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Evaluation and refinement of thermodynamic databases for mineral carbonation

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Abstract

Thermodynamic models are often used to quantify fluid-rock interactions. The validity of such models critically depends on the accuracy of the thermodynamic database used. This study evaluated the quality of existing PHREEQC databases (*phreeqc.dat*, *llnl.dat*, and *core10.dat*) through the analysis of mineral saturation states for various carbonates, sulfur-containing minerals, silicates, and hydroxides. The comparison between data from available equilibrated dissolution-precipitation experiments and predicted saturation states reveals: i) systematic deviations when using *phreeqc.dat* at temperatures higher than ~ 90 °C; ii) a lack of direct solubility measurements of numerous sulfide and silicate minerals; iii) systematic solubility underestimates for kaolinite and brucite. To address these issues the *carbfix.dat* database was created based on the *core10.dat* database, revising several mineral solubilities and aqueous species stabilities to improve our ability to model fluid-rock interactions during basalt-hosted mineral carbonation efforts.

Keywords: Geochemistry; Thermodynamics; Solubility; Speciation; Databases; Carbon sequestration

1. Introduction

   Geochemical modelling is widely used to quantify chemical reactions occurring between fluids and solid phases over a wide range of temperatures and pressures in the Earth. For example, carbon storage efforts in basalt rely on

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CO_2-water-basalt interactions to fix CO_2 as stable carbonate minerals [1,2]. To better understand such processes thermodynamic models are often used, however the quality of model results depends critically on the quality of the chosen thermodynamic database [3]. Over the past decades a number of thermodynamic databases have been created and compiled for different geochemical modelling codes such as EQ3/6 [4], WATCH [5], SUPCRT92 [6], PHREEQC [7], Geochemist's Workbench [8], Visual MINTEQ [9], TOUGHREACT [10,11], CHNOSZ [12], and GEMS [13,14]. This has enabled predictions of mineral solubility and aqueous solute speciation in an assortment of geochemical systems. Nevertheless, it is an essential step to evaluate the databases as new and/or improved thermodynamic data are continuously published. Given this, Gysi and Stefansson [15] and Aradóttir et al. [16] evaluated and compiled thermodynamic datasets of pertinent minerals for CO_2 mineral sequestration in basalts. Aradóttir et al. [16] created a new database in the TOUGHREACT format based on the EQ3/6 database and SUPCRT92, while Gysi and Stefansson [15] based their work on the *phreeqc.dat* database in PHREEQC.

In this study, this effort is revisited by focusing on mineral saturation states. Mineral saturation states are key parameters in geochemical studies and indicate how far a solution is from thermodynamic equilibrium with respect to a certain mineral. The saturation state is defined as $\Omega \equiv Q/K_{SP}$, where K_{SP} is the equilibrium constant of the mineral dissolution reaction, and Q is the corresponding reaction quotient of this reaction, calculated from the activities of all species involved in the dissolution reaction. At equilibrium, $Q = K_{SP}$ so that $\Omega = 1$. The saturation index, defined as $SI \equiv \log_{10} \Omega$, is used in many cases instead of Ω (e.g. in PHREEQC), so that at equilibrium $SI = 0$. A saturation index greater than zero indicates that an aqueous solution is supersaturated with a specific mineral, and $SI < 0$ indicates that the aqueous solution is undersaturated with respect to the mineral. The interpretation of saturation states and indices can be complicated by various factors; for example, a positive SI does not necessarily imply that the mineral will precipitate from the solution, as the slow precipitation kinetics may inhibit the precipitation, or favor precipitation of another mineral. Nevertheless, these parameters have proven to be useful indicators of equilibrium or disequilibrium in natural environments.

To evaluate the quality of predicted mineral saturation states, we calculated the saturation indices for sets of laboratory experiments in which thermodynamic equilibration between aqueous solutions and one or more minerals was likely achieved, and analyzed the accuracy, precision, as well as systematic deviations of predicted SI from zero. The PHREEQC software package, version 3 [7], was used together with different popular databases to carry out these thermodynamic calculations. Furthermore, a new database, *carbfix.dat*, was created, modifying and extending existing databases.

2. Thermodynamic databases used for evaluations

Several thermodynamic databases are available for PHREEQC, for which the standard state for solid phases and H_2O is the pure phase, while a hypothetical 1 mol/kg aqueous solution referenced to infinite dilution is chosen for unit activity of aqueous species, both at the temperature and pressure of interest.

The default PHREEQC database *phreeqc.dat* is derived from PHREEQE [17] and contains thermodynamic data for aqueous species and minerals relevant to natural fluid-rock interactions. Most equilibrium constants (K or $\log K$) in this database are extrapolated to temperatures other than 25 °C assuming that the enthalpy of reaction ($\Delta_r H$) does not vary with temperature (i.e. using the Van 't Hoff equation). Changes in $\Delta_r H$ are negligible for small temperature changes, but not so for larger temperature changes, so that calculations using *phreeqc.dat* become less reliable with increasing temperature.

The *llnl.dat* database for PHREEQC contains the vast amount of thermodynamic data compiled at the Lawrence Livermore National Laboratory for the *thermo.com.V8.R6.230* database of Geochemist's Workbench [7]. Many of the equilibrium constants in this database were calculated from thermodynamic properties of minerals and aqueous species using the SUPCRT92 software package [6]. For aqueous species, revised Helgeson-Kirkham-Flowers (HKF) equations [18,19] are used together with parameters regressed by a number of authors [e.g. 18,20–22] using a large set of experimental data that was available at that time. Similarly, mineral data are described by equations given in [23] and regressed data based on numerous experimental data. The resulting equilibrium constants are parameterized as a function of temperature in the *llnl.dat* database, allowing calculations over a larger temperature range compared to *phreeqc.dat*.

The *core10.dat* database is based on *llnl.dat*, but contains several modifications and improvements [24]. This database was developed with the application to icy world interiors in mind, but is applicable to other geochemical settings as well due to its similarity to *llnl.dat*. Importantly, it corrects several erroneous data, only contains data for which analytical expressions for equilibrium constants were available (as opposed to assumptions of constant $\Delta_r H°$ or constant K), and only contains phases and species for which molar volumes were available, allowing PHREEQC to estimate the pressure dependence of equilibrium constants.

2.1. The CarbFix database for PHREEQC

In this study, a new thermodynamic database for PHREEQC, *carbfix.dat*, was created based on the existing *core10.dat* database [24]. Compared to *core10.dat*, it contains additional mineral solubilites and aqueous species stability constants. Furthermore, selected mineral solubilites were revised based on the results of the evaluations presented below, and a typographical error was corrected in the former database (the second parameter of the analytical expression for the solubility product of saponite-Fe-Fe should read '-1.630e-1' instead of '-1.630-1').

Minerals added into *carbfix.dat* include 18 zeolite group minerals, whose thermodynamic properties were taken from Neuhoff [25]. The equilibrium constants for the dissolution reactions of these minerals were calculated using thermodynamic data for aqueous species taken from the OBIGT and SUPCRTBL thermodynamic databases together with the CHNOSZ package for the software R [12,26]. As these databases and the software package are based on SUPCRT92, these newly added mineral solubilites are expected to be internally consistent with the other data in *core10.dat*. The equilibrium constants calculated by CHNOSZ were fit to the analytical expression form of PHREEQC using the standard non-linear regression techniques in Wolfram Mathematica, and molar volumes were taken directly from Neuhoff [25]. Furthermore, the thermodynamic properties of ferro-actinolite and ankerite were taken from Holland and Powell [27] and integrated into the database using the same procedure. The solubilites of dolomite and siderite were re-calibrated using experimental data as explained in section 3.

Several metal-carbonate aqueous complexes were added to or revised in *carbfix.dat*. The parameters used to calculate the specific volumes of these species with a Redlich-type equation were taken from the OBIGT and SUPCRTBL databases. The equilibrium constant for formation of $CaHCO_3^+$ was taken from *llnl.dat*, for $NaCO_3^-$ and $NaHCO_3$ from Stefánsson et al. [28], for $MgCO_3$ and $MgHCO_3^+$ from Stefánsson et al. [29], and for $NaSO_4^-$ from McCollum and Shock [30] using CHNOSZ. Furthermore, the equilibrium constant for the formation of $Al(OH)_2^+$ was added from *llnl.dat* and the stability of the $AlH_3SiO_4^{2+}$ complex was parameterized using data of Pokrovski et al. [31]. Using CHNOSZ, stabilities and specific volumes of $AlSO_4^+$ and $NaAl(OH)_4$ [32], $Fe(OH)_2^+$, $Fe(OH)_3$, $Fe(OH)_4^-$, $Fe(OH)_2$, $Fe(OH)_3^-$, $HClO$, $HClO_2$, $HS_2O_3^-$, and KOH [33] were added to the database as well.

The resulting latest version of the *carbfix.dat* database is available at GitHub at the address https://github.com/CarbFix/carbfix.dat where the version described in this article can be accessed from release v1.0.0, or alternatively at http://carbfix.com.

3. Evaluation of predicted saturation indices

Mineral saturation indices (SI) were calculated using the databases described above for aqueous solutions used in laboratory experiments during which equilibration between the fluid and one or more minerals was approached. Calculations were carried out using the originally reported fluid compositions (such as pH, total aqueous concentrations of elements or species, temperature, etc.) to avoid dependence of the results on other thermodynamic data.

All experimental studies used for these evaluations were originally performed to determine mineral solubilites. However, as the achievement of thermodynamic equilibrium cannot be proven for these experimental studies, disequilibrium would lead to deviations of calculated SI from zero. Most studies aimed to achieve equilibrium from under- as well as supersaturation by carrying out both dissolution and precipitation experiments. This approach limits systematic errors in calculated solubilites and helps to estimate the uncertainties in experimentally determined parameters. If equilibration is attained only from one direction, the distance from equilibrium is difficult to estimate, as mineral-fluid reactions might proceed at rates significantly slower than changes observable over reasonable timespans and experimental and analytical uncertainties. Errors in the thermodynamic data or models represent further

potential uncertainties. Errors in solubilities (K_{SP}) directly affect calculated SI and thus represent a prime source for errors, but many calculations also depend on other equilibrium constants (e.g., of reactions between different aqueous species). Oversimplifications in the thermodynamic model, such as the approximation of activity coefficients or the assumption of a temperature-invariant $\Delta_r H$ (like in the case of many reactions in *phreeqc.dat*) may also lead to significant systematic errors, as illustrated below. Finally, experimental and analytical uncertainties lead to (mostly random) variability in calculated SI.

Except for disequilibrium, all potential reasons mentioned above for deviations of SI from zero equally apply when SI are calculated in geochemical studies. If errors due to disequilibrium in the employed experimental studies are small compared to the other sources of errors (i.e. errors in the thermodynamic database or model, and analytical uncertainties), the deviation from zero and the variability of the calculated SI for these experimental studies indicate the magnitude the uncertainty in calculated SI. Therefore, we calculated the mean saturation index ($\overline{SI}$) and the standard deviation (σ) for all experimental datasets as measures for the accuracy and precision of calculated SI, respectively. It should be noted however that some of the experimental datasets used for the evaluations only cover a limited range of temperature, outside of which larger uncertainties may occur as thermodynamic data is often less well constrained at increasing temperatures. Furthermore, most natural systems are chemically more complex than laboratory experiments, which likely leads to larger uncertainties when predicting SI for such systems. Therefore, the uncertainties estimated here should be regarded as minimum estimates of the uncertainties that must be anticipated for modelled SI.

3.1. Carbonate minerals

Due to the importance of carbonate minerals for carbon mineral storage, the quality of SI calculated for the minerals calcite, aragonite, dolomite, magnesite, siderite, and dawsonite was evaluated. From the results (Table 1, Fig. 1), it can be seen that $\overline{SI}_{Calcite}$ deviate by less than 0.097 from zero for all databases at < 90 °C, indicating a high level of accuracy of calculated SI. Standard deviations are equally low (≤ 0.061) in all cases, suggesting that $SI_{Calcite}$ can be predicted with a high level of accuracy and precision in simple, low-temperature fluids. Similarly, the mean SI calculated for aragonite solubility experiments of temperatures up to 90 °C are small (≤ 0.075). Note however, that these aragonite solubility experiments [34,35] were conducted in pure water, so that larger uncertainties are likely for more complex solutions. SI calculated for the high temperature calcite solubility experiments of [36] show larger deviations from zero, but standard deviations remain below 0.169 except for *phreeqc.dat*, for which SI are systematically negative. Similarly, deviations of $SI_{Dolomite}$ and $SI_{Siderite}$ from zero are largest using *phreeqc.dat*, where SI are close to zero at up to 90 °C but become increasingly negative with higher temperatures as shown with siderite in Fig. 2. This behavior can be explained by use of the assumption of constant $\Delta_r H$ for many reactions in *phreeqc.dat*, as explained in section 2. SI calculated using *lllnl.dat* and *core10.dat* for these two minerals, as well as for magnesite and dawsonite, are much closer to zero (Table 1, Fig. 1). However, $\overline{SI}$ for siderite is approximately -0.5, indicating a systematic deviation from zero, and σ for dolomite is relatively large (0.67). Therefore, the parameters for the analytical expressions of the solubilities as a function of temperature were re-calibrated for these two minerals in *carbfix.dat* using the same experimental datasets used for the evaluations [37,38]. The log K_{SP} were fit to the same form of expressions used in these original studies, resulting in

$$\log K_{SP}^{Dolomite} = 29.3854 - \frac{6474.23}{T} - 0.08464\ T \tag{1}$$

$$\log K_{SP}^{Siderite} = 349.432 - \frac{13573.8}{T} - 0.0362811\ T - 131.651 \log_{10} T \tag{2}$$

where T is temperature in Kelvin for the dissolution reactions

$$CaMg(CO_3)_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + 2\ CO_3^{2-} \tag{R1}$$

$$FeCO_3 \rightleftharpoons Fe^{2+} + CO_3^{2-} \tag{R2}$$

respectively. It can be seen from Table 1 and Fig. 1 that the SI predicted for these two minerals using *carbfix.dat* are an improvement over the other databases, which can be largely attributed to these re-calibrated solubility expressions. While the SI for dawsonite and magnesite also slightly deviate from zero using *core10.dat*, no re-calibration was necessary as several aqueous species were added to *carbfix.dat* (see section 2.1), improving the SI predicted using the latter database for these two minerals.

Table 1. Experimental studies of mineral solubilities used to in the present study to assess the quality of thermodynamic saturation index calculations using PHREEQC and different databases. The type refers to dissolution (D) and precipitation (P) experiments and N is the number of equilibrated aqueous solutions available in each study. $\overline{\overline{SI}}$ and σ refer to the sample mean and standard deviation of the saturation indices calculated for the experimental solutions using the different databases, respectively.

Mineral	Formula	Ref.	N	Type	T / °C	pH	phreeqc.dat		llnl.dat		core10.dat		carbfix.dat	
							$\overline{SI}$	σ	$\overline{SI}$	σ	$\overline{SI}$	σ	$\overline{SI}$	σ
Carbonates														
Calcite	$CaCO_3$	[34]	40	D/P	5-50	~ 6	-0.007	0.017	0.020	0.023	0.064	0.017	0.020	0.022
		[35]	141	D/P	0.1-90	~ 6	-0.003	0.045	0.017	0.061	0.097	0.051	0.019	0.061
		[36]	46	D	120-290	5-6	-0.411	0.605	0.170[a]	0.169[a]	0.277	0.179	-0.122	0.118
Aragonite	$CaCO_3$	[35]	205	D/P	0.7-90	6-8	0.001	0.001	0.022	0.029	0.075	0.040	0.023	0.029
Dolomite	$CaMg(CO_3)_2$	[37]	28	D/P	50-250	5-7	-3.337	2.359	-0.047	0.660	-0.030	0.666	-0.004	0.317
Magnesite	$MgCO_3$	[39]	25	D/P	50-200	5-8	-	-	0.078	0.298	0.112	0.310	0.074	0.305
Siderite	$FeCO_3$	[38]	21	D/P	50-250	5-6	-1.469	1.450	-0.484	0.332	-0.512	0.343	-0.005	0.310
Dawsonite	$NaAlCO_3(OH)_2$	[40]	30	D/P	50-200	4-10	-	-	0.238	0.484	0.350	0.441	-0.025	0.431
Sulfur-bearing minerals														
Anhydrite	$CaSO_4$	[41]	103	D	70-300	~ 7	0.100	0.268	0.541	0.399	0.388	0.372	0.377	0.357
		[42]	54	D	100-260	~ 7	-0.034	0.089	0.414	0.273	0.116	0.104	0.116	0.104
		[43]	11	D	65	~ 7	-0.190	0.090	-0.355	0.160	0.080	0.103	-0.383	0.161
Pyrrhotite	FeS	[44]	1	D	25-60	4	-	-	-1.215	-	-1.220	-	-1.220	-
Mackinawite	FeS	[44]	6	D/P	25	3-4	-0.058	0.459	-	-	-	-	-	-
FeS	FeS	[44]	4	P	25	3-4	0.383	0.173	-	-	-	-	-	-
Silicates														
Quartz	SiO_2	[45]	6	D	136-240	7	-0.009	0.016	0.068	0.049	0.066	0.047	0.066	0.047
		[46]	10	D	21-96	7	0.149	0.066	0.128	0.108	0.128	0.108	0.128	0.108
Am. SiO_2	SiO_2	[47]	20	D/P	8-300	7	-0.015	0.041	0.002	0.061	-0.002	0.062	-0.002	0.062
Kaolinite	$Al_2Si_2O_5(OH)_4$	[48]	16	D/P	25	~ 4	0.190	0.100	0.889	0.101	0.900	0.101	0.881	0.100
		[49]	7	D/P	80	~ 3	0.515	0.226	1.443	0.217	1.451	0.216	1.301	0.208
Analcime	$NaAlSi_2O_6·H_2O$	[50]	60	D/P	25-300	7-10	-	-	0.173	0.416	0.165	0.425	0.017	0.489
Hydroxides														
Gibbsite	$Al(OH)_3$	[51]	10	D/P	25	4-6	0.050	0.079	0.510	0.114	0.599	0.166	0.510	0.114
		[52]	180	D	50	3-9	-0.643	0.260	0.020	0.207	0.044	0.167	-0.017	0.209
Boehmite	AlOOH	[53]	496	D/P	100-290	2-10	-	-	-0.261	0.978	-0.324	1.181	-0.356	1.215
Brucite	$Mg(OH)_2$	[54]	13	D	22	9-11	-	-	0.693	0.058	0.693	0.058	0.693	0.058

[a]Aqueous solution densities necessary for the calculation of SI for the experimental data were calculated using *core10.dat*, as *llnl.dat* does not allow the calculation of densities.
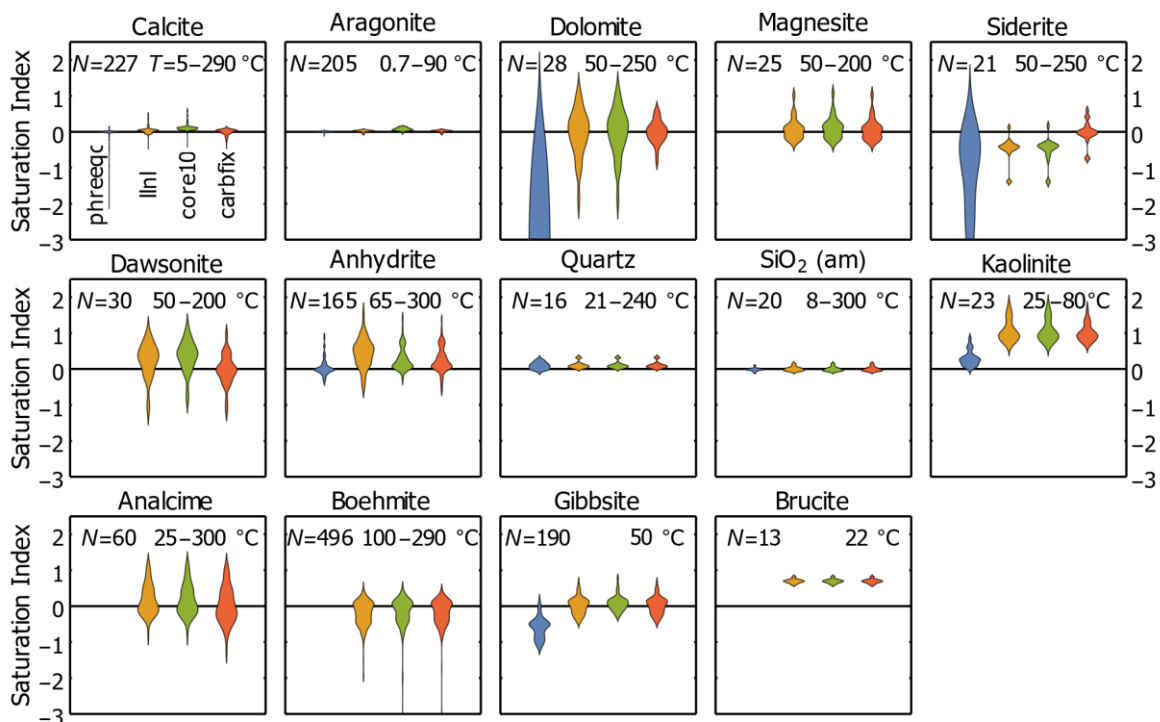
Fig. 1. Plot of the distributions of saturation indices (SI) calculated for aqueous solutions of studies that experimentally determined mineral solubilities. Thermodynamic SI calculations were carried out with PHREEQC using different databases shown in different colors as defined in the upper left-hand plot. The plotted distributions correspond to smoothed histograms, i.e. kernel density estimations of the probability density function.
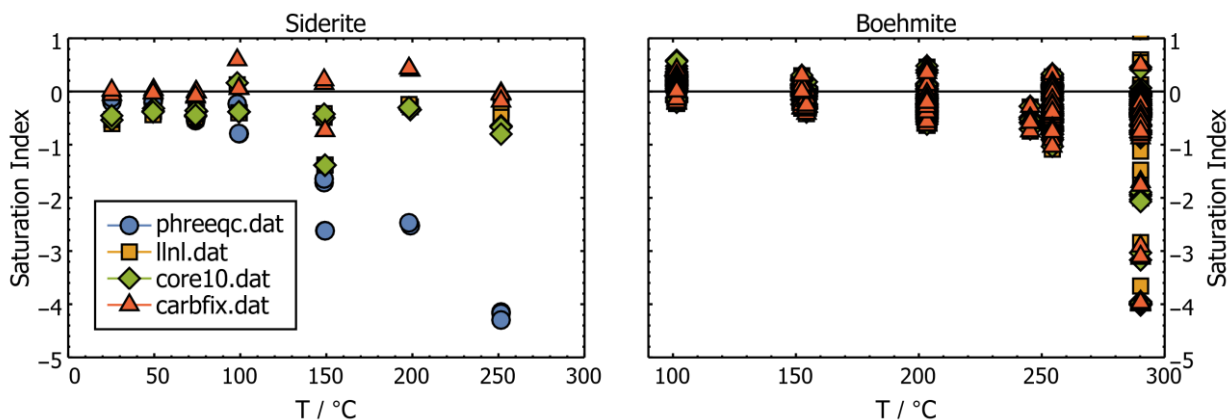

Fig. 2. Plots of saturation indices (SI) calculated for aqueous solutions of experimentally determined the solubilites of siderite (*left*) and boehmite (*right*) as a function of temperature. Thermodynamic SI calculations were carried out with PHREEQC using different databases shown in different colors as defined in the left-hand plot.

3.2. Sulfur-bearing minerals

A large number of experimental solubility experiments are available for the Ca-sulfate anhydrite (see Table 1). Mean SI calculated for data from the three experimental studies deviate from zero by less than 0.38, and standard deviations are smaller than 0.4, suggesting a reasonable accuracy and precision of the calculations over the temperature range 65-300 °C for simple aqueous solutions. Among the four tested databases, *phreeqc.dat* gives the best results and *llnl.dat* shows the largest variability.

On the other hand, the sulfide minerals are severely under-represented within the PHREEQC suite of databases due to the difficulties associated with the direct measurement of their solubility because of: i) their sluggish dissolution kinetics, which often prevents attainment of equilibrium at low temperatures; ii) the requirement of low redox potentials, which poses challenges to experimental and analytical techniques; iii) the potential release of toxic H_2S gas, which requires special experimental facilities; and iv) the electron configuration of some iron sulfide minerals such as pyrite which prevents solubility measurements at ambient temperatures [55]. Nevertheless, we calculated SI for pyrrhotite, mackinawite, and ferrous sulfide using experimental data of Berner [44] (Table 1). The single pyrrhotite experiment suggests an overestimation of its solubility in all three databases containing data for this mineral (*llnl.dat, core10.dat, carbfix.dat*), whereas data in *phreeqc.dat* for mackinawite and ferrous sulfide are in good agreement with the experimental data. However, no conclusive statement can be made about the accuracy and precision of the mineral solubilities of the sulfide minerals in any of these databases due to the lack of direct solubility measurements. These equilibrium constants are ultimately derived from indirect measurements (e.g., calorimetric measurements of the mineral properties).

3.3. Silicate minerals

Saturation states calculated for solubility experiments of quartz and amorphous SiO_2 are close to zero for all databases even at high temperatures (Table 1, Fig. 1), indicating a high degree of reliability of these SI, which can be explained by the relatively simple aqueous speciation of Si. The temperature dependence of the solubilities of these two minerals are widely used as geothermometers to calculate equilibration temperatures of natural fluids [45–47]. Thus, differences between such calculated equilibrium temperatures and measured experimental temperatures indicate minimum uncertainties that are to be expected from geothermometric calculations of natural fluids (assuming similar speciation and analytical uncertainties). Using *carbfix.dat*, we calculated the best-fit equilibrium temperatures (i.e. assuming SI=0) from the measured experimental SiO_2 concentrations within the temperature range of 8-300 °C; on average, they deviate from the measured experimental temperatures by 3 °C, with a standard deviation of 11 °C.

Direct solubility measurements of more complex silicate minerals are very limited, which is mainly due to 1) the sluggish dissolution/precipitation kinetics of many silicate minerals at low temperatures and 2) complications caused by synthesis and solid-solution formation, especially for sheet silicates like clays. Nevertheless, some experimental solubility measurements are available for kaolinite and analcime. For the former mineral, SI calculated from the experimental data of May et al. [48] and Nagy et al. [49] are close to zero for *phreeqc.dat* (Table 1, Fig. 1), whereas calculations with the other three databases are offset from zero by ~ 0.9 on average. However, it is unclear whether this difference is due to an incorrect solubility product (K_{SP}) or due to erroneous stability constants for aqueous alumina species, so that this solubility constant was not changed in *carbfix.dat*. It should be noted that all experiments were carried out at 25 to 80 °C, and that *phreeqc.dat* only contains a constant $\Delta_r H$ for the kaolinite dissolution reaction, so that calculated saturation indices are likely to show systematic errors at higher temperatures. Measured solubilities of analcime [50] at temperatures of up to 300 °C are reproduced relatively accurately by the three databases containing data for this mineral, as signified by the $\overline{\overline{SI}}$ close to zero (≤ 0.173, Table 1). However, the standard deviations are higher (~ 0.4), indicating that care must be taken when interpreting such saturation indices.

3.4. Hydroxide minerals

In general, aluminum hydroxide minerals are of great interest as Al is a major component in many natural rocks that interact with fluids, such as in geothermal reservoirs. Direct solubility measurements have been carried out for gibbsite and boehmite [51–53], and $\overline{\overline{SI}}$ calculated for these data range from ~ 0.1 to 0.6 (Table 1, Fig. 1), while standard

deviations are of similar magnitude (gibbsite) or slightly larger (boehmite). For the latter mineral, the errors of calculated SI significantly increase above 250 °C as shown in Fig. 2, which is likely caused by the increased errors in extrapolated aqueous speciation constants in thermodynamic databases.

The solubility of brucite is of importance because of its similarity to more complex clay minerals for which direct measurements are complicated by the complex chemistry and solid solutions [56], in addition to its use as backfill material in nuclear waste storage sites [54]. Brucite solubilites measured at room temperature [54] are systematically higher (~ 0.7 in SI) than indicated by *llnl.dat, core10.dat,* and *carbfix.dat* (all containing the same constant), but show a lower standard deviation. This implies, similar to silicate minerals, that uncertainties in saturation state calculations for these minerals must be considered. No correction of solubility products was attempted for these phases, as it is unclear whether errors are caused by aqueous complex stability constants or the solubility products themselves.

4. Conclusions

Saturation indices were calculated for aqueous solutions that directly determined the solubility of various minerals. Calculations were carried out with PHREEQC using its different thermodynamic databases to assess the quality of such predictions. The results reveal varying degrees of deviation of the predicted saturation indices from zero, which may be caused by errors in the thermodynamic database or model, analytical and experimental uncertainties, or departures from equilibrium in the experiments. While the *phreeqc.dat* database reproduces low-temperature data relatively well, systematic errors appear at higher temperatures for many minerals due to the assumption of a constant enthalpy of reaction ($\Delta_r H$). For carbonate minerals, the fit is best for calcite and aragonite, while dolomite, magnesite, siderite and dawsonite SI deviate from zero by approximately up to 1 to 2. A similar degree of variability can be seen for anhydrite, analcime, and the alumina hydroxide minerals gibbsite and boehmite. Experimentally determined quartz and amorphous silica solubilities are reproduced well by all databases, and geothermometric (equilibrium) temperatures calculated from the same data deviate from measured experimental temperatures by 3 °C on average, with a standard deviation of 11 °C. Systematic underestimation of solubilities by approximately one SI are seen for kaolinite and brucite. A new database for PHREEQC, *carbfix.dat*, was created based on the *core10.dat* database of Neveu et al. [24], adding several additional mineral solubilites and aqueous species stabilities relevant for fluid-rock interactions in basalt-hosted carbon sequestration efforts, as well as improving several equilibrium constants based on available data.

In general, the variability of calculated SI and their deviance from zero indicate that care must be taken when interpreting thermodynamically calculated SI for natural fluids. The variability shown in this study should be regarded as a minimum estimate of uncertainty, as fluid compositions are commonly much more complex in natural systems, so that errors in the stabilities of aqueous species stabilities are amplified. Furthermore, the experimental data used for our quality assessments do not span the full range of temperature and pressure that occur in natural systems. Therefore, larger errors likely prevail under such conditions since many thermodynamic constants are extrapolated over a wide range of conditions [3]. Moreover, for many of the more complex minerals (especially sheet silicates such as clays, and zeolites), no direct solubility measurements are available; consequently, solubilites in thermodynamic databases are calculated indirectly from thermodynamic properties of the minerals and aqueous species, potentially introducing large errors that are difficult to estimate. This highlights the need for further experimental studies directly measuring the solubilites of such minerals over a wide range of conditions (temperature, pressure, composition) along with the evaluation of solid solution properties. Finally, the creation of a fully internally consistent thermodynamic database for a large set of minerals and aqueous species, including uncertainties of parameters evaluated using statistical methods during the regression process, is yet to be achieved. Although such a database is available for petrological purposes [27], its applicability to low- to medium-temperature fluids of complex composition is currently limited due to the lack of many aqueous species in the database.

Acknowledgements

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