

## Water Rock Interaction [WRI 14]

# Water-rock interaction in the Long Valley Caldera (USA)

W.C. Evans<sup>a\*</sup>, S. Hurwitz<sup>a</sup>, D. Bergfeld<sup>a</sup>, J. Lewicki<sup>a</sup>, M.A. Huebner<sup>a</sup>, C.F. Williams<sup>a</sup>, S.T. Brown<sup>b</sup>

<sup>a</sup>*U.S. Geological Survey, Menlo Park, California, USA*

<sup>b</sup>*Lawrence Berkeley National Laboratory, Berkeley, California, USA*

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### Abstract

Water-rock interactions within the main thermal aquifer in the Long Valley Caldera are evaluated using water chemistry data from a new suite of samples. The results reflect the impact of increased geothermal production and major CO<sub>2</sub> loss, which appears to drive calcite precipitation in the aquifer. The study provides qualitative information on the rates of mineral reactions and the response times of chemical geothermometers to declining temperatures.

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### 1. Introduction

The Long Valley Caldera in eastern California hosts a large and well-characterized hydrothermal system (Fig 1a). The hottest water (~220°C), from well 44-16 in the west moat, most closely represents the deep reservoir fluid. This water flows eastward at ~370 kg/s in a permeable zone of tuff and rhyolitic rocks [1]. This lateral flow zone is tapped by several wells, some of which provide water to a geothermal plant at Casa Diablo. Most of the water discharges through large springs in Hot Creek Gorge, though a minor flow continues further eastward. On the long flow path, the thermal water experiences gradual dilution, and the temperature drops to near boiling. Many studies have focused on mixing, cooling, and water-rock interaction in the lateral flow zone [e.g., 1-3] but using water chemistry that predates current geothermal production and the resultant increased CO<sub>2</sub> loss from the aquifer [4]. Here we discuss data from samples collected between 2005 and 2009 using improved methodology, including samples from newly drilled wells, to re-evaluate water-rock interaction in the Long Valley hydrothermal system.

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\* Corresponding author. Tel.: 01-650-329-4514; fax: 01-650-326-4463.

E-mail address: [wcevans@usgs.gov](mailto:wcevans@usgs.gov).

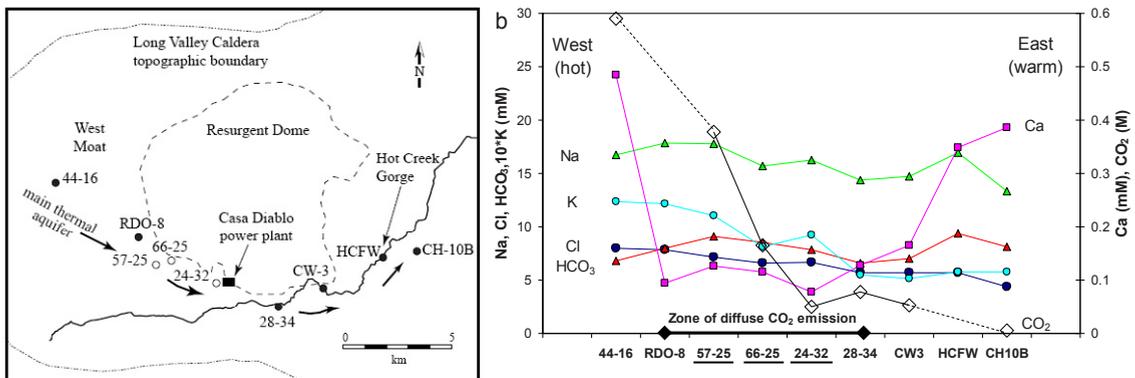


Fig. 1. (a) Location of sampled wells along the main thermal aquifer and the major discharge area in Hot Creek Gorge. Open dots are production wells. (b) Water chemistry from west to east (production wells underlined). HCO<sub>3</sub> is total alkalinity as bicarbonate. The zone of diffuse CO<sub>2</sub> emissions begins near 57-25 and continues past 24-32.

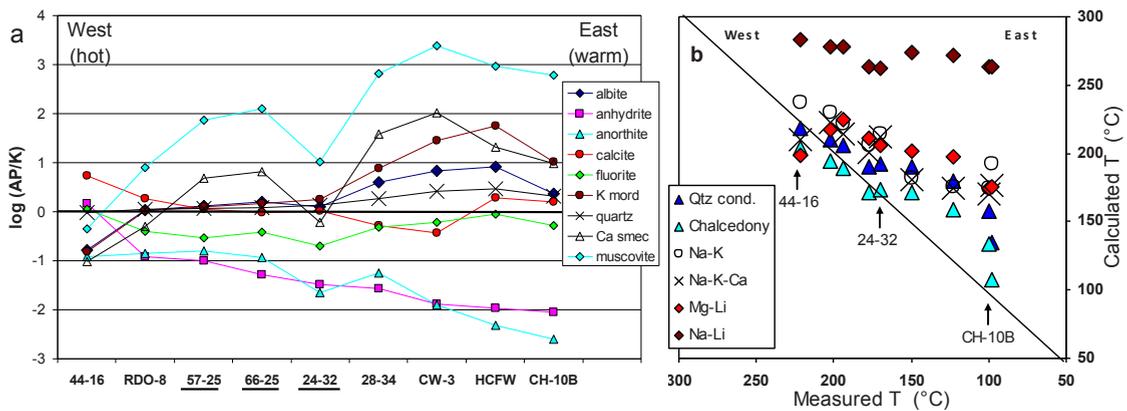


Fig. 2. SOLMINEQ.88 calculations of (a) mineral saturation indices from west to east (production wells underlined), and (b) geothermometer temperatures.

## 2. Methods and results

All samples discussed in this paper were collected from wells except for HCFW, which is a bubbling spring in Hot Creek Gorge (Fig 1a). Well samples were either collected under pressure from down-hole pumps or in a pre-evacuated down-hole sampler, allowing for an accurate measurement of dissolved CO<sub>2</sub> prior to any gas loss. Coupling the measured CO<sub>2</sub> concentrations with alkalinity values determined on-site constrains fluid pH. The analytical results were evaluated with the SOLMINEQ.88 computer code [5], which calculates pH, chemical speciation, and mineral saturation indices at aquifer temperatures.

Figure 1b shows the large drop in dissolved CO<sub>2</sub> concentration that occurs during eastward flow. In part this reflects pressure drawdown near the production wells, which allows vapor to form in the aquifer. The vapor rises to the surface and the CO<sub>2</sub> escapes diffusely through areas of hot ground [4]. The ~45% decline in Cl can be equated to dilution by low-Cl meteoric water [1,2]. Despite this dilution, HCO<sub>3</sub> increases significantly at the start and toward the end of the flow path, with Na following a similar pattern. Potassium follows the Cl trend but shows a greater decline, while Ca variations show no relation to any other species. Concentrations of Mg (not shown) are low (<0.02 mM) over the entire flow path.

Overall, these changes can be explained by silicate hydrolysis, converting  $\text{CO}_2$  to  $\text{HCO}_3^-$  and releasing cations into solution, with preferential scavenging of Mg and K into alteration minerals. The peculiar variation in Ca concentrations requires additional explanation.

### 3. Mineral stabilities and geothermometry

Saturation indices for selected minerals are shown in Figure 2a. The values for Al-containing minerals are based on the Al concentrations measured in filtered ( $0.45\mu$ ) acidified water, a recognized source of uncertainty [2]. The calculations benefit from the tight constraints on pH at down-hole conditions.

The hottest water from well 44-16 is near saturation with respect to quartz, fluorite, and anhydrite. Calcite is significantly oversaturated and some aluminosilicate minerals are undersaturated. However, all values are within  $\pm 1$  log unit of saturation, providing some justification for using measured Al values and supporting the view that this water is equilibrated reservoir fluid.

As this water flows eastward, it becomes undersaturated with fluorite and anhydrite but remains saturated with calcite past the production well-field. The water quickly reaches saturation with albite, K-mordenite, and Ca-smectite. Anorthite is undersaturated over the entire flow path. Progressive oversaturation in K-mordenite and Ca-smectite occurs, especially east of the production wells. Other end-members of the series (e.g., Na-mordenite, Na-smectite) that are not plotted behave similarly. The patterns in Figure 2a fit the mineralogy observed in drill core from Long Valley [1-3]. Albite is abundant and anorthite rare in feldspars, and alteration minerals include clays, zeolites, and calcite.

Although saturation indices do not provide a unique explanation for observed changes in water chemistry, the evolution of water chemistry in Figure 1b is consistent with the following scheme. Between wells 44-16 and RDO-8,  $\text{CO}_2$ -driven dissolution of albite increases Na and  $\text{HCO}_3^-$  concentrations. Because Ca-smectite is undersaturated, precipitation of calcite accounts for the observed drop in Ca. Albite appears to exert control over fluid chemistry between RDO-8 and the Casa Diablo power plant, perhaps in conjunction with K-mordenite. Over this same segment, calcite appears to control Ca concentrations at low levels. Note that Ca concentrations only begin to increase after calcite becomes undersaturated east of Casa Diablo, by which time Ca-smectite is greatly oversaturated. The escape of  $\text{CO}_2$  likely plays a big role in maintaining calcite saturation through the production well area because of its effect on carbonate speciation. Although total alkalinity ( $\text{HCO}_3^-$  in Figure 1b) changes by a small amount over this part of the flow path, the  $\text{CO}_3$  fraction increases by a factor of  $\sim 15$ .

Several common geothermometers (Fig 2b) are close to the maximum measured temperature in well 44-16, the “equilibrated” reservoir fluid. Only Na-Li gives a substantial overestimate. As the water cools on its eastward flow, the silica geothermometers based on quartz and chalcedony nearly keep pace with falling temperature through the production well area (dilution plays a small role). The Na-K geothermometer also keeps pace, even if consistently above measured temperatures. This is also the part of the flow path where mineral equilibria seem to exert greater control over water chemistry (Fig 2a). East of well 24-32, the chemical geothermometer temperatures exceed measured water temperatures, and mineral phases are out of equilibrium (Figs 2a,b), both likely due to kinetic constraints. For an indication of reaction rates, the flow time from 24-32 to CH-10B is  $\sim 10$ -20 years, based on fluid velocity in the aquifer [8]. Such sluggish kinetics, even for chalcedony, likely apply to other geothermal areas.

### 4. Comparison to other studies

Similar to this study, White and Petersen [2] linked the near saturation in quartz and calcite for wells in the production area to formation of these minerals in the aquifer. Using ion activity ratios instead of measured Al concentrations, they also modeled high-temperature equilibration with illite, based on

muscovite as its thermodynamic equivalent (c.f. Fig 2a). Most recently, Temple et al. [3] applied reactive transport modeling to the part of the system between RDO-8 and Casa Diablo, using water chemistry data from 1986. Major processes were dissolution of albite and formation of quartz and Ca-smectite. Interestingly, mass balance considerations required addition of CO<sub>2</sub> and dissolution of a small amount of calcite, the opposite of what seems to be occurring today. A new study of δ<sup>44</sup>Ca values [6] in the samples discussed herein also found evidence for calcite precipitation between 44-16 and 24-32, with likely dissolution of previously formed calcite further east. This scenario is consistent with our mineral stability data (Fig 2a), which show calcite undersaturation in wells 28-34 and CW-3.

About 24 tonnes/day of CO<sub>2</sub> escapes through thermal ground in and around the production well field [4,7], enough to decrease aquifer CO<sub>2</sub> by ~17 mmol/L. This is substantial, but only accounts for about 30% of the observed drop in CO<sub>2</sub> between wells 44-16 and 24-32 (Fig 1b). Water that feeds the binary geothermal plant is injected under pressure back into the aquifer, so no CO<sub>2</sub> loss occurs in this process. Vigorous steam vents occur in the Casa Diablo area, but these vents have very low gas/steam ratios [4] and are not thought to discharge huge amounts of CO<sub>2</sub>.

The increase in HCO<sub>3</sub> shown in Figure 1b represents the loss of several mmol/L of CO<sub>2</sub>, after correcting for dilution. The amount of CO<sub>2</sub> lost to calcite precipitation depends on the availability of Ca from various sources. The starting thermal water (represented by the water in well 44-16) contributes 0.5 mmol/L Ca (Fig 1b). The diluting water is unlikely to contribute more than this, given any reasonable assumption of Ca concentration. Anorthite abundance in the aquifer is low. The modeling by Tempel et al. [3] suggests that only 0.04 mmol of anorthite dissolves in each L of water, and the δ<sup>44</sup>Ca values [6] support this finding. Thus it seems like calcite precipitation cannot account for more than ~1 mmol/L reduction in CO<sub>2</sub>. Some additional study is clearly needed to account for the entire drop in CO<sub>2</sub> over the flow path. Regardless, it is worth noting that precipitation of calcite is not balanced by dissolution of anorthite and thus could ultimately lead to a decrease in aquifer permeability.

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