**Geochemical behavior of a hot dry rock geothermal reservoir**

Charles O. Grigsby, Fraser E. Goff, Trujillo, Patricio E., Jr., and Dale A. Counce, 1984, pp. 265-270


---

This is one of many related papers that were included in the 1984 NMGS Fall Field Conference Guidebook.

**Annual NMGS Fall Field Conference Guidebooks**

Every fall since 1950, the New Mexico Geological Society (NMGS) has held an annual *Fall Field Conference* that explores some region of New Mexico (or surrounding states). Always well attended, these conferences provide a guidebook to participants. Besides detailed road logs, the guidebooks contain many well written, edited, and peer-reviewed geoscience papers. These books have set the national standard for geologic guidebooks and are an essential geologic reference for anyone working in or around New Mexico.

**Free Downloads**

NMGS has decided to make peer-reviewed papers from our Fall Field Conference guidebooks available for free download. Non-members will have access to guidebook papers two years after publication. Members have access to all papers. This is in keeping with our mission of promoting interest, research, and cooperation regarding geology in New Mexico. However, guidebook sales represent a significant proportion of our operating budget. Therefore, only *research papers* are available for download. *Road logs, mini-papers, maps, stratigraphic charts,* and other selected content are available only in the printed guidebooks.

**Copyright Information**

Publications of the New Mexico Geological Society, printed and electronic, are protected by the copyright laws of the United States. No material from the NMGS website, or printed and electronic publications, may be reprinted or redistributed without NMGS permission. Contact us for permission to reprint portions of any of our publications.

One printed copy of any materials from the NMGS website or our print and electronic publications may be made for individual use without our permission. Teachers and students may make unlimited copies for educational use. Any other use of these materials requires explicit permission.
This page is intentionally left blank to maintain order of facing pages.
INTRODUCTION

Technical feasibility of the Hot Dry Rock (HDR) concept of geothermal-energy extraction was proved in 1978 (Tester and Albright, 1978). Since that time a series of experiments has been conducted in the first (Phase I) reservoir to assess reservoir performance. The geochemistry of fluids obtained during these early experiments has been discussed by Grigsby and others (1983) and Goff and Grigsby (1982). These authors noted that the chemistry of fluids was subtly different from the natural hydrothermal fluids originating in the nearby Baca geothermal field, Valles caldera. After additional experiments, and after obtaining samples of pore fluid from deeper wells at Fenton Hill, the differences between these two fluids are even more noteworthy than previously thought. Because of the attention now being focused on the Valles caldera due to geothermal activities and the growing Continental Scientific Drilling Program, it is appropriate that the fluid chemistry of the Fenton Hill pore fluids be contrasted here with the Baca geothermal waters.

BACKGROUND

The HDR concept of geothermal-energy production involves extracting energy from hot, impermeable rocks by a man-made geothermal system. First, fracture-flow paths are created by hydraulically fracturing the rock between two wellbores (Fig. 1). Cold water is pumped down one wellbore, through the fracture system where it is heated, and up the second wellbore. At the surface, the hot water is maintained under sufficient pressure to prevent flashing and the attendant problems of scale formation. Energy is transferred from the hot water to a refrigerant that drives a turbine in a separate, closed loop. Fresh water is added to the cooled production water as required to make up the permeation losses in the reservoir before it is recirculated through the fracture system (Smith and others, 1975).

Field-scale investigations of the HDR concept in low-permeability Precambrian basement rock are being conducted at Fenton Hill, located on the west flank of the Valles caldera in the Jemez Mountains of northern New Mexico (Fig. 2). The initial reservoir design consists of two holes connected by a fractured heat-extraction system that ranges in depth from 2.5 to 3 km. The first borehole, Geothermal Test-2 (GT-2), was drilled in 1974 to a depth of 2.98 km, where the temperature was 197°C. A second borehole, Energy Extraction-1 (EE-1), was directionally drilled to 3.06 km in 1975. These two boreholes and the man-made hydraulic fractures connecting them constitute the Phase-I system. A third well, EE-2, was completed to 4.4 km (14,400 ft true vertical depth) in 1980, and a fourth well, EE-3, was completed to 4.1 km (13,399 ft) in 1981. This second pair of wellbores constitutes the Phase-II system that is being developed to demonstrate the reservoir...
lifetimes required for commercial heat extraction. As of the preparation of this paper, however, the two Phase-I wells have not been hydraulically connected. Figure 3 shows a simplified geologic column from cores and cuttings taken during the drilling of GT-2, EE-1, EE-2, and EE-3. Superimposed on this figure is an elevation view of the four wellbore drilled at Fenton Hill. The temperature scale from a background temperature log of EE-2 is also shown in Figure 3.

The Phase-I reservoir originally consisted of a set of near-vertical fractures that crossed the EE-1 wellbore at 2.75 km (behind the EE-1 casing). The performance of this original system was evaluated by a 75-day heat-extraction test which began on January 28, 1978 (Tester and Albright, 1978; Albright, 1978; Murphy, 1978; Grigsby and Tester, 1978). Following this test, the EE-1 casing was recentered and re-fractured, and a new, larger reservoir was formed with an injection point at 2.93 km in EE-1. The production zones for the enlarged reservoir were the same zones that were active during the 75-day test of the smaller reservoir. Preliminary evaluation of the enlarged reservoir was accomplished during a 24-day heat-extraction experiment that began on October 23, 1979 (Murphy, 1980; Murphy and others, 1981). More extensive testing of the enlarged reservoir ran for 280 days from March 10 to December 16, 1980. Results of this extended test are described by Zvyvoloski (1981). A summary of the entire Phase-I experience is given by Dash and others (1983). Nominal values of various Phase-I operating conditions are given in Table 1.

Fluid samples from EE-2 and EE-3 have been collected during various experiments and workover operations. Three types of samples have been collected: (1) downhole samples collected at in-situ temperature and pressure using a one-liter high-temperature-fluid sampling tool developed by Los Alamos; (2) vent samples that result from the return of fluid that has been pumped downhole in a fracturing experiment; and (3) bottoms-up samples from reverse-circulating a wellbore to remove fluid that has been sitting in a wellbore prior to conducting workover operations (Fig. 4). Vent samples are typically collected at the liquid outlet of a steam separator, and they require correction for flashing. Bottoms-up samples have been cooled by counter-current flow of cold water as shown in Figure 4.

### FLUID GEOCHEMISTRY

Fluid samples (except for the EE-3 reverse-circulation samples) were collected according to procedures described previously by Grigsby and others (1983). The EE-3 samples that were not collected according to those procedures are “grab” samples that were filtered and acidified or diluted in the laboratory after a 24-48-hour delay. Results of these various analyses are reported in Table 2.

The predominant ions in solution are Na', C1, and HCO-. with , Ca', and SO, also present in significant concentrations. Important minor or trace elements are B, As, F, and Br. The high concentrations of all species, especially in the relatively undiluted EE-3 bottoms-up samples, are significant in that these are the most concentrated fluids ever observed in the Jemez Mountains (see Trainer, 1974; Goff and Grigsby, 1982; White and others, this guidebook). Because of the counterflow heat exchange that occurs in reversing out a well, this fluid arrives at the surface at temperatures substantially below the boiling point. There is no concentration effect due to steam loss or boiling. This is also evident from the low silica concentrations in the bottoms-up samples, although it is not clear at this time if some silica from these samples has polymerized before analysis.

Because of the addition of fresh make-up water of dilute chemical composition (i.e., C120 mg/l) to the Phase-I injected fluid and of similar fresh water to the Phase-II wellbores during drilling, workover, and fracturing operations, uncontaminated samples of formation fluids have never been obtained. Therefore, it is impossible to calculate the absolute concentration of species in the pore fluid at this time. Only the ratios of species can be defined with accuracy. The presence of a unique formation fluid or pore fluid in the Precambrian rocks is inferred from several lines of evidence:

1. Oxygen- and hydrogen-isotope shifts suggest that long-term exchange has occurred between water and the rock.
2. Mixing relationships indicate the presence of a concentrated parent fluid.
3. Similar behavior of several species in response to changing operational conditions.

Shifts in oxygen- and hydrogen-isotope ratios are shown in Figure 5 for produced, injected, and make-up samples from the 24- and 280-
TABLE 2. Chemical and water-isotope analyses of Fenton Hill fluid samples. Elemental analyses by P. Trujillo and D. Counce, LANL; isotope analyses by L. Merlivat, Departement de Recherche et Analyse, Saclay, France.

| Sample | Date    | Time   | pH | Conductivity | Na | K | Li | Ca | Mg | Fe | B | As | SO₄ | HCO₃ | Cl | F | Br | δ¹⁸O | δD |
|--------|---------|--------|----|--------------|----|---|----|----|----|----|----|----|----|-----|-----|----|---|----|-----|-----|
| GT-Z Production Fluid from 250-Day Experiment (Experiment 217) |
| 2      | 10 Mar 80 | 15:00  | 6.52 | 7500 | 250 | 1400 | 110 | 3.0 | 3.0 | 42.3 | n.d. | 341 | 538 | 1750 | 8.7 | 11.7 | 7.40 | -74.7 |
| 3      | 11 Mar 80 | 00:30  | 5.96 | 5600 | 245 | 1100 | 90  | 17.0 | 61  | 2.2 | 5.55 | 35.1 | n.d. | 250 | 513 | 1220 | 10.6 | 12.0 | n.d. | n.d. |
| 4      | 11 Mar 80 | 07:00  | 5.66 | 4500 | 232 | 855  | 75  | 14.0 | 42  | 1.6 | 5.83 | 25.0 | n.d. | 248 | 493 | 921  | 15.3 | 3.7  | 9.45 | -81.4 |
| 6      | 14 Mar 80 | 12:00  | 6.33 | 3100 | 214 | 750  | 53  | 9.5  | 26  | 0.8 | 1.00 | 14.5 | n.d. | 227 | 400 | 563  | 16.5 | 2.1  | 10.29 | -84.6 |
| 15     | 21 Mar 80 | 10:30  | 7.33 | 2900 | 214 | 554  | 48  | 8.8  | 28  | 0.6 | 0.64 | 13.5 | n.d. | 260 | 471 | 528  | 11.2 | 2.1  | 10.80 | -85.0 |
| 22     | 26 Mar 80 | 10:30  | 6.78 | 2500 | 209 | 485  | 46  | 7.8  | 24  | 0.5 | 0.58 | 12.0 | n.d. | 241 | 455 | 422  | 14.1 | 1.2  | n.d. | n.d. |
| 29     | 04 Apr 80 | 10:30  | 7.31 | 2400 | 213 | 470  | 47  | 7.6  | 26  | 0.5 | 0.42 | 10.9 | n.d. | 232 | 483 | 397  | 14.4 | 1.5  | 11.10 | -85.5 |
| 30     | 11 Apr 80 | 00:30  | 6.31 | 2800 | 232 | 490  | 49  | 7.9  | 27  | 0.6 | 0.64 | 11.4 | n.d. | 265 | 477 | 291  | 15.8 | 2.6  | n.d. | n.d. |
| 50     | 25 Apr 80 | 10:30  | 5.13 | 2500 | 227 | 485  | 47  | 7.8  | 24  | 0.5 | 0.30 | 11.1 | n.d. | 258 | 454 | 412  | 14.6 | 2.1  | -11.00 | -85.0 |
| 63     | 09 May 80 | 06:00  | 6.27 | 2900 | 233 | 475  | 48  | 8.6  | 28  | 0.6 | 0.39 | 13.4 | n.d. | 256 | 448 | 420  | 13.3 | 1.7  | n.d. | n.d. |
| 76     | 30 May 80 | 10:30  | 6.14 | 2900 | 233 | 535  | 48  | 8.6  | 28  | 0.6 | 0.39 | 13.4 | n.d. | 286 | 450 | 485  | 17.0 | 2.3  | -10.74 | -84.7 |
| 94     | 20 Jun 80 | 10:00  | 6.28 | 2400 | 228 | 490  | 46  | 7.8  | 25  | 0.6 | 0.23 | 11.8 | n.d. | 279 | 490 | 300  | 13.0 | 1.6  | -10.75 | -81.3 |
| 104    | 11 Jul 80 | 10:00  | 6.37 | 2300 | 211 | 402  | 39  | 6.8  | 21  | 0.5 | 0.20 | 9.6 | n.d. | 190 | 471 | 314  | 12.6 | 1.1  | -10.55 | -82.7 |
| 114    | 25 Jul 80 | 11:10  | 6.37 | 2300 | 225 | 398  | 39  | 7.1  | 19  | 0.5 | 0.21 | 10.9 | n.d. | 205 | 467 | 351  | 13.0 | 0.5  | -10.75 | -81.5 |
| 175    | 31 Oct 80 | 10:45  | 6.26 | 2000 | 204 | 350  | 35  | 6.0  | 19  | 0.5 | 0.18 | 8.7 | n.d. | 180 | 346 | 305  | 17.2 | 0.5  | -11.05 | -86.4 |
| 133    | 21 Nov 80 | 11:45  | 6.26 | 2000 | 199 | 409  | 38  | 6.3  | 20  | 0.5 | 0.18 | 8.7 | n.d. | 208 | 434 | 302  | 20.3 | 0.5  | -11.05 | -86.4 |

EE-Z Downhole Sample

n.d. - not determined

FIGURE 4. Reverse-circulating a well. "Bottoms-up" occurs when the fluid originally at the bottom of the well is displaced up the center pipe to the surface.

FIGURE 5. Oxygen- and hydrogen-isotope shifts for samples from the 280-day experiment.
day tests of the enlarged reservoir. Make-up samples consist of meteoric water that is pumped from the base of the volcanic section beneath Fenton Hill (approximate depth 780 m). These points cluster near the Craig meteoric-water line as they should (Craig, 1961). Injected fluid consists of produced fluid plus make-up water just before it is recycled through the system. Produced fluids (Fig. 5) represent a combination of pore fluid (formation fluid) that has resided in the reservoir rocks for extended periods of time and make-up fluid of meteoric composition. Early samples of the HDR produced fluids show enrichment in $^{18}$O of about 6.5 per mil relative to the make-up fluid. As recirculation continues, the formation fluid is diluted with meteoric water so that the "steady-state" produced fluid shows only a 1.5-2.0 per mil shift. Likewise, there is a 15-20 per mil shift in hydrogen-isotope ratios in the early samples, but with time this shift drops to only 5-10 per mil.

Also shown in Figure 5 are isotope analyses of samples from the Baca wells, tapping the deep geothermal system in the Valles caldera (see paper by White and others, this guidebook, for description of the major element chemistry in the Baca wells) and from derivative hot springs which discharge in Calle de San Diego (Goff and others, 1981; Goff and Grigsby, 1982). The similarity in oxygen- and hydrogen-isotope behavior between the Fenton Hill system and the Valles deep geothermal and derivative fluids, which appears in Figure 5, does not hold when ratios of other species are considered. Figure 6, for example, shows two unique mixing relationships between local, surface-meteoric water, Fenton Hill pore fluid, and Valles geothermal and derivative fluids. Notice that the ratios of B/Cl and Li/Cl in the Fenton Hill system are significantly different from the ratios in the Baca fluid. This mixing behavior is also observed in the Na/Cl and K/Cl ratios, but in these

\[
<C> = \frac{C(t) - C^*}{C^* - C_m}
\]  

where $C^*$ is the concentration of a species in the mature fluid, $C(t)$ is the concentration of that species in the produced fluid at time $t$, and $C_m$ is the concentration in the make-up fluid (Grigsby and others, 1983). A graph of $<C>$ for Na, K, Cl, and B is given in Figure 7 for the 280-day experiment. The values of $C(t)$ and $C_m$ are measured directly; $C^*$ cannot be measured directly, but is approximated by initial values of $C(t=0)$. Figure 7 shows that the dimensionless concentrations of all of these species are the same and that the response of each of the species to changes in operational conditions is identical. This is a clear indication of mixing of a concentrated fluid with a dilute fluid in the reservoir.
GEOCHEMICAL MODELING

The evidence discussed in the previous section indicates that a unique aqueous phase containing dissolved salts is present in the Precambrian granitic rocks, and this phase is distinct from the Valles geothermal fluids. Furthermore, this fluid is apparently being added to the fluid recirculating through the Phase-I system for the entire duration of the 280-day experiment.

The rate at which this fluid is added can be roughly calculated by considering the increase in concentration of the pore-fluid species in the circulating fluid as it passes through the downhole system. If we assume that the pore-fluid composition is constant and that the pore fluid initially present in the main-fracture system has been completely flushed out so that no increase in concentration of C1, B, etc. occurs in the system, then simple mixing of the fluid in the main-fracture flow path with the pore fluid can be used to determine the relative amounts of pore fluid and fresh fluid. This mixing relationship is simply expressed as a material balance

\[ (1 - x) C_{in} + (x) C_{c} = C_{out} \]  

where \( x \) is the fraction of pore fluid in the produced fluid, \( C_{c} \) is the injected concentration, and \( C_{out} \) is the produced concentration. A graph of \( x \) vs. time for the 280-day experiment is given in Figure 8. By integrating this curve (after changing the flow fraction to a flow rate) we find that the cumulative volume of pore fluid displaced from the Precambrian rocks is of the order of 6,700 m³ (1.8 x 10⁶ gal).

GEOTHERMOMETRY

Quartz is by far the most reactive mineral under conditions of recirculating water flow past granodiorite samples from GT-2 at 200°C (Charles, 1979). While quartz is exposed to recirculating fluid, the aqueous-silica activity is almost completely controlled by quartz dissolution. The solubility of quartz as a function of temperature is well known (Morey and others, 1962; Kennedy, 1950). Aqueous-silica solutions become metastable as they are cooled and become supersaturated. They do not immediately precipitate silica when the temperature is lowered, so the solubility vs. temperature relationship has been used as a means of estimating equilibration temperatures between quartz and water in wells and hot springs (Mahon, 1966; Fournier and Rowe, 1966). This quartz-geothermometer relationship is empirically expressed as

\[ T(C) = \frac{1309}{5.19 - \log_{10}[\text{SiO}_2]} - 273.15 \]  

where aqueous-silica concentration is in mg/l. This equation applies over the temperature range of 0-250°C, but works best for temperatures above 150°C.

![Figure 8. Fraction of produced fluid that was pore fluid in 280-day experiment.](image)

Another chemical geothermometer that is often used to predict reservoir temperatures is the Na—K—Ca geothermometer (Fournier and Truesdell, 1973), which predicts the temperature of equilibration from the ratios of Na/K and Na/Ca. These ratios are set by cation exchange among the feldspars and feldspar-alteration minerals (particularly at temperatures above 100°C). The Na—K—Ca geothermometer is written

\[ \Delta T(C) = \frac{1647}{\log_{10}(Na/K) + \beta[\log_{10}(Ca/Na)] - 2.06} + 2.47 \]  

where Na, K, and Ca are concentrations in mg/kg, and

\[ \beta = \frac{4/3, T < 100°C}{13}, \frac{T > 100°C}{47} \]

Because the Na—K—Ca geothermometer depends upon the ratios among several dissolved species, dilution of a hot fluid containing large amounts of dissolved Na, K, and Ca with a dilute fluid should not significantly affect the ratios of the ions. Therefore, the predicted Na—K—Ca temperature should be relatively unaffected by dilution with fresh water. The calculated Na—K—Ca temperatures range from 190 to 195°C in samples collected during the 280-day experiment, and these temperatures correspond to the measured initial rock temperature.

Changes in calcium concentration within the system by dissolution or precipitation of calcite can affect the accuracy of the Na—K—Ca-geothermometer prediction (Fournier and Truesdell, 1973). If calcite is precipitating in the reservoir, the rate of precipitation of calcite would be limited by the rate at which calcium is supplied either by feldspar alteration or by the make-up fluid. Feldspar alteration is a slow process relative to the recirculation rate, and the calcium concentration in the pore fluid is higher than in the make-up fluid so that the calcium activity is low. It is therefore expected that the Na—K—Ca geothermometer is relatively unaffected by calcite precipitation in this system.

Comparisons of the silica and the Na—K—Ca-geothermometer temperatures with actual measured temperatures from the 280-day experiment are shown in Figure 9. In general, Na—K—Ca geothermometer temperatures are higher than silica-geothermometer temperatures and are close to the initial rock temperature. This conclusion is not surprising, since the Na/K ratio is set in the fluid that has been in long-term residence in the Precambrian rock.

The behavior of the quartz-geothermometer predicted temperatures is more difficult to explain. It was originally thought that quartz dissolution in the main-fracture flow path provided the source of additional...
silica, which is observed in the production fluid. However, as shown by Grigsby (1983), the rate of quartz dissolution is much too slow and the residence time is much too short to account for the silica concentrations in the production fluid. Instead, some of the fluid injected into the reservoir must have sufficiently long residence time in regions that have not been thermally depleted so that the silica concentration can come to equilibrium at the initial rock temperature. This fluid is then mixed in the reservoir with water, which has a short residence time in cooler regions of the reservoir so that it contains only the silica concentration of the injected fluid. According to a simple mass-balance calculation, approximately 30% of the injected fluid must have a mean residence time greater than five days at temperatures of 1995°C to explain the silica behavior.

**DISCUSSION AND CONCLUSIONS**

A significant volume of a previously unknown geothermal fluid occurs in Precambrian basement rocks on the west flank of the Valles caldera. We suggest that this fluid has a different origin than the deep geothermal fluids inside the caldera. Moreover this in-situ fluid exerts a controlling influence over the observed fluid chemistry in the Fenton Hill HDR system. Detailed modeling of recirculated water in the deeper HDR reservoir may provide some clues about the origin of the in-situ fluid, but study and comparison of hydrothermal waters from additional deep wells drilled within and around the Valles caldera may ultimately be the key to addressing this problem.

**ACKNOWLEDGMENTS**

This project was sponsored by the U.S. Department of Energy, Division of Geothermal Energy. We thank Frank Trainer and Art White for reviewing this paper and thank Frank again for sharing with us the publication on saline waters from the Canadian shield. We also thank Marcia Jones for typing this manuscript and John Paskiewicz for drafting the figures.

**REFERENCES**


---, (ed.), 1980, Preliminary evaluation of the second hot dry rock geo-


