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Journal Article**Author(s):**

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Publication date:

2017-09-01

Permanent link:

<https://doi.org/10.3929/ethz-b-000191433>

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Originally published in:

American Journal of Science 317(7), <https://doi.org/10.2475/07.2017.01>

This is the Green Open Access version of: Miron, G. D., Wagner, T., Kulik, D. A., Lothenbach, B., 2017. An internally consistent thermodynamic dataset for aqueous species in the system Ca-Mg-Na-K-Al-Si-O-C-Cl to 800 °C and 5 kbar. *American Journal of Science*, v. 317, p. 755-806. Original publication see: <https://doi.org/10.2475/07.2017.01>

An internally consistent thermodynamic dataset for aqueous species in the system Ca-Mg-Na-K-Al-Si-O-C-Cl to 800 °C and 5 kbar

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Submitted to: American Journal of Science

Date: 28 April 2017

ABSTRACT

This study presents an internally consistent thermodynamic dataset for aqueous species in the system Ca-Mg-Na-K-Al-Si-O-H-C-Cl, obtained by adding species of calcium, magnesium and carbon to the core system Na-K-Al-Si-O-H-Cl (Miron and others, 2016). Critically evaluated experimental data on mineral solubility (Ca and Mg hydroxides, Ca and Mg silicates, anorthite, Ca and Mg carbonates) in water and aqueous electrolyte solutions over wide ranges in temperature and pressure were added to the database of experimental data. The complete experimental dataset was then used to simultaneously refine the standard state Gibbs energies of all aqueous ions and complexes in the framework of the revised Helgeson-Kirkham-Flowers (HKF) equation of state. The thermodynamic properties of the solubility-controlling minerals were accepted from the internally consistent dataset of Holland and Powell (1998; updated Thermocalc dataset ds55). The association equilibria of important hydroxide, chloride, carbonate and silicate complexes were critically reviewed, and their standard state properties and HKF parameters were independently derived from conductance, potentiometric and, in a few cases, solubility measurements. In a global optimization of standard Gibbs energies of aqueous species, performed with the GEMSFITS code (Miron and others, 2015), the association equilibria for aqueous complexes were always maintained. The new thermodynamic dataset reproduces all available fluid-mineral phase equilibria and mineral solubility data in the system Ca-Mg-Na-K-Al-Si-O-H-C-Cl with good accuracy over wide ranges in temperature (25 to 800°C), pressure (1 bar to 5 kbar) and composition (salt concentrations up to 5 molal). This makes it possible to perform geochemical and reactive transport modeling of processes in natural and engineered georeservoirs over wide ranges of conditions with an unprecedented level of accuracy and reliability and to address processes of fluid flow and fluid-rock interaction in the Earth's crust from a new perspective. Using the same strategy as applied in the present study, the internally consistent thermodynamic dataset can be further extended with additional major and trace elements, and the data refinement process can be repeated when new experimental data or next-generation equation of state or activity models for aqueous solutions become available.

INTRODUCTION

Thermodynamic modeling is an important approach for gaining fundamental understanding of chemical processes in natural and engineered geochemical systems such as the formation of hydrothermal ore deposits, mass transfer and hydrothermal convection at mid-ocean ridges, fluid production and transfer in subduction zones, fluid release during crystallization of igneous intrusions, fluid circulation in geothermal reservoirs, and carbon dioxide sequestration in deep geological formations. The results of thermodynamic modeling depend on the robustness of the geochemical models and on the quality and consistency of the thermodynamic parameters (Engi, 1992; André and others, 2006; Thien and others, 2015; Wolery and Colón, 2016). In our previous study (Miron and others, 2016), we have developed a strategy for generating an internally consistent thermodynamic dataset for aqueous species in the system Na-K-Al-Si-O-H-Cl at temperatures and pressures up to 600 °C and 5 kbar. A large amount of critically evaluated experimental mineral solubility data was used to refine the standard state Gibbs energies of aqueous ions and complexes while maintaining close agreement with the association equilibria for ion pairs and complexes as independently derived from the conductance and potentiometric data.

Calcium and magnesium are major components of most crustal rocks, and are commonly bound to silicates, or into calcite and magnesite in carbonate-bearing rocks. Fluid-mineral equilibria involving Ca and Mg carbonate minerals play a key role in geological processes such as regional metamorphism of metasediments (Baumgartner and Ferry, 1991; Bousquet and others, 2008; Whitney and others, 2008; Miron and others, 2013), mass transfer in the deep Earth carbon cycle (Dasgupta and Hirschmann, 2010; Manning and others, 2013; Facq and others, 2014; Sverjnesky and Huang, 2015; Galvez and others, 2016), formation of sediment-hosted hydrothermal ore deposits (Meinert and others, 2003; Baker and others, 2004), carbonate alteration of basalts in geothermal systems (for example Alfredsson and others, 2008), diagenesis and dolomitization of carbonate platforms (for example Wilson and others, 2001) and geochemical reactions related to cementitious systems in (radioactive) waste repositories (Berner, 1992; Kulik and Kersten, 2001; Lothenbach and Winnefeld, 2006; Lothenbach and others, 2012).

At elevated temperatures and pressures, crustal fluids become enriched in carbon bearing species, which impacts the solvation behavior of aqueous ions and affects the mobility of rock-

forming elements and trace ore metals (Kyser and Hiatt, 2003; Dasgupta and Hirschmann, 2010; Galvez and others, 2013). Carbon dioxide is initially taken up by rocks via reaction processes such as weathering or submarine alteration of oceanic basalts which can increase their carbon concentration from below 0.2 wt.% up to about 3 wt.% (Staudigel, 2003). Metamorphic pressure-temperature gradients during regional metamorphism or subduction-related high-pressure metamorphism result in dehydration and decarbonation of carbonate rocks. This causes the release of a fluid phase rich in water and carbon components (Plank and Langmuir, 1998), while part of the carbon is being transported into the mantle and fixed as graphite or diamond (Frezzotti and others, 2011; Galvez and others, 2013). The fluids released from the subducting slab cause metasomatism of the overlying mantle wedge. The carbon present in fluids in these environments has a major effect on the melting behavior of the rocks, element transport and fluid properties, and on the amount of carbon released during volcanic eruptions (Manning and others, 2013). Another major source of carbon is buried organic material present in sedimentary and metasedimentary rocks (Sephton and Hazen, 2013).

Improved understanding of the behavior of calcium, magnesium and carbon in aqueous fluids in a wide range of geological systems and at elevated temperatures and pressures requires a high-quality internally-consistent thermodynamic model for the solubility and aqueous speciation of these elements. In the present study, we therefore employ the strategy introduced by Miron and others (2016) and extend the chemical system by adding calcium, magnesium, and the oxidized species of carbon. The existing experimental data on the solubility of calcium, magnesium, and carbonate minerals (silicates, hydroxides, and carbonates) in water and different electrolyte solutions were critically assessed. Based on the experimental data, a speciation model that accounts for chloride, hydroxide, carbonate and silicate complexing has been developed. The standard state Gibbs energies of aqueous ions and complexes in the system Ca-Mg-Na-K-Al-Si-O-H-Cl were then globally optimized against selected experimental data covering a wide range of conditions. The resulting thermodynamic dataset is able to represent the majority of experimental solubility data within their stated uncertainty. The results also reveal important gaps and limitations in the available experimental fluid-mineral equilibria data, and provide some guidance for key future experimental studies.

THERMODYNAMIC FRAMEWORK

The thermodynamic framework and standard states used in this study are the same as the ones used in previous work (Miron and others, 2016). Thermodynamic properties of minerals in this study were taken from the Holland-Powell internally consistent thermodynamic dataset (Holland and Powell, 1998; updated Thermocalc dataset ds55) and the related thermodynamic framework. This dataset is referred to as HP02 in the remainder of this paper. In addition to the minerals used in the previous dataset for the system Na-K-Al-Si-O-H-Cl (Miron and others, 2016), the present study included the following pure minerals: anorthite, anthophyllite, antigorite, aragonite, brucite, calcite, chrysotile, enstatite, forsterite, magnesite, pyrophyllite, talc, tremolite, and wollastonite. The remaining Ca and Mg oxides, silicates and carbonates present in the HP02 database should also be consistent with the current dataset, but were not used in the study because no experimental solubility data are available for them. Portlandite is not included in the HP02 database and, although it was not used in the global optimization, it was an essential mineral in this study for constraining the calcium speciation model. The standard state properties for portlandite came from compilations of Robie and Hemingway (1995) and Thoenen and others (2014). The thermodynamic data for portlandite were employed in such a way that the final values of the Gibbs energies of the aqueous species are not dependent on them (see Discussion).

The properties of aqueous species were modeled within the framework of the revised Helgeson-Kirkham-Flowers (HKF) equation of state (Helgeson and Kirkham, 1974a, 1974b, 1976; Tanger and Helgeson, 1988; Shock and others, 1992). Activity coefficients for charged aqueous species were calculated with an extended Debye-Hückel equation (Helgeson and others, 1981). For solubility experiments done in CaCl_2 and MgCl_2 solutions, extended Debye-Hückel parameters were taken from Helgeson and others (1981). The ion size parameters $\bar{a}$ are 4.32 and 4.11, while the extended term parameters b_γ are 0.077 and 0.106 (assumed constant at any temperature and pressure) for CaCl_2 and MgCl_2 , respectively. The activity model uses a common background electrolyte b_γ (related to the predominant electrolyte in solution) (Helgeson and others, 1981). For the neutral species the activity coefficient is assumed to be a linear function of the ionic strength. In chemical systems where the CO_2 aqueous concentration exceeds 1.1 molal (2 mol%) the activity coefficient of CO_2 aqueous diverges from 1.0 and the extended Debye-Hückel model is not suitable for calculating activity coefficients. The calculations become even

more problematic when besides the amount of dissolved CO₂, the background electrolyte is present in concentrations over 0.1 molal (see the DISCUSSION section). Models which can reproduce solubilities, in concentrated CO₂ solutions, containing a small set of elements (C-O-H-Ca-Na-Cl), have been proposed (Duan and Sun, 2003; Duan and Li, 2008).

Standard state properties and fugacity coefficients of pure gas species in the gas phase (for modeling CO₂ solubility in water and NaCl solutions) were calculated using the compensated Redlich-Kwong (CORK) model, which is consistent with the HP02 dataset (Holland and Powell, 1991). Fugacity and activity coefficients for gas mixtures were calculated using the asymmetric formalism (Holland and Powell, 2003). These calculations were performed with the GEM-Selektor package and the GEMS3K code (Kulik and others, 2013) using the TSolMod library (Wagner and others, 2012).

CARBON DIOXIDE SOLUBILITY IN WATER

Carbon dioxide gas dissolves in aqueous solutions according to the initial reaction:

The solubility of CO₂ in pure water and electrolyte solutions has been extensively studied experimentally (for example Harned and Davis, 1943; Ellis and Golding, 1963; Takenouchi and Kennedy, 1964; Zawisza and Malesinska, 1981). Recent reviews of the experimental data and thermodynamic models were made by Diamond and Akinfiev (2003), Duan and Sun (2003) and De Visscher and others (2012). The CO₂ solubility experiments in water are typically used to extract Henry's law solubility constants, but the resulting constants are highly dependent on the aqueous electrolyte model used in evaluating the data (Plummer and Busenberg, 1982). Notwithstanding experimental and analytical problems, the extracted reaction constants are affected by the calculation of the activity coefficient of CO_{2(aq)} in the aqueous phase (which diverges from 1.0 above about 2 mol.% dissolved CO₂), the estimation of the CO₂ mole fraction in the gas phase, and the dissociation of CO_{2(aq)}, which was not taken into account in all experimental studies (Plummer and Busenberg, 1982; Diamond and Akinfiev, 2003; De Visscher and others, 2012).

Several models have been developed to calculate the solubility of CO₂ in water and electrolyte solutions. Akinfiev and Diamond (2003) proposed a virial-like equation of state (EOS) for calculating thermodynamic properties of aqueous nonelectrolytes over a wide range of

conditions. Their EOS is compatible with the HKF model for electrolytes, yields a good representation of solubility constants over wide ranges of temperature and pressure, and approaches the ideal gas limit at very low pressures. Duan and Sun (2003) proposed a model that combines the EOS for gaseous CO₂ from Duan and others (1992) with the Pitzer ion interaction model (Pitzer, 1973) for calculating the chemical potential of CO₂ in the aqueous phase. The HKF model (Tanger and Helgeson, 1988) developed for calculating standard chemical potentials of aqueous ions was empirically extended to calculation of the standard state properties of aqueous nonelectrolytes (Shock and others, 1989; Shock and Helgeson, 1990). However, experimental studies for the standard partial molar volume and heat capacity of aqueous nonelectrolyte solutions have convincingly demonstrated that the HKF model fails to correctly predict the standard state properties of nonelectrolytes close to the critical point of water (Plyasunov and Shock, 2001; Schulte and others, 2001; Akinfiev and Diamond, 2003; Plyasunov, 2015). Schulte and others (2001) and Plyasunov and Shock (2001) have revised the HKF parameters of CO_{2(aq)} to better reproduce the recent measurements (Hnědkovský and Wood, 1997) of partial molal heat capacity and partial molal volume of CO_{2(aq)}.

Figure 1 compares calculations using different thermodynamic models with experimental determinations of CO₂ solubility constants in water from 0 to 360 °C at saturated water vapor pressure. Properties of the gas phase were calculated with the CORK model (Holland and Powell, 1991). The agreement between different experimental datasets and model predictions is quite good below 100 °C, with somewhat larger differences between the data and their trends for higher temperatures. The maximum discrepancy is less than 0.1 log units.

We have made a comparison between experimentally measured dissolved aqueous CO₂ concentrations and calculated values using different sources for the thermodynamic properties of the CO_{2(aq)} species at different total pressures (fig. 2). The experimental dataset included CO₂ solubility in pure water and in NaCl solutions. A more detailed review of the experimental data can be found in Duan and Sun (2003). In our calculations, the activity coefficient of CO_{2(aq)} is assumed to be 1.0, which is a good approximation up to around 2 wt.% dissolved CO₂ (roughly equivalent to 1 mol/kg). It can be seen in figs. 1 and 2 that there is rather good agreement between different sources for the properties of CO_{2(aq)}. The best agreement between modeled and experimental CO₂ solubility data is achieved when the model of Akinfiev and Diamond (2003) is

used. We have therefore selected this model for calculating the properties for $\text{CO}_{2(\text{aq})}$ in this study.

Fig. 1. Comparison between calculated and experimentally measured solubility constants of $\text{CO}_{2(\text{g})}$ in water. Calculations were performed with thermodynamic models for $\text{CO}_{2(\text{aq})}$ from Akinfiev and Diamond (2003), Shock and others (1989) and Plyasunov and Shock (2001). Thermodynamic properties of gaseous CO_2 were calculated with the compensated Redlich-Kwong (CORK) equation of state (Holland and Powell, 1991).

CARBON SPECIES

The CO_2 solubility in aqueous solution increases as a function of the $\text{CO}_{2(\text{g})}$ partial pressure (Diamond and Akinfiev, 2003; Duan and Sun, 2003). The CO_2 that dissolves in an aqueous solution will partially dissociate into HCO_3^- and CO_3^{2-} according to two stepwise reactions:

For both reactions, an increase in pH will shift them to the right-hand side. At ambient pressure-temperature conditions and a pH of 6, the amount of $\text{CO}_{2(\text{aq})}$ and of bicarbonate is more or less equal. Carbonic acid dominates at low pH and the formation of bicarbonate is favored at high pH. In a closed fluid-rock system controlled by equilibria with carbonate minerals at temperatures below 200 °C, HCO_3^- is the dominant species, and above this temperature, $\text{CO}_{2(\text{aq})}$

becomes dominant. Bicarbonate and carbonate species can both form stable complexes with various metal cations.

Fig. 2. Comparison between calculated and experimentally determined solubility of $\text{CO}_2(\text{g})$ in water (A-D) and in NaCl solutions (E-F), at different temperatures and as function of total pressure. Calculations were performed with different thermodynamic models for $\text{CO}_{2(\text{aq})}$; thermodynamic properties of gaseous CO_2 were calculated with the compensated Redlich-Kwong (CORK) equation of state (Holland and Powell, 1991).

Carbonate and Bicarbonate

Values of the first dissociation constant reported in the literature were recently reviewed (Li and Duan, 2007; De Visscher and others, 2012; Stefánsson and others, 2013, 2014). There is a fairly good agreement between the experimental data and thermodynamic models at pressures of 1 bar and saturated water vapor pressure and at temperatures from 25 °C up to the critical point of water (fig. 3A). For subcritical conditions, Stefánsson and others (2013, 2014) reported new values of the first dissociation constant, which are in good agreement with previously determined values (Harned and Davis, 1943; Ellis, 1959a; Read, 1975; Patterson and others, 1982). The only high-pressure experimental studies on the dissociation constant were done by Ellis (1959a) up to 3000 bar and 65 °C and by Read (1975) up to 2000 bar and 250 °C using conductance methods. When comparing the available models with the experimental data at high pressures (figs. 3C and 3D), the predicted values are increasingly in disagreement with the experimental data of Read (1975) as pressure and temperature increase. Read (1975) used KCl and KHCO₃ solutions for the experiments, but did not consider the possibility that potassium carbonate species would form. Although in concentrated chloride bearing solutions these species have insignificant concentrations, they become more important in solutions with lower chlorinity. We refitted the HKF parameters for HCO₃⁻ in this study to better represent both the low pressure (Harned and Davis, 1943; Ellis, 1959a; Read, 1975; Patterson and others, 1982) and the high pressure data of Read (1975) and Ellis (1959a), but we retained the standard state properties ($\Delta_f G_{298,1}^0$, $S_{298,1}^0$, $Cp_{298,1}^0$, $V_{298,1}^0$) from Shock and Helgeson (1988).

The second dissociation constant of aqueous CO₂ was investigated experimentally only at pressures of 1 bar and at saturated water vapor pressure (fig. 3B). The agreement between different experimental studies is very good up to 125 °C (Stefánsson and others, 2013), but at higher temperatures the differences increase up to 0.5 log units. Patterson and others (1982, 1984) performed potentiometric measurements in NaCl solutions up to 5 molal concentration. Data on the high-pressure stability (> 10 kbar) of the bicarbonate complex was obtained from in situ Raman measurements (Facq and others, 2014), but these *P-T* conditions are outside the permissible range of the HKF model used in this study. The bicarbonate species is predicted to be important in aqueous solutions at very high pressures exceeding 30 kbar (Facq and others, 2014). The $Cp_{298,1}^0$ for CO₃²⁻ was previously determined by Shock and Helgeson (1988) based on

the data of Patterson and others (1982). In this study, we have refined the $Cp_{298,1}^0$ using the new data of Stefánsson and others (2013), Stefánsson and others (2014), and the data of Patterson and others (1982) with lower weight above 125 °C. The $S_{298,1}^0$ of CO_3^{2-} was adopted from the calorimetric measurements of Berg and Vanderzee (1978), while the other standard state properties were accepted from Shock and Helgeson (1988).

Fig. 3. Comparison between calculated and experimentally determined stability constants of carbonate and bicarbonate complexes. **(A)** Stability constant of HCO_3^- as function of temperature at saturated water vapor pressure. **(B)** Stability constant of CO_3^{2-} as function of temperature at saturated water vapor pressure. **(C)** Stability constant of HCO_3^- as function of temperature at pressures of 0.2 and 2.0 kbar. **(D)** Stability constant of HCO_3^- as function of pressure at temperatures of 55, 150 and 250 °C.

Metal-Bicarbonate and -Carbonate Complexes

While the metal-carbonate complexes are only significant at extremely low CO_2 partial pressure and at high pH, the metal-bicarbonate ion pairs exert a significant control on carbonate mineral

solubility and their dependence on CO₂ partial pressure (De Visscher and others, 2012). The physical existence of alkali metal bicarbonate and carbonate species has been confirmed by Raman spectroscopy (Capewell and others, 1999; Sipos and others, 2000) and atomistic simulations (Demichelis and others, 2011). Stability constants for metal-bicarbonate and metal-carbonate species derived from the experimental solubility data are largely dependent on the speciation model used, which, in turn, also affects the calculation of ionic strength and pH (Turner and others, 1981).

The speciation model in this study considers the first bicarbonate and carbonate complexes of the alkaline earth and alkali metals Ca, Mg, Na and K. The association reactions are

Ca complexes.---The complexes CaHCO₃⁺ and CaCO₃⁰ were identified by Raman measurements and by atomistic calculations (Demichelis and others, 2011). Caciagli and Manning (2003) suggested that at the pressure-temperature conditions (6-16 kbar, 500-800 °C) of their experiments, CO_{2(aq)} was the predominant species, while CO₃²⁻, CaHCO₃⁺, and CaCO₃⁰ were negligible (<1%). Conversely, Facq and others (2014) concluded that CaHCO₃⁺ would be more stable at pressures <30 kbar, while CaCO₃⁰ becomes more stable at higher pressures. They also noted that at high-pressure conditions, both carbonate and bicarbonate are major carbonate species, which also form complexes with calcium. They suggested that with increasing pressure (above 5 kbar), CO_{2(aq)} is initially replaced by HCO₃⁻ and finally by CO₃²⁻ as the predominant species. With the exception of high-pressure studies, all other experiments were done at pressures of 1 bar and at saturated water vapor pressure. There is considerable disagreement concerning the stability of CaHCO₃⁺, and the reported log *K* values for equation (4) range from 0.29 to 1.29 at 25 °C and 1 bar. There is reasonable agreement between two of the experimental

studies, which are the conductance measurements of Jacobson and Langmuir (1974) and the aragonite and calcite solubility data of Plummer and Busenberg (1982). By contrast, the study of Martynova and others (1974), which used an ion-selective electrode method over the temperature range 22-98 °C, resulted in log K data that are in disagreement with the two studies mentioned above (fig. 4A).

Stability constants for Ca bicarbonate and carbonate species derived from solubility data depend on the values used for the first and second dissociation constant of $\text{CO}_{2(\text{aq})}$. This should not affect the data from Plummer and Busenberg (1982) much, because their experiments were performed below 90 °C, where the agreement between different datasets for the dissociation constants of $\text{CO}_{2(\text{aq})}$ is good. For CaCO_3^0 , there is reasonable agreement between the potentiometric study of Reardon and Langmuir (1974) and the data derived by Plummer and Busenberg (1982) from the pH of $\text{CaCl}_2 + \text{K}_2\text{CO}_3$ solutions. The ion-selective electrode measurements of Martynova and others (1974) are again in disagreement with the other two studies (fig. 4B).

Fig. 4. Comparison between calculated and experimentally determined association constants of calcium carbonate and calcium bicarbonate complexes as functions of temperature at saturated water vapor pressure. (A) Association constant of CaHCO_3^+ . (B) Association constant of CaCO_3^0 .

For CaHCO_3^+ , we selected the standard state properties from the study of Duan and Li (2008), which are derived from both low- and high-pressure calcite solubility experiments at saturated CO_2 conditions. The $S_{298,1}^0$ of CaCO_3^0 was refined based on the reported log K values

for equation (5) of Reardon and Langmuir (1974), Plummer and Busenberg (1982), Felmy and others (1998) and Bychkov and others (2007). The remaining standard state properties and HKF parameters were accepted from Sverjensky and others (1997).

Mg complexes.---Since the extensive review of De Visscher and others (2012), new data for the association constants of the Mg complexes MgHCO_3^+ and MgCO_3^0 were retrieved by Stefánsson and others (2014) from potentiometric and spectrophotometric measurements. Their data are in good agreement with the potentiometric measurements of Siebert and Hostetler (1977) for both complexes and also with the potentiometric measurements of Reardon and Langmuir (1974) for MgCO_3^0 (fig. 5). Importantly, the data analysis of Stefánsson and others (2014) considered also the presence of MgOH^+ , MgCl^+ , NaHCO_3^0 and NaCO_3^- . They concluded that MgCl^+ , NaHCO_3^0 and NaCO_3^- are present in insignificant amounts at their experimental conditions. Other reported values for the association constants of MgHCO_3^+ and MgCO_3^0 are in disagreement with the above mentioned studies.

Fig. 5. Comparison between calculated and experimentally determined association constants of magnesium carbonate and magnesium bicarbonate complexes as functions of temperature at saturated water vapor pressure. (A) Association constant of MgHCO_3^+ . (B) Association constant of MgCO_3^0 .

We have therefore refined the $S_{298.1}^0$ of MgHCO_3^+ based on log K values for equation (6) from Siebert and Hostetler (1977) and Stefánsson and others (2014). The remaining standard state properties and the HKF parameters for this complex were taken from Sverjensky and others

(1997). For MgCO_3^0 , we have refined $S_{298.1}^0$ against the data of Siebert and Hostetler (1977) and Stefnsson and others (2014), while accepting the remaining standard state properties and HKF parameters from Sverjensky and others (1997).

Na complexes.---The existence of NaCO_3^- and NaHCO_3^0 complexes has been demonstrated by Raman spectroscopy studies (Capewell and others, 1999; Sipos and others, 2000). The only high temperature studies (at saturated water vapor pressure) that would constrain the stability of these complexes are the potentiometric and spectrophotometric measurements of Stefnsson and others (2013) that cover temperatures from 80 to 200 C, and the data of Bychkov and others (2007) as reported by Stefnsson and others (2013) from 100 to 160 C. For 25 C and 1 bar, Capewell and others (1999) calculated a $\log K$ value of 0.98 for NaCO_3^- from Raman spectroscopic data, while Wimberley and others (1985) calculated $\log K$ values for both NaCO_3^- and NaHCO_3^0 of 0.92 and -0.143 at 25 C and 1 bar from ion selective electrode measurements (fig. 6). These values agree within their uncertainties with extrapolations to 25 C using the data of Stefnsson and others (2013). Facq and others (2016) have retrieved the stability constant of NaHCO_3^0 at the temperature of 300 C and pressures above 10 kbar, above the applicability range of the HKF EOS used in this study. We have accepted the $\Delta_f G_{298.1}^0$ values for NaCO_3^- and NaHCO_3^0 derived from the study of Wimberley and others (1985). Subsequently, we have obtained the other standard state properties and HKF parameters of both species using the estimation methods from Sverjensky and others (1997). Then the $S_{298.1}^0$ values were regressed against the $\log K$ values reported by Wimberley and others (1985), Bychkov and others (2007) and Stefnsson and others (2014).

K complexes.---The possible presence of KHCO_3^0 and KCO_3^- complexes was identified in the Raman spectroscopic study of Sipos and others (2000), but the inferred stability of both species was lower than that of their Na counterparts. Wimberley and others (1985) derived values for the association constants of KCO_3^- and KHCO_3^0 as 1.025 and -0.26 at 25 C and 1 bar, using measurements with an ion selective electrode. To our knowledge, there are currently no experimental constraints on the stability of potassium bicarbonate and carbonate complexes at elevated temperatures and pressures. We have therefore accepted the $\Delta_f G_{298.1}^0$ values for KCO_3^-

and KHCO_3^0 derived from the study of Wimberley and others (1985) and estimated the remaining standard state properties and HKF parameters using the correlation methods of Sverjensky and others (1997).

Fig. 6. Comparison between calculated and experimentally determined association constants of sodium carbonate and sodium bicarbonate complexes as function of temperature at saturated water vapor pressure. (A) Association constant of NaHCO_3^0 . (B) Association constant of NaCO_3^- .

ION ASSOCIATION PROPERTIES OF Ca AND Mg WITH HYDROXIDE AND CHLORIDE
Standard state properties and HKF parameters of Ca and Mg hydroxide and chloride species were derived from the experimental data, where preference was given to conductance and potentiometric measurements in aqueous solutions with low concentrations of dissolved Ca and Mg. Most datasets are restricted to subcritical conditions, and there is a clear lack of experimental data at supercritical temperatures and high pressures. The speciation model of this study considers the first hydroxide complex and the first and second chloride complex of Ca and Mg. The association reactions are:

Hydroxide Species

While the concentrations of Ca and Mg hydroxide species are negligible at low temperatures and slightly alkaline pH (De Visscher and others, 2012), they become more important as temperature increases (Walther, 1986; Seewald and Seyfried, 1991), and at pH >12. The properties of CaOH^+ and MgOH^+ in the SUPCRT92 dataset are solely based on predictions using correlations between standard state properties of ions and those of hydroxide species. They were refined in this study, taking into account new experimental data that constrain their stability.

CaOH⁺ association constant.---Experimental data on the stability of CaOH^+ are only available at temperatures below 100 °C (fig. 7A). Experimental studies include potentiometric measurements by Bates and others (1959), electromotive force measurements by Gimblett and Monk (1954) and measurements using ion-selective electrodes by Martynova and others (1974). Additional studies that permit to derive the stability constant of CaOH^+ are portlandite solubility experiments. Felmy and others (1998) derived a log K value of -12.93 at 22 °C from portlandite solubility, while Baes and Mesmer (1981) report a value of -12.85 at 25 °C. Both values are in excellent agreement with the value of -12.86 at 25 °C and 1 bar that was reported by Bates and others (1959). Gimblett and Monk (1954) report a log K value of -12.63, which is in disagreement with all other studies.

At elevated temperatures and pressures, the stability of the CaOH^+ species was exclusively retrieved from portlandite solubility measurements (fig. 7B). At temperatures between 100 and 350 °C and at 500 bar pressure, stability constants for CaOH^+ have been extracted from the experiments by Seewald and Seyfried (1991). For processing their data at low concentrations, they employed the extended Debye-Hückel model from Helgeson and Kirkham (1974b), which is consistent with the activity model used in this study. Walther (1986) studied the solubility of portlandite from 300 to 600 °C and from 1 to 3 kbar. The possible formation of CaOH^+ was not considered in the data treatment; the agreement between calculated and measured solubility was achieved by adjusting the $\Delta_f G_{298.1}^0$ of the Ca^{2+} ion. Seewald and Seyfried (1991) reinterpreted the data from Walther (1986), taking into account the formation of CaOH^+ . They extracted log K values up to 425 °C from the solubility data, but could not obtain them for higher temperatures due to the lack of high-temperature heat capacity data for portlandite. We have refined the standard state properties and HKF parameters of CaOH^+ using

the low temperature data of Bates and others (1959) and the portlandite solubility data of Seewald and Seyfried (1991) and Walther (1986).

Fig. 7. Comparison between calculated and experimentally determined association constants of the calcium hydroxide complex CaOH^+ . (A) Association constant as function of temperature below 100 °C at saturated water vapor pressure. (B) Association constant as function of temperature from 100 to 600 °C and at pressures of 0.5, 1.0, 2.0 and 3.0 kbar.

MgOH⁺ association constant.---The stability of MgOH^+ has been studied using potentiometry by McGee and Hostetler (1975) from 10 to 90 °C and by Palmer and Wesolowski (1997) from 25 to 250 °C and at saturated water vapor pressure (fig. 8A). Both datasets have a slightly different trend with temperature and start to diverge above 60 °C, with a maximum difference of around 0.4 log units at 90 °C. At high temperatures and pressures, the log K values of MgOH^+ have been derived from brucite solubility measurements by Walther (1986) assuming that MgOH^+ is the dominant species (fig. 8B). The thermodynamic properties of brucite used by Walther (1986) were those from Helgeson and others (1978). We have refined the $S_{298.1}^0$ and the HKF parameters of MgOH^+ based on the accurate potentiometric data of Palmer and Wesolowski (1997). The pressure and temperature trends of the stability constant of MgOH^+ calculated with the properties from Shock and others (1997) and this study are substantially different from those of Walther (1986). The brucite solubility experiments of Walther (1986) were not explicitly used to extract the stability constants of MgOH^+ , but they were used in the global regression of all mineral solubility data (see below).

Fig. 8. Comparison between calculated and experimentally determined association constants of the magnesium hydroxide complex MgOH^+ . (A) Association constant as function of temperature below 300 °C at saturated water vapor pressure. (B) Association constant as function of temperature from 300 to 600 °C and at pressures of 1.0 and 2.0 kbar.

Ca and Mg Chloride Species

The standard state properties and HKF parameters of Ca and Mg chloride species present in the SUPCRT92 database were derived from a limited number of experimentally determined stability constants below 100 °C and from correlations between aqueous metal complexes (Sverjensky and others, 1997). The properties for both CaCl^+ and MgCl^+ were derived from the potentiometric measurements of Majer and Štulík (1982). As already noted by Méndez De Leo and Wood (2005) and Arcis and others (2014), the log K values reported by Majer and Štulík (1982) were not extrapolated to infinite dilution. This results in a systematic error for the properties of CaCl^+ and MgCl^+ reported by Sverjensky and others (1997). The same applies to the properties of the complexes SrCl^+ , BaCl^+ , MgF^+ , CaF^+ , BaF^+ , and SrF^+ , which are also based on the uncorrected data of Majer and Štulík (1982). The log K values for CaCl^+ and CaCl_2^0 at 25 °C and 1 bar were derived from the study of Ramette (1986) which were also not corrected to infinite dilution. Ramette (1986) derived the association constants of CaCl^+ , CaCl_2^0 and CaCl_3^- from solubility experiments performed at constant ionic strength of 5 molal. Ruaya (1988) employed an isocoulombic approach to estimate the properties of Ca chloride complexes, but also used the uncorrected log K values of Majer and Štulík (1982). Rard and Clegg (1997) reviewed the properties of aqueous CaCl_2 solutions and identified large inconsistencies between

different datasets for the association constants of calcium chloride complexes at low temperatures.

Frantz and Marshall (1982) derived the ionization constants for calcium and magnesium chloride species (the first and second association constants for both elements) from electrical conductance measurements at 400 to 600 °C and 1 to 4 kbar in solutions of low total concentrations (0.001-0.005 molal). They did not account for the formation of the hydroxide species CaOH^+ and MgOH^+ in their data treatment, which introduced systematic errors in the association constants for chloride ion pairs. While hydroxide species are rather insignificant in moderately to highly concentrated chloride solutions, they form in appreciable amounts in solutions with low total electrolyte concentrations. Calculating the equilibrium speciation of a fluid with 0.001 CaCl_2 or MgCl_2 (using the properties of the Ca and Mg species from this study) at 400 to 600 °C and pressures of 1.0 to 4.0 kbar demonstrates that Ca and Mg hydroxide species are not negligible. CaOH^+ accounts for 3 to 8 % of the total dissolved calcium and MgOH^+ accounts for 5 to 16 % of the total dissolved magnesium.

CaCl⁺ and CaCl₂⁰ association constants.---The stability of the CaCl^+ complex was studied at subcritical conditions by diverse experimental techniques. This included potentiometric measurements from 15 to 85 °C (Majer and Štulík 1982), flow calorimetric measurements from 250 to 325 °C and saturated water vapor pressure (Gillespie and others 1992), enthalpy of dilution measurements from 300 to 325 °C and saturated water vapor pressure (Oscarson and others 2001), and conductance measurements (Méndez De Leo and Wood 2005). The association constants from Oscarson and others (2001) are systematically lower than the ones reported by Gillespie and others (1992) at the same conditions (fig. 9A). At supercritical conditions (fig. 9B), the association constants of calcium chloride were derived from electrical conductance measurements at 400 to 600 °C and 1 to 4 kbar by Frantz and Marshall (1982). Williams-Jones and Seward (1989) extracted values for the first (at 150 °C only) and second association constant from solubility measurements of AgCl in HCl-CaCl_2 solutions from 0.3 to 3 molal, for temperatures of 100 to 360 °C and at saturated water vapor pressure. Their association constants depend highly on the values used for the properties of silver chloride complexes, the solubility product of AgCl(s) and the properties of the HCl^0 species. Their results may also be affected by

the activity model used (Helgeson and others, 1981) to calculate the mean activity for mixed HCl-CaCl₂ solutions.

Fig. 9. Comparison between the calculated and experimentally determined first and second association constants of calcium chloride complexes. (A) Association constant of CaCl^+ as function of temperature at saturated water vapor pressure. (B) Association constant of CaCl^+ as function of pressure at temperatures from 400 to 600 °C. (C) Association constant of CaCl_2^0 as function of temperature at saturated water vapor pressure. (D) Association constant of CaCl_2^0 as function of pressure at temperatures from 400 to 600 °C.

When regressing the experimental data above 150 °C, Williams-Jones and Seward (1989) assumed that CaCl^+ was present in insignificant amounts and that CaCl_2^0 is the only species that needs to be considered. Reflecting the large discrepancies between different datasets for the relative stability of both CaCl^+ and CaCl_2^0 , this assumption is valid for one particular set of thermodynamic properties of the Ca chloride only. This is straightforwardly demonstrated by comparing the species distribution in a 1 molal chloride solution obtained using the

thermodynamic data of Williams-Jones and Seward (1989) and those of Sverjensky and others (1997) at 150 °C and saturated water vapor pressure (fig. 10).

Fig. 10. Calculated species distribution (expressed as percentage of the total dissolved Ca) for a 0.1 molal calcium solution as function of increasing chlorinity (at 150 °C and saturated water vapor pressure).

The association constants of CaCl_2^0 were also determined by Popp and Frantz (1979) from solubility experiments of quartz+wollastonite in $\text{CaCl}_2\text{-HCl}$ solutions at supercritical conditions (425 to 600 °C, 1 to 2 kbar) using the Ag-AgCl buffer technique. Their results are strongly dependent on the properties used for the HCl^0 species and on the calibration of the Ag-AgCl buffer. Popp and Frantz (1979) have also calculated the difference between the standard state Gibbs energies of CaCl_2^0 and HCl^0 , which is as such independent of the absolute properties used. However, they only considered CaCl_2^0 as the major Ca species, and ignored the presence of CaCl^+ at the conditions of their experiments.

To overcome the large inconsistencies between different datasets for the Ca chloride species, we have re-fitted the standard state Gibbs energy, entropy, and HKF parameters of CaCl^+ using carefully selected experimental data. These include the data of Majer and Štulík (1982) corrected to infinite dilution, the data from high-precision conductance experiments of Méndez De Leo and Wood (2005), and the data from calorimetric measurements of Gillespie and others (1992). The $C_p^0_{298,1}$ and $V^0_{298,1}$ values were adopted from Sverjensky and others (1997). Because only few data are available for CaCl_2^0 , we accepted the Gibbs energy and entropy of

this complex from the recent study of Gruszkiewicz and others (2007). They used isopiestic measurements of concentrated CaCl_2 and mixed-electrolyte solutions and extracted thermodynamic properties using a well-calibrated Pitzer activity coefficient model. The association constants of CaCl_2^0 calculated with the data from this study result in a considerable disagreement with the data of Frantz and Marshall (1982) at supercritical conditions (fig. 9D). Similar discrepancies have been observed when comparing the association constants of HCl^0 from the critical review of Tagirov and others (1997) with the data reported by Frantz and Marshall (1984). However, as will be shown below, the new association constant data for CaCl^+ and CaCl_2^0 , in conjunction with the association constant data for CaOH^+ that are based on robust experiments, are able to simultaneously represent all experimental calcite and Ca-silicate solubility data.

MgCl⁺ and MgCl₂⁰ association constants.---The association constant of the MgCl^+ complex was studied from 15 to 85 °C (fig. 11A) using a potentiometric method by Majer and Štulík (1982). They did not correct their results to infinite dilution. We have approximated their log K values at infinite dilution by applying a correction of similar magnitude to what was used by Méndez De Leo and Wood (2005) to correct the CaCl^+ data to infinite dilution. This approach is justified because the same background electrolyte and ionic strengths were used by Majer and Štulík (1982) in the experiments with Mg and Ca chloride solutions.

At supercritical conditions, the association constants of Mg chloride species were derived from electrical conductance measurements at 400 to 600 °C and at 1 to 4 kbar by Frantz and Marshall (1982) (figs. 11B and 11D). Saccocia and Seyfried (1990) extracted the stability constants of MgCl^+ from solubility measurements of talc+quartz in NaCl-MgCl_2 solutions (300-400 °C, 0.5 kbar). They assumed that MgCl_2^0 is insignificant at their experimental conditions, and they used the properties for HCl^0 from Frantz and Marshall (1984). The association constants of MgCl_2^0 were extracted by Frantz and Popp (1979) from quartz+talc solubility experiments in $\text{MgCl}_2\text{-HCl}$ solutions (400 to 650 °C, 1 to 2 kbar) using the Ag-AgCl buffer technique. Their results depend strongly on the calibration of the Ag-AgCl buffer used. They assumed that MgCl_2^0 was the only chloride species present, which was subsequently demonstrated to be incorrect (Frantz and Popp, 1981). They also calculated the difference between the standard state Gibbs energy of MgCl_2^0 and HCl^0 .

Fig. 11. Comparison between calculated and experimentally determined first and second association constants of magnesium chloride complexes. (A) Association constant of MgCl^+ as function of temperature at saturated water vapor pressure. (B) Association constant of MgCl^+ as function of pressure at temperatures from 300 to 600 °C. (C) Association constant of MgCl_2^0 as function of temperature at saturated water vapor pressure. (D) Association constant of MgCl_2^0 as function of pressure at temperatures from 500 to 600 °C.

In this study, we have derived a new $\Delta_f G_{298,1}^0$ for MgCl^+ bringing it into agreement with the corrected log K value at 25 °C and 1 bar from Majer and Štulík (1982). The $Cp_{298,1}^0$ and $V_{298,1}^0$ values were accepted from Sverjensky and others (1997) and the $S_{298,1}^0$ is essentially identical to the value derived by Sverjensky and others (1997), because the temperature dependence of the log K values corrected to infinite dilution at 15-85 °C is approximately the same as that of the uncorrected data. The association constants of MgCl^+ and CaCl^+ calculated with the properties from this study agree within 0.1 log units and show identical temperature and pressure trends. This led us to the conclusion that there should be a similar agreement between the temperature

and pressure trends of the association constants for MgCl_2^0 and CaCl_2^0 . We have therefore re-fitted the standard state properties and the HKF parameters of MgCl_2^0 based on this assumption. The data of Frantz and Marshall (1982) for the H_2O - MgCl_2 system are affected by the same inherent problems as those for the H_2O - CaCl_2 system.

Ca AND Mg SILICATE SPECIES

The speciation model in this study considers the silicate complexes of Ca and Mg. The association reactions are:

Standard state properties and HKF parameters for calcium and magnesium hydrosilicate species (reactions 18 and 20) are reported by Sverjensky and others (1997). They adopted the $\Delta_f G_{298.1}^0$ values of CaHSiO_3^+ and MgHSiO_3^+ from the compilation of Turner and others (1981), which are in very good agreement with those reported in the recent critical evaluation of Thoenen and others (2014). Sverjensky and others (1997) estimated the $S_{298.1}^0$, $Cp_{298.1}^0$ and $V_{298.1}^0$ of these species from correlations that involve metal ions and complexes with chemically similar ligands. Because there are no new experimental data that would constrain the stability of Ca and Mg silicate complexes, we accepted the data from Sverjensky and others (1997).

There are no experiment based standard state properties and HKF parameters for CaSiO_3^0 and MgSiO_3^0 available, and the information on the stability of these species at ambient conditions and elevated temperature and pressure is very limited (Walker and others, 2016). They can become important at ambient conditions and at elevated pH (Walker and others, 2016) but can potentially play a role in hydrothermal systems that are buffered by calcium and magnesium silicates. Therefore, we have performed an estimation of the thermodynamic properties and HKF parameters of CaSiO_3^0 and MgSiO_3^0 (table 1) based on the very limited data at hand. For CaSiO_3^0 , the standard Gibbs energy of formation and the absolute entropy of CaSiO_3^0 were taken from the study of Walker and others (2016), who used the solubility of

calcium silicate-hydrate to constrain the stability of this species at ambient conditions. We have then adjusted the $Cp_{298,1}^0$ to reproduce the

Table 1. Standard state properties (partial molal entropy, heat capacity and volume), HKF, and Akinfiev and Diamond (2003) model parameters of CO₂(aq) used in this study. These values were not adjusted but taken from their original references.

Species	$S_{298,1}^0$	$Cp_{298,1}^0$	$V_{298,1}^0$	$a_1 \cdot 10$	$a_2 \cdot 10^{-2}$	a_3	$a_4 \cdot 10^{-4}$	c_1	$c_2 \cdot 10^{-4}$	$\omega_0 \cdot 10^{-5}$	
	(J/mol·K)	(J/mol·K)	(J/bar)	(cal/mol/bar)	(cal/mol)	(cal·K/mol/bar)	(cal·K/mol)	(cal/mol/K)	(cal·K/mol)	(cal/mol)	
(1)Ca ⁺²	-56.48	-30.92	-1.84	-0.1947	-7.2520	5.2966	-2.4792	9.00000	-2.5220	1.2366	
(1)Mg ⁺²	-138.07	-21.662	-2.2	-0.8217	-8.5990	8.3900	-2.3900	20.8000	-5.8920	1.5372	
(2)CaHSiO ₃ ⁺	-8.33	137.8	-0.67	1.0647	-5.1787	7.7785	-2.5649	30.8048	3.6619	0.5831	
(2)MgHSiO ₃ ⁺	-99.5	158.65	-1.08	0.6289	-6.2428	8.1967	-2.5209	36.7882	4.6702	0.9177	
<div><div>$Cp^0 = a_0 + a_1 \cdot T + a_2 \cdot T^{-2} + a_3 \cdot T^{-0.5} + a_4 \cdot T^2$</div><div><div>$a_0 \cdot 10^{-1}$$a_1 \cdot 10^2$$a_2 \cdot 10^{-5}$$a_3 \cdot 10^{-2}$$a_4 \cdot 10^6$</div><div>Empirical parameters</div></div></div>											
								ξ	a (cm ³ /g)	b (cm ³ ·K ^{0.5} /g)	
(3)CO ₂ (aq)	119.29	209.75	3.27	6.56823	1.11973	2.80403	-5.99129	-3.92	-0.085	-8.8321	11.2684

(1) Taken from Shock and others (1997)

(2) Taken from Sverjensky and others (1997).

(3) Taken from the model of Akinfiev and Diamond (2003). Molal thermodynamic properties of species in the ideal gas state are calculated through standard heat capacity integration, and the hydration properties are then added as a pressure correction. The Gibbs energy of hydration is calculated using the Akinfiev and Diamond (2003) model.

increase in wollastonite+quartz solubility above 500 °C observed in the experiments of Xie and Walther (1993b). The HKF parameters were estimated from correlations (Sverjensky and others, 1997). Because there is no data available for the stability of MgSiO_3^0 , we have assumed that its stability constants are the same as those for CaSiO_3^0 . They were subsequently used to regress the values of the standard state properties and HKF parameters of MgSiO_3^0 . The thermodynamic properties of the two species CaSiO_3^0 and MgSiO_3^0 generated in this study have very large associated uncertainties. These species were therefore not considered in the global optimization of solubility data and cannot be included in geochemical speciation models, as long as reliable experimental constraints on their stability at different conditions are not available and the presence of these species in crustal fluids is questionable.

SELECTION OF THE EXPERIMENTAL SOLUBILITY DATA

The available experimental solubility datasets that would constrain the stability of Ca and Mg aqueous species are much smaller in number than those for the previously evaluated system Na-K-Al-Si-Cl-O-H (Miron and others, 2016). In our selection, priority was given to experiments that demonstrated the attainment of equilibrium, used experimental techniques which were not affected by quenching problems, and sampled the aqueous solutions at equilibrium conditions.

System Ca-Mg-Al-Si-O-H

Fluid-mineral equilibria in the system Mg-Si-O-H in a wide range of temperatures and at pressures of 1 and 2 kbar were studied by Hemley and others (1977a) and Hemley and others (1977b). They used cold-seal pressure vessels with a rapid quench method for their experiments. The equilibrium was established by approaching it from different initial silica concentrations and they used both synthetic and natural minerals. For the same temperature-pressure conditions, the results using synthetic and natural mineral samples agree within their experimental uncertainty. Hemley and others (1977a, b) also investigated the possible loss of dissolved silica by precipitation during quench, but concluded that it did not occur.

Walther (1986) determined the solubility of brucite in water between 300 and 600 °C and at pressures of 1 to 3 kbar. The experiments were performed using an extraction quench hydrothermal apparatus. The aqueous phase was equilibrated with synthetic brucite, and the final material was analyzed optically and by X-ray diffraction to confirm that brucite was the only

mineral phase present in the run products. Equilibrium was considered to be approached from supersaturation if the Mg concentration decreased by more than 10% from the previous step, and from undersaturation if the concentration of Mg increased by more than 10%. The solubility of brucite at low temperatures in different electrolyte solutions has been extensively reviewed by Lambert and Clever (1992a). The solubility product of brucite is rather small and thus difficult to measure with sufficiently good precision (Lambert and Clever, 1992a).

Xie and Walther (1993b) studied the solubility of the assemblage wollastonite+quartz in water and NaCl solutions. The experiments in pure H₂O were performed at temperatures of 250 to 600 °C and pressures of 1 to 2 kbar. They used an extraction quench hydrothermal apparatus similar to the one used by Walther (1986) for brucite solubility experiments. The authors used natural wollastonite samples and they did not report the chemical composition of the mineral. They approached equilibrium from both undersaturated and supersaturated conditions by increasing or decreasing the concentration of Ca between different experiments. Wollastonite solubility experiments at very high pressures were done by Fockenberg and others (2006), but the experimental conditions are outside the permissible range of the HKF model for aqueous species used in this study.

Portlandite solubility experiments at hydrothermal conditions were performed by Seewald and Seyfried (1991) and Walther (1986). Seewald and Seyfried (1991) measured portlandite solubility in water and acetate solutions from 100 to 350 °C at 500 bar. Walther (1986) conducted solubility experiments between 300 and 600 °C and at pressures of 1 to 3 kbar. They report the results of experiments that approached equilibrium from both undersaturated and supersaturated conditions, based on the change in concentration of the sampled solution (increase or decrease by 10%). The experimental technique in both studies employed sample extraction at run conditions, thus avoiding possible errors related to quenching. The solubility of portlandite at low temperatures and in different electrolyte solutions has been reviewed by Lambert and Clever (1992b).

System Ca-Mg-Al-Si-Cl-O-H

The most comprehensive study in the Ca-Mg-Si-Cl-O-H system has been conducted by Luce and others (1985) who provided the solubility data which are critical for constraining the stabilities of calcium silicates involved into metasomatic skarn reactions. The studied fluid-mineral equilibria

comprise the mineral assemblages talc+quartz, tremolite+talc+quartz, diopside+tremolite+quartz, wollastonite+diopside+quartz, and wollastonite+quartz. The experiments were performed between 500 and 700 °C, at a pressure of 2 kbar and chloride concentrations from 0.03 to 6.0 molal. They used cold-seal pressure vessels, employed both natural and synthetic minerals as starting materials, and the solutions were analyzed after fast quench. Luce and others (1985) derived the concentration of HCl in their experiments using pH calibration curves, which were determined from known HCl concentrations in solutions with variable CaCl_2 and MgCl_2 concentrations. The experimental dataset of Luce and others (1985) was used as a reference dataset in the present study because it provides a great number of constraints on the stabilities of key aqueous species.

Roselle and Baumgartner (1995) studied the solubility of the anorthite+andalusite+quartz assemblage in supercritical chloride solutions. They used their results to derive the anorthite+andalusite phase equilibrium, to evaluate the stability of higher-order calcium chloride species CaCl_3^- and CaCl_4^{2-} , and to determine the stability constant of CaOH^+ . They used a cold-seal pressure vessel method comparable to that used by Hemley (1959). The actual H^+ concentration was derived using a calibration method of the pH electrode that accounts for salt and electrode specific effects. Synthetic anorthite and natural andalusite and quartz were used as starting materials. The equilibrium constants derived from their experiments depend strongly on the values used for the association constants of H_2O , HCl^0 , CaCl^+ , and CaCl_2^0 . They used a different set of association constants than was employed in this study.

Xie and Walther (1993a) studied the solubility of quartz+wollastonite in pure water and in NaCl solutions using an extraction quench method. They retrieved association constants for CaCl^+ and CaCl_2^0 from their experiments in NaCl solutions, using the properties of HCl^0 from Frantz and Marshall (1984). The resulting association constants for CaCl_2^0 are around 2 log units lower than the ones from Frantz and Marshall (1982) at similar conditions.

Saccocia and Seyfried (1990) studied the solubility of the assemblage talc+quartz between 300 and 400 °C and at 0.5 kbar in NaCl-MgCl₂ solutions. They employed a hydrothermal apparatus and extracted the solutions at run conditions. They performed experiments from both undersaturated and supersaturated conditions by changing the concentration of MgCl_2 and measured the pH of the extracted solutions at 25 °C. They derived the association constant for MgCl^+ using the properties of HCl^0 from Frantz and Marshall (1984)

without considering the formation of MgCl_2^0 . Their results are in disagreement with extrapolated data from Frantz and Marshall (1982), but in reasonable agreement with the results of Luce and others (1985).

Several studies of the solubility of calcium and magnesium silicates have been performed using the $\text{Ag(s)}\text{-AgCl(s)}$ acid buffer technique. This method allows controlling the activity of HCl at experimental run conditions, but it highly depends on the calibrations, on the thermodynamic properties of Ag(s) and AgCl(s) , those of the aqueous species, and those of the oxygen fugacity buffers. The $\text{Ag(s)}\text{-AgCl(s)}$ buffer method was re-calibrated in several studies (Frantz and Popp, 1979; Luce and others, 1985). The method has been employed in a number of studies, including the solubility of wollastonite+quartz in supercritical chloride solutions by Gunter and Eugster (1978) and Popp and Frantz (1979) and the solubility of talc+quartz in supercritical chloride solutions by Frantz and Popp (1979) and Grabman and Popp (1991). Grabman and Popp (1991) used NaCl-MgCl_2 solutions in their experiments and suggested that higher-order Mg chloride and mixed Na-Mg chloride species may form at temperatures above $500\text{ }^\circ\text{C}$. They concluded that at temperatures above $500\text{ }^\circ\text{C}$, higher-order chloride species are needed to explain their data.

System Ca-Mg-Cl-O-H-C

The most extensive reviews of solubility of alkaline earth metal carbonates in water and electrolyte solutions were presented by Duan and Li (2008), De Visscher and others (2012), and De Visscher and Vanderdeelen (2012). The majority of carbonate solubility experiments were done at temperatures up to $100\text{ }^\circ\text{C}$ and in a three-phase system (solid carbonate, aqueous solution and CO_2 -rich gas phase). A large number of calcite and aragonite solubility measurements below $100\text{ }^\circ\text{C}$ over a range in CO_2 partial pressure were performed by Plummer and Busenberg (1982). Segnit and others (1962) measured the solubility of calcite from 75 to $200\text{ }^\circ\text{C}$ and at CO_2 partial pressures of 6 to 63 bars. Ellis (1959b) measured the solubility of calcite from 100 to $302\text{ }^\circ\text{C}$ and at CO_2 partial pressures of 1 to 63 bars. The solubility of calcite at temperatures above $100\text{ }^\circ\text{C}$ in dilute NaCl solutions was measured by Ellis (1963) at a CO_2 partial pressure of 12.2 bar. Bychkov and others (2007) evaluated the solubility of calcite from pH measurements in NaCl solutions from 120 to $160\text{ }^\circ\text{C}$ at variable CO_2 partial pressures of $2\text{-}50$ bar. Their values are in good agreement with calculated solubility data using thermodynamic data from SUPCRT92

(Stefánsson and others, 2013). The authors concluded that calcium carbonate species are not important in controlling calcite solubility at these conditions. Calcite solubility in chloride brines at different CO_2 concentration was also measured by Malinin and Kanukov (1972) between 200 and 600 °C. Their measurements were done mostly at high CO_2 concentrations where the assumption of the activity coefficient of $\text{CO}_{2(\text{aq})}$ being equal to 1.0 is not valid. Experiments that involve only an aqueous solution and a carbonate mineral (but not a separate CO_2 -rich gas phase) are very challenging, because even a small external contamination with CO_2 can have a large impact on the measured solubility. This explains why the experimentally determined calcite solubility data below 100 °C show a considerable scatter (fig. 12). These data were therefore not included into our final experimental database used for the global regression of aqueous species thermodynamic data.

Fig. 12. Comparison between calculated and experimentally determined calcite and aragonite solubility in the system $\text{CaCO}_3\text{-H}_2\text{O}$ as function of temperature at saturated water vapor pressure. (A) Dissolved Ca concentration in equilibrium with calcite. (B) Dissolved Ca concentration in equilibrium with aragonite.

There are only three studies that determined the solubility of calcite in water and aqueous electrolyte solutions at supercritical conditions. The solubility experiments of Walther and Long (1986) were done at 300 to 600 °C and 1.0 to 3.0 kbar. Fein and Walther (1989) measured the solubility of calcite in water and in HCl-NaCl solutions at 2.0 kbar and temperatures up to 600 °C. Their calcite solubility data in water are systematically higher than the ones reported by Walther and Long (1986). Fein and Walther (1987) measured the calcite solubility in $\text{H}_2\text{O-CO}_2$ fluids at conditions above 2 mol.% CO_2 dissolved in the aqueous phase, where the assumption

that the activity coefficient of CO₂ aqueous species is close to 1.0 is not valid anymore. Consequently, experimental data obtained at more than 2 mol.% CO₂ were not considered in our data regression. Caciagli and Manning (2003) and Newton and Manning (2002) studied calcite solubility in H₂O and NaCl solutions at deep crustal and mantle pressures which exceed the applicability of the HKF equation of state that was used in this study.

The magnesite solubility under subcritical conditions was reviewed by De Visscher and others (2012). They point out that the data in the system open to CO₂, in pure water and in electrolyte solutions, are very limited and largely inconsistent. Bénézech and others (2011) measured the solubility of magnesite from 50 to 200 °C in 0.1 mol/kg NaCl aqueous solutions under different CO₂ partial pressures using the hydrogen electrode concentration cell and a batch Ti reactor. Based on carbon and magnesium species properties from the literature and their measured data, they retrieved the solubility products of magnesite and the standard state properties of magnesite at 25 °C and 1 bar.

Experimental studies of the solubility of dolomite have been mostly performed at ambient conditions, and in many cases they have addressed the dissolution-precipitation kinetics of dolomite (Michałowski and Ausero, 2012). The equilibrium solubility of dolomite is difficult to study especially at low temperatures, because of kinetic effects (pure dolomite dissolves more slowly than pure calcite), and because of temperature-dependent order-disorder of Ca and Mg in the dolomite structure. Morey (1962) reported values for the solubility of dolomite in CO₂-free water from 25 to 340 °C and at saturated water vapor pressure. The reported values of the logarithm of the solubility product of dolomite at 25 °C and 1 bar range over 3 orders of magnitude from -19 to -16 (Sherman and Barak, 2000). This large discrepancy is mainly due to one or several experimental problems, mainly the lack of attainment of equilibrium (Sherman and Barak, 2000). Sherman and Barak (2000) tried to better constrain the solubility product of dolomite and they report a best estimate of -17.2 ± 0.2 . Reflecting the inherent problems with the experimental determination of the dolomite solubility product, the available experimental data were not included in the global optimization. We have, however, compared calculations with the final thermodynamic dataset of this study with selected experimental and natural data for dolomite solubility (see Discussion).

PARAMETER OPTIMIZATION METHODS

We used the same global optimization method and settings that were utilized in the previous study addressing the thermodynamic data in the Na-K-Al-Si-O-H-Cl system (Miron and others, 2016). The standard state Gibbs energies of aqueous species were regressed with the GEMSFITS code (Miron and others, 2015), which uses the GEMS3K Gibbs energy minimization code (Kulik and others, 2013) and the TsolMod library of activity and equation of state models (Wagner and others, 2012). The chemical system definitions (lists of phases and species, initial thermodynamic properties of each species, bulk composition, pressure and temperature for each experimental data point) were prepared using the GEM-Selektor v.3 code package (<http://gems.web.psi.ch/GEMS3>) and then exported into text files that can be read by GEMS3K and GEMSFITS codes (Miron and others, 2015).

The final parameter values for aqueous species in the system Na-K-Al-Si-O-H-Cl from the previous study (Miron and others, 2016) were used as starting values for the new global optimization. The starting values for aqueous species related to calcium, magnesium and carbon were taken from Shock and Helgeson (1988), Shock and others (1989), Sverjensky and others (1997), Shock and others (1997), and Stefánsson and others (2014).

Standard state properties and the HKF parameters (other than $\Delta_f G_{298,1}^0$) for the aqueous species were taken from several sources (table 1) or were separately optimized in this study (table 2, section on carbon, calcium and magnesium species). These parameters were not refined during the global regression of mineral solubility data and only the $\Delta_f G_{298,1}^0$ values of the aqueous species were optimized. The program OptimB (Shvarov, 2015) was used for optimizing the HKF parameters of several aqueous complexes based on the critically evaluated datasets of association constants reviewed above.

The critically evaluated experimental dataset for the system Na-K-Al-Si-O-H-Cl (Miron and others, 2016) was accepted in this study, and only the new experimental data for the solubility of Ca-Mg silicate and carbonate minerals or mineral assemblages were added. In addition to freely optimized $\Delta_f G_{298,1}^0$ values in the system Na-K-Al-Si-O-H-Cl (those of Na^+ , K^+ , SiO_2^0 , HSiO_3^- , Al_3^+ , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^0$, $\text{Al}(\text{OH})_4^-$, $\text{NaAl}(\text{OH})_4^0$, KAlO_2^0), we have included the $\Delta_f G_{298,1}^0$ values for key Ca and Mg species (those of Ca^{+2} , Mg^{+2} , CaCl_2^0 , and MgCl_2^0) into the global optimization. Other calcium, magnesium and carbonate species considered in the

extended system Ca-Mg-Na-K-Al-Si-O-H-C-Cl were either adjusted through reaction constraints (Miron and others, 2015) or accepted from carefully evaluated datasets. There are only very limited and partly contradicting data available that would constrain the stability and standard state properties of CaCl_2^0 , and MgCl_2^0 independently of solubility data. As long as no new high-quality conductance experiments become

Table 2. Standard state properties (partial molal entropy, heat capacity and volume) and HKF parameters of aqueous species derived in this study from conductance, literature logKs, and solubility (portlandite) data. The values presented for CaSiO_3^0 and MgSiO_3^0 are tentative, and were not included in the global optimization. For details on how the properties and parameters were generated, see the sections on carbon, calcium, and magnesium species.

Species	$S_{298,1}^0$ (J/mol·K)	$CP_{298,1}^0$ (J/mol·K)	$V_{298,1}^0$ (J/bar)	$a_1 \cdot 10$ (cal/mol/bar)	$a_2 \cdot 10^{-2}$ (cal/mol)	a_3 (cal·K/mol/bar)	$a_4 \cdot 10^{-4}$ (cal·K/mol)	c_1 (cal/mol/K)	$c_2 \cdot 10^{-4}$ (cal·K/mol)	$\omega_0 \cdot 10^{-5}$ (cal/mol)
CaOH^+	36.47	-78.41	1.096	3.9385	-1.1019	6.1831	-2.7334	-9.5888	-2.6253	0.4190
CaCl^+	-2.97	73.33	0.556	2.7406	-1.0897	6.1783	-2.7340	21.5880	0.5240	0.5626
CaCl_2^0	67.73	129.52	3.265	6.2186	7.4024	2.8406	-3.0850	23.9609	3.2720	-0.0380
CaHCO_3^+	66.27	234.27	1.328	3.7000	1.2579	5.2520	-2.8310	43.1120	7.7228	0.3113
CaCO_3^0	20.11	-123.86	-1.565	-0.3907	-8.7325	9.1753	-2.4179	-11.5309	-9.0641	-0.0380
MgOH^+	-67.36	129.1	0.166	2.2937	-2.1809	6.6072	-2.6888	31.5415	3.2394	0.7950
MgCl^+	-79.5	104.96	0.125	2.2809	-2.3585	6.6770	-2.6815	28.5471	2.0579	0.8389
MgCl_2^0	-11.57	170.77	2.825	5.6165	5.9323	3.4184	-3.0242	29.7395	5.2804	-0.0380
MgHCO_3^+	-19.11	254.69	0.934	3.3000	0.1608	5.6868	-2.7875	47.5204	9.3524	0.6204
MgCO_3^0	-102.57	-114.64	-1.827	-0.7355	-9.5745	9.5062	-2.3831	-9.8914	-8.6160	0.0000
NaCO_3^-	56.09	-82.31	-0.152	2.0000	-2.3350	6.6714	-2.6825	7.7693	-7.1095	1.4265
NaHCO_3^0	158.66	201.84	3.182	6.1192	7.1597	2.9359	-3.0750	34.4381	6.7919	0.0000
KCO_3^-	76.32	-112.85	0.829	3.4128	0.5540	5.5266	-2.8018	2.7390	-8.5569	1.3525
KHCO_3^0	208.74	134.95	4.319	7.6623	10.9298	1.4497	-3.2307	24.7193	3.5355	-0.0380
CO_3^{2-}	-50	-322.65	-0.606	2.8524	-3.9844	6.4142	-2.6143	-7.9872	-18.8139	3.3914
HCO_3^-	96.62	-34.85	2.421	2.9936	4.9787	23.5905	-2.9848	12.994	-4.7579	1.2792
CaSiO_3^0	-20.54	-179	1.57	3.1272	-10.5859	42.3257	-2.3414	61.9110	-51.1046	0.0935
MgSiO_3^0	-102	-169.9	1.21	0.8426	-11.069	52.9604	-2.3216	68.7194	-53.9981	-0.0445

available, the values of CaCl_2^0 , and MgCl_2^0 need to be included into the regression in order to achieve a sufficiently good representation of the experimental Ca and Mg silicate and carbonate solubility data.

The overall quality of the fit for each individual experimental dataset related to Ca-Mg silicate and carbonate solubility is reported in table 3 and defined by the normalized-root-mean-square-error (*NRMSE*):

$$NRMSE = \sqrt{\frac{\sum_i^N [y(i) - f(i)]^2}{\sum_i^N y(i)^2}} \quad (22)$$

This evaluation of the quality of the fit is performed after the GEMSFITS optimization and is not equivalent to the objective function that is used by the optimization algorithm.

RESULTS

The experimental solubility data are compared with their calculated counterparts in figures 13 through 23. In these figures, full symbols always denote experimental data points used in the global optimization, while open symbols denote data points that were not used and are included for comparison. The final regressed $\Delta_f G_{298.1}^0$ values of aqueous species obtained from the global optimization of all mineral solubility data, including refined data for the species included in the earlier study of the system Na-K-Al-Si-O-H-Cl (Miron and others, 2016), are summarized in tables 4 and 5. These tables also list all thermodynamic properties of the species that were fixed during fitting, and those which were constrained using association reaction constants.

System Ca-Mg-Al-Si-O-H

There is a fairly good agreement between the calculated and the measured silica concentration data for fluid-mineral equilibria experiments in the system Mg-Si-O-H (fig. 13A). There are some small differences for experiments involving talc+antigorite (fig. 13B), enstatite+forsterite and talc+anthophyllite assemblages. Considering the good agreement with all the other experimental data involving Ca and Mg silicates, these differences could be at least partly related to the thermodynamic properties of the minerals which were accepted from the Holland-Powell mineral dataset (Holland and Powell, 1998), or to some unresolved issues with the experiments.

Reference	System	Number of data points used	⁽¹⁾ Direction of equilibrium	Temperature range (deg. C)	Pressure range (kbar) / Partial pressure gas (bar)	Dataset total error (eq. 22)
Hemley and others (1977a)	talc-chrysotile-forsterite-H ₂ O	38	U	90 – 600	1bar – 2.0	Si: 0.035
Hemley and others (1977b)	talc-forsterite-antophyllite-enstatite-H ₂ O	55	U	300-720	1.0 – 2.0	Si: 0.064
Walther (1986)	brucite-H ₂ O	39	U-S?	350-630	1.0-2.9	Mg: 0.045
Luce and others (1985)	talc-wollastonite-diopside-tremolite-quartz-MgCl ₂ -CaCl ₂ -H ₂ O	68	U	500-700	2.0	Log(Ca/Mg): 0.086 Log(Ca/H ²): 0.032 Log(Mg/H ²): 0.125
Fein and Walther (1989)	calcite-H ₂ O-HCl-NaCl	65	U	400-600	2.0	Ca: 0.031
Plummer and Busenberg (1982)	calcite-H ₂ O-CO ₂	141	U	0-90	1 / ⁽²⁾ PCO ₂ 1 – <0.01	Ca: 0.019
Plummer and Busenberg (1982)	aragonite-H ₂ O-CO ₂	205	U	1-90	1 / PCO ₂ 1 – <0.01	Ca: 0.017
Ellis (1959b)	calcite-H ₂ O-CO ₂	59	U	98-302	⁽³⁾ SWVP / PCO ₂ 1 – 62	Ca: 0.021
Bénézech and others (2011)	magnesite-H ₂ O-NaCl-CO ₂	34	U	50-202	SWVP / PCO ₂ 13 – 30	Mg: 0.078

Table 3. Summary of experimental solubility datasets selected for the global optimization.

⁽¹⁾ U: equilibrium approached from undersaturation; S?: was considered that the equilibrium was approached from supersaturation if the measured concentration decreased by 10% from previous measurements (in a continuous series of varying conditions).

⁽²⁾ PCO₂: partial pressure of carbon dioxide gas.

⁽³⁾ SWVP: Saturated water vapor pressure

Table 4. Final values of the standard-state molal Gibbs energy for aqueous species related to calcium, magnesium, and carbon, optimized using the experimental datasets presented in this study (Table 3). Gibbs energy values need to be combined with standard state entropy, volume, heat capacity, and HKF parameters from Tables 1 and 2. The standard deviation of optimized parameters was calculated from 500 Monte Carlo simulation runs, and the 95% confidence interval - using the Student's t-distribution.

Species	$\Delta_f G_{298,1}^0$ (J/mol) this study	Standard deviation	95% confidence interval	Optimization mode
Ca ⁺²	-552821	50	100	Optimized
CaOH ⁺	-716750	-	-	(1)Constrained
CaCl ⁺	-689297	-	-	(1)Constrained
CaCl ₂ ⁰	-795990	985	1933	Optimized
CaHCO ₃ ⁺	-1145214	-	-	(1)Constrained
CaCO ₃ ⁰	-1099084	-	-	(1)Constrained
CaHSiO ₃ ⁺	-1575097	-	-	(2)Constrained
CaSiO ₃ ⁰	-1515154	-	-	(1)Constrained
Mg ⁺²	-456005	519	1019	Optimized
MgOH ⁺	-626503	-	-	(1)Constrained
MgCl ⁺	-592204	-	-	(1)Constrained
MgCl ₂ ⁰	-696566	957	1879	Optimized
MgHCO ₃ ⁺	-1048857	-	-	(1)Constrained
MgCO ₃ ⁰	-1000992	-	-	(1)Constrained
MgHSiO ₃ ⁺	-1479708	-	-	(2)Constrained
MgSiO ₃ ⁰	-1418335	-	-	(1)Constrained
NaCO ₃ ⁻	-789833	-	-	(1)Constrained
NaHCO ₃ ⁰	-842065	-	-	(1)Constrained
KCO ₃ ⁻	-810746	-	-	(1)Constrained
KHCO ₃ ⁰	-862284	-	-	(1)Constrained
CO ₃ ⁻²	-527983	-	-	(3)Fixed
HCO ₃ ⁻	-586855	-	-	(4)Fixed
CO _{2(aqueous)}	-386030	-	-	(5)Fixed

(1)Constrained to properties of the respective ions by the reactions presented in Section 4 consistent with the standard state properties and HKF parameters from Tables 1 and 2.

(2)Constrained to properties of Ca⁺², Mg⁺², and SiO₂⁰ by the reaction: Ca⁺² + H₂O + SiO₂⁰ = CaHSiO₃⁺ + H⁺, Mg⁺² + H₂O + SiO₂⁰ = MgHSiO₃⁺ + H⁺ and equilibrium constants consistent with the standard state properties and HKF parameters from Table 1 taken from Sverjensky and others (1997).

(3)Taken from Shock and others (1997).

(4)Refined in this study against literature logK values, -586940 J/mol reported by Shock and others (1997).

⁽⁵⁾Taken from the model of Akinfiev and Diamond (2003).

Table 5. Final values of the standard-state molal Gibbs energy for aqueous species that were previously refined in Miron et al. (2016), and the new optimized values obtained using the experimental datasets both from Miron et al. (2016) and this study (Table 3). Gibbs energy values need to be combined with standard state entropy, volume, heat capacity and HKF parameters from Table 1 (ion pairs of main electrolytes) and Table 5 (other aqueous species) from Miron et al. (2016). The standard deviation of parameters was calculated from 500 Monte Carlo simulation runs, and the 95% confidence interval - using the Student's t-distribution.

Species	$\Delta_f G_{298,1}^0$ (J/mol) Miron et al. (2016)	$\Delta_f G_{298,1}^0$ (J/mol) this study	Δ 2016-this study	Standard deviation	95% confidence interval	Optimization mode
Al ³⁺	-486627	-486594	-33	258	507	Optimized
AlOH ²⁺	-695574	-695541	-33	543	1077	⁽¹⁾ Constrained
Al(OH) ₂ ⁺	-898295	-898292	-3	1339	2627	Optimized
Al(OH) ₃ ⁰	-1105801	-1105813	12	944	1852	Optimized
Al(OH) ₄ ⁻	-1305097	-1305097	0	229	450	Optimized
NaAl(OH) ₄ ⁰	-1562121	-1562083	-38	944	1853	Optimized
AlH ₃ SiO ₄ ²⁺	-1782516	-1782421	-95	-	-	⁽²⁾ Constrained
KAlO ₂ ⁰	-1100293	-1100134	-159	2423	4751	Optimized
K ⁺	-276893	-276870	-23	643	1261	Optimized
KOH ⁰	-431656	-431633	-23	-	-	⁽³⁾ Constrained
KCl ⁰	-402544	-393521	-23	-	-	⁽³⁾ Constrained
Na ⁺	-256169	-256142	-27	644	1263	Optimized
NaOH ⁰	-411594	-411567	-27	-	-	⁽³⁾ Constrained
NaCl ⁰	-383091	-383064	-27	-	-	⁽³⁾ Constrained
NaHSiO ₃ ⁰	-1283076	-1282987	-89	-	-	⁽⁴⁾ Constrained
HSiO ₃ ⁻	-1015237	-1015175	-62	-	-	⁽⁵⁾ Constrained
SiO ₂ ⁰	-834103	-834041	-62	34	67	Optimized
Cl ⁻	-131290	-131290	0	-	-	⁽⁶⁾ Fixed
HCl ⁰	-127240	-127240	0	-	-	⁽⁷⁾ Fixed
OH ⁻	-157287	-157287	0	-	-	⁽⁶⁾ Fixed
H ⁺	0	0	0	-	-	⁽⁸⁾ Fixed
H ₂ O	-237183	-237183	0	-	-	⁽⁹⁾ Fixed

⁽¹⁾ Constrained to properties of Al³⁺ by the reaction: AlOH²⁺ + H⁺ = Al³⁺ + 2 H₂O, using equilibrium constant values from Palmer and Wesolowski (1993).

⁽²⁾ Constrained to properties of Al³⁺ and SiO₂⁰ by the reaction: Al³⁺ + 2 H₂O + SiO₂⁰ = AlH₃SiO₄²⁺ + H⁺, and equilibrium constants from Tagirov and Schott (2001), extracted from Pokrovski and others (1996) and Salvi and others (1998).

⁽³⁾ Constrained to properties of Na⁺, K⁺, OH⁻, and Cl⁻ using the equilibrium constants determined from the new standard state properties of ion pairs extracted from the conductance data (Table 1).

- (4) Constrained to properties of Na^+ and SiO_2^0 by the reaction: $\text{Na}^+ + \text{H}_2\text{O} + \text{SiO}_2^0 = \text{NaHSiO}_3^0 + \text{H}^+$, using equilibrium constants from Sverjensky and others (1997), extracted from Seward (1974).
- (5) Constrained to properties of SiO_2^0 by the reaction: $\text{SiO}_2^0 + \text{H}_2\text{O} = \text{HSiO}_3^- + \text{H}^+$, using equilibrium constants from Busey and Mesmer (1977).
- (6) Taken from Shock and Helgeson (1988).
- (7) Taken from Tagirov and others (1997).
- (8) Conventional value.
- (9) Taken from Johnson and others (1992).

Fig. 13. Comparison between calculated and experimentally determined phase equilibria and dissolved silicon concentrations in the Si-Al-Mg-H-O system (Hemley and others, 1977a; 1977b) as function of temperature at 1 kbar pressure. (A) Phase equilibria below 600 °C. (B) Phase equilibria between 600 and 800 °C.

Calculated Mg concentrations for the brucite solubility equilibrium at different temperatures and pressures are in reasonably good agreement with the experimental data (fig. 14) from Walther (1986). The agreement between calculated and measured data is better for the dataset from this study, compared to calculations using the aqueous species data from Shock and others (1997). Calculated wollastonite solubility using data from Shock and others (1997) underestimates the experimentally measured solubility in pure water by around 0.3 log units. Calculating the wollastonite solubility with the data from this study results in moderate underestimation of the experimental solubility as well (fig. 15). The discrepancy between calculated and measured solubility increases with temperature.

Fig. 14. Comparison between calculated and experimentally determined brucite solubility (concentration of total dissolved Mg in water) (Walther, 1986) as function of temperature. (A) Brucite solubility at 1 kbar pressure. (B) Brucite solubility at 2 kbar pressure.

Fig. 15. Comparison between calculated and experimentally determined wollastonite+quartz solubility (concentrations of total dissolved Ca and Si) in water (Xie and Walther, 1993b) as function of temperature and 2 kbar pressure. Calculations were performed with the thermodynamic data for aqueous species from this study, (A) those from SUPCRT92 and (B) with the stability of CaHSiO_3^+ complex increased by 20 kJ/mol and with the complex CaSiO_3^0 added to the speciation model (reaction (19): $\log K = -5.06$).

The refined thermodynamic properties of CaOH^+ result in a good agreement between the calculated portlandite solubility and the experimental data from Walther (1986) and Seewald and Seyfried (1991) for temperatures between 100 and 500 °C and pressures of 0.5 and 1.0 kbar (fig. 16). The agreement is much better than for calculations that use the CaOH^+ properties from Shock and others (1997). There remains, however, some disagreement between calculated and

experimentally measured portlandite solubility for 2.0 and 3.0 kbar. While the experimental results of Walther (1986) at these two pressures may not be necessarily incorrect, they are discrepant with their data at lower pressures and the results of the study of Seewald and Seyfried (1991). We note that it is not possible to reconcile these discrepancies within the thermodynamic framework of this study.

Fig. 16. Comparison between calculated and experimentally determined portlandite solubility in water (Walther 1986; Seewald and Seyfried 1991), expressed as total dissolved Ca as function of temperature at pressures of 0.5, 1.0, 2.0 and 3.0 kbar. Solid symbols represent experimental data points which were used to refine the properties of the CaOH^+ complex, while open symbols represent experimental data points which were not used.

System Ca-Mg-Al-Si-Cl-O-H

The calculated decimal logarithm of the total calcium to hydrogen ratios, $\log(\text{Ca}/(\text{H})^2)$, for fluid-mineral equilibria involving different Ca and Mg silicate assemblages are in good agreement (fig. 17) with the experimental data from Luce and others (1985) at all temperatures. By contrast, calculations with the aqueous species data from SUPCRT92 show only good agreement with the experimental data from Luce and others (1985) at 600 °C (fig. 17). The agreement between the calculated logarithm of the total magnesium to hydrogen ratios, $\log(\text{Mg}/(\text{H})^2)$, and their experimental counterparts (Luce and others, 1985) is good for the data at 600 and 700 °C, but not as good for the data at 500 °C.

Fig. 17. Comparison between calculated and experimentally determined $\log(\text{Ca}/\text{H}^2)$ and $\log(\text{Mg}/\text{H}^2)$ values in the system Ca-Mg-Si-Al-OH-Cl (in 1 molal CaCl_2 or MgCl_2 solutions), as function of temperature at a pressure of 1 kbar. Equilibrium assemblages: (A) talc+quartz. (B) tremolite+talc+quartz. (C) diopside+talc+quartz. (D) wollastonite+diopside+quartz. (E) wollastonite+quartz. Solid symbols represent experimental data points which were used in the global data regression, while open symbols represent experimental data points which were not used.

The wollastonite+quartz solubility experiments of Xie and Walther (1993b) in NaCl solutions are not well reproduced by calculations with the data from this study (fig. 18). There is a disagreement in terms of the absolute Ca concentration data, but also in terms of the temperature dependence at different NaCl concentrations. Interestingly, at 1.0 kbar pressure (and NaCl concentration of 0.83 molal), the measured Ca concentration is overestimated, while at 2.0 kbar the total Ca is underestimated by the calculations. This would imply that the pressure dependence of the solubility is not well reproduced by the thermodynamic properties of the aqueous species.

Fig. 18. Comparison between calculated and experimentally determined wollastonite+quartz solubility (expressed as total dissolved Ca) in NaCl solutions of different concentrations (Xie and Walther, 1993b), plotted as function of temperature. (A) Solution of 0.49 mol/kg NaCl at 1 kbar pressure. (B) Solution of 0.833 mol/kg NaCl at 1 kbar pressure. (C) Solution of 0.833 mol/kg NaCl at 2 kbar pressure.

Fig. 19. Comparison between calculated and experimentally determined (Plummer and Busenberg, 1982) calcite and aragonite solubility (expressed as total dissolved Ca concentration) in the system $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$, as function of temperature ($<100\text{ }^\circ\text{C}$) and at different CO_2 partial pressures (at a total system pressure of 1 bar), in equilibrium with (A) calcite and (B) aragonite.”

System Ca-Mg-Cl-O-H-C

There is very good agreement between calculated calcite and aragonite solubility and the experimental data from Plummer and Busenberg (1982). The agreement is good for all experimental data points over a considerable range of CO_2 partial pressure (fig. 19). The calculations do also show a good agreement with the calcite solubility experiments in water at different CO_2 partial pressures at temperatures of 100 to $300\text{ }^\circ\text{C}$ from Ellis (1959b). The calculated solubility is slightly overestimated compared to the measured one at a CO_2 partial pressure of 63 bar, and this could be due to activity coefficient effects of $\text{CO}_{2(\text{aq})}$ becoming important (fig. 20A). The calcite solubilities in NaCl solutions from Ellis (1963) are somewhat overestimated by the calculations using the thermodynamic dataset of this study. The difference amounts to about 0.1 log units in 0.2 molal NaCl solution at $120\text{ }^\circ\text{C}$ and to 0.4 log units in 1 molal NaCl solution at $320\text{ }^\circ\text{C}$ (fig. 20B). We note that the experimental data of Ellis (1963) were not included into the final experimental database and global optimization of the $\Delta_f G_{298.1}^0$ of the aqueous species.

At higher temperatures and pressures, the calculated calcite solubilities in water are systematically higher than those experimentally determined by Walther and Long (1986). It is important to note that the experimental data of Walther and Long (1986) are also in disagreement

with the subsequent calcite solubility study of Fein and Walther (1989), and some experimental problems encountered in Walther and Long (1986) have been discussed by Fein and Walther

(1989). There is fairly good agreement between the calculated and the measured calcite solubility data in water from 400 to 600 °C and at 2.0 kbar (Fein and Walther, 1989), using the properties of calcium and carbonate species from this study (fig. 21). The agreement between calculations and experimental results is much better than with the thermodynamic data from SUPCRT92, including calcite solubility in pure H₂O and in NaCl solutions (fig. 22).

Fig. 20. Comparison between calculated and experimentally determined calcite solubility (expressed as total dissolved Ca concentration) as function of temperature. (A) Calcite solubility in water at different CO₂ partial pressures from 1 to 62 bar. (B) Calcite solubility in NaCl solutions of 0.2, 0.5 and 1.0 molal at a CO₂ partial pressure of 12 bar. The calculations were performed with the thermodynamic dataset of this study. (C) Calcite solubility in NaCl solutions of 0.2, 0.5 and 1.0 mol/kg at a CO₂ partial pressure of 12 bar. The calculations were performed with

the thermodynamic dataset of this study, but using an ion size parameter of 5.9 in the Debye-Hückel activity model and without the CaCl^+ complex included into the speciation model.

Fig. 21. Comparison between calculated and experimentally determined calcite solubility in the $\text{CaCO}_3\text{-H}_2\text{O}$ system as function of temperature and at a pressure of 2 kbar.

Fig. 22. Comparison between calculated and experimentally measured calcite solubility in HCl and NaCl solutions (expressed as total dissolved Ca concentration) as function of Cl molality at a pressure of 2 kbar. (A) Calcite solubility in HCl solutions at 400 °C. (B) Calcite solubility in NaCl solutions at 400 °C. (C) Calcite solubility in NaCl solutions at 500 °C. (D) Calcite solubility in NaCl solutions at 600 °C.

Finally, there is good agreement between the calculated and the experimentally determined magnesite solubility data from Bénézeth and others (2011). The agreement is good for all experimentally studied temperatures from 50 to 200 °C and at saturated water vapor pressure (fig. 23). Unfortunately, there are no experimental magnesite solubility data available for supercritical conditions and predictions using the thermodynamic data from this study cannot be tested at higher temperatures and pressures.

Fig. 23. Comparison between calculated and experimentally determined (Bénézeth and others, 2011) magnesite solubility constants as function of temperature and at saturated water vapor pressure.

DISCUSSION

System Ca-Mg-Al-Si-O-H

The CaOH^+ complex becomes increasingly important with increasing temperature at alkaline pH (Seewald and Seyfried, 1991). The existing standard state properties and HKF parameters for CaOH^+ are only based on correlations and low temperature association constant data (25 °C) and have a rather large uncertainty. Because portlandite is not included in the Holland-Powell thermodynamic database, the portlandite solubility experiments were not used in the global optimization process. Rather, the data from the two experimental datasets (Walther, 1986; Seewald and Seyfried, 1991) at 0.5 and 1.0 kbar were used to independently retrieve the association constant of CaOH^+ . In the absence of other experimental constraints, these values were subsequently used to refine the standard state properties and HKF parameters of CaOH^+ .

There are differences between the reported values for the $\Delta_f G_{298.1}^0$ of portlandite. Walther reports a $\Delta_f G_{298.1}^0$ value of -898.4 kJ/mol, whereas the data compilation of Robie and Hemingway (1995) gives a value of -898.0 kJ/mol. Thoenen and others (2014) report a value of -897.0 kJ/mol, which is consistent with a $\log K$ of 22.8 for the reaction $\text{Ca}(\text{OH})_2(\text{cryst.}) + 2 \text{H}^+ = \text{Ca}^{2+} + 2 \text{H}_2\text{O}$ at 25 ° and 1 bar. This value is based on a number of critical data evaluations and compilations (Baes and Mesmer, 1976; Duchesne and Reardon, 1995; Nordstrom, 2013), and can be calculated from the $\Delta_f G_{298.1}^0$ of portlandite from Robie and Hemingway (1995) and the

$\Delta_f G_{2981}^0$ values of Ca^{2+} and H_2O from Cox and others (1989). In order to maintain consistency with the generally accepted value for the solubility product of portlandite, we have accepted the $\Delta_f G_{2981}^0$ value of portlandite from Thoenen and others (2014). The standard state entropy, molar volume, and heat capacity of portlandite were then adopted from Robie and Hemingway (1995). Figure 16 compares the solubility product of portlandite, calculated with the thermodynamic data of this study, with the experimental data at elevated temperatures and pressures. The agreement is very good at pressures of 0.5 and 1.0 kbar up to 500 °C. This highlights the strong interdependence of the thermodynamic properties used for all the aqueous species, complexes and solid phases in the solubility model.

The solubility of the wollastonite+quartz assemblage in water, calculated using the thermodynamic data from this study, somewhat underestimates the experimentally measured values (fig. 15). This may be related to the standard state properties and HKF parameters of the calcium silicate complex (CaHSiO_3^+) being not well constrained by independent experimental data (Sverjensky and others, 1997). If the stability of CaHSiO_3^+ would be increased by about -20 kJ/mol, this would result in a much better agreement between calculated and experimental wollastonite+quartz solubility data up to 500 °C. Discarding possible issues with the wollastonite+quartz experiments, the measured calcium concentrations above 500 °C can only be accounted for if an additional higher-order Ca silicate species becomes important at the highest temperatures. A likely candidate would be the neutral calcium silicate complex CaSiO_3^0 . If included into the speciation model, this complex would bring the calculated solubility of wollastonite+quartz into a good agreement with the experimental data (fig. 15B). However, because there are no independent solubility data (linked to minerals present in the Holland-Powell database) that could constrain the stability of the calcium silicate complex CaSiO_3^0 , we have not included this species into the final speciation model and have therefore not used the wollastonite+quartz solubility data in the global data regression.

Altmaier and others (2003) suggested that the logK (25 °C, 1 bar) of 16.3 of brucite (fig. 24) calculated with the thermodynamic data from SUPCRT92 is inconsistent with the results of several solubility studies. The value of logK (25 °C, 1 bar) of 17.1 ± 0.2 derived in their study agrees very well with the values of 17.11 ± 0.16 and 17.05 ± 0.2 reported by McGee and Hostetler (1977) and Xiong (2008) obtained from solubility experiments. It also agrees very well with the value of 17.13 reported by Brown and others (1996) obtained by extrapolation of high-

temperature potentiometric titration data. In contrast, Thoenen and others (2014) report the logK (25 °C, 1 bar) of 16.84 for brucite. The logK (25 °C, 1 bar) of 16.3 is calculated when using the thermodynamic data from SUPCRT92, and a value of 16.48 is obtained when using the properties of H₂O and Mg²⁺ from SUPCRT92, but the $\Delta_f G_{2981}^0$ of brucite from the Holland-Powell database. This suggests that either the $\Delta_f G_{2981}^0$ of Mg²⁺ or the one of brucite are inconsistent with the experimentally determined solubility constant at 25 °C. Figure 24 compares the brucite solubility products obtained from experimental studies (McGee and Hostetler, 1977; Brown and others, 1996) with calculations using different thermodynamic datasets. The difference between calculated and measured data can be accommodated by an adjustment of the $\Delta_f G_{2981}^0$ of Mg²⁺ of around 3 to 4 kJ/mol or by a change in the properties of brucite. After the global optimization performed in this study, the refined $\Delta_f G_{2981}^0$ value of Mg²⁺ is 2 kJ/mol more negative, compared to the value reported in SUPCRT92, resulting in a logarithm of the solubility product of brucite of 16.85, which is in reasonably good agreement with the experimental data. Using the properties for Mg²⁺ from CODATA (Cox and others, 1989), a value of -455.4 ± 1.8 kJ/mol was calculated for $\Delta_f G_{2981}^0$, which is very close to the one obtained in this study.

System Ca-Mg-Al-Si-Cl-O-H

There is good agreement between calculated and experimentally measured (Luce and others (1985) mineral solubility data in chloride solutions at temperatures above 500 °C, while the agreement is not as good at 500 °C and below. The disagreement at lower temperatures could be related to the thermodynamic properties of calcium and magnesium chloride complexes, in particular to the HKF parameters that define the temperature and pressure dependence of the standard state Gibbs

Fig. 24. Comparison between calculated and experimentally determined brucite solubility constants as function of temperature and at saturated water vapor pressure. The experimental data include potentiometric (Brown and others, 1996) and solubility measurements (McGee and Hostetler, 1977).

energies. This issue could also be responsible for the observed disagreement between calculated and experimentally determined $\log(\text{Ca}/\text{H}^2)$ and $\log(\text{Mg}/\text{H}^2)$ ratios.

There is no clear explanation for the disagreement between calculated and measured Ca concentrations for the wollastonite+quartz solubility experiments in NaCl solutions (Xie and Walther, 1993b). Close inspection of the experimental data reveals a considerable scatter, with measured Ca concentrations for P - T conditions and input solution compositions that are very close to each other varying by as much as 0.5 log units (fig. 18). Another problematic feature of the data of Xie and Walther (1993b) is the very large pressure dependence of the solubility. Increasing the experimental pressure from 1 to 2 kbar results in an increase in the dissolved Ca concentration by one order of magnitude. A pressure dependence of such magnitude has not been reported from any other silicate mineral solubility study so far. Considering the large variations in measured Ca concentrations for approximately similar state points, the unreasonably large pressure dependence and the absence of a clear temperature trend suggests that at least some experimental runs of Xie and Walther (1993b) did not attain equilibrium.

A major problem in the chloride-bearing systems is the lack of sufficient independent constraints on the stability of the aqueous Ca and Mg chloride complexes CaCl^+ , CaCl_2^0 , MgCl^+ and MgCl_2^0 . Despite substantial efforts, it was not possible to reconcile the association constant data from the conductance study of Frantz and Marshall (1982) with those from conductance

experiments at lower temperatures (Méndez De Leo and Wood, 2005). The association constants for CaCl^+ and CaCl_2^0 from Frantz and Marshall (1982) are also discrepant with the temperature and pressure trends of chloride complexes predicted by Sverjensky and others (1997) and with trends shown by other well-studied electrolyte solutions. Most likely, the discrepancies relate to the method that was used for extracting the association constants from the conductance experiments of Frantz and Marshall (1982). Values for the limiting equivalent conductance of the CaCl_2 and MgCl_2 electrolytes and the method used for extracting the molar conductance appear to be correct, in view of the fact that the limiting equivalent conductance for CaCl_2 from Frantz and Marshall (1982) agrees well with the results of molecular dynamics simulations by Lee (2004).

However, retrieving association constants from the conductance data in the Ca and Mg chloride systems depends largely on the speciation model employed. Frantz and Marshall (1982) assumed that only the first and the second chloride complex would form in their experiments, but ignored the important formation of the hydroxide species CaOH^+ and MgOH^+ . The data reduction method used by Frantz and Marshall (1982) may have also resulted in large errors for the association constants of the chloride complexes. When retrieving association constants from the experiments in the $\text{CaCl}_2\text{-H}_2\text{O}$ system, they first modeled the measured molar conductance data for a speciation model with only Ca^{2+} and Cl^- , and then separately for one with only CaCl^+ and Cl^- . Subsequently, they assumed that all measured conductance values lying between these two end-member cases would contain Ca^{2+} , CaCl^+ , and Cl^- ions. Only for conductance values below those of the model with CaCl^+ and Cl^- , they used a model with CaCl^+ , Cl^- , and CaCl_2^0 but not Ca^{2+} instead. In fact, they never modeled any of their experiments with a full speciation model that would include Ca^{2+} , CaCl^+ , CaCl_2^0 and Cl^- . This potentially resulted in an underestimation of the relative stability of CaCl_2^0 compared to that of the CaCl^+ complex.

In figure 25, the measured $\log(\text{Ca}/\text{H}^2)$ and $\log(\text{Mg}/\text{H}^2)$ ratios are compared with their calculated counterparts using association constants for the Ca and Mg chloride species from Frantz and Marshall (1984) and HCl^0 association constants from Frantz and Marshall (1984). Experimental values are poorly reproduced by the modeled data, but when the $\log(\text{Ca}/\text{H}^2)$ and $\log(\text{Mg}/\text{H}^2)$ values are calculated with a speciation model that only accounts for CaCl^+ and MgCl^+ , the calculated data agree very well with the experimental ones. This strongly supports the conclusion that the data reduction method used by Frantz and Marshall (1982) has resulted in

incorrect association constant data for the Ca and Mg chloride species, by underestimating the relative stability of CaCl_2^0 compared to that of the CaCl^+ complex.

Fig. 25. Comparison between calculated and experimentally determined $\log(\text{Ca}/\text{H}^2)$ values in the system diopside+talc+quartz. Calculations were performed with three alternative thermodynamic datasets for the association constants of the Ca chloride complexes CaCl^+ and CaCl_2^0 as well as the HCl^0 ion pair.

System Ca-Mg-Cl-O-H-C

Refining the thermodynamic properties of the CaOH^+ complex has brought the calculated and experimentally determined calcite solubility data in water and chloride solutions into very good agreement. The improvement is substantial compared to calculations with the properties of CaOH^+ from Shock and others (1997). Their data predict much larger stability of CaOH^+ , which has a strong impact on the calculated calcite solubility. This outcome highlights that regression of the standard state properties and HKF parameters of aqueous complexes should also take advantage of available solubility data. This particularly applies to cases such as CaOH^+ where no independent experimental information such as conductance or potentiometric data is available.

The solubility of calcite and magnesite in sodium chloride solutions at saturated CO_2 conditions is somewhat overestimated by the thermodynamic data of this study. This could be related to an overestimation of the stability of some of the Ca complexes or to limitations of the activity coefficient model employed. With increasing NaCl concentration, the calculated stability of CaCl^+ for the conditions of the experiments of Ellis (1963) increases and it becomes the predominant Ca complex in 1 molal solutions above 140 $^{\circ}\text{C}$. If calcite solubility is calculated

without inclusion of the Ca chloride complexes into the speciation model, the modeled Ca concentrations are still higher than the experimentally determined values (fig. 20B). At these conditions, the stability of the CaCl^+ complex is in agreement with association constants derived from the experiments of Majer and Štulík (1982), Gillespie and others (1992) and Méndez De Leo and Wood (2005). We have investigated the relative impact of the activity coefficient model by regressing the calcite solubility data using different values of the ion size parameter in the extended Debye-Hückel equation. The results show that the agreement between calculated and experimental data becomes very good if the ion size parameter is increased to a value of 5.9 (fig. 20C). We have also investigated the effect of the extended term parameter of the Debye-Hückel model, and the results show that it is very insensitive to the calcite solubility data. It was not possible to arrive at realistic values for the ion size parameter (<20) when the CaCl^+ complex was included into the speciation model. Until more experimental data become available that would constrain the activity coefficients and association constants in the $\text{CaCl}_2\text{-H}_2\text{O-CO}_2$ system, we suggest to maintain the standard state properties of calcium carbonate and chloride species as presented in this study.

Calculating magnesite solubility in water and NaCl solutions at saturated CO_2 conditions results in a moderate underestimation of the experimentally determined values (Bénézech and others, 2011). We note that those experiments, which were performed in a hydrogen electrode concentration cell containing no gas phase saturating the CO_2 partial pressure in solution, are better modeled by the thermodynamic data of this study. Magnesite solubility is also overestimated when modeling the experiments under CO_2 saturated conditions in NaCl solutions reported by Bénézech and others (2011). Conversely, the magnesite solubility experiments performed in the hydrogen electrode concentration cell without a gas phase saturating the CO_2 partial pressure in solution, are not overestimated by the calculations with the thermodynamic dataset of this study.

A possible explanation for the disagreement between calculated and measured calcite solubility data in concentrated NaCl solutions could be that the extended Debye-Hückel model (Helgeson and others, 1981) is inadequate for the aqueous carbonate species in systems saturated with CO_2 . The activity coefficient of $\text{CO}_{2(\text{aq})}$ and of other neutral complexes is assumed to be close to unity (only the solution concentration effect is taken into account). The activity coefficients of charged species are calculated by the extended Debye-Hückel model using

parameters for the background electrolyte for all species. This approach may not be suitable for electrolyte solutions that contain large concentrations of $\text{CO}_{2(\text{aq})}$ buffered by a CO_2 -rich gas phase. Resolving the remaining disagreements between calculated and measured solubility may require to develop an improved thermodynamic model for calculating activity coefficients in aqueous electrolyte solutions with high concentrations of dissolved chlorides and carbonates in the framework of the revised HKF model, which is beyond the scope of the present study. An alternative approach would be to use local-composition based activity coefficient models such as eNRTL or rEUNQUAC (for example Chen and Song, 2004; Hingerl and others, 2014) in conjunction with the speciation model employed in this study. To help improve the model predictions or to resolve the existing discrepancies in the carbonate systems, more experimental data is necessary. Solubility experiments in the $\text{Ca-CO}_2\text{-H}_2\text{O}$ and $\text{Ca-CO}_2\text{-NaCl-H}_2\text{O}$ dilute systems are lacking, especially at supercritical conditions. Experiments in the system $\text{Ca-CO}_2\text{-KCl-H}_2\text{O}$, dilute solutions could be used to constrain the potassium carbonate species. This type of experiments can be used to test the limits of the extended Debye-Hückel activity model.

For dolomite bearing systems, we have compared calculated and measured (Morey, 1962) solution compositions (total dissolved Ca and Mg) in equilibrium with dolomite at elevated temperatures (fig. 26). Although the experimental dolomite solubility data were not included into the global optimization, the agreement is remarkably good and well comparable to the agreement between calculated and measured calcite solubility. The equilibrium constant (at 25 °C) calculated with the thermodynamic data from this study is -17.0, which is in excellent agreement with the recommended value of -17.2 ± 0.2 from Sherman and Barak (2000), and the value of -17.1 ± 0.4 from Hemingway and Robie (1994). Furthermore, in figure 26B we compare the calculated $\log(\text{Ca/Mg})$ values of fluids in equilibrium with dolomite+calcite with those of natural sedimentary fluids buffered by calcite and disordered dolomite (Hyeong and Capuano, 2001). The results show very good agreement within analytical uncertainty over the temperature interval 50-150 °C. This demonstrates that the internally consistent thermodynamic dataset generated in this study is able to quantitatively predict experimental and natural fluid-mineral equilibria which were not included into the data regression procedure. It also shows convincingly that thermodynamic calculations using this dataset are relevant to natural fluid-rock systems.

Standard State Properties of Ca and Mg Ions

The $\Delta_f G_{298,1}^0$ of the Ca^{2+} ion in the SUPCRT92 database was calculated from the $\Delta_f H_{298,1}^0$, the $S_{298,1}^0$ and the standard third-law entropies of the elements from the CODATA compilation (Cox and others, 1989). The values of $\Delta_f H_{298,1}^0$ and $S_{298,1}^0$ are -543.1 ± 0.8 kJ/mol and -56.6 J/(mol·K) in Cox and others (1989) and -542.8 kJ/mol and -53.1 J/(mol·K) in the report of Wagman and others (1982). The reported $\Delta_f H_{298,1}^0$ of Ca^{2+} from Cox and others (1989) was derived from calcite solubility data (Langmuir, 1968; Jacobson and Langmuir, 1974) and the enthalpy of dissolution of portlandite (Hopkins and Wulff, 1965; Langmuir, 1968). The standard state properties of calcite have been accurately known since the determinations of Bäckström (1925a, 1925b). Their measured value of -178.24 ± 0.8 kJ/mol for the heat of oxide reaction to form calcite ($\text{CaO}_{(s)} + \text{CO}_{2(g)} = \text{CaCO}_{3(s)}$) is almost identical to the value of -178.3 ± 1.2 kJ/mol (Chai and Navrotsky, 1993) that was adopted by Holland and Powell (1998).

Fig. 26. (A) Comparison between calculated and measured dolomite solubility (total Ca and Mg concentrations) as function of temperature (and at a pressure of 203 bars). (B) Comparison between calculated and measured log(Ca/Mg) molar ratios from sedimentary fluids in equilibrium with calcite and disordered dolomite, at temperatures of 50-150 °C and at saturated water vapor pressure.

Using the Gibbs energy effect of reaction for the portlandite solubility product reported by Hopkins and Wulff (1965) of 29.7 kJ/mol and the thermodynamic data for portlandite from Langmuir (1968), results in a $\Delta_f G_{298,1}^0$ of the Ca^{2+} ion of -553.9 kJ/mol. Combining this value for the Ca^{2+} ion with the $\Delta_f G_{298,1}^0$ of the CO_3^{2-} ion of -527.9 kJ/mol (Langmuir, 1968) and the Gibbs

energy effect of reaction for the calcite solubility product at 25 °C and 1 bar, the $\Delta_f G_{298,1}^0$ of calcite is calculated as -1129.8 kJ/mol. The difference between this value and the $\Delta_f G_{298,1}^0$ value of -1128.8 kJ/mol from Holland and Powell (1998) is only around 1 kJ/mol. This difference is almost identical to the difference between the $\Delta_f G_{298,1}^0$ value of Ca^{2+} calculated above (-553.9 kJ/mol) and the value of -552.8 kJ/mol reported by Cox and others (1989). The $S_{298,1}^0$ of Ca^{2+} reported by Cox and others (1989) is consistent with the accepted third-law entropy value of 83.4 J/(mol·K) of portlandite and the entropy difference of the portlandite dissolution of 159.8 J/(mol·K) as calculated by Hopkins and Wulff (1965). These connections provide support for the fact that the thermodynamic properties of calcite and all aqueous Ca and carbonate and silicate species derived in this study are fully consistent with each other.

The $\Delta_f G_{298,1}^0$ of the Mg^{2+} ion in the SUPCRT92 database was calculated from the $S_{298,1}^0$ of Mg^{2+} , the standard third-law entropies of elements from the CODATA compilation (Cox and others, 1989) and the $\Delta_f H_{298,1}^0$ of Mg^{2+} from Shin and Criss (1979). They evaluated the $\Delta_f H_{298,1}^0$ of the Mg^{2+} ion from the enthalpy of formation of $\text{MgCl}_{2(s)}$ in acid HCl solutions and from the enthalpy of dilution of $\text{MgCl}_{2(s)}$ in pure water. They used these experimental data to calculate the standard state enthalpy of $\text{MgCl}_{2(aq)}$ at 25 °C and 1 bar (and at infinite dilution). Using the enthalpy of $\text{MgCl}_{2(aq)}$, the $\Delta_f H_{298,1}^0$ of the Cl^- ion from CODATA and applying the additivity principle, they calculated the $\Delta_f H_{298,1}^0$ value of the Mg^{2+} ion.

The standard partial molal entropy of Mg^{2+} in SUPCRT92 comes from the compilation of Parker and others (1971), who did not report the exact source for their thermodynamic data. Stephenson (1946) calculated the $S_{298,1}^0$ and $\Delta_f G_{298,1}^0$ of Mg^{2+} from the measured heats of reaction and heats of formation for different magnesium compounds available at that time (using a thermochemical cycle). They arrived at an $S_{298,1}^0$ value of -136.8 ± 4.2 J/(mol·K), which is very close to the value of -138.1 J/(mol·K) reported by Parker and others (1971). However, the determination of the standard enthalpy and entropy from a thermochemical cycle results in accumulation of rather large errors amounting from the imprecise heat of reaction data. In addition, the heats of formation of all the reaction participants do introduce additional errors.

The standard partial molal heat capacity $Cp_{298,1}^0$ and the c_1 and c_2 HKF parameters for the Ca^{2+} and Mg^{2+} ions were derived by Tanger and Helgeson (1988) from isobaric heat capacity measurements of aqueous calcium and magnesium electrolyte solutions. For the Mg^{2+} ion, the standard state partial molal volume $V_{298,1}^0$ and the HKF parameters a_1 , a_2 , a_3 and a_4 that describe the pressure dependence were derived by Tanger and Helgeson (1988) from the experimental data on partial molal volume and isothermal compressibility of aqueous magnesium electrolyte solutions at 1 bar and different temperatures below 150 °C. For the Ca^{2+} ion, the $V_{298,1}^0$ was derived by Tanger and Helgeson (1988) using the partial molar volume data of calcium electrolyte solutions. They employed estimation techniques for the missing data for the isothermal compressibility of aqueous calcium electrolyte solutions. Shock and Helgeson (1988) used the standard partial molal compressibility for Ca^{2+} reported by Millero (1982) and correlations between the a_1 , a_2 , a_3 , and a_4 parameters, the isothermal compressibility, and the partial molal volumes of other ions to estimate the HKF parameters for the Ca^{2+} ion. The Born coefficients ω_0 for both the Ca^{2+} and Mg^{2+} ions originate from the work of Helgeson and Kirkham (1976), who calculated them from the effective electrostatic radii of the ions.

The adjustment of around 2 kJ/mol to the $\Delta_f G_{298,1}^0$ of Mg^{2+} , which resulted from the global optimization of solubility data in this study, is well within the uncertainties associated with the thermochemical cycles used in the extraction of the ion properties. For the Ca^{2+} ion, the thermodynamic properties are strongly connected with the properties of the minerals and their solubility products, resulting in an insignificant change after the optimization process (only tens of J/mol).

CONCLUSIONS AND OUTLOOK

- (1) Critically evaluated experimental solubility data in the Ca-Mg-Na-K-Al-Si-O-H-C-Cl system covering a wide range of pressure-temperature conditions were used to simultaneously refine, in an internally consistent way, the standard state Gibbs energies of aqueous ions and complexes. The refined properties of aqueous species are consistent with the Holland-Powell internally consistent dataset for minerals.
- (2) The thermodynamic database presented in this study is compatible with the open-source freely available GEMS3 geochemical modeling software (available at: <http://gems.web.psi.ch/>)

and enables calculation of aqueous-mineral equilibria in the system Ca-Mg-Na-K-Al-Si-O-H-Cl at temperatures up to 1000 °C, pressures up to 5 kbar, and salt concentrations up to 5 molal.

(3) Major discrepancies were identified for the properties of Ca and Mg hydroxide and chloride species, amounting to several orders of magnitude of uncertainty in solubility predictions at supercritical conditions. More experimental data are needed to resolve the disagreement between the association constant data for the Ca and Mg chlorides from different studies. New experimental studies at subcritical and supercritical conditions that are independent from solubility are essential for constraining the stability of the CaCl_2^0 and MgCl_2^0 species. Additional studies should investigate the possible formation of higher order chloride species, which could play an important role in concentrated chloride brines, especially at temperature and pressure conditions of the deep Earth. New experimental data are also needed for evaluating the stability constants of the hydroxide species CaOH^+ and MgOH^+ , because at supercritical conditions there are no association constant data available that would be independent from solubility.

(4) The properties of carbonate species derived in this study are consistent with the properties of $\text{CO}_{2(\text{aq})}$ calculated with the Akinfiyev-Diamond model for aqueous nonelectrolytes. Calculations with this model predict CO_2 solubilities in water that are in a very good agreement with the experimental data. Only limited data are available for the association constants for alkali and alkaline earth metal carbonate and bicarbonate complexes, and future experimental studies should specifically address their stability at supercritical conditions.

(5) More solubility experiments are needed to resolve discrepancies between calculated and experimentally measured Ca silicate solubilities, highlighted by the substantial disagreement found for the system wollastonite+quartz+ H_2O . The discrepancies could be reconciled by accounting for silicate complexes that are not included in the current speciation model, such as CaSiO_3^0 and MgSiO_3^0 . This would require constraining the stability of such complexes from additional independent experiments.

(6) The refined and extended thermodynamic dataset from this study makes it possible to perform geochemical and reactive transport modeling of processes in natural and engineered georeservoirs over wide ranges of conditions with an unprecedented level of reliability, and to address processes of fluid flow and fluid-rock interaction in the Earth's crust from a new perspective.

(7) Using the same strategy as applied in the present study, the internally consistent thermodynamic dataset can be further extended with additional major and trace elements, and/or the data refinement process can be repeated when new experimental data or next-generation equation of state or activity models for aqueous solutions become available.

ACKNOWLEDGEMENTS

This project was supported by funding from ETH Zurich, ETHIIRA grant number ETH-19 11-2, and by NANOCHEM internal project (Thermodynamic dataset for modelling CASHNK aqueous-solid solution systems - extension of the SNF-Sinergia project). The authors would like to thank Christoph A. Heinrich for his outstanding support during the course of this project. D.J. Wesolowski and D.A. Sverjensky are thanked for their reviews, as well as the associate editor for handling the manuscript.

Appendix Table A. Standard state properties (partial molal entropy, heat capacity and volume) and HKF parameters of aqueous species reported by Miron and others (2016), to be used together with the Gibbs free energy values, at 25 °C, reported in table 5 to calculate the Gibbs free energy values at elevated temperature and pressure.

Species	$S_{298,1}^0$	$CP_{298,1}^0$	$V_{298,1}^0$	$a_1 \cdot 10$	$a_2 \cdot 10^{-2}$	a_3	$a_4 \cdot 10^{-4}$	c_1	$c_2 \cdot 10^{-4}$	$\omega_0 \cdot 10^{-5}$
	(J/mol·K)	(J/mol·K)	(J/bar)	(cal/mol·bar)	(cal/mol)	(cal·K/mol·bar)	(cal·K/mol)	(cal/mol·K)	(cal·K/mol)	(cal/mol)
Al ³⁺	-339.74	-119.34	4.53	-3.3984	-16.0789	12.0699	-2.1143	14.4295	-8.8523	2.7403
AlOH ²⁺	-181.13	-37.44	-2.06	-0.4532	-8.8878	9.2434	-2.4116	15.4131	-4.8618	1.5897
Al(OH) ₂ ⁺	-27.53	40.86	0.385	2.4944	-1.6909	6.4146	-2.7091	16.7439	-1.0465	0.5324
Al(OH) ₃ ⁰	5.16	248.56	3.07	6.1977	8.2816	2.4950	-3.1214	71.1003	-1.0644	1.0461
Al(OH) ₄ ⁻	103.55	96.54	4.63	8.4938	12.9576	0.6570	-3.3147	55.7265	-11.4047	1.0403
NaAl(OH) ₄ ⁰	204.18	134.56	5.36	9.1267	14.3411	0.1121	-3.3719	60.7157	-14.0523	0
AlH ₃ SiO ₄ ²⁺	56.78	-300.67	1.396	0.1600	-7.2300	8.6100	-2.4800	37.0700	-49.6600	0.8800
KAlO ₂ ⁰	149.37	18.05	3.114	6.0070	6.8858	3.0436	-3.0637	1.3940	1.2120	-0.0500
K ⁺	101.04	8.39	0.901	3.5590	-1.4730	5.4350	-2.712	7.4000	-1.7910	0.1927
KOH ⁰	90.6	41.47	1.41	3.7562	1.3900	5.2037	-2.8365	13.499	-1.0192	0.1665
KCl ⁰	182.16	33.32	2.99	5.8341	7.0550	2.9771	-3.0707	-5.7084	7.6228	0.1996
Na ⁺	58.41	38.12	-0.121	1.8390	-2.2850	3.256	-2.7260	18.1800	-2.9810	0.3306
NaOH ⁰	42.4	113.5	-0.023	1.7792	-3.4372	7.1010	-2.6369	22.8222	2.6543	0.1189
NaCl ⁰	110.8	47.52	2.4	5.0828	4.629	3.9306	-2.9704	13.6339	-0.7212	0.0889
NaHSiO ₃ ⁰	41.84	102.95	1.273	3.4928	0.7500	5.4483	-2.8100	20.2395	1.9785	-0.0380
HSiO ₃ ⁻	19.7	-38.47	0.5	3.3090	-0.5201	5.9467	-2.7575	15.0000	-4.9202	1.5583
SiO ₂ ⁰	75.31	-318.48	1.61	1.9000	1.7000	20.000	-2.7000	29.1000	-51.2000	0.1291
Cl ⁻	56.74	122.49	1.734	4.0320	4.8010	5.5630	-2.847	-4.4000	-5.7140	1.4560
HCl ⁰	1.76	149.5	1.64	16.1573	-11.4311	-46.1866	-2.3036	46.4716	-5.2811	0
OH ⁻	-10.71	136.34	-0.471	1.2527	0.0738	1.8423	-2.7821	4.1500	-10.346	1.7246

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How to TBD

1. Download the zip file, extract the files into the /Resources/DB.default/ (from GEM-Selektor installation folder)
2. Run GEMS using the desktop icon (GEMS3.3) – or from command prompt using: `./gems3 -d`

3. Create a new project with all the options turned off (not ticked/selected) – Click New Project
4. Select the database (only Aqueous electrolyte, Gas mixture, Non-ideal fluids, and Crystalline

solids in the left panel):

5. Select aqueous and gas options (click Check button after you made the selections):

Setup of aqueous and gas phases in project: test2

Select Aqueous Electrolyte Model | Select Gas/Fluid Mixture Model

☐ Ion-association (IA) with Davies equation, D (default)

☒ IA with extended Debye-Hueckel equation (Helgeson), common b_{gamma} and a_0 , H

☐ IA with extended Debye-Hueckel equation (Shvarov), common b_{gamma} and a_0 , Y

☐ IA with extended Debye-Hueckel equation (Karpov), common b_{gamma} , individual a_0 , 3

☐ IA with Debye-Hueckel equation, no b_{gamma} , individual a_0 , 2

☐ IA with Debye-Hueckel limiting law (very low ionic strength), 1

☐ Do not generate; select a user-defined Phase record from database (Q, S, Z), U

☐ Do not include aqueous electrolyte phase into the system definition, N

Phase record key: a AQELIA aq_gen aq EDH_H

Parameters for the aqueous phase model

$b_{\text{gamma}}(1,298)$ value: 0.064

$b_{\text{gamma}}(P,T)$ mode: NaCl

Common a_0 value: 3.72

Gamma (neutral species): Calculate as $b_{\text{gamma}} \cdot IS$

Gamma (water solvent): From osmotic coefficient

Molality conversion: Applied to all species

OK Cancel Check Learn more

Aqueous:

Gas (do not generate: select a user-defined Phase from database):

Setup of aqueous and gas phases in project: xxxx

Select Aqueous Electrolyte Model | Select Gas/Fluid Mixture Model

☐ Ideal mixture of gaseous components, I (default)

☐ Churakov-Gottschalk (CG) multicomponent fluid EoS model, E

☐ Peng-Robinson (PR) multicomponent fluid EoS model, Z

☐ Peng-Robinson-Stryjek-Vera (PRSV) multicomponent fluid EoS model, P

☐ Soave-Redlich-Kwong (SRK) multicomponent fluid EoS model, E

☒ Do not generate; select a user-defined Phase record from database, U

☐ Do not include gas/fluid mixture phase into the system definition, N

Phase record key: g GASMIXID gas_gen gm Ideal

OK Cancel Check Learn more

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