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Possible evidence for fluid-rock oxygen isotope disequilibrium in hydrothermal systems

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**ABSTRACT:** There is ample evidence from geothermal systems that isotope temperatures estimated from the oxygen isotope fractionation between alteration phases and coexisting aquifer fluids agree closely with measured bore-hole temperatures. Similar, but limited evidence is found in epithermal vein deposits where isotope temperatures agree well with fluid inclusion homogenization temperatures. Conversely, many hydrothermal systems exhibit varying degrees of fluid-rock oxygen isotope equilibration (measured  $\alpha_{r-w}$  equilibrium  $\alpha_{r-w}$ ). There appears to be a crude relationship between increasing degree of equilibration and increasing temperature and salinity. The observed variations in the degree of exchange may have resulted from local, self-sealing of the fracture network prior to equilibration. The ability for fractures to remain open or to propagate allowing continued fluid flow may be the deciding factor in the attainment of isotopic equilibration.

1. INTRODUCTION

During fluid flow, the most important process by which the oxygen isotopic composition of the hydrothermal fluid may be altered prior to mixing and boiling at or near the surface, is through oxygen isotope exchange with silicates and carbonates at depth (Craig, 1963). The magnitude of the oxygen isotopic shifts in waters and rocks is controlled by the temperature of the interaction, the relative proportions of rock and fluid, the initial difference in the  $\delta^{18}O$  values between the rock and fluid, and whether the system is open or closed to flow. The final rock-fluid isotope fractionation ( $\alpha_{r-w}$ ) is dependent only upon temperature for systems that have attained equilibrium. For non-equilibrium rock-fluid interaction, isotopic exchange is influenced not only by temperature, but also fluid composition, mineralogy, fluid/rock ratio, surface area (permeability) and time. The purpose of this communication is three fold. First, we will assess the degree of isotopic equilibration between alteration phases (veins, pore-filling, matrix) and co-existing fluids. If we can demonstrate that a fluid of known isotopic composition has equilibrated with a given alteration assemblage, then we can assess the reaction progress or degree of exchange between bulk

rock and fluid, knowing that the two are related temporally. Upon demonstration that a given system exhibits fluid-rock isotope disequilibrium, we can begin to examine the relationships between the degree of exchange and variables such as temperature, solution composition and permeability. This approach differs from that described by Blattner (1985), who used an equilibrium model to assess the magnitude of incremental isotope shifts in fluids and rocks from selected geothermal systems.

2. ISOTOPIC DATA

Isotopic data on fluids and solids were selected from both active and fossil hydrothermal systems where a single fluid-type dominated (e.g., meteoric water, seawater) and the host rocks were igneous derived - i.e., volcanic, plutonic, or their weathered equivalents. For the fossil systems, we assumed that vein fluids approximated wall-rock fluids, thereby allowing use of fluid inclusion information (temperatures, compositions). Wherever possible, the effects of boiling and mixing on isotope budgets have been accounted for so that reservoir isotope values for the fluids were used in the model calculations. The isotope compositions of unreacted

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fluids and solids are known or can be inferred quite accurately for all of the systems studied. Isotope compositions of bore-hole fluids are used for the geothermal systems, whereas calculated fluid isotope compositions (in equilibrium with vein assemblages) are used for the epithermal ore deposits. With the exception of the Reykjanes, Iceland geothermal system, fluids from the remaining 11 geothermal areas and 7 ore systems exhibit characteristic  $^{18}\text{O}$  shifts, with little or no D/H shift.

### 3. MINERAL-FLUID ISOTOPE FRACTIONATION

In order to directly compare fluid isotope shifts with those measured in the bulk rock, we need to demonstrate that some or preferably all of the alteration phases have equilibrated with a common fluid of known origin and composition. This will give us a strong indication that the fluid and altered rock are related temporally. Figure 1 shows isotopic temperatures plotted against measured temperatures for a variety of geothermal systems. An agreement of  $\pm 30^\circ\text{C}$  (dashed lines) is considered evidence for equilibration given the errors in both the fractionation factors and measured down-hole temperatures. Data on Fig. 1a-c indicate that the agreement between isotopic and measured temperatures is good for all phases examined from most of the geothermal systems suggesting that the bore-hole fluids and the observed alteration are temporally related. This is particularly true for Wairakei, Cerro Prieto, Reykjanes, Svartsengi, and Krafla. Notable exceptions include the lower chlorite and calcite-fluid temperatures estimated for the Roosevelt Hot Springs system and lower quartz-fluid isotope temperatures for Broadlands and Salton Sea.

### 4. ROCK-FLUID ISOTOPE FRACTIONATION

The oxygen isotope fractionations ( $\alpha_{T-w}$ ) between the altered rocks and coexisting fluids have been calculated for the geothermal systems and epithermal vein deposits, and are plotted against measured temperatures on Figs. 2a and 2b, respectively. Also shown for reference are the equilibrium isotope fractionation curves for the systems: (1) granite/rhyolite-, (2) granodiorite/dacite-, and (3) andesite/basalt-fluid. These curves are based on equilibrium alteration mineral assemblages predicted from rock-water interaction simulated through mass transfer

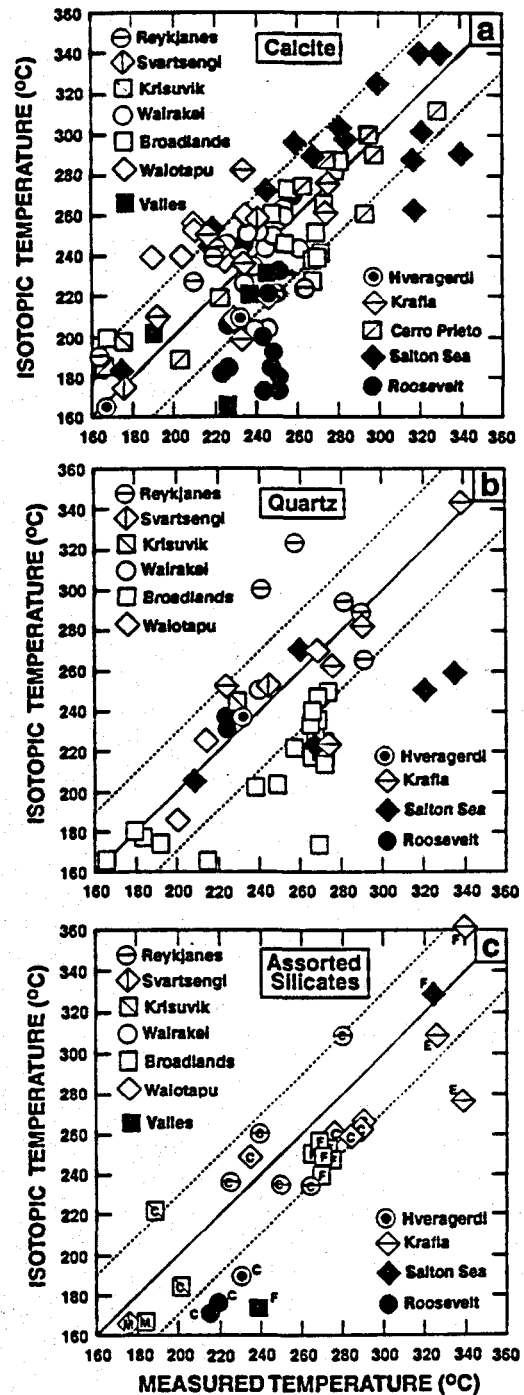


Fig. 1 Mineral-fluid isotope temperatures versus bore-hole temperatures. (a) calcite, (b) quartz, (c) assorted silicates.

computations (Bowers and Taylor, 1985; Cole et al, 1987, 1992). With the exception of the Salton Sea, all of the geothermal systems exhibit some degree of deviation from equilibrium isotope fractionation. For example, equilibrium fractionation between altered granite/rhyolite and water is about 6 per mil at 250°C, but rhyolitic systems such as Wairakei and Valles yield maximum fractionations of 10 and 14 per mil, respectively. For any given system, typical deviations from equilibrium rock-fluid fractionation range from a few per mil to over 8 per mil.

The observed rock-fluid isotopic fractionations in the vein-type ore deposits, detailed in Fig. 2b, also show apparent disequilibrium tendencies. For example, fractionation at Goldfield ranges from 8.3 to 14.4 per mil, whereas the expected equilibrium value at 250°C is 5.1 per mil. Most of these deposits exhibit a significant range in rock-fluid fractionation, similar in magnitude to ranges observed in the geothermal systems. We might conclude from this analysis that within a given hydrothermal system, isotope equilibrium may occur in some locales (or depths) but not others. In some deposits, such as Sunnyside, the degree of equilibration varies considerably over distances of only a few meters.

## 5. DISCUSSION

The extent of fractional approach to oxygen isotope equilibrium in these hydrothermal systems can be expressed in the familiar form of  $F$ , as derived by Northrop and Clayton (1966):

$$F = (\alpha^t - \alpha^f) / (\alpha^t - \alpha^{eq}) \quad (1)$$

where the  $\alpha$ 's are the isotopic fractionation factors between rock and fluid at time  $t$  ( $\alpha^t$ ), at time=0 ( $\alpha^f$ ) and  $t$ - $\alpha^{eq}$ ). We have used the following equilibrium isotope fractionation equations to estimate the  $\alpha$ 's for granite/rhyolite (Cole et al, 1992) and andesite/basalt (Cole et al, 1987), respectively.

$$1000 \ln \alpha_{gran-f} = 2.68(10^6/T^2) - 3.57 \quad (2)$$

$$1000 \ln \alpha_{bas-f} = 2.75(10^6/T^2) - 7.25 \quad (3)$$

Curves have also been calculated for compositions intermediate to these two end-members.

Values for the degree of equilibration ( $F$ ) fall between about 0.45 and 1.0 for the Hveragerdi, Iceland vary from 0.45 to about

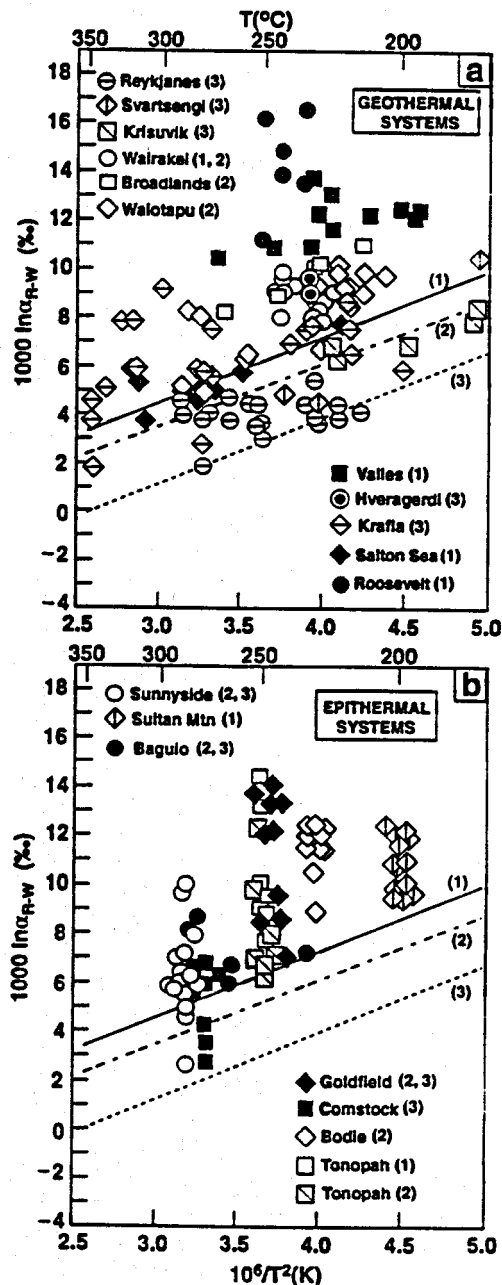


Fig. 2 Isotope fractionation between rocks and fluids in (a) geothermal or (b) epithermal systems.

hydrothermal systems under consideration, with each system exhibiting its own distinct range. For example,  $F$  values from

