SPREADSHEETS FOR GEOTHERMAL WATER AND GAS GEOCHEMISTRY

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ABSTRACT

Two Excel spreadsheets released with this paper support many of the common graphical analyses of water and gas chemistry used to interpret hot spring, fumarole and well samples in geothermal exploration and development. Cross-plots and ternary diagrams are generated from measured concentrations of chemical species using formulas based on equilibrium reactions and empirical relationships. Typical applications include geothermometry, fluid and gas space and time trend characterization, and data quality assessment. The spreadsheets provide charting capability compatible with all versions of Excel from 1997 to 2007.

Liquid_Analysis_v1_Powell-2010-StanfordGW.xls takes tabulated water chemistry data input in ppm weight and stable isotope data in per mil and tabulates geothermometers and quality assurance parameters. Explanations for the calculations are referenced. Charts include the ubiquitous Giggenbach Na-K-Mg geothermometer ternary, three temperature "geoindicator" cross-plots, $\delta^{18}O$-δD, Cl-enthalpy, and four commonly used trace element ternary plots. Brief outlines of applications reference publications that provide more detailed case histories.

Gas_Analysis_v1_Powell-2010-StanfordGW.xls takes gas analyses from steam samples in a variety of commonly reported units, makes an air correction (if needed) and plots four common ternaries, three3 "Y-T" gas geothermometer grids and two gas ratio geothermometer grids, mainly derived from the work of Werner Giggenbach. Typical applications of the graphical analyses provided in this gas spreadsheet are briefly summarized based on an earlier paper.

These spreadsheets are offered as freeware, without warranty of fitness for any purpose under the GNU General Public License 3, subject to users' reference to this paper in initial publications of work based on these spreadsheets.

INTRODUCTION

The genesis of this paper was the interest expressed by many people, particularly the second author, in a review paper that would describe the Excel spreadsheets that the first author developed as an aid to geothermal geochemistry interpretation. The Stanford Workshop on Geothermal Reservoir Engineering seemed an appropriate forum because the spreadsheets themselves could be included with this explanatory paper in the freely available online version of the Workshop Proceedings.

As a cursory outline of geochemistry interpretation tools, this paper uses references to clarify their application. A few texts have been written on the subject of geothermal geochemistry, although only Arnórsson (2000) is still in print. Despite being out-of-print, Nicholson (1993) is still a reasonably current general reference on geothermal geochemistry that can sometimes be found used. Ellis and Mahon (1977) is less current but often cited. Henley et al. (1984) is a useful teaching resource and reference for geothermal geochemistry problems and is available in digital form from the Society of Economic Geologists online bookstore.

Klein (2007) provides a summary and bibliography on established applications and applied research on geothermal geochemistry. Most of the landmark papers by Giggenbach are available in digital form, although some are published in academic journals to which geothermal professionals are unlikely to subscribe. However, the widely cited report by

Giggenbach and Goguel (1989) on sampling and analysis is out-of-print. Tutorial references that are freely available online include Fournier (1989) on cation and silica geothermometry and Powell (2000) on gas geothermometry. We hope this paper inspires others to publish case histories and tutorials that illustrate the integration of geothermal geochemistry with geoscience data in building resource conceptual models directed at geothermal exploration and development.

The two Excel spreadsheets described by this paper provide a way to quickly plot chemical analyses on many commonly used geothermal geochemistry plots. Most of these plots were developed in the 1980s and early 1990s by the late Werner Giggenbach based on his work and the research of many others as indicated, for example, by the reference lists in Arnórsson (2000) and Fournier (1989). The spreadsheets omit some plots that can be easily customized to meet particular needs using the basic graphing tools of Excel, such as plots where one quantity is plotted against another on linear axes. In addition, by removing the protection from the spreadsheet, users can adapt the graphics to create similar plots using other chemical species. Owing to the inventiveness of Giggenbach and the extended slump in geothermal industry activity that only recently ended, the graphics included in these spreadsheets generally remain state-of-the-art for the conceptual interpretation of geothermal geochemistry directed at the exploration of geothermal reservoirs.

These spreadsheets can be used to analyze water and gas chemistry data from both wells and surface manifestations. However, there is no provision for calculating liquid chemistry corrections for steam fraction loss during well discharges; Therefore, these adjustments need to be calculated separately. The analyses tools in the spreadsheets are directed at understanding the natural, near-equilibrium properties of geothermal reservoirs that are relevant to both exploration and development. However, geochemistry graphics directed at understanding changes with respect to time in geothermal reservoirs under production are not included.

Probably the most common errors encountered by users of these spreadsheets are related to confusion over units, often due to poorly annotated source data. Although extensive case history experience specific to geothermal resources is sometimes needed to sort out poor labeling, a basic text on water analysis such as Hem (1970) can often resolve problems with units, or a web search can help with questions like converting mmoles/litre to mg/kg. Nicholson (1993) provides a detailed review of units and conversions in a geothermal context and Henley et al. (1984) also addresses the issue.

Both spreadsheets are in Excel97 format, so as to be compatible with both current versions of Excel and the earliest versions typically in use. Calculations are protected to prevent overwriting of spreadsheet calculations but no password is used to allow their modification if the user chooses. The spreadsheets are offered as freeware, without warranty of fitness for any purpose under the GNU General Public License 3, subject to users' reference to this paper in the initial publications of work based on these spreadsheets.

SAMPLING AND MEASUREMENT

Giggenbach and Goguel (1989) present a detailed discussion of appropriate analytes, sampling techniques and analysis methods. Updates and clarifications to these methods have been proposed (e.g. Arnórsson, 2000) and several of these are highlighted below. Safety training should be taken seriously when sampling any geothermal fluid capable of causing serious burns.

Liquid sampling and measurement

Water analyses for exploration interpretation, geothermometers and the charts presented here need, at a minimum, pH, SiO_2, the major cations and anions (Na, K, Ca, Mg, Cl, SO_4, HCO_3/CO_3) and a few key trace elements (Li, Rb, Cs, B, F). A separate acidified or diluted sample is needed for SiO_2. Other analyses might be valuable in certain situations, especially if chemical modeling is contemplated (e.g. Al and Fe), or if there are environmental concerns (e.g. As, Hg). Field analyses or hermetically sealed samples may be needed for gassy waters or waters that are likely to change by oxidation while in transit (i.e. Fe or H_2S rich fluids). Field pH measurement and sample temperature is useful to determine changes to sample chemistry between field and lab.

Conductance measured in the field and entered on the field sample sheet is recommended for quality control since conductance reported in microSeimens per cm is usually about 100 times the sum of cations or anions (in milliequivalents per litre, Hem, 1970). Conductance, as an independent approximate measure of sample concentration, can also help sort out sample mix-ups and labeling problems.

A shortcoming of water laboratories that do not specialize in geothermal analyses is that they may be unable to measure some species with the required resolution. For example, because water from surface aquifers usually has orders of magnitude more Mg than geothermal reservoir water, most laboratories that primarily do water quality analysis will have a detection limit for Mg higher than the 0.1 mg/L needed to provide useful results for important plots such as the Na-K-Mg ternary diagram.

Water samples should also be collected for stable isotope analyses ($\delta^{18}O$ and δD). If dissolved H_2S is suspected (by smell), a short length of bare copper wire should be added to the sample to combine with the sulfide, because sulfide will sometimes interfere with ^{18}O analyses. It is important to also collect a sample of local meteoric water, ideally from a cold spring, to determine this end member composition.

Gas sampling and measurement

Gas sample measurements should include, at a minimum, CO_2, H_2S, NH_3, N_2, CH_4, H_2, Ar and O_2. Although He, CO, Ne, SO_2 and He isotopes are sometimes useful, they will usually require a special bottle. Meaningful interpretation of N_2, Ar, He and Ne requires extreme care to prevent air contamination during sampling and extensive experience and/or training is required to ensure reliable gas sampling from many types of features. CO degrades in caustic soda, so it is sampled either in a separate bottle or its concentration is corrected for degradation (B. Christenson, GNS Science, pers. comm.). SO_2 is useful in distinguishing between volcanic and hydrothermal sources, but also requires a separate sample. Samples for He isotopes are sampled in a special (borosilicate) glass flask or copper tube sealed with refrigeration clamps. Although He-isotope sampling is commonly completed and interpretations have regional significance, the results are seldom given much emphasis in developing conceptual resource models for reservoirs and so He-isotope analysis is a lower priority for this purpose.

Fumarole steam should be condensed and cooled to below 40°C to minimize fractionation to escaped water vapor. Analyses of steam condensate of superheated fumaroles have the potential to contain dissolved solids not scrubbed out by co-existing condensate in the subsurface. These can be particularly important when a volcanic source is suspected. Analytes should include pH, Cl, F, B and Na. Stable isotope (H, O) analyses of steam condensate from saturated (boiling point temperature) freely flowing fumaroles are also useful. It is important that these samples not be pumped if flow is weak because the pressure change at the vent will change the isotopic content.

If the updated versions of the procedures recommended by Giggenbach and Goguel (1989) are followed, the quality of collected water samples will likely be reliable. The gas spreadsheet includes input cells for all of the chemical species relevant to most geothermal geochemistry analyses excepting those needed for helium isotopes interpretation.

LIQUID ANALYSIS

Liquid_Analysis_v1_Powell-2010-StanfordGW.xls is an Excel spreadsheet that contains an input sheet, a geothermometry report sheet, ten charts, an information "how to use" sheet (including details on many reporting conventions and unit conversions), and two hidden data reference sheets. The hidden reference sheet "Tgrid" provides the coordinates to draw the ternary diagrams and "Ref" provides plotting data for rocks, tie-lines and equilibrium lines in the charts. The hidden sheets can be customized to provide alternative analysis capabilities by removing the protection from the spreadsheet and "unhiding" them.

Input

The data input sheet allows for 30 water and/or stable isotope (δD and $\delta^{18}O$) analyses. In order to illustrate its use, the provided spreadsheet includes analyses from Giggenbach and Goguel (1989). The plots generated by the spreadsheet can be compared to the plots in the original publication. The provided data can be deleted or overwritten without disturbing the computation in the protected spreadsheet. To make interpretation plots, chemical analyses data are input or copied into data rows and the spreadsheet calculates their geothermometers and plot parameters in hidden columns to the right. Hidden columns AG to BJ read the input rows by fixed cell address to prevent accidental moves of data in the input field which can mix up cell addresses; a common problem with spreadsheets. All further plots and analyses are read from these hidden columns.

As a quality control check, the sum of cations, the sum of anions and the charge balance are calculated. A common source of confusion is that, although cations and anions are input as mg/kg, the sum of cations and anions is reported in meq/kg, that is, the measured data in mg/L or mg/kg divided by the milliequivalent weight in mg/meq for the species being analyzed.

To adjust the plots to fit more dilute or concentrated ranges of water analyses or to differentiate tight clusters of points, multiplier factors for the ternary plots can be changed in the table above the data input rows. These also allow users to change the locations of reference features on the isotope plots.

More than 30 data points can be analyzed by copying the formulas in columns to right of the data input range (columns AG to BJ) to rows below the first 30. Because the charts are written to only display the ranges up to 30, the data ranges will also need to be modified for each plot. However, experience suggests that, in most cases, editing the data to a representative subset may assist the interpretation because plots with more than 30 labeled points are often too cluttered to illustrate trends.

Report: Liquid Geothermometers

The "Report" sheet shows values for the common geothermometers. Fournier (1989) provides an excellent introduction to the models, derivations and assumptions used for the most widely used silica and cation liquid geothermometers. For those unfamiliar with the context of these plots, geothermometers work because the relative equilibrium concentrations of chemical species change with respect to temperature. The rates at which different species react also vary, with cations like sodium and potassium adjusting more slowly than silica. Therefore, the cation geothermometry has a longer "memory" and typically reflects the temperature of a more distant or deeper source fluid. In contrast, the silica geothermometer reflects the temperature of a nearby aquifer. The graphs combine species with different sensitivity to temperature, mixing and other processes in order to resolve trends in geothermal reservoirs and their shallow manifestations.

Choices in Geothermometers

Tables that list most of the geothermometers proposed by investigators tend to mask trends indicated by the more reliable geothermometers. Therefore, geothermometers that have a poor record of prediction or an unclear context of application have been omitted. Researchers can remove the spreadsheet protection and add these alternatives to investigate how they might be improved or in what context they might be effective. However, because this spreadsheet is primarily intended to be a practical tool, analyses and plots that have not proven to have a reliable application in the authors' experience are omitted.

Silica

Geothermometer temperatures are calculated for amorphous silica, chalcedony, quartz via conductive cooling and quartz via adiabatic cooling (boiling). Geothermometers have been proposed based on the silica phases α-cristobalite, β-cristobalite and tridymite, but results are seldom interpreted in terms of these phases because they are rarely found as a hydrothermal alteration product. The Fournier and Potter (1982) quartz geothermometer is chosen over the earlier Fournier (1981) formula due to its higher temperature range (up to 330ºC versus 250ºC) and its accuracy in comparison to measured well temperatures. The quartz maximum steam loss geothermometer, based on the 1981 quartz formula, is included here because it is more appropriate for boiling hot springs than the formula for conductive cooling.

Cations

The cation geothermometers include the empirical Na-K-Ca geothermometer of Fournier (1981), which has been found to be consistent with measured well temperatures. The β factor for the formula is calculated in hidden columns assuming that, if the calculated temperature based on $\beta = 4/3$ is less than 100ºC and the term [log ($\sqrt{Ca}/Na$) +2.06] is positive, then $\beta = 4/3$, otherwise $\beta = 1/3$. The magnesium correction to the formula is also calculated using the rules of Fournier (1981).

Three different versions of the Na/K geothermometer are presented, yielding temperature differences of 20 to 30ºC. These are probably not accurate below about 150ºC and are commonly greater than the maximum measured temperatures found in drill holes.

Other omitted geothermometers

A few commonly cited geothermometers have been omitted from the spreadsheet because experience suggests that they are either too often unreliable (Na/Li) or difficult to use outside of a research context (sulfur isotopes).

Charts for Water Chemistry Interpretation

The charts have been programmed to automatically include labels from the label column on the input sheet for each plotted point. There are drawbacks to this and one often gets unwanted labels for various reasons. An alternative would be to use an X-Y plot labeling add-in, such as the one available (as freeware) by AppsPro:
www.appspro.com/Utilities/ChartLabeler.htm

Map

This sheet is a simple map of sample points, based upon the UTM northing and easting coordinates input with the chemical analysis. Axis ranges in the attached sheets are set to the example data points in the input sheet and should be reset for other data. To fix the scales of the coordinate axes in Excel, an empty text box with equal height and width has been added to the NW corner of the map. This can be resized in the format menu of the text box to act as a guide to make the map axes equal.

Tcsh

The ubiquitous $Cl-SO_4-HCO_3$ ternary plot illustrates the proportions of the major anions present in geothermal water in a format based on Giggenbach (1991a). Labels on the plot indicate associations with different parts of a geothermal system or different types of geothermal systems. A hot spring with significant chloride, moderate bicarbonate and minimal sulfate is consistent with outflow from a geothermal reservoir. It will be much more likely to

provide reliable cation geothermometry than a spring that is mainly bicarbonate or sulfate.

Figure 1: Cl- SO₄-HCO₃ ternary anion plot. Data from Giggenbach and Goguel (1989).

Although high temperature bicarbonate reservoir fluids provide valid geothermometry in fields like Beowawe, Nevada, this type of reservoir is uncommon near andesitic volcanoes. In this volcanic context, a bicarbonate hot spring with some sulfate and no chloride is more likely related to groundwater heated by steam from a deeper reservoir. A high sulfate spring is likely to be associated with a deeper boiling zone. Of course, such possible associations are more definitive when combined with analyses of other water and gas constituents and with other geoscience data sets, including geology, alteration, resistivity and structural patterns. These types of data provide an underlying context for the geochemistry interpretation that should always be considered.

Tclb

The ternary of chloride, lithium and boron in the form presented in Giggenbach (1991a) is used to distinguish fluids from different sources, to reveal fractionation associated with boiling or mixing with fluids that have boiled, or fluids generated by different sources of high temperature steam. In Powell et al. (2001), for example, it is used to distinguish geothermal waters influenced by absorption of high temperature steam from differing sources.

Tcfb

This ternary of chloride, fluoride and boron is useful in tracing sources of water, because, in the absence of relatively rare fluorite with which to re-equilibrate, fluoride can be expected to be conservative. Figure 2 shows an example where this ternary was used to illustrate different sources of two closely associated sets of hot spring water in New Zealand.

Figure 2: Cl-F-B ternary plot from O'Brian et al. (2009).

Tnkm

The Na-K-Mg graphic is probably the most widely used cation geothermometry plot, a ternary combining the sodium-potassium (Na-K) geothermometer with the potassium-magnesium (K-Mg) geothermometer. Immediately after being presented by Giggenbach, successive versions of this plot were adopted by the geothermal industry so rapidly that it became known as "the" Giggenbach plot, although it was merely the most widely used of many effective cross-plots developed by Giggenbach. The version here is similar to that of Giggenbach (1991a). Giggenbach called this type of plot a "geoindicator" because it organizes the plotted data points in a manner that illustrates both the evidence that supports the interpretation of equilibrated water at high temperature but also the influence of shallow processes and possible equilibration at lower temperature.

Figure 3: Na-K-Mg ternary geothermometer plot.

Some interpreters directly interpret mixing from this plot but because re-equilibration can produce a similar pattern, to verify such a claim, species

characteristic of the proposed mixing process should be plotted.

Numerous case histories have illustrated the utility and limitations of this plot for interpreting the chemistry of neutral water from thermal springs and exploration wells. Barnett et al. (2005), Mariner and Janik (1995) and Maturgo et al. (2000) demonstrate that extrapolations of a geothermometer trend based on shallow samples can have excellent agreement with both geothermometers and measured temperatures from produced wells in the reservoir. A very recent case history by Casteel et al. (2010) illustrates the utility of this plot in the exploration of hidden geothermal systems and the development of conceptual models.

Xkms

This cross-plot of the K-Mg geothermometer and the quartz (conductive) geothermometer is from Giggenbach and Goguel (1989). The plot uses the chalcedony geothermometer, which is often more appropriate to use than quartz for water from a lower temperature source. By comparing two low temperature geothermometers, it increases confidence in both if they agree. Disagreement between these two geothermometers might be due to dilution, equilibration with amorphous silica, or perhaps some residual effect of an acid zone that invalidates the geothermometry even though the water has been neutralized.

Xkmc

Giggenbach and Goguel (1989) refer to this cross-plot as a "geoindicator" rather than a geothermometer plot because it juxtaposes the potassium-magnesium geothermometer with a measure of the partial pressure of CO_2 based upon equilibrium between K-feldspar, calcite and K-mica on one side and dissolved Ca^{+2} and K^+ on the other. The purpose of the cross-plot is to determine the partial pressure of CO_2 at the last temperature of the water equilibration with rock, as determined by the K-Mg geothermometer. In that values of the CO_2 partial pressure (P_{CO_2}) assume equilibrium between calcite and the other mineral phases, P_{CO_2} of analyses plotting outside the "calcite formation" field can only be interpreted qualitatively. This being the case, this plot is probably limited to assessments of whether the sampled fluid is likely to be in equilibrium with calcite in the subsurface.

Xmckn

This Na-K/Mg-Ca diagram, presented in Giggenbach and Goguel (1989), is another "geoindicator" plot that could be viewed as an elaboration of the Na-K-Mg plot. It juxtaposes the Na-K geothermometer with equilibration of the system Mg-Ca. Its most widespread application is the determination of the influence of shallow, low temperature processes, which have particular influence on the apparent Mg-Ca equilibrium. It may be appropriate for reservoirs in carbonate rocks or fluids dominated by rock chemistry rather than geothermal equilibration.

XClHqtz

This is the commonly used chloride-enthalpy diagram for hot spring samples, with enthalpy based upon quartz geothermometer temperature. Enthalpy is derived from the Fournier and Potter (1982) quartz geothermometer using a fourth order polynomial curve fit of the enthalpy of pure water between 80°C and 340°C. The position of steam (2800 kJ/kg) is set with a data point on the "enthalpy" axis, representative of steam separated between 200°C and 260°C. Considering the scale of the enthalpy axis, the error introduced by steam separated at different temperatures will be small. This plot is commonly useful in areas where steam separation and dilution are suspected and where there are many fluid sources for sampling, including wells. Maturgo et al. (2000) demonstrate an application.

Iso

This is a standard cross-plot of the stable isotopes of water ($\delta^{18}O$ – δD). It includes the World Meteoric Trend line, the range of andesitic water as proposed by Giggenbach (1992a) and a cluster showing steam-water equilibrium fractionation end members at different temperatures based upon data from Henley et al (1984). The positions of the meteoric trend line label and the fractionation cluster can be modified in cells above the isotope data entry columns on the input sheet.
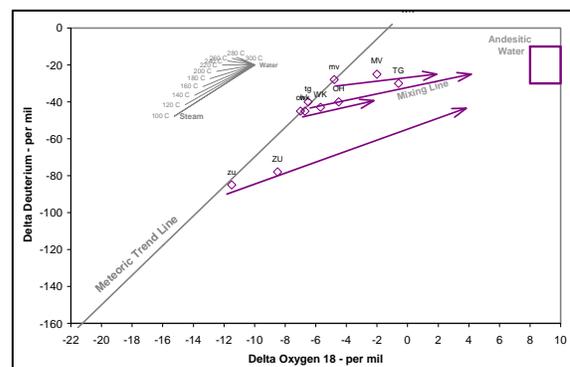

Figure 4: $\delta^{18}O$ – δD stable isotope plot.

Interpretation is often difficult since small amounts of evaporation, boiling, rock exchange, or mixing can all affect the relatively imprecise analyses that are commonly available. In the absence of boiling or evaporation a line of analyses related to mixing or exchange can point to a cold water source area and to the most highly exchanged or hottest sample.

Arnórsson (2000) illustrates issues and applications of such plots.

GAS ANALYSIS

The Gas_Analysis_v1_Powell-2010-StanfordGW.xls spreadsheet contains an input sheet, an information sheet, four ternary diagrams, five geothermometer grids and three hidden reference sheets. Reference sheet "Ggrid" provides the coordinates of the gas geothermometry grids, "Tgrid" the coordinates of the ternary diagrams, and "Ref" the tie-lines and reference lines for the ternary charts. Gas geothermometer equations used to plot geothermometer grids in the "Ggrid" sheet are those from Powell (2000) and the references in that earlier paper provide the supporting background details.

Input

The overall format of the gas geochemistry spreadsheet is similar to the water geochemistry spreadsheet discussed in the last section. For example, multipliers for the different components of the ternary plots can be changed in the boxes above the input field. The input sheet allows for 30 gas analyses, preloaded with gas analyses from Rotorua area hot springs and wells as tabulated in Giggenbach and Glover (1992). This data set more comprehensively illustrates the characteristics of the gas spreadsheet and charts than is true of the data preloaded in the companion water spreadsheet.

As with the liquid analysis spreadsheet, more analyses can be accommodated by copying down the formulae in the hidden columns to the right of the analyses input area and increasing the plot ranges of the charts. Hidden rows Y to AM read input rows by fixed cell address to prevent accidental data moves from mixing up the data for the analysis.

Gas specie data are input as mole percent of dry gas, with the gas concentration entered as either gas/steam ratio (ppm molar), mole percent gas in steam or weight percent gas in steam. The spreadsheet looks for an entry in one of these three columns (under "Total Noncondensible Gas") and uses this to calculate the gas/steam ratio of the individual gases. The spreadsheet calculates the sum of the individual gases to check that they sum to close to 100%.

Nicolson (1993) provides details needed to convert data to one of the three formats accommodated by the spreadsheet. For example, gas analysis data in New Zealand is commonly reported in millimoles gas/100 moles H_2O. This can be converted to ppm molar gas/steam ratio by multiplying all the gas concentrations by 10, summing them to find the ppm molar gas to steam ratio of the total gas, then dividing the ppm molar concentration of each gas by the ppm molar total gas to find the mole percent of each gas in the total. With a customized spreadsheet, this can be done efficiently and accurately provided that a check is made with respect to independently derived results.

The percent air contamination in the sample is calculated based upon the oxygen content of the sample. The percent of total N_2 and Ar that is contributed by air contamination in the sample is removed from the analytical results to provide corrected values. If the fractions of air in these two analyses are large, as indicated by large percentages of air N_2 and air Ar (say greater than 10-20%), then the plots involving these species are less useful.

Charts for Gas Chemistry Interpretation

The descriptions of the following plots are particularly brief if they have been already described in Powell (2000).

Tnha

This N_2, He and Ar ternary plot is used to determine likely sources of geothermal waters and to indicate if air contamination might adversely effect the interpretation of the chemistry. The tie-lines here are from Giggenbach and Goguel (1989). The N2/Ar ratio is useful in showing the relative contributions of magmatic and meteoric fluids.

Tnca

This ternary of N_2, Ar, and CO_2 is similar to the Tnha plot and has similar application, but uses CO_2 instead of He, as presented in Giggenbach (1992b).

Tcch

Tcch is a ternary of CH_4, CO_2 and H_2S, which is useful for examining the process of degassing of a shallow thermal aquifer. It was used successfully by Giggenbach and Glover (1992) on the Rotorua system in New Zealand. The left side of the ternary shows a CO_2-CH_4 geothermometer grid, assuming an R_H (log fugacity(H_2)/fugacity(H_2O)) for the system. R_H is a measure of redox potential and can be specified on the input sheet (Giggenbach, 1989; Powell 2000). In the absence of information about the specific redox potential of the hot spring environment, -2.8 has been proposed by Giggenbach and Goguel (1989) as representative of most volcanic-hosted geothermal systems.

Besides the RHA, the starting reservoir temperature for the thermal aquifer can be specified. Temperature of boiling for the aquifer can be changed on the "Ref" sheet.

Tchn

Tchn is a simple ternary of CO_2, H_2S and NH_3 that is used to examine the chemical differences between

gas samples. These three gases have very different solubilities in water, sometimes supporting interpretations of condensation or boiling processes.

CAR-HAR

As a gas ratio geothermometer plot involving gases with low solubility, this grid does not require the interpreter to specify the steam fraction where the gas equilibrated, unlike the Y-T gas grid geothermometers (Giggenbach and Glover, 1992). CAR-HAR juxtaposes a CO_2 geothermometer with a H_2 geothermometer, using argon concentration as a proxy for gas-steam ratio. R_H can be specified for the grid on the input page, but the default –2.8 is proposed to be representative for most systems. Proposed exceptions are discussed by Urzua et al. (2002). Due to the low solubility of the three gases involved, the grid does not suffer significantly from gas solubility differences between steam and water and is expected to be useful for both hot springs and fumaroles. Due to its reliance on argon concentration, however, it is quite susceptible to air contamination, as the arrow on argon error suggests in Figure 5. Points that plot between the equilibrated vapor and equilibrated liquid lines show evidence of two-phase conditions in the subsurface. However H_2 and CO_2 equilibrate at very different rates (H_2 quicker than CO_2) so that gases that plot in the two-phase field may be related to changes in H_2 that are not fully accommodated by CO_2 reaction in a liquid phase reservoir.
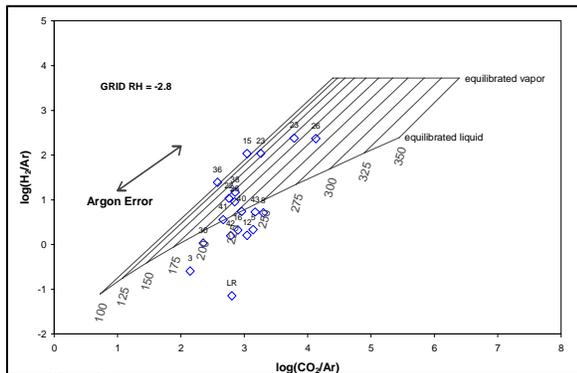

Figure 5: CAR-HAR geothermometer grid with data from Giggenbach and Glover (1992).

COCOCHCO

Like CAR-HAR, this gas ratio grid geothermometer does not require an estimation of steam fraction. COCOCHCO is a geothermometer grid juxtaposing the CO/CO_2 geothermometer with a CH_4/CO_2 geothermometer developed by Giggenbach (1991b). CO is typically found in very low concentration, so the spreadsheet only places plot labels on analyses that are above detection. This plot is commonly used

to interpret fumarole and well gases and can reveal deep reservoir temperatures (Urzua et al., 2002).

FT-HSH

FT-HSH is a geothermometer grid juxtaposing a geothermometer based upon the Fischer-Tropsch reaction ($CO_2 + 4H_2 = CH_4 + 2H_2O$) and a geothermometer based upon $H_2 – H_2S$ equilibria in the presence of magnetite and pyrite. The grid plots temperature versus "Y value", which is defined as the fraction of steam resident in the reservoir and with gas content in equilibrium with reservoir water, and are sometimes called "Y-T" grids. Powell (2000) provides a more detailed discussion of these.

This geothermometer has limited usefulness in the analysis of surface manifestations because it requires an accurate gas/steam ratio, which is often only available in superheated fumaroles or wells. As can be seen in the spreadsheet, none of the thermal features in Rotorua actually plot on the grid. Therefore, the primary use of this spreadsheet is in interpreting well discharges. Of course, even in areas where no thermal manifestations exist, an exploration drilling program can be guided by the results of these types of analyses of production tests, for example, a range of geothermometers can be used to assess whether measured well temperatures are close to the maximum and typical resource temperatures.

FT-CO$_2$

FT-CO$_2$ is another "Y-T" grid juxtaposing the Fischer-Tropsch geothermometer with one proposed by Giggenbach based upon CO_2 concentration. In this case, a number of the analyses from Rotorua plot on the grid, but do not make a coherent pattern. Again, this grid needs an accurate gas/steam ratio to be applicable, and is therefore best suited to use in well discharges.

FT-H2S

FT-H2S is similar to the CO_2 version, but with the H_2S geothermometer of Giggenbach (1997), and is similar to the FT – HSH geothermometer grid.

CONCLUSIONS

The spreadsheets described in this paper provide geochemistry interpretation tools with proven value in exploring and characterizing the properties of both volcanic and forced convection geothermal reservoirs, including "blind" systems as illustrated by the case history of a "blind" system currently under development (Casteel et al., 2010).

An exploration program that integrates geochemical indications of aquifer geometry and temperature with geophysics, geology, well targeting and well testing,

is likely to lower the cost of building sufficient confidence in resource conceptual models capable to commit to a generation capacity and plan well targets for development.

We hope that this cursory introduction to graphics tools commonly used in geothermal geochemistry interpretation, along with spreadsheets that implement them, supports further publications of case histories and tutorials that illustrate the integration of geothermal geochemistry in resource conceptual models.

ACKNOWLEDGEMENTS

REFERENCES

Arnórsson, S. (Ed.) (2000), "Isotopic and Chemical Techniques in Geothermal Exploration, Development and Use. Sampling Methods, Data Handling, Interpretation," *International Atomic Energy Agency*, Vienna, 351p.

Barnett, P., Clotworthy, A., Bogie, I., Talebi, B. Khosrawi, K. (2005), Stage 2 Exploration and Development, NW Sabalan Geothermal Field, Iran. *Proceedings World Geothermal Congress 2005*.

Casteel, J., Trazona, R., Melosh, G., Niggemann, K. and Fairbank, B. (2010), "A Preliminary Conceptual Model for the Blue Mountain Geothermal System, Humboldt County, Nevada" Accepted in: *Proceedings World Geothermal Congress 2010*.

Ellis, A.J., Mahon, W.A.J. (1977), "Chemistry and Geothermal Systems," *Academic Press*, NY, 392p.

Fournier R.O. (1981), "Application of water geochemistry to geothermal exploration and reservoir engineering," in *Geothermal Systems: Principles and Case Histories*, Ryback and Muffler eds., John Wiley and Sons, NY, 109-143

Fournier R.O. (1989), "Lectures on geochemical interpretation of hydrothermal waters," *UNU Geothermal Training Programme, Reykjavik, Iceland.* Report 10, 1989. . www.unugtp.is/solofile/33667 www.unugtp.is/solofile/33668

Fournier R.O. and Potter R.W. II (1982), "A revised and expanded silica (quartz) geothermometer," *Geothermal Resources Council Bulletin*, **11**, 3-12

Giggenbach, W.F. (1980), "Geothermal gas equilibria," *Geochem Cosmochem Acta*, **44**, 2021-2032.

Giggenbach, W.F. (1988), "Geothermal solute equilibria," *Geochem Cosmochem Acta*, **52**, 2749-2765.

Giggenbach, W.F. (1991a), "Chemical techniques in geothermal exploration," *in UNITAR/UNDP Guidebook:* Application of geochemistry in resources development, 119-144.

Giggenbach, W.F. (1991b), "The composition of gases in geothermal and volcanic systems as a function of tectonic setting," in *Water-Rock Interactions*, Kharaka and Maest eds., Balkema Rotterdam, 873-878.

Giggenbach, W.F. (1992a), "Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin", *EPSL* **113**, 495-510.

Giggenbach, W.F. (1992b), "Magma degassing and mineral deposition in hydrothermal systems along convergent plate boundaries," SEG distinguished lecture; *Economic Geology*, **87**, 1927-1944.

Giggenbach, W.F. (1993), "Redox control of gas compositions in Philippine volcanic-hydrothermal systems," *Geothermics*, **22,** 575-587.

Giggenbach, W.F. (1997), "The origin and evolution of fluids in magmatic-hydrothermal systems," in *Geochemistry of Hydrothermal Ore Deposits, 3rd edition*, H.L. Barnes ed., John Wiley and Sons, NY, June 1997.

Giggenbach, W.F. and Glover, R.B. (1992), "Tectonic regime and major processes governing the chemistry of water and gas discharges from the Rotorua geothermal field, New Zealand," *Geothermics*, **21**, 121-140.

Giggenbach, W.F. and Goguel, R.L. (1989), "Collection and analysis of geothermal and volcanic water and gas discharges," *DSIR report CD 2401, 4th ed.*, Pentone, New Zealand.

Hem, J.D., 1970, "Study and Interpretation of the chemical characteristics of natural water," *US Geological Survey Water Supply Paper 1473*, reprinted 2005 by University Press of the Pacific, Honolulu, Hawaii.

Henley, R.W., Truesdell, A.H. and Barton, P.B. Jr., (1984), "Fluid-mineral equilibria in hydrothermal systems," *Reviews in Economic*

Geology Vol 1, Soc Econ Geol, Univ Texas, El Paso, TX, 267p.

Klein C. (2007), "Advances in the Past 20 Years: Geochemistry in Geothermal Exploration, Resource Evaluation and Reservoir Management," *Geothermal Resource Council Transactions.*

Mariner, R.H. and Janik, C.J. (1995), "Geochemical data and conceptual model for Steamboat Hills geothermal system, Washoe County, Nevada," *Geothermal Resource Council Transactions.*

Maturgo, M., Zaide-Delfin, Layugan, D. and Catane, D. (2000), "Characteristics Of The Volcanic-Hydrothermal System In Mt. Labo, Philippines: Implications To Development," *Proceedings World Geothermal Congress 2000.*

Nicholson, K. (1993), "Geothermal fluids: Chemistry and exploration techniques," *Springer-Verlag*, 263p.

O'Brian J., Horton, T., Cole, J., Powell, T. (2009), "Hydrogeochemical characterization of the Ngatamariki geothermal field and a comparison with the Orakeikorako thermal area, TVZ, NZ," P*oster, NZ Geochemical and Mineralogical Society meeting*, Napier, 8-10 November 2009.

Powell, T. (2000), "A Review of Exploration Gas Geothermometry," *Proceedings, 25th Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, CA, SGP-TR-165.

Powell, T., Moore, J., DeRocher, T., McCulloch, J., (2001), "Reservoir Geochemistry of the Karaha - Telaga Bodas Prospect, Indonesia," *Geothermal Resource Council Transactions* **25**.

Urzua, L., Powell, T., Cumming, W., and Dobson, P. (2002), Apacheta, a New Geothermal Prospect in Northern Chile. *Geothermal Resources Council Annual Meeting Transactions*, **26**.