GeoT User's Guide
A Computer Program for Multicomponent Geothermometry and Geochemical Speciation
Version 1.4

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1 Introduction

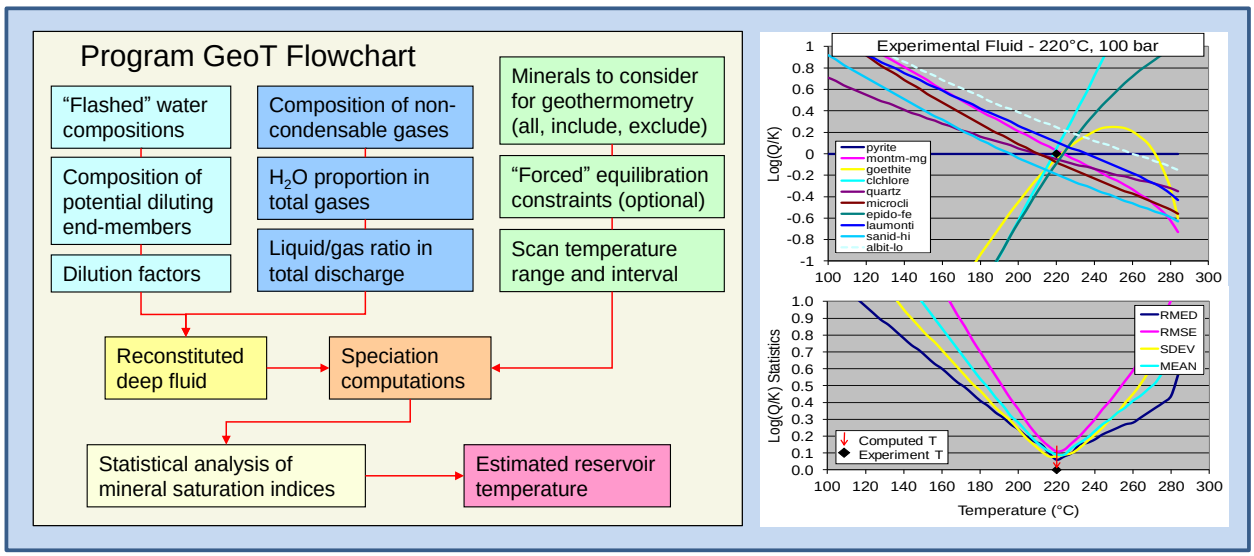
Solute geothermometers have been used for decades to infer the temperature of deep geothermal reservoirs from analyses of fluid samples collected at ground surface from springs and exploration wells (e.g., Fournier and Rowe, 1966; Fournier and Potter, 1982; Fournier, 1977; Fournier and Truesdell, 1973; Fournier 1979; Giggenbach, 1988; Fouillac and Michard, 1981). These "classical" geothermometers and several of their modifications have been successfully applied to many geothermal waters, and have become important and essential geothermal exploration tools. However, in their simplicity, these geothermometers can fail because the (semi-)empirical correlations on which they are based are not always valid for all geochemical systems. Also, geothermal fluids ascending to ground surface are typically affected by gas loss, mixing and/or dilution with shallower waters, masking their deep geochemical signatures.

The multicomponent chemical geothermometry method presented by Reed and Spycher (1984) and further developed by Pang and Reed (1998) and Palandri and Reed (2001) presents advantages over classical geothermometers because it relies on complete fluid analyses and a solid thermodynamic basis, rather than (semi-) empirical correlations, and thus in principle apply to any geochemical system. The method consists of using full chemical analyses of water samples to compute the saturation indices (log(Q/K)) of reservoir minerals over a range of temperatures (e.g., 25 to 300°C). The saturation indices are graphed as a function of temperature, and the clustering of log(Q/K) curves near zero at any specific temperature (for a group of certain reservoir minerals) is inferred to yield the reservoir temperature. Prior to computing saturation indices, the composition of the deep fluid is reconstructed by applying corrections for any dilution and/or mixing effects and by numerically adding back (to the analyzed fluid composition) any gases that may have exsolved from the deep fluid on its way to the ground surface. If unknown, input parameters necessary to reconstruct the deep fluid composition can be estimated by adjusting these parameters to minimize the cluster of mineral saturation indices near zero. This approach was shown to work well to "un-dilute" and re-carbonate geothermal waters (Reed and Spycher, 1984; Pang and Reed, 1998) and oil field brines (Palandri and Reed, 2001) affected by mixing and degassing.

The method of Reed and Spycher (1984) was developed for single-point fluid analyses and requires somewhat tedious data processing followed by temperature estimations relying on fairly subjective "eyeballing" of the clustering of computed log(Q/K) curves. For these reasons, GeoT (Spycher et al., 2011; Figure 1-1) was developed to automate this method into a practical software tool that uses a

set of objective criteria to estimate reservoir temperatures from computed mineral saturation indices, given any input water composition. Because it is a stand-alone program, GeoT can also be integrated with separately available parameter estimation software (e.g., PEST, Doherty, 1998; iTOUGH2, Finsterle and Zhang, 2010) to optimize the clustering of mineral saturation indices near zero for geothermometry computations. This allows a larger number of parameters to be estimated than can be done manually by trial-and-error, and can be accomplished for several water compositions simultaneously if these waters are all believed to originate from one common geothermal reservoir. GeoT can also be used as a geochemical speciation tool to process one or more water analyses simultaneously and to quickly evaluate the saturation indices of a large number of minerals over various ranges of temperature.

Figure 1—1 Structure of the geothermometry computer program GeoT and example computations



See Figure 3-1 for the temperature estimation methodology

2 Requirements

2.1 Computer Requirements

GeoT is written in FORTRAN 77 with Fortran-90/95 extensions. It has been tested on various computer platforms (Microsoft Windows- and Linux-based PCs, Apple Macintosh G4, G5, and Intel-based computers). On most machines the code should compile without errors using Fortran 95 and Fortran 90 compilers. GeoT requires 64-bit arithmetic (8 byte word length for floating point numbers) for successful execution. The source code includes IMPLICIT DOUBLE PRECISION (A-H, O-Z) and IMPLICIT INTEGER*8 (I-N) statements that will automatically generate 64-bit arithmetic on 32 bit

processors. The distribution files folders include documentation (this manual), test problems, and executable files generated with compilers described in accompanying README files.

2.2 Memory Requirements

The required computer memory depends on the problem size. PARAMETER statements are specified in an INCLUDE file (chempar.inc) to define array dimensions. The current version allows for processing 100 water analyses, each with a maximum number of 50 primary species, 800 secondary species, 500 minerals, and 10 gases. Temperature scans can span a maximum of 300 temperature steps, and up to 5 end-member water compositions can be specified for "de-mixing" computations. At the beginning of a model run, the program automatically checks the array dimensions and stops if the dimensions are insufficient for the specific problem, with a message describing the exceeded array size. The memory requirement for this program is about 4 Mb.

2.3 User Knowledge Requirements

Estimated temperatures are sensitive to the mineral assemblage used to run the geothermometry computations. The concentrations of trace elements such as Al and Mg, as well as input thermodynamic data, can also affect temperature estimations. Therefore, the successful implementation, setup, problem formulation, and interpretation of the results of GeoT require a solid background in hydrothermal geochemistry and familiarity with geochemical modeling.

3 Technical Approach

GeoT (Figure 1-1) was developed drawing on existing routines and methods implemented into programs TOUGHREACT (Xu et al., 2011), SOLVEQ/CHILLER (Reed, 1982, 1998) and GEOCAL (Spycher and Reed, unpublished, U. Oregon, 1985). The core of the software is essentially a homogenous geochemical speciation algorithm solving mass-balance/mass-action equations by Newton-Raphson iterations (e.g., Reed, 1982). Using complete fluid analyses, the saturation indices of minerals ($\log(Q/K)$) are obtained from the computed ion activity product (Q) and thermodynamic equilibrium constant (K) of each considered mineral. Data for the computation of activity coefficients together with equilibrium constants for aqueous complexes and minerals at various temperatures are read from an external thermodynamic database. The pH at high temperatures is calculated from the total numerical H^+ concentration computed from the input (known) low-temperature pH, following the method of Reed and Spycher (1984). The program allows for simultaneous regression of multiple waters, automatic

reconstitution of deep fluid compositions, and estimation of reservoir temperature from statistical evaluation of computed mineral saturation indices as described below.

3.1 Deep fluid reconstruction

Input water compositions are corrected for gas loss, dilution or concentration (by some factor), and/or mixing with other waters. If known, the gas phase composition and its proportion in the fluid, the dilution/concentration factor, and/or compositions and fractions of mixing water end-members are entered into the calculations (Figure 1-1). Following Reed and Spycher (1984), gases are numerically added back to the fluid in their respective stoichiometric forms (as defined in the input thermodynamic database; e.g., H_2S as $1\times HS^-$ and $1\times H^+$; CO_2 as $-1\times H_2O$, $1\times HCO_3^-$ and $1\times H^+$), after calculation of the total numerical H^+ of the solution from a given pH. The new total numerical H^+ of the solution, after gas addition, is then used to compute the pH of the reconstructed fluid. The "de-mixing" of a particular end-member solution is carried out essentially in the same manner, by removing or adding a particular component in given input stoichiometric proportions.

Unknown concentrations of one or more specific elements in the deep fluid can be optionally computed by assuming that the concentration of each element is constrained by thermodynamic equilibrium between that element and a respective mineral. This follows the approach presented by Pang and Reed (1998) for aluminum ("Fix-Al" method), and Palandri and Reed (2001) for silica. This equilibrium constraint can be applied over the entire scanned temperature range, only at the initial speciation temperature, or in both instances, as chosen for each dissolved species.

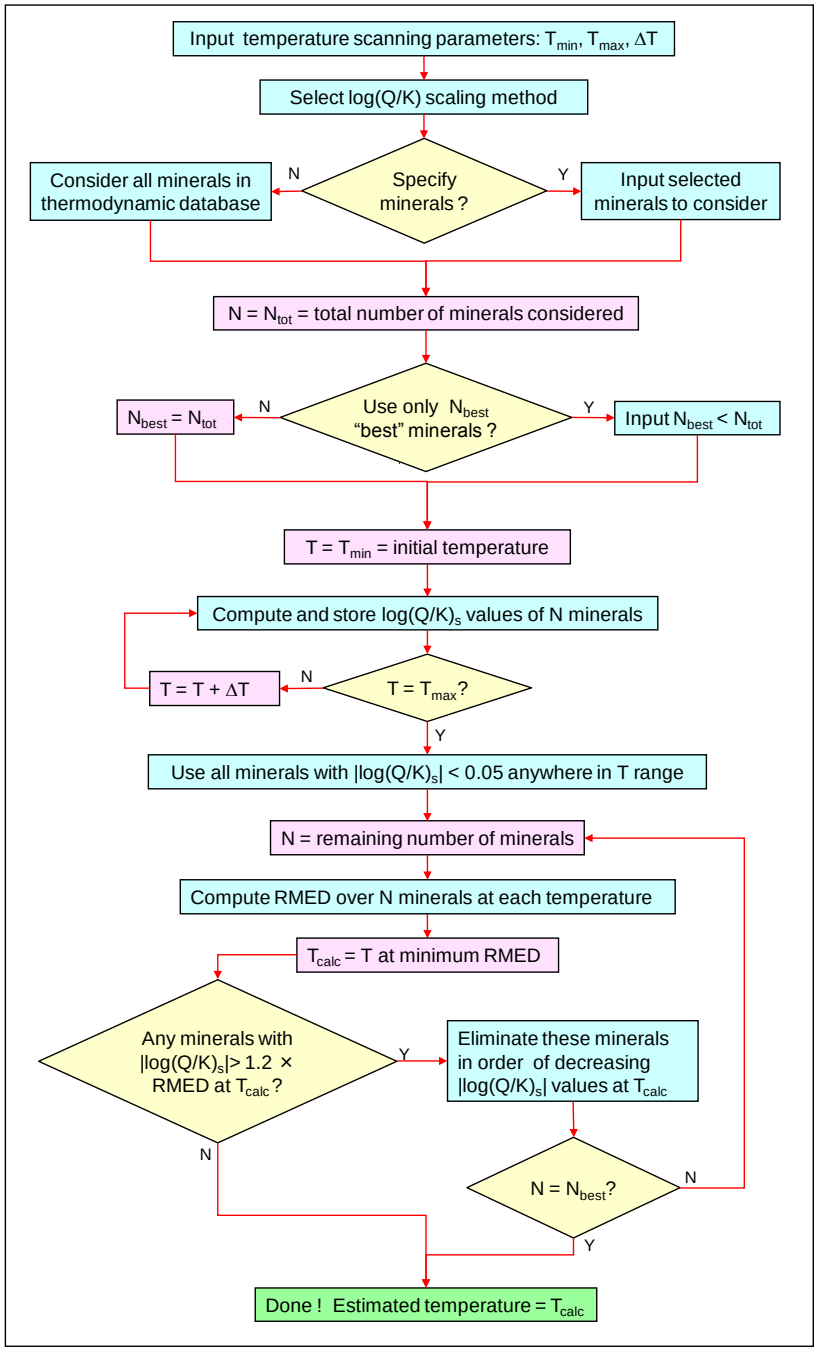
3.2 Temperature estimation from the clustering of saturation indices

Several schemes were evaluated to estimate reservoir temperatures based on the saturation indices of a group of mineral. Best results were obtained by taking the temperature at which the absolute value of the median of computed saturation indices (for a group of minerals) is minimum, after applying an optional elimination algorithm to select a certain number (N_{best}) of "best-clustering" minerals (Figure 3-1). The temperature estimation can be based on a given suite of specific minerals, or applied "blindly" using all minerals available in a separate thermodynamic database. The number of "best-clustering" minerals can be specified (e.g., of a suite of 15 input minerals, only $N_{best} < 15$ minerals are used for the final temperature determination) or defaults to the total number of considered minerals. The program first eliminates all minerals whose absolute value of saturation indices remain at or above 0.05 (an arbitrary but near-zero cut-off value) over the entire temperature range considered. For remaining minerals, the median of the absolute values of saturation indices (RMED) is then evaluated at all temperatures.

Optionally (and recommended), the list of minerals contributing to the temperature estimation is further narrowed down by eliminating minerals with saturation indices exceeding RMED × 1.2 (an arbitrary value > 1 tested to yield satisfactory results). This is done in an iterative manner during which RMED is continuously re-evaluated (Figure 3-1). The temperature at which the final RMED value is minimum is then inferred as the reservoir temperature. The temperatures at which other statistical parameters are minimum (mean, standard deviation, and mean-root-square error) are also computed to provide information on the quality of the clustering (e.g., Figure 1-1). In the case of perfect clustering, all these statistical parameters become zero at the same temperature. However, only the median is used for the final temperature determination, because this non-parametric value ensures that large saturation indices of minerals falling significantly off-cluster do not bias the temperature estimation.

Mineral saturation indices are a direct expression of reaction thermodynamic affinity (Gibbs free energy of reaction), and therefore are extensive variables that are function of the mineral formula. The temperature at which log(Q/K)=0 (equilibrium point) for a given mineral is not function of the mineral formula, but the log(Q/K) values away from this equilibrium point (more precisely, the slopes of the log(Q/K) values with temperature around the equilibrium point, e.g. Figure 1-1, right) are function of the mineral formula. For example, defining a clay or a zeolite mineral on the basis of a different total number of silica or oxygen atoms (as is often the case) yields different log(Q/K)≠0 values, which in some cases can affect the mineral selection and minimization procedure described above. For this reason GeoT implements two optional log(Q/K) scaling approaches. The first one consists of dividing log(Q/K) values by the molecular weight of the mineral. The second (preferred) method is applied only to silicate minerals, and consists of dividing log(Q/K) values by the number of silicon atoms in the mineral formula. These schemes are similar in nature to the scaling approach implemented by Wolery (1979) and Reed (1982, 1998), which consists of dividing log(Q/K) values by the sum of absolute values of the stoichiometric coefficients of species in the reaction expressing mineral dissolution. The advantage of our approach is that the scaling depends only on mineral unit formula and not on the type of species used to describe a mineral (e.g., as when calcite is expressed as a function of Ca^{+2} and CO_3^{-2} versus H^+, HCO_3^-, and Ca^{+2}).

Figure 3—1 Flowchart of algorithm implemented to estimate reservoir temperatures



Saturation indices are optionally scaled ($\log(Q/K)_s$). RMED is the median of absolute values of saturation indices.

3.3 Optimization and temperature-related outputs

If unknown, input parameters necessary to reconstruct the deep fluid composition can be estimated by adjusting these parameters to minimize the cluster of mineral saturation indices near zero. This approach was shown to work well to "un-dilute" and re-carbonate geothermal waters (Reed and Spycher, 1984; Pang and Reed, 1998) and oil field brines (Palandri and Reed, 2001) affected by mixing and degassing. Here, because the calculations to reconstruct the deep fluid, and the geothermometry computations, are performed by one stand-alone program (Figure 1-1), optimization of the clustering can be carried out numerically using external software (e.g., PEST, Doherty, 1998; iTOUGH2, Finsterle and Zhang, 2010). This allows a larger number of parameters to be estimated than manually by trial-and-error, and can be accomplished for several water compositions simultaneously if these waters are all believed to originate from one common geothermal reservoir. In principle, any input parameter could be estimated by numerical optimization, however the optimization may not be successful if too many input parameters were to be estimated simultaneously.

The program computes various statistical parameters that can be used to formulate objective functions for numerical optimization. Main output parameters include the median (RMED), mean (MEAN), standard deviation (SDEV) and root mean-square error (RMSE) of saturation indices and the temperatures at the minimum value of these statistical parameters (T_{RMED}, T_{SDEV}, T_{MEAN}, T_{RMSE}, respectively) (e.g., Figure 7.1-1b, Table 7.1-2). Several other clustering measures are computed, including the spread of temperatures (DT) given by the points at which log(Q/K)=0 for each individual mineral, and the average and standard deviation of these temperatures (T_{DT} and σ_{DT}, respectively) (e.g., Table 7.1-2). For a perfectly clustered system, T_{RMED}, T_{SDEV}, T_{MEAN}, T_{RMSE} and T_{DT} should all be identical, and DT and σ_{DT} should both equal zero. Therefore, when processing each individual water analysis, these outputs can be used directly for numerical optimization, by simultaneously: 1) taking T_{RMED} as the estimated temperature, 2) minimizing DT or σ_{DT}, and 3) minimizing the difference between T_{RMED} and the average of T_{SDEV}, T_{MEAN}, T_{RMSE}. When processing more than one water analysis, the mean and standard deviation of T_{RMED} and DT values computed for all the different water compositions are also output to provide additional parameters for use in a global optimization.

4 General Description of Inputs and Outputs

4.1 Input Files

GeoT requires only one main input file, which is assigned a fixed name (*geot.inp*; e.g., Tables 7.1-1, 7.2-1). This name cannot be changed by the user. This file mainly includes the type and number of aqueous component species, minerals, and gases considered in the simulation. It also includes the compositions of waters to be processed. This file has a "free" format, with inputs described in Section 5.1.

In addition to the *geot.inp* file, the program requires a thermodynamic database file with a file name that is specified in the *geot.inp* file. This file contains reaction stoichiometries, dissociation constants (log(K)), and regression coefficients of log(K) as a function of temperature. This is also a "free"-format file. Its inputs are described in Section 5.2 and shown in Table 5.2-1.

4.2 Output Files

Three output files are generated by GeoT. Each ouput file is assigned a fixed name. These names cannot be changed by the user:

runlog.out – Log of all inputs and of the progress of the calculations, including record of geochemical speciation convergence. It also lists all run-related messages, including error messages.

speciate.out – Chemical speciation data. This file contains results of geochemical speciation calculations for each input water composition, including mineral saturation indices. It also lists these data for waters and temperatures at which chemical convergence failed. Depending of the value of flag IPRT-SPC in file *geot.inp*, geochemical speciation results are output only at the initial speciation temperature, at all scanned temperatures, or at specific temperature increments.

geot.out – Geothermometry results and tabulation of mineral saturation indices. If the flag GEOT is set to "yes" or "y" in file *geot.inp*, a record of geothermometry computations are output in this file. These include estimated temperatures from the statistical analyses of computed mineral saturation indices (see Section 3.2), temperatures from classical geothermometers (using reconstructed water analyses to account for gas loss and/or dilution), as well as an ordered list of mineral saturation indices and their statistical parameters as a function of temperature (e.g., Table 7.1-2), which can be used for plotting.

4.3 Convergence parameters

The maximum number of iterations allowed for Netwton-Raphson iterations in GeoT is fixed at 300 iterations. Non-convergence should therefore be assumed for program runs that display 300 iterations.

The convergence citeria for Netwton-Raphson iterations in GeoT is also fixed, at a value of 10^{-6}. This value represents the *relative* change in concentrations from one iteration to the next, and has been tested to provide a good balance between computing speed and accuracy.

4.4 Suppression of screen inputs and outputs

Upon execution, GeoT sends various informations to the standard screen output and prompts the user to press a key to continue. To run the program in "batch" mode, without screen inputs or outputs, the string "*BATCH*" (no quotes needed) needs to appear anywhere in the TITLE record (see Section 5.1). This is needed, for example, when running GeoT with parameter estimation software for numerical optimization.

5 Formats and Contents of Input Files

5.1 Main input file (*geot.inp*)

All variables in this file are input in free format. Input character variables, if including blanks, must be enclosed in quotes.

The names of all aqueous species, gases, and minerals input in this file are internally converted to lower case characters. The electronic charge in the names of cations and anions are also internally converted to display the charge sign followed by the number of charges (for example, 'CO3--' is converted to 'co3-2' and 'Al+++' is converted to 'al+3'. This allows for input flexibility and maintains internal consistency. Examples of input files are given in Tables 7.1-1 and 7.2-1.

One or more heading (comment) line can precede each record described below (see inputs for the sample problems). A comment line must begin with the character "#" followed by one blank (without quotes). Any blank record is also skipped on input. These "skip" records can be inserted anywhere in the

file, except within input blocks that end with the '*' string. These "skip" records can be used for data source references, or for documenting inputs.

1st Entry (single record): Title

Variable: TITLE

Format: A (free format, first 80 characters will be retained)

TITLE: title and comments in one line. If this record contains the string *BATCH*, all screen prompts will be suppressed, such that GeoT can be run in batch mode from another program (as needed for example, for numerical optimization)

2nd Entry (single record): Thermodynamic database file name

Variable: FILE_NAME

Format: A (free format, maximum 20 characters)

FILE_NAME: name of input thermodynamic database file (maximum 20 characters)

3rd Entry (block of records): Primary aqueous species (one species per record; list must end with '*')

Variable: NAPRI

Format: A (free format, one record per primary species)

NAPRI: name of the primary species (enclosed in quotes if including blanks, truncated after 20 characters). It must match exactly the names in the thermodynamic database file, except for upper or lower case and charge notation (e.g., Al+++, Al+3, al+++, or al+3 are all assumed the same).

A record starting with '*' is needed to indicate the end of the list of the primary species.

4th Entry (block of records): Minerals (one mineral per record; list must end with '*')

Variable: NAMIN

Format: A (free format)

NAMIN: name of the mineral, (in quotes if including blanks, truncated after 20 characters). It must be consistent with the names in the thermodynamic database, except for upper or lower case.

If no minerals are given, all possible minerals from the database will be considered in the temperature estimations.

Other optional entries are as follow (either or both options, in the order shown):

– If the first mineral entry is "include_minerals": all minerals from the database will be considered but the minerals listed in subsequent records will always be included in the temperature estimations, regardless if they cluster or not.

– If the first mineral entry is "skip_minerals": all minerals from the database will be considered but the minerals listed in subsequent records will be excluded in the temperature estimations.

A record starting with '*' is needed to indicate the end of the list of minerals, even if no minerals are listed. If using an “include_minerals” list followed by a “skip_minerals” list, both lists must end with a '*' record.

5th Entry (block of records): Gases (one gas per record; the list must start with H_2O gas and must end with ‘*’)

Variable: NAGAS CONCG

Format: A F (free format)

NAGAS: name of the gas (in quotes in including blanks, truncated after 20 characters). The name must match the gas names in the thermodynamic database, except for upper or lower case. H_2O gas must be included, and must come first in the list.

CONC

– For H_2O gas (first record in list): mole fration of H_2O in wet gas. This value can be estimated using the ideal gas law and the often reported measurement of liters of gas per kilogram condensate.

– For other gases (must be listed after H_2O): dry gas compositions in mole % (which is also equal to volume %)

If no gases are listed, no gases will be included in the computations.

A record starting with '*' is needed to indicate the end of the list of gases, even if no gases are listed.

6th Entry (single record): Print flags

Variable: IPRT-SPC TINCP

Format: F F(free format)

IPRT-SPC: 0 full speciation results are output (in file *speciate.out*) only at the initial temperature (and not after addition of gases)

1 full speciation results are output (in file *speciate.out*) at the initial temperature for both the no-gas and added-gas cases

2 full speciation results are output (in file *speciate.out*) at temperature intervals equal to TINCP

TINCP: temperature increment at which to output tabulated mineral saturation indices (in file *geot.out*). This parameter must be greater or equal to TINC defined below. This increment is used only for output, as opposed to TINC (below), which is used for calculations. TINCP is used to reduce the size of output when TINC is small.

7th Entry (single record): Geothermometry flags

Variable:	GEOT	Tstart	Tend	TINC	MIN_ELIM	ISCALE
Format:	A	F	F	F	I	I (free format)

GEOT: flag set to 'yes' or 'y' to perform geothermometry computations and tabulate mineral saturation indices as a function of temperature. Set to 'no' or 'n' to skip geothermometry computations.

Tstart and Tend: starting and ending temperature for geothermometry calculations (typically 100 and 300°C, respectively; also depending on the temperature range of input thermodynamic data; these parameters correspond to T_{min} and T_{max} on Figure 3-1). This temperature range will be scanned in increments of TINC, and mineral saturation indices will be computed at all temperature increments for geothermometry computations.

TINC: temperature increment at which to compute saturation indices (suggested 2 or 4°C; this parameter corresponds to ΔT on Figure 3-1). This increment will be used for geothermometry computations.

MIN_ELIM: if >3, the list of minerals from which to infer temperature will be narrowed to the first min_elim number of minerals that cluster the best (suggested 6 to 10) (this parameter corresponds to N_{best} on Figure 3-1)

ISCALE: 0 no scaling of saturation indices

1 scale saturation indices of silicates to the number of silica in formula (suggested)

2 scale saturation indices of all minerals by their molecular weight divided by 100

8th Entry (one or more blocks of records): Water compositions (one block per water)

1st Sub-entry (single record) : Water-specific parameters

Variable:	ID	TC	KEEPIC	STWF	CFACT	PMIX(n=1 to number of end-members)
Format:	A	F	I	F	F	nF (free format)

ID: 20-character water ID (in quotes if it includes blanks)

TC: initial speciation temperature in (C)

KEEPIC: currently unused

STWF: steam (total gases) weight fraction in total discharge. This parameter is used to add gases back into solution in the correct proportions (if zero, no gas is added).

CFACT: concentration/dilution factor (this parameter multiplies input concentrations)

1 The input water composition is not changed

>1 The input water composition is concentrated by CFACT (to correct for dilution)

<1 The input water composition is diluted by CFACT (to correct for evaporative concentration)

PMIX: (optional) mixing proportions for each mixing endmember (0 or blank = none, 2 = 2:1 mixing etc.) One PMIX value must be entered per mixing water composition entered at bottom of file. This option is enabled if MIXFLAG (10th entry) is set to 'yes'or 'y'.

Next sub-entries (block of records): water composition (one species per record; end list with '*')

Variable:	NAME_S	ICON	TRIAL_C	INPUT_C	NAME_EQ	LOGQK
Format:	A	I	F	F	A	F (free format)

NAME_S: name of primary species (at minimum H^+ and H_2O), in any order

ICON: flag to specify the meaning of each input concentration

1 Input concentration is total moles for solutes, and kilograms for water (generally 1kg)

2 Total concentration will be calculated to yield a saturation index value of LOGQK for specified mineral NAME_EQ, at the initialization temperature TC.

3 Input concentration is activity of the actual species. For pH, use ICON=3 and input 10^{-pH}. The total concentration of the species will be computed from its input activity, at the initialization temperature TC.

4 The input total concentration will be adjusted for charge balance (at all temperatures). If the species charge sign is the same as the charge imbalance, the computations will not converge, in which case pick a species with an opposite charge (an error message to this effect will appear).

5 Same as 2, but the equilibrium constrain with the specified mineral is applied only at temperatures from Tstart to Tend. Use this option in case options 2 or 6 yield convergence problems at the (generally low) initialization temperature TC.

6 Same as 2, but the equilibrium constrain with the specified mineral will apply at all temperatures

TRIAL_C: initial trial value of speciated (true) concentration. The value of TRIAL_C does not affect speciation results, but it affects convergence speed (and can result in non-convergence). It cannot be negative, in which case it is reset to 1.E-10. If set greater than INPUT_C, it is automatically reset to INPUT_C/10. Generally use the same value as the input concentration INPUT_C, or 10x smaller.

INPUT_C: moles of solute or kilograms of water, unless specified differenty by ICON above. This is the input water composition, from which speciation and geothermometry will be computed. Note that if the composition of the deep fluid is reconstructed (from entered gas, dilution/concentration, or mixing data), these concentrations will be corrected for the effect of gas loss, dilution/concentration, or mixing. Also note that classical geothermometers are applied to the reconstructed water (not to these input concentrations).

NAME_EQ (optional): name of mineral used to fix the concentration of that species (enabled when ICON = 2, 5 or 6)

LOGQK (optional): desired saturation index of the constraining mineral, generally 0 for equilibrium (enabled when ICON = 2, 5, or 6)

A record starting with '*' is needed to indicate the end of the list of species.

9th Entry (single record): trailer for list of waters (this record is needed after the last water block)

Variable: LABEL

Format: A (free format)

LABEL: must contain string ‘end_waters’

10th Entry (single record): Mixing end-member option

Variable: MIXFLAG

Format: A (free format)

LABEL: ‘yes’or ‘y’to enable de-mixing of specific water end-member compositions. ‘no’ or ‘n’ to skip this option, in which case this is the last record in the file.

11th Entry (one or more blocks of records, optional): Mixing endmember(s) compositions(s) (one block per water)

1st Sub-entry (single record) : endmember parameters

Variable: IDmix TCmix

Format: A F

IDmix: 20-character end-member ID (in quotes if it includes blanks)

TCmix: initial speciation temperature (in °C). If TC is zero, the speciation of this endmember water will skipped, and only the primary species of interest should be listed. For example, if de-mixing an NaCl component, TC is set to 0 and only records for species Na and Cl need to be entered below.

Next sub-entry (one block of records) : endmember water composition (one species per record; list must end with ‘*’)

Variable:	NAME_S	ICON	TRIAL_C	INPUT_C	NAME_EQ	LOGQK	
Format:	A	I	F	F	A	F	(free format)

Parameter definitions are the same as for the input water composition blocks (see 8th entry above). If TCmix is zero, all components do not need to be entered, and the entered concentrations will not be speciated (and only NAME_S and INPUT_C matter).

Concentrations entered for mixing endmember waters will be "un-mixed" from the original input water compositions, in proportions PMIX defined for each input water composition (see 8th entry). This option is still being tested. If the concentration of an endmember constituent is larger than its concentrations in the original input water (after adjustment by PMIX), un-mixing will result in negative concentrations and convergence will fail.

A record starting with '*' is needed to indicate the end of the list of species.

12th Entry (single record): trailer for list of endmember waters (this record is needed after the last endmember water block)

Variable: LABEL

Format: A (free format)

LABEL: must contain string ‘end_mix’

5.2 Thermodynamic Database

Aqueous species, minerals, and gases read in file *geot.inp* must correspond to names found in the thermodynamic database file. The name of the database file is specified in file *geot.inp*. The format of the database file is free, and values for all input data (even if zero) must be supplied, unless specifically indicated otherwise. If any aqueous species, mineral, or gas is not in the supplied database, or one desires to use different thermodynamic data, users must add these data to the database.

Because multicomponent geothermometry is based on thermodynamic equilibrium computations, the method is sensitive to input thermodynamic data. The GeoT example problems (Section 7) were run with thermodynamic data from the compilation by Reed and Palandri (2006) (*soltherm.h06*). This database was selected because it was developed primarily for high temperature applications (to 350°C along the saturation pressure of water) and was found to provide satisfactory results. This database relies on Gibbs free energy data primarily from Holland and Powell (1998) for minerals, and from SUPCRT92 (Johnson et al., 1992) for aqueous species. Other databases may also be used, as long as they conform to the formats described below. Note that these formats are the same as those required for thermodynamic data input into TOUGHREACT V2 (Xu et al., 2011).

Spelling convention for reactants/products names

The names of all reactants and products must be input within quotes. On input, these strings are all converted to lower case characters. In addition, any multiple electronic charge incorporated into the names of cations and anions are converted to one charge sign followed by the number of charges. For example, ‘CO3--’ is converted to ‘co3-2’ and ‘Al+++’ is converted to ‘al+3’. All names must be no more than 20 characters long. Longer names will be truncated. The use of a consistent spelling in the database is recommended, although the internal conversion to lower case characters and unique style for charge allow for input flexibility.

The following aqueous and gas species require specific spelling for proper internal handling:

water	‘H2O’ or ‘h2o’
hydrogen ion	‘H+’ or ‘h+’

End-of-header record (first record):

Variable: 'DUMMY'

Format: A

DUMMY: a label used to indicate the start of the database. This label must start with the string '!end-of-header', without quotes. All inputs prior to this record are skipped. All records after this record must follow the formatting and record order described below.

Temperature record:

Variable: 'DUMMY', NTEMP, (TEMPC(i), i=1,NTEMP)

Format: A, I, NTEMP(F)

DUMMY: a label (in quotes) used to describe the data for this record.

NTEMP : the number of TEMPC values to read.

TEMPC : temperatures (ºC) at which the log(K) data are listed in this file, at a given reference pressure P^0 (P^0=1 bar at T<100°C, and the saturation pressure of pure water at T≥100°C). TEMPC values must be listed in order of increasing temperature. These values are used to constrain log(K) extrapolation within this temperature range. Log(K)'s are not extrapolated outside this temperature range. For example, if the maximum TEMPC is 150ºC but the computed system temperature is 250ºC, log(K)'s will be extrapolated only to 150ºC (i.e. the geochemical speciation will be computed at 150ºC, not 250ºC). *Therefore, users must make sure that simulation temperatures are within the range of thermodynamic data temperatures.*

Primary species records:

Primary-1.

Variable: 'NAME', REJ, Z, MWT

Format: A, 3F (one record per primary species)

NAME : name or chemical formula of aqueous primary species, in quotes (truncated after 20 characters).

REJ : Ion effective or hydrated radius used to compute the Debye-Hückel a0 parameter (see Appendix H for details). For neutral species other than typical dissolved gases, if REJ > 100, the value of REJ is used to compute a salting-out coefficient K_i equal to REJ – 100, i.e., salting-out coefficients for neutral species can be entered as values of REJ equal to 100+K_i where K_i x ionic strength = log10(activity coefficient).

Z : the ion electric charge

MWT : Molecular weight of the aqueous species (g/mol).

This record is repeated as many times as the number of primary species.

Trailer record after primary species records:

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes. This record indicates the end of the list of primary species, and must appear directly after the last primary species.

"Skip" records:

Starting from this point, any record beginning with either # (without quotes), or * followed by one blank (without quotes), or any blank record will be skipped on input. These "skip" records can be inserted anywhere in the database (after the first trailer record closing the list of primary species), as long as they are not inserted within records pertaining to the same reaction (i.e., these records can be inserted only between sets of records that pertain to one reaction). These "skip" records can be used for comments, data source references, or simply to clear the appearance of the database.

Secondary (derived) species records:

The data for each secondary species are input as a set of 3 records, as follows:

Sec-1.

Variable: 'NAME', Xmwt, REJ, Z, NCPS, (STQS(i), 'NAM(i)', i=1,NCPS)

Format: A, 3F, I, NCPS(F, A)

NAME : chemical formula of secondary species, in quotes (truncated after 20 characters).

Xmwt : molecular weight of the aqueous species (g/mol).

REJ : ion effective or hydrated radius (Angstrom) used to compute the Debye-Hückel a0 parameter (see Appendix H for details). For neutral species other than typical dissolved gases (see Section H.3 of Appendix H), if REJ > 100, the value of REJ is used to compute a salting-out coefficient K_i equal to REJ – 100, i.e., salting-out coefficients for neutral species can be entered as values of REJ equal to 100+K_i where K_i x ionic strength = log10(activity coefficient).

Z : ion electric charge.

NCPS : number of primary species defining the secondary species.

STQS: stoichiometric coefficients of component (primary) species NAM included in the dissociation reaction of the derived species (negative and positive values for reactants and products, respectively). The derived species is always assumed to have a stoichiometric coefficient of -1.0, which is not included in STQS.

NAM: name of the reactant or product, in quotes (truncated after 20 characters; must match one of the primary species).

Sec-2.

Variable: 'NAME', (AKLOG(i), i=1,ntemp)

Format: A, ntemp(F)

NAME : name or chemical formula of secondary species, as in Sec-1.

AKLOG : contains the equilibrium constants (log(K) in base 10) for the given reaction at each discrete temperature listed in record Temp-1 above (at a reference pressure P^0). These data are generally skipped on input if log(K) regression coefficients as a function of temperature are entered on record Sec-3 (the discrete log(K) values should, however, always be included in the file to provide for easy reference to the data). If no regression coefficients are given on record Sec-3, AKLOG values are used to internally regress log(K) as a function of temperature on input. Note that AKLOG values equal to 500 are interpreted as "no data".

Sec-3.

Variable: 'NAME', (AKCOES(i), i=1,5), (AKCOP(i), i=1,5)

Format: A, 5(E), 5(E)

NAME : name or chemical formula of secondary species, as in Sec-1.

AKCOES : contains regression coefficients a, b, c, d, and e to calculate $\log_{10}(K)$ as a function of temperature (at a reference pressure P^0) with $\log_{10}(K)_{T,P0} = a*\ln(T_k) + b + c*T_k + d/T_k + e/T_k^2$, where T_k is absolute temperature (K), and *ln* stands for natural logarithm. Values must be entered for all coefficients. If all coefficient values are omitted, the coefficients will be internally computed from AKLOG values input on record Sec-2.

Records Sec-1, Sec-2, and Sec-3 are repeated as sets of triplets, as many times as the number of secondary species. Each set can be spaced by as many "skip" records as desired.

Trailer record after secondary species records:

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes. This record indicates the end of the list of secondary species, and must appear anywhere between the last secondary species and first mineral.

Mineral Records:

The data for each mineral are input as a set of 3 records, as follows:

Mineral-1.

Variable: 'NAME', MOLWT, VMIN, NCPM, (STQM(i), 'NAM(i)', i=1,NCPM)

Format: A, 2F, I, NCPM(F, A)

NAME : name or chemical formula of a mineral, in quotes (truncated after 20 characters).

MOLWT : molecular weight (g/mol).

VMIN : molar volume (cm3/mole).

NCPM : the number of component species defining the mineral.

STQM : contains the stoichiometric coefficient of primary species NAM in the dissociation (hydrolysis) reaction of the mineral (negative and positive values for reactants and products, respectively). The mineral species is always assumed to have a stoichiometric coefficient of -1.0, which is not included in STQM.

NAM: name of the reactant or product, in quotes (truncated after 20 characters; must match one of the primary species).

Mineral-2.

Variable: 'NAME', (AKLOG(i), i=1,ntemp)

Format: A, ntemp(F)

NAME : name or chemical formula of the mineral, as in Mineral-1.

AKLOG : contains the equilibrium constants (log(K) in base 10) for the reaction at various temperatures. See record Sec-2 for formatting and other details.

Mineral-3.

Variable: 'NAME', (AKCOEM(i), i=1,5), (AKCOP(i), i=1,5)

Format: A, 5(E)

NAME : name or chemical formula of the mineral, as in Mineral-1.

AKCOEM : contains regression coefficients a, b, c, d, and e to calculate $\log_{10}(K)$ as a function of temperature. See record Sec-3 for formatting and details.

AKCOP : (optional) contains regression coefficients a, b, c, d, and e to calculate ΔV for the reaction (in cm^3/mol) as a function of temperature. See record Sec-3 for formatting and details.

Records Mineral-1, Mineral-2, and Mineral-3 are repeated as sets of triplets, as many times as the number of secondary species. Each set can be spaced by as many "skip" records as desired.

Trailer record after Mineral records:

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes. This record indicates the end of the list of minerals, and must appear anywhere between the last mineral and first gas.

Gas records:

The data for each gas species are input as a set of 3 records, as follows:

Gas-1.

Variable: 'NAME', DMOLWT, DMDIAM, NCPG, (STQG(i), 'NAM(i)', i=1,NCPG)

Format: A, 2F, I, NCPG(F, A)

NAME : name or chemical formula of a gas species, in quotes (truncated after 20 characters).

DMOLWT : molecular weight (g/mol)

DMDIAM: molecular diameter (m) (not used with GeoT)

NCPG : the number of primary species defining the gas.

STQG : contains the stoichiometric coefficient of component species NAM in the dissociation reaction of the gas (negative and positive values for reactants and products, respectively). The gas is always assumed to have a stoichiometric coefficient of -1.0, which is not included in STQG.

NAM: name of the reactant or product, in quotes (truncated after 20 characters; must match one of the primary species).

Gas-2.

Variable: 'NAME', (AKLOG(i), i=1,ntemp)

Format: A, ntemp(F)

NAME : name or chemical formula of the gas, as in Gas-1.

AKLOG : contains the equilibrium constants (log(K) in base 10) for the reaction at various temperatures. See record Sec-2 for formatting and other details.

Gas-3.

Variable: 'NAME', (AKCOEG(i), i=1,5), (AKCOPG(i), i=1,5)

Format: A, 5(E)

NAME : name or chemical formula of the gas, as in Gas-1.

AKCOEG : contains regression coefficients a, b, c, d, and e to calculate $\log_{10}(K)$ as a function of temperature. See record Sec-3 for formatting and details.

Records Gas-1, Gas-2, and Gas-3 are repeated as sets of triplets, as many times as the number of secondary species. Each set can be spaced by as many "skip" records as desired.

Trailer record 1 after Gas records:

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes. This record indicates the end of the list of gases, and must appear anywhere between the last gas and first surface complex.

Final trailer record (2nd trailer record):

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes. This record indicates the end of the list of secondary species, and must appear anywhere after the last surface complex.

Table 5.2—1 Example thermodynamic database input file.

```
Any text here, for any number of records

!end-of-header     Do not remove this record!
'Temperature points:' 8 0.01 25.0 60.0 100.0 150.0 200.0 250.0 300.0
'H2O'                              0.00  0.00     18.015
'Ca++'                             2.87  2.00     40.078
'Cl-'                              1.81 -1.00     35.453
'Fe++'                             2.62  2.00     55.845
'H+'                               3.08  1.00      1.008
'HCO3-'                            2.10 -1.00     61.017
'K+'                               2.27  1.00     39.098
'Na+'                              1.91  1.00     22.990
'Hfo_sOH'                          0.00  0.00      0.000
'null'

####################
# Aqueous species #
####################
'CO2(aq)'       44.010  0.00  0.00    3  -1.00000 'H2O'  1.00000 'H+'  1.00000 'HCO3-'
'CO2(aq)' -6.5804   -6.3447   -6.2684   -6.3882   -6.7235   -7.1969   -7.7868   -8.5280
'CO2(aq)' 0.10476478E+03 -0.67138541E+03 -0.10862163E+00 0.38868294E+05 -0.26528340E+07
#  Data source:     EQ3/6 database data0.ymp.R5 YM Project SN0612T0502404.14

'NaSO4-'        119.053  1.81 -1.00    2   1.00000 'Na+'  1.00000 'SO4--'
'NaSO4-'  -0.6765   -0.7000   -0.8416   -1.0629   -1.3893   -1.7724   -2.2416   -2.8730
'NaSO4-' 0.15443167E+03 -0.98620007E+03 -0.14872193E+00 0.56350439E+05 -0.34707590E+07
#  Data source:     EQ3/6 database data0.ymp.R5 YM Project SN0612T0502404.14

'null'

####################
#   Minerals      #
####################

'Calcite'  100.087    36.934    3  -1.00000 'H+'  1.00000 'Ca++'  1.00000 'HCO3-'
'Calcite'  2.2257    1.8487    1.3330    0.7743    0.0999   -0.5838   -1.3262   -2.2154
'Calcite' 0.14237876E+03 -0.90313945E+03 -0.14436024E+00 0.50619704E+05 -0.29300495E+07
#  Data source:     EQ3/6 database data0.ymp.R5 YM Project SN0612T0502404.14

'Carnallite' 277.853 172.580 4 1.00000 'K+' 1.00000 'Mg++' 3.00000 'Cl-'  6.00000 'H2O'
'Carnallite' 500.0000 4.2721 500.0000  500.0000  500.0000  500.0000  500.0000  500.0000
'Carnallite' 0.00000000E+00 0.42721000E+01 0.00000000E+00 0.00000000E+00 0.00000000E+00
#  Data source:     EQ3/6 database data0.ymp.R5 YM Project SN0612T0502404.14



'null'
####################
#   Gases         #
####################

'CO2(g)' 44.010 2.5e-10 3 -1.00000 'H2O' 1.00000 'H+' 1.00000 'HCO3-'
'CO2(g)'  -7.7695 -7.8257 -8.0437 -8.3390 -8.7356 -9.2136 -9.7552 -10.3962
'CO2(g)' 9.833583157 -59.02305875 -0.026997768 950.3210943 0.0
#  Data source:     Regressed from Spycher and Pruess (2009)
#  Note, these values are for the CO2(g)=>CO2(aq) reaction

'null'

'null'
```

6 Error Messages

All execution stops built into GeoT are accompanied by a message indicating why the execution was aborted. These messages are written to file *runlog.out* and generally also to the screen, and are mostly self explanatory. Other error messages do not lead to a program interruption. Two main convergence-related error messages are briefly discussed below.

Warning!! Charge balancing using ____ is not working. Try balancing with an opposite-charged species

Execution stop: yes. This error occurs when the charge-balancing ion (listed with ICON=4 in *geot.inp*) does not have the correct sign of charge to allow charge balancing. In this case, use a species with an opposite charge.

***** !! Warning !! Convergence problem with water ___ at temp (C)= ____*
Program execution was not aborted. Check results!

Execution stop: no. Check the *speciate.out* file for clues on why convergence was not reached (e.g., addition of an unrealistic gas composition, unrealistic mineral equilibrium constraints, etc.) You may need to adjust trial concentrations (TRIAL_C) or use smaller temperature increments in file *geot.inp*. Mineral equilibrium constrains using ICON = 2, 5, or 6 can also yield convergence problems. If using ICON=6 (equilibrium constrain at all temperatures), try to switch to ICON=5 so the constrain is applied only at elevated temperature (for example, constraining the concentration of Al^{+3} by equilibration with an aluminum silicate may create problems at low temperature (during the initial speciation) but not at higher temperatures.

7 Sample Problems

We present below two examples of applications of GeoT. The studies of Reed and Spycher (1984), Pang and Reed (1998), and Palandri and Reed (2001) have documented the merits of multicomponent geothermometry and its application to a wide range of natural thermal waters. Users are recommended to familiarize themselves with these earlier studies prior to work with GeoT.

7.1 Problem 1

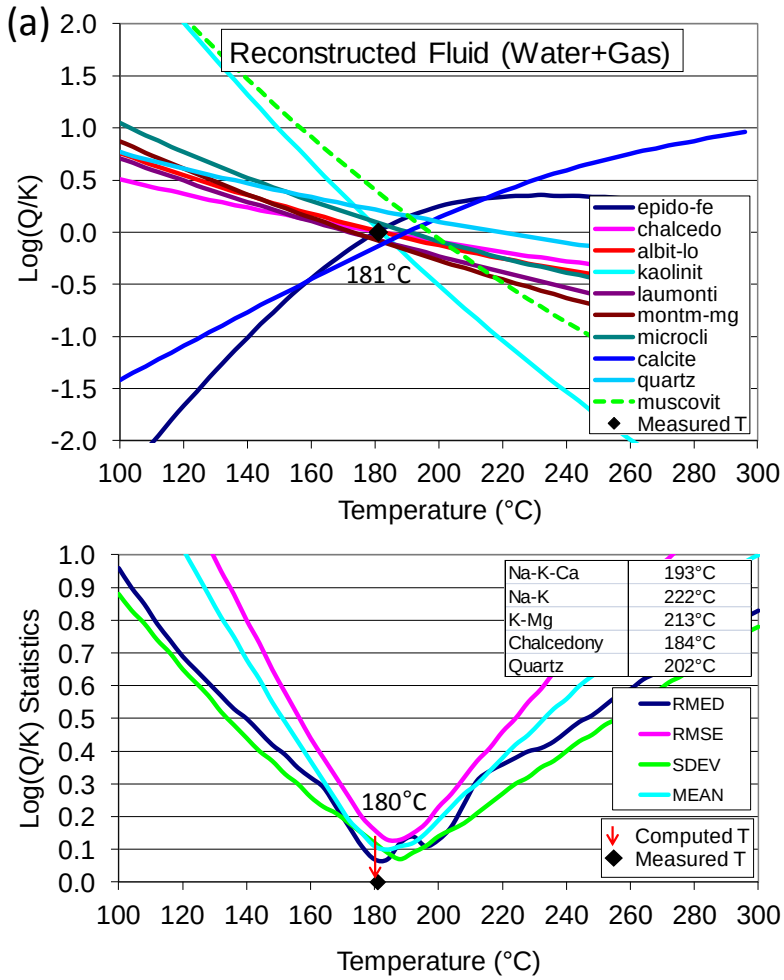
This first problem is adapted from Reed and Spycher (1984). The deep temperature of a geothermal fluid is computed using water and gas analyses from Arnorsson et al. (1983) for a geothermal well in Iceland. In the present case, fifteen minerals, initially, were specified as potential reservoir minerals, and the deep fluid temperature was computed from the ten (MIN_ELIM=10) "best" clustering minerals (those shown on Figure 7.1-1, automatically selected following the procedure shown in Figure 3-1; the other minerals considered were goethite, illite, chlorite, anhydrite and fluorite). This yielded a temperature (at minimum RMED) of T_{RMED} = 172°C with a range of temperatures averaging ($T_{DT} \pm \sigma_{DT}$) 180 ± 17°C (not shown). The problem was then refined by optimizing the input water mole fraction in the gas phase, using the ten selected minerals. This yielded T_{RMED} = 180°C and a temperature range averaging ($T_{DT} \pm \sigma_{DT}$) 188 ± 14°C (Figure 7.1-1, Table 7.1.-2). In absence of measurements, the steam weight fraction in the total (water+steam) discharge was estimated (STWF~0.04) using the enthalpy of pure water at the measured downhole fluid inflow temperature (181°C) and the enthalpy of pure water and steam at the sampling pressure, assuming adiabatic flashing (Arnorsson et al., 1983). The amount of H_2O gas in the steam was initially calculated (CONCG(1)=0.9992 mole fraction) using the ideal gas law and the reported proportions of gas and condensate (1.06 L gas per kg condensate). This value was then refined by optimization (yielding CONCG(1)~0.9986, the value used for this example).

In this example the temperature is scanned in steps of 2°C (TINC=2), over the temperature range TSTART=100 to TEND=300°C. Full speciation results are output every 2°C in file *speciate.out* (IPRT_SPC=2), and saturation indices are tabulated at every 4°C in file *geot.out* (TINCP=4). The saturation indexes of silicates are scaled by the number of silica in their formula (ISCALE=1). The water is not concentrated nor diluted (CFACT=1).

The results of classical geothermometers for this case vary (Figure 7.1-1b). Chalcedony indicates a temperature consistent with the measured value of 181°C. The Na-K geothermometer shows the largest deviation (about 40°C higher than measured).

The input and output files for this problem are shown on Tables 7.1-1 and 7.1-2, respectively, in a truncated format for space. Explanation of output parameters are shown on Table 7.1-2 in italic fonts.

Figure 7.1—1 Problem 1 – Application to an Icelandic geothermal water



(a) Computed saturation indices, log(Q/K), as a function of temperature, showing clustering near zero close to the measured temperature (181°C). (b) Statistical analyses of saturation indices: median (RMED), mean root square error (RMSE), standard deviation (SDEV) and average (MEAN) of absolute log(Q/K) values. The reservoir temperature is inferred from the temperature at which RMED is minimum. Results of classical geothermometers are also shown for comparison, calculated using the reconstituted deep fluid composition (Na-K-Ca, Fournier and Truesdell, 1973; Na-K, Giggenbach, 1988; chalcedony, Fournier, 1977; quartz, Fournier and Potter, 1982).

Table 7.1—1 Problem 1 – Input file (*geot.inp*)

```
# Title comes first (one record below)
Geothermal Water   Hveragerdi Well 4

# thermodynamic database
tk-slt.h06.dat

# PRIMARY AQUEOUS SPECIES - always end the list with a star (in quotes or not)
H+
H2O
Cl-
 ..... etc.
F-
'*'

# MINERALS - always end the list with a star (in quotes or not), even if no minerals are listed
chalcedo
albit-lo
epido-fe
 ..... etc.
muscovit
'*'

# GASES - always end the list with a star (in quotes or not), even if no gases are listed
# nagas     concg
'H2O GAS'  .99862
'CH4 GAS'  0.331
'CO2 GAS'  93.3
'H2 GAS'   3.09
'H2S GAS'  3.31
'*'

# PRINT FLAGS
#iprt-spc  tincp
    2       4.

# GEOTHERMOMETRY FLAGS
#geot  tstart  tend   tinc   min_elim   iscale
 yes    100.    300.    2.      10        1


# WATER COMPOSITIONS
# ID                tc     keepic        stwf         cfact    pmix(1 to nmix)
Hveragerdi_W4       20.0      1         0.04          1.0

#name  icon  guess(molal)    input(mol)     constr.  sat.
H+       3    1.00E-09       1.514E-09     pH = 8.82  thus H+ = 10^-8.82 with ICON=3
H2O      1    1.00           1.000
Cl-      1    1.00E-04       3.09E-03
SO4--    1    1.00E-06       4.55E-04
 ..... etc.
F-       1    1.00E-06       9.59E-05
Below is an example record for forced mineral equilibria between Tstart=100 and Tend=300C
Al+++    5       1.00E-08          1.00E-08       'albit-lo'  0.0
'*'

end_waters

#OPTIONAL MIXING END-MEMBERS
no
```

Table 7.1—2 Problem 1 – Annotated ouptut file (*geot.out*)

```
Geothermal Water   Hveragerdi Well 4
******************************************************************************
Geothermometry calculations using the flagged minerals below

Water   1     ID: Hveragerdi_W4
----------------------------
Classical geothermometers (C) (for info only, reconstructed water, 0. if no data)
  Quartz (Four&Pott82)  202. (no steam loss)
  Am.Silica (Four77)     77.
  Chalcedony (Four77)   184.
  Na-K-Ca (Four&True73) 193.
  Na-K (Gigg88)         222.  (Four79) 206.
  K-Mg (Gigg88)         213.
  Na-Li (Foui&Mich81)     0.

Estimated equilibrium temperature (C): 180.
```

(T_{RMED}) This is the estimated reservoir temperature

*This is the temperature at the minimum value of RMED (median of absolute value of log(Q/K)'s). RMED and other statistical parameters are computed for the MIN_ELIM number of best clustering minerals (those shown with * or ** below). In this example, MIN_ELIM is set to the same number as the total number of input minerals, therefore all minerals are used in the statistics.*

```
Log(Q/K) minimum RMED:   0.069   RMSE:   0.163   SDEV:   0.124   MEAN:   0.113
```

These are the statistics on the log(Q/K) absolute values at the estimated temperature (at minimum RMED). RMED is median, RMSE is mean root-squared error and MEAN is average (in log(Q/K units, scaled as specified on input).

T(C) cross average	188.40	*Average of temperatures shown by each individual (selected) mineral (T_{DT})*
T(C) at minimum RMSE	186.00	*(T_{RMSE})*
T(C) at minimum SDEV	188.00	*(T_{SDEV})*
T(C) at minimum MEAN	182.00	*(T_{MEAN})*

If the clustering was perfect, all these temperatures would be identical

T range:	174.00 to 222.00	*Range of temperatures (°C) shown by each individual (selected) mineral*
T spread	48.00	*Spread of these temperatures, i.e., 174 – 220 = 48°C (DT)*
T stdev:	14.07	*Standard deviation of these temperatures (σ_{DT} in °C)*

`Trmed-Tstatav = 0.533333E+01` *Estimated temperature at minimum RMED minus the average of temperatures at minimum RMSE, SDEV and MEAN. Perfect clustering would yield 0.*

`RMED/nmin = 0.686038E-02` *Minimum RMED (at estimated temperature) divided by the number of seleted minerals (average log(Q/K)units per mineral)*

Temperature (C) --->	100.00	104.00	108.00	112.00	....etc.	300.00
Gas sat. P(bar) --->	1.2	1.4	1.5	1.7	....etc.	85.2
Iterations	21	5	5	5	....etc.	7
pH	6.53	6.55	6.57	6.59	....etc.	8.13
RMED	0.96	0.90	0.85	0.79	....etc.	0.83
RMSE	1.63	1.54	1.46	1.37	....etc.	1.25
SDEV	0.89	0.84	0.79	0.75	....etc.	0.78
MEAN	1.40	1.32	1.25	1.17	....etc.	1.00

```
Saturation indices:  * (or **) if mineral selected for statistics, ** if sat index is within +-
rmed at selected T
```

*Minerals below are listed in order of increasing log(Q/K) absolute values at the estimated temperature (T_{RMED}). * or ** indicates these were (automatically) selected for statistics (see Figure 3-1). ** for minerals with log(Q/K) values within RMED at the estimated temperature. Log(Q/K units are scaled as specified on input.*

chalcedo	**	0.51	0.48	0.45	0.42	....etc.	-0.49

```
epido-fe            **  -2.41     -2.26     -2.11     -1.97  ....etc.      0.25
albit-lo            **   0.76      0.72      0.67      0.63  ....etc.     -0.59
laumonti            **   0.71      0.67      0.62      0.58  ....etc.     -0.96
kaolinit            **   2.76      2.61      2.46      2.31  ....etc.     -2.82
montm-mg            *    0.87      0.82      0.76      0.71  ....etc.     -1.08
microcli            *    1.05      0.99      0.93      0.88  ....etc.     -0.70
calcite             *   -1.43     -1.36     -1.30     -1.23  ....etc.      0.99
quartz              *    0.77      0.73      0.70      0.67  ....etc.     -0.34
muscovit            *    2.71      2.58      2.45      2.32  ....etc.     -1.81

                     Mole fractions
```

Computed at saturation pressure (see above) assuming non-ideal gases but ideal mixing

```
h2o gas                 0.8508    0.8644    0.8768    0.8881 ....etc.     0.9974
ch4 gas                 0.0000    0.0000    0.0000    0.0000 ....etc.     0.0000
co2 gas                 0.1415    0.1289    0.1173    0.1067 ....etc.     0.0024
h2 gas                  0.0000    0.0000    0.0000    0.0000 ....etc.     0.0002
h2s gas                 0.0076    0.0067    0.0059    0.0052 ....etc.     0.0000

 *******************************************************
 Global optimization data (to use with multiple waters):
```

These can be used for numerical optimization when multiple waters (presumably from the same reservoir) are input into the computations. Here only one water is used, so standard deviations (stdev) are 0. Averages are over all input waters. All temperatures in °C.

```
Average estimated T =   180.000  stdev =   0.000000
Average T other stat=   185.333  stdev =   0.000000
```

Average of temperatures at minimum RMSE,SDEV, and MEAN

```
Average of T range  =   188.400  stdev =   0.000000
```

Average of "T(C) cross average" (T_{DT}) values

```
Average T cross     =    48.000  stdev =   0.000000
```

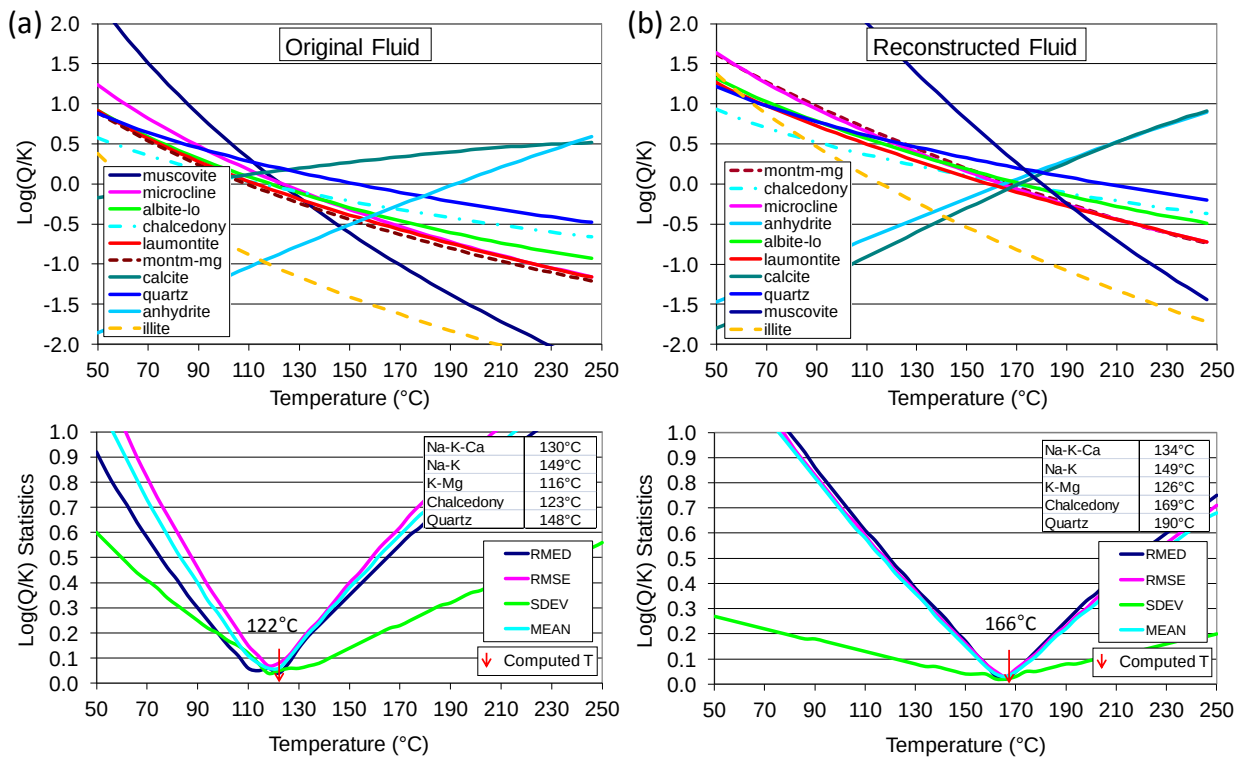
Average of temperature spread values

7.2 Problem 2

This second problem consists of a geothermal water from Klamath Falls, Oregon (Janik et al., 1984) previously used by Pang and Reed (1998) to illustrate the reconstruction of a deep fluid after loss of CO_2 and dilution. These authors corrected the composition of the sampled water by numerically titrating CO_2 into the water until its pH matched the value measured in the field (6.3 at 84°C versus 8.6 in the laboratory at 25°C). They then concentrated the solution (by a factor ~2, determined by trial and error) until a good clustering of mineral saturation indices was obtained. In doing so these authors obtained estimated reservoir temperatures between 160 and 190°C for this fluid. This example is revisited, this time optimizing the problem using GeoT coupled with iTOUGH2. The measured water composition is specified, including the laboratory-measured pH. Ten potential reservoir minerals are given (Figure 7.2-1), and the temperature is determined from the six best-clustering minerals. Under these conditions (un-reconstructed fluid), a temperature (T_{RMED}) of 122°C is computed, with temperatures ($T_{DT} \pm \sigma_{DT}$) averaging 118 ± 6°C, displaying a relatively poor clustering of saturation indices (Figure 7.2-1a). As such, the measured field pH value cannot not be reproduced. The problem is then run again, this time adding a gas phase consisting of 99 vol.% H_2O with pure CO_2, and estimating by numerical optimization the steam weight fraction of the discharge (yielding ~ 0.003) as well as a concentration factor (yielding

~1.9). The proportion of water in the gas phase is somewhat arbitrary (but predominantly water as would be expected in steam from a geothermal well), and the estimated steam weight fraction in this case serves only as a practical parameter (without quantitative relevance to field conditions) to numerically re-carbonate the water. In doing so, a better clustering is obtained yielding a temperature (T_{RMED}) of 166°C, and an average temperature ($T_{DT} \pm \sigma_{DT}$) 167 ± 4°C (Figure 7.2-1b). The reconstructed fluid yields a pH value at 84°C (6.2) that is consistent with the measured value in the field (6.3), and a concentration factor and reservoir temperature in agreement with results optimized by trial-and-error by Pang and Reed (1998). In this case there are no deep temperature measurements to verify the model, and the computations serve only as an example of automated fluid reconstruction with deep temperature prediction. Classical geothermometry yields temperatures within about 32°C from the computed temperature (T_{RMED}), and good agreement with the chalcedony geothermometer.

Figure 7.2—1 Problem 2 – Example fluid reconstruction



(a) Results using the original fluid composition. (b) Results after correcting for dilution and CO_2 loss by numerical optimization. The temperature is determined from the saturation indices of the six best clustering minerals (the top six listed in the legend) (min_elim=6; same as N_{best} on Figure 3-1) out of 10 specified minerals. Results of classical geothermometers are also shown for comparison, calculated using fluid compositions before and after optimization (see caption of Figure 7.1-1 for references on these geothermometers).

Table 7.2—1 Problem 2 – Input file (*geot.inp*)

```
# Title comes first (one record below)
Geothermal Water   Klamath Falls      from Pang & Reed 1998

# thermodynamic database
tk-slt.h06.dat

# PRIMARY AQUEOUS SPECIES - always end the list with a star (in quotes or not)
H+
H2O
Cl-
 ..... etc.
Na+
'*'

# MINERALS - always end the list with a star (in quotes or not), even if no minerals are listed
albit-lo
microcli
muscovit
 ..... etc.
laumonti
'*'

# GASES - always end the list with a star (in quotes or not), even if no gases are listed
'H2O GAS'  0.99
'CO2 GAS'  100.0
'*'

# PRINT FLAGS
#iprt-spc  tincp
    2       4.

# GEOTHERMOMETRY FLAGS
#geot  tstart  tend   tinc   min_elim   iscale
 yes    50.     250.    2.     6        1


# WATER COMPOSITIONS
# ID                tc      keepic        stwf         cfact    pmix(1 to nmix)
KF-original       25.0      0         0.00           1.0

#name  icon  guess(molal)    input(mol)     constr.  sat.
H+       3    1.00E-07       2.512E-9
H2O      1    1.00           1.00
Cl-      1    1.00E-3        1.14e-3
SO4--    1    1.00E-4        4.68e-3
 ..... etc.
Na+      1    1.00E-3        9.80e-3
'*'


# ID                tc      keepic        stwf         cfact    pmix(1 to nmix)
KF-optim          25.0      0         .00268       1.89

#name  icon  guess(molal)    input(mol)     constr.  sat.
H+       3    1.00E-07       2.512E-9
H2O      1    1.00           1.00
Cl-      1    1.00E-3        1.14e-3
SO4--    1    1.00E-4        4.68e-3
 ..... etc.
Na+      1    1.00E-3        9.80e-3
'*'

end_waters

#OPTIONAL MIXING END-MEMBERS
no
```

8 Concluding Remarks

GeoT (Spycher et al., 2011) was developed by automating the multicomponent chemical geothermometry method of Reed and Spycher (1984). As needed, this program can be integrated with parameter estimation software. Without optimization, GeoT is useful for fast geothermometry computations with fluid compositions from single locations, and for independently processing fluids from multiple locations in one single program run. Numerical optimization can considerably extend the power of this software because it allows the estimation of unknown or poorly known parameters that are needed to compute reservoir temperatures. This includes, for example, estimating the proportion and/or chemical composition of gases lost before sampling, or the concentrations of some elements such as Al and Mg which are typically poorly constrained.

It must be made clear that GeoT is not intended to replace classical geothermometry, which remains an important and essential tool in geothermal exploration. Classical geothermometers can yield erroneous temperatures, for example in cases when concentrations of major cations are not controlled primarily by feldspars and Mg phases such as chlorite and illite (assumptions on which most classical geothermometers rely, e.g., Giggenbach, 1998), or when fluids are affected by dilution and gas loss as they ascend to the surface from a deep reservoir. In this case, multicomponent geothermometry can significantly improve on classical geothermometry. This is not to say that multicomponent geothermometry cannot yield erroneous results. In fact, when applied carelessly, this method can also fail, such as when selecting inappropriate minerals or relying on Al and/or Mg concentrations that do not reflect reservoir conditions (e.g., Pang and Reed, 1998). When coupled with numerical optimization, the convergence of the method to an incorrect solution (local minima) can also yield erroneous results. Therefore, the method should never been applied blindly or taken as a new fail-proof solution to the challenging problem of solute chemical geothermometry.

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