

New Developments in Multicomponent Geothermometry

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Keywords: geothermometer, GeoT, iGeoT, modeling, water chemistry, solute, reservoir temperature, saturation index

ABSTRACT

The multicomponent geothermometry computer program GeoT was upgraded to allow for reaction of one or more minerals when making temperature estimations, to take into account the effect of potential re-equilibration of fast-reacting minerals (e.g., calcite) along the cooling path of deep fluids on their way to ground surface. An option was also added into GeoT to iteratively estimate steam weight fraction for degassed samples, assuming iso-enthalpic boiling from the estimated temperature at saturation pressure (pure water), down to a given sampling pressure. Finally, the numerical optimization engine of iTOUGH2 was integrated into a standalone computer program, iGeoT, which enables the estimation of input parameters necessary for the reconstruction of deep fluid chemistries without having recourse to separate numerical optimization software. Various examples using both real and synthetic geothermal waters are discussed, including the effect of different optimization methods, objective functions, mineral-fluid reactions, and input thermodynamic databases on estimated deep reservoir temperatures.

1. INTRODUCTION

The computer program GeoT (<http://esd.lbl.gov/technology/geot/>; Spycher et al., 2011, 2013, 2014) was developed after the method of Reed and Spycher (1984) to reconstruct the composition of deep geothermal fluids prior to degassing and mixing during their ascent to shallow depths, and to estimate deep reservoir temperatures from the computed saturation indices of multiple minerals using complete fluid analyses collected from wells or springs. This geothermometry tool provides a more integral approach to estimate reservoir temperatures than traditional geothermometers alone, particularly for fluids that have not fully equilibrated with reservoir minerals and/or that have been subject to dilution and degassing (Peiffer et al., 2014; Gherardi and Spycher, 2014; Batistel et al., 2014). In addition, the use of GeoT with the iTOUGH2 numerical optimization software (<http://esd.lbl.gov/iTOUGH2>; Finsterle, 2007a,b,c; 2004) has shown promising results to estimate unknown parameters necessary for the chemical reconstruction of deep fluids (e.g., dilution factor, composition and amounts of exsolved gases) and thus to better constrain estimates of deep reservoir temperatures. A similar optimized multicomponent geothermometry approach using the Geochemist Workbench (www.gwb.com) and parameter estimation software PEST (Doherty, 2008; <http://pesthompage.org/>) has since been explored by others also with good results (Palmer et al., 2014; Neupane et al., 2015).

The assumption of fluid-mineral equilibrium (on which all solute geothermometry methods rely), uncertainties in model input parameters (including thermodynamic data), and different optimization methods all introduce uncertainties in this new geothermometry approach. In this study we report on recent capabilities implemented into GeoT and ongoing investigations to assess and minimize these uncertainties, with the goal of expanding the practical and technical applicability of the optimized multicomponent geothermometry method.

2. NEW CODE DEVELOPMENTS

Details on GeoT have been provided elsewhere (Spycher et al., 2013, 2014) and are briefly summarized here. GeoT is a computer program that automatically reconstructs the deep-reservoir composition of geothermal fluids and then estimates the reservoir temperature by computing the saturation points of multiple minerals as a function of temperature. The temperature is estimated by computing various measures of the clustering of mineral saturation indices near a value of zero, which represents the theoretical equilibrium point for each mineral. Besides full water compositions, GeoT inputs include the amount of dilution (or evaporative concentration) that waters may have been subjected to before sampling and analysis, as well as the composition and amount of gases that may have exsolved from these fluids. These typically unknown or poorly constrained input parameters can be estimated by numerical optimization. The simultaneous processing of multiple water compositions is possible and minimizes the degrees of freedom in these inversions. Previously, the automatic estimation of these parameters with GeoT required an external numerical optimization software. The newly developed iGeoT (discussed below) incorporates its own optimization engine.

GeoT has been upgraded to allow for the back-reaction of one or more minerals when making temperature estimations for cases when fluids are suspected to have re-equilibrated with certain minerals upon cooling and degassing. A new option also allows for the iterative estimation of steam weight fraction assuming iso-enthalpic boiling, which is primarily intended for geothermal wells. A more significant upgrade was the development of iGeoT, a version of GeoT that incorporates the numerical optimization engine of iTOUGH2 into one standalone program. These upgrades are further discussed below.

2.1 Mineral Re-Equilibration Option

The results of all solute geothermometers can be strongly affected by mineral re-equilibration upon cooling and/or degassing of deep fluids on their way to ground surface. For example, the concentrations of Al and Mg in geothermal fluids are typically small and can be particularly affected by the dissolution/precipitation of small amounts of Al- and Mg-bearing phases (Giggenbach, 1988; Pang and Reed, 1998; Peiffer et al., 2014; Wanner et al., 2014). Therefore, geothermometry approaches based on computed saturation indices of Al and Mg silicate minerals are quite sensitive to the concentration of these elements. To circumvent this difficulty, the aqueous concentration of an element such as Al or Mg can be assumed to remain controlled by equilibrium with a specific mineral when making temperature estimations. This approach (the Fix-Al method of Pang and Reed, 1998) is implemented into GeoT and greatly helps solving this problem. However, this method can suffer from difficult numerical convergence, and its application to more than one element (requiring a different mineral specified for each element) does not always yield a unique solution (Bethke, 1992). Furthermore, the re-equilibration of one mineral in a real system can significantly affect the concentration of more than one aqueous species, such as the dissolution/precipitation of calcite potentially affecting not only Ca, but also pH and/or dissolved carbonate. For this reason, GeoT was upgraded with an option to model the full equilibrium reaction of one or more minerals with any given water composition, at all temperature steps when evaluating for the clustering of mineral saturation indices as a function of temperature.

This option was tested with both a synthetic water and an actual thermal spring water (Figure 1). In the first case, a synthetic water was created by (numerically) equilibrating an actual geothermal water with several minerals at 250°C (plausible phases for the system considered), then cooling the resulting fluid to 50°C while keeping the fluid at equilibrium with calcite along the cooling path. The reservoir temperature was then back-calculated from the 50°C fluid composition, first ignoring (Figure 1a, top) and then including (Figure 1a, bottom) the back-reaction of calcite with the fluid. In this extreme case, the clustering of saturation indices was lost when ignoring the reaction of calcite, which also biases the Na-K-Ca temperature to low values and (by pH effect) slightly increases the equilibration temperatures of the feldspars (Figure 1a, top). In the second case, GeoT was applied to a hot spring water sample from Breitenbush, Oregon (Mariner et al., 1993), first using the Fix-Al method to compute Al concentration from equilibrium with K-feldspar, without further reconstruction (Figure 1b, top). The temperature estimation was then repeated, this time specifying back-reaction of calcite and K-feldspar, yielding an improved clustering and an estimated temperature (176°C) close to that calculated using the SO₄-H₂O δ¹⁸O equilibrium temperature (178°C, Mariner et al., 1993) (Figure 1b, bottom).

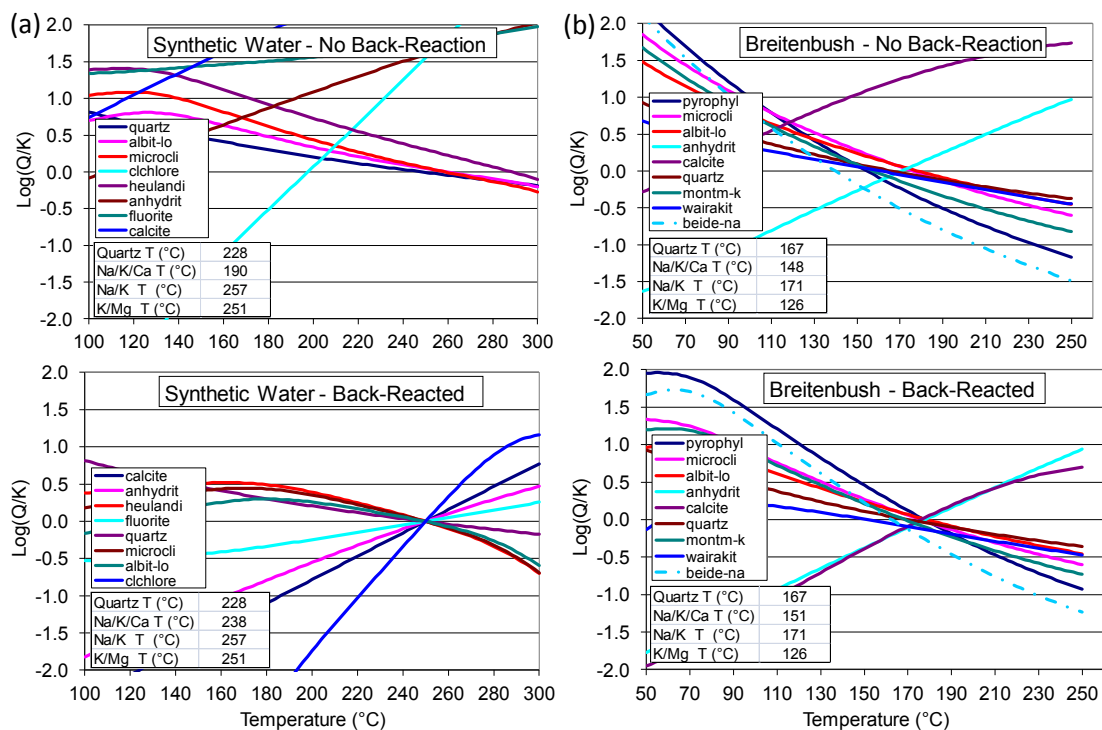


Figure 1: Computed mineral saturation indices ($\log(Q/K)$) as a function of temperature for a synthetic water originally equilibrated with reservoir minerals at 250°C then cooled to 50°C while reacting calcite (a), and an actual hot spring water from Oregon (b), in each case ignoring (top) or including (bottom) the re-equilibration of calcite. The Al concentration in the hot spring water (b) is fixed by equilibration with K-feldspar (top, with no convergence above 250°C) and alternatively by full reaction with K-feldspar (bottom). Traditional geothermometers computed using the unreconstructed (top) and reconstructed (bottom) waters are also shown on the graphs (Na-K-Ca, Fournier and Truesdell, 1973; Na-K, K-Mg, Giggenbach, 1988; quartz, Fournier and Potter, 1982).

2.2 Steam Weight Fraction Computation Option

For waters that have boiled/degassed on their way to the surface, GeoT allows for input of a gas composition and a steam fraction, defined as the weight fraction of total gases (H_2O and non-condensables) in the total discharge (water and gases). Although this parameter can be estimated by trial-and-error or numerical optimization (e.g. Spycher et al., 2014), a more practical option (and potentially more rigorous for geothermal wells) was implemented into GeoT to estimate the steam fraction in tandem with temperature. When this option is enabled, GeoT first estimates a reservoir temperature with a trial 1% steam fraction to reconstruct the composition of the deep fluid; a new steam fraction is then computed assuming iso-enthalpic boiling from this first estimated temperature, at the saturation pressure of water, down to an input sampling pressure (at corresponding saturation temperature), using pure-water liquid and vapor enthalpy data (e.g. Arnorsson and Sigurdsson, 1982); the composition of the deep fluid is then recalculated using the new steam fraction, and the reservoir temperature is estimated again (new clustering) for this new fluid composition; from the new estimated temperature, a new steam fraction for iso-enthalpic boiling is evaluated, and so on. This iterative procedure continues as long as the clustering of mineral saturation indices near zero improves, in this case computed as the spread in the equilibration temperatures of all minerals considered in the temperature estimation. This option is intended only for fluids from high-temperature wells or from boiling springs (near $100^\circ C$) for which the assumption of iso-enthalpic boiling can be presumed reasonable. If this is not the case, the steam fraction is preferably estimated using numerical optimization.

2.3 Seamless Numerical Optimization with iGeoT

GeoT's multicomponent geothermometry computations have been integrated into the iTOUGH2 simulation-optimization framework to automatically estimate some of GeoT's input parameters (e.g., steam weight fraction, concentration/dilution factor, input concentrations) without recourse to a separate iTOUGH2 version or other optimization software. iTOUGH2 is a computer program for parameter estimation, sensitivity analysis, and uncertainty propagation analysis (Finsterle, 2007a, b, c). It contains a number of local and global minimization algorithms for automatic calibration of a model against measured data, or for the solution of other optimization problems. The combination of iTOUGH2 and GeoT into a standalone program has been named iGeoT; it enables the automatic estimation of input parameters by minimizing the statistical measures (Spycher et al., 2014) that describe the clustering of mineral saturation indices near zero. iGeoT can be run in two modes:

- *Expert Mode* The user controls the optimization by supplying a command file containing standard iTOUGH2 instructions. In this mode, the user has access to all options for specifying inputs, selecting algorithms, and performing additional analyses (e.g., sensitivity and uncertainty quantification analyses).
- *Automatic Mode* The user indicates in a standard GeoT input file (using special characters) which of its input parameters shall be considered uncertain and thus estimated by minimizing appropriate clustering measures. iGeoT automatically sets up suitable iTOUGH2 instructions for the optimizations. In this mode, the user has access to iTOUGH2 optimization without the need to be proficient in the use of iTOUGH2. Moreover, the iTOUGH2 command file that is automatically generated by iGeoT in Automatic Mode can be used as a template for further analyses to be conducted in Expert Mode.

Like its predecessor, iGeoT has been tested using both synthetic and actual geothermal water compositions. One of these tests involved the temperature estimation of the same synthetic water considered in Figure 1 (equilibrated at $250^\circ C$), but this time using two waters derived (numerically) from this parent water: one diluted two times and cooled/degassed to atmospheric CO_2 pressure at $50^\circ C$, and another diluted 3 times and cooled/degassed to $25^\circ C$ also at atmospheric CO_2 pressure. The reconstruction of the parent water was achieved by estimating dilution factors and steam weight fractions for each derived water in one simultaneous iGeoT inversion, using an objective function that considers the saturation index clustering of both waters as well as the deviation between estimated temperatures for each water (Figure 2). In doing so, even though the two derived waters have lost all their original mineral equilibration temperatures (Figures 3a and 3b), the optimization recovers quite closely the signature of the parent water (Figures 3c and 3d).

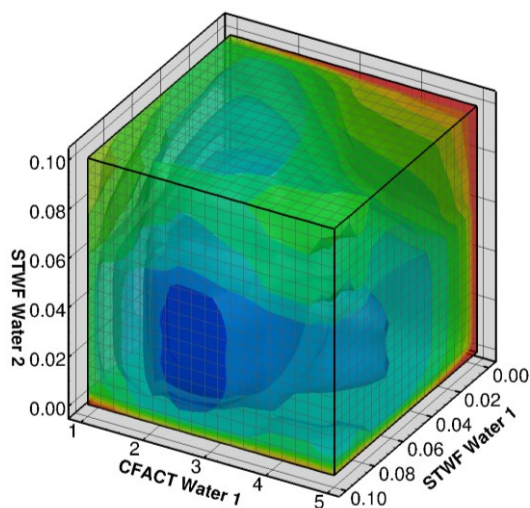


Figure 2. Objective function of the iGeoT inverse problem in three-dimensional parameter space combining the steam weight fraction (STWF) and dilution factor (CFACT) of two waters derived from one parent water.

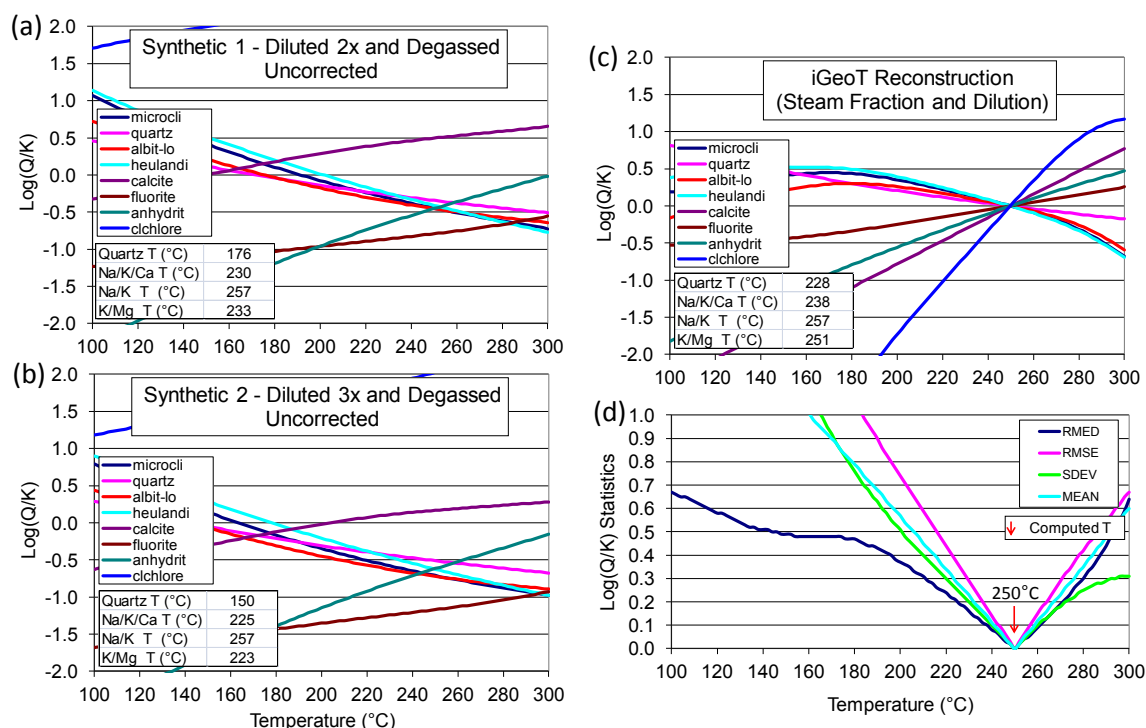


Figure 3. Computed mineral saturation indices ($\log(Q/K)$) as a function of temperature for two waters (a and b) derived by numerically cooling, degassing, and diluting a synthetic parent water originally equilibrated with reservoir minerals at 250°C, and for the parent water as reconstructed with iGeoT (c). Saturation indices clustering indicators are shown for the reconstructed water (d) (median RMED, root-mean-square RMSE, standard deviation SDEV, and average MEAN). Traditional geothermometers calculated with each water composition are also shown (see caption of Figure 1 for source).

Even though optimized multicomponent geothermometry shows promising results, it should not be considered as a fail-safe approach or as a replacement of more traditional (and practical) geothermometers. In many (but not all) cases, the combination of both approaches by applying classical geothermometers to the reconstructed water compositions can be useful to build confidence in temperature estimations. This is the case with the example in Figure 3, which shows that the different classical geothermometers yield more consistent temperatures once the parent water has been reconstructed (as would be expected). In some cases, estimating an “a-priori” dilution factor from the Na/K temperature (dilution independent) and quartz temperature (dilution dependent) can also be useful as a first-guess to reconstruct a reservoir water composition using iGeoT.

As with any solute geothermometry methods, the multicomponent geothermometry approach should not be applied blindly and without a good understanding of underlying uncertainties, especially when combined with numerical optimization. These uncertainties are further examined below.

3. KEY METHOD UNCERTAINTIES

The large number of inputs required for multicomponent geothermometry (compared to traditional geothermometers) presents both positive and negative aspects. On one hand the reliance on full water compositions makes this method more integral and applicable to a wider range of mineral-water interactions than traditional geothermometers, which are limited to reactions involving only one or a few specific minerals. On the other hand, the reliance on a larger number of inputs inherently has the potential to increase uncertainty when these inputs are poorly constrained. Besides uncertainties in parameters necessary for the reconstruction of deep fluids, such as dilution factor and steam fraction, which can be optimized as discussed previously, inherent uncertainties also exist related to the 1) the nature of minerals controlling the reservoir fluid chemistry, 2) the search method, parameters, and objective function(s) required for numerical optimization, and 3) the thermodynamic data of minerals and aqueous species needed for computations of saturation indices, as discussed below.

3.1 Mineral Assemblage

The mineral assemblage selected for temperature estimations obviously can affect temperature estimations from computed mineral saturation indices, as discussed in earlier studies (Reed and Spycher, 1984; Pang and Reed, 1998). The Phase Rule should dictate exactly how many minerals can be at equilibrium with the solution under the given temperature, pressure, and composition conditions and this rule can help in narrowing down a list of suitable minerals (e.g., Palmer et al., 2014). However, “exact” equilibrium is rarely

achieved in natural systems. We have shown with kinetic reactive transport simulations and experiments (Spycher et al., 2014) that water-rock reactions can yield a suite of minerals nearly, but not exactly, at equilibrium with the solution, with near-zero saturation indices that closely bracket the “true” reservoir temperature. In addition, because similar types of minerals have similar thermodynamic properties, we have observed that the saturation indices of similar minerals are often near zero close to the “true” temperature, even when not truly belonging to the observed assemblage. This argues in favor of the use of proxy minerals (e.g. for clays and micas) when detailed mineralogical information or thermodynamic data are not available. Nevertheless, it must be recognized that uncertainties regarding a reservoir mineral assemblage directly translate to uncertainties in predicted temperatures.

If a sampled thermal water needs reconstruction to account for boiling or dilution, the uncertainty resulting from an unknown mineral assemblage may be compounded by the reconstruction procedure. For example, using GeoT with iTOUGH2, Fowler et al. (2015) reported two possible reservoir temperatures for a thermal water sampled in an exploration well at Surprise Valley (Phipps #2 well; Sladeck et al., 2004): 190°C when chalcedony was taken as the stable silica polymorph, versus 228°C when quartz was considered instead (the hottest reported temperature to date in this well is ~170°C). We further tested iGeoT using the same Phipps #2 well water, considering similar minerals as in the quartz assemblage used by Fowler et al. (2015) but adding anhydrite in one case (Figure 4a) then keeping anhydrite but replacing talc by laumontite in another case (Figure 4b). In both cases the solutions were back-reacted with calcite, K-spar and Mg montmorillonite using the new GeoT option described earlier, and the amount of gas loss was estimated by optimization (steam weight fraction of a gas with pure CO₂ and 99 vol% steam). Because the concentration of Al was not measured, and that of Mg was below the detection limit, the computed concentrations of these elements could not be compared to measured data. For both cases a relatively good clustering was obtained, although yielding two different temperatures (216 and 201°C, respectively; Figure 4) resulting primarily from the different solubility of talc and laumontite, but also from the different optimized steam fraction values resulting from the use of these different minerals (thus a coupled effect). Neither talc nor laumontite has been reported in this well, although one could argue that talc is a reasonable proxy for clays, and laumontite for zeolites. This example illustrates the need to carefully assess model inputs and results when running optimized multicomponent geothermometry computations with limited mineralogical and/or water analytical data, and to test as many inversions as possible to assess the sensitivity of temperature estimations with respect to different plausible mineral assemblages. In the present case, the smaller computed margin of error favors the first inversion (Figure 4a), although different optimization methods and/or initial guesses for estimated parameters can also yield differences in results with similarly good clustering (Figures 4c and 4d), as discussed further below.

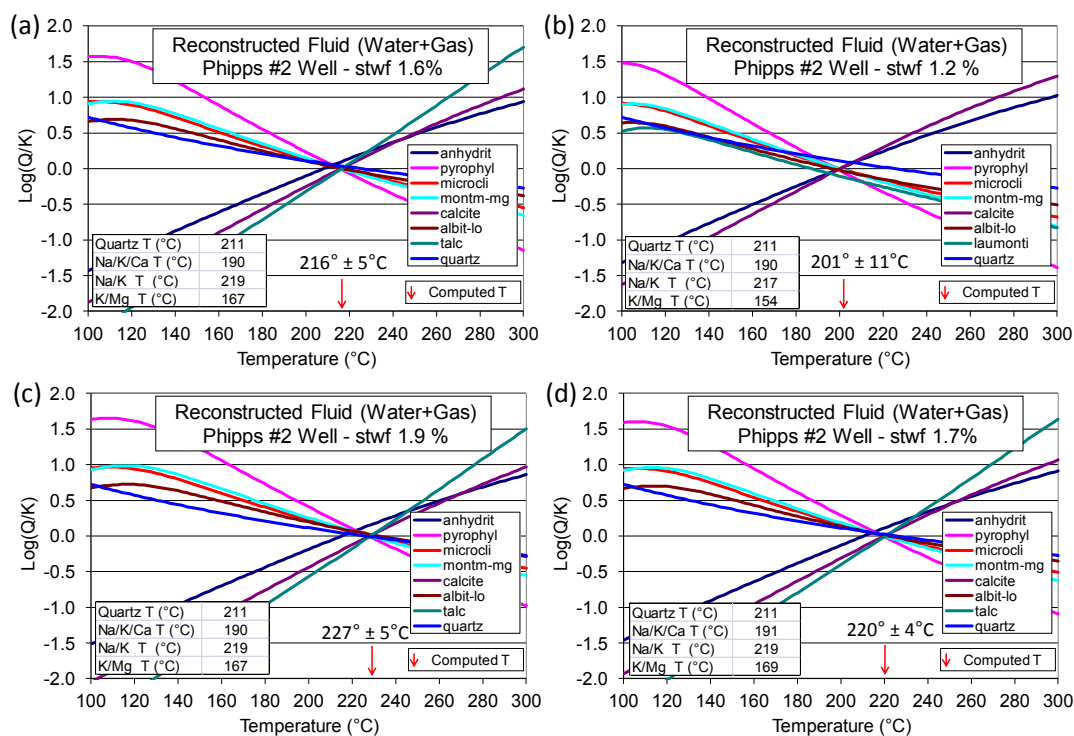


Figure 4. Computed mineral saturation indices ($\log(Q/K)$) as a function of temperature for a geothermal water from Surprise Valley, California, after correction for CO₂ loss (estimation of steam weight fraction, stwf) and re-equilibration of certain minerals (see text) using iGeoT. Temperature estimations are shown assuming mineral assemblages including talc (a) or laumontite (b), a different initial guess for steam fraction (c), or a different optimization search procedure (d; grid search versus Levenberg–Marquardt for the other cases).

3.3 Optimization Parameters

The type of search procedure and initial guesses to estimate input parameters by numerical optimization can also affect computed reservoir temperatures (Figures 4c and 4d) and so do other parameters specific to the various optimization methods available with iGeoT. This is because the clustering parameters used for optimization (measures of saturation indices spread, median, standard deviation, and root-mean-square error; see Figure 1d, also Spycher et al., 2014) may not always yield an objective function as smooth as that shown on Figure 2, particularly when reaction/equilibrium constraints are applied during the inversion. For this reason, iGeoT should never be applied blindly and without at least a basic understanding of implemented optimization algorithms and their input requirements. Although iGeoT’s “Automatic” mode was preset to yield reasonable optimization results in many typical applications, taking full advantage of its “Expert” mode can significantly increase its range of application and reduce the potential for convergence to a false minimum.

3.1 Thermodynamic Data

We previously investigated the effect of different thermodynamic databases on temperature estimations using early versions of GeoT (Spycher et al., 2011). This previous and rather cursory assessment showed that despite decades of ongoing geochemical modeling studies, there remain significant differences between various databases compiled by various groups. Here and in previous studies we have used the SOLTHERM thermodynamic database (Reed and Palandri, 2006) based in large part on the internally consistent mineral data set of Holland and Powell (1998) and aqueous species data from Shock et al. (1997). To evaluate uncertainties related to the use of different databases, the Phipps #2 water used for the example in Figure 4 was re-run with iGeoT, this time using another commonly distributed alternative database (SNL, 2007). In this case, a temperature within the range of previously obtained temperatures was computed, but only after replacing talc with illite (Figure 5), illustrating differences in thermodynamic properties of minerals between databases, particularly for mixed phases such as clays.

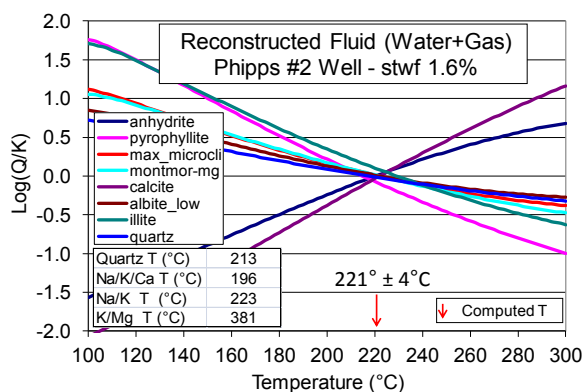


Figure 5. Computed mineral saturation indices (log(Q/K)) as a function of temperature for a geothermal water from Surprise Valley, California, as described for Figure 4a but using a different thermodynamic database, and switching talc for illite.

To further investigate differences in GeoT results when using alternative databases, two synthetic waters were created, each reflecting equilibrium with the same propylitic mineral assemblage at 250°C. The first synthetic water was created using our “base-case” database (Reed and Palandri, 2006) (Figure 6a). The second water was created using the alternative database from SNL (2007) (Figure 6b). In doing so two different waters were created, each reflecting equilibrium with the same suite of minerals at about the same pH (6.7 and 6.8) but each with somewhat different compositions reflecting the differences in thermodynamic databases used to create them. GeoT was then applied to back-calculate the temperature of these waters, but after switching databases, i.e., running with the alternative database the water created with the base-case database (Figure 1b), then running with the base-case database the water created with the alternative database (Figure 1d). By applying classical geothermometers to each synthetic water, the consistency of the databases with these geothermometers could be assessed. Results show (Figure 5) that both waters yield Na/K temperatures (Giggenbach, 1988) close to their 250°C equilibration temperatures. The water created with the base-case database yields significantly lower Na-K-Ca (Fournier and Truesdell, 1973) and quartz (Fournier and Potter, 1982) temperatures, and higher K-Mg (Giggenbach, 1998) temperatures than its 250°C equilibration temperature (Figures 6a or 6b). A similar trend but better agreement is found with the use of the alternative database (Figures 6c or 6d). The K/Mg geothermometer is observed to yield inconsistent results, yielding good equilibration temperatures with the synthetic water shown in Figure 1a, but not with the water in Figure 6a, even though both waters were equilibrated with mostly similar minerals using the same thermodynamic database. It should also be noted that the differences in quartz solubility between the two databases considered here reflect the reevaluation of quartz solubility by Rimstidt (1997), which led to a re-assessment of the Gibbs free energy of aqueous silica (SNL, 2007; Gunnarsson and Arnórsson, 2000) that was taken into account in more recent databases (although introducing the potential for losing the self-consistency of older databases). In both cases, the equilibration temperatures recomputed with GeoT after switching databases vary (Figure 6b and 6d), with a better median temperature in the first case (Figure 6b) and better average temperature in the second case (Figure 6d). This exercise illustrates the need and

importance in continuing the development and refinement of thermodynamic data for geothermal applications, even though such activity is no longer considered “fashionable” by the scientific community.

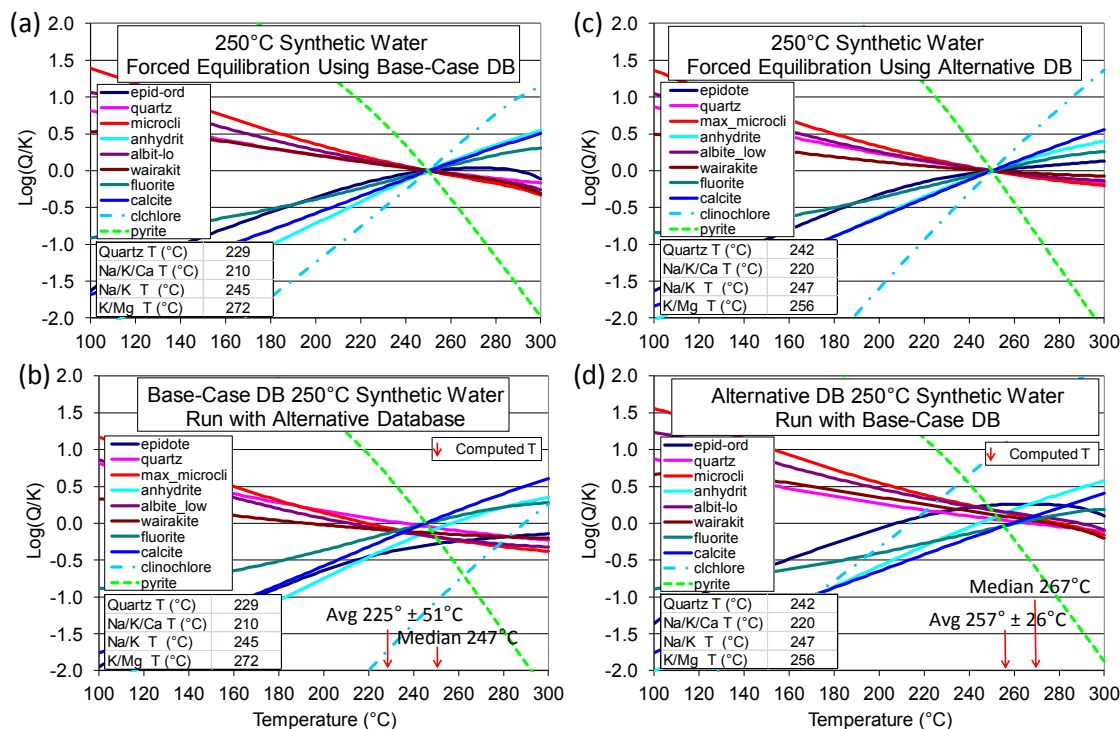


Figure 6. Computed mineral saturation indices ($\log(Q/K)$) as a function of temperature for two synthetic waters derived by numerically equilibrating each solutions at 250°C with the same mineral assemblage, but using two different thermodynamic databases (a and c), then re-computing the equilibration temperatures of these solutions after switching databases (b and d).

4. CONCLUSION

The GeoT computer program has been upgraded with new options, and a new standalone iGeoT version has been developed that incorporates the numerical optimization engine of iTOUGH2. These new developments increase the range of applicability and ease the use of the optimized multicomponent geothermometry approach towards reconstructing the composition of deep geothermal reservoir fluids and estimating their deep temperature. This method, however, should not be applied blindly, as we and others have shown that it holds the potential to yield variable results owing primarily to uncertainties related to 1) the selected mineral assemblage for temperature estimations, 2) the optimization procedure and its input parameters, and 3) uncertainty in thermodynamic data that are needed for this type of computations. Nevertheless, when used in conjunction with, and not instead of, more traditional geothermometry approaches, optimized multicomponent geothermometry presents significant advantages over classical methods in that it allows to estimate the temperature of deep geothermal reservoirs in a more integral manner than previously achieved. Recommendations to minimize uncertainties and maximize confidence in the results of this approach include:

- The temperature of measurement should always be reported when measuring pH – both these parameters are required as input to the computations and have a significant effect on computing multicomponent equilibria at elevated temperatures (Reed and Spycher, 1984).
- As complete as possible water analyses should be obtained, including concentrations of Mg and Al, preferably filtered (<0.2m) and unfiltered to help constrain computed values if these need to be optimized (e.g., Peiffer et al., 2014).
- The method should be applied using alteration mineral assemblages when known (preferentially to primary minerals), and as many plausible assemblages as possible should be tested for the system of interest.
- When using numerical optimization, several inversions should be carried out using different initial guesses to ensure convergence to a plausible solution; if estimating only one or two parameters, using a grid-search procedure is practical to guarantee finding the optimization minimum.

- Gas analyses should be obtained when possible for waters suspected to have boiled and/or exsolved gases, to more accurately reconstruct the composition of deep fluids.
- If field data suggest that several springs may originate from the same parent reservoir fluid, optimizations using water analyses from multiple springs simultaneously can significantly help constraining temperature estimations. However doing so also increases the complexity of the inverse problem and thus the potential for false optimization minima.

Uncertainties related to thermodynamic data are more difficult to tackle. These can only be addressed by continued testing of various databases against well-constrained data from natural systems, and upgrading thermodynamic data as necessary. Mixing data from various databases is not recommended without a clear understanding of data sources (including original reference properties used in various sources) and of the potential for loss of internal consistency.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), Geothermal Technologies Office (GTO) under Contract No. DE-AC02-05CH11231 with Lawrence Berkeley National Laboratory.

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