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Isotopic Constraints on the Chemical Evolution of Geothermal Fluids, Long Valley, CA

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ABSTRACT

A spatial survey of the chemical and isotopic composition of fluids from the Long Valley hydrothermal system was conducted. Starting at the presumed hydrothermal upwelling zone in the west moat of the caldera, samples were collected from the Casa Diablo geothermal field and a series of monitoring wells defining a nearly linear, ~14 km long, west-to-east trend along the proposed fluid flow path (Sorey et al., 1991). Samples were analyzed for the isotopes of water, Sr, Ca, and noble gases, the concentrations of major cations and anions and total CO₂. Our data confirm earlier models in which the variations in water isotopes along the flow path reflect mixing of a single hydrothermal fluid with local groundwater. Variations in Sr data are poorly constrained and reflect fluid mixing, multiple fluid-pathways or water-rock exchange along the flow path as suggested by Goff et al., (1991). Correlated variations among total CO₂, noble gases and the concentration and isotopic composition of Ca suggest progressive fluid degassing (loss of CO₂, noble gases) driving calcite precipitation as the fluid flows west-to-east across the caldera. This is the first evidence that Ca isotopes may trace and provide definitive evidence of calcite precipitation along fluid flow paths in geothermal systems.

Introduction

The efficiency of heat extraction from geothermal reservoir rocks is limited by chemical processes and the physical characteristics of the reservoir. Specifically, mineral dissolution and precipitation and the geometry of heat and mass exchange between fluids and the reservoir lithologies of fractured dominated systems define the long term efficiency of heat extraction but are difficult to quantify and therefore predict. Increased knowledge about the water-rock exchange in geothermal systems and the size and

spacing of the major fluid transporting fractures would be valuable information that impact decisions guiding the management of natural and enhanced geothermal systems.

The chemical composition of a geothermal fluid records the net product of mineral dissolution and precipitation, but does not provide information regarding the relative importance of mineral dissolution and precipitation along and affecting the fluid flow path. Isotopic systems, such as oxygen and strontium (a trace element in natural waters), provide additional constraints on the processes occurring as a result of water-rock exchange. Perhaps the best example is the well known shift in water oxygen isotopes as the ¹⁸O depleted water exchanges with ¹⁸O-enriched reservoir minerals. The extent of the oxygen shifts provides constraints on water/rock ratios and temperature of exchange (Craig, 1956). The isotopic composition of Sr in fluids has been used to track mineral dissolution along a flow path (Goff et al., 1991; Johnson and DePaolo, 1994; 1996). Recently, evidence has been found that calcium, a major cation in most natural waters, can be fractionated during the precipitation of calcite (Jacobson and Holmden, 2008). In this case, the precipitated calcite is depleted in the heavier isotopes of calcium while the residual Ca in the fluid is enriched. Therefore, calcium isotope data may preserve a record of mineral precipitation.

In addition to information about water-rock ratios and mass exchange, coupled isotopic systems can provide important constraints on reservoir characteristics. For instance, it has been recently proposed (DePaolo, 2006) that the rate (or length scale) of isotopic exchange between fluid and reservoir rock is related to the ratio of the diffusive reaction length into the reservoir matrix to the average fracture spacing of the reservoir. In theory the isotopic compositions of two elements with different reaction lengths could be used to calculate the size and spacing of the primary fluid carrying fractures. When combined with a tracer determined sweep volume, the average fracture spacing can be used to estimate the surface area of mass and heat exchange along the primary flow paths.

In the following contribution we test the ideas of using isotopic data to constrain the chemical processes and properties of geothermal reservoirs using samples collected during 2005-2007 from

production and monitor wells in the geothermal system in Long Valley caldera, California, USA.

Geologic Setting

The Long Valley caldera is a ~540 km² depression located on the border between the Sierra Nevada and Basin and Range physiographic provinces. The caldera formed during the eruption of the Bishop Tuff approximately 0.76 ma (Bailey et al, 1976). Subsequent volcanism included extensive post caldera rhyolite and basalt in the west and south moat regions of the caldera. Smaller eruptions have formed the resurgent dome, Mammoth Mountain, and the Mono-Inyo chain. The present phase of geothermal activity in Long Valley has been active for the last 30-40 ka based on tufa deposits and hydrothermally altered sediments (Sorey et al., 1991 and references therein).

Meteoric recharge of the geothermal system is thought to occur in the northwestern rim of the caldera, likely along the caldera ring fracture (White et al, 1990). The hottest geothermal water samples have been observed at Shady Rest well RDO-8 and Unocal 44-16 (Figure 1). Sorey et al. (1991) suggest that the up flow region for geothermal waters must be west of RDO-8 and likely south of 44-16 based on potentiometric surface and fluid temperatures. Once geothermal waters enter the upper-most Bishop Tuff and lower post caldera rhyolites out-flow of geothermal water is thought to be from northwest to southeast (Sorey et al, 1991; Goff et al, 1991). Our sampling focuses on wells southeast of the proposed source region, including new production wells in Basalt Canyon, the main Casa Diablo well field and monitoring wells southeast of the production field. In all, samples cover approximately 14 km along the proposed out-flow path (Figure 1).

Results

The water isotopic compositions from this study and literature data (White et al., 1990; Sorey et al., 1991) are shown in Figure 2. As previously argued (Sorey et al., 1991), the data are consistent

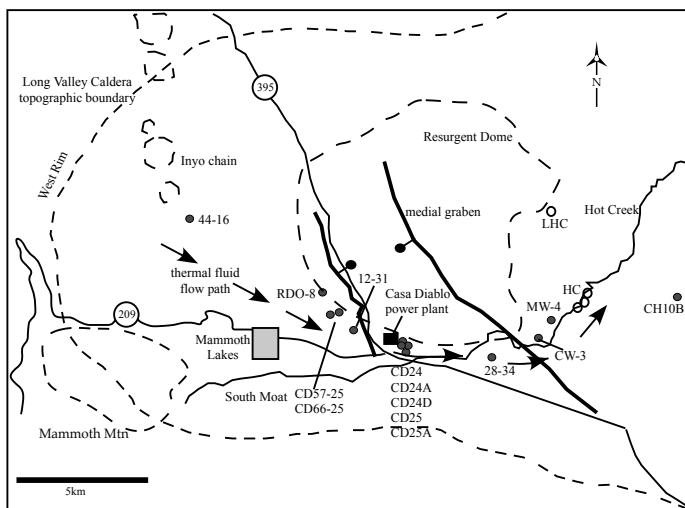


Figure 1. Map of Long Valley caldera showing the proposed flow path of the Long Valley hydrothermal fluid (arrows) that emerges in the west moat near well 44-16 and locations of geothermal well samples (gray circles).

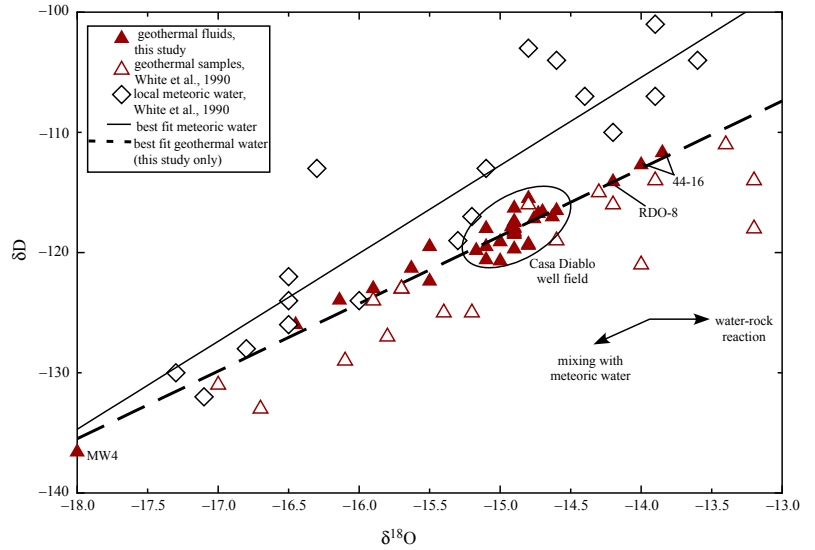


Figure 2. Water isotope data from this study and White et al., 1990.

with mixing of two waters: a geothermal fluid displaced from the meteoric water line by water rock interaction and local meteoric water. Water samples from wells RDO-8 and 44-16 are the least diluted and most displaced from the local meteoric waterline as defined by White et al (1990). Moving eastward samples become progressively lighter in δ¹⁸O and δD as the contribution from meteoric water increases.

The strontium isotopic data, including data from Goff et al. (1991), are summarized in Figure 3 as a function of distance from well 44-16, following the proposed flow path of the hydrothermal fluid. The range in Sr isotopic composition of the reservoir lithologies [Bishop Tuff (BT) and Early Post-caldera Rhyolites (EPCR)] is shown for comparison. Strontium isotopic compositions in geothermal waters are expected to reflect the addition of Sr by mineral dissolution as the fluid equilibrates with reservoir rock lithologies (Goff et al., 1991; Johnson and DePaolo, 1994; 1996). Although there appears to be a general trend of declining ⁸⁷Sr/⁸⁶Sr along the flow path from the section 25 wells (CD57-25 and CD65-25) to CW-3 that is consistent with the gradual isotopic

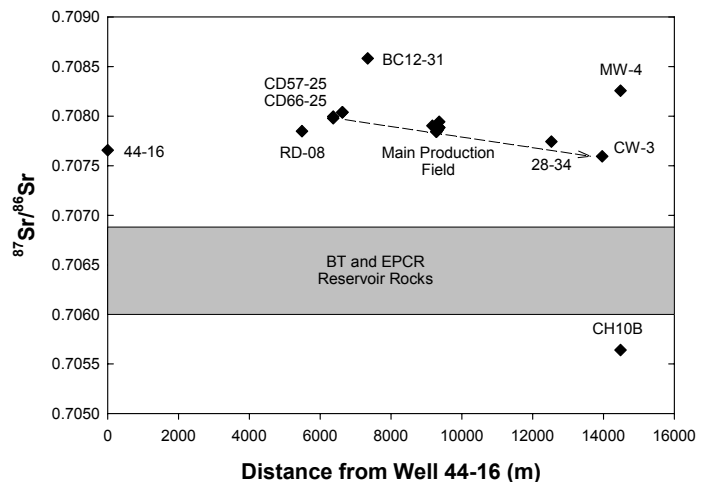


Figure 3. Sr isotope data vs distance from well 44-16 across Long Valley along the proposed fluid flow path.

equilibration of the fluid with the reservoir rocks, overall the data are inconsistent with a single “flow path”. Note, for instance, that wells 44-16 and RDO-8 located near the fluid upwelling zone have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the main geothermal field to the east. The high value for BC12-31 is thought to reflect contamination with drilling mud and/or water as evident from other chemical anomalies encountered in this well.

Along the flow path from west-to-east there is a marked decline in the concentrations of Ca and CO_2 (Figure 4). Although the decline could result from fluid mixing between a CO_2 -Ca-rich geothermal fluid and a dilute (meteoric) water, consistent with the water isotope data (Figure 2), co-variations between CO_2 and $^4\text{He}/^{36}\text{Ar}$ ratios [$F(^4\text{He})$, Figure 5] are inconsistent with mixing

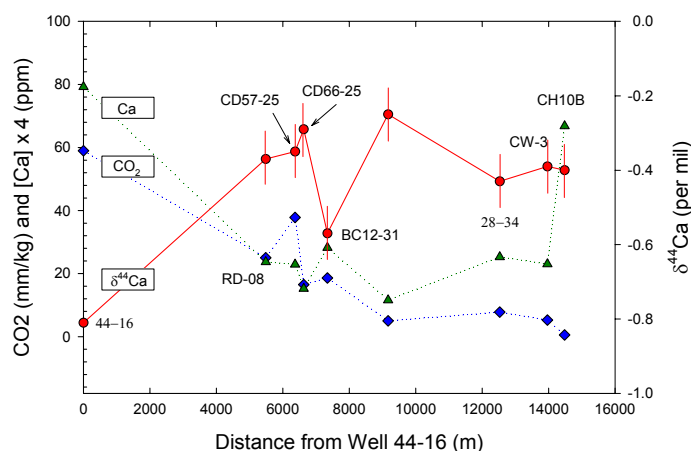


Figure 4. Covariations between the concentrations of Ca and CO_2 and the Ca isotopic composition ($\delta^{44}\text{Ca}$) along the proposed flow path. The $\delta^{44}\text{Ca}$ values are negatively correlated with Ca and CO_2 concentrations, consistent with Ca isotope fractionation due to precipitation of calcite.

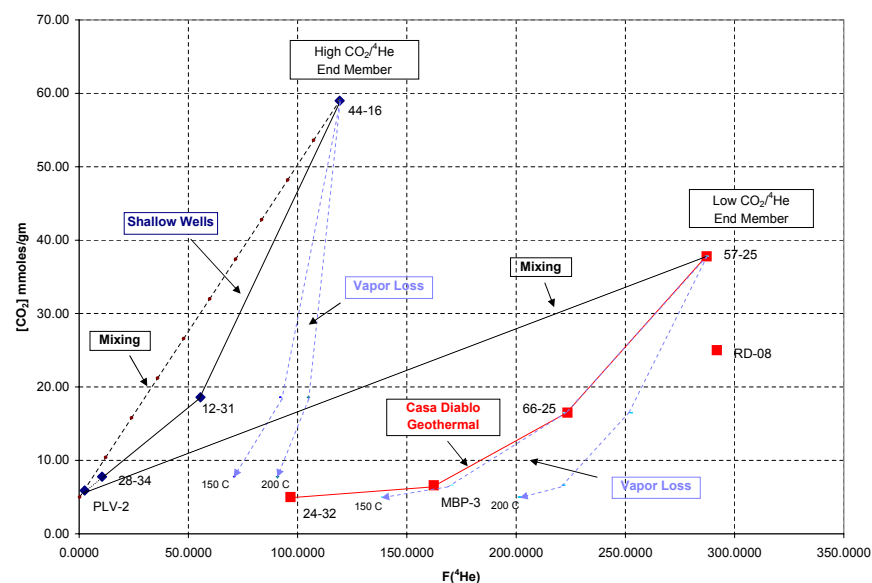


Figure 5. $F(^4\text{He})$ and CO_2 concentrations in Long Valley geothermal waters discriminate into two separate trends: monitoring wells (solid diamonds: 44-16, 12-31, 28-34, PLV-2) and wells from the geothermal field and a nearby exploratory well (solid squares: 57-25, 66-25, MBP-3, 24-32 and RDO-8). The $F(^4\text{He})$ value is the $^4\text{He}/^{36}\text{Ar}$ ratio normalized to the same ratio in air. The non-linear nature of the compositional trends rules out mixing of CO_2 - ^4He -rich fluids with dilute (meteoric) water. Instead, both trends are likely the result of degassing of geothermal fluids.

and require that the decline in CO_2 is driven primarily by vapor loss (degassing, Bergfeld et al., 2006). Coinciding with the decline in CO_2 and Ca concentrations, the Ca isotopic composition of the fluid becomes progressively enriched in the heavier ^{44}Ca isotope: $\delta^{44}\text{Ca}$ increases from -0.8‰ to -0.3‰ . The enrichment of the heavy Ca isotopes is consistent with calcite precipitation (Lemarchand et al., 2004; Tipper et al., 2006).

Discussion

Goff et al (1991) interpreted the west to east decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ as a progressive reaction between geothermal fluids and the reservoir rocks along the flow path of the hydrothermal fluid. In general, our Sr isotope data for geothermal wells (Figure 3) are consistent with the west to east trend as described by Goff et al (1991), but in detail are inconsistent with equilibration along a single flow path. Furthermore, if water-rock reaction in the out-flow zone is an important process then it results in only a small change in the Sr isotope compositions of the geothermal fluids over distances of several kilometers making it difficult to isolate this process from other processes that introduce variability into the dataset, such as multiple flow paths or fluid mixing. A model for water rock reaction based on a filtered data set of the Casa Diablo samples and the wells 28-34 and CW-3 east of the well field produces a coherent trend which yields reaction length scale estimates on the order of tens of kilometers, much larger than expected for meteoric-hydrothermal systems (DePaolo, 2006). Previous estimates of the fluid flux through the Long Valley geothermal system of $\sim 400\text{ L s}^{-1}$ and fluid velocities of 400-4000 m/yr (Evans et al, 2004) and the small shifts in $^{87}\text{Sr}/^{86}\text{Sr}$ imply that a relatively limited amount of reaction between geothermal fluids and reservoir rock occurs in the out-flow zone in Long Valley. Other processes like mixing may have a stronger influence on the initial variability and evolution of Sr isotopes in the thermal fluids. For example, well MW-4, which is similar to the proposed meteoric component based on water isotopes, has $^{87}\text{Sr}/^{86}\text{Sr} = 0.7083$. The addition of a cold meteoric component with relatively radiogenic Sr to the out-flow zone would obscure some of the expected isotopic shift due to water-rock reaction. Thus processes like mixing make the application of a dual porosity model difficult to apply in Long Valley using Sr isotope data alone. Geothermal systems with different flow regimes may be better candidates for dual porosity modeling.

This and previous studies of Long Valley geothermal fluids have concluded that mixing between a thermal fluid and cold meteoric water is the dominant process based on the water isotope data and concentration gradients for boron and Cl- (Sorey et al, 1991; Goff et al, 1991; White et al, 1990). Goff et al. (1991) attribute a shift in Sr isotopes to water-rock reaction, however more extensive sampling presented in this contribution has shown that the Sr data are not entirely consistent with any single process and likely records multiple processes such as mixing and water-rock reaction. In contrast, noble gas and CO_2 data (Figure 5) are inconsistent with the thermal-meteoric

water mixing model. Instead these data indicate that degassing of the geothermal fluid(s) is an important process in the west moat and eastward along the proposed thermal fluid flow path.

The correlation between stable Ca isotope data and concentrations of Ca and CO₂ in geothermal wells adjacent to the Casa Diablo power plant imply calcite precipitation in the geothermal reservoir. The fractionation of Ca isotopes due to inorganic calcite precipitation has been previously suggested for non-thermal groundwater and riverine systems (Tipper et al, 2006; Jacobson and Holmden, 2008) however this is the first evidence that Ca isotopes may trace calcite precipitation in geothermal systems. The rapid decline in Ca and CO₂ concentrations and increase in δ⁴⁴Ca is consistent with a change in Ca solubility associated with degassing of the geothermal reservoir and calcite precipitation occurring over the first 5-10 km of flow across the reservoir. Just east of the main well field samples 28-34 and CW-3 indicate a slight increase in Ca and CO₂ and decrease in δ⁴⁴Ca. At this time it is unclear why Ca and CO₂ concentrations might increase east of the production field, though the Ca isotope data imply that this could be due either to the input of small amounts of additional undegassed geothermal fluids or to the dissolution of previously precipitated (isotopically light) fracture-filling calcites. Further east in the caldera well CH10B has δ⁴⁴Ca similar to the other wells east of Casa Diablo despite a much higher Ca concentration. This suggests that the addition of Ca to the reservoir in the eastern portion of the caldera with a different isotopic signature from the west moat area. Interestingly, a spring in the eastern caldera has the high ³He/⁴He ratio than found anywhere along the west moat flow path. Additional measurements of Ca isotopes to characterize the reservoir rocks and fracture filling calcites would help further constrain the processes occurring east of the geothermal reservoir.

Conclusions

An isotopic study of hydrothermal fluids from Long Valley Caldera has shown that for water isotopes and possibly Sr isotopes mixing between meteoric and hydrothermal fluids dominates over water-rock reactions in the out-flow zone. Other tracers like noble gases and stable Ca isotopes, which are more sensitive to changes in gas solubility show evidence for degassing and calcite precipitation in the thermal reservoir.

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