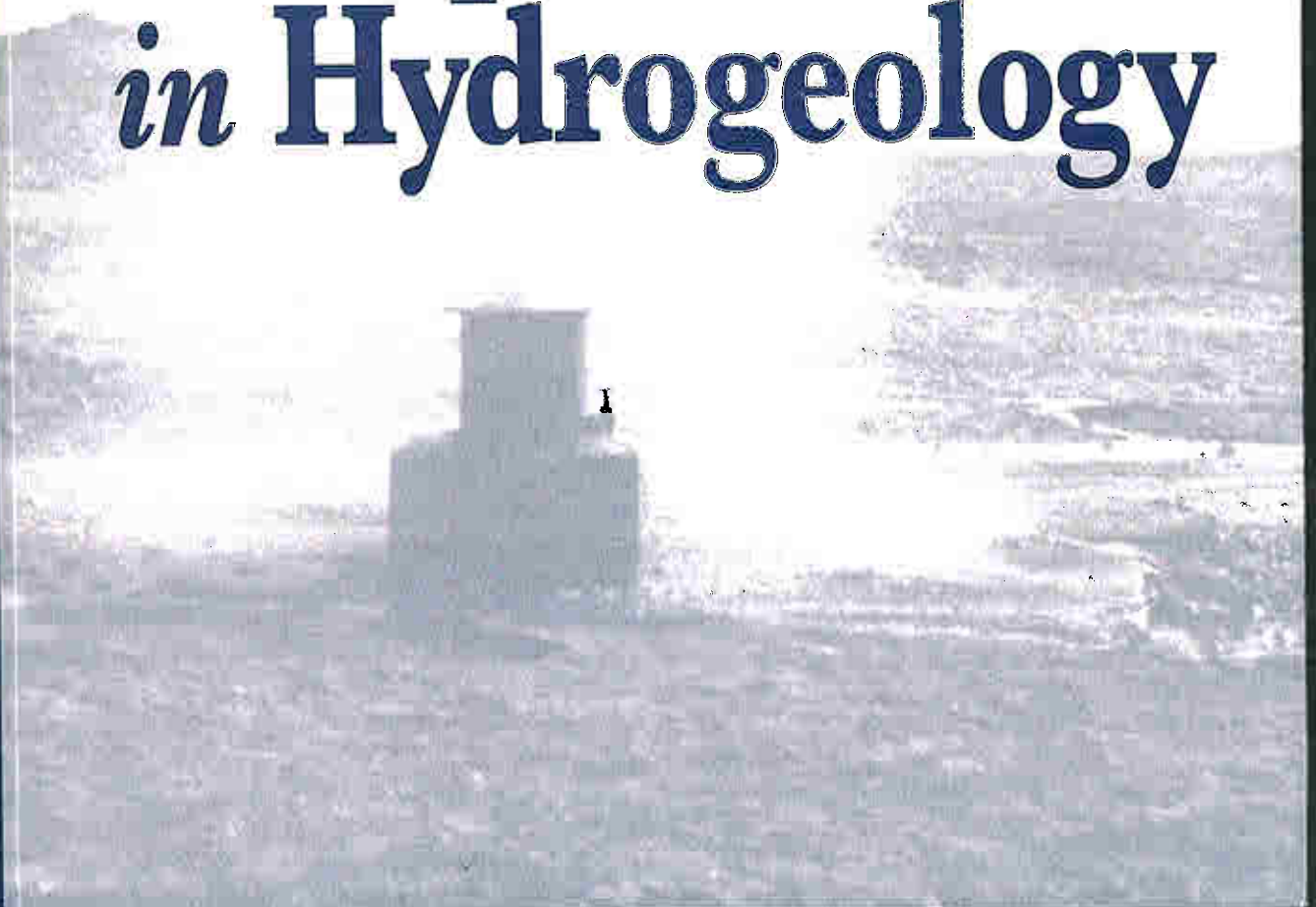# Ian Clark
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Environmental
Isotopes
in Hydrogeology

Subsurface steam separation

A second subsurface process that can affect the isotopic composition of thermal waters is steam loss in the subsurface. During ascent, >100°C a fraction of a geothermal water will flash to steam as the pressure diminishes. Fractionation during boiling imparts an enrichment on the residual liquid. Although the fractionation between water and steam is greatest at low temperature, it is significant at geothermal temperatures. For ^{18}O it is 5‰ at 100°C, and a little over 2‰ at 200°C (Table 1-4 and associated equations). Steam separation can take place as single step, multi-step or continuous processes (Truesdell et al., 1977), all of which affect the isotopic composition of the residual water. Arnason (1977) calculates the change in ^{18}O or ^2H contents of the liquid phase according to the following equation, which assumes that the steam and water remain in contact (closed system equilibrium conditions):

$$\delta_{w-low\,T} - \delta_{w-high\,T} = (1000 + \delta_{w-low\,T}) \cdot (1-[f + (1-f)/\alpha_{v-w}])$$

where high T and low T are the initial and steam-separation temperatures, respectively, and α_{v-w} is the vapour-water fractionation factor for the temperature of separation.

Depending on the degree of steam separation, which is a function of the initial and final temperature, the isotopic composition of the remaining thermal water may be enriched by up to several permil in ^{18}O. The isotopic composition of the geothermal waters in MC1 (Fig. 9-7) was calculated in this manner, from isotope measurements of post-flash (100°C) waters (Ghomshei and Clark, 1993).

Geothermometry

Maximum subsurface temperatures experienced by geothermal waters can be recorded by ionic and stable isotope ratios in solutes and the water itself. Such information is important in geothermal resource evaluation. It also reflects on depth of groundwater circulation, based on an understanding of regional tectonics and geothermal gradients. Geochemical and isotopic geothermometers developed over the past two decades rely on the assumptions that the two species or compounds coexisted and have equilibrated within the geothermal reservoir, that temperature is the main control on their ratio, and that re-equilibration has not occurred during ascent and discharge.

Cationic relationships: Studies of Na, K and Ca in aqueous systems suggest that cation concentrations are controlled by temperature-dependent equilibrium reactions with feldspars, mica and calcite. Several semi-empirical equations for the temperature have been determined on the basis of cation ratios (in ppm):

$$T°C = \frac{1217}{log(Na/K) + 1.483} - 273 \qquad \text{(Ellis and Mahon, 1967)}$$

$$T°C = \frac{1647}{log(Na/K) + \beta\,[log(\sqrt{Ca}/Na) + 2.06] + 2.47} - 273$$

where $\beta = \frac{1}{3}$ for Na waters and $\beta = \frac{4}{3}$ for Ca waters   (Fournier and Truesdell, 1973)

At temperatures less than about 200°C, the solubility of magnesium silicate increases and Mg plays a role in the controlling reactions, which must be accounted for (Fournier and Potter, 1979). In lower temperature or high salinity systems, other cations relationships including Na/Li and Mg/Li are important, e.g.:

$$T°C = \frac{2200}{\log(\sqrt{Mg} / Li) + 5.47} - 273 \qquad \text{Kharaka and Mariner (1987)}$$

The principal drawback to these chemical geothermometers is that given time or low water-rock ratios, re-equilibration can occur through exchange reactions at lower temperatures during ascent.

Silica solubility: The increased solubility of quartz and its polymorphs at elevated temperatures has been used extensively as an indicator of geothermal temperatures (Truesdell and Hulston, 1980; Fournier and Potter, 1982). In systems above about 180 to 190°C, equilibrium with quartz has been found to control the silica concentration, whereas at lower temperatures, chalcedony is the controlling phase (Arnasson, 1976). These relationships are graphically presented in Fig. 9-6. Temperature can be derived from the following relationships for equilibrium with these silica polymorphs from 0 to 250°C, where Si concentrations are in ppm (from Fournier, 1981):

Quartz (no steam loss) $\quad T°C = 1309/(5.19 - \log Si) - 273$

Quartz (max. steam loss) $\; T°C = 1522/(5.75 - \log Si) - 273$

Chalcedony $\qquad\qquad\quad T°C = 1032/(4.69 - \log Si) - 273$

Amorphous silica $\qquad\quad T°C = 731/(4.52 - \log Si) - 273$

$\Delta^{18}O$ in sulphate-water exchange: Although several isotope exchange reactions can be used as indicators of subsurface temperatures, the exchange of ^{18}O between dissolved sulphate and water is often the most useful because equilibration is rapid at reservoir temperatures greater than about 200°C and pH less than 7, conditions that favour SO_4^{2-}–H_2O exchange. Below reservoir temperatures of 150 to 200°C, the abiotic exchange half-time increases exponentially from several years to some 10^6 years at 100°C and pH 7 (Chiba and Sakai, 1985). Only during bacterial sulphate reduction can accelerated ^{18}O exchange take place. Recall from Chapter 6 that during this process $\delta^{18}O_{SO_4}$ increases asymptotically towards an equilibrium value with the water at the ambient temperature. If sulphate reduction in the discharge area is not important, then a measure of the reservoir temperature is often preserved. These two equations provide similar estimates:

$$10^3 \ln\alpha^{18}O_{SO_4\text{-}H_2O} = 3.251 \cdot 10^6\, T^{-2} - 5.1 \qquad \text{(Mitzutani and Rafter, 1969)}$$

$$10^3 \ln\alpha^{18}O_{SO_4\text{-}H_2O} = 2.88\ \cdot 10^6\, T^{-2} - 4.1 \qquad \text{(McKenzie and Truesdell, 1977)}$$

$\Delta^{34}S$ in SO_4^{2-}-H_2S exchange: In geothermal systems where both dissolved sulphate and sulphide are present, the large temperature-dependent fractionation of ^{34}S can be a useful geothermometer. Exchange is fast under acidic conditions, although exchange at near-neutral pH can take hundreds of years (Truesdell and Hulston, 1980) and so ascending fluids can preserve their temperature record. The exchange follows the following reaction:

$$10^3 \ln\alpha_{SO_4\text{-}H_2S} = 5.07 \cdot 10^6\, T^{-2} + 6.33 \qquad \text{(Robinson, 1973)}$$

$\Delta^{13}C$ *in CO_2-CH_4 exchange:* In groundwaters where methane coexists with dissolved inorganic carbon, ^{13}C will exchange through the reaction:

$$CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2H_2O$$

The temperature of equilibration can be calculated from the relationship of Bottinga (1969):

$$10^3\,ln\alpha^{13}C_{CO_2\text{-}CH_4} = 2.28\,(10^6\,T^{-2})^2 + 15.176\,(10^6\,T^{-2}) - 8.38$$

or of Richet et al. (1977):

$$10^3\,ln\alpha^{13}C_{CO_2\text{-}CH_4} = -0.62 \cdot 10^9\,T^{-3} + 6.616 \cdot 10^6\,T^{-2} + 6.04 \cdot 10^3\,T^{-1} - 3.08$$

At high temperature, isotopic equilibrium is achieved quickly and is preserved in gases discharging from geothermal systems. However, re-equilibration often takes place as geothermal waters move into shallower zones at lower temperatures during ascent. In low temperature systems, isotopic equilibrium between CO_2 and CH_4 can be achieved during bacterial activity (Truesdell and Hulston, 1980).

Δ^2H *in H_2-H_2O exchange:* The H_2-H_2O pair is one of the few that give consistent agreement. Equilibration is faster for this exchange reaction than other geothermometers. Consequently, calculated temperatures are often closer to discharge temperatures than reservoir temperatures. Calculations can be made using a combination of the temperature equations for ^2H fractionation between H_2O vapour and water, and between H_2 and H_2O vapour (Table 1, inside front cover).

Low Temperature Water-Rock Interaction

The "geothermal shift" observed for $\delta^{18}O$ in geothermal groundwaters is a trend towards isotopic equilibrium between ^{18}O-depleted meteoric waters and ^{18}O-enriched rocks at high temperature. In lower temperature environments, however, the reverse can be observed. Increased fractionation between water and minerals results in ^2H-enriched and ^{18}O-depleted waters that plot above the meteoric water line. Retrograde exchange between water and primary silicate minerals, and hydration of primary silicates, are the two dominant exchange reactions.

Two conditions are required if significant shifts are to be observed: (i) very low water-rock ratios where the rock reservoir dominates in exchange reactions, and (ii) geological time scales, because rates of exchange and hydration are slow at low temperature. The crystalline rocks of most shield terrains host brines that meet these criteria, and exhibit these trends.

Hydration of primary silicate minerals

Below temperatures of about 300°C, the hydration of silicate minerals becomes an important reaction affecting the isotopic evolution of water in crystalline rocks. Reactions such as the alteration of feldspar (anorthite) to clay (kaolinite):

$$CaAl_2Si_2O_8 + 3H_2O \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4 + 2OH^-$$
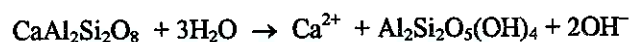
result in a significant uptake of water. Fractionation of ^{18}O occurs between the fluid and the silicate structure as well as between the fluid and mineral hydration water. For ^2H, fractionation