

# Evidence for SiO<sub>2</sub>-NaCl complexing in H<sub>2</sub>O-NaCl solutions at high pressure and temperature

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## ABSTRACT

Experimental studies reveal complex dissolution behavior of quartz in aqueous NaCl solutions at high temperature and pressure, involving variation from salting-in to salting-out that changes with temperature, pressure, and salt concentration. The behavior is not explainable by traditional electrostatic theory. An alternative hypothesis appeals to complexing of SiO<sub>2</sub> with NaCl and can explain the observations. However, the hypothesis of complexing, as previously applied, is inadequate in several respects: it neglects polymerization of solute silica, regards the SiO<sub>2</sub>-NaCl hybrid complex(es) as anhydrous, which seems unlikely, and invokes an incorrect stoichiometry of the hydrated silica monomer, now known to be Si(OH)<sub>4</sub>•2H<sub>2</sub>O. These neglected features can be incorporated into the complexing model in a revised formulation based on a simple thermodynamic analysis using existing quartz solubility data. The analysis leads to a quasi-ideal solution model with silica monomers, dimers, and two distinct hydrous SiO<sub>2</sub>-NaCl hybrid complexes with overall NaCl:H<sub>2</sub>O = 1:6, one Na-bearing and one Cl-bearing. Their (equal) molar concentrations ( $X_{hc}$ ) are governed by a pressure- and temperature-dependent equilibrium constant,  $K_{hc} = X_{hc}^2 / (a_{NaCl} a_{H_2O}^6)$ , where  $a_{NaCl}$  and  $a_{H_2O}$  are the respective activities of the solvent components. The stability of the hybrid complexes (i.e., their concentration) is very sensitive to H<sub>2</sub>O activity. The entire set of experimental quartz-solubility data at 700°C, 1–15 kbar, is reproduced with high fidelity by the expression  $\log K_{hc} = -4.585 + 0.2691P - 2.023 \times 10^{-3}P^2$  ( $P$  is pressure in kbar), including the transition from low-pressure salting-in to high pressure salting-out. The results indicate that hybrid SiO<sub>2</sub>-NaCl complexes are the main hosts for dissolved silica at NaCl concentrations greater than 6 wt%, which are likely common in crustal fluids. At higher temperatures, approaching the critical end point in the system SiO<sub>2</sub>-H<sub>2</sub>O, the model becomes progressively inaccurate, probably because polymers higher than the dimer become significant as SiO<sub>2</sub> concentration increases.

Key words: aqueous geochemistry, brines, crustal fluids, quartz solubility, thermodynamic models

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## INTRODUCTION

Silica is a major solute in crustal fluids, but its concentration depends strongly on fluid composition. At quartz saturation, silica solubility in H<sub>2</sub>O increases strongly with rising temperature ( $T$ ) and pressure ( $P$ ) (Kennedy 1950; Morey & Hesselgesser 1951; Wyart & Sabatier 1955; Khitarov 1956; Kennedy *et al.* 1962; Weill & Fyfe 1964; Anderson & Burnham 1965; Hemley *et al.* 1980; Walther & Orville 1983; Manning 1994; Newton & Manning 2008; Hunt & Manning 2012). At fixed  $P$  and  $T$ , addition of CO<sub>2</sub> causes solubility to decline (Novgorodov 1975,

1977; Walther & Orville 1983; Newton & Manning 2000, 2009). However, more complex behavior is observed in alkali- or alkaline-earth halides. For example, in H<sub>2</sub>O-NaCl solutions at low  $P$  and moderate to high  $T$ , quartz solubility initially increases as NaCl is added to H<sub>2</sub>O (i.e., silica ‘salts in’) (Fournier *et al.* 1982; Saccocia & Seyfried 1990; Xie & Walther 1993; Newton & Manning 2000; Shmulovich *et al.* 2006). A maximum is reached at an intermediate NaCl mole fraction ( $X_{NaCl}$ ), and then solubility declines (silica ‘salts out’). The extent of the initial salting-in diminishes as  $P$  increases, until at high  $P$ , quartz solubility declines exponentially with rising  $X_{NaCl}$ . In other

halide solutions, intriguing variations exist: CaCl<sub>2</sub> solutions show no quartz solubility enhancement at any  $P$ , whereas CsCl solutions show initial enhancement followed by salting-out at high salinity at all  $P$  up to 9 kbar (Shmulovich *et al.* 2006). The behavior of quartz solubility in H<sub>2</sub>O-salt solutions has defied clear theoretical understanding, which limits our ability to develop robust thermodynamic models for the transport of one of the most important solutes in crustal fluids.

Two general approaches have been used to model quartz solubility in salt solutions. The first is based on Setchénov's (1892) treatment of the solubility of organic compounds in salty fluids (Shmulovich *et al.* 2006). The other emphasizes reactions of quartz with solvent constituents to form soluble SiO<sub>2</sub>-NaCl-(H<sub>2</sub>O) complexes (Evans 2007). Comparison and critique of the merits and shortcomings of these approaches are given in Newton & Manning (2010).

The Setchénov-type formulation provides a mathematically useful description of the experimental data, but is lacking in theoretical underpinnings. In particular, there is no input of pertinent thermodynamic properties such as standard-state properties or measured activities of H<sub>2</sub>O and saline components, data which exist for NaCl and KCl solutions. The latter restriction ignores the fact that the  $P$ -induced transition from salting-in to salting-out coincides with the  $P$ -induced decrease in H<sub>2</sub>O activity at about 4 kbar, attributed to the ionization of NaCl (Aranovich & Newton 1996). This change in the solvent would be expected to have a major effect on the solubility of minerals. Also, the formulation gives no account of speciation or polymerization of solute SiO<sub>2</sub>.

The alternative approach of Evans (2007) is based on solute-solvent interaction and provides a more intuitive basis for understanding quartz solubility behavior. In her model, quartz solubility is governed by a set of homogeneous and heterogeneous equilibria involving quartz and aqueous species. A key feature is the formation of one or more hybrid SiO<sub>2</sub>-NaCl complexes of the general form SiO<sub>2</sub>· $x$ NaCl· $y$ H<sub>2</sub>O. If such a solvent-solute interaction governs quartz dissolution in H<sub>2</sub>O-NaCl solutions, then  $P$ -induced changes in the activities of the solvent components, such as the rather sudden decreases in H<sub>2</sub>O and NaCl activities near 4 kbar (Aranovich & Newton 1996), would affect the stability of the hybrid complex(es) and therefore might account for the pattern of quartz solubility as a function of  $P$ ,  $T$ , and NaCl mole fraction. Evans (2007) was able to fit Newton & Manning's (2000) quartz solubility data reasonably well over a broad range of  $P$  and  $T$  with suitable choices of the coefficients  $x$  and  $y$ ; she chose the proportions  $x = 1/2$  and  $y = 0$  for a single hybrid complex, with the SiO<sub>2</sub> species in the NaCl-free system assumed to consist entirely of Si(OH)<sub>4</sub>·1H<sub>2</sub>O.

The formulation of Evans (2007) is advantageous due to its flexibility and rigorous formalism. However, for convenience in developing her model, Evans (2007) neglected silica polymerization and assumed that any hybrid complex was anhydrous. In addition, the stoichiometry of H<sub>2</sub>O solvation of the silica monomer is now known to be constant at Si(OH)<sub>4</sub>·2H<sub>2</sub>O over a wide range of  $P$  and  $T$  (Newton & Manning 2009). The purpose of the present work is to show that these neglected features can be incorporated into an Evans-type model using existing quartz solubility data and that they lead to a more comprehensive description of quartz solubility in NaCl-H<sub>2</sub>O solutions at high  $T$  and  $P$ , with consistent definition of possible solute species.

## THE MODEL

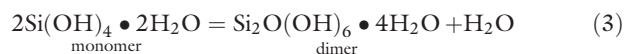
Over a range of crustal  $P$  and  $T$ , the silica monomer in H<sub>2</sub>O has the stoichiometry Si(OH)<sub>4</sub>·2H<sub>2</sub>O (Walther & Orville 1983; Newton & Manning 2009). The concentration of the monomer in quartz-saturated solutions of decreasing H<sub>2</sub>O activity is controlled by the reaction:



with an equilibrium constant:

$$K_{qm} = \frac{a_m}{a_{\text{H}_2\text{O}}^4} \quad (2)$$

where the subscripts  $q$  and  $m$  denote quartz and the monomer, and  $a_m$  and  $a_{\text{H}_2\text{O}}$  are, respectively, the activities of the monomer and H<sub>2</sub>O. With increasing concentration of SiO<sub>2</sub>, increasing amounts of the silica dimer are produced:



with an equilibrium constant:

$$K_{md} = \frac{a_d a_{\text{H}_2\text{O}}}{a_m^2} \quad (4)$$

where the subscript  $d$  denotes the dimer. Newton & Manning (2002, 2003, 2010) used SiO<sub>2</sub> solubility measurements on various silica-buffering assemblages to show that the activities of the monomer and dimer in H<sub>2</sub>O can be replaced by their mole fractions with a high degree of consistency; that is, these species mix ideally in H<sub>2</sub>O. They formulated  $K_{md}$  as:

$$\log K_{md} = 1.480 + 0.0012T + (0.000119T - 0.1685)P \quad (5)$$

where  $T$  is in Kelvin and  $P$  is in kbar. Equations 1–5 demonstrate that any assessment of the importance of hybrid SiO<sub>2</sub>-NaCl complexes must account for the silica hydration number and polymerization.

We postulate that there exists in H<sub>2</sub>O-NaCl solutions at elevated  $T$  and  $P$  some species of silica complexed with the solvent components. The postulated complexes coexist with the hydrous silica species (Newton & Manning 2002, 2003, 2009) and could account for the salting-in behavior of quartz solubility in the low pressure range. We also hope to explain the relationship that must exist between the sudden pressure-induced decrease in the activities of NaCl and H<sub>2</sub>O that occurs near 0.4 GPa (Aranovich & Newton 1996), and the equally sudden transition from salting-in to salting-out of quartz solubility that occurs in the same pressure range (Newton & Manning 2000). Following Evans (2007), the solute complexes are formed by the reaction:



This general type of reaction has been used to model the solubilities of several different minerals in NaCl solutions at elevated  $T$  and  $P$ , especially for those minerals that show solubility enhancement by the presence of NaCl (Newton & Manning 2010, and references therein).

Assuming that the ideal solution relation used for the silica polymers holds for the hybrid complexes also, there exists an equilibrium constant  $K_{\text{hc}}$  for Eq. 6 involving the concentration of hybrid complexes ( $X_{\text{hc}}$ ):

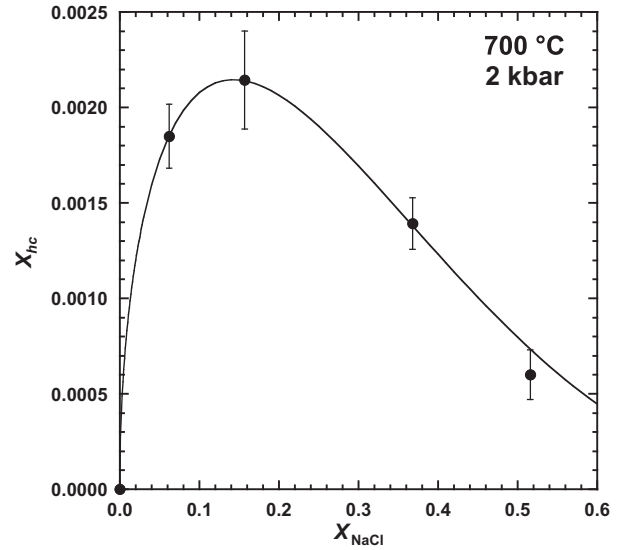
$$K_{\text{hc}} = \frac{X_{\text{hc}}^n}{a_{\text{NaCl}}^x a_{\text{H}_2\text{O}}^y} \quad (7)$$

$K_{\text{hc}}$  depends on  $T$  and  $P$  but not on the concentration factors.

The contribution of the postulated hybrid species to the total silica concentration, irrespective of the stoichiometric number of Si they contain, is given by

$$X_s = X_{\text{hc}} + X_m + 2X_d \quad (8)$$

where  $X_s$  is the total molar silica concentration, and  $X_m$  and  $X_d$  are the respective monomer and dimer concentrations. Note that Eq. 8 is applicable only where the concentration of higher Si polymers (trimers, etc.) is negligible. Figure 1 shows the concentration of the hybrid species at 0.2 GPa and 700°C. At these conditions, the activities of H<sub>2</sub>O and NaCl are indistinguishable from their mole fractions,  $X_{\text{H}_2\text{O}}$  and  $X_{\text{NaCl}}$  (Aranovich & Newton 1996), and the NaCl is inferred to exist in solution as undissociated molecules. It is evident from Fig. 1 that the solute complex(es) must be substantially hydrous, as there is strong control on the concentration by H<sub>2</sub>O activity. The location of the solute maximum, near 15 mol%, suggests that the overall NaCl:H<sub>2</sub>O molar ratio of the complexes is 1:6 (Newton & Manning 2010). With increasing salinity, the mole fraction of hybrid complexes drops off sharply, reflecting the strong dependence on H<sub>2</sub>O activity.



**Fig. 1.** Mole fraction of silica in the form of hybrid complex(es) ( $X_{\text{hc}}$ ) formed by quartz dissolution in H<sub>2</sub>O-NaCl fluids at 700°C and 2 kbar, as a function of NaCl mole fraction. Data points derived from experimental data of Newton & Manning (2000) and Eq. 8, text. Curve is calculated with Eq. 7, text, assuming  $n = 2$ . Error bars reflect  $1\sigma$  errors in  $X_s$ ,  $K_{\text{md}}$  and  $a_{\text{H}_2\text{O}}$  and were derived as follows:  $\sigma(a_{\text{H}_2\text{O}})$  was set to 0.010 for all salinities (Aranovich & Newton 1996),  $\sigma(X_s)$  was taken from solubility determinations of Newton & Manning (2000), and  $\sigma(K_{\text{md}})$  was derived from the average uncertainty in calculated  $\log K_{\text{md}}$  of 7.0% (Newton & Manning 2002), which is larger than the 4.4% difference between fitted and derived  $\log K_{\text{md}}$  values using Eq. 4.

**Table 1** Correlation coefficients ( $R^2$ ) of fits for various combinations of the constants  $y$  and  $n$  at  $x = 1$  in Eq. 7.

$n$	$y = 5$	6	7	8
1	0.902	0.762	0.499	0.209
2	0.922	0.998	0.960	0.810
3	0.902	0.949	0.957	0.910

Data source: 2 kbar, 700°C data of Newton & Manning (2000).

Assuming that mixing of SiO<sub>2</sub> species, H<sub>2</sub>O, and NaCl molecules is ideal and that solute species possess integer stoichiometry, the values of the coefficients  $x$ ,  $y$ , and  $n$  may be estimated by plotting the numerator of Eq. 7 against the denominator, with trial combinations of integers, and searching for the highest straight-line correlation indicating closest approach to a constant value of  $K_{\text{hc}}$ . As we are interested mainly in the ratios of the integers, we may take  $x$ , the overall stoichiometric coefficient of NaCl in the complex(es), to be unity. Table 1 shows the correlation factor  $R^2$  for various combinations of  $y$  and  $n$ . It is observed that the correlation is very high for the combination  $y = 6$ ,  $n = 2$ , and poor to nonexistent for all other plausible combinations. The high degree of consistency of this model with the experimental data is shown in Figs 1

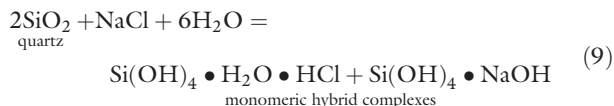
and 2. This result is strong evidence in favor of dissociation of NaCl in the complexing process. Presumably, two hydrous SiO<sub>2</sub> complexes are formed, one with Na and one with Cl.

The predicted contributions of the monomer, dimer, and the hybrid complex(es) to the total dissolved silica are shown in Fig. 3. Hybrid complexes become predominant at  $X_{\text{NaCl}} > 0.02$ . That is, the hybrid SiO<sub>2</sub>-NaCl complex(es) will be the main host for dissolved silica at all dissolved NaCl concentrations greater than about 6 wt%. This is relatively modest salinity that is common in crustal fluids at elevated *P-T* conditions (Yardley & Graham 2002).

## IDENTIFICATION OF THE HYBRID COMPLEXES

Even if mixing is not strictly ideal, the relationships in Fig. 2 still strongly imply that there are two hybrid complexes formed for every NaCl reacted, which is indeed the ratio preferred by Evans (2007). This result is also consistent with the neutral pH observed in quench fluids (Newton & Manning 2006) because it is likely that any HCl and NaOH liberated during the quenching process will maintain acid-base neutrality.

If fractional molecules are avoided, the derived values of *y* and *n* would seem to mean that the NaCl must dissociate in the reaction to form one silica species with Na and one with Cl. Assuming neutral monomeric complexes, a reaction which satisfies these conditions is:



The HCl in one complex is postulated to play the same energetic role as a H<sub>2</sub>O molecule; the other hybrid complex is some very soluble Na silicate. While Eq. 9 is the simplest equilibrium that can be written, it is not unique. For example, two monovalent species of opposite charge, for example  $\text{Si(OH)}_4 \bullet \text{H}_2\text{NaO}^+$  and  $\text{Si(OH)}_4 \bullet \text{H}_2\text{ClO}^-$ , could maintain overall electrical neutrality. An alternative dissolution reaction proposed by Anderson & Burnham (1967) for quartz solubility experiments in KCl-H<sub>2</sub>O would generate two solute species for each KCl reacted, an alkali silicate, and HCl. This reaction would yield strongly acidic quenched fluids, which seems unlikely in view of the results for NaCl-H<sub>2</sub>O. Regardless of the identities of the hybrid species, it should be emphasized that the values of *x*, *y*, and *n* implied by the solubility data must be satisfied.

## EXTENSION TO HIGHER AND LOWER PRESSURES

The quartz solubility data at 700°C and higher pressures may be analyzed by the same methods. There is ambiguity regarding the mole fractions of species as NaCl begins to dissociate with increasing pressure. Following Evans (2007), we take mole fractions among all molecules and ions, so that the mole fractions depend on the degree of dissociation of NaCl. The activity-concentration relations

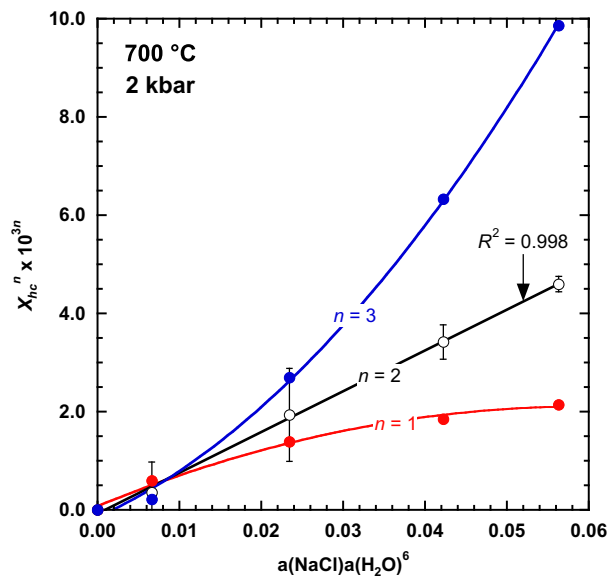


Fig. 2. Plot of Eq. 7, text, from quartz solubility data of Newton & Manning (2000) at 700°C and 2 kbar, assuming  $n = 1, 2,$  and  $3$ . The model most consistent with an equilibrium constant,  $K_{\text{hc}}$ , in Eq. 7 should yield a straight line through the origin and is seen to be the model corresponding to  $n = 2$ , or double dissociation of NaCl in forming hybrid complexes.  $1\sigma$  errors propagated as described in Fig. 1, caption.

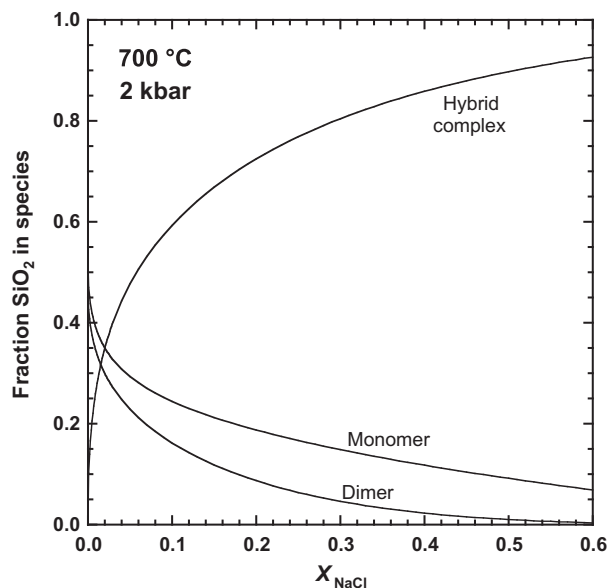


Fig. 3. Contributions of monomer ( $X_m$ ), dimer ( $X_d$ ), and hybrid complex(es) ( $X_{\text{hc}}$ ) to the total dissolved silica in H<sub>2</sub>O-NaCl solutions at 700°C and 2 kbar in the presence of quartz.

of Aranovich & Newton (1996) give, to a first approximation, the degree of dissociation of NaCl, modeled by the parameter  $\alpha$ , in the solutions:

$$a_{\text{H}_2\text{O}} = \frac{X_{\text{H}_2\text{O}}}{1 + \alpha X_{\text{NaCl}}} \quad (10)$$

$$a_{\text{NaCl}} = \left( \frac{(1 + \alpha) X_{\text{NaCl}}}{1 + \alpha X_{\text{NaCl}}} \right)^{(1 + \alpha)}$$

If there were ideal mixing among H<sub>2</sub>O, undissociated NaCl, Na<sup>+</sup> and Cl<sup>-</sup>, the dissociation parameter  $\alpha$  should run from zero for undissociated NaCl to unity for complete dissociation. In fact, Aranovich & Newton (1996) found that  $\alpha$  becomes larger than unity at  $P > 1.0$  GPa, exceeding the theoretical limit for complete dissociation. This is a defect of the Aranovich & Newton (1996) theoretical treatment of their activity–concentration measurements, according to which the dissociation factor,  $\alpha$ , is a function of only  $P$  and  $T$ , but not salinity. In the present discussion, the dissociation factor is, for purposes of calculating mole fractions, limited to the range  $1 \geq \alpha \geq 0$ , although, in order to reproduce the activity data correctly,  $\alpha$  has to be 1.22 at 10 kbar and 1.49 at 15 kbar. In spite of this inconsistency, the formulation of  $K_{\text{hc}}$  in Eq. 9 with  $n = 2$ ,  $x = 1$ ,  $y = 6$  appears to work well with the solubility data of Newton & Manning (2000), as shown in Fig. 4. The model reproduces the data of Newton & Manning (2000) to within 5% relative at 2–15 kbar and from pure H<sub>2</sub>O to halite saturation.

Values of  $K_{\text{hc}}$  increase with rising  $P$  at 700°C. A quadratic fit to calculated  $\log K_{\text{hc}}$  values yields

$$\log K_{\text{hc}} = -4.585 + 0.2691P - 2.023 \times 10^{-3}P^2 \quad (11)$$

( $P$  in kbar,  $R^2 = 0.9998$ ), shown in Fig. 5. The model predicts that at constant  $X_{\text{NaCl}}$  and quartz saturation, the fraction of dissolved silica in hybrid complexes ( $F_{\text{hc}}$ ) decreases with increasing  $P$  at low  $X_{\text{NaCl}}$ ; however, at high  $X_{\text{NaCl}}$ ,  $F_{\text{hc}}$  is roughly independent of  $P$  over the investigated range. As expected,  $F_{\text{hc}}$  increases with  $X_{\text{NaCl}}$  at all  $P$ .

A test of the extrapolability of the model may be made with reference to the data of Xie & Walther (1993) at 1 kbar and low salinity. Their data in the range 425–575°C and  $m_{\text{NaCl}} = 0.83$  ( $X_{\text{NaCl}} = 0.0147$ ) were extrapolated with small uncertainty to 700°C by a least-squares fit of  $\log m_{\text{SiO}_2}$  versus  $1/T$  (Fig. 6), yielding  $X_s = 0.00152$  under these conditions. Extrapolating our trend of  $\log K_{\text{hc}}$  versus  $P$  at 700°C in Fig. 5 to 1 kbar yields  $X_s = 0.00148$  at  $m_{\text{NaCl}} = 0.83$ , in nearly perfect agreement with extrapolation of the Xie & Walther (1993) data.

Several features are of interest in the model results presented in Fig. 4. The 1 kbar quartz solubilities are predicted to flatten out and become nearly invariant over a wide range of salt concentration,  $0.05 < X_{\text{NaCl}} < 0.30$ .

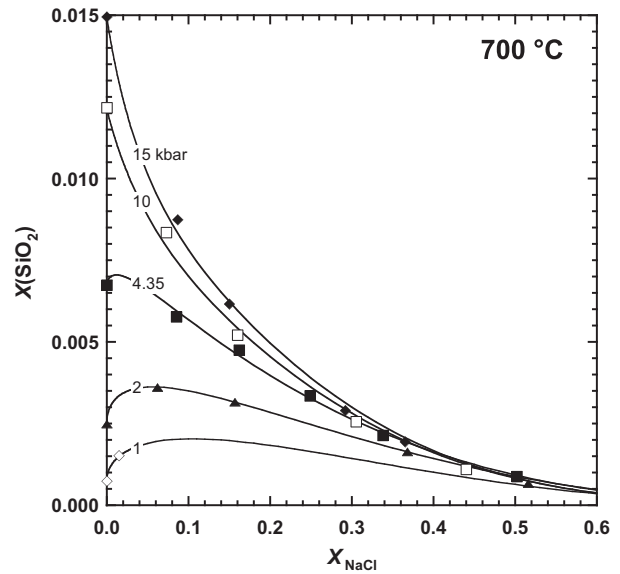


Fig. 4. Model quartz solubility curves assuming hybrid complexes composed of 6 H<sub>2</sub>O and one dissociated NaCl ( $n = 2$ ) for each two SiO<sub>2</sub> dissolved. Each curve involves only a single adjustable parameter, the equilibrium constant  $K_{\text{hc}}$  (see text). Experimental data points are from Newton & Manning (2000). The 1 kbar curve is an extrapolation from the higher  $P$  trends and is supported by the experimental solubility data of Xie & Walther (1993).

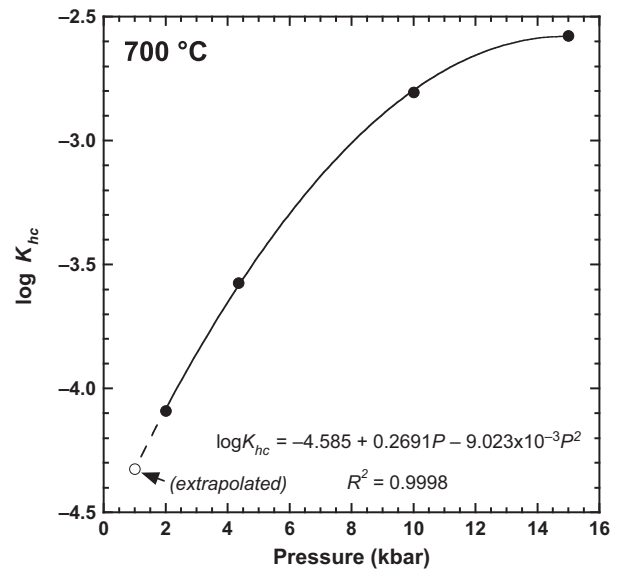


Fig. 5. Trend of the equilibrium constant for formation of the hybrid complexes in equilibrium with quartz (Eq. 11, text). The curve assumes that  $n = 2$ ; that is, that two complexes are formed for each NaCl reacted. A short extrapolation to 1 kbar is made with the quadratic fit in  $X_{\text{NaCl}}$ .

This behavior is testable by further solubility experiments. It seems doubtful that the high SiO<sub>2</sub> solubility in a fused salt-like mixture of 50 wt. % NaCl could be simply the

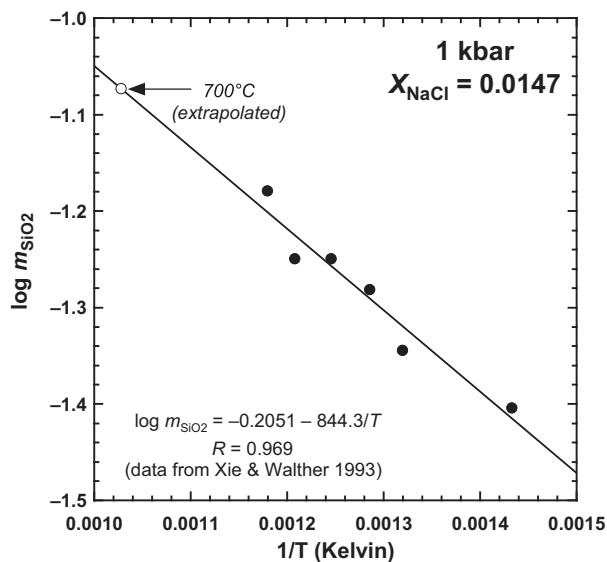


Fig. 6. The extrapolation of Xie & Walther's (1993) quartz solubility data at 1 kbar and constant salinity ( $m_{\text{NaCl}} = 0.83$ ), to estimate a solubility at 700°C. The extrapolated solubility agrees closely with that predicted by the present model.

result of electrostatic modification of the H<sub>2</sub>O component, as Xie & Walther (1993) attempted to show for their data at low salinity; rather, it implies a substantial reaction with the solvent resulting in stable hybrid species. The trend at 4.35 kbar is predicted to have a very small maximum at low salinity, although the experimental data are not sufficient to show this. The twenty-parameter numerical fit to all of the experimental data of Newton & Manning (2000) does, in fact, yield a small maximum at 4 kbar and 700°C (their Fig. 5a). The solubility curves converge strongly at high salinity such that, at  $X_{\text{NaCl}} > 0.4$ , there is little  $P$  effect on the SiO<sub>2</sub> solubility. Finally, the higher  $P$  fits are better if the low salinity points are omitted from the regressions. This is to be expected because such fluids are highly ionized so that the assumption of ideal mixing may be inappropriate, and/or because more extensive polymerization of the hybrid complexes is likely at high SiO<sub>2</sub> concentration.

The latter point is illustrated at 800°C and 10 kbar, where Newton & Manning (2000) have the most comprehensive coverage (Fig. 7). The fit is acceptable if all of the solubility data are included in the regression, but if the low-salinity data are excluded, the fit to the rest of the data is much better (Fig. 7). Again, this behavior probably reflects the inadequacy of the model at high SiO<sub>2</sub> concentrations. At 850 and 900°C and 10 kbar, no good correlations could be made using  $n = 2$ ,  $x = 1$ , and  $y = 6$ . This is likely a consequence of more extensive polymerization of silica species at the higher concentrations characteristic of these conditions (Cruz & Manning 2015).

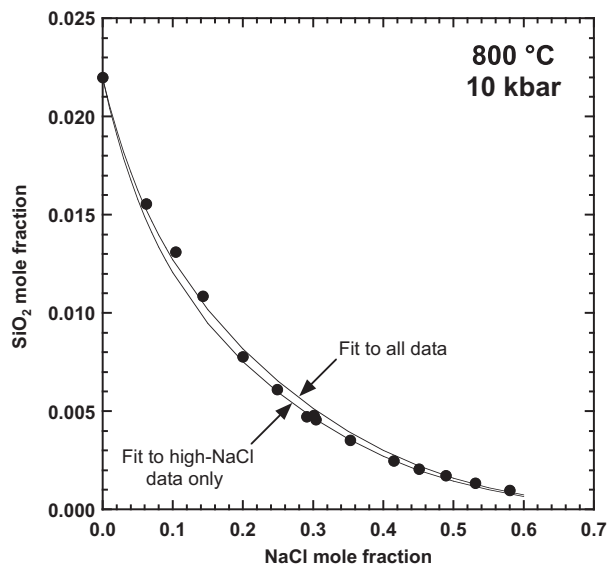


Fig. 7. Test of the quartz dissolution model at 800°C and 10 kbar with the experimental data of Newton & Manning (2000). The model with  $n = 2$  gives a reasonable fit when all of the data are regressed, but fits the solubility data at high salinity better. This probably means that the model is less valid for solutions of high SiO<sub>2</sub> and high H<sub>2</sub>O mole fraction, indicating that the fused salt-like ideal solution model fails at low salinity, that polymers higher than the dimer become important or that the hybrid complexes are polymerized at high concentration.

## CONCLUSIONS

The present analysis improves on the treatment of Evans (2007) by adopting an updated silica hydration number, using measured values of the activities of H<sub>2</sub>O and NaCl as input, and by allowing for polymerization of the silica and the possibility of hydrous solute species. The analysis shows that the concept of hybrid SiO<sub>2</sub>-NaCl-H<sub>2</sub>O complexes leads to a natural interpretation of the salting-in to salting-out transition with increasing salinity at low pressure, and also the lapse of the salting-in effect at pressures above about 4 kbar, where ionization of aqueous NaCl becomes important. The inferred hybrid complexes must be substantially hydrous. Assuming a quasi-ideal solution model of SiO<sub>2</sub> complexes, H<sub>2</sub>O molecules, and undissociated NaCl molecules at low pressure, the solubility data strongly favor a model in which two complexes are formed for each NaCl reacted, one complex Na-bearing and the other Cl-bearing. The inference of separate Na-silica and Cl-silica complexes is upheld by the observed pH neutrality of quenched solutions in NaCl-H<sub>2</sub>O quartz solubility experiments (Newton & Manning 2006). With increasing temperature, pressure, and SiO<sub>2</sub> concentration, which becomes very high at low salinity, the simple mixing model becomes inadequate, indicating that mixing mole fractions and activities are uncertain because of NaCl dissociation

and/or polymerization of SiO<sub>2</sub>, possibly including the hybrid complexes.

## ACKNOWLEDGEMENTS

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## REFERENCES

- Anderson GM, Burnham CW (1965) The solubility of quartz in supercritical water. *American Journal of Science*, **263**, 494–511.
- Anderson GM, Burnham CW (1967) Reactions of quartz and corundum with aqueous chloride and hydroxide solutions at high temperatures and pressures. *American Journal of Science*, **265**, 12–27.
- 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.
- Cruz MF, Manning CE (2015) Experimental determination of quartz solubility and melting in the system SiO<sub>2</sub>-H<sub>2</sub>O-NaCl at 15–20 kbar and 900–1100°C: implications for silica polymerization and formation of supercritical fluids. *Contributions to Mineralogy and Petrology*, **170**, 35.
- Evans K (2007) Quartz solubility in salt-bearing solutions at pressures to 1 GPa and temperatures to 900°C. *Geofluids*, **7**, 451–67.
- Fournier RO, Rosenbauer RJ, Bischoff JL (1982) The solubility of quartz in aqueous sodium chloride solution at 350°C and 180 to 500 bars. *Geochimica et Cosmochimica Acta*, **46**, 1975–8.
- Hemley JJ, Montoya JW, Marineko JW, Luce RW (1980) Equilibria in the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O and some general implications for alteration/mineralization processes. *Economic Geology*, **75**, 210–28.
- Hunt JD, Manning CE (2012) A thermodynamic model for the system SiO<sub>2</sub>-H<sub>2</sub>O near the upper critical end point based on quartz solubility experiments at 500–1100°C and 5–20 kbar. *Geochimica et Cosmochimica Acta*, **86**, 196–213.
- Kennedy GC (1950) A portion of the system silica-water. *Economic Geology*, **45**, 629–53.
- Kennedy GC, Wasserburg GJ, Heard HC, Newton RC (1962) The upper three-phase region in the system SiO<sub>2</sub>-H<sub>2</sub>O. *American Journal of Science*, **260**, 501–21.
- Khitarov NI (1956) The 400°C isotherm for the system H<sub>2</sub>O-SiO<sub>2</sub> at pressures up to 2,000 kg/cm<sup>2</sup>. *Geochemistry*, **1956**, 55–61.
- Manning CE (1994) The solubility of quartz in H<sub>2</sub>O in the lower crust and upper mantle. *Geochimica et Cosmochimica Acta*, **58**, 4831–9.
- Morey GW, Hesselgesser JM (1951) The solubility of some minerals in superheated steam at high pressures. *Economic Geology*, **46**, 821–35.
- Newton RC, Manning CE (2000) Quartz solubility in H<sub>2</sub>O-NaCl and H<sub>2</sub>O-CO<sub>2</sub> solutions at deep crust-upper mantle pressures and temperatures: 2–15 kbar and 500–900°C. *Geochimica et Cosmochimica Acta*, **64**, 1993–3005.
- Newton RC, Manning CE (2002) Solubility of silica in equilibrium with enstatite, forsterite, and H<sub>2</sub>O at deep crust/upper mantle pressures and temperatures and an activity-concentration model for polymerization of aqueous silica. *Geochimica et Cosmochimica Acta*, **66**, 4165–76.
- Newton RC, Manning CE (2003) Activity coefficient and polymerization of aqueous silica at 800°C, 12 kbar, from solubility measurements on SiO<sub>2</sub>-buffering mineral assemblages. *Contributions to Mineralogy and Petrology*, **146**, 135–43.
- Newton RC, Manning CE (2006) Solubilities of corundum, wollastonite and quartz in H<sub>2</sub>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 (2008) Thermodynamics of SiO<sub>2</sub>-H<sub>2</sub>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 (2009) Hydration state and activity of aqueous silica in H<sub>2</sub>O-CO<sub>2</sub> fluids at high pressure and temperature. *American Mineralogist*, **94**, 1287–90.
- Newton RC, Manning CE (2010) Role of saline fluids in deep-crustal and upper-mantle metasomatism: insights from experimental studies. *Geofluids*, **10**, 58–72.
- Novgorodov PG (1975) Solubility of quartz in H<sub>2</sub>O-CO<sub>2</sub> mixtures at 700°C and pressures of 3 and 5 kbar. *Geochemistry International*, **12**, 122–6.
- Novgorodov PG (1977) On the solubility of quartz in H<sub>2</sub>O + CO<sub>2</sub> and H<sub>2</sub>O + NaCl at 700°C and 1.5 kb pressure. *Geochemistry International*, **14**, 191–3.
- Saccoccia PJ, Seyfried WE (1990) Talc-quartz equilibria and the stability of magnesium chloride complexes in NaCl-MgCl<sub>2</sub> solutions at 300, 350, and 400°C, 500 bars. *Geochimica et Cosmochimica Acta*, **54**, 3283–94.
- Setchénow M (1892) Action de l'acide carbonique sur les solutions des sels forts. *Annales de Chimie et de Physique*, **25**, 225–70.
- Shmulovich KI, Yardley BWD, Graham CM (2006) 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*, **6**, 154–67.
- Walther JV, Orville PM (1983) The extraction-quench technique for determination of the thermodynamic properties of solute complexes: application to quartz solubility in fluid mixtures. *American Mineralogist*, **68**, 731–41.
- Weill DF, Fyfe WS (1964) The solubility of quartz in H<sub>2</sub>O in the range 1000–4000 bars and 400–550°C. *Geochimica et Cosmochimica Acta*, **28**, 1243–55.
- Wyart J, Sabatier G (1955) Nouvelles mesures de la solubilité du quartz, de la tridymite et de la cristobalite dans l'eau sous pression au-dessus de la température critique. *Académie des Sciences, Comptes Rendus*, **240**, 1905–7.
- 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.

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