Implications of the redissociation phenomenon for mineral-buffered fluids and aqueous species transport at elevated temperatures and pressures

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Abstract

Aqueous species equilibrium constants and activity models form the foundation of the complex speciation codes used to model the geochemistry of geothermal energy production, extremophilic ecosystems, ore deposition, and a variety of other processes. Recently, researchers have shown that a simple three species model (i.e., Na^+ , Cl^- , and NaCl(aq)) can accurately describe conductivity measurements of concentrated NaCl and KCl solutions at elevated temperatures and pressures (Sharygin et al., 2002). In this model, activity coefficients of the charged species (e.g., Na^+ , K^+ , Cl^-) become sufficiently low that the complexes must redissociate with increasing salt concentration in order to meet equilibrium constant constraints. Redissociation decreases the proportion of the elements bound up as neutral complexes, and thereby increases the true ionic strength of the solution. In this contribution, we explore the consequences of the redissociation phenomenon in albite-paragonite-quartz (APQ) buffered systems. We focus on the implications of the redissociation phenomenon on mineral solubilities, particularly the observation that, at certain temperatures and pressures, calculated *activities* of charged ions in solution remain practically constant even as element *concentrations* increase from <1 molal to 4.5 molal. Finally, we note that redissociation has a similar effect on pH, and therefore aqueous speciation, in APQ-hosted systems. The calculations and discussion presented here are not limited to APQ-hosted systems, but additionally apply to many others in which the dominant cations and anions can form neutral complexes.

1. Motivation

High-temperature hydrothermal systems embody many scientifically, societally, and economically important processes. These systems can host a variety of extremophilic organisms (Jørgensen and Boetius, 2007); are proposed to be exploited for both CO_2 - and water-based geothermal energy (Barbier, 2002; Fridleifsson and Elders, 2005; Pruess, 2006; Randolph and Saar, 2011); and

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concentrate significant amounts of valuable metals (Simmons and Browne, 2000; Yardley, 2005; Williams-Jones and Heinrich, 2005; Williams-Jones et al., 2012). The aqueous fluids involved in these processes generally contain chlorine as their dominant anion, and many common cations tend to form charged and/or neutral complexes with chlorine at elevated temperatures and pressures. Because cation-chloride complexing tends to increase the solubility of minerals and elements in geological fluids, it is one of the most fundamental processes controlling mass transfer in high temperature hydrothermal systems (e.g., Helgeson, 1964; Quist and Marshall, 1968; Helgeson, 1969; Gunter and Eugster, 1980; Helgeson, 1992; Sverjensky et al., 1997; Ho et al., 1994; Ho and Palmer, 1997; Ho et al., 2001; Yardley and Bodnar, 2014, and sources therein).

One of the most striking examples of the importance of cation-chloride complexing in geologic systems is the control that complex formation exerts on solution pH. Measurements of in situ pH in seafloor hydrothermal vents on the Juan de Fuca Ridge and East Pacific Rise indicate “near-neutral” values of 4.35-5.4, but measurements of the pH of these fluids at ambient temperatures indicate much more acidic fluids, in the range of 3.2-3.9 (Ding et al., 2005). The difference between these in situ and ambient values (up to 2 orders of magnitude in the activity of H^+) can be attributed almost entirely to the complete dissociation of the $HCl(aq)$ complex at ambient temperature. The fact that the in situ values are only weakly acidic places constraints on mineral solubilities and elemental speciation and fluxes through these systems. In turn, these effects play a role in the formation of ore deposits (Reed, 1997; Yardley and Bodnar, 2014) and development of diverse, geologically-fueled ecosystems (Jørgensen and Boetius, 2007).

2. Background

2.1. Ionic strength and cation-chloride complexing

Because of their ability to regulate mineral and gas solubility and transport processes in a wide range of geological solutions, the association constants of certain chloride complexes (e.g., $NaCl$, KCl , HCl) and their activity coefficients and those of their constituent ions have been extensively studied (Quist and Marshall, 1968; Helgeson, 1969; Helgeson et al., 1981; Frantz and Marshall, 1984; Pitzer and Pabalan, 1986; Pabalan and Pitzer, 1987; Sverjensky et al., 1991; Archer, 1992; Oelkers and Helgeson, 1993a,b; Pokrovskii and Helgeson, 1997; Ho and Palmer, 1997; Tagirov et al., 1997; Pokrovskii, 1999; Ho et al., 2001; Sharygin et al., 2002; Zimmerman et al., 2012; Tutolo

et al., 2014). Commonly, chloride complex association constants are obtained using conductance measurements in static or flow-through cells (e.g., Quist and Marshall, 1968; Frantz and Marshall, 1984; Ho and Palmer, 1997; Ho et al., 2001; Sharygin et al., 2002; Zimmerman et al., 2012), although some researchers have attempted to use mineral-fluid equilibria to extract association constants and activity coefficients from supercritical solutions (e.g., Frantz and Popp, 1979; Gunter and Eugster, 1978; Popp and Frantz, 1979, 1980; Sverjensky et al., 1991; Xie and Walther, 1993; Aranovich and Newton, 1996, 1997; Walther, 1997; Tutolo et al., 2014). Overall, measurements and calculations indicate substantial association of the chloride complexes at elevated temperature, although the degree to which these complexes form is dependent upon the temperature and pressure and concentration of the solution.

Ionic strength is the measure of the amount of charged solutes dissolved in a solvent. There are two methods for calculating ionic strength: “stoichiometric ionic strength”, I , which assumes that all complexes in solution are completely dissociated, and “true ionic strength”, $\bar{I}$, which takes speciation and complex association into account. $\bar{I}$ is calculated according to:

$$\bar{I} = \frac{1}{2} \sum_i m_i z_i^2, \quad (1)$$

where m_i and z_i are the molality and charge, respectively, of the i^{th} charged species. Because the formation of neutral chloride complexes tends to decrease the number of charged species in solution, $\bar{I}$ is typically considerably smaller than I . Importantly, however, calculations and experimental measurements indicate that, at certain temperatures and pressures, $\bar{I}$ actually begins to increase relative to I with increasing NaCl molality such that the two can become nearly equivalent.

2.2. Modeling the aqueous speciation of cation-chloride complexes

Extensive effort has been devoted towards developing and utilizing thermodynamic models to understand and predict the behavior of cation-chloride complexing at elevated temperatures and pressures. The goal of these models is to utilize a simplistic microscopic description to capture important macroscopic phenomena, such as the effects of cation-chloride interactions on solution pH, ionic strength, fluid density, and boiling and freezing points. In the case of the NaCl(aq) system, there are an infinite number of individual species that may exist in solution at the molecular scale (e.g., NaCl(aq), Na^+ , Cl^- , Na_2Cl^+ , NaCl_2^- , ...), but it is both impractical and unnecessary to produce measurements and thermodynamic descriptions of the behavior of each of these individual

species. Indeed, researchers have shown that the behavior of NaCl in solution can be accurately modeled at many commonly encountered temperatures, pressures, and NaCl concentrations using only three species (NaCl(aq) , Na^+ , and Cl^-) and an appropriate activity model. Thus, thermodynamic models are a “useful fiction” in this regard, because, although they may not necessarily capture the molecular-scale phenomena occurring in a system, they can be calibrated to reproduce and accurately predict processes occurring in natural systems.

Although they have been studied in extensive detail, several aspects of the thermodynamics of chloride complex association remain uncertain. One specific example relates to the neutral and charged species activity model and the number of species that need to be included in the model in order to capture the relevant processes. Based upon examination of a large volume of experimental conductance data, Oelkers and Helgeson proposed, in the early 1990s, a model for cation-chloride complexes at elevated temperatures and pressures that involved substantial activity coefficients of the neutral complex and formation of polynuclear and triple ion complexes (e.g., Na_2Cl^+ , NaCl_2) (Oelkers and Helgeson, 1990, 1991, 1993a,b). Additionally, Driesner et al. (1998) presented molecular dynamics simulation results that support the extensive multi-ion clustering proposed by Oelkers and Helgeson. In the latter case, the authors note that their study is somewhat preliminary, and Sharygin et al. (2002) have pointed out that the modeling results hinge on potentially uncertain parameters. Furthermore, it is important to note that the Oelkers and Helgeson analysis was based upon data obtained at chloride molalities <0.1 molal, and therefore calculations at higher ionic strengths had to be based upon model extrapolations.

The advent of field and experimental devices for measuring the in situ speciation and pH of hydrothermal solutions has increasingly provided the requisite data for discerning the thermodynamics of chloride complexes at elevated temperatures, pressures, and concentrations. A more recent reexamination of the Oelkers and Helgeson model by Sharygin et al. (2002) indicates that the observed phenomena can potentially be explained using a simpler model than that suggested by Oelkers and Helgeson. Notably, Sharygin et al. (2002) suggest that: a) based upon statistical mechanical calculations, the high neutral chloride complex activity coefficients proposed by Oelkers and Helgeson (1991) yield distances of closest approach that are physically unrealistic, and b) the Oelkers and Helgeson speciation model involving a number of multi-ion complexes cannot match their (Sharygin et al., 2002) conductance measurements of NaCl and KCl solutions up to

4.5 molal without the use of the unphysically large salting out coefficients. Based on this analysis, they suggest that the activity coefficient of the neutral complex can be assumed equal to 1 and a simple speciation model involving only Na^+ , Cl^- , and NaCl(aq) can fit the measurements within the experimental uncertainty, except in solutions with exceptionally low dielectric constants. Their proposed speciation model uses the extended Debye-Hückel equation (Helgeson et al., 1981) with extended parameters calculated using the revised Helgeson-Kirkham-Flowers (HKF) equation of state (Tanger and Helgeson, 1988) by Oelkers and Helgeson (1990) to calculate the charged species (Na^+ , K^+ , Cl^-) activity coefficients.

At certain temperatures and pressures, this aqueous speciation model calculates low charged species activity coefficients, which, combined with constraints placed upon the fluid by aqueous species association constants, yields an increasing degree of redissociation of the chloride complexes with increasing chloride molalities. Sharygin et al. (2002) show that their model is able to fit their conductivity measurements with a high degree of accuracy for all but one of their measurements, which was obtained at an extreme condition where the fluid was very close to phase separation behavior (397°C, 280 bar) and the solute interactions are calculated to be the strongest. The overall agreement of their proposed model with their experimental data indicates that it has robust capacity for calculating charged species activity coefficients and fluid speciation over a wide range of conditions. Nonetheless, the effects of redissociation processes on geochemical fluxes have not been thoroughly examined, likely because of the historical uncertainty surrounding their occurrence. Here, we attempt to stimulate thought and continued experimental study by producing calculations and hypotheses that explore the consequences of redissociation in geological systems.

3. Methods

3.1. Aqueous Speciation

Sharygin et al. (2002) only reported association constants at a number of discrete points and did not produce a parameterization for extrapolating their measurements to other conditions. Nonetheless, their reported association constants are in good agreement with those calculated according to the Ho et al. (1994) density model, suggesting that the latter (which was calibrated using considerably more dilute solutions) has robust calculation capabilities. Therefore, we use the Ho et al. (1994) model to calculate NaCl association constants in the present study. Density is calculated

using a Matlab implementation (Junglas, 2009) of the IAPWS-95 formulation (Wagner and Pruss, 2002). Additionally, although their effects are minor compared with those of NaCl association, the association constants of water and HCl(aq) are calculated according to Marshall and Franck (1981) and Ho et al. (2001), respectively. Mineral hydrolysis constants are calculated according to the Tutolo et al. (2014) thermodynamic data set. Where required, speciation calculations are performed using a Matlab implementation of the EQBRM package (Anderson and Crerar, 1993).

3.2. Activity coefficients of charged aqueous species

Activity coefficients are typically utilized to account for departures from the thermodynamic reference state resulting from increasing ionic strength of the solvent. The activity coefficient of an aqueous species, γ_i , may be defined as:

$$\gamma_i = \frac{a_i}{m_i}, \quad (2)$$

where a_i and m_i are its activity and molality, respectively. Two main types of models exist for calculating activities of solutes in geological fluids: “Pitzer-style” formulations, which are based on specific ion interaction approaches (e.g., Pitzer, 1973; Harvie et al., 1984), and formulations based on Debye-Hückel theory and its extensions (e.g., Helgeson, 1969; Helgeson et al., 1981). Both styles of models have their limitations, but, generally, “Pitzer-style” formulations are better suited to the calculation of ion activities in concentrated electrolyte solutions. Nonetheless, the “Pitzer-style” models are typically characterized by their complexity, and large amounts of data are required for their implementation. Due to the relative lack of the requisite data to parameterize “Pitzer-style” models at elevated temperatures and pressures, their applications in geochemical modeling are generally limited to near-ambient conditions (e.g., Harvie et al., 1984; Møller, 1988; Duan and Sun, 2003; Zhang et al., 2006).

Thus, because of its generality and versatility, many geochemical models utilize the extended Debye-Hückel equation to calculate the activity coefficients of charged aqueous species. The mean ionic activity coefficient¹ of a charged ion in an electrolyte solution, $\gamma_{\pm}^*$, can be approximated

¹The “mean” ionic activity coefficient represents the activity coefficients of all charged species in the NaCl solutions considered here (Helgeson et al., 1981; Oelkers and Helgeson, 1990). In mixed electrolytes, other forms of this equation must be employed (Helgeson et al., 1981).

according to Helgeson et al. (1981):

$$\log \gamma_{\pm}^* = -\frac{z_i^2 A_{\gamma} \bar{I}^{1/2}}{1 + \bar{a} B_{\gamma} \bar{I}^{1/2}} + b_{\gamma,i} \bar{I} + \Gamma_{\gamma}, \quad (3)$$

where z_i is the charge of the i^{th} electrolyte, $\bar{a}$ is the ion size parameter for the solution, Γ_{γ} is mole fraction to molality conversion factor:

$$\Gamma_{\gamma} = -\log(1 + 0.180153m^*), \quad (4)$$

where m^* is the sum of molalities of all species in solution, A_{γ} and B_{γ} are T -, P -specific constants, and $b_{\gamma,i}$ is an electrolyte-specific “extended term parameter”. Values of A_{γ} and B_{γ} can be calculated according to (Helgeson and Kirkham, 1974):

$$A_{\gamma} \equiv \frac{(2\pi N)^{1/2} e^3 \rho^{1/2}}{\ln(10)(1000)^{1/2} (\epsilon k T)^{3/2}} = \frac{1.825 \times 10^6 \rho^{1/2}}{(\epsilon T)^{3/2}}, \quad (5)$$

and

$$B_{\gamma} \equiv \left(\frac{8\pi N \rho e^2}{1000 \epsilon k T} \right)^{1/2} = \frac{5.029 \times 10^9 \rho^{1/2}}{(\epsilon T)^{1/2}}, \quad (6)$$

where N is Avogadro’s number, e is the absolute electron charge, k is the Boltzmann constant, and ρ and ϵ are the density and dielectric constant of pure water, respectively, at the T and P of the calculation. Here, values of ϵ are calculated according to equations Johnson and Norton (1991) implemented in SUPCRT92, and the ion size parameter is calculated according to the HKF equation of state (Oelkers and Helgeson, 1990; Shock et al., 1992). For NaCl solutions, $\bar{a}$ is calculated as the sum of the effective electrostatic radii of Na^+ and Cl^- , which can be calculated according to equations and parameters presented by Shock et al. (1992). At most pressures, values of the electrostatic radii of both Na^+ and Cl^- in liquid water remain constant to at least 300°C, and therefore $\bar{a}$ differs negligibly from 3.72 Å at these conditions (Shock et al., 1992). Nonetheless, $\bar{a}$ does deviate slightly from this value at some of the conditions considered here (Shock et al., 1992), and we have therefore included a provision to calculate its value using the HKF equation of state here.

Due to the high probability that most geologic solutions contain NaCl as the dominant electrolyte, $b_{\gamma,i}$ is often taken equal to $b_{\gamma,\text{NaCl}}$. Versions of Eq. 3 for NaCl solutions have been parameterized by several researchers. For example, Helgeson (1969) utilized a simplified version of Eq. 3) in which Γ_{γ} was assumed to be equal to 0 to calculate activity coefficients of charged aqueous

species. Helgeson (1969) calculated values of $b_{\gamma,i}$ from 0-300°C based upon data and extrapolations and the assumption that γ for NaCl(aq) could be taken as equal to values of γ calculated from experimental measurements of CO₂ solubility in NaCl solutions (thus putting it at odds with the Sharygin et al. (2002) model). Helgeson (1969) suggested that solutions deviate negligibly from Debye-Hückel theory at T>300°C and that $b_{\gamma,i}$ should therefore be set to 0. Values of $b_{\gamma,\text{NaCl}}$ over the entire range of applicability of the HKF were later recalculated by Helgeson et al. (1981) using a full implementation of Eq. 3. More recently, Oelkers and Helgeson (1990) recalculated values of $b_{\gamma,\text{NaCl}}$ to reflect revisions to the HKF equation of state (Tanger and Helgeson, 1988; Shock et al., 1992). A validation of the implementation of our activity coefficient model is included in Appendix A. In this study, we employ Eq. 3 with $b_{\gamma,\text{NaCl}}$ values presented by Oelkers and Helgeson (1990) parameters for all relevant calculations.

4. Implications of neutral complex redissociation for mineral solubilities

4.1. Aqueous chemistry of mineral-buffered systems

The redissociation phenomenon can affect the evolution of water-rock-gas interactions and elemental fluxes in a variety of geologic settings. One important example (and the one that we will rely upon here) involves silicate-fluid interactions, which are ubiquitous throughout Earth's crust and upper mantle. Geologic formations containing felsic mineral assemblages such as those plotted in Fig. 1 (i.e., alkali feldspar-mica-quartz) host a plethora of geothermal energy and hydrothermal ore deposition systems (e.g., Hemley, 1959; Hemley and Jones, 1964; Montoya and Hemley, 1975; Merino, 1975; Giggenbach, 1988; Sverjensky et al., 1991; Yardley and Bodnar, 2014). When these assemblages interact with chloride brines, Na⁺ and K⁺ are the dominant cations and Cl⁻ is the dominant anion. Based on charge balance constraints, therefore, Na⁺ + K⁺ = Cl⁻, and the total solubility of the alkali feldspar-mica-quartz assemblage is fixed by the chlorinity of the fluid. Furthermore, dependent upon the equilibrium mineralogical assemblage, the ratio of the activities of Na⁺ and/or K⁺ relative to the activity of H⁺ will be fixed by the equilibrium constants forming the boundaries of the stability fields in Fig. 1. Thus, because the equilibrium constant is fixed by the temperature and pressure conditions, the pH should decrease with increasing Cl concentration. Furthermore, because pH fixes the speciation and fluxes of many of the more minor solutes, this combined chlorinity-activity constraint plays an important role in the fluxes of elements through

Figure 1: Activity diagram showing silicate mineral buffering of fluid compositions at 350°C and steam saturation pressure, calculated using the thermodynamic data set presented by Tutolo et al. (2014).

many geological systems.

4.2. An example: the albite-paragonite-quartz system

Importantly, the “chlorinity constraint” discussed above fixes Na and K *concentrations*, but the “equilibrium constant constraint” fixes Na^+ , K^+ , and H^+ *activities*. The difference between these values is affected not only by the departures from ideality resulting from the elevated ionic strength of the solution (accounted for by activity coefficients), but also by the degree of association of neutral ion pairs. As redissociation processes increasingly dominate the speciation of the system, the activity of Na^+ becomes increasingly independent of the NaCl concentration. In other words, at certain temperatures and pressures, the activity of Na^+ remains virtually constant, even when the Na molality is greatly increased. We can examine the temperature and pressure conditions at which this behavior will occur by using the example of the albite-paragonite-quartz equilibrium:

which is not only a common fluid-buffering assemblage in the field but is also commonly employed to fix pH in hydrothermal experiments (e.g., Woodland and Walther, 1987; Saccocia and Seyfried, 1994; Tagirov et al., 2002). The fact that this reaction may be metastable at some of the conditions

examined here is irrelevant for the purposes of the present discussion; we could have just as easily used any reaction represented in Fig. 1 to portray these phenomena.

In order to exhibit the redissociation phenomenon, we calculate the fraction of NaCl in solution present as neutral complexes, $\alpha_{\text{NaCl(aq)}}$, according to:

$$\alpha \equiv \frac{m_{\text{NaCl(aq)}}}{m_{\text{NaCl,tot}}}, \quad (8)$$

where $m_{\text{NaCl(aq)}}$ is the calculated molality of the neutral complex and $m_{\text{NaCl,tot}}$ is the total NaCl molality. Accordingly, the fraction of NaCl in solution that does not exist as a charged species is equivalent to one minus α . At steam saturation pressures and NaCl concentrations from 0-4.5 molal (the limit of the Sharygin et al. (2002) measurements), the redissociation phenomenon is only evident (i.e., α peaks and begins to decline within our modeled range of concentrations) at temperatures greater than $\sim 300^\circ\text{C}$ (Fig. 2a). However, at 1 kbar pressure and those same NaCl molalities, redissociation processes begin to dominate NaCl speciation at significantly higher temperatures, greater than $\sim 400^\circ\text{C}$. Furthermore, below these temperature cutoffs in both scenarios, the molality of Na^+ in solution increases with a near-constant slope with increasing NaCl molality. However, above this temperature, the calculated Na^+ molalities demonstrate increasingly positive slopes with increasing NaCl molality, with higher temperatures exhibiting more dramatic slope increases (Fig. 3a,b). Unlike their molalities, the activities of Na^+ and Cl^- remain linear with increasing NaCl molality at all modeled temperatures and pressures. This behavior results from the constraints placed upon the activities of these individual ions by the equilibrium constant for NaCl association, which is only a function of temperature and pressure, and not NaCl concentration. Importantly, in the solutions where significant redissociation is calculated to occur, the activities of these ions remain virtually constant with increasing NaCl molality.

The calculations presented in Figs. 2 and 3 demonstrate that the redissociation phenomenon is a result of the competing effects of activity coefficient decreases and molality increases. The high NaCl molalities, combined with the fact that a larger proportion of the total NaCl in solution is present as the charged ions Na^+ and Cl^- , lead to elevated values of $\bar{I}$ and therefore lower values of the activity coefficient (Eq. 3). Nonetheless, it is additionally apparent that the redissociation phenomenon is not only tied to the salinity of the fluid, but also closely linked to both temperature and pressure (Figs. 2 and 3). Based on the experimental observations of Sharygin et al. (2002) and the calculations performed here, redissociation predominantly occurs in solutions with relatively

Figure 2: Fraction of total NaCl in solution present as NaCl(aq) (α , see Eq. 8) in 0-4.5 molal NaCl solutions at: a) 25°C-350°C and pressures along the steam saturation curve, and b) 250-550°C and 1 kbar. Lines colors represent temperature and pressure conditions where redissociation does (black) or does not (gray) occur.

low densities and dielectric constants. As these values decrease, the salinity at which the fluid begins to demonstrate redissociation behavior also becomes lower, such that, at 350°C and steam saturated pressure, where the density of pure water is 0.57 g/cm³, redissociation begins to occur at ~0.5 molal NaCl (Fig. 2a). However, at 1 kbar, the redissociation phenomenon does not occur in 0-4.5 molal NaCl solutions at this same temperature (Fig. 2b). At 1 kbar and 550°C, where the density of pure water is 0.44 g/cm³ however, solutions under 0.5 molal NaCl are very strongly associated and become increasingly dissociated with increasing NaCl concentration.

If we now assume, as discussed above, that the fluids plotted in Figs. 2 and 3 are in equilibrium with the mineral assemblage represented by Reaction 7, we can examine how the pH may vary as a function of salinity at these temperatures and pressures. As may be expected from a direct relationship between NaCl concentration and fluid pH, fluids at relatively low temperatures generally decrease in pH as salinity increases (Fig. 4). This style of behavior occurs in fluids at steam saturated pressures and temperatures up to ~250°C, and in fluids at 1 kbar at temperatures up to ~400°C. However, at elevated temperatures, where redissociation begins to have a major effect on the fluid speciation, the increasing salinity has very little, and, for the most part, immeasurable effect on pH, even as NaCl molality increases from <0.25 to 4.5 molal NaCl.

The concept that solutions with cation-chloride concentrations up to (and likely greater than) 4.5

Figure 3: Molality (a,b) and activity (c,d) of Na^+ in 0-4.5 molal NaCl solutions up to 350°C at steam saturation pressures calculated using the speciation model discussed in Section 3. The panels on the left side (a,c) illustrate calculations performed at 25°C-350°C at pressures along the steam saturation curve, and the panels on the right side (b,d) illustrate calculations performed at 250-550°C at 1 kbar.

Figure 4: Calculated pH in equilibrium with an albite-paragonite-quartz assemblage (Reaction 7) in 0-4.5 molal NaCl solutions at: a) 250-350°C and steam saturation pressures, and b) 250-550°C and 1 kbar.

molal can have approximately the same activity of their dominant cation, and, in our example, pH, as a solution containing <1 molal of the same elements (Fig. 3) is counter-intuitive if redissociation processes are not considered. These calculations suggest that solutions existing along any of the mineral-mineral boundaries in Fig. 1 can have concentrations of [Na + K] and Cl anywhere over the range from <1 to >4.5 molal and still have virtually the same pH. These calculations therefore suggest that, in instances where substantial redissociation is calculated to occur, the solubility of the aluminosilicate assemblages plotted in Fig. 1 and others is, indeed, dependent upon the concentration of the Cl ligand, but pH is not. Thus, in situations where a phase-separated vapor and brine equilibrate with an equivalent mineral assemblage at temperatures and pressures where redissociation is calculated to occur, it is likely that both fluids will have equivalent pH. This has implications for the chemistry of fluids sampled at seafloor hydrothermal vents (e.g., Ding et al., 2005; Pester et al., 2014) as well as in active geothermal systems (e.g., Reed, 1997; Simmons and Browne, 2000).

4.3. Extension to other systems and trace element transport

Although we have specifically focused on the albite-paragonite-quartz equilibrium, it is likely that analogous considerations apply to the K-feldspar-muscovite-quartz system and many others in which redissociation can affect the speciation of the dominant cations and anions in solution. Furthermore, the speciation of many geologically important trace elements, such as Al and B, is strongly

pH-dependent. Therefore, the considerations discussed above regarding the pH-independent nature of redissociated solutions can affect the transport and flux of these elements in geological environments.

5. Uncertainties and future work

Although the redissociation phenomenon has a number of important implications for describing elemental fluxes through geologic systems, its effects and applicability vary depending on the temperature and pressure conditions of the system. It must therefore be emphasized that the results reported here are dependent upon the accuracy of the model that we have employed. The experimental measurements of Sharygin et al. (2002) show that this model can effectively match the conductivities that they have observed experimentally. However, they also provide measurements at temperature and pressure conditions where the model employed here cannot account for the behavior of the solution. Considering that Sharygin et al. (2002) made this observation based upon conductivity measurements of solutions with up to 1.0 molal NaCl at 397°C, 280 bar, where the density and dielectric constant of water are calculated to be 0.3 g/cm³ and ~5, respectively, indicates that some relationship between density, dielectric constant, and model applicability must exist. Tutolo et al. (2014) offer further evidence of regions where the transition from single ion pair to multiple ion association may occur. Using measurements of mineral-buffered solutions at elevated temperatures and pressures, Tutolo et al. (2014) have shown that the single ion pair model with the assumption of $\gamma_{\text{KCl(aq)}} = \gamma_{\text{HCl(aq)}} = 1$ cannot reproduce the measured solubilities to an increasing degree with increasing temperature and decreasing density. Notably, the solutions that deviate most significantly from the single ion pair model have similar densities and dielectric constants to the measurement by Sharygin et al. (2002), suggesting that similar processes (i.e., multiple ion clustering or salting out/in of neutral species) are governing solution chemistry. Further experimental work will be required to improve our ability to model these processes. The approaches advocated by both Sharygin et al. (2002) and Tutolo et al. (2014) can likely be used in tandem to further advance our understanding of redissociation processes.

6. Conclusion

Consideration of the experimental measurements of Sharygin et al. (2002) and the simple calculations that we have performed here suggest the redissociation phenomenon is important to consider in a variety of geological systems. Specifically, because, at certain temperatures and pressures, calculated *activities* of ions in solution remain practically constant even as element *concentrations* increase from <1 molal to 4.5 molal, this phenomenon could significantly affect mineral and gas solubilities as well as elemental fluxes. In turn, these effects play a role in the formation of ore deposits (Reed, 1997; Yardley and Bodnar, 2014) and development of diverse, geologically-fueled ecosystems (Jørgensen and Boetius, 2007). Nonetheless, the full region of applicability of the types of calculations performed here is not yet clear. Our hope is that the calculations and hypotheses included herein will stimulate continued experimental and numerical study examining the limits of the the speciation model employed here in order to improve the certainty with which geochemical speciation codes may be applied to geological problems.

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8. Disclaimer

Dr. Saar has a significant financial and business interest in TerraCOH, Inc., a company that may commercially benefit from the results of this research. The University of Minnesota has the right to receive royalty income under the terms of a license agreement with TerraCOH, Inc. These relationships have been reviewed and managed by the University of Minnesota in accordance with its conflict of interest policies.

Appendix A. Validation of the activity coefficient formulation

To test the accuracy and correct implementation of Debye-Hückel activity coefficient models in the present study, we compare them with another published, calibrated model (Archer, 1992). Because it is based on a modified form of the Pitzer ion-interaction model (Pitzer, 1973; Archer, 1991), the Archer (1992) model is formulated based upon I , the stoichiometric ionic strength of the solution and we must therefore derive a relationship between the two ionic strength scales in order to yield a meaningful comparison.

In NaCl-dominated solutions where H^+ and OH^- contribute negligibly to ionic strength, we can assume:

$$\bar{I} = m_{Na^+} \quad (A.1)$$

and

$$I = m_{Na}. \quad (A.2)$$

Further, by defining $\gamma_{\pm}$ as the activity coefficient on the stoichiometric ionic strength scale (i.e., those reported by Archer (1992)) and keeping in mind that a_{Na^+} must be consistent regardless of whether the activity model is employing I or $\bar{I}$, we can write:

$$\gamma_{\pm}^* m_{Na^+} = \gamma_{\pm} m_{Na}. \quad (A.3)$$

Lastly, by plugging Eqs. A.1 and A.2 into Eq. A.3, we have:

$$\gamma_{\pm} I = \gamma_{\pm}^* \bar{I}, \quad (A.4)$$

which allows us to compare values of $\gamma_{\pm}^*$ calculated using Eq. 3 with values of $\gamma_{\pm}$ calculated using the Archer (1992) model.

Figure A.1: Comparison between calculations of mean ionic activity coefficients for 0.5, 1, 3, and 6 molal NaCl solutions using extended Debye-Hückel equations parameterized by Helgeson (1969) (A) and Helgeson et al. (1981) (B) (lines) and Archer (1992) (symbols) for equivalent true ionic strengths (see text).

Comparisons between values calculated from Eq. 3 using both the Helgeson (1969) and Oelkers and Helgeson (1990) parameters and those calculated from the parameterization of Archer (1992) indicate varying degrees of agreement and disagreement over the range of calculated temperatures and ionic strengths (Fig. A.1). At lower temperatures, the Helgeson (1969) formulation agrees well with the Archer (1992) formulation up to NaCl molalities of ~ 1 , and the Oelkers and Helgeson (1990) parameters are in agreement up to NaCl molalities of ~ 3 . At higher temperatures, both formulations are in better agreement with the Archer (1992) calculations, and the Oelkers and Helgeson (1990) parameters appear to be in very good agreement with the Archer (1992) calculations up to 6 molal NaCl. This conclusion is in accord with the assertion by Helgeson and Kirkham (1974) that the dielectric constant of water and values of parameters in Eq. 3 change in such a way as to extend the region of applicability of Debye-Hückel theory to progressively more concentrated solutions with increasing temperature and/or decreasing pressure.

The Helgeson (1969) calibration of Eq. 3, which is implemented in many geochemical speciation codes (e.g., EQ3/6 (Wolery, 1992), PFLOTRAN (Hammond et al., 2012), and the Geochemist's Workbench (Bethke and Yeakel, 2012)), was limited by the relatively few experimental measurements available at the time it was produced. The Helgeson (1969) calibration was therefore superseded by the Oelkers and Helgeson (1990) formulation, which employed experimental

data acquired over a much wider range of temperature, pressure, and concentration conditions. Nonetheless, although the Oelkers and Helgeson (1990) formulation yields activity coefficients in significantly better agreement with the Archer (1992) formulation and is therefore more accurate, it has been shown that the error in mineral solubility calculations resulting from even the relatively large inter-model variations in $\gamma_{\pm}^*$ shown in Fig. A.1 is relatively minor (e.g., Manning, 2013). Therefore, either the Helgeson (1969) or Oelkers and Helgeson (1990) parameters may be used without introducing undue uncertainty in speciation calculations. In this study, we employ the Oelkers and Helgeson (1990) parameters for all relevant calculations.

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