FLUID-MINERAL EQUILIBRIA IN GREAT BASIN GEOTHERMAL SYSTEMS: IMPLICATIONS FOR CHEMICAL GEOTHERMOMETRY

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ABSTRACT
Partial to nearly full fluid-mineral equilibrium exists between common aqueous species in reservoir fluids and the mineral assemblage quartz (chalcedony), Na-feldspar, K-feldspar, K-mica, Mg-chlorite (clinochlore), calcite, and heulandite in Great Basin geothermal systems. For chemical geothermometry, the silica geothermometer based on quartz/chalcedony solubility appears to be the most reliable indicator of reservoir temperature. Although Na/H vs K/H ratios plot on the Na-feldspar-K-feldspar equilibrium line (~250°C), application of the Na-K geothermometer overestimates reservoir temperature, possibly because equilibration occurs at conditions that are hotter and deeper than existing feed points in geothermal wells. A linear trend in Na/K versus temperature permits formulation of a new empirical geothermometer

\[ t^\circ C = \frac{315}{\log \left( \frac{Na}{K} \right)} - 273 \]

that has yet to be tested and proven. Modest to low confidence in the application of the K-Mg geothermometer is expected because the reservoir K/Mg ratios are scattered with respect to Mg-chlorite-K-mica-K-feldspar-quartz equilibria.

INTRODUCTION
Chemical geothermometers have been available since the 1960s, providing a cost effective means of estimating the temperature of a geothermal reservoir during exploration, development, and on going management of a resource. The most widely used geothermometers (i.e., Na-K, K-Mg) are based on fluid-mineral equilibria, relating to hydrothermal minerals that are commonly found in altered volcanic rocks (e.g., Fournier, 1981, 1991; Giggenbach, 1988, 1991). By contrast the geothermometers based on aqueous silica concentrations and the solubilities of quartz or one of its polymorphs can be applied to geothermal reservoirs with quartz-bearing rock types (Fournier, 1981; 1985). The still widely used Na-K-Ca geothermometer (Fournier and Truesdell, 1973) is an empirical geothermometer, which lacks thermodynamic underpinning and functions as a complicated version of the Na-K geothermometer (Giggenbach, 1988).

The results reported below represent preliminary outcomes of a DoE funded project to identify new hydrogeochemical indicators of geothermal resources in the Great Basin. One of the major goals is to improve confidence in the application and interpretation of chemical geothermometers. Accordingly, the states of fluid-mineral equilibria in reservoirs were assessed, using public domain data sets of fluid compositions and reservoir temperatures for Beowawe, Dixie Valley, Mammoth-Long Valley, Raft River, and Roosevelt. The results build on earlier work (Capuano and Cole, 1982; Tempel et al., 2011; White and Petersen, 1991) and were used to determine the applicability of aqueous geothermometers. They also provide insights regarding the minerals that are likely to be influencing the chemical compositions of deep geothermal waters in the Great Basin.

DATA SETS
Geothermal reservoir water compositions (Table 1) that represent a spectrum of geothermal reservoirs of low to high temperature across the Great Basin were evaluated. All the waters are near neutral pH. Chloride (350 to >3000 mg/kg Cl) is the dominant anion at Dixie Valley, Roosevelt, and Raft River, whereas bicarbonate (145–>400 mg/kg HCO₃) is the dominant anion at Beowawe and Long Valley-Mammoth. Sulfate is a minor anion, with concentrations (30 to >200 mg/kg SO₄) that are subequal with bicarbonate (30 to <500 mg/kg HCO₃).
Temperature data (Table 1) represent maximum measurements from well surveys or interpretations from well enthalpy data. All reservoirs are assumed to comprise a single phase liquid, with no free vapor or gas.

Mineralogical analyses (XRD, thin section petrography) of drill cuttings from Beowawe, Dixie Valley, Mammoth, and Roosevelt confirm that quartz, feldspars (Na-feldspar, K-feldspar, plagioclase), illite (K-mica), chlorite, and calcite are common minerals in the reservoir rocks, despite variability in rock types and stratigraphic sequences that characterize each geothermal system.

**COMPUTATIONS**

Speciation calculations were undertaken using the computer code WATCH 2.0 (Iceland Geosurvey; http://geothermal.is/software/software); the most recent version is modified and updated from the one that was initially written by Stefán Arnórsson, Sven Sigurdsson and and Hórdur Svararson (e.g., Arnórsson et al., 1982, 1983a, 1983b). For Dixie Valley, gas and water data (Goff et al., 2002) were combined to formulate representative reservoir water compositions using heat and mass balance constraints (e.g., Henley et al., 1984).

WATCH input requires fluid analyses, pH, temperature/pressure of sampling, and well enthalpy or reservoir temperature. The concentrations, activity coefficients, and activities of aqueous species at reservoir conditions are determined by an iterative process that involves simultaneous solution of mass balance and mass action equations, input from a standard set of thermodynamic data, and a model of ion-ion interactions based on the extended Debye-Hückel equation (e.g., Garrels and Christ, 1965). The output gives concentrations of analytes at reservoir conditions, activity coefficients of aqueous species (69 total), partial pressures of dissolved gas species, and reservoir pH, which are used to compute activities and activity ratios of aqueous species. These computed values are plotted on phase diagrams showing the compositional and thermal stability fields of silica polymorphs (quartz, chalcedony, cristobalite), calcite, and alumino-silicate minerals. SOLVEQ (Reed and Spycher, 1984) is a computer code that is similar to WATCH, containing more aqueous and gaseous species in the database, but the input files require more time to set up. A comparative analysis of outputs from SOLVEQ and WATCH using data from Dixie Valley showed that computed activities of major species are within a few percent.

Phase diagrams were computed using Geochemists Workbench (Bethke, 1996) based on thermodynamic data from SUPCRT (Johnson et al., 1992). For these phase diagrams, certain zeolites, clays, feldspars and calcium alumino-silicates (i.e., beidellite, saponite, clinoptilolite, margarite, grossular, high albite, maximum microcline) were suppressed in order to most closely match the minerals occurring in the reservoir rocks.

**RESULTS**

A series of phase diagrams (Figs. 1-7), which show the positions of mineral stability fields with respect to reservoir water compositions, are used to assess the state of fluid-mineral equilibria. Silica phases and calcite are evaluated first, followed by assessment of sodium, potassium, calcium, and magnesium alumino-silicates. Na/K and K/Mg ratios are plotted as a function of well temperature to determine applicability of conventional geothermometers based on equilibrium with hydrothermal feldspars, clays, and quartz/chalcedony.

**Silica**

Since silicic acid (H$_2$SiO$_3$) is a neutral species in solution (acid to near neutral pH), the computed value of activities for SiO$_2$(aq) are within a few percent of the analyzed concentrations of SiO$_2$(aq), and analytical data, corrected for steam loss, can be plotted directly on phase diagrams to evaluate equilibrium with respect to quartz, chalcedony, and cristobalite (Fig. 1). Most of the waters plot on or between chalcedony and quartz solubility curves, suggesting that these two phases are the main control on silica concentrations in geothermal reservoirs. Beowawe data are scattered with two analyses plotting near or above the cristobalite solubility curve; the only analysis from Roosevelt also plots near the cristobalite solubility curve.

**Calcite**

As shown by Ellis (1959), calcite solubility at hydrothermal conditions is mainly a function of temperature and aqueous CO$_2$ concentration (Fig. 2). The activity products ([Ca$^{2+}$][HCO$_3^-$]) for waters from all the geothermal reservoirs plot close to calcite saturation curves based on the concentrations of reservoir aqueous CO$_2$. All of the WATCH/SOLVEQ calculations indicate the waters are supersaturated in calcite. There is nil likelihood of forming a geothermometer based on calcite solubility.

**Na-, K-, Ca-, & Mg-Alumino Silicates**

Four similar phase diagrams (Fig. 3) portray the stability fields of alumino-silicate minerals as a function of silica activity/concentration (log [SiO$_2$]) and cation-hydrogen ion activities. The positions of
Figure 1: Aqueous silica concentrations versus temperature with reference to the experimentally determined quartz, chalcedony, and cristobalite solubility curves (Fournier, 1985).

Figure 2: Product of calcium and bicarbonate activities versus temperature with reference to calcite saturation curves as a function of aqueous CO$_2$ concentration (after Ellis, 1959).
Figure 3: Log activities of Na/H, K/H, Ca/H, and Mg/H versus log activity of silica, showing compositions of reservoir waters with respect to the stability fields of aluminosilicate minerals, quartz, and chalcedony at 150°, 200°, and 250°C.

Figure 4: Log activities of Na/H versus K/H showing the compositions of reservoir waters with respect to the stability fields of Na- and K-bearing feldspars and micas (quartz saturation) at 150°, 200°, and 250°C.
Figure 5: Log activity of K/H versus temperature showing the compositions of reservoir waters with respect to the stability fields of K-bearing feldspars and micas.

Figure 6: Log activity of Na/K versus temperature showing the compositions of reservoir waters with respect to the stability fields of Na- and K-bearing feldspars (solid line). The dashed line that is reported as equation 1 in the text represents a simple linear regression of the aqueous Na/K ratios. Modified from Giggenbach (1988).
Figure 7: Log activity of Mg/K versus temperature showing the compositions of reservoir waters with respect to the stability fields of K-feldspar and K-mica plus Mg-chlorite at quartz saturation. Modified from Giggenbach (1988).

Table 1: Water analyses for Beowawe, Dixie Valley, Mammoth-Long Valley, Roosevelt, and Raft River.

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the water compositions plot within or near the stability fields of K-feldspar, K-mica, albite, heulandite, and Mg-chlorite, and within the range of quartz-chalcedony solubility for respective reservoir temperatures.

**Na/H & K/H Activity Ratios**

Figure 4 shows the positions of geothermal waters with respect to the stability fields of Na-feldspar (albite), K-feldspar, K-mica, Na-mica (paragonite), and kaolinite. The waters form a linear trend that coincides with the Na-feldspar-K-feldspar boundary, suggesting that Na/K ratios are controlled by fluid-mineral equilibria involving these feldspars at ~250°C. This is true even for Mammoth where because the [H+] ion activity is elevated, the waters plot in the K-mica field; a similar trend has been noted in high temperature geothermal reservoirs from New Zealand (e.g., Simmons and Browne, 2000).

Figure 5 shows the positions of geothermal waters with respect to the stability fields of K-feldspar, K-mica, and kaolinite. The data plot about the K-feldspar-K-mica boundary, suggesting these two minerals moderate reservoir fluid pH.

**Na/K & Mg/K Activity Ratios**

Figure 6 shows the positions of geothermal waters with respect to the stability fields of Na-feldspar and K-feldspar as a function of temperature, which is the basis for the Na-K geothermometer (e.g. Giggenbach, 1988). The data form a low angle linear trend that plot well within the K-feldspar stability field, intersecting the Na-feldspar-K-feldspar boundary around 250°C close to where the Dixie Valley data plot. This Na/K trend seems to contradict the results of Figure 4, and it is possible that Great Basin feed temperatures and depths may be cooler and shallower than the environment in which equilibrium is established. Alternatively, geothermal waters are out of equilibrium with Na-feldspar and K-feldspar. Regardless of the correct explanation, a linear regression of the Na/K vs temperature trend yield an empirical relationship that can be tentatively used as a substitute geothermometer:

\[
T^\circ = \frac{315}{\log \frac{\text{Na}}{\text{K}} + 0.467} - 273 \quad (1)
\]

However, for a small range of Na/K values (e.g., due to analytical error or natural variation) there is a large range of corresponding temperatures that could easily exceed several tens of degrees (°C), hence the usefulness of this empirical relationship needs to be proven.

Figure 7 shows the positions of geothermal waters with respect to an equilibrium condition controlled by K-mica, K-feldspar, Mg-chlorite, and quartz, which forms the basis for the K-Mg aqueous geothermometer (Giggenbach, 1988). The array of K-Mg water data are scattered. Dixie Valley and Roosevelt Log [Mg]/[K] values, however, plot close or on the equilibrium line. Overall the results are mixed, and they offer modest to poor confidence in the application of a K-Mg chemical geothermometer.

**DISCUSSION & CONCLUSIONS**

These preliminary results show that despite variability in the rock types and stratigraphic columns of geothermal reservoirs across the Great Basin, quartz (chalcedony), Na-feldspar, K-feldspar, and K-mica influence the compositions of thermal waters via fluid-mineral equilibria. Accordingly, the quartz-silica and Na-K geothermometers should yield reliable temperatures, even if they reflect different temperatures and depths of equilibration.

The preceding analysis assumes the water data and temperature profiles contain minimum analytical errors. Some of the data are several decades old, and the details of measurements are missing or poorly documented. For example, some of the aqueous silica data from Roosevelt and Beowawe are too high with respect to quartz solubility. Other sources of potential error might lie in pH measurements, and/or analyses of Mg and CO$_2$HCO$_3$ concentrations. New samples and analyses are required to confirm the trends identified in this report.

Some of the future avenues for research include investigation of: 1) the origin(s) of the linear Na/K vs temperature relationship; 2) the control of depth and temperature on equilibration points for the various mineral-aqueous ion reactions; 3) the role that shallow saline ground waters play in modifying geothermal water compositions during fluid movement to the surface.

**ACKNOWLEDGMENTS**

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**REFERENCES**


