Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators

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Abstract—Relative Na, K, Mg, and Ca contents of thermal waters in full equilibrium with a thermodynamically stable mineral system derived through isochemical recrystallisation of an average crustal rock are, at a given temperature and salinity, uniquely fixed. Together with the compositions of waters resulting from isochemical rock dissolution, they provide valuable references for the assessment of the degree of attainment of fluid-rock equilibrium. In geothermal systems, the pair K-Na reaches its equilibrium contents as governed by

$$L_{kn} = \log\,(c_K/c_{Na}) = 1.75 - (1390/T)$$

most slowly (c_i in mg/kg, T in K). The quotient c_K^2/c_{Mg} adjusts much faster and to low temperatures ($<100°C$) according to

$$L_{km} = \log\,(c_K^2/c_{Mg}) = 14.0 - (4410/T).$$

The system K-Ca is sensitive to variations in f_{CO_2} with

$$L_{kc} = \log\,(c_K^2/c_{Ca}) = \log f_{CO_2} + 3.0.$$

These subsystems are combined to obtain graphical techniques for the evaluation of deep temperatures and CO_2-partial pressures by use of Na, K, Mg and Ca contents of geothermal water discharges.

INTRODUCTION

IN DYNAMIC HYDROTHERMAL alteration systems overall fluid-rock equilibrium is rarely attained and the fluids sampled are likely to have reached some complex steady-state composition reflecting the combined effects of initial fluid composition, the kinetics of primary mineral dissolution and secondary mineral deposition at changing temperatures and pressures, in addition to vapor loss, dilution and mixing with fluids of different origin. In the midst of all these complexities two limiting processes controlling the chemistry of thermal fluids may be distinguished: The first of these more or less hypothetical processes corresponds to isochemical dissolution of the rock material in contact with the rising fluid; the other to eventual equilibration of the fluid with the thermodynamically stable alteration assemblage resulting from isochemical recrystallisation of the primary rock at a given temperature and pressure, a process likely to come to completion only in stagnant systems of infinite age (GIGGENBACH, 1984). The chemical composition of fluids and minerals resulting from both these reference processes, however, are accessible to rigorous evaluation.

By exploiting differences in the thermodynamic properties and relative abundances of the four major cations encountered in crustal rocks and geothermal waters, Na, K, Mg and Ca, an attempt is made to derive geoindicators allowing water-rock equilibration conditions and the position of a given water sample with respect to the above two limiting states to be evaluated.

POTENTIAL PROCESSES AFFECTING THE CHEMICAL COMPOSITION OF THERMAL WATERS DURING THEIR MOVEMENT THROUGH THE CRUST

In an earlier investigation into mass transfer processes in hydrothermal systems involving the rise of initially magmatic fluids through intermediate to acid crustal rocks (GIGGEN-BACH, 1984), four major alteration processes and associated environments were identified:

1. Potassium metasomatism accompanied by silicification in major upflow zones.

2. Hydrogen metasomatism caused by the attack of CO_2 on Ca-aluminium silicates leading to the formation of calcite and Al-enriched, argillic to phyllic alteration assemblages principally over parts of the hydrothermal system subject to rapid conductive cooling or dilution adjacent to major upflow zones.

3. Sodium, magnesium, calcium metasomatism associated with descending and heating solutions and, therefore, affecting rock over the meteoric recharge zones at the periphery of a hydrothermal system.

4. Isochemical recrystallisation and hydration over close to stagnant parts of a hydrothermal system.

In conjunction with findings on active volcanoes (GIGGEN-BACH, 1975a, 1987), a fifth alteration process, likely to prevail over the deep magmatic to hydrothermal transition zones of a hydrothermal system with close volcanic-magmatic associations, may be defined. It consists of the attack of strong acids (HCl, H_2SO_4, HF) formed through absorption of magmatic gases into deeply circulating groundwater and leads to wholesale rock destruction, advanced argillic alteration and silicification.

The alteration patterns thus delineated may be used to construct a revised and more detailed version of an earlier schematic diagram (GIGGENBACH, 1981) depicting the theoretical distribution of alteration zones in a hydrothermal system as shown in Fig. 1. Again the top of the degassing magma is placed at an arbitrary but reasonable depth of 8 km, isotherms were drawn by assuming uniform and isotropic permeability conditions and a geothermal gradient of 50°/km

apparent approach to fluid/rock-equilibrium, those from Te Aroha (TE) and Radkersburg (RA) (Fig. 9), give equilibration temperatures of around 130° at CO_2-fugacities of 0.9 and 10 b, respectively. Both are associated with active deposition of calcite at the surface thus confirming calcite supersaturation, at least under surface discharge conditions. Deposition of calcite at shallow levels or even during sampling may then be responsible for the very low Ca-content of the Radkersburg sample and the correspondingly very high apparent CO_2-fugacity. The CO_2 pressure indicated for the Te Aroha water of around 1 bar is that expected for such lower temperature, calcite depositing springs.

From the above findings it can be concluded that evaluation of f_{CO_2} by use of K-Ca contents of discharge waters is only reliable for data points close to the full equilibrium line. For data points deviating significantly, the full equilibrium line may be taken to separate waters from two distinct alteration environments: those plotting below in Fig. 10 are likely to come from an alteration system dominated by acid fluids, those plotting above from a rock dominated, CO_2-deficient environment.

PRACTICAL APPLICATIONS

The wide range of chemical geothermometers hitherto proposed and to varying degrees presently in use may be subdivided into several categories, depending on the number of components involved in their formulation. The most simple ones are those based on uni-variant reactions such as the silica geothermometer and a number of gas geothermometers as proposed by ARNORSSON et al. (1983a,b) and discussed by ARNORSSON and SVAVARSSON (1985). Their major disadvantage is their high sensitivity to secondary processes such as dilution, and in the case of gas geothermometers, to vapor loss or condensation and errors in the estimates of vapor-liquid ratios.

At the other end of the spectrum are "global" techniques involving a large number of constituents and based on the inherent assumption that all these constituents have been in equilibrium simultaneously at some stage and that their compositions are still representative of the conditions in this deeper equilibration zone. Examples are gas geothermometers proposed by GIGGENBACH (1980) on the basis of reactions involving the formation of CH_4 and NH_3, or those based on the reconstruction of the deep equilibrium fluid as proposed, e.g., by MICHARD and ROEKENS (1983) and REED and SPYCHER (1984).

Application of these techniques is valid in the case of deep well discharges likely to be representative of the deep equilibrium environment, but questionable in the case of natural surface discharges. For these fluids, subject to secondary processes such as partial re-equilibration to lower temperatures, dilution or steam loss, the results become inconclusive. Major disadvantages of these multicomponent techniques then are their dependence on virtually complete and representative analyses of thermal discharges and on the availability of reliable thermodynamic information for a large number of mineral and fluid phase species, their limited ability to allow any further ready interpretation or intercomparison among a large number of samples and their general unwieldiness. A useful aspect of these global techniques is their ability to reveal attainment of equilibrium among a large number of fluid and mineral components. Under these circumstances, however, any geoindicator based on a suitable subsystem,

involving much fewer components, would have given the same answer.

Most of the drawbacks of single species and global techniques are overcome by the use of isomolar concentration ratios in the case of gases (GIGGENBACH, 1987) or isocoulombic concentration quotients, as discussed above, in the case of ionic solutes. These approaches are in accordance with the general rule that comparison of analytical and theoretical information in geochemical systems should be carried out as much as possible on the basis of actually measured variables and variable by variable (GIGGENBACH, 1987). The two diagrams represented by Figs. 9 and 10, based on readily available analytical information, fulfil this condition; the overall treatment essentially preserves the identity of each variable and allows secondary processes affecting each variable to be assessed individually.

The above findings also show that one of the most important additional requirements in the formulation of a geoindicator is the strict delineation of its limits of applicability. In the graphical evaluation of water-rock equilibration by use of Fig. 9, two areas marked partially equilibrated waters and immature waters were distinguished. They are defined by the full equilibrium line and another apparently quite arbitrary curve separating the area where the Na-K-Mg-geothermometer may be applied with confidence from one representing immature waters likely to reflect the effects of rock dissolution rather than rock equilibration. In order to facilitate numerical evaluation, a "maturity index" measuring the degree of attainment of water-rock equilibrium would be useful. Such an index may be obtained by first combining the Na-K- and K-Mg-geothermometers as represented by the equations

$$t_{kn} = 1390/(1.75 - L_{kn}) - 273.2 \qquad (24)$$

$$t_{km} = 4410/(14.0 - L_{km}) - 273.2 \qquad (25)$$

to form a temperature independent equation for the full equilibrium curve according to

$$L_{kn} = 0.315L_{km} + 2.66 = sL_{km} + MI \qquad (26)$$

or

$$c_{Na} = 457c_K^{0.37}c_{Mg}^{0.315} = mic_K^{(1-2s)}c_{Mg}^s. \qquad (27)$$

The coefficient $s = 0.315$ represents the ratio of van't Hoff slopes for the two geothermometers, the value of $mi = 457$ the concentration of sodium required for given values of $c_K^{0.37}c_{Mg}^{0.315}$ to obtain full equilibrium. As discussed in detail above (Fig. 8), the major cause of non-attainment of water-rock equilibrium in geothermal solutions approaching full equilibrium is the slowness of the process supplying the comparatively large equilibrium contents of Na especially in lower temperature solutions. Lack of equilibrium, therefore, is likely to be reflected in Na-contents of the waters being too low. The apparently quite arbitrary line in Fig. 9 separating immature from partially equilibrated waters actually corresponds to a value of MI, the "maturity index", of 2.0 according to

$$MI = 0.315L_{km} - L_{kn} = 2.0 \qquad (28)$$