

Mechanisms and Rates of Oxygen Isotope Exchange in Experimental Hydrothermal Systems.

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In order to use isotopic exchange between rocks and fluids as an effective monitoring and predictive tool in dynamic hydrothermal systems, the isotopic shifts accompanying the interaction must be quantified as a function of the chemical and physical parameters which control the system. An isotopic study was undertaken to quantify the influence of temperature, solution chemistry, rock type, surface area, system size and time on the isotopic shifts during granite-water interaction. Specifically, changes in solution chemistry, mineralogy and the isotopic compositions of solutions and rocks were monitored through time as alteration reactions proceeded. This information was used to determine the mechanisms and rates of oxygen isotopic exchange reactions during alteration.

A total of 34 granite (microcline)-water experiments were conducted at temperatures of 200° to 300°C. Solution compositions were varied from pure water to 1m NaCl, with times of interaction ranging from 35 to 1006 hours. The experiments were carried out in either Barnes-type rocking autoclaves, circulating or static hydrothermal apparatus, with water/rock mass ratios ranging from 0.3 to 10.

The experimental interaction of granitic rock with hydrothermal solutions resulted in the production of propylitic alteration assemblages dominated by chlorite, zeolites, sericite, hematite and albite. The abundances of these minerals increased with an increase in temperature, surface area of rock, time

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and salinity of the solution. The magnitudes of isotopic shifts in fluids and rocks accompanying alteration also increased with increasing temperature, salt concentration, surface area and time (see Fig. 1). Solution compositions came to steady state after a few weeks and were shown to be in equilibrium both chemically and isotopically with many of the alteration phases observed in run products.

In order to quantify the isotopic exchange process, a model was developed to describe the kinetics of rock (mineral)-water reactions, which is applicable to isotopic exchange accompanying alteration. The equation for the oxygen isotopic exchange reaction between rock and water can be given as:



where r_1 and r_2 are the rates of the forward and reverse reactions, respectively. The parameters W_1 and W_2 are the number of atoms of ^{16}O and ^{18}O in the water, respectively, and R_1 and R_2 are the number of atoms of ^{16}O and ^{18}O in the rock, respectively. From this relationship, an equation has been derived to express the rate of isotopic exchange between solids and fluids:

$$r_1 = \frac{-\ln(1-F)}{W + R} \left(\frac{WR}{A} \right) \left(\frac{1}{t} \right) \quad (2)$$

The rate of exchange (r_1) is shown to be proportional to the degree of disequilibrium ($1-F$, where F is the fraction of exchange) and the product of the number of moles of oxygen in water (W) and rock (R), and inversely proportional to the surface area of the rock (A , in m^2), the sum of the moles of oxygen in water and rock and reaction time (t , in seconds).

Estimates of rate constants (moles/ m^2 sec) obtained from our experimental data indicate that whole rock-solution isotopic exchange rates are several orders of magnitude faster than isotopic exchange controlled by diffusion. In addition, the whole rock-water exchange rates are comparable to rates

predicted by equation (2) for oxygen exchange in mineral-water systems dominated by hydrolysis or dissolution reactions described in the literature (see Fig. 2). The fractions of exchange (F) were taken directly from the data tables given in each paper, with the WR, W+R and A values estimated from their experimental conditions. Whole rock and mineral-water reactions dominated by hydrolysis and dissolution exhibit activation energies (E_{act}) of 9 to 17 Kcal/mole, while diffusion-controlled oxygen exchange reactions in feldspars have E_{act} values ranging from 21 to 27 Kcal/mole.

By rearranging the isotopic rate equation(2), the time of interaction can be solved as a function of surface area, system size (WR/W+R) and rate at a particular temperature. Thus, the time to isotopic equilibration (F=1.0) was found to increase with decreasing surface area and decreasing temperature. However, if the system size was increased, the time to isotopic equilibrium decreased.

Model calculations were performed to compare the times required to attain a certain fraction of exchange for alteration and diffusion-controlled reactions. For example, if a K-feldspar grain with a radius of 0.05cm is reacted with a 1m NaCl solution at 350°C and a water/rock mass ratio of 1, approximately 80% of the isotopic exchange will occur in 3 years. If the oxygen isotopic exchange occurs through a diffusional mechanism, 80% exchange is not achieved until 8×10^4 years. These calculations suggest that in natural systems, isotopic exchange proceeds in two stages. The earlier stage is alteration controlled, with the attainment of isotopic equilibrium occurring between minerals and solutions. After the alteration is completed, oxygen diffusion between unaltered, residual minerals and solution controls the second stage of rock equilibration with the fluid.

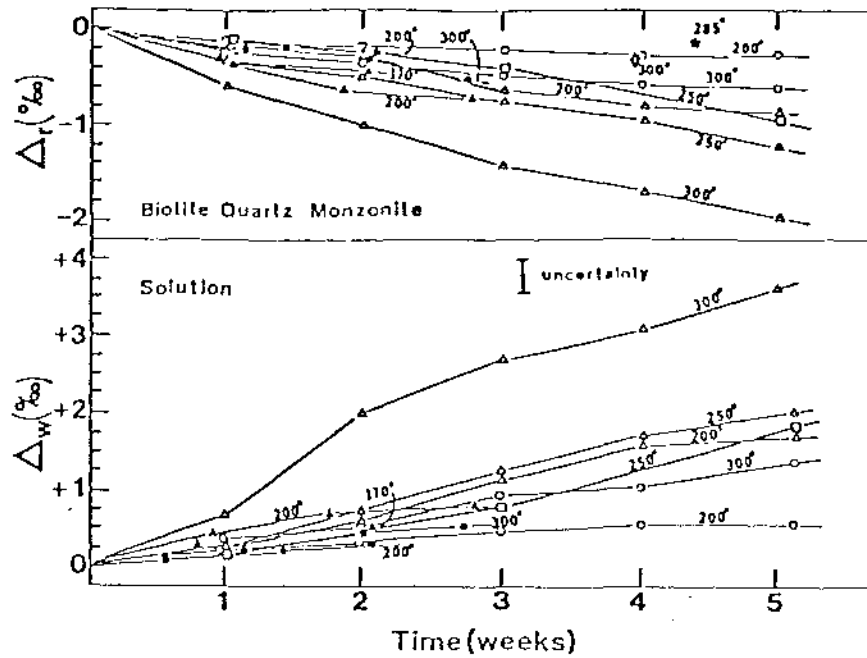


Figure 1. Changes in the oxygen isotopic composition of biotite quartz monzonite (Δ_r) and solutions (Δ_w) as a function of reaction time, temperature and solution type. Circle = pure water, triangle = 0.1m NaCl, square = 0.1m KCl, star = 0.1m NaCl(Disc run), diamond = 1.0m NaCl(Disc run). The open symbols = static system, solid symbols = circulating system.

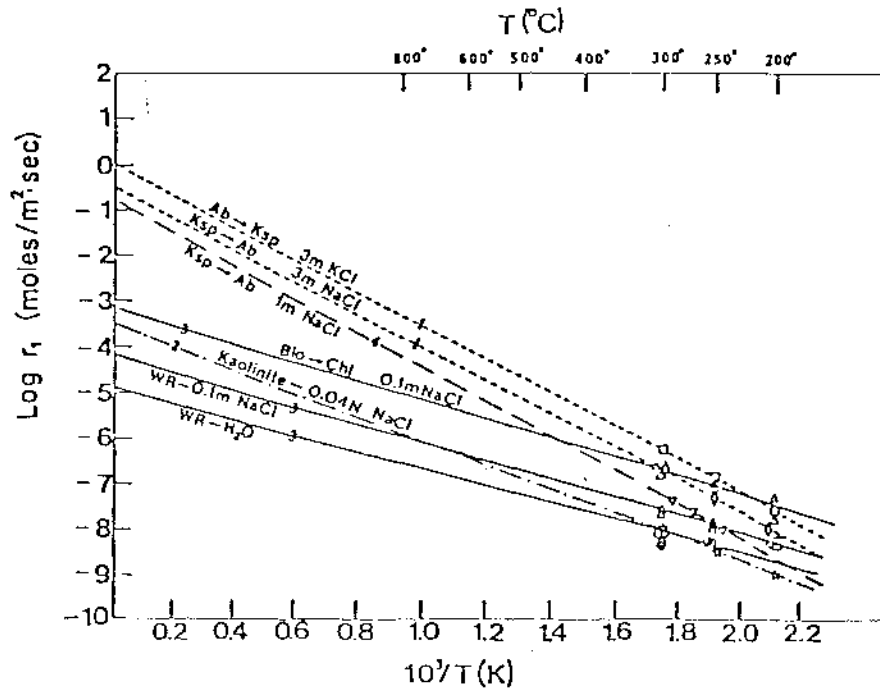


Figure 2. Arrhenius plot of experimentally determined oxygen isotopic rate constants. Circle = pure water, triangle = 0.1m NaCl, star = 0.04N NaCl, inverted triangle = 1.0m NaCl, square = 3.0m KCl, diamond = 3.0m NaCl, line (1) computed from the data of O'Neil and Taylor(1967), (2) computed from O'Neil and Kharaka(1976), (3) and (4) are from this study.