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Comparison of different thermodynamic databases used in a geothermometrical modelling calculation

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Abstract

Different thermodynamic databases usually have common thermodynamic data for some minerals or aqueous species, but in many cases they present important differences. Four different thermodynamic databases (WATEQ4F, LLNL, DATA0.YMP.R5 and SOLTHERM) have been used in a geothermometrical modelling problem and they are compared in this work. The main differences found in the thermodynamic data are related to the order, degree, crystallinity and composition of the considered aluminosilicate phases and the effects of these properties in the experimental, or theoretical, data used for the fitting of the equilibrium constant at different temperatures.

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1. Introduction

The geothermometrical modelling is a useful technique to study and characterise a thermal system. It allows estimating the reservoir temperature of the waters from the study of the evolution of the saturation states of different mineral phases when an increase of the temperature of the waters is simulated.

This kind of determination is carried out by using geochemical modelling codes such as PHREEQC[1] or GeoT[2] among others, which are provided with different databases that contain the thermodynamic data for minerals, gases and aqueous species. The fact that these databases can present significant differences in their data, which would affect the temperature prediction[3], makes the selection of the most adequate one according to the characteristics of the studied waters and minerals in contact to, a necessary task.

The aim of this study is to present the differences found when performing the geothermometrical modelling of a

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thermal water by using four of the most commonly used thermodynamic databases in this type of calculations, and explain the main reason for that. The water sample selected for this study belongs to a low temperature carbonate evaporitic system (Arnedillo thermal system), located in La Rioja, Spain. The water is of chloride – sodium type with a spring temperature of 45.3 ºC and TDS value of 7352 ppm.

2. Materials and methods

2.1. Geothermometrical modelling

The geothermometrical modelling is a kind of reaction path calculation which allows estimating the temperature of the thermal water in the reservoir from the chemical analysis of a water[4]. In order to do this, it is necessary to assume that thermal waters have not changed their composition while ascending. Then, a temperature increase is simulated and the final temperature is found when the set of minerals, previously selected as present in the reservoir, converge towards equilibrium simultaneously.

2.2. *Databases*

The four thermodynamic databases compared in this work are: WATEQ4F[5] and LLNL[6] databases, which have been used with the PHREEQC code[1], and DATA0.YMP.R5[7] and SOLTHERM[8] used with the code GeoT[2].

The WATEQ4F database has been developed by the U.S. Geological Survey and it contains most of the major and trace species, mineral and gas phases in natural water systems. It was developed to be used in a temperature range of 0 to 100 ºC, and care should be taken when outside this range[5]. In any case, it can be used for the study of a wide range of natural waters, including waters from low enthalpy geothermal systems. Among the four databases compared in this work, WATEQ4F is the only one that uses, mainly, the Van't Hoff equation for the calculation of the equilibrium constants at different temperatures. Some exceptions are the cases of calcite, anhydrite or quartz, for which the calculation is through a polynomic K(T) expression fitted to experimental data. That is the main procedure for the other three databases used in this work.

The LLNL includes reliable data for a vast number of minerals and aqueous species in a temperature range of 0 to 300 ºC[6]. The DATA0.YMP.R5 in one of the versions performed for the Yucca Mountain Project and it has also been prepared to be used for a temperature range of 0 – 300 ºC[7]. Finally, the SOLTHERM database is derived from the databases of Holland and Powell[9] and the SLOP.98[10]. It was developed to be applied in a temperature range from 25 to 300 ºC[8]. For the activity coefficient calculations all databases rely on different extensions of the Debye-Hückel equation (Davis, B-dot, etc.). The ionic strength of the studied waters is 0.13 molal and, therefore, the different equations are not expected to promote important differences in the calculations[4].

Most of the data contained in these databases present important differences regarding 1) the solubility constant and composition of certain minerals and 2) the aqueous species dissociation constants[3]. Furthermore, these databases do not contain data for the same minerals and, therefore, only common or equivalent minerals included in the four databases have been selected for comparison in the geothermometrical modelling performed in this work. The selected minerals are anhydrite, quartz, calcite, dolomite (disordered dolomite), albite (low temperature albite in all cases except from the WATEQ4F database, which only contents one type of albite), K-feldspar (maximum microcline in DATA0.YMP.R5, microcline in SOLTHERM, and adularia in WATEQ4F since it does not contain other K-feldspar), and some aluminosilicates like laumontite, pyrophylite, kaolinite and illite.

3. Results

The modelling results obtained with the four different databases are presented in Table 1 and Figure 1 (as the evolution of the SI values, log IAP/K(T), for the selected minerals). There are not significant differences in the results obtained for anhydrite (differences of 7 ºC), and slightly larger for quartz (up to 14 ºC). However, the differences found in results obtained for the rest of the minerals are more important. The results for calcite vary in a range of 17 ºC. For dolomite three of the results vary in a range of 8 ºC whilst with the WATEQ4F database this mineral is always undersaturated. Something similar happens for albite and K-feldspar, they are undersaturated

when the WATEQ4F database is used, while using the other databases these minerals are in equilibrium in a range of 24 and 20 ºC, being DATA0.YMP.R5 and LLNL in a better agreement and SOLTHERM giving the highest value obtained. The major differences have been found in the case of laumontite, with differences of 106 ºC, kaolinite with 38 ºC, illite with 40ºC, and phyrophyllite, always oversaturated if the calculations are done with the WATEQ4F database, and showing differences of 24 ºC when using the other three databases.

Table 1. Temperatures (ºC), predicted by geothermometrical modelling, by using the different database, at which the different mineral phases considered reach the equilibrium with waters.

	WATEQ4F	LLNL	DATA0.YMP	SOLTHERM
Anhydrite	88	81	82	82
Quartz	97	90	83	96
Calcite	85	79	96	92
Dolomite	- [a]	98	102	106
Albite	- [a]	79	72	96
K-feldspar	- [a]	80	75	95
Laumontite	58	77	164	89
Pyrophyllite	- [b]	89	85	109
Kaolinite	88	103	102	126
Illite	56	96	95	69

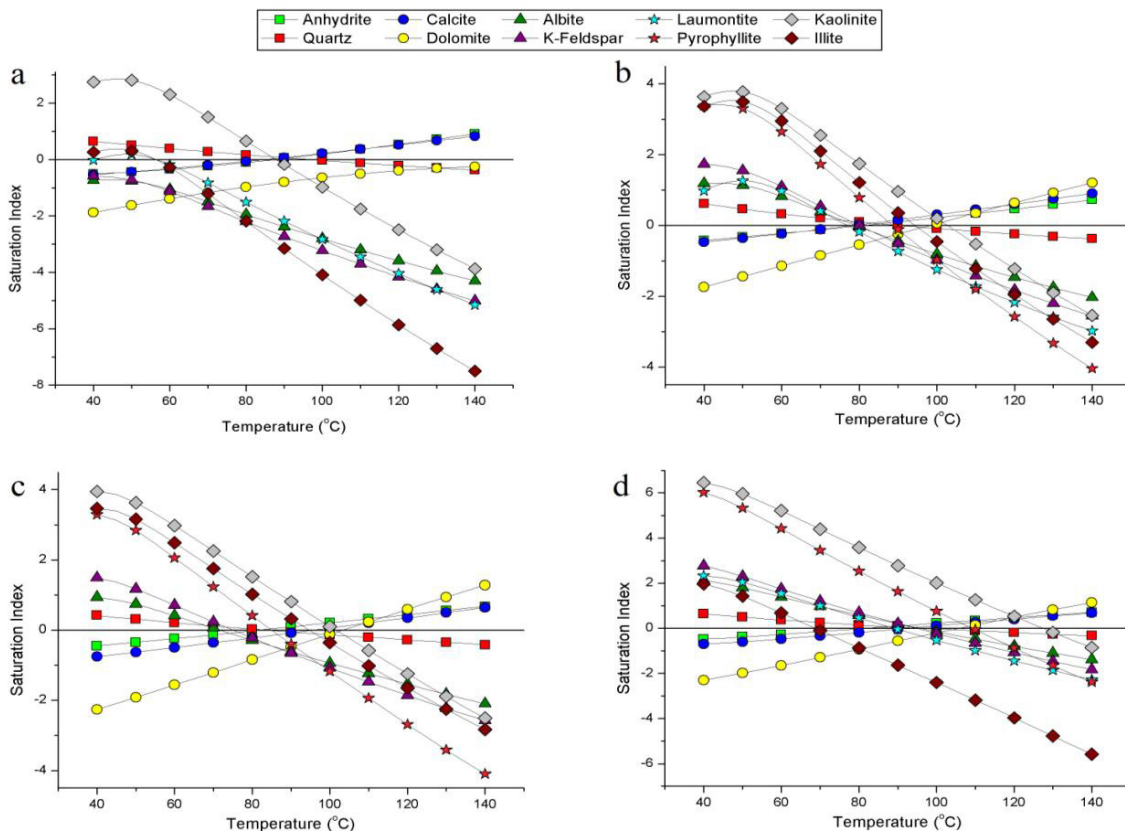*Notes: [a] always undersaturated; [b] always oversaturated.*

Figure 1. Graphical representation against temperature of the saturation indices of the different minerals considered in the study. (a) Results obtained with WATEQ4F database; note that phyrophyllite does not appear in the representation since it is always oversaturated with a Saturation Index close 10. (b) Results with LLNL database. (c) Results with DATA0.YMP.R5 database; note that laumontite does not appear since it is oversaturated in the considered temperature range, it reaches equilibrium at 164 ºC. (d) Results with SOLTHERM database.

4. Discussion and conclusions

The main differences in the results obtained when using the four thermodynamic databases have been found for the aluminosilicates. This is due to the fact that the solubility of those phases (and its variation with temperature) presents important uncertainties related to the compositional variability and/or the degree of crystalinity[11]. That is, depending on the similarity between the characteristics of the phase considered in the different databases and the phase involved in the study, the results will be more or less accurate.

The differences found in the results obtained for the rest of the considered phases seem to be related to the experimental data used for them and the mathematical fitting to those data. An additional cause of differences is the fact that the WATEQ4F database uses the Van't Hoff equation to calculate the equilibrium constant at different temperatures for some phases. However, the saturation states of calcite, anhydrite and quartz are not calculated using the Van't Hoff equation, but a polynomic K(T) expression from experimental data which are fitted in the temperature range of 0 – 90ºC[12], 25 – 56 ºC[13] and 70 – 250 ºC[14], respectively.

In the case of dolomite, in which the disordered phase has been selected in all cases, the differences found seem to be due to differences in the polynomic expression used for the calculation of the equilibrium constant at different temperatures. Nonetheless, the largest difference has been found when using the WATEQ4F database, which is the only one that calculates the saturation state of this phase with the Van't Hoff equation.

In any case, despite the differences found, the results obtained with the different databases would allow establishing a temperature in the reservoir of about 90 ºC (obviously excluding some of the results obtained with some aluminosilicates phases). Two additional conclusions are that there is not a thermodynamic database more reliable than other for this type of systems, and that it is necessary to be careful when selecting the aluminosilicate phases to consider in the modelling due to their high uncertainties.

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