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OXYGEN ISOTOPE EXCHANGE IN RELATION TO HYDROTHERMAL ALTERATION OF ROCKS

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ABSTRACT

Oxygen isotope data from unaltered 'to intensely altered rocks indicate that substantial ^{18}O-exchange precedes the visible effects of hydrothermal alteration. The cumulative water to rock mass ratios calculated from the ^{18}O-data are generally less than 1; values more than 1 are less sensitive to ^{18}O-exchange. These ratios correspond to tines when rock and fluid attained δ^{18}O compositions close to their current values, a situation that probably occurs during the early part of the history of most geothermal systems. Water/rock ratios which are calculated on the basis of leaching and addition of some common and rare alkalies during hydrothermal alteration, however, are in comparison higher by two orders of magnitude. This is because these latter ratios relate to much slower processes and are affected by subsequent fluid throughput during the entire history of the system.

INTRODUCTION

Several factors, varying in relative importance between geothemal fields affect the formation of hydrothermal minerals and shifts in oxygen isotope composition of reservoir rocks. These factors are temperature, rock type, permeability, fluid composition and duration of activity. The two processes of hydrothermal alteration and ^{18}O -exchange therefore, are normally assumed to be comparable, and most extreme shifts in the ^{18}O composition would therefore be expected in rocks showing intense hydrothermal alteration. However, this is not necessarily true. In the Wairakei geothermal field, for example, andesite and ignimbrite cores with almost unaltered plagioclase record the lowest δ^{18}O values, 2.6 to 3.3‰ SMOW, i.e. they are depleted by *4* to 5‰ (Clayton and Steiner, 1975). Such contrasts in the intensity of alteration and extent of 180-exchange may be a function of chemical and isotopic composition of the fluid. For example, calcic plagioclase may persist to a temperature of 323°C even in intensely altered rocks due to high Ca^{++}-activity in the fluid (Muffler and White, 1969). Similarly, K-feldspar may be stable in high pH and K^+-activity fluids. Such a feldspar, however, will tend to .exchange its ^{18}O depending on the δ^{18}O composition of the fluid and the prevailing temperature; it could end up with an appreciably depleted value in spite of being mineralogically unaltered.

Contrary to this, an uncommon situation could exist where hydrothermally altered rocks display very little or no 180-shift. An example for such a case is the Ngawha geothermal field, NZ, where basement' greywackes and argillites have hydrothermal mineral assemblages comprising quartz-calcite-chlorite-illite-epidote-clinozoisite (Browne, 1981), but still retain their original δ^{18}O value of ~12‰ (Blattner, 1985A) due to the presence of a fluid, with δ^{18}O = +5.5‰ (Sheppard, 1984), not capable of exchanging ^{18}O with the basement rocks. Except for such rare situations, ^{18}O-shift always accompanies hydrothermal alteration, but the two may not correspond to one another. The intensity of alteration need not necessarily correspond to the cumulative fluid throughput due to stability of feldspars in **some** fluid environments, but ^{18}O-exchange between feldspars and fluid always will under the temperature conditions of geothermal systems. Current work on the ^{18}O - composition of the greywacke basement underlying geothermal fields in the Taupo Volcanic Zone (Absar, unpublished data, Blattner 1985B) strongly suggests that feldspars are, in general, metastable under prevailing conditions and get appreciably depleted in their ^{18}O content before being visibly altered. This is because the ^{18}O-exchange between fluid and minerals (particularly feldspars) is faster than their hydrothermal alteration.

RELATIVE RATES OF ^{18}O-EXCHANGE AND HYDROTHERMAL ALTERATION

Quartz and feldspars make up to 75% of rocks such as greywackes and argillites. Quartz is well known to retain its ^{18}O-composition under geothermal conditions, however, feldspars have a very fast rate of 180-exchange and will attain equilibrium with the fluids even under laboratory conditions (O'Neil and Taylor, 1967). The δ^{18}O values of a number of slightly altered greywacke samples from the Kawerau and Broadlands geothermal fields indicate that most of the feldspar fraction must have exchanged Oxygen isotopes with solutions to attain near equilibrium values. Greywacke samples from wells KA-22 and 31 at Kawerau, with unaltered to partially altered feldspar grains, have δ^{18}O values of 4.8 to 5.01‰. It is impossible to account for such low whole rock δ^{18}O values (depleted by> 5‰) without attributing a value of ~3‰ to the feldspar fraction, as quartz which makes up to 20% of the rock still retains its original value of ~12‰. Similarly, 3 Broadlands greywacke samples (wells BR-24, *43* and *44)* with primary quartz contents of 15 to 20% and unaltered feldspar grains among others partially or totally altered, have δ^{18}O values of 2.28 to **3.83‰**. Assuming as at Kawerau, that the quartz still retains its original δ^{18}O value, the ^{18}O-composition of the feldspar fraction in these samples can be calculated as *0.4* to 1.5‰, i.e. it is in equilibrium with the fluid of δ^{18}O = -4.5‰ (measured by Giggenbach (1971)).

These samples from Kawerau and Broadlands geothermal fields clearly indicate that substantial ^{18}O-shift of 4 to 5‰ or greater could precede alteration in feldspars. This is further substantiated by the oxygen isotope analysis of **a** greywacke core from the Rotokawa geothermal field (RK-4/2577m). The primary feldspars in this sample are relatively little altered (Browne, 1984), yet the whole rock δ^{18}O value of the sample is 4.82‰; this comprises 25% quartz with δ^{18}O =11.7‰ and a 75% 'feldspar' fraction' with δ^{18}O = 2.5‰ (Blattner, 1985B). The feldspars therefore have been shifted from 8 to 2.5‰ i.e. by -5.5‰. Regardless of the extent of mineralogical alteration, therefore, if a rock has been depleted in ^{18}O, this isotope must have been removed by the fluid. This indicates that for the feldspars, 180-exchange is **a** faster process than the accompanying hydrothermal alteration.

WATER TO ROCK RATIOS

Taylor (1971) used ^{18}O data as evidence **for** large scale interaction between meteoric groundwaters and igneous intrusions, and calculated the water to rock mass ratios responsible for ^{18}O-**shift** in these epizonal bodies. Taylor's model was modified by Blattner (1981, 1985A) for more direct application to geothermal systems and estimation of the fraction of 180–exchange towards equilibrium. According to this zero dimensional 'nixed–model':

$$\Phi = -\ln\left(\frac{\sigma_R}{P} + 1\right) \qquad (1)$$

where Φ = water to rock ratio in terms of atom % oxygen

σ_R = δ Rock Final $-\delta$ Rock Initials
negative shift in the rock

P = (δRock Initial $-\delta$Water Initial)
− (δRock Final $-\delta$ Water Final)

= δ Rock Initial − &water Initial $-\Delta$,
isotope shifting potential

Δ = δ Rock Final $-\delta$Water Final,
equilibrium isotope fractionation

Equation 1 can be written as:

$$\frac{\sigma_R}{\ } = (e^{-\Phi} - 1)$$

This ratio, $-(\sigma_R/P)$ is the 'fraction of ^{18}O-**exchange** as it is zero **when** $\sigma_R = 0$, i.e., there is no shift in the rock, and 1 when rock is shifted down by the value equal to P. Figure 1 plots $-(\sigma_R/P)$ against 4 and water to rock mass ratio (W/R). The curve shows that ^{18}O-**exchange** is very fast in the beginning but gradually slows with increasing cumulative fluid throughput. By the time the W/R ratio reaches the value of 1 ($\Phi = 2$), more than 85% of 180–exchange has already taken place. The rate of 180–exchange decreases drastically beyond the mass ratio of 1 on the flat portion of the curve and 99.75% exchange is attained at a mass ratio of 3. Theoretically, 100% exchange takes place when W/R ratio reaches 7.5 (Φ =15). No more 180–exchange is then possible. It is possible that an 180–exchange of 90 to 95% never takes place due to the exceptionally slow rate of exchange resulting from the exhausted isotope shifting capacities of the rock and water. This is indicated by calculated W/R ratios for the various geothermal fields (Blattner, 1985A) and epizonal igneous intrusions (Taylor 1979), which are generally less than, or near to 1.

These W/R ratios with a typical value of 1 do not even compare with W/R ratios calculated on the basis of leaching and addition of some common and rare alkalies during hydrothermal alteration for Wairakei and Broadlands geothermal fields; these have W/R values of 100 (Goguel, 1983). Very high values, up to infinity, of W/R ratios may be calculated if it is assumed that the meteoric water entering the reservoir 'pre–shifted' to, or close to, its present value. This has been suggested by Goguel (1983) as a compromise between ratios calculated from the isotope data and hydrothermal alteration. This suggestion can be easily analysed in the light of ^{18}O-**data** from Rawerau and Broadlands fields. The lowest $\delta^{18}O$ vnlues for the greywacke in these two fields are 2.9‰ and 1.5‰ , respectively. Such low values can not be attained by exchanging with fluids of $\delta^{18}O$ value higher than −4.35‰ for Kawerau and −5.75‰ for Broadlands. These values are only 1.25‰ higher than the respective meteoric waters and define the maximum permissible limit of 'pre–shifting'. Using the $\delta^{18}O$ values of the 'pre–shifted' meteoric water, high W/R ratios of 3.5 may be Calculated instead of the values shown (Fig. 1), but not higher by the orders of magnitude as suggested by Goguel (1983).

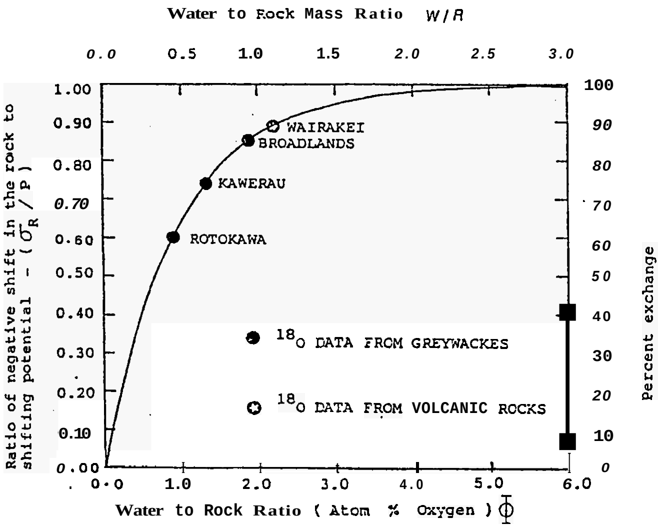

Fig. 1: Oxygen isotope exchange in the reservoir rocks of geothermal systems as a function of cumulative water to rock ratio. Note that exchange to 85% requires a water to rock mass ratio of only 1 under ideal conditions. The distribution of four New Zealand geothernal fields along the curve suggests their respective approach towards a near equilibrium condition.

DISCUSSION

The W/R ratios calculated from the ^{18}O-data and those from leaching and addition of cations during hydrothermal alteration are greatly different. The reason **for** their not being comparable is depicted in Fig. 1. Exceptionally low ratios, calculated from the isotope data, point to a very fast rate of ^{18}O-exchange which substantiates the argument presented earlier that feldspars register the effect of ^{18}O-exchange long before their hydrothermal alteration products become conspicuous. This, in turn, indicates that rock and fluid tend to attain ^{18}O compositions close to their current values during the early history of a geothermal system. This is evidenced by 2 to 3% vein calcite with a $\delta^{18}O$ value(s) being in equilibrium with present day fluid, circulating in the greywackes at Kawerau and Broadlands. From the calcite solubility data of Ellis (1963) it can be calculated that W/R ratios of 150 may be responsible for the precipitation of observed content of calcite. This means that for a period corresponding to a cumulative W/R ratio of 150 the average $\delta^{18}O$ **value** of the fluid, and consequently of the rock, has remained nearly constant. The process of hydrothermal alteration has obviously continued uninterrupted during this period resulting in the precipitation of calcite incorporating Ca^{++} released into the solution through alteration of plagioclase to illite.

CONCLUSIONS

1. Substantial isotope exchange precedes the first appearance of hydrothermal alteration products.

2. Slightly altered rocks which record ^{18}O-**shifts** similar to those of intensely altered rocks probably did not remain in contact with thernal fluid long enough to register pronounced effects of alteration, due to sealing of fractures with precipitated minerals. Before the circulation ceased, rocks had already attained $\delta^{18}O$ composition close to their observed values.

3. Water–to–rock mass ratios calculated from ^{18}O-data are generally less than 1. Values more than 1 **are** rare, and above 7.5, not possible.

4. The W/R ratios calculated from the ^{18}O data and hydrothermal alteration correspond to two different periods during the history of a geothermal system. The W/R (isotope) ratios correspond to a time when rock and fluid attained ^{18}O compositions close to their observed values, an event that occurred in the early history of a geothermal system. The W/R (alteration) ratios on the other hand reflect cumulative fluid throughput during the entire life of the system.

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