt type,  $T$  (in  $^\circ\text{C}$ ) and  $P$  (in GPa). Filled circles data at  $700^\circ\text{C}$ ,  $0.2$  GPa, from Newton & Manning (2000).

solubility in different salt solution indicates complex interaction that may have to do with complexing, polymerization, hydration state, mixing statistics (possibly including or excluding ionized units) and local electrical environment of the  $\text{SiO}_2$  units. Shmulovich *et al.* (2006) showed that, to a good approximation, the solubility of quartz at a given  $P$  and  $T$  in a mixed-salt solution is proportional to the sum of the solubilities in the individual salt solutions. This applies also to solvent mixtures of salt and  $\text{CO}_2$ .

There are several empirical formulations of the variation in quartz solubility with salt concentration (e.g. Fournier *et al.* 1982; Fournier 1983; Shibue 1996), but more recent efforts have focused on developing models that explicitly account for the physical chemistry of salting-in and salting-out behavior. The salting-out of silica is readily understood if the solute silica consists of hydrated species, because of the decrease in  $\text{H}_2\text{O}$  activity. The physical chemical explanation for salting-in is, however, the subject of ongoing debate. Current hypotheses can be regarded as falling into two categories:

- (1) the effect is a property of the solvent; i.e. salt components alter electrostatic properties of  $\text{H}_2\text{O}$ , especially the dielectric constant, so that uncharged species like silica become more compatible with the hydrous matrix; and
- (2) the effect is a property of the solute, in that more soluble species are formed by reaction of the silica with salt constituents.

Resolution of this question will require additional accurate and specifically directed solubility and spectroscopic studies.

#### Solubility enhancement as solvent modification

A conventional line of approach followed by several authors (Xie & Walther 1993; Shmulovich *et al.* 2001, 2006) makes use of a parameter first defined by Setchénov (1892) to understand the effect of dissolved ionic salts on the solubility of organic compounds. Departures from ideal mixing behavior (i.e. solubility negatively proportional to the mole fraction or molality of the salt) are embodied in the expression:

$$\log \gamma_i = B_i I \quad (7)$$

where  $\gamma_i$  is the activity coefficient of the organic (or uncharged) solute,  $I$  is the ionic strength of the solution (for alkali halides simply the salt molality) and  $B_i$  is the Setchénov coefficient, unique to each salt and uncharged solute and generally a function of  $T$  and  $P$ . This approach cannot explain salting-in followed by salting-out at higher salt concentration unless the Setchénov coefficient is also made a function of salt concentration. For quartz solubility in salt solutions, the expression of Shmulovich *et al.* (2006) is:

$$\log m_{\text{SiO}_2} = \log m_{\text{SiO}_2}^0 + 3.5 \log X_{\text{H}_2\text{O}} + a m_i^b \quad (8)$$

where  $m_i$  indicates total molality of the subscripted constituent, and the superscript zero refers to initially pure  $\text{H}_2\text{O}$ . The third term on the right embodies the Setchénov concept while allowing the term to be a function of salinity and, through the empirical parameters  $a$  and  $b$ , pressure and to a lesser extent temperature. The second term describes the effect of decreasing  $\text{H}_2\text{O}$  activity with salinity, and models the average total hydration number ( $n$ ) of solute silica as 3.5. The parameter  $b$  must be less than unity when salting-in occurs (almost always at low  $\text{H}_2\text{O}$  density). The authors give a table from which to obtain  $a$  and  $b$  by interpolation in the pressure range 1–9 kbar and temperature range  $400$ – $800^\circ\text{C}$ . Figure 4 compares the quartz solubility predictions of Shmulovich *et al.* (2006) for various salt solutions,  $T$  and  $P$ .

The advantage of this method is that it assigns all non-ideality in the solubility calculation to a term which is effectively a function of  $\text{H}_2\text{O}$  activity. A disadvantage, noted by Evans (2007), is that the model does not directly address the dissociation of  $\text{NaCl}$  at high pressures and concentrations, so that the mole fraction of  $\text{H}_2\text{O}$  is ambiguous (taken by Shmulovich *et al.* 2006; to be  $1 - X_{\text{NaCl}}$ ). Therefore, the model is to some extent non-physical. Also, no account is taken of polymerization of  $\text{SiO}_2$  in solution, which is an important contributor to  $\text{SiO}_2$  solution non-ideality at the high concentrations associated with elevated  $P$  and  $T$  (Newton & Manning 2002a, 2003). Shmulovich *et al.* (2006) maintain that neglect of these factors is necessary for a unified account of their experimental results for a variety of salts, since

activity coefficients and  $\text{SiO}_2$  speciation are not as yet known for most salt solutions at high  $T$  and  $P$ . Akinfiyev & Diamond (2009) proposed a similar reconstruction. They showed that experimental measurements on quartz solubility in ionic fluids at high  $T$  and  $P$  can equally well be represented with  $n = 2$ .

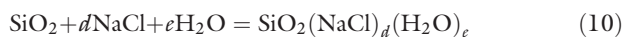
#### Solubility enhancement as solvent interaction

A different approach implies that salting-in is due to a reaction of  $\text{SiO}_2$  with salt (and possibly  $\text{H}_2\text{O}$ ) to produce soluble hybrid species. Tanaka & Takahashi (1999) showed by high-resolution mass spectrometry at ambient conditions of quartz-saturated NaCl solutions that there is considerable complexing of Na with polymeric silica forms (monomer, dimer and tetramer). Anderson & Burnham (1967) suggested that enhancement of quartz solubility in KCl solutions at 3 kbar and  $600^\circ\text{C}$  could be explained by a reaction:



The postulated solvent interaction should therefore generate acid solutions under  $P$ - $T$  conditions where salting-in occurs; this has not yet been verified for quartz solubility (e.g. by pH measurements, either *in situ* or on quenched solutions). Anderson & Burnham (1967) did not attempt to show that their hypothesis could account for the phenomenon of salting-in followed by salting-out at higher salinity. Several experimental and theoretical studies (summarized in Frank *et al.* 2003) have shown that, if Al is present, as in aluminosilicate minerals and melts, acid solutions are generated by reaction with NaCl.

Another approach was adopted by Evans (2007). She postulated the dissolution reaction:



which implies that NaCl is complexed as an undissociated unit. All species in solution are regarded as an ideal mixture, including  $\text{H}_2\text{O}$ , NaCl,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SiO}_2 \cdot 3\text{H}_2\text{O}$  (the assumed hydration state of the monomeric complex), and the postulated hybrid complex in Equation 10. Her formulation incorporates non-ideality of the  $\text{H}_2\text{O}$ -NaCl solutions as a consequence of pressure-induced ionization, but does not use measured activity values of  $\text{H}_2\text{O}$  as primary input; rather, she uses the dissociation constant  $\alpha$  as a fitting parameter. Evans (2007) was able to obtain reasonable fits to the solubility data of Newton & Manning (2000) and Shmulovich *et al.* (2006) with a broad range of  $d$  and  $e$  values; she chose the values  $d = 0.5$  and  $e = 0$ . Figure 5 compares the predictions of Evans (2007) for NaCl- $\text{H}_2\text{O}$  at  $700^\circ\text{C}$  and various pressures with the experimental data of Newton & Manning (2000). The main advantage of her

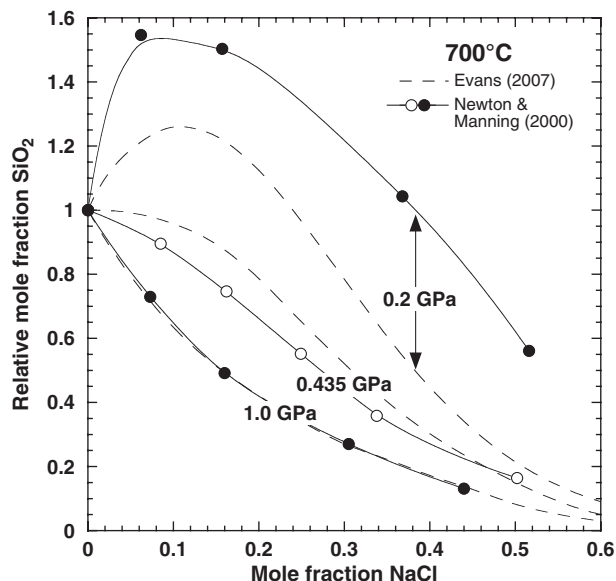


Fig. 5. Variation in quartz solubility with NaCl mole fraction and pressure at  $700^\circ\text{C}$ . Circles and solid lines are from Newton & Manning (2000); dashed lines from Evans (2007). Relative mole fractions are normalized to values in initially pure  $\text{H}_2\text{O}$ .

method is that change of the activity coefficients of  $\text{H}_2\text{O}$  and dissolved salts is explicitly taken into account; indeed, Evans (2007) showed that this effect can account for the transitions from salting-in at low pressure to salting-out at high pressures. This is evident from Equation 10, where it is seen that decreasing the activity of both NaCl and  $\text{H}_2\text{O}$ , which decrease occurs with increasing pressure, destabilizes the hybrid complex.

Newton & Manning (2006) attempted to incorporate both pressure-induced ionization of NaCl and polymerization of  $\text{SiO}_2$  in a single theory. This formalism uses  $\text{H}_2\text{O}$  activity measurements of Aranovich & Newton (1996) and makes the assumption that solute  $\text{SiO}_2$  forms an ideal substituent among all other solution entities ( $\text{H}_2\text{O}$ , NaCl,  $\text{Na}^+$ , and  $\text{Cl}^-$ ) subject to the formula:

$$X_{\text{SiO}_2} = \frac{m_{\text{SiO}_2}}{m_{\text{SiO}_2} + 55.51 \left[ 1 + \frac{(1+\alpha)X_{\text{NaCl}}}{X_{\text{H}_2\text{O}}} \right]} \quad (11)$$

where mole fraction and molality of  $\text{SiO}_2$  refer to total silica in solution and  $\alpha$ , the dissociation parameter, characterizes the non-ideality of NaCl solutions (Aranovich & Newton 1996). Theoretically,  $\alpha$  should run from zero for undissociated NaCl to unity for completely dissociated NaCl. In fact,  $\alpha$  as fitted by Aranovich & Newton (1996) to their activity data actually exceeds unity by about 10% at the highest pressures (15 kbar). At 10 kbar and  $800^\circ\text{C}$  it is almost exactly unity. This assumption and the polymerization model of Newton & Manning (2002a, 2006) lead to the formula:

$$a_{\text{SiO}_2} = X_m = \frac{(1 + 8X_{\text{SiO}_2} K_{md}/a_{\text{H}_2\text{O}})^{\frac{1}{2}} - 1}{4K_{md}/a_{\text{H}_2\text{O}}} \quad (12)$$

where  $a_{\text{H}_2\text{O}}$  is closely equal to  $X_{\text{H}_2\text{O}}/(2 - X_{\text{H}_2\text{O}})$ , again subject to the same ideal solution model of all ions and neutral molecules and  $K_{md}$  is the equilibrium constant for dimer formation, Equation 2, assumed to apply to  $\text{SiO}_2$  solutions in  $\text{H}_2\text{O}$ – $\text{NaCl}$  solvents.

#### *Critique of the quartz solubility models*

All of the above attempts to quantify quartz solubility and silica activity in salt solutions in terms of physical chemical properties have advantages in data organization, but also significant defects. The Newton & Manning (2006) model yields a Walther–Orville slope of 1.86 (Fig. 2B), very near 2, suggesting that  $n = 2$  in Equation 2a, and consequently that there no hydrogen-bonded  $\text{H}_2\text{O}$  molecules in monomeric silica. The parameter  $n = 2$ , together with Equations 11 and 12, fits the Newton & Manning (2000) experimental quartz solubility data at 800°C and 10 kbar very well. However, the hypothesis leads to a contradiction in that, at the limit of  $\text{NaCl}$  dilution, the number  $n$  must be 4 to be in accord with the results for  $\text{H}_2\text{O}$ – $\text{CO}_2$  solubility (Newton & Manning 2009). Such a change of Walther–Orville slope at low  $X_{\text{NaCl}}$  is not evident in the Newton & Manning (2000) data. It seems probable either that the assumption of ideal mixing of neutral silica complexes with charged ions is incorrect or that there is indeed some additional complexing with  $\text{NaCl}$ , in the manner envisioned by Evans (2007).

The quartz solution hypothesis of Anderson & Burnham (1967) embodied in Equation 9 supposes that quite acid solutions result from the dissolution of quartz in alkali halide solutions. Newton & Manning (2006) tested this hypothesis by measuring the pH of quenched fluid from a solubility experiment at 10 kbar and 800°C and  $X_{\text{NaCl}} = 0.17$ . Their measurement of pH 7 was not significantly different from acid–base neutrality at 25°C. However, pH measurements have not been performed on fluids quenched from low-pressure quartz solubility experiments; it is possible that Anderson & Burnham's (1967) model may apply to quartz solubility in the 'salting-in' range.

Shmulovich *et al.* (2006) ascribe the effect of dissolved salts on quartz solubility to change in solute properties, according to Setchénow's formulation. Their discussion is more comprehensive than that of Newton & Manning (2006), who considered only  $\text{NaCl}$  solutions or than that of Anderson & Burnham (1967), who considered only  $\text{KCl}$  solutions, but takes no account of such phenomena as hydration state, polymerization or ionization of the salts. Also, as Evans (2007) pointed out, the Setchénow coefficient must change drastically with pressure and salt concentration in order to explain the transition from salting-in to

salting-out. Therefore, much of the utility of the Setchénow formulation is lost.

The hypothesis of Evans (2007) that  $\text{SiO}_2$  reacts with dissolved  $\text{NaCl}$  to form a neutral hybrid solute complex has the ability to explain salting-in to salting-out in terms of changing  $\text{NaCl}$  and  $\text{H}_2\text{O}$  activities. Her hypothesis also supposes that the  $\text{SiO}_2$ –salt complex is neutral, which supports the observation of pH-neutral quenched fluid observed by Newton & Manning (2006). However, her formalism does not take into account what must be one of the most important properties of solute silica, that of polymerization.

In summary, the physical–chemical basis for quartz dissolution in natural fluids, at high  $P$  and  $T$ , and especially those containing ionized salts, is currently in an imperfect state. Although key data, such as pH measurements, are lacking, empirical equations predict quartz solubility adequately in a variety of simple media which contain both neutral and ionized constituents.

## SOLUBILITY ENHANCEMENT OF ROCK-FORMING MINERALS BY $\text{NaCl}$

In addition to quartz, the solubilities of various simple oxides or silicate minerals in concentrated  $\text{NaCl}$  solutions have now been measured, though data are still sparse. Nevertheless, the data are sufficient to reveal a general pattern of the enhancement of mineral solubility in  $\text{H}_2\text{O}$ – $\text{NaCl}$  relative to that in pure  $\text{H}_2\text{O}$  at high  $P$  and  $T$ . Shmulovich *et al.* (2001) found marked increase in the solubility of diopside,  $\text{CaMgSi}_2\text{O}_6$ , at 5 kbar and 650°C in aqueous fluids of salinity up to  $X_{\text{NaCl}} = 0.26$ , and Macris & Manning (2006) found a similar enhancement at 800°C and 10 kbar. The dissolution is incongruent: the Ca–silicate portion is more soluble and forsterite is left as a residue. Wollastonite ( $\text{CaSiO}_3$ ), corundum ( $\text{Al}_2\text{O}_3$ ), and grossular ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) show even greater enhancement, reaching concentrations of up to 10 times the pure- $\text{H}_2\text{O}$  solubility at 800°C and 10 kbar (Fig. 6; Newton & Manning 2006, 2007). The only silicate mineral investigated thus far which does not show enhancement by  $\text{NaCl}$  is zircon ( $\text{ZrSiO}_4$ ; Newton *et al.* 2010).

The marked solubility enhancements cannot result simply from alteration of the solvent properties, but must reflect strong reactions of the mineral constituents with the dissolved salt components. The example of wollastonite is instructive. The initial salting-in with increasing  $\text{NaCl}$  concentration is followed by a flat maximum at about  $X_{\text{NaCl}} = 0.35$  and then a salting-out at still higher salinity (Fig. 6). Quenched fluids are strongly basic (pH 11–12), which indicates that when Ca enters the solution some  $\text{OH}^-$  is created in the dissolution reaction. We adopt an approach similar to that of Evans (2007) and postulate a wollastonite dissolution reaction of the form:

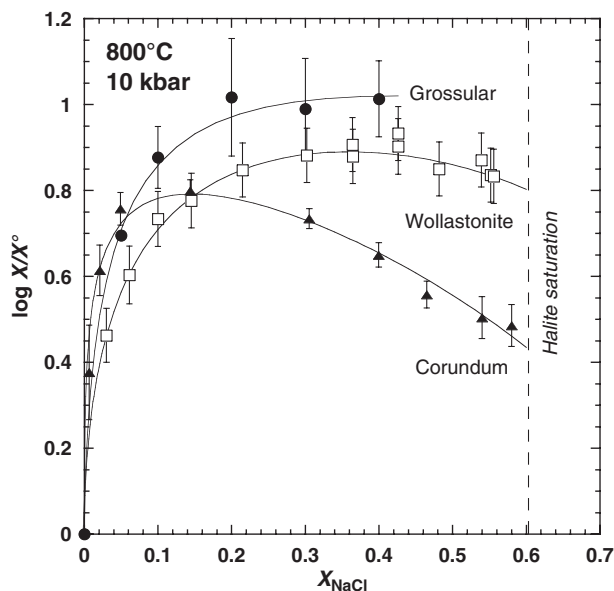
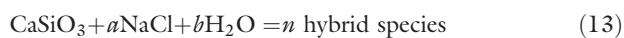


Fig. 6. Enhancement of solubilities of corundum, wollastonite and grossular by NaCl in NaCl-H<sub>2</sub>O solutions. All solubilities are observed mole fraction relative to that in initially pure H<sub>2</sub>O. Data from Newton & Manning (2006, 2007). Dashed vertical line is halite saturation.



It may be shown quite generally that, if wollastonite solubility as a function of  $X_{\text{NaCl}}$  has a maximum (salting-in going to salting-out), then, the maximum in solubility occurs at a NaCl content ( $X_{\text{NaCl}}^*$ ) determined from the reaction coefficients by:

$$X_{\text{NaCl}}^* = \frac{a}{a+b} \quad (14)$$

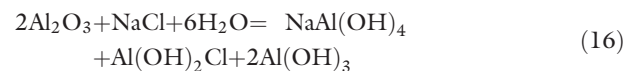
Equations 13 and 14 state that solubility enhancement is eventually arrested and reversed by decreasing H<sub>2</sub>O activity with increasing salinity. The observed maximum in the wollastonite solubility curve near  $X_{\text{NaCl}}^* = 0.35$  can be explained most simply by the dissolution reaction:



wherein  $X_{\text{NaCl}}^* = 1/3$  and the basic nature of the quenched fluids is explained. The neutral complex H<sub>3</sub>NaSiO<sub>4</sub> is analogous to that previously postulated by Anderson & Burnham (1967) for quartz solubility in KCl solutions (see Equation 9).

Corundum dissolution in NaCl solutions at 10 kbar and 800°C shows a different behavior. There is a nearly ten-fold increase in solubility over that in pure H<sub>2</sub>O with a maximum near  $X_{\text{NaCl}} = 0.15$  (Fig. 6), if, following Evans (2007), the mole fraction of Al<sub>2</sub>O<sub>3</sub> is taken with respect to

all molecules and ions in the solution (NaCl counts for two mixing units, Na<sup>+</sup> and Cl<sup>-</sup>, in a completely dissociated aqueous fluid). In Newton & Manning's (2006) corundum solubility measurements, quench pH was 7, implying that neither H<sup>+</sup> or OH<sup>-</sup> are involved in the dissolution reaction. A reaction which satisfies the above observations is:



(Newton & Manning 2006), for which  $a = 1$ ,  $b = 6$ , and  $X_{\text{NaCl}}^* = 0.143$ . The neutral complex NaAl(OH)<sub>4</sub> was proposed by Walther (2001) in his study of corundum solubility in NaCl solutions at low  $P$  and  $T$ .

When SiO<sub>2</sub> is added to the system Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O-NaCl, Al<sub>2</sub>O<sub>3</sub> solubility enhancement becomes very strong and, in fact, quartz solubility is simultaneously enhanced over that at the same salinity in the absence of Al<sub>2</sub>O<sub>3</sub> (Newton & Manning 2008b). This mutual enhancement culminates in the precipitation of albite at higher salinities and SiO<sub>2</sub> contents of the fluid (Fig. 7). Quenched solutions are very acid (pH 1–2), implying that the dissolution reaction of corundum involves complexing with Na and Si, leaving an excess of Cl<sup>-</sup>. A consistent dissolution reaction must be something like the following:

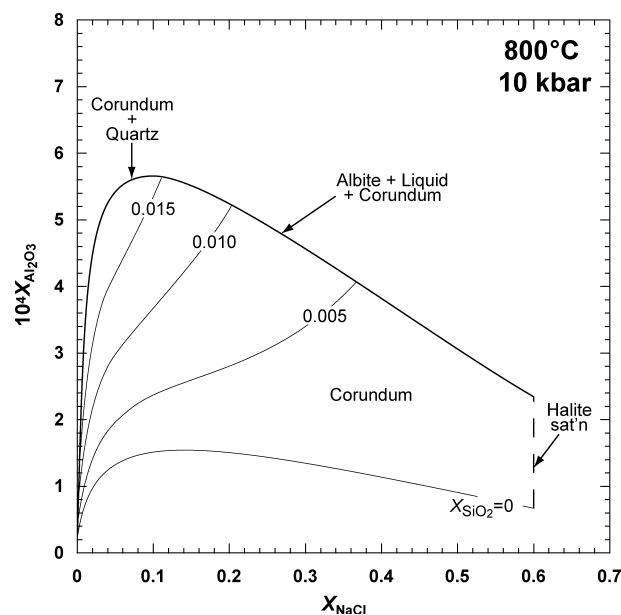
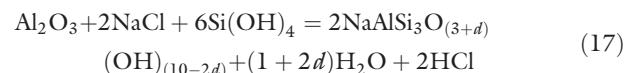


Fig. 7. Variation in corundum solubility (as  $10^4$  times mole fraction of Al<sub>2</sub>O<sub>3</sub>) with NaCl and SiO<sub>2</sub> concentration at 800°C, 10 kbar. The light solid lines are lines of constant SiO<sub>2</sub> mole fraction, and the bold solid line is quartz or albite + silicate liquid saturation; the transition between saturating phases occurs at the maximum in solubility. Dashed vertical line is halite saturation.

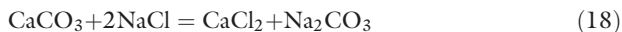


The average Si/Al ratio of the solute aluminosilicate species estimated by mass balance by Newton & Manning (2008b) is near three at albite precipitation, which supports the hypothesis of Anderson & Burnham (1983) that Al can exist in Si and Na bearing fluids in the form of a feldspar-like molecule. The hydration state of the complex, characterized by the parameter  $d$ , is indeterminate.

In view of the marked enhancement of  $\text{CaSiO}_3$  and  $\text{Al}_2\text{O}_3$  solubility in aqueous NaCl and NaCl– $\text{SiO}_2$  solutions at high  $P$  and  $T$ , the solubility of a compound of these components, such as grossular garnet ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), is of interest. Newton & Manning (2007) found that grossular solubility is congruent even at very high salinity, with relative enhancement greater than either wollastonite or corundum (Fig. 6). The solubility of  $\text{Al}_2\text{O}_3$  can be enhanced over that of corundum in pure  $\text{H}_2\text{O}$  by a factor of nearly 100 in solutions containing also NaCl and  $\text{CaSiO}_3$  (Newton & Manning 2007). Quenched fluids were very basic, showing that Ca–chloride production drives the high solubility. Interestingly, similar enhancement by NaCl solutions at high  $P$  and  $T$  of the analogous  $\text{Fe}^{3+}$  garnet, andradite, does not occur; evidently,  $\text{Fe}_2\text{O}_3$  is a much more refractory component than  $\text{Al}_2\text{O}_3$  in salty solutions of calc-silicates (Wykes *et al.* 2008).

### SOLUBILITY ENHANCEMENT OF Ca SALTS BY NaCl

The greatest solubility-enhancements by brines are found in systems with calcium carbonate, sulfate, fluoride and phosphate. Figure 8 shows enhancement factors for calcite, anhydrite, fluorite and fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ . The solubility versus  $X_{\text{NaCl}}$  curves are strongly convex to salinity, indicating that the  $\text{H}_2\text{O}$  activity is not a major influence, which in turn suggests that the solute species are not hydrates and that multiple hybrid species form upon dissolution. For calcite, the dissolution reaction must be something like:



In this reaction calcite, a mineral very insoluble in pure  $\text{H}_2\text{O}$ , becomes very soluble in concentrated NaCl solutions at high  $T$  and  $P$ . Anhydrite undergoes a similar dissolution reaction, but solubility enhancement is extreme. In both systems the solubility becomes so high at high salinity and temperature that critical mixing between saline fluids and mixed-salt melts is anticipated at moderately high temperatures and salinities (probably 900–1000°C and  $X_{\text{NaCl}}$  of 0.3–0.4; Fig. 9).

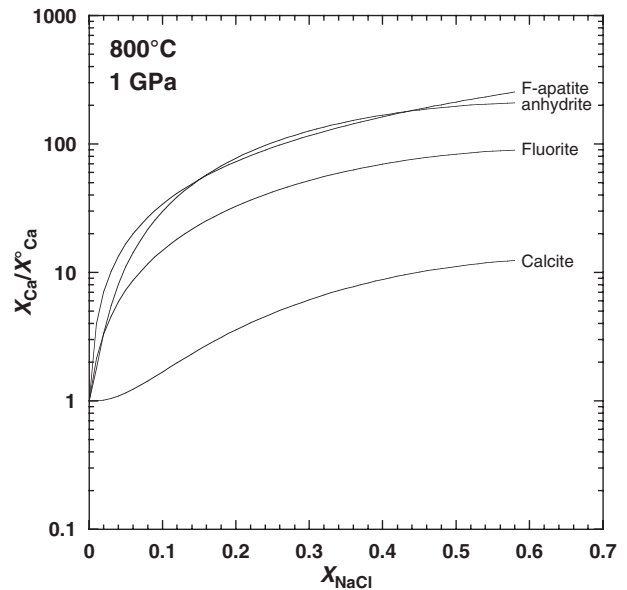


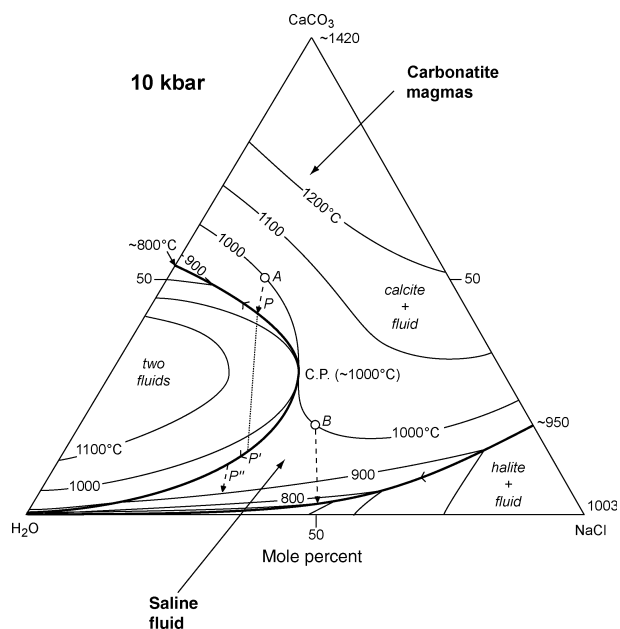
Fig. 8. Solubility enhancement of Ca salt and oxysalt minerals, including calcite, fluorite, fluorapatite and anhydrite, at 800°C, 10 kbar. Enhancement, as mole fraction relative to that in initially pure  $\text{H}_2\text{O}$ , was calculated using equations given in Newton & Manning (2002b, 2005), Tropper & Manning (2007) and Antignano & Manning (2008).

### APPLICATIONS TO PETROLOGY

Solubility studies of various minerals in salty fluids over the last decade have suggested that such fluids may be important agents in petrogenesis, capable of explaining some oft-observed metasomatic phenomena that may not be otherwise readily interpreted. A few examples are discussed below.

#### Deep-crustal fluids in general

Various mechanisms have been suggested for the origin of concentrated brines in deep-crustal igneous and metamorphic processes, including involvement of deeply-buried evaporites (e.g. Yardley & Graham 2002), downward circulation of dissolved salts of surficial origin in thermally excited convection cells (McLelland *et al.* 2002) and magmatic fluids emitted in the late stages of crystallization of igneous rocks at depth (Ryabchikov & Hamilton 1971; Hansteen & Burke 1990). The last hypothesis has gotten considerable momentum from the experiments of Webster *et al.* (1999), which have shown that concentrated brines can be emitted from Cl-saturated magmas at depth, most abundantly from basaltic intrusions. Whatever the sources of the salty fluids, their high affinity for carbonate and sulfate militates that they must become complex brines in their passage through crustal rocks. The properties of low  $\text{H}_2\text{O}$  activity yet relatively high solution capability for



**Fig. 9.** Schematic CaCO<sub>3</sub>-NaCl-H<sub>2</sub>O pseudo-ternary showing solubilities at 10 kbar, from Newton & Manning (2002b). Critical mixing between a hydrous, NaCl-bearing carbonatite liquid and a CaCO<sub>3</sub>-rich hypersaline aqueous solution may occur near 1000°C and 30 mol % NaCl, 25 mol % CaCO<sub>3</sub>. A hydrous carbonatite liquid (composition A) with calcite at 1000°C will, upon cooling to 950°C (point P), emit a concentrated salt solution (point P'). Both fluids will crystallize calcite upon further cooling over a narrow *T* interval. At P', only the CaCO<sub>3</sub>-rich brine phase remains and deposits most of solute CaCO<sub>3</sub> in cooling only 200°C further. A calcite-saturated brine of composition B, generated at 1000°C, will avoid the two-fluid region and deposit nearly all of its substantial solute carbonate in isobaric cooling past 800°C.

quartz and silicate minerals, including actual enhancement for some rock components, indicate that the concentrated brines must be important in rock alteration and mass transport in the deeper parts of the crust.

#### Carbonatite-fenite complexes and carbonated shear zones

The association of carbonatite intrusions of obviously igneous origin surrounded by wide tracts of alkali-metasomatized rocks has been described from many localities (e.g. Alnö Island, Sweden: Morogan & Wooley 1988). Students of these complexes have largely come to the conclusion that they result from fluid immiscibility in the intrusion process between carbonate-rich and saline aqueous components (e.g. Hamilton *et al.* 1979). Figure 9 shows a semi-quantitative diagram of the pseudo-ternary system CaCO<sub>3</sub>-NaCl-H<sub>2</sub>O at 10 kbar, after Newton & Manning (2002b). The very high solubility of calcite in NaCl-H<sub>2</sub>O solutions at high *T* and *P* indicates that such *T*- and/or *P*-dependent fluid immiscibility must take place in this model carbonatite-fenite system. Depending on the initial bulk composition, a supercritical carbonatite magma may either split

into carbonate-rich and NaCl-rich fractions during cooling (path A), in which case a carbonatite-fenite association may develop, or pass continuously into ultrasaline fluids (path B) capable of voluminous carbonate alteration of country rocks, as in the carbonate-metasomatized mega-shear zones like the Attur Fault Zone of South India (Wickham *et al.* 1994).

#### Sulfur-rich magmatism

The anhydrite solubility study of Newton & Manning (2005) suggested a new mode of anhydrite involvement in Mt. Pinatubo-type S-rich volcanism. Many authorities now envision a 'basalt trigger' for the massive 1991 eruption in the Philippines (e.g. Pallister *et al.* 1992) and, in view of the findings of Webster *et al.* (1999) of Cl-induced early magmatic outgassing, the possibility arises that the sulfur could have originally been released as sulfate in a magmatic brine. The highly oxidizing fluids which apparently affected the rocks under Mt. Pinatubo (Cameron & Hattori 1994) and which were ultimately vented massively to the surface in the form of sulfate aerosols, could have been in the form of a concentrated brine of magmatic origin.

Hattori & Keith (2001) imagined a close genetic connection between Mt. Pinatubo-type eruptions and the porphyry Cu-Mo ores of western North America, which are invariably found in the aureoles of small Late Mesozoic and Tertiary granitic intrusions. These sulfide ore vein deposits are always characterized by massive oxidation and anhydrite deposition. It seems reasonable to suppose that Cl- and S-laden basaltic magmas 'triggered' the hypabyssal intrusions in much the same manner as for the Mt. Pinatubo dacite eruptions.

#### Fluid-present granulite-facies metamorphism

Deep-crustal granulite-facies metamorphism, which generated the extensive high-grade terranes characteristic of the Precambrian shields of all continents, yields mineral assemblages that indicate formation at low H<sub>2</sub>O activity, yet possess geochemical and petrological characteristics which in some cases require interaction with a mobile fluid phase (Newton *et al.* 1998). This evidence, for example from the Archean craton of southern India, includes orthopyroxene-bearing metasomatic rocks, massive quartz veins with orthopyroxene-bearing selvages (Fig. 10), whole-rock depletions of Rb and Th across isograds (Hansen *et al.* 1995), and incipient charnockitic alteration of amphibole-biotite gneisses, as at the amphibolite facies-granulite facies boundary in southern India (Hansen *et al.* 1987). Early models invoked CO<sub>2</sub>-rich fluids to explain much of the metasomatism associated with granulite metamorphism (e.g. Newton *et al.* 1980). Petrologic considerations posed problems for this simple model (e.g. Lamb *et al.* 1987;



Fig. 10. Synmetamorphic quartz vein in charnockite with orthopyroxene selvage from near Dharmapuri, Tamil Nadu, South India. Knife for scale.

Yardley & Valley 1997); however, mounting evidence suggests that  $\text{CO}_2$ -rich fluids coexisted with an immiscible alkali-halide-rich solution, consistent with the large miscibility gap in the  $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$  system at high  $P$  and  $T$  (Johnson 1991; Gibert *et al.* 1998; Heinrich 2007).

Studies of mineral solubility in saline fluids offer insights on the granulite-fluid controversy. Early models were heavily influenced by the plethora of dense  $\text{CO}_2$ -rich fluid inclusions found in many or most granulites, first recognized by Touret (1971). Concentrated brine inclusions in quartz have also been reported from granulites (Touret 1985; Crawford & Hollister 1986); these are rarer and less well preserved than the  $\text{CO}_2$  inclusions. The fluid inclusion evidence may be questioned in light of the demonstrated likelihood of postentrapment alteration (Sterner & Bodnar 1989; Barker 2007). However, saline fluids trapped in minerals undergoing granulite-facies metamorphism must originally have been very concentrated if they coexisted with an immiscible  $\text{CO}_2$ -rich fluid. The importance of salty fluids has probably been underestimated because of difficulty of capture as fluid inclusions – brines have much greater wetting ability for grain boundaries in silicate mineral aggregates and quartz than does dense  $\text{CO}_2$  (Watson & Brenan 1987). It is clear from the solubility studies that halide ( $\pm$ carbonate,  $\pm$ sulfate) solutions at high  $T$  and  $P$  are much more efficient than dense  $\text{CO}_2$  in promoting mineral reactions and performing mass transport in the deeper parts of the crust. The amounts of the fluids need not have been excessive to perform important functions such as desiccation and trace element depletion (Aranovich & Newton 1996). For instance, the high solubility of apatite, a principal rare-earth-element carrier, in high  $P$ - $T$  brines could explain REE mobility inferred in some granulite terranes (Pan & Fleet 1996). The great wetting ability of salt solutions for mineral grain boundaries, in contrast to  $\text{CO}_2$ , may also be an important factor in deep-crustal metasomatism.

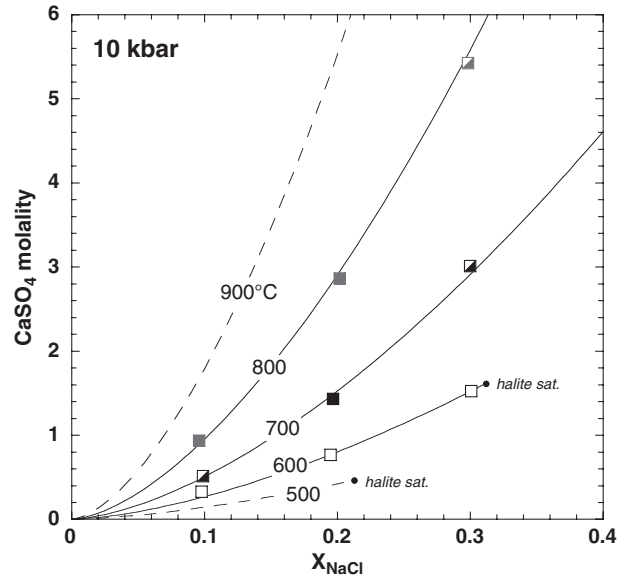


Fig. 11. Variation of the solubility of anhydrite with NaCl concentration and temperature at 10 kbar, from Newton & Manning (2005). Experiments were unbuffered, but  $f_{\text{O}_2}$  is inferred to be near Ni-NiO equilibrium.

The high solubility of  $\text{CaSO}_4$  in alkali halide solutions (Fig. 11) could be a factor in the origin of some highly oxidized terranes, like Wilson Lake, Labrador (Currie & Gittens 1988) and Labwor, Uganda (Sandiford *et al.* 1987). These extensive Precambrian terranes reveal high oxidation states in their high  $\text{Mg}/(\text{Mg} + \text{Fe})$  ratios of silicates, even in felsic compositions and in the compositions of the Fe, Ti oxide minerals, including, in some cases, modal hematite. This oxidation could only be the result of pervasive infiltration of highly oxidizing solutions at high grade conditions; highly oxidized protoliths as envisioned by Arima *et al.* (1986) could not account consistently for the syndrome of related phenomena, which include profound shearing deformation with related vein mineralization, high positive gravity anomalies centered upon the granulites and Archean age of some, in spite of the reducing surficial weathering conditions that prevailed at that time. Cameron & Hattori (1994) ascribed the oxidizing metamorphism to the passage of  $\text{SO}_2$ -bearing fluids released from underplated basaltic magmas; Newton & Manning (2005) modified this concept to include the action of orthomagmatic brines carrying concentrated sulfate.

Wannamaker *et al.* (2004) present evidence from magnetotelluric sounding data that the lower crust under the Great Basin of the western US contains highly conductive, interconnected pore fluids and they suggest that these fluids have their origin in underplated basaltic intrusions. Such a view of regional deep-crustal fluid action is consonant with the 'Basin-and-Range' model of granulite-facies metamorphism advanced by Hopgood & Bowes (1990).

### Aluminum mobility in high-grade metamorphism

The element Al has long been thought to be effectively inert in metasomatic processes. The assumption of fixed Al in metasomatic mass transfer has been used to anchor calculations of mineral reactions in high-grade rocks in open systems (e.g. Hansen *et al.* 1987). This point of view has been influenced in part by the low hydrothermal solubility of corundum compared to that of quartz at high  $P$  and  $T$ . However, many authors have pointed to the existence of widespread Al-silicate veining in high-grade terranes (Kerrick 1988; McLelland *et al.* 2002), where Al transport seems to have been a major process. Anderson & Burnham (1983) argued for the transport of solute Al in the form of feldspar-like complexes. Simpler complexes arising from interaction between Si and Al in alkali-free fluids have also been inferred (Manning 2007). The possible role of Al-Si and alkali-Al-Si complex transport has received only limited attention (e.g. Manning *et al.* 2010), chiefly because the basic thermodynamic properties of such species are still not tabulated; however, there is evidence that such transport may be further promoted at elevated salinity.

The sillimanite-quartz veins described by McLelland *et al.* (2002) (Fig. 12) are characterized by very salty fluid inclusions in quartz with up to 25 wt% NaCl equivalent. It is possibly significant that this concentration range is the location of a very sharp Al solubility maximum (Fig. 7), according to the solubility experiments of Newton & Manning (2008b). We can propose a scenario in which brines, liberated from the abundant intrusions in the area, increased in salinity as H<sub>2</sub>O was absorbed into migmatites in the country rocks and the NaCl concentration increased until Al was more or less suddenly mobilized at about 25 wt% NaCl. Further increase in salinity would then begin to have a decreasing effect on Al solubility.

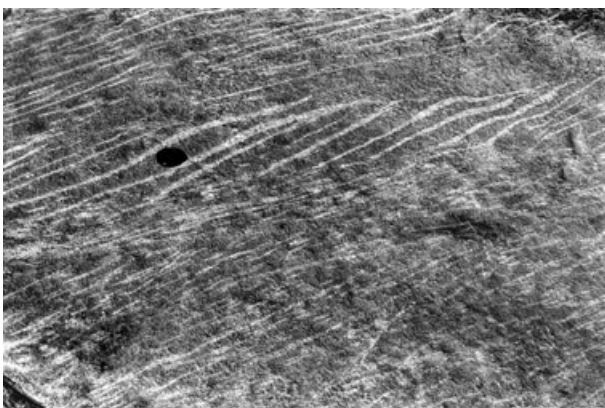


Fig. 12. Sillimanite-quartz vein network in Lyon Mountain granitic gneiss, Adirondack Mountains, New York, USA. Courtesy J. McLelland (McLelland *et al.* 2002). Lens cap for scale.

The grossular solubility study of Newton & Manning (2007) showed that Ca-Al silicates are also quite soluble in concentrated brines at high  $T$  and  $P$ . In the case of calc-silicates, the driving force of Al solubility enhancement is the formation of CaCl<sup>+</sup> ion, creating very basic fluids in the dissolution process. Chemical studies of calc-silicate lenses in granulites from Australia (Buick *et al.* 1993) showed that Al is a relatively mobile component, whereas Fe<sup>3+</sup> is more inert, tending to remain at fixed levels in calc-silicate lenses interacting with surrounding quartzofeldspathic rocks. This observation concurs with the finding of low solubility of Fe<sup>3+</sup> in high  $P$ - $T$  NaCl solutions at least at relatively high oxygen fugacity (Wykes *et al.* 2008). Iron becomes much more soluble at lower oxygen fugacity and lower-grade conditions in rock compositions (Althaus & Johannes 1969; Chou & Eugster 1977).

### SUMMARY

Solubility studies lead to the conclusion that concentrated brines may be important agents in metasomatic alteration of deep-seated rocks. While providing low H<sub>2</sub>O activity, which is necessary that aqueous fluids be compatible with anhydrous silicate minerals, especially pyroxenes and garnets, they nevertheless retain relatively high solubility for silicate constituents, high Al-transporting ability in either calcareous or aluminous rocks and high affinity for other salt components, which makes them effective in trace-element mobilization. These specific properties contrast with the limited ability of CO<sub>2</sub>-rich solutions to mobilize rock constituents.

The solubility enhancements by alkali halide solutions at high  $P$  and  $T$  show contrasting mechanisms in aluminous versus calcareous rocks. Acid solutions are generated in aluminous rocks due to the stability of soluble Na-Al complexes, as shown by a number of earlier workers (Candela 1990; Frank *et al.* 2003). In calcareous rocks, the stability of Ca ions in chloride solutions drives solubility enhancement.

It is certain that concentrated brines will strongly inhibit critical phenomena in rock-H<sub>2</sub>O systems; this narrows the geologic opportunities for critical mixing between silicate-rock melts and intergranular fluids in the crust, because all such fluids are likely to be salty to some degree. However, the high solubility of rock materials in such fluids shows that they are capable of extensive metasomatism under some conditions such that the affected rocks can be reconstituted to almost the same degree as by actual rock melting. Study of trace element behavior and fluid inclusions will doubtless further elucidate the comparative roles of mineralizing fluids and rock melting in the deep crust and upper mantle.

## ACKNOWLEDGEMENTS

This work was supported by National Science Foundation grant EAR-0711521. The manuscript was completed while CEM was in residence at the Bayerisches GeoInstitute through the auspices of the Humboldt Foundation. Two anonymous reviewers provided invaluable information and advice.

## REFERENCES

- Akiniev NN, Diamond LW (2009) A simple predictive model of quartz solubility in water-salt-CO<sub>2</sub> systems at temperatures up to 1000 °C and pressures up to 1000 Mpa. *Geochimica et Cosmochimica Acta*, **73**, 1597–608.
- Althaus E, Johannes W (1969) Experimental metamorphism of NaCl-bearing aqueous solutions by reaction with silicates. *American Journal of Science*, **267**, 87–98.
- Anderson GM, Burnham CW (1965) The solubility of quartz in supercritical water. *American Journal of Science*, **263**, 494–511.
- Anderson GM, Burnham CW (1967) Reaction of quartz and corundum with aqueous chloride and hydroxide solutions at high temperatures and pressures. *American Journal of Science*, **265**, 12–27.
- Anderson GM, Burnham CW (1983) Feldspar solubility and the transport of aluminum under metamorphic conditions. *American Journal of Science*, **283-A**, 283–97.
- Antignano A, Manning CE (2008) Fluorapatite solubility in H<sub>2</sub>O and H<sub>2</sub>O-NaCl at 700 to 900 °C and 0.7 to 2.0 GPa. *Chemical Geology*, **251**, 112–19.
- Aranovich LY, Newton RC (1996) H<sub>2</sub>O activity in concentrated NaCl solutions at high pressures and temperatures measured by the brucite-periclase equilibrium. *Contributions to Mineralogy and Petrology*, **125**, 200–12.
- Aranovich LY, Newton RC (1999) Experimental determination of CO<sub>2</sub>-H<sub>2</sub>O activity-composition relations at 600–1000 °C and 6–14 kbar by reversed decarbonation and dehydration reactions. *American Mineralogist*, **84**, 1319–32.
- Arima M, Kerrich R, Thomas A (1986) Sapphirine-bearing paragneiss from the northern Grenville Province in Labrador, Canada. Protolith compositions and metamorphic P-T conditions. *Geology*, **14**, 884–87.
- Barker AJ (2007) Post-entrapment modification of fluid inclusions due to overpressure: evidence from natural samples. *Journal of Metamorphic Geology*, **13**, 737–50.
- Bowers TS, Helgeson HC (1983) Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H<sub>2</sub>O-CO<sub>2</sub>-NaCl on phase relations in geologic systems. Equation of state for H<sub>2</sub>O-CO<sub>2</sub>-NaCl fluids at high pressures and temperatures. *Geochimica et Cosmochimica Acta*, **47**, 1247–75.
- Buick IS, Hardy SL, Cartwright IC (1993) Granulite facies metasomatism: Zoned calc-silicate boudins from the Rauer group, East Antarctica. *Contributions to Mineralogy and Petrology*, **113**, 557–71.
- Cameron EM, Hattori K (1994) Highly oxidized deep metamorphic zones: occurrence and origin. *Mineralogical Magazine*, **58A**, 142–43.
- Candela PA (1990) Theoretical constraints on the chemistry of the magmatic aqueous phase. *Geological Society of America Special Paper*, **246**, 11–20.
- Chou IM, Eugster HP (1977) Solubility of magnetite in supercritical chloride solutions. *American Journal of Science*, **277**, 1296–314.
- Crawford ML, Hollister LS (1986) Metamorphic fluids, the evidence from fluid inclusions. In: *Fluid-Rock Interactions During Metamorphism* (eds Walther JV, Wood BJ), pp. 1–35. Springer-Verlag, Berlin.
- Currie KL, Gittens J (1988) Contrasting sapphirine parageneses from Wilson Lake, Labrador and their tectonic applications. *Journal of Metamorphic Geology*, **6**, 609–22.
- Duan Z, Møller N, Weare JH (1995) Equation of state for NaCl-H<sub>2</sub>O-CO<sub>2</sub> system. Prediction of phase equilibria and volumetric properties. *Geochimica et Cosmochimica Acta*, **59**, 2869–82.
- Evans K (2007) Quartz solubility in salt-bearing solutions at pressures to 1 GPa and temperatures to 900 °C. *Geofluids*, **7**, 1–17.
- Fournier RO (1983) A method of calculation of quartz solubilities in aqueous sodium chloride solution. *Geochimica et Cosmochimica Acta*, **47**, 579–86.
- Fournier RO, Rosenbauer RJ, Bishoff JL (1982) The solubility of quartz in aqueous sodium chloride solution at 350 °C and 180 to 500 bars. *Geochimica et Cosmochimica Acta*, **46**, 1975–78.
- Frank MB, Candela PA, Piccoli PM (2003) Alkali exchange equilibria between a silicate melt and coexisting magmatic volatile phase: an experimental study at 800 °C and 100 MPa. *Geochimica et Cosmochimica Acta*, **67**, 1415–27.
- Fu B, Touret JLR, Zheng YF (2001) Fluid inclusions in coesite-bearing eclogites and jadeite quartzite at Shanghe, Dabie Shan (China). *Journal of Metamorphic Geology*, **19**, 529–45.
- Gibert R, Guillame D, LaPorte D (1998) Importance of fluid immiscibility in the H<sub>2</sub>O-NaCl-CO<sub>2</sub> system and selective CO<sub>2</sub> entrapment in granulites: experimental phase diagram at 5–7 kbar, 900 °C and wetting textures. *European Journal of Mineralogy*, **10**, 1109–23.
- Hamilton DL, Freestone IC, Dawson JB, Donaldson CH (1979) Origin of carbonatites by liquid immiscibility. *Nature*, **279**, 52–54.
- Hansen EC, Janardhan AS, Newton RC, Prame WKBN, Ravindra Kumar GR (1987) Arrested charnockite formation in southern India and Sri Lanka. *Contributions to Mineralogy and Petrology*, **96**, 225–44.
- Hansen EC, Newton RC, Janardhan AS, Lindenberg S (1995) Differentiation of Late Archean crust in the Eastern Dharwar Craton, Krishnagiri-Salem area, South India. *Journal of Geology*, **103**, 629–51.
- Hansteen TH, Burke EAJ (1990) Melt-mineral-fluid interaction in the Oslo Rift, southeast Norway. II. High-temperature fluid inclusions in the Eikorn-Skrim complex. *Norges Geologiske Undersøkelse Bulletin*, **417**, 15–32.
- Hattori K, Keith JF (2001) Contribution of mafic melt for porphyry deposits; evidence from Pinatubo and Bingham. *Mineralium Deposita*, **36**, 799–806.
- Heinrich W (2007) Fluid immiscibility in metamorphic rocks. *Reviews in Mineralogy and Geochemistry*, **65**, 389–430.
- Hopgood AM, Bowes DR (1990) Contrasting structural features in the granulite-gneiss-charnockite-granite complex, Lake Baikal, USSR: evidence for diverse geotectonic regimes in early Proterozoic times. *Tectonophysics*, **174**, 279–99.
- Izraeli ES, Harris JW, Navon O (2001) Brine inclusions in diamonds: a new upper mantle fluid. *Earth and Planetary Science Letters*, **187**, 323–32.
- Izraeli ES, Harris JW, Navon O (2004) Fluid and mineral inclusions in cloudy diamonds from Koffiefontein, South Africa. *Geochimica et Cosmochimica Acta*, **68**, 2561–75.
- Johnson EL (1991) Experimentally determined limits for H<sub>2</sub>O-CO<sub>2</sub>-NaCl immiscibility in granulites. *Geology*, **19**, 925–8.

- Kennedy GC, Wasserburg GJ, Heard HC, Newton RC (1962) The upper three-phase region in the system  $\text{SiO}_2\text{-H}_2\text{O}$ . *American Journal of Science*, **260**, 501–21.
- Kerrick DM (1988)  $\text{Al}_2\text{SiO}_5$ -bearing segregations in the Lepontine Alps, Switzerland: aluminum mobility in metapelites. *Geology*, **16**, 636–40.
- Klein-BenDavid O, Izraeli ES, Hauri E, Navon O (2007) Fluid inclusions in diamonds from the Diavik mine, Canada and the evolution of diamond-forming fluids. *Geochimica et Cosmochimica Acta*, **71**, 723–44.
- Kullerud K (1996) Chlorine-rich amphiboles: interplay between amphibole composition and an evolving fluid. *European Journal of Mineralogy*, **8**, 355–70.
- Lamb WM, Valley JW, Brown PE (1987) Post-metamorphic  $\text{CO}_2$ -rich inclusions in granulites. *Contributions to Mineralogy and Petrology*, **96**, 485–95.
- Macris CA, Manning CE (2006) The solubility of diopside in  $\text{H}_2\text{O-NaCl}$  fluids at 800 °C and 10 kbar. *Eos, Transactions of the American Geophysical Union*, **87**. Fall Meeting Supplement, Abstract MR43C-1091.
- Manning CE (1994) The solubility of quartz in  $\text{H}_2\text{O}$  in the lower crust and upper mantle. *Geochimica et Cosmochimica Acta*, **58**, 4831–9.
- Manning CE (2007) Solubility of corundum + kyanite in  $\text{H}_2\text{O}$  at 700°C and 10 kbar: evidence for Al-Si complexing at high pressure and temperature. *Geofluids*, **7**, 258–69.
- Manning CE, Antignano A, Lin HA (2010) Premelting polymerization of crustal and mantle fluids, as indicated by solubility of albite + paragonite + quartz in  $\text{H}_2\text{O}$  at 1 GPa and 350–620 °C. *Earth and Planetary Science Letters*, in press.
- Markl G, Bucher K (1998) Composition of fluids in the lower crust inferred from metamorphic salt in lower crustal rocks. *Nature*, **391**, 781–3.
- Markl G, Ferry JM, Bucher K (1998) Formation of saline brines and salt in the lower crust by hydration reactions in partially retrogressed granulites from the Lofoten Islands, Norway. *American Journal of Science*, **298**, 705–57.
- McLelland J, Morrison J, Selleck B, Cunningham B, Olson C, Schmitt K (2002) Hydrothermal alteration of late- to post-tectonic Lyon Mountain Granite Gneiss, Adirondack Mountains, New York: origin of quartz-sillimanite segregations, quartz-albite lithologies and associated Kiruna-type low-Ti oxide deposits. *Journal of Metamorphic Geology*, **20**, 175–90.
- Mora C, Valley JW (1989) Halogen-rich scapolite and biotite: Implications for metamorphic fluid-rock interaction. *American Mineralogist*, **74**, 721–37.
- Morogan V, Wooley AR (1988) Fenitization in the Alnö Complex, Sweden: distribution, mineralogy and genesis. *Contributions to Mineralogy and Petrology*, **100**, 169–82.
- Munoz JL (1981) Chloride-hydroxyl exchange in biotite and estimation of relative HCl/HF activities in hydrothermal fluids. *Economic Geology*, **76**, 2212–21.
- Newton RC, Manning CE (2000) Quartz solubility in  $\text{H}_2\text{O-NaCl}$  and  $\text{H}_2\text{O-CO}_2$  solutions at deep crust-upper mantle pressures and temperatures: 2–15 kbar and 500–900 °C. *Geochimica et Cosmochimica Acta*, **64**, 2993–3005.
- Newton RC, Manning CE (2002a) Solubility of enstatite + forsterite in  $\text{H}_2\text{O}$  at deep crust/upper mantle conditions: 4 to 15 kbar and 700 to 900 °C. *Geochimica et Cosmochimica Acta*, **66**, 4165–76.
- Newton RC, Manning CE (2002b) Experimental determination of calcite solubility in  $\text{H}_2\text{O-NaCl}$  solutions at deep crust/upper mantle temperatures and pressures: Implications for metasomatic processes in shear zones. *American Mineralogist*, **87**, 1401–9.
- Newton RC, Manning CE (2003) Activity coefficient and polymerization of aqueous silica at 800 °C, 12 kbar, from solubility measurements on  $\text{SiO}_2$ -buffering mineral assemblages. *Contributions to Mineralogy and Petrology*, **146**, 135–43.
- Newton RC, Manning CE (2005) Solubility of anhydrite,  $\text{CaSO}_4$ , in  $\text{NaCl-H}_2\text{O}$  solutions at high pressures and temperatures; applications to fluid-rock interaction. *Journal of Petrology*, **46**, 701–16.
- Newton RC, Manning CE (2006) Solubilities of corundum, wollastonite and quartz in  $\text{H}_2\text{O-NaCl}$  solutions at 800 °C and 10 kbar: Interaction of simple minerals with brines at high pressure and temperature. *Geochimica et Cosmochimica Acta*, **70**, 5571–82.
- Newton RC, Manning CE (2007) Solubility of grossular,  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ , in  $\text{H}_2\text{O-NaCl}$  solutions at 800 °C and 10 kbar, and the stability of garnet in the system  $\text{CaSiO}_3\text{-Al}_2\text{O}_3\text{-H}_2\text{O-NaCl}$ . *Geochimica et Cosmochimica Acta*, **71**, 5191–202.
- Newton RC, Manning CE (2008a) Thermodynamics of  $\text{SiO}_2\text{-H}_2\text{O}$  fluid near the upper critical end point from quartz solubility measurements at 10 kbar. *Earth and Planetary Science Letters*, **274**, 241–9.
- Newton RC, Manning CE (2008b) Solubility of corundum in the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-NaCl}$  at 800 °C and 10 kbar. *Chemical Geology*, **249**, 250–61.
- Newton RC, Manning CE (2009) Hydration state and activity of silica in  $\text{H}_2\text{O-CO}_2$  fluids at high temperatures and pressures. *American Mineralogist*, **94**, 1287–90.
- Newton RC, Smith JV, Windley BF (1980) Carbonic metamorphism, granulites, and crustal growth. *Nature*, **288**, 45–50.
- Newton RC, Aranovich LY, Hansen EC, Vandenhoevel BA (1998) Hypersaline fluids in Precambrian deep-crustal metamorphism. *Precambrian Research*, **91**, 41–63.
- Newton RC, Manning CE, Hanchar JM, Colasanti CV (2009) Free energy of formation of zircon based on solubility measurements at high temperature and pressure. *American Mineralogist*, doi: 10.2138/am.2010.3213.
- Nijland TG (1993) Halogen geochemistry of fluid during amphibolite-granulite metamorphism as indicated by apatite and hydrous silicates in basic rocks from the Bamble sector, south Norway. *Lithos*, **30**, 167–89.
- Novgorodov PG (1977) On the solubility of quartz in  $\text{H}_2\text{O} + \text{CO}_2$  and  $\text{H}_2\text{O} + \text{NaCl}$  at 700 °C and 1.5 kb pressure. *Geochemistry International*, **14**, 191–3.
- Pallister JS, Hoblitt RP, Reyes AG (1992) A basalt trigger for the 1991 eruptions of Pinatubo volcano? *Nature*, **356**, 426–8.
- Pan Y, Fleet ME (1996) Rare earth element mobility during prograde granulite facies metamorphism: significance of fluorine. *Contributions to Mineralogy and Petrology*, **123**, 251–62.
- Philippot P, Selverstone J (1991) Trace element-rich brines in eclogitic veins: implications for fluid composition and transport during subduction. *Contributions to Mineralogy and Petrology*, **106**, 417–30.
- Quist AS, Marshall WL (1968) Electrical conductances of aqueous sodium chloride solutions from 0 to 800 °C and at pressures up to 4000 bars. *Journal of Physical Chemistry*, **72**, 684–703.
- Ryabchikov ID, Hamilton DL (1971) Possibility of separation of concentrated chloride solutions in course of acid magma crystallization. *Doklady Akademii Nauk SSSR*, **197**, 933–7.
- Sandiford M, Neall FB, Powell R (1987) Metamorphic evolution of aluminous granulites from Labwor Hills, Uganda. *Contributions to Mineralogy and Petrology*, **95**, 217–25.

- Setchénow M (1892) Action de l'acide carbonique sur les solutions des sels acides forts. *Annales de Chimie et de Physique*, **25**, 225–70.
- Shibue Y (1996) Empirical expressions of quartz solubility in H<sub>2</sub>O, H<sub>2</sub>O + CO<sub>2</sub>, and H<sub>2</sub>O + NaCl fluids. *Geochemical Journal*, **30**, 339–54.
- Shmulovich KI, Graham CM, Yardley BWD (2001) Quartz, albite and diopside solubilities in H<sub>2</sub>O-NaCl fluids at 0.5–0.9 GPa. *Contributions to Mineralogy and Petrology*, **141**, 95–108.
- Shmulovich KI, Yardley BWD, Graham CM (2006) The solubility of quartz in crustal fluids: experiments and general equations for salt solutions and H<sub>2</sub>O-CO<sub>2</sub> mixtures at 400–800 °C and 0.1–0.9 GPa. *Geofluids*, **7**, 1–17.
- Smit CA, Van Reenan DD (1997) Deep crustal shear zones, high-grade tectonites, and associated metasomatic alteration in the Limpopo Belt, South Africa. *Journal of Geology*, **105**, 37–58.
- Sommerfeld RA (1967) Quartz solution reaction: 400–500 °C, 1000 bars. *Journal of Geophysical Research*, **72**, 4253–57.
- Stern SM, Bodnar RJ (1989) Synthetic fluid inclusions: VII. Re-equilibration of fluid inclusions in quartz during laboratory simulated metamorphic burial and uplift. *Journal of Metamorphic Geology*, **7**, 243–60.
- Tanaka M, Takahashi K (1999) The identification of chemical species of silica in sodium hydroxide, potassium hydroxide and sodium chloride solutions by FAB-MS. *Analytical Sciences*, **15**, 1241–50.
- Touret JLR (1971) Le faciès granulite en Norvège Méridionale. *Lithos*, **4**, 239–249.
- Touret JLR (1985) Fluid regime in Southern Norway: the record of fluid inclusions. In: *The Deep Proterozoic Crust in the North Atlantic Provinces* (eds Tobi AC, Touret JLR), pp. 517–49. Reidel, Dordrecht.
- Touret JLR, Huizenga JM (1999) Precambrian intraplate magmatism: high temperature, low pressure crustal granulites. *Journal of African Earth Sciences*, **28**, 367–82.
- Tropper P, Manning CE (2004) Paragonite stability at 700 °C in the presence of H<sub>2</sub>O-NaCl fluids: constraints on H<sub>2</sub>O activity and implications for high-pressure metamorphism. *Contributions to Mineralogy and Petrology*, **147**, 740–9.
- Tropper P, Manning CE (2007) The solubility of fluorite in H<sub>2</sub>O and H<sub>2</sub>O-NaCl at 0.5–2 GPa, 600–1000 °C. *Chemical Geology*, **242**, 299–306.
- Van den Berg R, Huizenga JM (2001) Fluids in granulites of the Southern Marginal Zone of the Limpopo Belt, South Africa. *Contributions to Mineralogy and Petrology*, **141**, 529–45.
- Walther JV (2001) Experimental determination and analysis of the solubility of corundum in 0.1 and 0.5 m NaCl solutions between 400 and 600 °C from 0.5 to 2.0 kbar. *Geochimica et Cosmochimica Acta*, **65**, 2843–57.
- Walther JV, Orville PM (1983) The extraction-quench technique for determination of the thermodynamic properties of solute complexes: applications to quartz solubility in fluid mixtures. *American Mineralogist*, **68**, 731–41.
- Wannamaker PE, Caldwell TG, Doerner WM, Jiracek GR (2004) Fault zone fluids and seismicity in compressional and extensional environments inferred from electrical conductivity: the New Zealand southern Alps and US Great Basin. *Earth, Planets and Space*, **56**, 1171–76.
- Watson EB, Brenan JM (1987) Fluids in the lithosphere: 1. Experimentally-determined wetting characteristics of CO<sub>2</sub>-H<sub>2</sub>O fluids and their implications for fluid transport, host-rock physical properties and fluid inclusion formation. *Earth and Planetary Science Letters*, **85**, 497–515.
- Webster JD, Kinzler RJ, Mathez EA (1999) Chloride and water solubility in basalt and andesite liquids and implications for magmatic degassing. *Geochimica et Cosmochimica Acta*, **63**, 729–38.
- Weill DF, Fyfe WS (1964) The solubility of quartz in H<sub>2</sub>O in the range 1000–4000 bars and 400–500 °C. *Geochimica et Cosmochimica Acta*, **28**, 1243–55.
- Wickham SM, Janardhan AS, Stern RJ (1994) Regional carbonate alteration of the crust by mantle-derived magmatic fluids, Tamil-Nadu, south India. *Journal of Geology*, **102**, 379–98.
- Wykes JL, Newton RC, Manning CE (2008) Solubility of andradite, Ca<sub>3</sub>Fe<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>, in a 10 mol% NaCl solution at 800 °C and 10 kbar: Implications for the metasomatic origin of grandite garnet in calc-silicate granulites. *American Mineralogist*, **93**, 886–92.
- Xie Z, Walther JV (1993) Quartz solubilities in NaCl solutions with and without wollastonite at elevated temperatures and pressures. *Geochimica et Cosmochimica Acta*, **57**, 1947–55.
- Yardley BWD, Graham JT (2002) The origins of salinity in metamorphic fluids. *Geofluids*, **2**, 249–56.
- Yardley BWD, Valley JW (1997) The petrologic case for a dry lower crust. *Journal of Geophysical Research*, **102**, 173–85.
- Zotov N, Keppler H (2000) In-situ Raman spectra of dissolved silica species in aqueous fluids to 900 °C and 14 kbar. *American Mineralogist*, **85**, 600–4.
- Zotov N, Keppler H (2002) Silica speciation in aqueous fluids at high pressures and high temperatures. *Chemical Geology*, **184**, 71–82.