Energy and Mineral Resources of New Mexico

Overview of the Valles Caldera (Baca) Geothermal System

Fraser Goff and Cathy J. Goff

VOLUME F

NEW MEXICO BUREAU OF GEOLOGY AND MINERAL RESOURCES
Memoir 50F
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Special Publication 13F

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Overview of the Valles Caldera (Baca) Geothermal System

Fraser Goff and Cathy J. Goff

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Cover: Sulphur Springs, main fumarole (December 2008). *Photo by Fraser Goff. Cover design by Brigitte Felix.*

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PREFACE

Virginia T. McLemore, Ronald F. Broadhead, Gretchen K. Hoffman, and Fraser Goff

New Mexico is called the Land of Enchantment, in part because of the diverse geologic formations of the state, which give rise to spectacular landscapes of mountains, valleys, mesas, canyons, rivers, deserts, and plains. Major cities are concentrated along the Rio Grande, including Albuquerque, Las Cruces, Rio Rancho, and Santa Fe, with smaller population centers in the southeast, eastern plains, and northwest, such as Roswell, Hobbs, Alamogordo, Carlsbad, Clovis, and Farmington (Fig. 1). New Mexico is the 5th largest state in terms of land area in the lower United States and contains five major physiographic provinces (Fig. 2): Great Plains, Basin and Range, Transition Zone, Colorado Plateau, and Southern Rocky Mountains. The rocks, which date back nearly two billion years, have undergone multiple major tectonic events that were accompanied by faulting and igneous activity (Figs. 3, 4). This rich geologic history has yielded a diversity of valuable energy and mineral deposits, which occur in all of the physiographic provinces in New Mexico, and in a variety of tectonic and geologic settings (Fig. 3). For more information on the geology of New Mexico, see Mack (1997), Mack and Giles (2004), and Price (2010). In addition, mining districts and prospect areas are shown and briefly described in McLemore (2017).

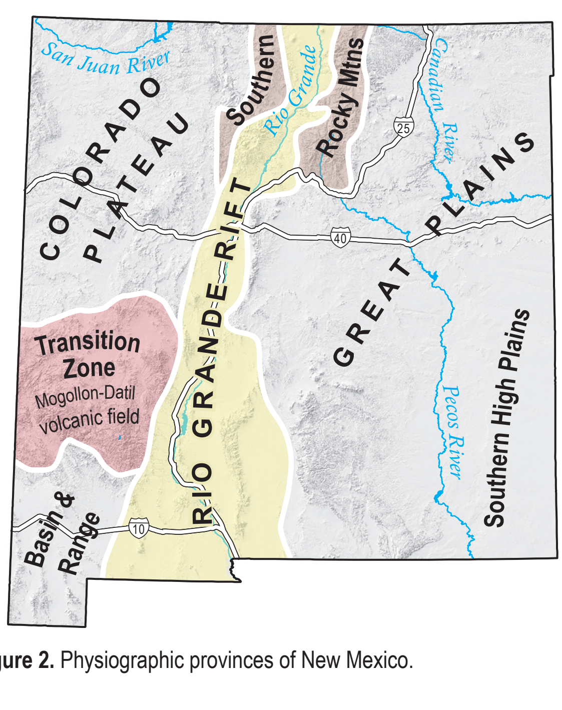

Figure 2. Physiographic provinces of New Mexico.

Rock collecting (or rock hounding), prospecting, and non-commercial gold panning are considered a casual use of public lands under most circumstances. **However, it is up to each individual to know the laws and land ownership.** For more information on mining claims and mineral leasing in New Mexico see McLemore (2017), BLM website (http://www.blm.gov/lr2000/), and New Mexico Mining and Minerals Division website (http://www.emnrd.state.nm.us/MMD/MARP/marpmainpage.html).

Importance of Energy and Minerals in New Mexico

New Mexico's mineral wealth is among the richest of any state in the United States. Oil and gas are the most important extractive industries in New Mexico in terms of production value (McLemore, 2017). In 2015, New Mexico ranked 6th in oil production, 8th in gas production, 10th in coal production, and 15th in non-fuel minerals production. Most of the state's mineral production comes from oil, gas, coal, copper, potash, industrial minerals and aggregates (Tables 1, 2). Other important commodities include a variety of industrial minerals (perlite, cement, zeolites, etc.), sulfuric acid, molybdenum, gold, uranium, and silver. New Mexico is fortunate to have geothermal resources in many locations. In December 2013, the Dale Burgett Geothermal Plant in the Animas Valley of southwest New Mexico started delivering up to 2 MW of electricity to the Public Service Company of New Mexico. Development of the Lightning Dock No. 2 project is underway with an additional 6 MW of generation planned.

A healthy energy and mineral industry is vitally important to the economy of New Mexico and to maintenance of public education and services (Table 2). The minerals industries provide property and corporate income taxes, while their ~35,000 direct employees contributed millions of dollars of personal

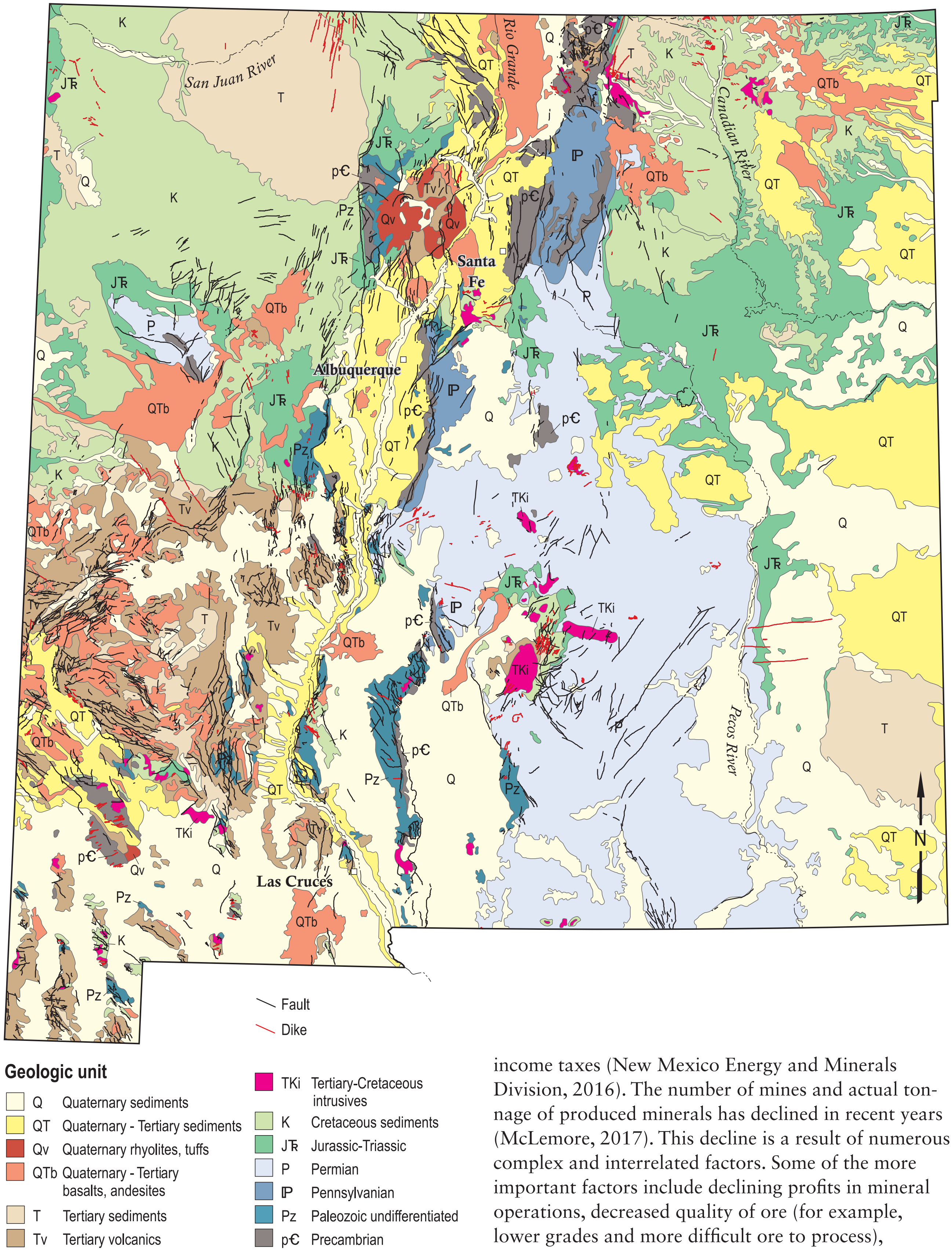

Figure 3. Simplified geologic map of New Mexico.

income taxes (New Mexico Energy and Minerals Division, 2016). The number of mines and actual tonnage of produced minerals has declined in recent years (McLemore, 2017). This decline is a result of numerous complex and interrelated factors. Some of the more important factors include declining profits in mineral operations, decreased quality of ore (for example, lower grades and more difficult ore to process), competition from the global market, and a shift from coal-generated electricity to alternative energy sources.

Table 1. Estimated total production of major commodities in New Mexico, in order of estimated cumulative value (data from USGS, 1902–1927; USBM, 1927–1990; Kelley, 1949; Harrer, 1965; USGS, 1965; Howard, 1967; Harben et al., 2008; Energy Information Administration, 2015; New Mexico Energy, Minerals and Natural Resources Department, 1986–2016). Figures are subject to change as more data are obtained. Estimated cumulative value is in real, historic dollars at the time of production and is not adjusted for inflation.

Commodity	Years of production	Estimated quantity of production	Estimated cumulative value ($)
Natural Gas	1921–2015	>75 trillion cubic feet	$169 billion
Oil	1922–2015	>6.4 billion barrels	$119 billion
Coal	1882–2015	>1.46 billion short tons	>$21.7 billion
Copper	1804–2015	>11.7 million tons	>$21.6 billion
Potash	1951–2015	>113 million short tons	>$15.6 billion
Uranium	1948–2002	>347 million pounds	>$4.8 billion
Industrial minerals**	1997–2015	>41 million short tons	>$2.7 billion
Aggregates***	1951–2015	>674 short tons	>$2.6 billion
Molybdenum	1931–2013	>176 million pounds	>$852 million
Carbon dioxide	1931–2015	>3.3 trillion cubic feet	>$726 million
Gold	1948–2015	>3.3 million troy ounces	>$486 million
Zinc	1903–1991	>1.51 million tons	>$337 million
Silver	1848–2015	>119 million troy ounces	>$280 million
Lead	1883–1992	>367,000 tons	>$56.7 million
Iron	1888–2015	>6.7 million long tons	>$23 million
Fluorspar	1909–1978	>721,000 tons	$12 million
Manganese	1883–1963	>1.7 million tons	$5 million
Barite	1918–1965	>37,500 tons	>$400,000
Tungsten	1940–1958	113.8 tons (>60% WO_3)	na
Niobium-tantalum	1953–1965	34,000 pounds of concentrates	na
TOTAL	**1804–2015**	**—**	**>$359 billion**

*Oil and gas values are estimated from production data provided by https://wwwapps.emnrd.state.nm.us/ocd/ocdpermitting/Reporting/Production/ProductionInjectionSummaryReport.aspx (New Mexico Oil Conservation Division Natural Gas and Oil Production, continuously updated, accessed 2/1/16) and estimated average commodity price. Minerals data are from New Mexico Energy, Minerals and Natural Resources Department (2016). **Industrial minerals include the combined total of several industrial minerals (e.g., perlite, cement, decorative stone, pumice, zeolites, etc.), but excluding potash and aggregates. ***Aggregates include only sand and gravel from 1951–1997, after 1997 aggregates include crushed stone and scoria. na–not available.

Table 2. Summary of mineral production in New Mexico in 2015, including oil and natural gas (New Mexico Energy, Minerals and Natural Resources Department, 2016, https://wwwapps.emnrd.state.nm.us/ocd/ocdpermitting/Reporting/Production/ProductionInjectionSummaryReport.aspx; Gould, 2015). na—not available.

Mineral	Production in 2015	Production rank in the U.S. in 2015	Production value in NM in 2015	Employment in NM (# full time jobs)	Reclamation employment in NM (# full time jobs)	State revenue generated from extractive industries	Federal revenue generated from extractive industries
Oil	147 million bbls oil	6	~$7,143,000,000	~30,000*	na	~$1,600,000,000*	na
Gas	1.23 trillion ft^3 gas	8	~$6,470,000,000	—	na	—	na
Copper	397,441,145 lbs	2	$996,838,033	1,878	4	$8,086,903	—
Coal	19,676,277 short tons	12	$691,047,434	1,341	118	$17,656,313	$10,243,850
Gold	20,438 troy oz	—	$23,708,980	—	—	$191,947	—
Industrial minerals	1,411,731 short tons	—	$87,305,356	413	11	$269,261	$213,816
Aggregates	8,169,753 short tons	—	$62,625,896	837	53	$3,092,285	—
Other metals (iron, manganese)	18,358 short tons	—	$165,223	18	—	$761,027	—
Potash	1,433,245 short tons	1	$659,505,518	1,194	12	$6,542,580	$8,133,012
Silver	56,983 troy oz	—	$895,610	—	—	$9,737	—
Uranium	none	—	—	11	11	—	—
Carbon dioxide	106 billion ft^3	—	$112,000,000	—	—	—	na
Total	**—**	**15 (excluding oil, gas, and coal)**	**~$16,247,000,000**	**~35,000**	**209**	**~$1,636,000,000**	**$18,590,678**

*Estimate includes oil, gas, and carbon dioxide.

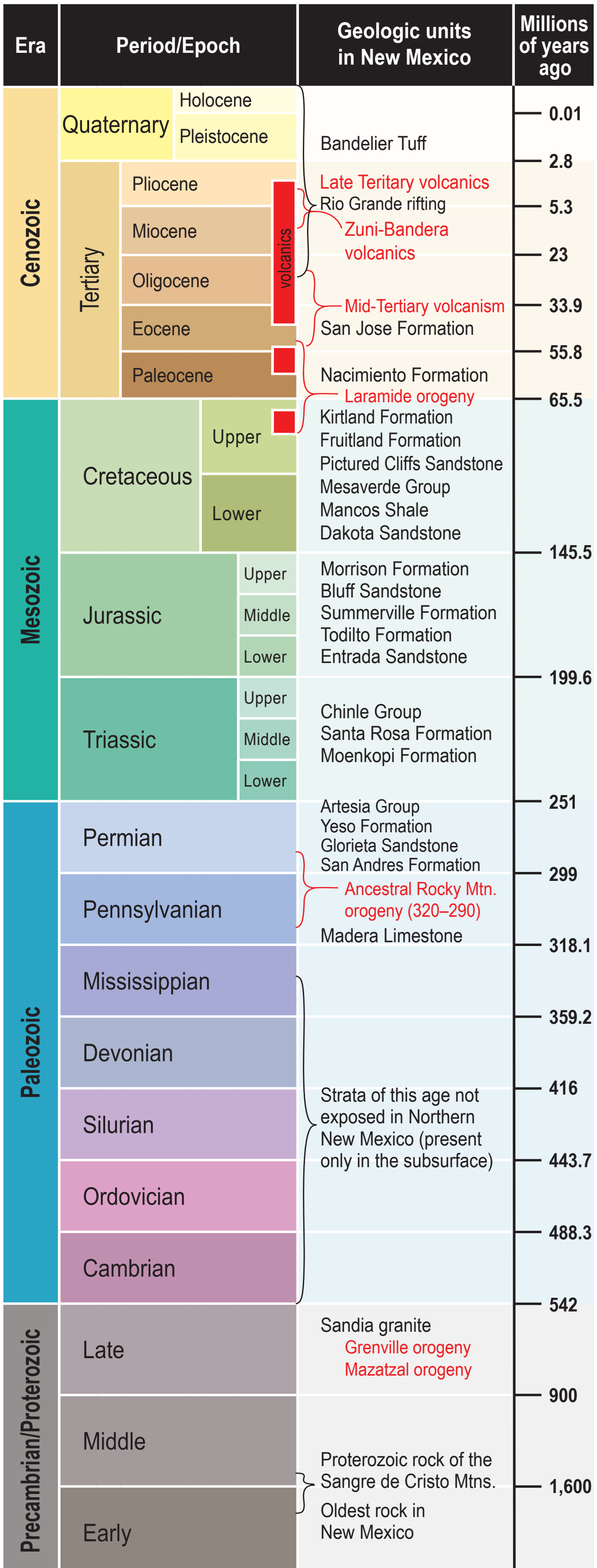

Figure 4. Geologic time scale. "Tertiary" is often used in these chapters to describe timing of events in the Paleogene and Neogene geologic periods.

New mines and petroleum drilling face a multitude of challenges, including water availability, water rights issues, public perceptions, a complex regulatory process and public opposition to petroleum drilling and mining.

Minerals and Society

The minerals industries (including oil and gas) play a vital role in the world economy by filling a persistent demand for the raw materials that are the foundation of our civilization. Our modern lifestyles are heavily dependent upon mining commodities that Americans use on a daily basis (Table 3). For example, petroleum, metals, and industrial minerals are used in every sector of construction and manufacturing. Coal, oil, gas, and uranium provide electricity and fuels. They are used in urban and industrial applications. Geothermal resources also provide electricity and heating (Table 3). Agriculture depends upon minerals for fertilizers and pesticides.

Mineral production in New Mexico and the world has increased dramatically in the last 100 years (Fig. 5, Wagner, 2002). Most industries no longer follow the casual mining and safety practices of the past. "*One of the greatest challenges facing the world today is integrating economic activity with environmental*

Table 3. Selected uses of commodities found in New Mexico.

Commodity	Selected Uses
Oil	Fuel, electricity generation, pesticides, fertilizers, chemicals, plastics
Gas	Fuel, electricity generation
Copper	Electrical wire, pipe, plumbing, motors, machinery, computers
Coal	Electricity generation, steel production, manufacture of cement, liquid fuel, chemical and pharmaceutical industries
Aggregates	Manufacture concrete and cement, road construction, railroad ballast
Molybdenum	Stainless and structural steel, superalloys, chemicals, cast iron
Potash	Agricultural fertilizers
Silver	Currency, jewelry, electronics, photography, silverware, mirrors
Gold	Currency, jewelry, electronics, computers, dentistry, glass
Uranium	Fuel for nuclear reactors, projectiles, shielding of radioactive materials
Perlite	Building construction materials, soil amendment, filter aid
Zeolites	Water purification, animal feed, sorbents
Rare earth elements	Catalyst, glass, polishing, re-chargeable batteries, magnets, lasers, glass, TV color phosphors
Geothermal resources	Electricity generation, space heating, greenhouse heating, aquaculture (fish farms), spas, and bath houses

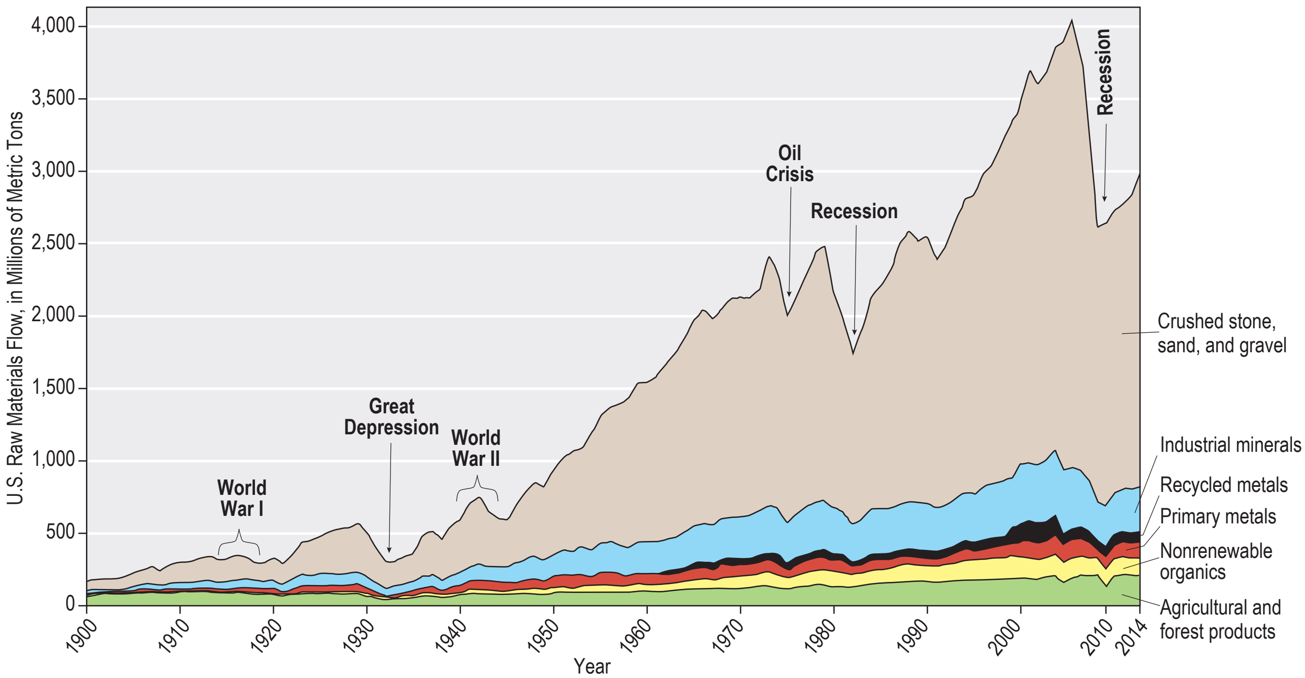

Figure 5. United States flow of raw materials by weight from 1900–2014. The use of raw materials increased dramatically during the last 100 years (modified from Wagner, 2002).

integrity and social concerns… The fulfillment of 'needs' is central to the definition of sustainable development" (IIED, 2002). The permitting process applied to most extractive industries includes archeological surveys, identification of rare and endangered species, and environmental monitoring during and after production. Today, another important aspect of mine planning in a modern regulatory setting is the philosophy, and often the requirement, that new mines and mine expansions must have plans and designs for closure. This philosophy is relatively new. It attempts to prevent environmental accidents common in the past and has increased the cost of mining.

Organization of this Series

This Memoir/Special Publication is the first modern summary of New Mexico's energy and mineral resources since work by the U.S. Geological Survey (USGS, 1965) and Howard (1967). This series of volumes is a joint publication of the New Mexico Bureau of Geology and Mineral Resources and the New Mexico Geological Society. This publication consists of six individual volumes under the theme of Energy and Mineral Resources of New Mexico.

Energy and Mineral Resources of New Mexico,
New Mexico Bureau of Geology and Mineral Resources, Memoir 50
New Mexico Geological Society, Special Publication 13

- **Petroleum Geology**
  by Ronald F. Broadhead, ***Volume A***
- **Coal Resources**
  by Gretchen K. Hoffman, ***Volume B***
- **Uranium Resources**
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- **Industrial Minerals and Rocks**
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- **Overview of the Valles Caldera (Baca) Geothermal System**
  by Fraser Goff and Cathy J. Goff, ***Volume F***

SUMMARY

High-temperature geothermal systems (≥150°C) are economically important because they have the potential to produce "renewable" electric power. Valles caldera is a large, Quaternary silicic volcanic complex (1.25 Ma to 70 ka) that contains a hot, but relatively small, geothermal system circulating at 210°C to about 300°C at 600 to 3,000 m depth. Reservoir fluids consist of dilute sodium-potassium-chloride-bicarbonate brines. The geothermal system also contains a vapor-phase cap with fumaroles and acid-sulfate springs; dilute thermal springs in the north, west and south caldera moat; and a hydrothermal outflow plume southwest of the caldera derived from the deep reservoir. Hydrothermal alteration mimics mineral assemblages found at many exhumed, volcanic-hosted, epithermal ore deposits. A residual magma body at 7 to 15 km beneath the southwestern sector of the caldera provides heat for the geothermal system.

The Valles system was "discovered" after drilling 15 deep wells in the southwestern caldera from 1960 to 1978. The end of this period coincided with the first United States "energy crisis," and the developer Union Oil Company of California (UNOCAL) claimed that Valles contained 400 MWe of geothermal resource. UNOCAL, the U.S. Department of Energy, and Public Service Company of New Mexico then signed a joint venture agreement in 1978 to develop the resource and build an initial 50 MWe power plant. However, the joint venture was terminated in January 1982 because UNOCAL could prove a resource of only 20 MWe and had become legally embroiled regarding impacts on local hot springs. The U.S. Continental Scientific Drilling Program commenced research activities at Valles in 1984, funding three core holes to better define the geothermal structure and plumbing of the caldera and to develop high-temperature coring and testing methods. This effort culminated in 1988 with well VC-2B, which at one time, was the hottest and deepest continuously cored hole in the U.S. (295°C at 1,762 m).

Valles caldera became a National Preserve in 2000 and a National Park in 2015. The geothermal resource was retired from commercial development in 2006 and, like similar National Parks (e.g., Yellowstone, Lassen, etc.), the geothermal system is now protected. In spite of these new realities, geothermal developers want to lease National Forest lands in the north and northwest sectors of the caldera and caldera flanks along the boundary with the new National Park. Their intent is to produce electric power.

DEDICATION

The authors wish to dedicate this
contribution to the memory of
Jamie Neal Gardner
(deceased, January 2015) who worked
with us for many, many years on
the Valles caldera geothermal system.

Photo by Fraser Goff.

I. INTRODUCTION

New Mexico's geothermal resources are currently utilized by several direct-use applications to grow greenhouse flowers and vegetables, to raise tilapia fry, and to provide warm water for spas (Witcher, 2007). In fact, New Mexico leads the nation in geothermal direct use for greenhouse heating. However, New Mexico also contains a famous, high-temperature geothermal system capable of electricity production but whose development ended in surprising failure, the Valles caldera. This result is unfortunate because in 2015 worldwide geothermal energy production accounted for about 11,800 MWe of electric power annually, equivalent to 205 million barrels of petroleum (Stimac et al., 2015).

Valles caldera is the only Quaternary (≤2.5 Myr) caldera in New Mexico and the American Southwest. Large Quaternary magma-hydrothermal systems and continental rifts have tremendous potential for worldwide production of geothermal energy (Duffield et al., 1994; Goff and Janik, 2000; Duffield and Sass, 2003; Stimac et al., 2015). The Valles caldera, located adjacent to the Rio Grande rift, is the most recent part of a large Quaternary caldera complex within the Jemez Mountains volcanic field and contains well-defined geothermal targets that have been explored for development. The most ambitious of these ventures included exploration of the small, liquid-dominated geothermal reservoir in the southwest sector of the caldera (a.k.a., the Baca geothermal system) from the 1960s to early 1980s, and scientific research and engineering of the prototype Hot Dry Rock geothermal project on the west flank of the caldera from the 1970s to late 1990s. Additional exploration and scientific drilling projects were conducted throughout the caldera and its margins during the 1980s and early 1990s. The results of these projects show that the Valles geothermal system is by far the hottest in New Mexico and the adjacent Southwest (≤300°C), surpassing the temperature of the only other southwestern system, Roosevelt Hot Springs geothermal field in Utah (about 230°C). None of these projects produced electricity or sufficient quantity of fluids for space heating, although they vastly improved our knowledge of the geothermal system itself.

The Baca name originates from a Hispanic ranching family, who was legally awarded the land grant and ranch in the 1870s. This name persisted until the U.S. Government purchased the Baca in 2000. Now the Valles Caldera National Preserve (a unit of the National Park Service), the ranch landholdings roughly coincide with the present caldera boundary. The purpose of this volume is to review the geothermal characteristics of the Valles caldera, to differentiate the natural thermal waters and gases and their geothermal indicators, and to describe the exploration history and status of the Valles (Baca) geothermal system.

Redondo Peak looking NE from Fenton Hill. *Photo by Fraser Goff.*

Bandelier Tuff from Jemez State Monument. *Photo by Fraser Goff.*

II. GEOLOGIC OVERVIEW

The Valles caldera is a 22-km-diameter resurgent cauldron that formed in the approximate center of the Jemez Mountains volcanic field circa 1.25 Ma (Figs. 1 and 2; Smith and Bailey, 1968; Phillips et al., 2007; Goff et al., 2011). The Jemez Mountains volcanic field consists primarily of calc-alkaline basalt, andesite, dacite, and rhyolite erupted from about 14 Ma to 70 ka (Gardner et al., 1986; Toyoda et al., 1995; Reneau et al., 1996; Goff and Gardner, 2004; Kelley et al., 2013a; Zimmerer et al., 2016). Volumetrically, two-pyroxene andesite domes and lavas are most abundant (about 1,000 km^3). Volcanism culminated with formation of the Valles and the comparably sized, but nearly obliterated, Toledo caldera (1.64 Ma; Spell et al., 1996; Goff et al., 2014) comprised of high-silica rhyolite ignimbrites (Bandelier Tuffs), and post-caldera rhyolitic products (≥800 km^3) (Gardner et al., 1986; Goff and Gardner, 2004; Goff, 2010).

The Jemez Mountains volcanic field lies at the intersection of the Jemez lineament and the western margin of the Rio Grande rift (Fig. 1). The Jemez lineament is an alignment of volcanic centers formed in Miocene to Holocene time along what is thought to be a reactivated Precambrian structure (Aldrich, 1986). There are no age or compositional progressions along the lineament, but by far the largest volume of erupted material occurs in the Jemez Mountains volcanic field. The Rio Grande rift is an intraplate zone of east-west extension and consists of a series of half-grabens extending from southern Colorado into northern Mexico. The northern Rio Grande rift formed about 27 to 30 Ma (Moore, 2000;

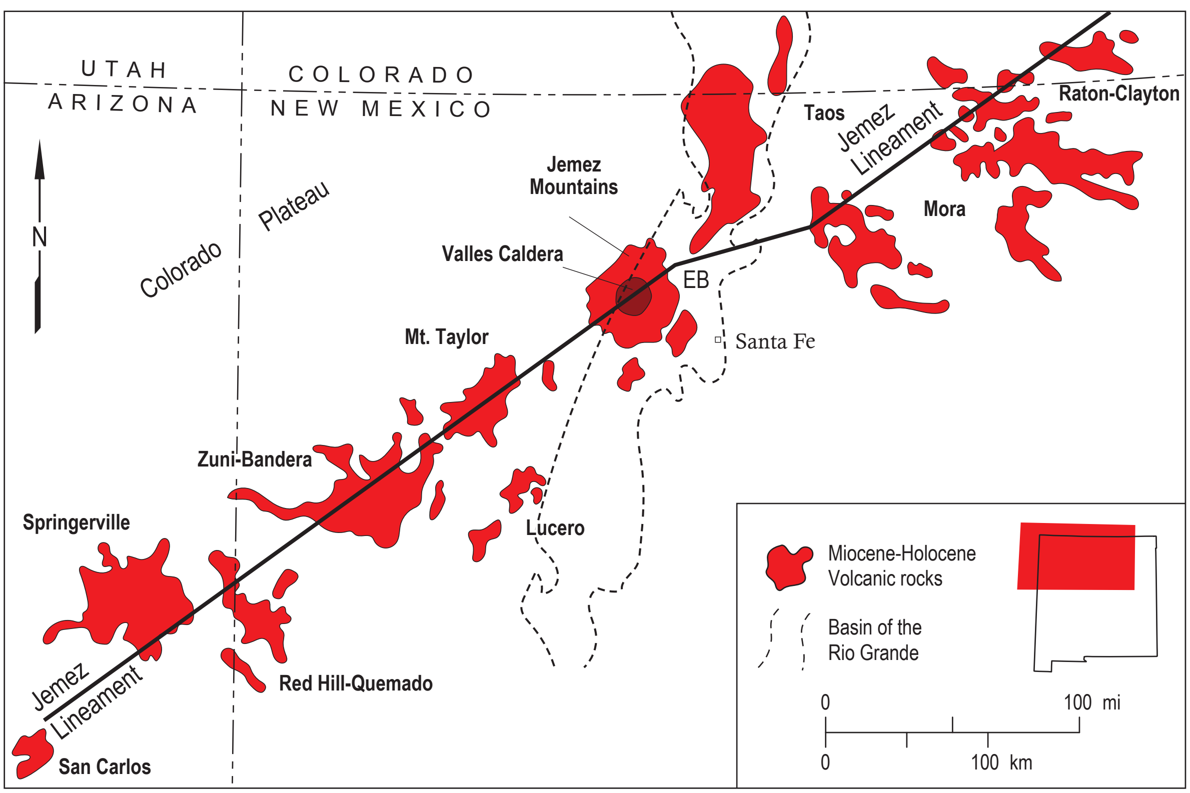


Figure 1. Location map showing the Jemez Mountains and Valles caldera with respect to other volcanic centers along the Jemez lineament, the Colorado Plateau and the Rio Grande rift. The Rio Grande rift in northern New Mexico is shown with a dashed outline. EB = the Española Basin segment of the rift.

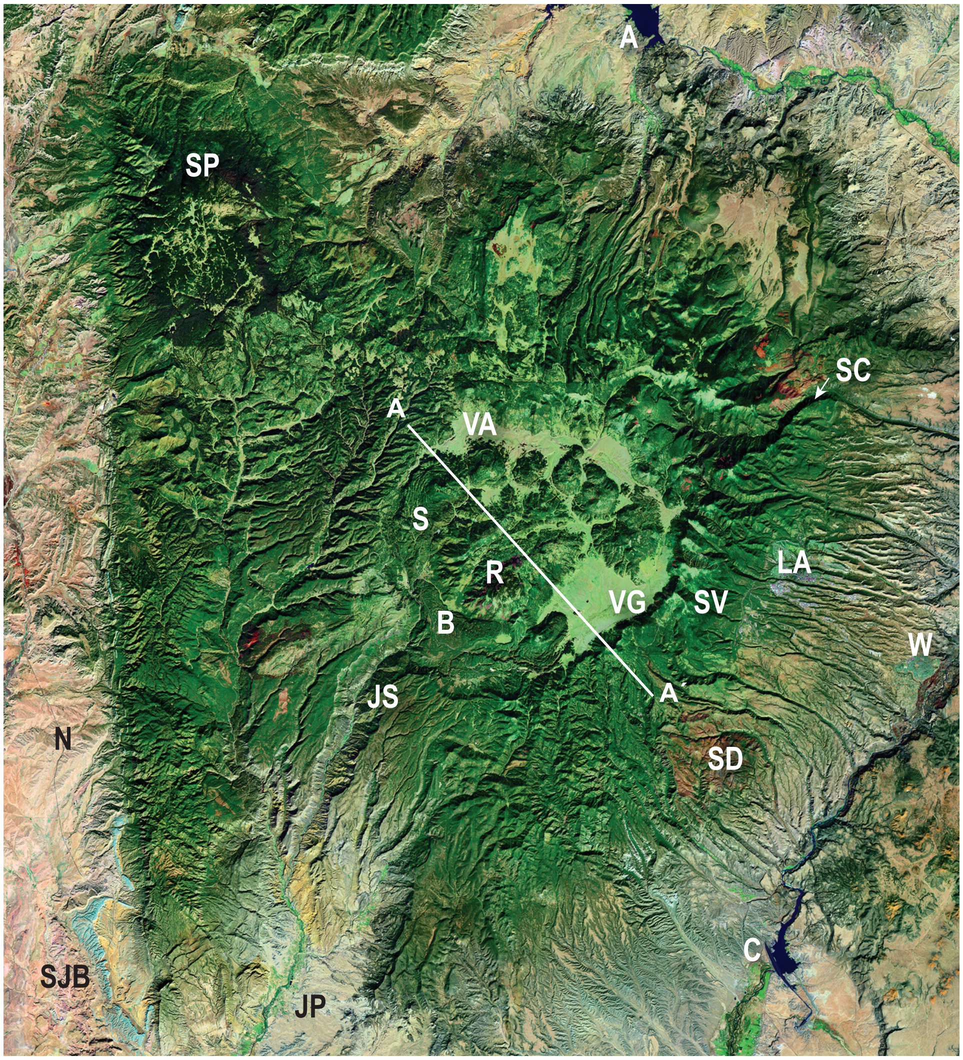


Figure 2. Color-enhanced LANDSAT photo shows the Valles caldera region, New Mexico. The caldera is approximately 22 km in diameter. Linear feature labeled N is the Nacimiento fault zone. Other labels: A = Abiquiu Reservoir, north side of Jemez Mountains, B = Banco Bonito lava flow (about 70 kyr), C = Cochiti Reservoir on the Rio Grande, JP = Jemez Pueblo on the Rio Jemez, JS = town of Jemez Springs, LA = city of Los Alamos, R = Redondo Peak, highest point on resurgent dome (3,430 m), S = Sulphur Springs acid-sulfate hot spring system, SC = Santa Clara Canyon, SD = St. Peters Dome, SJB = southeastern San Juan Basin, SP = San Pedro Park, SV = Sierra de los Valles, VA = Valle San Antonio, VG = Valle Grande, and W = community of White Rock. Cross section labeled A-A' shows approximate location of seismic line in Fig. 3.

Smith et al., 2002; Kelley et al., 2013b). Pleistocene volcanism associated with the Rio Grande rift has been predominately basaltic (Riecker, 1979; Baldridge et al., 1984).

Underlying Magma Body

The eruption of more than 800 km^3 of silicic pyroclastic flows and associated volcanics during the formation of the Valles and Toledo calderas implies the existence of a large underlying magma body (Smith, 1979; Goff et al., 2014). Several geochemical and geophysical studies show that the Valles caldera is, in fact, underlain by shallow magma (Goff and Gardner, 1994; Steck et al., 1998). For example, Valles intracaldera gases have $^3He/^4He$ ratios of ≤6.2 R/RA, where R/RA is the helium ratio of a sample of gas divided by the helium ratio of air. These values are similar to those of mid-ocean ridge basalt (MORB) and many arc (subduction zone) volcanoes indicating a mantle/magmatic source for the excess helium-3 (Goff and Janik, 2002). In addition, the $\delta^{15}N$-N_2 values of Valles intracaldera gases average -1.7 ± 1‰, close to the MORB value of -5 ± 3‰ (Fischer and Goff, 2007). Modeling of the nitrogen and helium data show that sedimentary rocks contribute only 20% of the nitrogen in Valles gas samples. The remaining 80%

of nitrogen must originate from a mantle source. The combined isotope data indicate that the Valles is underlain by a magma body periodically replenished by mantle basalt (Goff and Janik, 2002). Nonetheless, drilling to depths of 3.2 km within the resurgent dome has not penetrated dikes, sills, plugs, or laccoliths of mafic or silicic composition (Nielson and Hulen, 1984).

The caldera is aseismic and contains multiple low velocity zones identified as magma extending down to the upper mantle (Fig. 3; Steck et al., 1998; Aprea et al., 2002). Steck et al. (1998) concluded that the minimum melt fraction is roughly 13% and Aprea et al. (2002) determined that the top of the present magma chamber lies at 7 ±1 km depth. This chamber is centered beneath the southwest sector of the caldera, coincident with the youngest post-caldera ring-fracture eruptions and the deep geothermal system (Figs. 2 and 3). Convective heat flow at Sulphur Springs within the caldera exceeds 5,000 mW/m^2 (Morgan et al., 1996), whereas deep heat flow within the western caldera exceeds 450 mW/m^2 (Fig. 4; Sass and Morgan, 1988; Goff et al., 1989). Petrologic models suggest that the youngest post-caldera rhyolites erupted at 70 ka represent a new magma batch separate from magma generated in the original Bandelier magma chamber (Wolff and Gardner, 1995). Thus, the magma chamber defined by seismic studies probably represents this much younger magma batch.

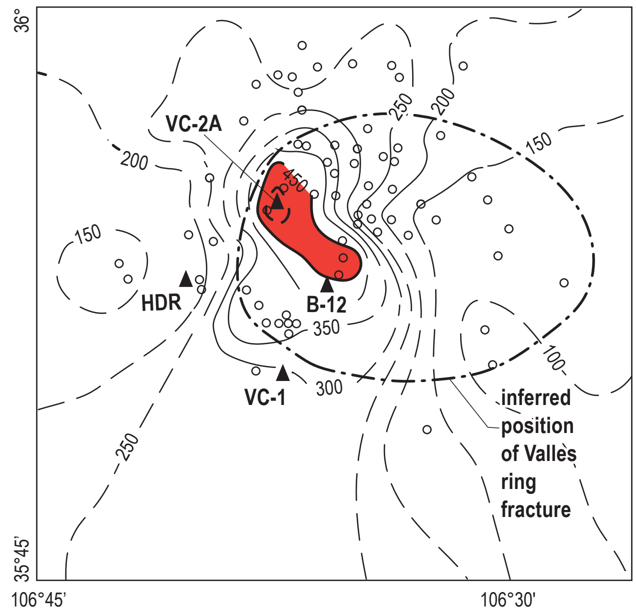


Figure 4. Contour map of shallow temperature gradients (°C/km) in and around the Valles caldera (modified from Sass and Morgan, 1988). Open circles show locations of temperature gradient wells. Triangles show selected deep geothermal and scientific wells mentioned in text (HDR = Hot Dry Rock wells at Fenton Hill; VC-1 and VC-2A= Continental Scientific Drilling Program wells; and B-12 = well Baca 12 in geothermal reservoir). For reference, these wells and the Valles ring fracture are shown on Figure 5. Red area highlights a zone with gradients above 450°C/km that extends from Sulphur Springs to Redondo Creek.

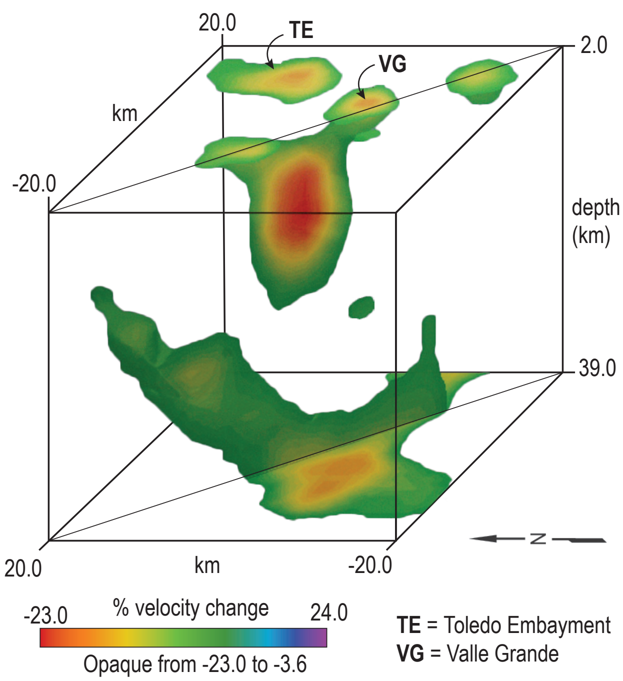


Figure 3. Block diagram showing three-dimensional low velocity seismic anomalies beneath Valles caldera (modified from Steck et al., 1998). Note that north is to the left and the displayed depth is from 2.0 to 39.0 km. Warmer colors indicate increasing seismic delay (slower seismic velocity). A partially solidified magma body exists beneath the southwest sector of the caldera at 7 to 15 km depth.

Cross Section

Geothermal and scientific drilling from 1960 to 1988 produced enormous amounts of information on the internal stratigraphy, structure, geophysical character, hydrothermal alteration, and hydrothermal fluids within the Valles caldera (Nielson and Hulen, 1984; Goff et al., 1989; Goff and Gardner, 1994). A generalized east-to-west cross section of the caldera region (Fig. 5) shows the relations among the major stratigraphic groups of the Jemez Mountains volcanic field and the relations to Tertiary basin-fill rocks of the Rio Grande rift, Paleozoic to Mesozoic rocks of the Colorado Plateau, and Precambrian basement. Detailed cross sections can be found in Goff et al. (2011). Drilling and gravity investigations reveal that the Valles caldera floor is structurally asymmetric. It is

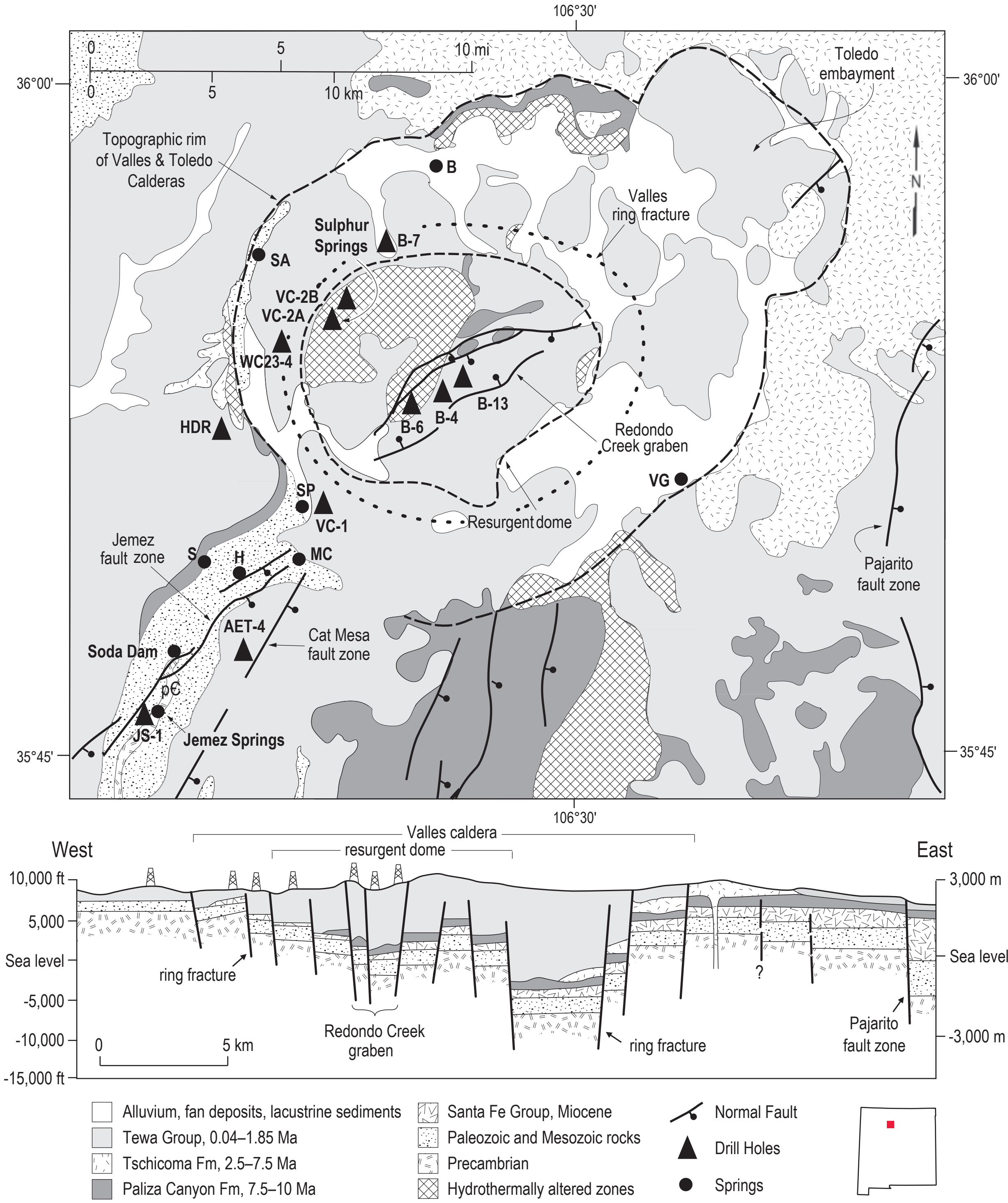


Figure 5. Generalized geologic map and east-west cross section of the Valles caldera region showing stratigraphic relations among major rock units and structural relations between the caldera and the Rio Grande rift. Well symbols shown on cross-section denote zone of subsurface stratigraphic control and do not necessarily denote any particular well. Geothermal and scientific drilling combined with gravity data reveal the "trap door" structure of the caldera, which has been since ascribed to down-to-the-southeast Rio Grande rift faulting combined with collapse of the earlier Toledo caldera (Goff et al., 2011). The data also reveal a relative horst occupied by the Sierra de los Valles (see Fig. 2) between the east caldera wall and central Rio Grande rift. On the map, B-4, B-7, etc. show locations of selected Baca geothermal wells. B-6 corresponds with the site of the failed 50 MWe geothermal power plant. Also shown are locations of the three Continental Scientific Drilling Program core holes (VC-1, VC-2A and VC-2B), the Fenton Hill Hot Dry Rock site (HDR), the JS-1 well at Jemez Springs and wildcat wells WC23-4 and AET-4. Springs highlighted in Tables 1 and 2 include Bathhouse Spring (B), McCauley Spring (MC), Sino Spring (S), San Antonio Hot Spring (SA), Spence Hot Spring (SP) and Valle Grande Spring (VG). H marks location of Hummingbird Fumarole. Figure modified from Goff and Gardner (2004, fig. 4).

much deeper on the east than on the west due to pre-existing Rio Grande rift structures and the collapse of the earlier Toledo caldera (Goff et al., 1989, fig. 9; Goff et al., 2014, fig. 12). Miocene sedimentary rocks of the Rio Grande rift thicken eastward toward the axis of the rift. Particularly noteworthy is the relative horst between the eastern caldera ring fracture and the Pajarito fault zone (Figs. 2 and 5). The Pajarito fault zone bounds the western and deepest part of the Española Basin segment of the Rio Grande rift. Because of this relative horst, the caldera depression and the Rio Grande rift form separate hydrologic basins.

Rift structures formed during the late Tertiary have been overprinted by Quaternary caldera structures formed during eruption of the Bandelier Tuff and subsequent events. The floor of the caldera collapsed hundreds to thousands of meters during and after these eruptions, producing a series of ring faults (Smith et al., 1970; Goff et al., 2011). After collapsing, the caldera floor was uplifted (a process called resurgence) about 1,000 m in 50,000 years or less (Phillips et al., 2007) by rising volatile depleted residual magma (Smith and Bailey, 1968). Finally, the moat zone between the resurgent dome and the caldera walls was partially filled with a complicated sequence of rhyolite domes, flows, pyroclastic rocks, lacustrine rocks, volcaniclastic sediments, and landslide deposits (Goff et al., 2011).

The uplift of the resurgent dome produced a multitude of normal faults with many orientations, but the major internal structure is the northeast-trending Redondo Creek graben. This structure parallels the northeast trend of the gravity signature, shown by Goff et al. (1989), indicating some faults within the resurgent dome are controlled by pre-existing rift structures. The northeast-trending Sulfur Creek and Redondo Creek grabens have the most impressive thermal features found in the caldera, but the east-west trending Alamo Graben cutting the western resurgent dome also displays notable hydrothermal phenomena (Fig. 6).

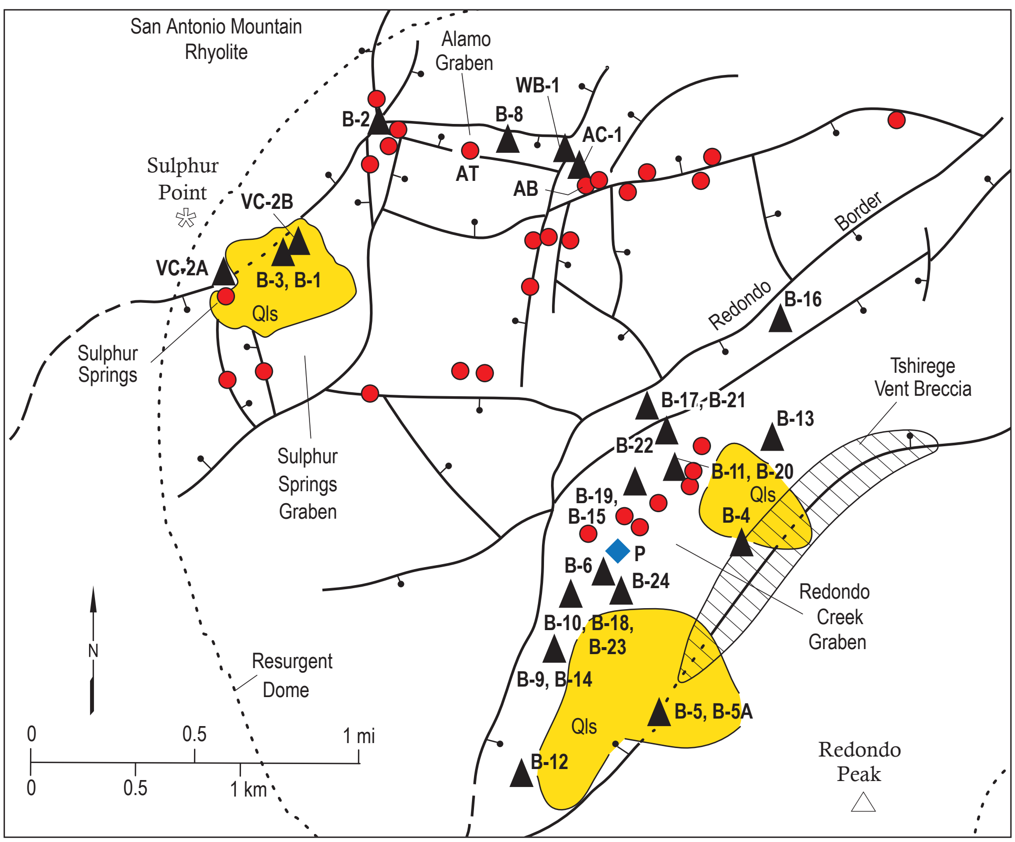


Figure 6. Simplified fault map of the southwestern resurgent dome area showing locations of H_2S-rich fumaroles and gas vents (red circles). Locations of the majority of geothermal and scientific wells are shown as black triangles. Largest landslides (Qls) are yellow, which disguise some of the larger faults. A small blue square by the letter P shows proposed location of 50 MWe power plant. This area coincides with zones of active argillic to advanced argillic alteration from acid groundwater mixed with fumarole emissions (see Charles et al., 1986 for geochemical details). Most of the gas vents have never been sampled or studied. An elliptical zone of Tshirege vent breccia (Goff et al., 2014) may coincide with a major upflow of geothermal fluids from depth (Hulen and Nielson, 1990). AB = Alamo Bog and AT = Alamo Tank. Figure adapted from Goff et al., 2011; ball and bar is on downthrown side of fault.

Geochemistry team collects samples from miniseparator during May 1991 flow test of VC-2B: Technician on left collects gas sample into special bottle, student on right is reading the temperature and pressure gauges. Cathy Janik-Goff is taking notes. Flow from the well moves to left toward the weir box steaming away in background. *Photo by Fraser Goff.*

Fraser Goff sampling Zia hot well in 1979. *Photo by Chuck Grigsby (formerly of LANL).*

III. SETTING, GEOCHEMISTRY AND USES OF THERMAL FEATURES

Three types of natural thermal fluids are found in the Valles caldera region (Fig. 7; Tables 1 and 2). Each possesses distinct geologic and structural controls, and displays unique chemical and isotopic signatures. Goff and Grigsby (1982) identified these as 1) acid-sulfate waters, 2) thermal meteoric waters and 3) deep geothermal and derivative waters. These water types are typical of those at geothermal systems hosted by Quaternary volcanoes (Goff and Janik, 2000). A fourth type of thermal fluid issues southwest and west of the Valles region at Jemez Pueblo and from down-faulted sediments west of the Nacimiento fault (Fig. 2). These sediments occur in the southeast portion of the San Juan Basin, a broad region covering most of northwest New Mexico. Waters in this fourth category most resemble sedimentary basin brines and have little or no affinity to the Valles hydrothermal system (Vuataz and Goff, 1986). Tables 1 and 2 also list some comparative analyses of waters and gases from the Fenton Hill Hot Dry Rock site on the western margin of the caldera (Fig. 5, labeled as HDR). These tables are by no means comprehensive and the interested researcher should consult several earlier reports to obtain additional analytical data (e.g., Goff et al., 1981, 1988; Goff and Gardner, 1994; Goff and Janik, 2002; Truesdell and Janik, 1986: Vuataz and Goff, 1986; White, 1986; White et al., 1984).

Acid-Sulfate Waters

Acid-sulfate waters commonly form in the cap rocks of high-temperature geothermal systems (White et al., 1971; Goff and Janik, 2000; Stimac et al., 2015). Rising H_2S gas from the underlying reservoir is oxidized to form sulfuric acid, which mixes with various proportions of local meteoric water. Acid-sulfate waters are restricted to the interior of the Valles caldera, where they discharge from faults and fractures within the western half of the resurgent dome (Goff et al., 1985; Goff and Janik, 2002). The most impressive group of fumaroles, acid springs, and mud pots emerge at Sulphur Springs (Figs. 7A and 7B) where several faults and fractures intersect. Weaker acidic features, gaseous cold springs, and gas vents discharge along the Alamo graben, the Redondo Creek graben, and small faults in between (Figs. 6, 7C, 7D, and 7E). These springs and vents discharge primarily from faulted intracaldera Bandelier Tuff, overlying tuffs of the Deer Canyon Formation, intracaldera debris flows and sediments, and young landslides (Goff et al., 2011). Flow rates and temperatures are seasonal, with the lowest flows and highest temperatures occurring during early summer and late fall-early winter, respectively. Most fumarole areas are characterized by multi-colored (white, yellow, and orange) hydrothermal alteration, dead vegetation, and the “rotten-egg” smell of H_2S. Pale yellow H_2S-loving filamentous bacteria thrive in some springs and pools. Sulfur speciation and biological conditions in these springs have been studied as possible analogues for acid-sulfate hydrothermal conditions on the planet Mars (Szynkiewicz et al., 2012b).

Sulphur Springs contains impressive acid-sulfate springs and mud pots, generally characterized by low pH (≤2), relatively high SO_4 (≤7,000 mg/kg, Table 1, but other analyses exceed 10,000 mg/kg Total Dissolved Solids (TDS)), and low Cl (≤10 mg/kg). The SiO_2 concentration is highly variable, as it is controlled by acidic reactions as well as temperature. Dissolved Al+Fe are often the dominant cations. Commonly, K concentrations exceeds Na, and Ca+Mg may exceed K+Na. Temperature sensitive trace element concentrations of B, Br, and Li are about the same as cold background waters because temperatures in acid-sulfate springs are usually less than boiling. Acid-sulfate waters may contain slightly high As and Hg because these elements are more volatile than most others.

Valles acid-sulfate waters have the distinction of containing the highest neodymium (Nd) and rare earth elements (REE) concentrations of any analyzed hydrothermal fluids (Michard, 1989). They have much higher concentrations of these elements than underlying geothermal reservoir waters (e.g., Baca-13)

Table 1. Chemical and stable isotope analyses of selected spring and well waters discussed in this paper; values in mg/kg and per mil (SMOW) unless otherwise stated.

Type	Background	Background	Acid-sulfate	Acid-sulfate	Acid-sulfate	Acid-sulfate	Thermal meteroic	Thermal meteroic	Thermal meteroic	Thermal meteroic
Name	**Sino Spg**	**Valle Grande Spg**	**Tony's Spg**	**Footbath Spg**	**Alamo Tank**	**Alamo Bog**	**Spence Hot Spg**	**San Ant Hot Spg**	**McCauley Spg**	**Bathhouse Spg**
UTM Northing	3965238	3969006	3974718	3974747	3975808	3975709	3968274	3978306	3965253	3981700
UTM Easting	348385	369074	354241	354261	355812	356161	352904	351811	353027	359291
Site	San Diego Canyon	E Valle Grande	Sulphur Spgs	Sulphur Spgs	L Alamo Canyon	U Alamo Canyon	Source	Source	Source	Source
Date	1979-1993	1979-2005	1993	1993	1979	2002	1988–1999	1988–1994	1978–1999	1979–1990
Rocks	Andes/redbeds	Alluv/colluv	Caldera fill	Landslide	Alluvium	Alluvium	Rhyo/red beds	Rhyo/red beds	Rhyo/red beds	Rhyolite
Analyses (n)	5	4	1	1	1	1	6	6	5	6
Depth (m)	surface	surface	surface	surface	surface	surface	surface	surface	surface	surface
Temp. (°C)	19±3	15.2±0.5	41.2	25	6.7	11.4	43.1±1.4	41.1±0.2	31.9±0.5	38.0±0.4
Flow (l/min)	50±30	30±5	≤1	≤1	1	≤1	100±40	150±25	500±150	12±6
pH	7.45±0.32L	7.0±0.3F	1.22L	1.54L	5.2F	2.81L	6.6±0.4F	6.6±0.4F	6.7±0.8F	7.6±0.2L
SiO_2	79±3	53.7±1.3	233	113	51	16.9	65.0±4.4	77.6±1.6	53.6±1.5	102±3
Na	14±2	7.7±1.5	4.7	18.9	32.8	14.7	52.8±2.8	22.1±0.8	19.9±1.1	29.8±5.2
K	1.0±0.4	1.4±0.2	49.2	64.1	7.9	14.8	1.58±0.12	2.02±0.25	1.0±0.1	4.5±1.5
Li	0.05±0.02	0.02±0.01	0.02	0.12	0.08	0.030	0.67±0.08	0.04±0.03	0.26±0.03	0.09±0.05
Ca	11.8±0.6	4.8±0.7	4.5	83.7	83.5	44.2	6.2±0.6	3.1±0.1	8.8±1.1	5.5±0.5
Mg	3.65±0.32	1.42±0.22	5.49	18.9	12.0	8.55	1.64±0.08	0.27±0.09	4.67±0.25	0.48±0.08
Sr	0.06±0.02	0.02±0.01	0.13	0.37	0.68	0.34	0.03±0.01	0.02±0.01	0.03±0.01	0.04±0.02
Fe	<0.01	0.01	54.1	309	0.28	34.7	*0.02*	0.05±0.03	0.01±0.01	*0.01*
Al	0.001	0.004±0.002	261	186	na	13.2	*0.02*	*0.01*	*0.05*	*0.04*
F	0.54±0.21	0.24±0.05	1.21	5.11	0.23	<0.01	0.62±0.05	0.75±0.05	0.86±0.07	1.5±0.2
Cl	4±1	1.1±0.3	<0.5	4.13	7.2	4.08	7.18±0.44	2.11±0.23	3.4±0.6	4.6±2
Br	0.06±0.02	0.01	<0.05	<0.05	na	0.04	0.06±0.03	0.04±0.01	0.02±0.01	*0.06*
I	<0.01	nd	<0.01	<0.01	na	<0.01	<0.01	<0.01	<0.01	<0.01
HCO_3	80±9	41±8	0	0	178	0	140±8	61.3±7.1	94.5±14.5	75±12
CO_3	0	0	0	0	0	0	0	0	0	0
SO_4	4.3±0.7	1.0±0.2	6230	4985	254	399	15.2±0.3	6.20±0.54	5.5±0.8	13.8±1.1
As	0.001	0.0004±0.0001	0.34	0.064	na	0.0013	*0.05*	*0.03*	0.02	<0.05
B	0.02±0.01	0.005±0.001	<0.05	<0.05	<0.1	0.035	0.25±0.22	*0.28*	0.047±0.005	*0.18*
Ba	0.02±0.01	0.003±0.001	0.03	0.03	<0.12	0.065	*0.005*	*0.005*	0.003	*0.01*
Cs	<0.002	≤0.002	0.028	0.01	na	0.0018	0.010±0.004	0.004±0.003	0.004	*0.02*
Mn	*0.01*	<0.001	0.67	3.06	0.96	0.92	*≤0.01*	*≤0.01*	*≤0.005*	*<0.01*
NH_4	*0.03*	≤0.05	89.2	0.07	na	0.17	0.08±0.06	0.06±0.03	0.12±0.08	*0.05*
Rb	0.006±0.002	0.005±0.001	0.36	0.52	na	0.034	0.011±0.003	0.012±0.004	0.007±0.002	0.025±0.020
TDS	203±10	116±13	6935	5795	628	552	284±15	179±8	194±17	260±25
δD-H_2O (‰)	-87.7±0.6	-85.2±0.2	-59.8*	-92.7 to -71.8*	-97.3	-83.1	-86.8±3.1	-91.6±0.6	-89.7±1.6	-86.7±1.7
$\delta^{18}O$-H_2O (‰)	-12.1±0.2	-12.55±0.15	-11.6*	-23.4 to -18.5*	-13.45	-12.0	-12.21±0.10	-12.83±0.08	-12.52±0.8	-12.1±0.3
^3H-H_2O	0.23±0.11	1.4±0.4	5.57*	5.4 - 17.0*	na	na	0.21±0.18	0.66±0.07	2.0±0.7	0.26±0.16
He 3/4			6.2	5.16				0.18		

Italicized values are best estimates from the available data; na = not analyzed; UTM coordinates are in NAD 27; F= field measurement; L= lab measurement

All analyses by Dale Counce and P.E. Trujillo, Jr., LANL. Geochemcial data from Shevenell et al. (1987), Musgrave et al. (1989), Meeker et al. (1990) and unpublished data.

*Isotope data from summer 1988 (Meeker et al., 1990); **Value too high due to reaction with casing.

Table 1. Continued.

Type	Reservoir	Reservoir	Reservoir	Reservoir	Reservoir	Reservoir	Derivative	Derivative	Derivative	Derivative
Name	**VC-2A well**	**Baca-3 well**	**VC-2B well**	**VC-2B well**	**Baca-13 well**	**Baca-15 well**	**VC-1 well**	**Soda Dam**	**Hidden Spg**	**Jemez Spg**
UTM Northing	3974755	3974902	3974933	3974933	3973399	3973083	3967306	3962001	3961953	3959782
UTM Easting	354291	354669	354669	354669	358460	357366	353665	347624	347626	347222
Site	Sulphur Spgs	Sulphur Spgs	Sulphur Spgs	Sulphur Spgs	Redondo Graben	Redondo Graben	SW caldera	Main Spring	Soda Dam area	Gazebo
Date	1987	1988	1990	1991–1992	1982–1988	1982–1988	1985	1991–2004	1992	1983–1992
Rocks	Band tuff	Band tuff	Precambrian	Tuff to lmst	Tuff/andes/ss	Tuff/andes	Limestone	Gneiss/lmst	Alluv/lmst	Alluvium
Samples	7	1	1	6	5	5	1	10	1	6
Depth (m)	410	546	1760	5 feed zones	≥1000	≥1000	483	surface	surface	surface
Temp. (°C)	210	190	295	225	278	267	111	46.9±0.3	33.2	74±0.5
Flow (l/min)	flow tests	in situ	in situ	flow tests	flow tests	flow tests	in situ	60±20	6±2	20±10
pH	8.66±0.15L	6.92L	5.06L	5.80±0.52L	8.56L	7.97L	7.07L	6.6±0.4F	7.25L	6.7±0.2F
SiO_2	310±26	255	882	400±39	515±30	492±49	74	47.5±2.9	41	91±1
Na	1825±126	1310	2350	1695±68	1156±29	1390±170	883	1006±47	882	644±21
K	306±20	158	700	389±51	218±23	274±38	85	179.5±5.5	158	69±8
Li	26.6±1.6	18.2	32.8	22.6±1.1	17.2±1.2	17.9±2.5	8.0	12.8±0.5	10.8	8.5±1.0
Ca	6.3±1.7	31.6	78.5	79.4±11.1	3.1±0.3	11.9±0.3	49.0	331±13	316	129±4.5
Mg	0.12±0.05	0.26	0.76	0.14±0.05	0.06±0.05	0.02	17.8	23.6±1.9	19.1	4.66±0.28
Sr	0.67±0.24	2.40	1.22	1.72±0.31	0.19±0.04	0.22±0.06	1.33	1.50±0.11	1.31	0.61±0.03
Fe	0.32±0.06	1.34**	0.47	0.27±0.09	0.010±0.006	0.010±0.006	<0.1	0.07±0.03	0.45	0.08±0.03
Al	*0.4*	<0.1	0.4	0.26±0.05	0.22±0.06	0.19±0.12	0.1	*0.3*	<0.1	*0.2*
F	6.13±1.14	10.6	5.67	2.75±1.12	7.2±0.2	5.5±0.9	3.94	3.30±0.52	2.67	5.25±0.73
Cl	2880±210	1780	4150	3050±160	1955±55	2420±300	964	1513±41	1345	905±38
Br	5.8±0.3	5.8	13.6	9.15±0.46	5.0±0.6	7.0±0.8	2.8	4.54±0.27	4.10	2.55±0.26
I	0.20±0.02	0.1	0.21	0.17±0.01	0.14	0.15	na	0.07±0.02	<0.02	0.04±0.01
HCO_3	59.4±19.8	588	105	115±29	174±7	59±13	942	1527±6	1198	729±28
CO_3	111±19	0	0	0	56	30	0	0	0	0
SO_4	54.7±6.2	66.8	7.8	14.5±2.7	37.8±2.7	29.4±5.1	56.8	35.3±0.09	47.0	41.5±2.4
As	1.81±0.32	1.23	2.7	0.98±0.35	2.2±0.3	2.6±0.2	0.8	1.75±0.15	1.11	0.8±0.2
B	25.0±1.9	18.4	29.6	24.0±2.8	15.0±1.2	18.8±2.8	8.55	13.9±0.5	11.9	7.09±0.38
Ba	0.010±0.03	0.08	0.32	0.79±0.16	0.02	0.02±0.01	0.78	0.43±0.02	0.38	0.23±0.03
Cs	3.27±0.21	2.08	5.45	3.80±0.37	2.1	3.9±1.1	0.19	1.75±0.27	1.90	1.01±0.25
Mn	0.05±0.05	0.30	0.014	0.15±0.07	0.01	0.010	0.55	0.53±0.05	0.50	0.19±0.12
NH_4	0.69±0.14	0.57	2.49	4.14±0.87	*0.3*	0.42±0.20	1.1	0.77±0.31	0.54	0.34±0.07
Rb	4.23±0.21	2.52	11.5	6.26±1.20	3.0±0.6	4.0±0.7	0.77	2.23±0.38	2.40	0.84±0.25
TDS	6640±900	4554	8410	5805±165	3870±350	4540±630	3120	4590±195	4045	2610±50
δD-H_2O (‰)	-72.6±4.4	-81.8	-85.2	-82.1±1.3	-86.4±2.2	-84.4±1.3	-88.0	-85.0±0.5	-86.0	-82.1±0.5
$\delta^{18}O$-H_2O (‰)	-6.94±0.63	-8.88	-7.50	-7.82±0.56	-9.92±0.16	-8.57±0.10	-11.35	-10.60±0.23	-10.64	-10.63±0.37
^3H-H_2O	0.47	0.55	0.77	0.44±0.23	0.61	0.18	0.66	1.48±0.15	3.63	1.20
He 3/4	≤5.0 (n=4)		<5.4 (n=6)		4.75	4.14		0.84		1.27

Italicized values are best estimates from the available data; na = not analyzed; UTM coordinates are in NAD 27; F= field measurement; L= lab measurement
All analyses by Dale Counce and P.E. Trujillo, Jr., LANL. Geochemcial data from Shevenell et al. (1987), Musgrave et al. (1989), Meeker et al. (1990) and unpublished data.
*Isotope data from summer 1988 (Meeker et al., 1990); **Value too high due to reaction with casing.

Table 1. Continued.

Type	Derivative	Pre-cambrian	Pre-cambrian	Pre-cambrian	Pre-cambrian	Basin brine	Basin brine	Basin brine	Basin brine	Basin brine	Basin brine	Basin brine
Name	**JS-1 well**	**WC23-4 well**	**EE-3 well**	**EE-2 well**	**EE-3 well**	**Salt Spg**	**JP-1 well**	**C Spg**	**Big Mama Spg**	**Tufa pool**	**L Double Spg**	**Zia hot well**
UTM Northing	3959796	3974933	3971780	3971781	3971780	3940555	3939701	3935059	3940677	3941152	3940108	3946080
UTM Easting	347236	352789	348850	348848	348850	340571	341340	334449	331159	331902	331078	329012
Site	Jemez Spgs	Thomp. Ridge	Fenton Hill	Fenton Hill	Fenton Hill	Jemez Pueblo	Jemez Pueblo	SE SJ Basin	SE SJ Basin	SE SJ Basin	SE SJ Basin	SE SJ Basin
Date	1979	1983	1983	1991	1994	1991	1991	1992	1996	1996	1996	1992
Rocks	Limestone	Granite/ gneiss	Gneiss/ schist	Gneiss/ schist	Gneiss/ schist	Alluv/ redbeds	Tert SS	Evap/SS/ Carb	Evap/SS/ Carb	Evap/SS/ Carb	Evap/SS/ Carb	Evap/SS/ Carb
Samples	1	1	1	5	1	1	1	1	1	1	1	1
Depth (m)	152	1921	>4000	3660	>3660	surface	≤73	surface	surface	surface	surface	surface
Temp. (°C)	60.5	233	>250	≥240	≥240	18	57.8	18.9	22.5	24.2	28	54.9
Flow (l/min)	flowing	in situ	pumped	circulation	circulation	seep	≥75	1	2	1	1.5	240±80
pH	6.69F	7.10F	6.67F	6.15 ±0.08L	6.88L	7.46L	7.61L	6.5F	7.27L	7.49L	7.16L	7.53L
SiO_2	36	450	*400*	419±10	389	6.3	39	14	17.6	36.8	23.8	38
Na	185	5890	4830	812±63	1890	822	1148	2240	3210	2170	2895	3320
K	29.9	1020	730	84±3	159	62	67	80.3	79.1	57.9	101	63.3
Li	2.27	68	106	14.3±1.8	35.6	3.44	6.09	6.15	5.62	3.85	6.62	4.20
Ca	120	46.0	140	15.2±1.4	48.0	170	69.5	363	392	289	467	282
Mg	9.31	0.45	9.8	0.22±0.09	2.78	32.9	12.7	84.5	60.5	57.9	64.8	54.8
Sr	0.40	1.98	na	0.53±0.14	2.14	3.16	2.76	6.57	7.75	6.36	6.69	7.47
Fe	0.39	0.25	na	5.5±3.4	5.02	0.36	0.11	1.31	0.03	0.05	0.04	1.24
Al	*0.1*	0.54	na	0.9±0.2	0.14	<0.1	<0.1	<0.1	0.16	0.14	0.13	<0.1
F	3.3	13.8	2.3	15.7±0.4	9.52	3.84	6.68	2.24	2.09	2.76	2.47	2.67
Cl	243	9960	10,500	1050±29	2520	878	1196	2055	2670	1985	2065	2890
Br	*1.2*	27	71	5.64±0.17	13.1	2.55	3.33	4.98	3.97	3.64	3.83	4.67
I	na	na	na	0.09±0.01	0.18	<0.02	0.08	0.04	<0.05	<0.05	<0.05	0.15
HCO_3	479	382	1100	454±36	1010	1160	1132	1565	1435	1305	2005	1445
CO_3	0	0	0	0	0	0	0	0	0	0	0	0
SO_4	49.9	95	51	230±8	350	256	254	1970	3315	1540	2915	3030
As	*0.4*	7.8	18.3	2.8±0.6	7.9	<0.1	0.4	0.28	0.06	0.18	0.12	0.41
B	2.2	96.2	272	36.6±1.3	76.7	5.53	8.46	9.42	7.47	5.10	8.44	6.94
Ba	<0.12	1.17	na	0.15±0.06	0.25	0.06	0.09	0.01	<0.01	0.01	0.01	0.06
Cs	na	na	na	na	1.84	0.47	0.23	0.38	0.24	0.25	0.23	0.11
Mn	0.02	1.08	na	0.10±0.05	0.11	0.04	0.04	0.63	0.44	0.28	0.23	<0.01
NH_4	0.3	na	na	1.12±0.19	0.92	0.06	0.59	0.12	0.24	0.11	0.17	0.59
Rb	na	*15*	na	na	1.84	0.52	0.46	0.53	0.35	0.46	0.60	0.28
TDS	1140	18,100	18,230	3150±130	6500	3407	3948	8404	11,210	7816	8555	11,150
δD-H_2O (‰)	-85.9	-71.5	na	-80.2	na	-90.8	-88.9	-85.2	-88.0	-83.0	-88.0	-86.3
$\delta^{18}O$-H_2O (‰)	-11.8	-5.05	na	-7.71	na	-12.0	-11.24	-10.32	-11.5	-11.5	-11.3	-11.1
^3H-H_2O	1.75	na	na	na	na	na	0.07	0.36	2.9±0.11	0.45±0.09	0.82±0.09	0.05
He 3/4								0.32				0.23

Italicized values are best estimates from the available data; na = not analyzed; UTM coordinates are in NAD 27; F= field measurement; L= lab measurement

All analyses by Dale Counce and P.E. Trujillo, Jr., LANL. Geochemcial data from Shevenell et al. (1987), Musgrave et al. (1989), Meeker et al. (1990) and unpublished data.

*Isotope data from summer 1988 (Meeker et al., 1990); **Value too high due to reaction with casing.

Photographs of Valles caldera and regional thermal features: **Figure 7a**—Sulphur Springs, main fumarole (December 2008) discharges deep steam (H_2O vapor) mixed with CO_2 and H_2S at boiling temperatures. Sublimed sulfur collects around the gas vents. *Photo by Fraser Goff.*

Figure 7b—Anna Szynkiewicz, geochemist at University of Tennessee, Knoxville, precipitates sulfur in a flask containing $CdCl_2$ at Footbath Spring to analyze $\delta^{34}S$-H_2S of deep gas (July 2014). Precipitated $CdCl_2$ is yellow-orange in color. Sulfur-rich acidic water in Footbath Spring was once used as a natural fungicide during the resort era before 1960. *Photo by Fraser Goff.*

Figure 7c—Alamo Tank (December 2008), a former stock-watering pond along Alamo Creek that coincides with an area of H_2S-rich gas vents. Note bubbles of gas disrupting water surface, and the turquoise-blue color of water, caused by filamentous bacteria and colloidal silica from acid-dissolution of rock. *Photo by Fraser Goff.*

Figure 7d—Gas vents at east end of Alamo Bog (December 2008; see Fig. 6). Note abundant pale yellow filamentous bacteria and gas bubbles. *Photo by Fraser Goff.*

Figure 7e—Diffuse gas vent in Redondo Creek graben (July 2014). H_2S-rich gas reacts with oxygen in groundwater and soil bacteria to form sulfuric acid that kills vegetation and bleaches rocks white (White et al., 1971; Szynkiewicz, 2012b). Sulfur, amorphous silica and natural sulfates are common. Tree damage on left side of photo is from a forest fire in 2013. *Photo by Fraser Goff.*

Figure 7f—Bathhouse Spring along the north edge of San Antonio Creek (Fig. 5) looking west (July 2014). Warm Spring rhyolite dome is to right; Cerro Seco rhyolite dome is to left; northwest caldera wall is in distance. Thermal water in the bathhouse has issued at 38°C for the last 36 years. *Photo by Fraser Goff.*

Figure 7g—Spence Hot Spring (July 2014; legs of bather for scale) issues from rhyolite rubble at contact of Banco Bonito vitrophyre lava and underlying Permian red-beds. Man-made pools catch dilute thermal water that averaged around 43°C before 1999. Now only 38°C, Spence is cooling down for reasons yet unknown. *Photo by Fraser Goff.*

Figure 7h—Family enjoys the source pool of McCauley Spring just as a thunderstorm begins (July 2014). Maximum measured temperature remains at about 32°C for the last 36 years. Tropical fish (tetras) and fish-tank grasses released by an unknown person have made a home in the spring waters for an equal amount of time. *Photo by Fraser Goff.*

Figure 7i—Photo looking northwest of the Main Spring, Soda Dam (July 2014), which issues from the Jemez fault zone southwest of Valles caldera (Fig. 5). Revered by the local Pueblo cultures, the mineral waters of Soda Dam became a focus of legal debate during the early years of geothermal development at the "Baca." Active deposit in photo is 2 m tall. *Photo by Fraser Goff.*

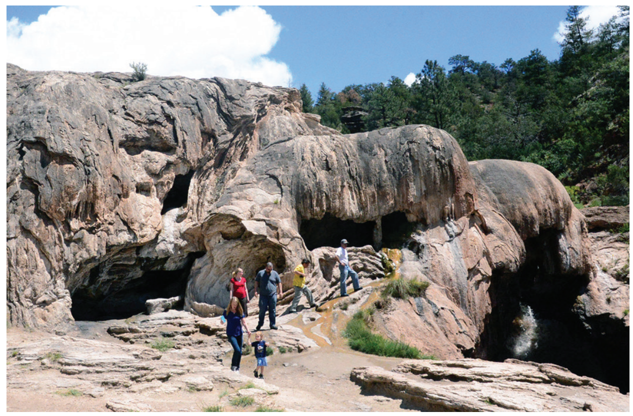


Figure 7j—Photo of Soda Dam travertine (mostly $CaCO_3$) bridging the Rio Jemez (July 2014); orange discoloration on right side of dam marks the location of Grotto Spring inside the dam. Recent work by Tafoya (2012) indicates this travertine formed in the last 10 kyr. *Photo by Fraser Goff.*

Figure 7k—Photo of what remains of the JS-1 geothermal well (July, 2014) drilled in 1977–1978 at Jemez Springs (Goff et al., 1981). Excess water issues from a pressure release pipe, but most water is piped to the gazebo of the "main" spring, actually a hand-dug well. *Photo by Fraser Goff.*

Figure 7l—Photo of Travertine Mound Spring, a low discharge, 75°C spring depositing travertine by the Rio Jemez at Jemez Springs (July 2014). *Photo by Fraser Goff.*

Figure 7m—William Inskeep, geochemist at Montana State University, measures field parameters at the JP-1 geothermal well (57.8°C) along the Rio Jemez in Jemez Pueblo (May 2010). Nearby hot springs once used by the Pueblo (Trainer, 1984; Trainer et al., 2000) ceased to flow once the well was drilled in 1991. Consequently, local inhabitants opened the unlocked well to let it flow into temporary pools built by the riverside. *Photo by Fraser Goff.*

Figure 7n—Photo of C Spring looking west (May 2010). This and other tepid mineralized seeps (19 to 28°C) issue from structurally deformed sediments at the SE edge of the San Juan Basin and Nacimiento fault system (see Fig. 2, site SJB for general location). Strata in the background consist of evaporites of Jurassic Todilto Formation overlying Jurassic Entrada sandstone and late Triassic Chinle Formation. *Photo by Fraser Goff.*

Table 2. Geochemistry of selected gas samples in Valles caldera and nearby areas. Values are reported in mol-% dry gas except where noted. Data are from Goff and Janik (2000, 2002, and unpublished files).

Site	Sulphur Spgs	Alamo Graben	VC-2A Well	VC-2B Well	Baca Wells	Soda Dam	Jemez Spgs	HDR Wells	C Spg	Double Spg	Zia Hot Well
Location notes	Women's Bath	Alamo Bog	flowing	in situ	flowing	main spg	gazebo	flowing	pool	pool	pool
UTM Northing	3974587	3975709	3974755	3974933	Various	3962001	3959782	3971780	3935059	3940108	3946080
UTM Easting	354191	356161	354291	354669	Locations	347624	347222	348850	334449	331078	329012
Analyses (n)	4	2	7	3	10	3	2	13	1	1	1
Temp (°C)	88±5	12.7	210	295	270±24	47±0.4	75±0.5	various	19	28	54
CO_2	98.5±1.2	97.88±0.16	97.1±1.4	96.9±0.8	98.8±0.4	98.4±1.3	99.1±0.6	95.5±3.8	97.7	72.3	87.6
H_2S	0.71±0.36	1.30±0.16	0.72±0.16	0.81±1.1	0.47±0.35	0.02±0.01	0.063±0.02	0.030±0.03	<0.02	0.013	0.068
H_2	0.10±0.04	*0.14*	0.25±0.24	1.85±1.44	0.62±0.34	0.005±0.002	0.0001±0.0001	0.21±0.5	<0.005	0.0000	0.0000
CH_4	0.016±0.002	0.050±0.008	0.017±0.014	0.24±0.12	0.20±0.20	0.004±0.001	0.005±0.0004	0.097±0.3	0.004	0.0000	0.0226
NH_3	0.0017±0.002	<0.0002	0.84±0.65	nd	0.29±0.29	0.002±0.001	0.0008±0.005	0.005±0.009	nd	0.0000	0.0059
N_2	0.69±0.9	0.746±0.008	0.94±0.67	0.29±0.09	0.47±0.25	1.10±1.0	0.71±0.6	3.3±2.8	1.97	24.9	11.3
O_2	0.0041±0.0040	0.003±0.001	0.0005±0.001	0.11±0.2	0.04±0.07	0.32±0.15	0.14±0.11	0.29±0.4	0.14	0.622	0.0379
Ar	0.01±0.01	0.0102±0.0007	0.016±0.009	0.0066±0.004	0.013±0.012	0.02±0.005	0.012±0.005	0.09±0.09	0.05	0.395	0.243
He	0.0040±0.0018	0.0040±0.0001	0.0020±0.0009	0.0051±0.005	0.0038±0.0021	0.002±0.001	0.0011±0.005	0.69±1.1	0.04	1.82	0.597
Total (dry)	100.04	100.13	99.89	100.21	99.91	99.87	100.03	100.21	99.90	100.05	99.87
H_2O (%)	na	na	99.4±0.6	na	98.9±0.5	na	na	na	na	na	na
He$^{3/4}$ (R/R$_A$)	6.16±0.19	nd	5.00±0.30	5.72±0.26	4.75±0.08	0.84±0.05	1.27±0.08	nd	0.32±0.03	nd	0.23±0.01
$\delta^{13}C$-CO_2 (PDB)	-3.60	nd	-4.99	-3.30	-4.95	-4.90	-5.15	-3.94	-5.25	nd	-6.77
$\delta^{34}S$-H_2S (CDT)	3.1±1.4*	4.2**	0.8±0.1	2.5±0.1	nd	-0.3	nd	nd	nd	nd	nd

Italicized values are best estimates from the available data; na = not applicable and nd = not determined; UTM coordinates are in NAD 27; *Data from Szynkiewicz et al. (table 1, 2012b), samples were taken from main fumarole; **Data from Szynkiewicz et al. (table 1, 2012b).

or other geothermal waters in the western United States (Wood and Shannon, 2003). These high REE concentrations are the result of acidic fluids interacting with the intracaldera Bandelier Tuff, which has high concentrations of these elements (F. Goff and R.G. Warren, unpub. data). Even so, the concentrations are low, with a maximum of 0.2 ppb cerium (Ce) and 0.09 ppb neodymium (Nd) in acid-sulfate waters (Michard, 1989).

Isotope variations in acid-sulfate waters are tremendous, especially in oxygen-18 (Fig. 8), which shows effects of evaporation and unusual low-temperature isotope fractionation between CO_2-H_2O (e.g., Footbath Spring, Vuataz and Goff, 1986; Meeker et al., 1990). However, Goff et al. (1985) showed that the isotope composition of fumarole steam at Sulphur Springs can be derived by boiling of underlying reservoir fluid at 200–220°C.

Gas compositions from acid-sulfate features (Table 2) consist of roughly 98 mol-% CO_2, 1 mol-% H_2S, and 1 mol-% other gases, on a water free basis. $^3He/^4He$ ratios up to 6.2 R/RA indicate a mantle magmatic source for the He (Goff and Gardner, 1994). These values are the highest measured in the caldera and the highest measured in New Mexico. Nonetheless, most gas vents east of Sulphur Springs, including those along Redondo Creek graben, have diffuse upflow and have never been successfully sampled. Recent geologic mapping has identified at least 20 previously unrecognized H_2S-emitting gas vents (Fig. 6; Goff et al., 2011) that have the usual small volume acid seeps, whitish acid alteration, dead vegetation, and "rotten-egg" smell.

Sulphur Springs is privately owned and composed of two 20-acre patented mining claims. About 200,000 lbs (91 metric tons) of native sulfur were mined at this site from 1902 to 1904 (Summers, 1976). Sulfur and other sublimates are deposited in shallow cracks and at the mouths of fumaroles (Charles et al., 1986). A small resort once utilized the thermal features at Sulphur Springs for bathing and

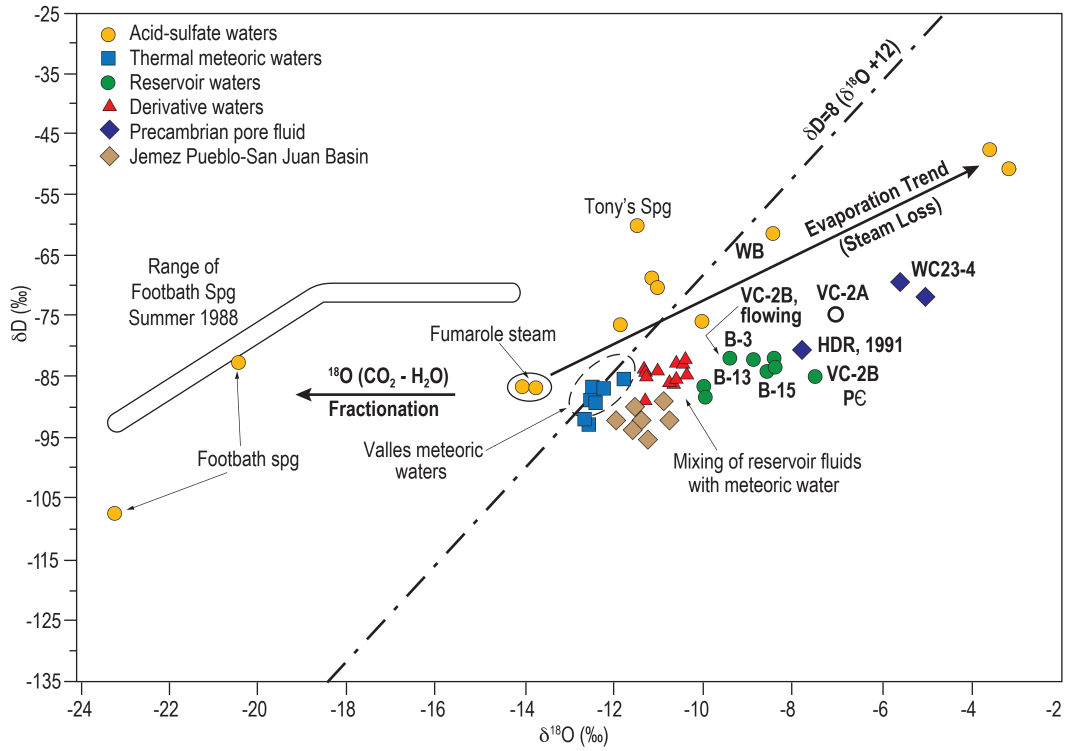


Figure 8. Plot of δD versus $\delta^{18}O$ (‰, SMOW) showing stable isotope relations among various thermal water types in the Valles caldera region. The black dashed line $\delta D = 8\delta^{18}O + 12$ is the Jemez Mountains meteoric water line derived by Vuataz and Goff (1986). Black dashed oval shows range of cold meteoric waters at elevations equivalent to the caldera. Valles geothermal reservoir waters show typical oxygen-18 enrichment relative to local meteoric water caused by high-temperature rock-water isotopic exchange; those circulating in Precambrian rocks tend to show the most enrichment. Derivative waters such as Soda Dam and Jemez Springs (red triangles) are mixtures of Valles geothermal reservoir water and local meteoric water. Acid-sulfate waters exhibit the most isotope variation. Fumarole steam can be derived from 200–220°C boiling of underlying reservoir water (Goff et al., 1985). Steam then mixes with surface meteoric water, but boiling and evaporation cause dramatic increases in both δD and $\delta^{18}O$, such as shown by Women's Bathhouse Hot Spring (WB). The big exception is Footbath Spring water, which undergoes oxygen-18 fractionation between CO_2-H_2O, thus decreasing $\delta^{18}O$ values (Goff et al., 1985; Vuataz and Goff, 1986). Four samples of Footbath Spring water collected during summer of 1988 show tremendous isotope variation caused by fractionation described above, mixing with water from thunderstorms, and evaporation (Meeker et al., 1990).

occasional drinking (Summers, 1976), but the buildings have been completely destroyed. As of 2015, Sulphur Springs is rarely visited and the springs are not suitable for bathing because of neglect. A detailed map of separate hot springs and other features can be found in Goff and Janik (2002, fig. 3).

Thermal Meteoric Waters

Four dilute springs with temperatures between 31 and 45°C and Cl concentrations ≤10 ppm discharge from isolated locations within the western moat and ring-fracture zone of the Valles caldera (Goff and Grigsby, 1982; Vuataz and Goff, 1986; Goff et al., 1988; Figs. 5, 7F, 7G, 7H). Each spring has a slightly different chemical composition and each likely originates from unique groundwater sources. Little scientific research has been conducted on these springs. San Antonio Hot Spring is the largest and presently the hottest of the four thermal meteoric springs. It issues from the east wall of San Antonio Canyon at the contact of Redondo Creek rhyodacite and underlying Permian red beds. Spence Hot Spring flows from the contact of Banco Bonito rhyolite and underlying Permian rocks. It was the hottest of the four springs until the late 1990s (45–42°C) but as of this writing discharges at only 38°C. McCauley Hot Spring issues from poorly exposed Valles moat sediments sandwiched between Banco Bonito rhyolite and Permian red beds. There is no evidence of faulting or fault-controlled discharge. Bathhouse Hot Spring issues from the fractured porphyritic rhyolite of Warm Springs dome and flows into San Antonio Creek. This dome grew along the ring-fracture system of the Toledo caldera at 1.26 Ma, prior to the Valles caldera eruption (Goff et al., 2014). Possibly, warm water rises along fractures related to this early fault system. A warm water well is documented by Summers (1976) in Valle San Antonio about 2 km west of the Bathhouse Spring.

Thermal meteoric waters are dilute (≤300 mg/kg TDS). Concentrations of major constituents and contents of B, Br, Li and As are slightly higher than those of cold background waters (Table 1). SiO_2 contents of thermal meteoric waters are slightly higher than cold background waters because the former are warmer. Similarly, the isotopic composition of thermal meteoric waters (blue squares) resembles background cold waters in the Valles region (the cloud named Valles Meteoric Waters, Fig. 8). Thermal meteoric waters do not discharge free gas. However, San Antonio hot spring water has a $^3He/^4He$ ratio of 0.18 R/RA in dissolved helium (F. Goff, unpublished data) indicating that it contains a small component of mantle/magmatic He. This value is considerably less than those for gases at Sulphur Springs, 2 km to the southeast, indicating that thermal meteoric waters have little connection to the deep geothermal system.

Bathhouse Spring and San Antonio Hot Spring are partially protected by a small cabin and a concrete crib, respectively, but Spence Hot Spring and McCauley Hot Spring are still relatively undeveloped (i.e. "wild"). The latter three sites belong to the U.S. Forest Service, while Bathhouse Spring is in the northwestern Valles Caldera National Preserve. All of these springs are used for bathing, although access to Bathhouse Spring is restricted. Bathers, hikers, and campers have constructed and otherwise modified the rock-lined pools at the two unprotected sites and below the San Antonio crib over the years. There are no hydrothermal alterations or hot spring deposits at these sites, except for minor opaline silica and calcite formed by evaporation.

Deep Geothermal Waters

Conventional geothermal wells were drilled in the resurgent dome of the Valles caldera from 1960 to 1982 (Baca-1, Baca-4, etc.) to explore and develop the deep geothermal system (Figs. 5 and 6). Maximum drilled depth and temperature are 3.2 km and 342°C in Baca-12 (Nielson and Hulen, 1984). Three scientific core holes (VC-1, VC-2A and VC-2B) were drilled in the caldera (Fig. 5) in 1984, 1986 and 1988 to examine the hydrothermal outflow plume, the vapor cap, the underlying liquid-dominated reservoir, and secondary mineralization analogous with fossil ore deposits (Goff et al., 1986; Hulen et al., 1987; Goff and Gardner, 1994). Maximum depth and temperature of the scientific wells were 1.76 km and 295°C in VC-2B, just northeast of Sulphur Springs.

Deep geothermal waters are found beneath the Redondo Creek graben, the Sulphur Springs area, and the Alamo graben (Fig. 6). These fluids (Table 1) are near neutral in pH and consist of Na-K-Cl-HCO_3 brines (3.8 to 9 x 10^3 mg/kg TDS). Deep geothermal waters contain substantial amounts of SiO_2 (≤880 mg/kg) and high concentrations of B, Br, Li, and As (as well as Cs and Rb). Concentrations of Na+K are much greater than Ca+Mg (particularly Mg) because of inverse solubility of divalent carbonates and sulfates at higher temperature. At temperatures exceeding 200°C, the ratio of Na/K decreases to values <10 and commonly <5. The $\delta^{18}O$ values of deep geothermal waters are shifted to the right (oxygen-18 enriched) relative to the local meteoric water line by more than 2‰ (Fig. 8) resulting from high-temperature isotopic exchange between water and rock (Craig, 1961). In contrast, the δD-H_2O values of deep geothermal waters resemble those of local meteoric water, a characteristic of many hydrothermal systems composed almost entirely of local meteoric water recharge (Goff and Janik, 2000).

All deep geothermal waters produce gases that can be sampled using steam separators (two phase conditions) or from gas-tight in situ samplers that prevent gas release during withdrawal to surface conditions. Gas compositions from the deep geothermal wells are extremely similar to compositions in the overlying acid-sulfate fumaroles, acid springs, and mud pots (Goff and Janik, 2002). On a triangular diagram of relative CO_2-H_2S-CH_4 (Fig. 9), Valles intracaldera gases plot along the join between CO_2 and H_2S, as do most geothermal system gases hosted in volcanic rocks. Thus, Valles geothermal gases resemble those from Yellowstone and Long Valley calderas. VC-2B gas from Precambrian basement (Table 2) is a little more H_2S rich than average gas from all Valles wells (W) and average gas from Valles acid-sulfate springs (S). Note that geothermal systems hosted in sedimentary rocks tend to contain substantially more CH_4 than volcanic hosted systems (e.g., The Geysers, Cerro Prieto).

On a triangular plot of relative N_2-He-Ar (Fig. 10), Valles intracaldera gases plot close to the join between a deep mantle or crustal component (high relative helium) and air saturated meteoric water (high relative argon). Valles intracaldera gases have low relative N_2 compared to geothermal system

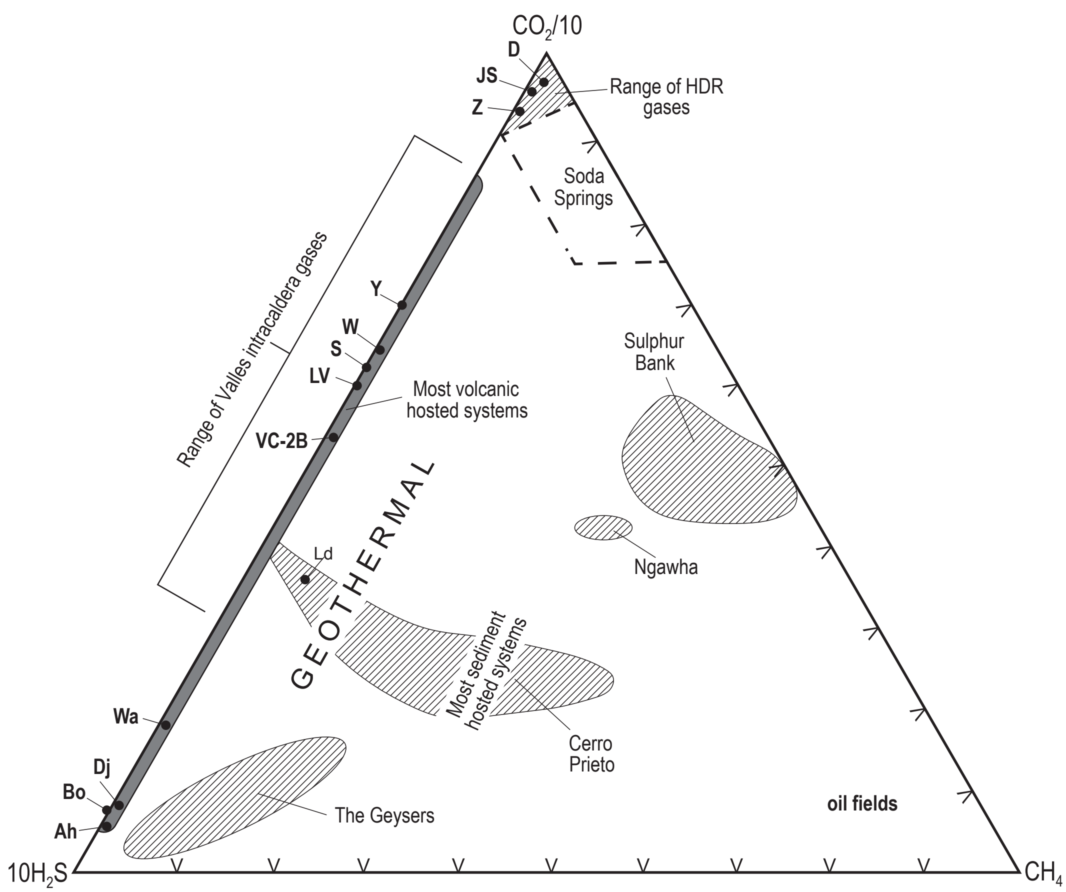


Figure 9. Triangular plot of CO_2/10-10H_2S-CH_4 shows gas compositions typical for geothermal systems, soda springs, and oil fields. Tic marks on the axes of this plot (and Fig. 10) show relative gas proportions in increments of 10%. Most volcanic hosted geothermal systems like Valles caldera have relatively low CH_4 and plot along the axis between CO_2- and H_2S-rich compositions. Other examples include Yellowstone (Y), Long Valley (LV), Wairakei, New Zealand (Wa), Ahuachapán, El Salvador (Ah), Borateras, Peru (Bo), Darajat, Indonesia (Dj). Sediment hosted geothermal systems like The Geysers and Sulphur Bank, California, Larderello, Italy (Ld), Ngawha, New Zealand and Cerro Prieto, Mexico, contain considerably more CH_4. Gases from Hot Dry Rock (HDR) site, Jemez Springs (JS) and the San Juan Basin (Z and D) resemble soda spring gases because of very high CO_2. W = average Valles intracaldera well (including VC and Baca wells), S = average Valles acid-sulfate spring; VC-2B = in situ gas from Precambrian interval (modified from Goff and Janik, 2002).

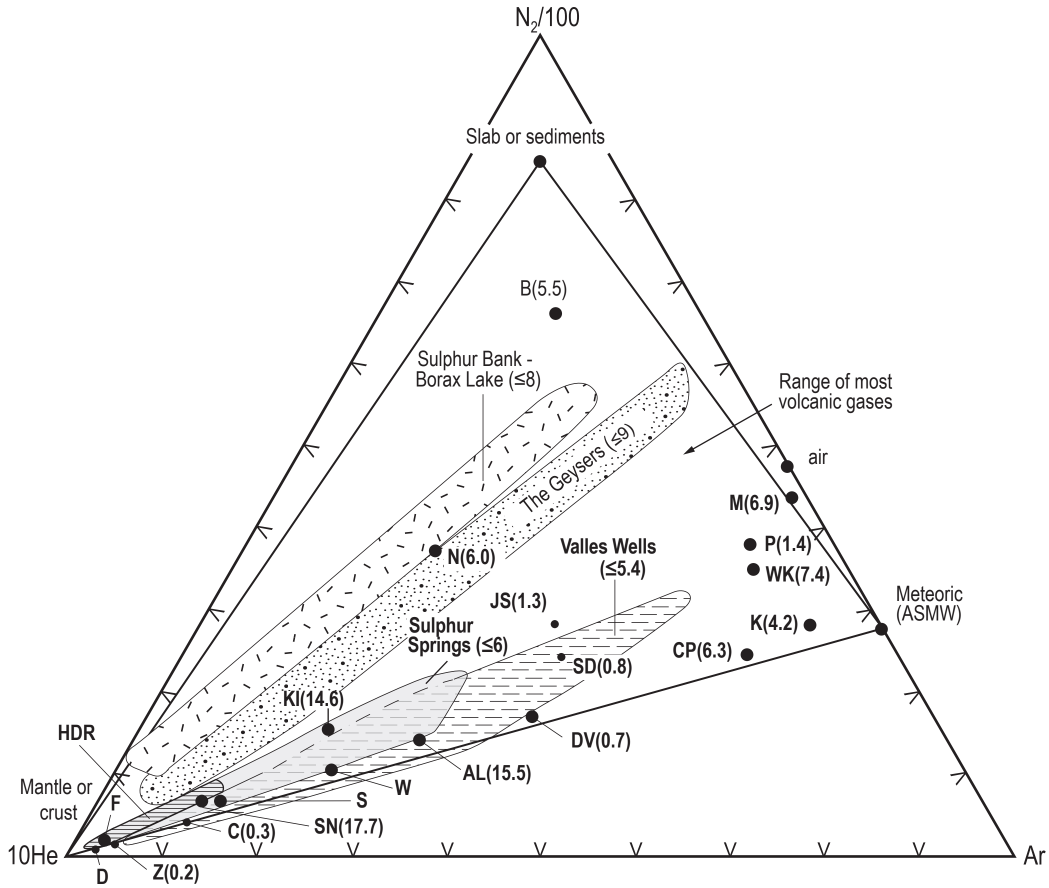


Figure 10. Triangular plot of N_2/100-10He-Ar showing relative contributions of gas from subducted slab or sediments (N_2-rich), mantle or crust (He-rich), or air saturated meteoric water (ASMW, Ar-rich). The R/R_A values for the $^3He/^4He$ ratios (shown in parentheses) are used to assess mantle versus crustal sources of He. Gases from Valles caldera geothermal wells (average = W) and acid-sulfate springs (average = S) have high $^3He/^4He$ ratios and plot along the join between mantle and ASMW, resembling those from Hot Spot volcanoes like Kilauea (Kl), Sierra Negra (SN) and Alcedo (AL). Soda Dam (SD) and Jemez Springs (JS) fall on the same trend but contain much less mantle He. Geothermal systems hosted in sedimentary rocks like The Geysers, Sulphur Bank-Borax Lake, Ngawha (N), and Broadlands (B) contain considerably more nitrogen but still have high mantle He. A surprising number of high-temperature geothermal systems contain relatively large amounts of recycled air or air saturated meteoric water (ASMW). Examples include Cerro Prieto (CP), Kawerau (K), Miravalles (M), Platanares (P), Dixie Valley (DV), and Wairakei (WK). Gases from Fenton Hill Hot Dry Rock (HDR) site contain high He (average = F), but unfortunately we have no $^3He/^4He$ analyses to discriminate between a mantle and crustal source. San Juan Basin sites (C, D and Z) have high He but low $^3He/^4He$ ratios, indicating that the He originates mostly from a crustal source (modified from Goff and Janik, 2002).

gases originating in sedimentary rocks (e.g., The Geysers and Sulphur Bank Mine-Borax Lake). Note also that Valles intracaldera gases are similar to those produced from hot spot volcanoes such as Kilauea in Hawaii, Sierra Negra, and Alcedo in the Galapagos. Geothermal systems associated with subduction zone volcanoes contain more relative N_2 derived from the underlying subducted slab (e.g., Broadlands; Miravalles).

Figure 10 also includes the $^3He/^4He$ ratios (R/RA) from each system to display mantle versus crustal helium (He) inputs. Even though C Spring and Zia hot well from the San Juan Basin have high concentrations of helium, their low R/RA ratios indicate primarily crustal origins for the gas. The $^3He/^4He$ ratios of Valles intracaldera gases range from 4 to 6, indicating that a substantial amount of mantle/magmatic helium reaches the reservoir (Smith and Kennedy, 1985).

Derivative Waters

Derivative waters are formed by mixing higher concentration deep geothermal waters with various types of dilute and bicarbonate-rich cooler fluids in the hydrothermal outflow plume (Fig. 5; Goff et al., 1981; 1988). Thermal features from the outflow plume emerge along or near strands of the Jemez fault zone, more than 10 km away from the caldera (Figs. 2 and 5), and intersect in the VC-1 well at ≥480 m depth just outside the southern ring fracture. Surface springs (derivative waters) from the outflow plume precipitate copious deposits of travertine (e.g., Soda Dam, Figs. 7I, 7J) caused by dissolution of $CaCO_3$ as the waters flow through Pennsylvanian carbonates outside the caldera. At Soda Dam, a widespread cluster of derivative springs issue from a splay of the Jemez fault zone, which displaces Precambrian gneiss against Paleozoic limestone. The fault or fracture system controlling surface discharge of the Jemez Springs is not exposed. Drilling of the JS-1 well in 1979 (Fig. 7K) showed that the source fluids for these springs circulate at 24 m depth at the contact of alluvium and underlying limestone (Goff et al., 1981). Another aquifer at 152 m depth was also intersected by the well (Table 1). The Jemez Springs also deposit travertine (Fig. 7L). Interestingly, waters at Soda Dam (Tmax = 48°C) are more concentrated but have lower temperatures than those at Jemez Springs (Tmax = 75°C), which is more distant from the caldera. This indicates that the two spring systems originate from different strands of the Jemez fault zone because the hottest fluids are furthest from the source (Goff et al., 1988).

Compared to Valles deep geothermal waters, derivative waters contain substantially less SiO_2, Na, K, and Cl, but substantially more Ca, Mg, Sr and HCO_3. Importantly, ratios of Na/K and B/Cl, Li/Cl, Br/Cl and As/Cl are nearly the same. Consequently, Cl-variation diagrams of these constituents produce mixing lines (Fig. 11) that help differentiate deep geothermal and derivative waters from other Valles region water types (discussed below). The end-member fluids are deep geothermal waters in the caldera and relatively dilute meteoric water from various sources. However, it should be noted that the trend of deep geothermal-derivative waters on the Br vs. Cl plot is very similar to a mixing line between seawater and dilute meteoric water. Apparently, this signature originates from solutes that are leached out of Paleozoic marine rocks. Isotopically, derivative waters plot between deep geothermal waters and local meteoric water (Fig. 8), providing more evidence for mixing of the two likely end-members.

Copious amounts of CO_2-rich gas are released from both Soda Dam and Jemez Springs (Table 2). In contrast with deep geothermal gases, which are relatively H_2S-rich, derivative gases are relatively poor in H_2S, H_2, CH_4 and NH_3. On the CO_2-H_2S-CH_4 plot (Fig. 9), derivative gases resemble those emitted from typical soda springs the world over (Goff and Janik, 2002). On the N_2-He-Ar plot (Fig. 10), Soda Dam and Jemez Springs fall on the more Ar-rich end of the trend of Valles intracaldera gases, indicating some origin within the caldera. The $^3He/^4He$ ratios are 0.84 and 1.27 R/RA at Soda Dam and Jemez Springs, respectively, which is considerably lower than values for Valles deep geothermal gases but greater than the 0.18 R/RA recorded at San Antonio Hot Spring.

A single zone of weak, dispersed gas emissions, with obvious H_2S odor and acid-altered rock, discharges at Hummingbird fumarole, which is located between Soda Dam and VC-1 (H, Fig. 5). Gas at this site has been extremely difficult to collect, particularly during wet periods when rainwater soaks the ground and scrubs water-soluble components. A sample collected in late August 1984 contained 96.1 mol-% CO_2 and 0.47 mol-% H_2S (Shevenell et al., 1987) indicating that this gas is similar to those in the deep geothermal system. Hummingbird fumarole gas probably originates by boiling of relatively undiluted, unreacted deep geothermal water from the underlying outflow plume. In the years since 1984, Hummingbird fumarole has been bulldozed and hand modified to prevent casual tourists from walking into low areas or small caverns, getting gassed and passing out.

The Soda Dam site has also been abused over the years by disturbance from road building and aggressive climbing (e.g., Goff and Shevenell, 1987, p. 295), even though most local inhabitants revere the waters and unique rock formations. The travertine deposits extend several hundred meters above the west side of the present hot springs and record a long history of deposition and incision along the Jemez River (Goff and Shevenell, 1987; Tafoya, 2012). Goff and Shevenell (1987) linked the travertine deposits to initial formation of the Valles geothermal system roughly 1 Ma. Tafoya (2012) showed that the intermediate level deposits on the east side of the river provide a robust incision rate of 160 m/Ma for the last 200 ka.

Jemez Springs contains a spa that has been in continuous operation since 1876. Another small spa (confusingly named Sulphur Spring) once operated a mere 200 m south of Jemez Springs but was defunct by the 1970s. This spa was "revived" in the late 1990s and is known as Giggling Springs, but has not been sampled for water and gas.

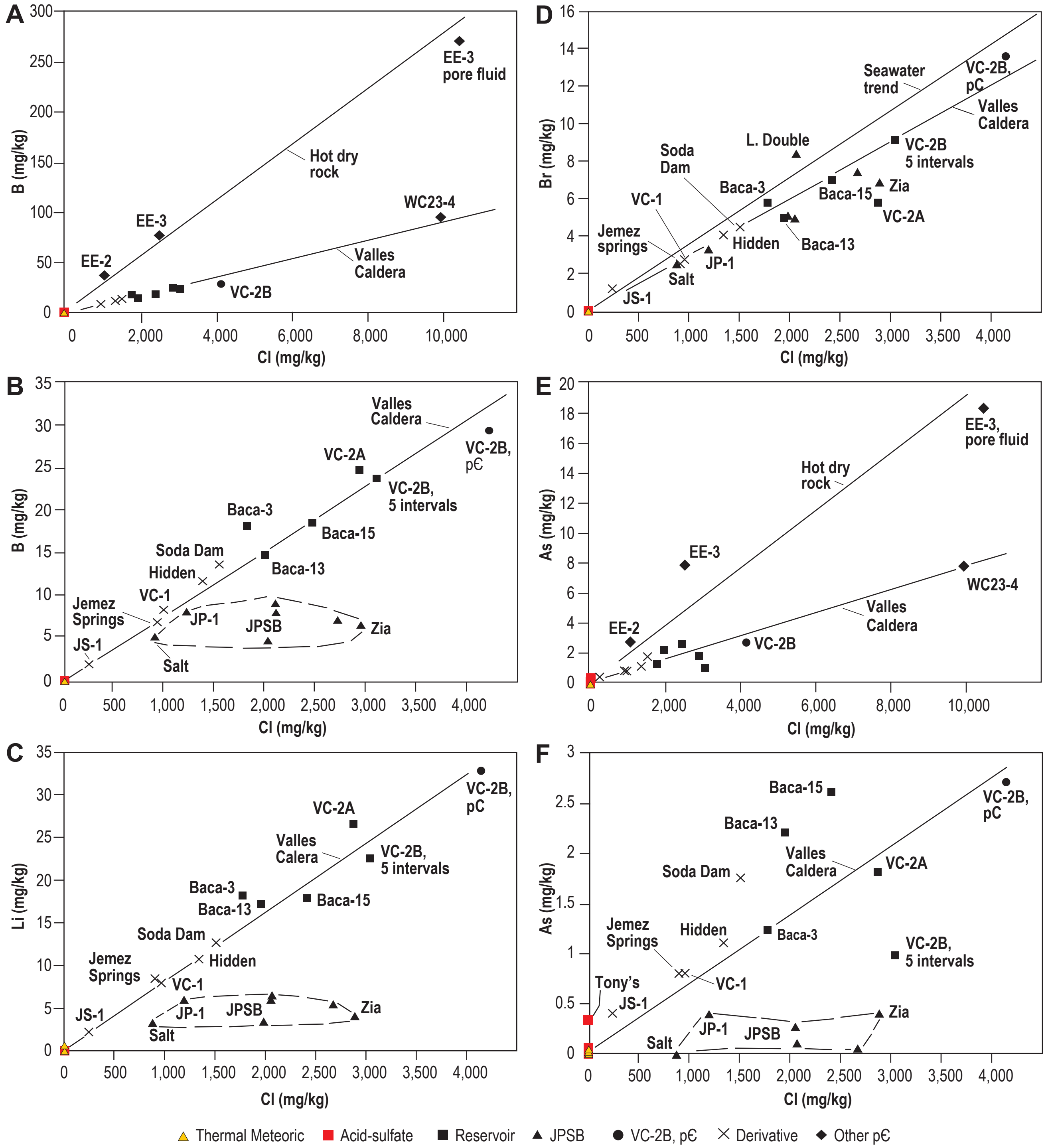


Figure 11. Chloride variation diagrams for water types listed in Table 1: **A**—Boron versus chloride shows two distinct trends for Valles caldera deep geothermal-derivative waters and Hot Dry Rock fluids. **B**—Boron versus chloride at different scale shows that Jemez Pueblo-San Juan Basin waters have different ratios than those from the Valles caldera. The two trend lines seemingly intersect at the composition of the JP-1 well and Salt Spring, suggesting these two sites are at the terminus of the Valles hydrothermal outflow plume. **C**—Li versus Cl also shows two distinct trends: one for Valles caldera waters and one for Jemez Pueblo-San Juan Basin waters. In this plot, JP-1 well and Salt Spring do not fall on the Valles trend. Key is same as Figure 11B. **D**—Br versus Cl shows the Valles caldera and Jemez Pueblo-San Juan Basin trends are similar to a hypothetical mixing trend for seawater and meteoric water. Key is same as Figure 11B. **E**—As versus Cl again shows the distinct difference between the Valles caldera and the Hot Dry Rock waters. Key is same as Figure 11A. **F**—As versus Cl at different scale shows difference between the Valles caldera trend and Jemez Pueblo-San Juan Basin trend. Note scatter in data for the Valle trend. Arsenic is reactive with iron casing in waters of standing wells, and can carry over in steam separators during flashing (Goff et al., 1994). The most consistent trend is observed in the derivative waters. Note relatively high arsenic in Tony's Spring. Arsenic is a volatile element sometimes slightly enriched in acid-sulfate waters. Key is same as Figure 11B.

Other Thermal/Mineral Waters

Wildcat wells

Two wildcat geothermal wells were drilled on the south and west margins of the Valles caldera in the early 1980s (Shevenell et al., 1988). The most interesting well was the WC23-4 well drilled on Thompson Ridge just outside the caldera ring fracture (Fig. 5; see cross sections in Goff et al., 1988; 2011). This well penetrated a thick interval of Precambrian crystalline rocks and a few producing fractures, but could not sustain commercial flow. In situ samples obtained by Los Alamos National Laboratory (LANL) show that the lowermost fracture (233°C) contains geothermal brine that has more than twice the salinity of any deep geothermal fluids within the caldera (Table 1), but resembles Valles geothermal fluids with respect to key chemical ratios (Fig. 11). Isotopically, WC23-4 fluids are the "heaviest" ever reported from the deep Valles geothermal system (Fig. 8), showing about 7‰ enrichment in $\delta^{18}O$ and 10 to 15‰ enrichment in δD relative to local meteoric water. Unfortunately, acceptable gas samples were never recovered from this well.

The AET-4 wildcat well was drilled on Cat Mesa to a depth of 1,211 m in Precambrian metamorphic rocks (Fig. 5) but could not flow. Temperature logs run several years after drilling show a maximum temperature of 129°C at 880 m in Pennsylvanian limestone, and a small temperature reversal below. This temperature peak was interpreted to result from the Valles hydrothermal outflow plume (Goff et al., 1988). Unfortunately, the well had several completion problems that prevented sampling of uncontaminated fluids. The AET-4 was drilled just west of the Cat Mesa fault zone (Fig. 5) but it is not known if this fault system contains hydrothermal fluids at depth. No active thermal springs, gas vents, or fumaroles discharge along the Cat Mesa fault zone.

Hot Dry Rock wells

The Hot Dry Rock geothermal concept (HDR) was first developed and tested at Fenton Hill by Los Alamos National Laboratory from 1972 to 1998 in Precambrian igneous and metamorphic rocks beneath the west margin of the caldera (Fig. 5; Heiken and Goff, 1983; Smith, 1983; Grigsby et al., 1984). During circulation experiments, cold water was pumped down an injection well, forced through artificially fractured reservoir rocks, and extracted from a nearby production well. The cold water dissolved minerals lining the fractured rocks and absorbed CO_2 and other gases while reaching thermal equilibrium (T≥160°C). Two experimental systems were constructed. The Phase I system consisted of the GT-1 injection and EE-1 production well pair completed in 1977 (about 2.6 to 3.0 km depth and Tmax = 200°C) whereas the Phase II system consisted of the EE-2 injection and EE-3 production well pair (3.5 to 4.2 km, Tmax = 300°C). Details of this project are summarized in many papers, most recently by Brown and Duchane (1999, and references therein).

Fluid variations observed in the Phase I system were discussed by Grigsby et al. (1984) who noted differences in B/Cl and Li/Cl ratios between Hot Dry Rock and Valles deep geothermal fluids and extreme shifts in $\delta^{18}O$ relative to the local meteoric water line (as much as 5.5‰). Reported here are three water analyses obtained from the Phase II wells during various experiments (Table 1). The 1983 EE-3 sample is water that sat in the bottom of the well and was pumped out prior to conducting various flow tests. It is the most Cl-rich Hot Dry Rock sample and contains exceptionally high concentrations of B, As (Fig. 11A, E), Br, and Li. The sample is also more saline than any of the typical reservoir fluids in the Valles and more enriched in trace elements than the WC23-4 Precambrian pore fluid. The analysis of EE-2 collected in 1991 is the average of five vent samples collected toward the end of a circulation experiment. The last sample is EE-3 vent fluid collected in 1994 during the beginning of a circulation experiment. These three samples form a trend on the Cl-variation diagrams (Fig. 11) that is completely different from the Valles deep geothermal and derivative trend. Unfortunately, very little isotope data was obtained on EE-2 and EE-3 samples.

Gases produced during Hot Dry Rock circulation experiments and during static conditions contain mostly CO_2 and N_2 (Table 2). They contain less H_2S and H_2, but more CH_4 and He, than Valles deep geothermal gases. Hot Dry Rock gases most resemble Soda Spring gases rather than high-temperature geothermal gases (Fig. 9). Hot Dry Rock gases contain high relative He, indicating a large crustal or mantle component of He (Fig. 10). Unfortunately, no samples were ever collected to measure $^3He/^4He$ ratios.

The Hot Dry Rock experiments at Fenton Hill ended in the late 1990s. All wells were plugged and abandoned, which was a great loss because EE-2 and EE-3 are among the deepest and hottest wells ever drilled in Precambrian rock. The Hot Dry Rock concept has since been renamed Enhanced Geothermal

Systems. Hot Dry Rock - Enhanced Geothermal Systems projects have been attempted in Japan, England, Germany, France, Sweden and Australia (see Geothermics, 1996). The most successful of these has been the Soultz-Sous-Forêts project along the western Rhine graben in France (Geothermics, 2006).

Jemez Pueblo-San Juan Basin springs and wells

An extensive group of mineralized fluids ranging from tepid to about 60°C discharges from a small structural rift basin in the area of Jemez Pueblo and along the southern end of the Nacimiento fault zone in the southeastern San Juan Basin (Fig. 2). These fluids circulate in a variety of non-volcanic rocks. The two samples from Jemez Pueblo emerge from alluvium (Fig. 7M) and early Miocene Zia Sandstone, a basin fill unit of the Rio Grande rift. The others discharge from Mesozoic-Paleozoic marine strata that include the Jurassic Todilto Formation, an evaporite sequence rich in salt and gypsum (Fig. 7N). As a result, the two Jemez Pueblo samples have lower Cl and SO_4 contents than other members of this group. The two areas are probably separate systems of thermal/mineral discharge, but because their waters are geochemically similar, they are lumped as one water type for the purpose of this paper.

Waters of the Jemez Pueblo-San Juan Basin type contain relatively high Cl and HCO_3, moderate to high amounts of SO_4, modest concentrations of B, Li, and Br, and relatively low As. Compared to other thermal waters in the region, the Jemez Pueblo-San Juan Basin fluids have less K with respect to Na and considerably more Ca, Mg, and Sr. Therefore, they resemble dilute sedimentary basin brines. On Cl-variation plots, they form a trend distinct from the Valles or Hot Dry Rock mixing trends, with the exception of the Br vs. Cl plot (Fig. 11D). On this plot, Valles deep geothermal-derivative and Jemez Pueblo-San Juan Basin type waters display similar Br/Cl ratios to each other and to seawater because of interaction with ancient marine strata. Isotopically, Jemez Pueblo-San Juan Basin waters have slightly lower δD and $\delta^{18}O$ values with respect to most Valles geothermal reservoir and derivative samples, even though they discharge at lower elevations. Phillips et al. (1986) claim that San Juan Basin brines were recharged in the early Pleistocene when isotope signatures were different than today.

Several Jemez Pueblo-San Juan Basin type waters are associated with emissions of free gas (Table 2), but these emissions are compositionally variable and consist mostly of CO_2 and N_2. Jemez Pueblo-San Juan Basin gases resemble those emitted from typical soda springs (Fig. 9). Compared to Valles deep geothermal-derivative gases, they contain very little (if any) H_2S, H_2, and CH_4, and do not resemble high-temperature geothermal gases hosted in either volcanic or sedimentary terrains. The most interesting component in Jemez Pueblo-San Juan Basin gases is their relatively high helium (≤1.8 mol%), which is a common characteristic of sedimentary basin and oil field gases. However, their $^3He/^4He$ ratios are ≤0.32 R/RA and indicate little mantle input of helium-3 (Fig. 10).

The JP-1 well listed in Table 1 (Fig. 7M) was drilled in January 1991 to a depth of 73.2 m in the Zia Sandstone adjacent to the Jemez River and Indian Hot Spring (Witcher et al., 1992). Drilling of the well resulted in eventual loss of the hot spring, which was previously used for bathing. Presently, the well is not locked and residents let the water flow into hand-dug pools that are used for bathing. Renewed exploration for geothermal resources at Jemez Pueblo began in 2010 (Albrecht et al., 2011), which resulted in a 1,600+ m hole drilled in late 2013. The BHT of this well is disappointing (<100°C). Research on this endeavor has not been completed due to lack of funding.

The Zia hot well (aka Kaseman #2 well or "Warm Spring") was originally drilled as an oil test in 1926 (Summers, 1976; Kelly, 1996). Total depth is 612 m, bottoming in the Pennsylvanian Madera Group but most water now originates from Permian and higher strata. The artesian well formed the basis for a spa that was abandoned by the mid-1970s. The outflow of the well is now diverted to a crude pool used for bathing. None of the waters in the Jemez Pueblo-San Juan Basin group are potable due to high TDS, although a few are occasionally used for bathing.

Flow test of HDR (hot dry rock) well back in the early 1990s, EE-2 is brown tower on right, EE-3 is on left. *Photo by Don Brown (LANL, retired).*

VC-2A during first geysering, 1987. *Photo by Fraser Goff.*

IV. GEOTHERMOMETRY

Temperature estimates based on chemical and isotope geothermometers have been calculated for all of the thermal water types listed in Table 1 and are shown in Table 3. Appendix 1 contains the equations and original papers describing the geothermometers and their application. Interpretation of geothermometer results is complicated, except for high-temperature fluids (≥150°C) for which most geothermometers are

Table 3. Calculated geothermal reservoir temperatures of Valles caldera region waters listed in Table 1 using a standard suite of chemical geothermometers (values in °C). Values in parentheses violate rules of application except for the Mg correction, which is the amount subtracted (see equations and original papers listed in Appendix 1). Values in boldface type are preferred estimates. Chemical and isotope geothermometers are not designed for acid-sulfate waters (Goff and Janik, 2000).

Type	Measured	Quartz	Chalcedony	Na/Kf	Na/Kt	Na/Li	Na-K-Ca	Na-K-Ca	Na-K-Ca (Mg Correction)		Li/Mg	K/Mg	$\delta^{18}O$-SO_4 [a]
							(β=1/3)	(β=4/3)	R-value	Tmg-corr			
Deep Geothermal Waters													
VC-2A (n=7)	210	**212**	196	**266**	**251**	**313**	**280**	(483)	0.12	280 (0)	341	271	**208**
Baca-3	190	**197**	179	**234**	**209**	**306**	**228**	(280)	0.38	228 (0)	288	216	
VC-2B, in-situ	295	**310**	318	**333**	**345**	**307**	**300**	(383)	0.29	300 (0)	292	265	**252**
VC-2B, flowing (n=6)	225	**233**	221	**300**	**299**	**314**	**269**	(312)	0.08	269 (0)	323	280	
Baca-13 (n=5)	278 to 292	**255**	249	**278**	**268**	**316**	**287**	(481)	0.09	287 (0)	334	271	**288 ±1** (n=2)
Baca-15 (n=5)	267 to 281	**251**	243	**283**	**274**	**295**	**277**	(400)	0.02	277 (0)	380	321	**295 ±5** (n=4)
Derivative Waters													
VC-1, 483 m	111	121	**93**	214	183	250	201	(207)	24.1	**76 (-125)**	**94**	**114**	163
Soda Dam Main (n=10)	46.9 ± 0.3	99	**69**	272	260	294	222	(179)	8.43	**172 (-50)**	**163**	**133**	
Hidden Spring	33.2	93	**62**	273	260	288	220	(172)	7.35	**180 (-40)**	**160**	**132**	
Jemez Spring, Gazebo	74.0 ± 0.5	132	**105**	223	195	299	192	(155)	2.28	**192 (0)**	**178**	**128**	
JS-1, 152 m	60.5	87	**56**	262	246	289	192	(104)	10.2	**142 (-50)**	**120**	**94**	
Other Geothermal Waters													
WC23-4 well	233	**243**	234	**269**	**255**	**280**	**287**	(526)	0.13	287 (0)	362	304	
EE-3, 1983	>250	**233**	221	**255**	**237**	382	**257**	(371)	3.05	257 (0)	285	203	
EE-2, 1991	≥240	**237**	226	**220**	191	343	**216**	(256)	6.19	186 (-30)	279	191	
EE-3, 1994	≥240	**230**	218	**203**	170	354	**208**	(268)	3.42	208 (0)	258	166	
Thermal Meteoric Waters													
San Antonio Hot Spring	41.1 ± 0.2	124	95	209	178	110	(157)	**71**	9.72	**≤70**	61	71	
Spence Hot Spring	43.1 ± 1.4	114	86	132	86	293	(115)	**58**	27.8	**≤70**	109	46	
McCauley Spring	31.9 ± 0.5	105	75	164	124	297	(121)	**31**	45.3	**≤70**	71	27	
Bathhouse Spring	38.0 ± 0.4	138	112	255	237	179	(208)	**53**	9.21	**≤70**	73	83	
Jemez Pueblo-San Juan Basin Waters													
JP-1 Well	57.8	91	**60**	175	136	193	175	(185)	16.8	100 (-75)	147	112	(92)
Salt Spring	18.0	48	**15**	162	120	164	174	(205)	24.1	71 (-101)	141	111	
C Spring	18.9	56	**24**	157	115	182	148	(149)	25.6	64 (-92)	128	92	
Big Mama Spring	22.5	59	**26**	121	74	108	136	(151)	18.7	86 (-50)	119	95	
Tufa Pool (Spring)	24.2	88	**57**	125	79	109	136	(140)	23.1	51 (-85)	108	87	
Lower Double Spring	28	70	**38**	141	96	125	149	(156)	17.1	84 (-65)	123	100	
Zia Hot Well	54.9	89	**59**	107	59	88	127	(152)	22.3	**67 (-60)**	112	90	
Seawater (F. Goff unpub. data)													
Satsuma Iwo-Jima, Japan	22	0.6	<0	145	102	5	175	(273)	(76.8)	**cold**	13	98	
Galapagos, Ecuador	27	<0	<0	136	91	<0	166	(257)	(79.3)	**cold**	7	91	

[a] Values for $\delta^{18}O$-SO_4 geothermometer from Truesdell and Janik (1986) and F. Goff (unpub. data).

designed (Fournier, 1981; Goff and Janik, 2000). In general, Valles deep geothermal and Hot Dry Rock waters provide high temperature estimates that consistently match reservoir temperatures measured in wells, regardless of the geothermometer used. Derivative waters yield high-temperature estimates for cation geothermometers (excluding those with magnesium) because their cation ratios of sodium, potassium, and lithium are not greatly affected by dilution. However, silica geothermometer temperatures are much lower because dilution lowers the silica content of these fluids. Geothermometers that use magnesium provide lower temperature estimates that reflect re-equilibration due to mixing. Chemical geothermometers are not designed for acid-sulfate waters and yield inconsistent results for thermal meteoric waters. Connate water (fossil seawater), sedimentary basin brines, and metamorphic water yield spurious and questionable chemical geothermometer estimates (Goff and Janik, 2000). For example, seawater produces a Na-K-Ca temperature estimate of 165 to 175°C.

Waters from the Jemez Pueblo-San Juan Basin (JPSB) group yield low or confusing temperature estimates from chemical geothermometers. This is because they are chemically akin to sedimentary basin brines where the silica is low, Na/K ratios are high, and total Ca+Mg contents are high. Thus, the temperature estimates show little agreement. These fluids probably did not equilibrate much above 60 ±20°C at depth. Interpretation of calculations from the JP-1 well at Jemez Pueblo (Table 3) would yield an estimate of 90°C at best.

Subsurface reservoir temperatures are also evaluated using the relative Na-K-Mg triangular plot of either Giggenbach (1988; Fig. 12) or Fournier (1990). This plot takes into account the concentration of Mg, which is not very abundant in high-temperature geothermal fluids (Table 1). Figure 12 shows that Valles deep geothermal waters plot as "fully," to "partially equilibrated waters," at 260 to 320°C, with VC-2B Precambrian fluid indicating the highest temperature. In contrast, the Borateras hot spring system in Peru (Bo) has never been drilled, but the expected reservoir temperature is around 200°C. For comparison, several other high-temperature, fully equilibrated geothermal fluids are shown on the diagram and their measured reservoir temperatures more or less match the indicated temperature on the plot (e.g., Ahuachapán, El Salvador (Ah) at 255°C; Miravalles, Costa Rica (MI) at 240°C; etc.).

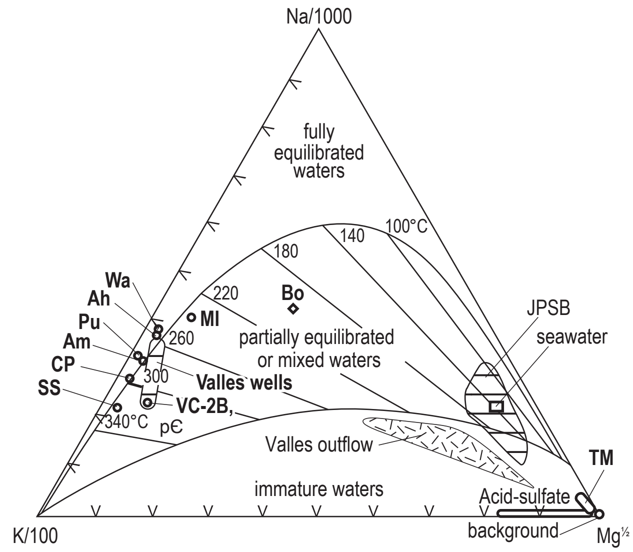


Figure 12. Triangular plot of Na/1000-K/100-$Mg^{1/2}$ devised by Giggenbach (1988) to discriminate among fully equilibrated high-temperature geothermal waters and other types of geothermal waters. Valles deep geothermal well waters plot as fully to partially equilibrated in a region of 260 to 320°C, essentially identical to their measured temperature. Other high-temperature reservoir waters have similar characteristics (i.e., Ahuachapán (Ah); Amatitlan (Am); Cerro Prieto (CP); Miravalles (MI); Puna, Hawaii (Pu); Salton Sea (SS); Wairakei (Wa)). Borateras, Peru (Bo) is a geothermal site that has not been drilled but seems to be partially equilibrated at 200°C. Waters of the Valles outflow plume are considered "immature," but trend toward their parent compositions hosted within the caldera. Jemez Pueblo-San Juan Basin (JPSB) waters fall in a separate group showing a spread of lower indicated temperatures but resemble seawater on this plot. We believe JPSB waters have equilibrated at temperatures less than ≤100°C (modified from Stimac et al., 2015, fig. 46.11).

Derivative waters from the Valles outflow plume plot as "immature waters" on Figure 12 because they are mixed with water containing calcium and magnesium derived from Paleozoic limestone, yet they form a trend pointing toward the parent Valles deep geothermal fluids. Thermal meteoric waters, acid-sulfate waters, and background cold waters from Table 1 plot very close to the magnesium apex of the diagram, indicating they are not derived from high-temperature sources. The Jemez Pueblo-San Juan Basin fluids form a separate group that plots on a different and much cooler trend than the Valles outflow plume. The Jemez Pueblo-San Juan Basin fluids most resemble sedimentary basin brines. Note that seawater plots in the middle of this group at an apparent equilibrium temperature of 140°C. Thus, this plot is not designed for sedimentary basin brines.

V. DISCHARGE OF VALLES GEOTHERMAL SYSTEM

The total discharge of the Valles geothermal system is impossible to measure directly because some of the flow is confined to subsurface aquifers west and east of San Diego Canyon and the Jemez fault zone (Trainer, 1974; Goff et al., 1988). It is also not known if the Cat Mesa fault system is a conduit for deep thermal water (Fig. 5), although there are no thermal waters, gas vents, or fumaroles that discharge along its trace. Several workers (Table 4) have estimated the discharge of hydrothermal fluids into the Jemez River from the major spring groups and from other groundwater input. The estimates vary and the best use ion balance calculations from river samples upstream and downstream of thermal inflow areas (Table 4) because much of the input occurs below river level. The estimate by Erickson (1977) used arsenic concentrations that are much lower than what is found in samples using modern analytical techniques. Those made by Reid et al. (2003) for June 1996 took advantage of low stream flow during a relatively dry month. Thus, arsenic concentrations that are much lower in the Jemez River below Soda Dam, were three times higher than normal (140 versus about 50 µg/kg), providing a more accurate estimate of discharge. Using parameters in Reid et al. (2003), roughly 1,600 L/min of thermal water discharges from the Soda Dam group and another 200 L/min are contributed by the Jemez Hot Springs group. Compared to an end-member composition of the parent fluid similar to Baca-15 (2,400 mg/kg Cl), Soda Dam (1,500 mg/kg Cl) is 63% parent fluid and Jemez Hot Springs (900 mg/kg Cl) is 38% parent fluid. The combined discharge of parent fluid from the caldera would then be about 1,000 L/min at Soda Dam and 75 L/min at Jemez Hot Springs, or a total of 1,075 L/min of parent fluid from the hot springs. Because the estimates rely on the composition of the parent end-member, using the value of Cl in Baca-13 or VC-2B fluids would raise or lower the estimates, respectively.

Table 4. Estimated discharge of Valles hydrothermal outflow plume.

Date	Solute used	Rate (l/min)	Conditions	Source of data
1973–1974	Cl	1500	Soda Dam Group only	Trainer, 1984
pre-1977	As	620[a]	From caldera margin to a point downstream of Jemez Springs	Erickson, 1977
pre-1980	Cl, B	1380	From caldera margin to a point downstream of Jemez Springs	Balleau, 1984
Jun-96	As	1660 ± 10%[b]	From Soda Dam to Jemez Ranger Station	Reid et al., 2003
Jun-96	Cl	1565 ± 10%[c]	From Soda Dam to Jemez Ranger Station	Reid et al., 2003
Jun-96	SO_4	1489?[d]	From Soda Dam to Jemez Ranger Station	Reid et al., 2003

[a] Uses values for arsenic that are much lower than those measured by more recent techniques.

[b] Uses 1.77 mg/kg As in Soda Dam fluid, 0.140 mg/kg As in Jemez River fluid and 350 l/min Jemez River flow rate. Error is estimated at 10% mostly in flow rate.

[c] Uses 1,530 mg/kg Cl in Soda Dam fluid, 114 mg/kg Cl in Jemez River fluid and same flow rate as above. Error is estimated at 10%.

[d] Uses 42.3 mg/kg SO_4 in Soda Dam fluids, a corrected value of 3 mg/kg SO_4 in Jemez River fluid and same flow rate as above. Error is estimated at >10%.

As mentioned above, drilling has shown that the hydrothermal outflow plume extends to the west and east of the Jemez fault zone within a few kilometers of the caldera margin (Goff et al. (1988). Using a 3-D finite element model, Faust et al. (1984) calculated that the total discharge of the Valles hydrothermal plume was 3,080 L/min, but he didn't account for the mixing that goes on in the plume. Thus, his estimate is probably too high.

Using data in Reid et al. (2003), the mass flux of arsenic, chloride, and other constituents in the Jemez River was calculated at Jemez Ranger Station in June 1996. For arsenic, the value is 6 kg/day, and for chloride, the value is 4,890 kg/day. Yearly flux rate calculations must consider varying discharge rates of the river. In contrast, the hot springs have very constant discharge rates. For the Soda Dam system, the arsenic flux is 1.5 metric tons/year and the chloride flux is 1,285 metric tons/year. These values seem rather impressive, and virtually all this mass originates from the Valles caldera geothermal system.

Determining the sulfate mass flux is much more complicated because there are several sulfate-rich sources upstream of Soda Dam (e.g. altered rocks at Hummingbird fumarole, acid-sulfate springs at Sulphur Springs) that affect the sulfate load in the Jemez River. This extra sulfate in the river must be eliminated from mass flux calculations to obtain a reasonable value of mass flux from Soda Dam. For example, if the sulfate content measured at the Jemez

River below Soda Dam in June 1996 is corrected to 3 mg/kg (from 8 mg/kg), the estimated discharge of thermal water at Soda Dam is about 1,490 L/min. However, this value is much less accurate than those obtained from calculations using arsenic and chloride. From Reid et al. (2003), the estimated sulfate flux from Soda Dam is 36 metric tons/year. For comparison, Szynkiewicz et al. (2012a) estimate that 16.4 metric tons/year sulfate is removed from the Valles caldera by the surface hydrologic cycle, with 11.5 metric tons/year sulfate coming from intracaldera acid-sulfate systems.

San Antonio Hot Spring during the early 1980s. *Photo by Fraser Goff.*

VI. GEOTHERMAL EXPLORATION OF "THE BACA"

The Early Years, 1960–1978

The first geothermal well in "the Baca" was spudded (began drilling operations) in 1960 as an oil test in Alamo graben on the west flank of the resurgent dome (Fig. 6). We can only speculate what the justification might have been for oil and gas exploration. Perhaps these early entrepreneurs thought the resurgent dome was a hydrocarbon trap. Instead of oil, the Westates-Bond #1 (WB-1) struck superheated water (~200°C) at relatively shallow depths (Dondanville, 1971), vented uncontrolled steam and brine for a short period of time (blew out), and killed a small cluster of nearby aspen trees.

By 1963, the Bond family, who were primarily sheep and cattle ranchers, sold the 100,000-acre Baca Ranch to James P. "Pat" Dunigan, the wealthy president of the Dunigan Tool & Supply Company in Abilene, Texas. Dunigan continued most of the established uses of the ranch, namely cattle ranching, logging, hunting, and fishing. However, because of his interest in geothermal development, Dunigan financed drilling of the next three geothermal wells. These wells were located near Sulphur Creek within the area of most obvious fumaroles, acid springs, and bleached rock. Baca-1 was drilled to a depth of 780.5 m in the summer of 1963 in what was later mapped as a stable landslide complex, just upstream of Sulphur Springs (Goff et al., 2011). A "steam zone" was intersected at 439 m (about 165°C), but the hole was lost while trying to run casing. In these early days of geothermal drilling technology, Baca-1 was eventually plugged with the aid of a ponderosa pine log dropped down the well bore.

Baca-2 was drilled from July to October 1964 at the mouth of Alamo Canyon (Fig. 6) where it intersects Sulphur Creek, in an area of widespread acid-sulfate alteration, gas emissions, and high-angle faults (Dondanville, 1971; Goff et al., 2011). This well is stratigraphically significant because it penetrates a complete section of intracaldera volcanic and volcaniclastic rocks, intersecting the Santa Fe Group at 732 m. The well also penetrates Permian and Pennsylvanian rocks, intersects the Precambrian at roughly 1,525 m, and bottoms at 1,725 m depth. Several small fluid entries were logged and maximum temperature was 218°C, but the well could not sustain commercial flow. To our knowledge, Baca-2 was never plugged.

Drilling returned near the Baca-1 site in late 1964 when the Baca-3 well was drilled to a depth of 671 m reaching a maximum temperature of 200°C. Again, some small fluid entries were found, but the well could not sustain commercial flow. Baca-3 was never plugged by Baca Land and Cattle Company and was re-entered in 1988 by LANL geoscientists who obtained bailer and in situ samples from the well during the drilling of VC-2B (see Table 1).

Having achieved little practical success in the Sulphur Springs and Alamo graben areas, Dunigan moved to the Redondo Creek graben where weaker thermal manifestations occur, but where surface hydrothermal alteration along faults is still rather extreme (Fig. 7E; Goff et al., 2011). Baca-4, drilled from September to October 1970, was a roaring success and remains one of the best wells ever drilled in Valles caldera. It is considered to be the "discovery well" of the producible geothermal system in the Redondo Creek area (Dondanville, 1978). Total depth is 1,854 m and the bottom hole temperature (BHT) approaches 300°C. Initial cuttings were examined by geologist R.L. Smith of the U.S. Geological Survey (USGS) who was greatly surprised by the thickness of intracaldera tuff (personal letter dated November 12, 1970, reproduced in Dondanville, 1971), because the thickness greatly exceeded what was shown in cross sections of the geologic map of the Jemez Mountains (Smith et al., 1970). The cuttings were later re-logged by Nielson and Hulen (1984).

At this point Dunigan terminated his drilling program and struck a contract with Union Oil Company of California (UNOCAL), who had a stellar reputation because they had successfully developed much of The Geysers, CA. The Geysers, now producing 700 MWe, is the first successful geothermal development for electricity in the United States and is the largest commercial geothermal field in the world. It provides a yardstick for exploration and development. UNOCAL began by determining the probable limits to the "reservoir" (Figs. 5, 6). Baca-5 and -5A were drilled south of Baca-4 on the southeast edge of the Redondo Creek graben and Baca-6 was drilled in the center of the graben, west of Baca-4. Baca-7 was drilled outside the northwest margin of the resurgent dome (Fig. 5), and Baca-8 was drilled within the Alamo graben between WB-1 and Baca-2. All of these wells were hot, ≥175°C at depths of 1 km above sea level (Vonder Haar, 1980). However, none except possibly Baca-6 could sustain commercial flow. Isotope and alteration studies showed that temperatures in Baca-7 and -8 approached 300°C in the past, but had cooled since their maximum temperatures were achieved (Lambert and Epstein, 1980; Hulen and Nielson, 1986b). Temperatures fell off rapidly southeast of Baca-5. The next eight wells (Baca-9 through -16) were located within the Redondo Creek graben to determine the dimensions of the "reservoir" encountered in Baca-4. Only five of the 11 wells drilled into the Bandelier Tuff beneath the Redondo Creek area flowed at commercially acceptable rates and pressures. All wells were hot, ≥230°C at 1 km above sea level (Vonder Haar, 1980).

From October 1975 to April 1976, UNOCAL conducted an interference test in the Baca field using three wells as production wells, three wells for injection, and four wells for observation (Bodvarsson et al., 1980). Only one observation well showed a distinct pressure response during the test. Nonetheless, using data from this single well, the area of the resource was calculated to be 110 km^2 (43 mi^2) with a minimum reservoir capacity of 2.13 x 10^9 metric tons (4.69 x 10^{12} lbs) of fluid. These large estimates cover nearly half of the caldera and assume the total mass of fluid exists as liquid water, but do not consider the fluid temperature or the effective permeability of the system. In retrospect, it was surprising how optimistic UNOCAL was about the future of geothermal development in the Valles caldera (Dondanville, 1978).

Joint Venture, 1978 to January 1982

The Baca cooperative geothermal demonstration project in Valles caldera began in July 1978. It was jointly sponsored by the U.S. Department of Energy (DOE), UNOCAL, and the Public Service Company of New Mexico (PNM). When the project began, UNOCAL claimed that a 400-megawatt electrical (MWe) resource existed within the caldera. Because of the "oil crisis" of the late 1970s, the Carter administration provided ample funding for alternate energy projects in both public and private sectors. The three parties above, particularly the DOE, were encouraged to showcase production of electricity from a liquid-dominated reservoir by construction of an initial 50 MWe power plant in the Redondo Creek area.

Another 13 wells were drilled in a short period of time, mostly in the Redondo Creek graben, and PNM began construction of a site for the first power plant. The exception was Alamo Canyon-1 (AC-1), which was drilled in 1979 a few hundred meters southeast of WB-1 in the Alamo graben. Very little is known about this well except that the stratigraphy was radically different from that logged in WB-1, putting both logs in question. Baca-12 (Figs. 4, 6) was deepened to 3,155 m to test permeability in Precambrian rocks, but this effort was not successful. Fracture stimulation experiments to increase permeability in wells Baca-20 and Baca-23 were not successful (Morris and Bunyak, 1982; Morris et al., 1982). A slightly permeable interval in Baca-20 from 1,488 to 1,561 m was stimulated, but only 30 m opened up at the bottom of the interval. Productivity of the well remained poor because of low permeability in the surrounding rock (intracaldera Bandelier Tuff). At the time, this was the hottest "frac job" (hydraulic fracturing) ever conducted in the United States (282°C). The fracturing experiment conducted in Baca-23 produced 15 seismic events that were identified by the seismic station at the nearby Fenton Hill Hot Dry Rock site and were similar in seismic signature to hydraulic fracturing experiments conducted at that site (Pearson, 1981).

Bodvarsson et al. (1980; 1982) made a revised estimate of reservoir capacity and an initial estimate of reservoir longevity using published geoscientific data, well logs, and a two-phase numerical simulator (SHAFT79). From their evaluations, the reservoir area was 40 km^2, only 36% of the earlier UNOCAL estimate. However, they deduced an average reservoir thickness of 610 m (2,000 ft), an assumed porosity of 5%, and a porosity-thickness product of 30.5 m (100 ft). From this evaluation, the calculated reservoir capacity is about 1.0 x 10^9 metric tons (2.2 x 10^{12} lbs), a value that is 45% of the previous UNOCAL estimate. This amounts to 2.7 km^3 of fluid. To estimate reservoir longevity, Bodvarsson et al. (1980) used a number of complicated assumptions and parameters and plugged them into the SHAFT79 simulator. The results are striking. A plot of production rate vs. time (Fig. 13) shows a 65% drop in

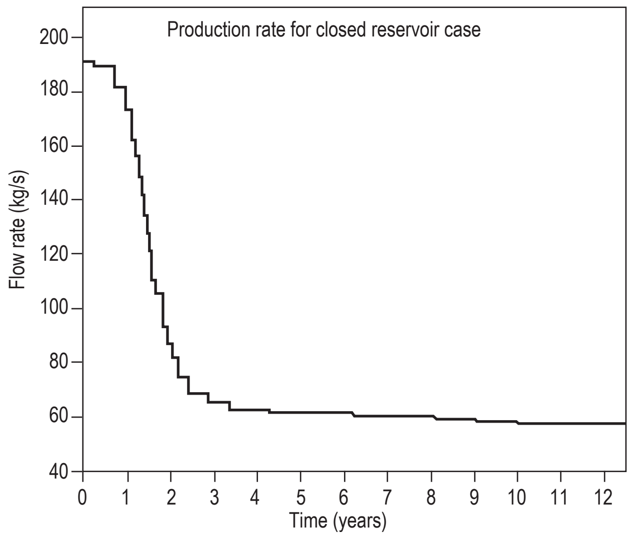


Figure 13. Plot of flow rate versus time for the "closed reservoir case" of the Baca geothermal reservoir determined from the two-phase numerical simulator SHAFT79 (Bodvarsson et al., 1980, 1982). Using parameters and permeability data obtained for the reservoir, the SHAFT model indicates rapid decreases in flow rate after only 2 to 3 years of production.

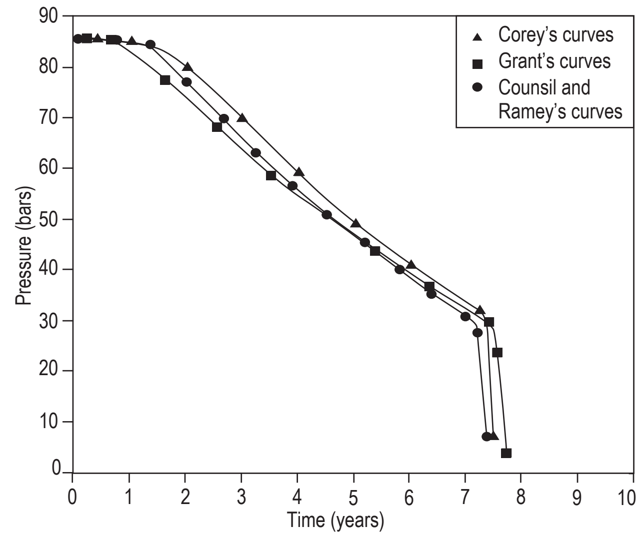


Figure 14. Plot of pressure versus time for the Baca geothermal reservoir using three permeability curves and the SHAFT79 simulator. The SHAFT model predicts a drastic decrease in reservoir pressure in 7 to 8 years. See Bodvarsson et al. (1980, 1982) for details on the model and derivation of the permeability curves.

flow rate in only two to three years. Additionally, the simulation predicts a 65% drop in pressure in roughly seven years (Fig. 14). Bodvarsson et al. (1982) concluded that it was questionable whether the geothermal field could supply enough steam to power a 50 MWe plant for 30 years.

A crude estimate of reservoir volume, or reservoir fluid capacity, can be calculated using tritium data (assuming that discharge from the reservoir is equal to recharge) and using the mean residence time of water in the reservoir (Pearson and Truesdell, 1978; Goff et al., 1991, p. 116; Shevenell and Goff, 1995, 1996). The reservoir volume in the Redondo Creek area is estimated at between 2.2 and 2.8 km^3 using a well-mixed reservoir model, the discharge rate of 1,500 L/min estimated by Trainer (1984), and values of 0.47 to 0.61 TU (tritium units where 1 TU equals 1 tritium atom in 10^{18} hydrogen atoms) obtained from Redondo Creek wells. This volume is roughly equivalent to that determined by Bodvarsson et al. (1980, 1982), but Shevenell and Goff (1995, 1996) point out that there are many variables to consider in such an estimate using tritium.

In January 1982, the joint project was terminated by mutual agreement because UNOCAL had only proven ≤20 MWe of resource (see discussion below). After this agreement was signed, only one of 13 new wells was deemed successful (Baca-24). UNOCAL drilled roughly 23 wells and re-drills during their lease of the Baca geothermal rights from 1971 to 1984. All the wells were hot, but few wells (five, possibly six) encountered sufficient permeability to be considered production wells. PNM actually bought two 25 MWe low-pressure steam turbines for use with the initial power plant. When the Baca project terminated, these turbines, which were the last low-pressure geothermal turbines manufactured by Westinghouse Corp., were sold to the Mexican government for pennies on the dollar. Those turbines are now operating at the Los Azufres geothermal field, Mexico. The Baca project, which was supposed to showcase development of liquid-dominated geothermal reservoirs, became extremely frustrating, expensive, and non-productive. The unfortunate history of these efforts is documented in several reports (Kerr, 1982; Goldstein and Tsang, 1984; Mangold and Tsang, 1984).

Published Information After 1982

Grant et al. (1984) prepared a conceptual model of the Baca geothermal field using drilling records, down-hole surveys, and surface discharge measurements from wells in the Redondo Creek area made through 1981. They determined that a two-phase region exists within the reservoir that is strongly influenced by the CO_2 content of the reservoir fluid. They also delineated two principal flow zones: an upper zone in fractured Bandelier Tuff and a lower zone near the interface with Bandelier Tuff and underlying

Paliza Canyon Formation andesite. Their model suggests that upwelling fluids in the Sulphur Creek area recharge the Redondo Creek reservoir.

Five wells were sampled from June to October 1982 (White, et al., 1984; White, 1986; Truesdell and Janik, 1986) as a cooperative project among Lawrence Berkeley Laboratory (LBL), LANL, USGS and UNOCAL. Samples were taken to obtain a uniform set of geochemical analyses. Additional repeat analyses were performed on preserved samples from each well test in 1985 by LANL (F. Goff, unpub. data; see Table 1). The data indicate that two reservoir fluids are present in the Redondo Creek graben: a higher enthalpy, lower chloride fluid to the east (Baca-4 and -13), and a lower enthalpy, higher chloride fluid to the west (Fig. 15). Noble gas data presented by Smith and Kennedy (1985) also indicate that two fluids exist in the Redondo Creek reservoir. White (1986) stated that the lower temperature, more concentrated fluids, evolved by boiling. In contrast, Truesdell and Janik (1986) reinterpreted data published by Grant et al. (1984) stating that the two types of fluids originated from a 335°C deep parent fluid beneath the Redondo Creek graben by different flow paths and reaction mechanisms (Fig. 16). Resolution of these contrasting views can only be reconciled by long-term production, which never occurred. All groups of researchers agree that the geochemical data verify a mixing relation of deep geothermal waters with cooler derivative fluids southwest of the caldera.

A summary of production characteristics of wells in the Redondo Creek portion of the Valles geothermal system is listed in Table 5. Only six wells were considered commercially viable: Baca-4, -6, -11,-13, -15, and -24. Two wells, B-11 and B-15, are excess enthalpy wells that produce from both liquid and steam zones (Atkinson, 1980). Production enthalpy of wells in the liquid dominated reservoir is approximately 1,150 KJ/kg. Baca-6 was at the limit of commercial viability because of marginal wellhead

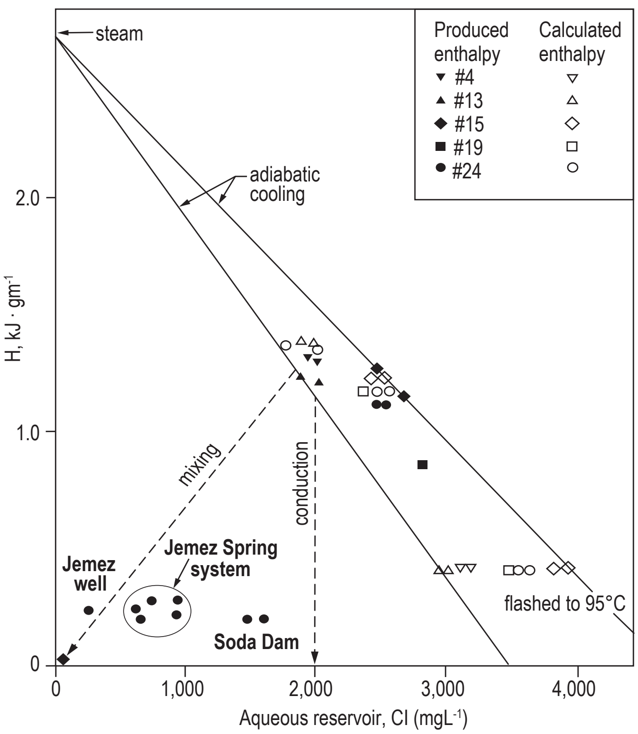


Figure 15. Enthalpy (H) versus chloride (Cl) relations showing fluid types in the Valles geothermal system (White et al., 1984). Produced enthalpy is determined from the measured down-hole temperature. Calculated enthalpy is determined from the chemical analysis of the well fluid and the Na-K-Ca chemical geothermometer (Fournier and Truesdell, 1973). Values of H from each method and each well sampled are more or less equal and show two types of reservoir fluid: a higher H, lower Cl fluid in the east (#4 and #13 refer to Baca-4, -13) and a relatively lower H, higher Cl fluid in the west (#15, #19 and #24 refer to Baca-15, -19, -24). Hot springs at Soda Dam and Jemez Springs cannot form by simple adiabatic cooling of reservoir fluid. Rather, they form by a combination of mixing with cooler meteoric waters and conductive cooling of heat to surrounding rocks. Conductive cooling is obviously a more important process for Soda Dam water. "Jemez Well" refers to the 152 m thermal aquifer in the JS-1 well at Jemez Springs (Table 1; Goff et al., 1981).

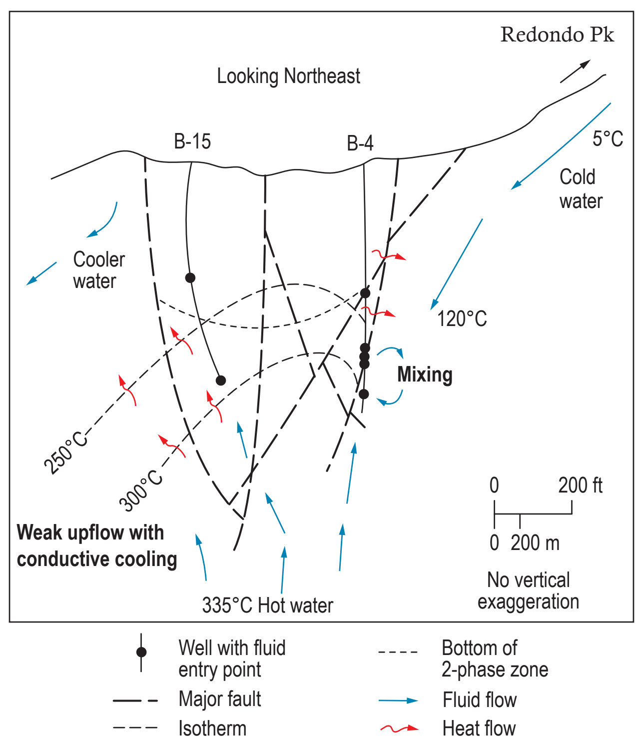


Figure 16. Conceptual-model cross section of Truesdell and Janik (1986) looking northeast across the Redondo Creek graben using additional data from Grant et al. (1984). Fluid and heat flows for dilution and conductive cooling are shown in the diagram.

pressure (0.66 MPa). According to Atkinson (1980), the minimum pressure required to run the power plant was about 0.69 MPa ±10% gauge (100 psig), with 0.97 MPa (140 psig) preferred. Although each well and steam separator had specific settings, we can estimate the power output (P) of the six wells using:

$$P = F\ (\Delta H)$$

where F is the total flow and ΔH is the enthalpy difference between separated steam and ambient steam (see Goff and Janik, 2000, p. 831—steam tables are required for the calculations). Assuming the separators are set at 170°C and the ambient enthalpy of steam wasted at the power plant corresponds with T = 25°C, the combined output of the liquid dominated fraction is roughly 10 MWe. However, two wells provide excess enthalpy from steam zones, thus the vapor-rich fraction of the reservoir is capable of another 8–10 MWe, equivalent to a total power output of 18-20 MWe.

Nielson and Hulen (1984) published their work on the stratigraphy of Baca wells 4 to 24 and their ideas on growth of the resurgent dome. Their paper is still important for examination of stratigraphy and fault structure. However, two of their geologic units are either not recognizable from surface mapping (Upper Tuff) or non-existent by reinterpretation of core (Lower Tuff). The former appears to be Deer Canyon Tuff, a post-caldera lithic-rich rhyolite tuff (Goff et al., 2011), and the latter appears to be part of the Otowi Member of the Bandelier Tuff, at least in the vicinity of the geothermal area (Warren et al., 2007, fig. 2).

Hulen and Nielson (1986a) followed up with their study of the hydrothermal alteration structure within the geothermal field (Fig. 17). The top of the system is characterized by argillic (smectite-rich) alteration to depths of 300–500 m and is underlain by weak to strong propylitic (calcite–quartz–illite–chlorite–albite) alteration to ≥2,500 m. Faults and fractures

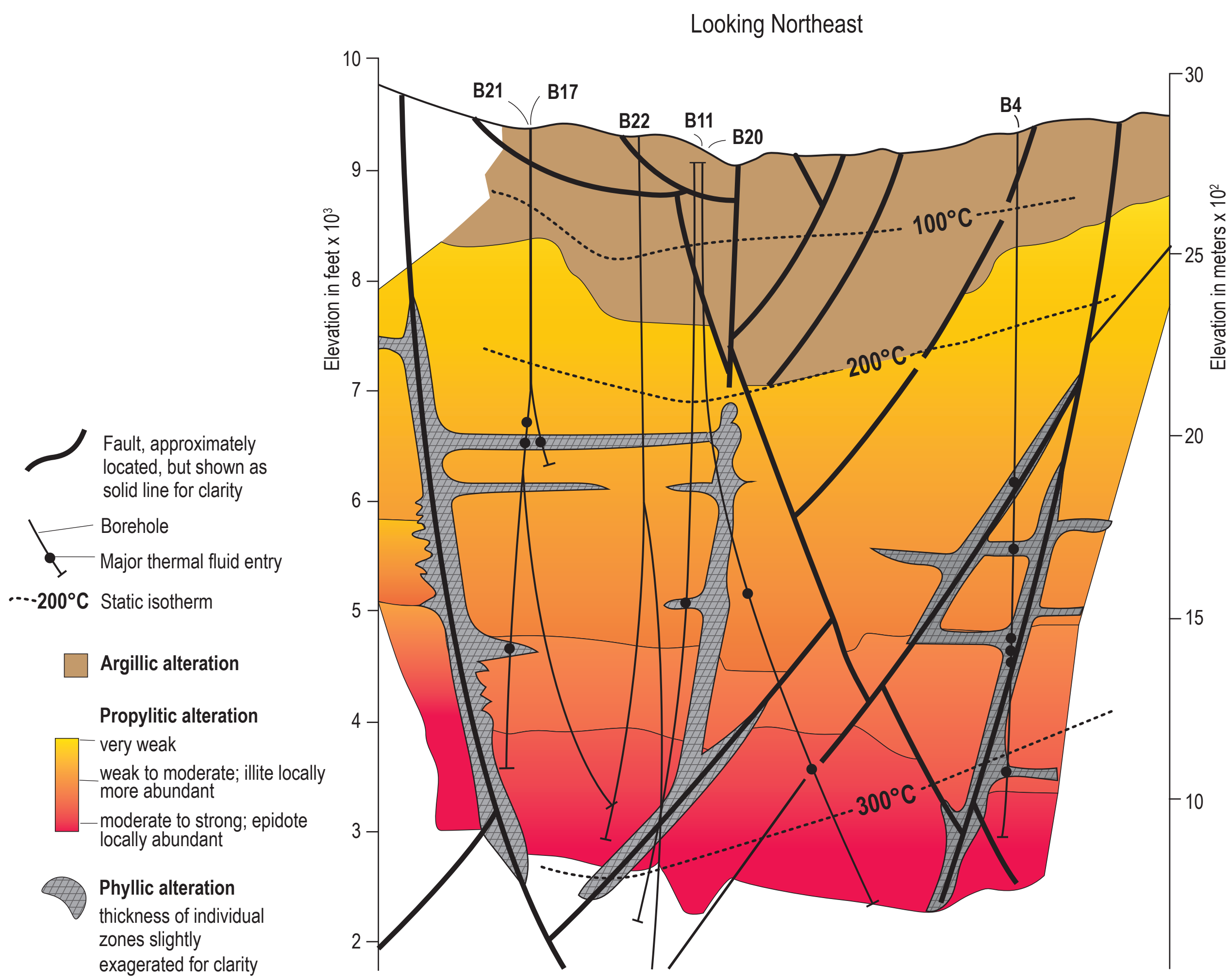


Figure 17. Generalized cross section of hydrothermal alteration through the Redondo Creek graben sector of the Valles geothermal system (from Hulen and Nielson, 1986a). The line of the section can be ascertained by examination of the well locations in Figure 6.

show intense but localized phyllic alteration (quartz–sericite–pyrite). Many of the best fluid entries in Baca geothermal wells are associated with phyllic alteration.

Later, Hulen and Nielson (1990) proposed that a possible feed zone (upflow plume) for the Redondo Creek reservoir existed beneath Redondo Peak to the east of wells Baca-4 and Baca-13 (see Fig. 6). This plume was identifiable by prominent subsurface pressure and temperature anomalies in the viable wells. The structures allowing upflow were not obvious, but Hulen and Nielson (1990, fig. 6) suggested that upflow was controlled by sub-circular volcanic vents that erupted the plinian phase of the Tshirege Member of the Bandelier Tuff. The postulated plinian vent is located somewhere beneath Redondo Peak (Self et al., 1986). Upflow might also be linked to centralized vents that had erupted upper flow units (ignimbrites) of the Tshirege Member, particularly Unit 4u (Goff et al., 2014, fig. 12e).

Additional Baca Controversies

Along with the drilling and development problems faced by UNOCAL, legal and economic controversies arose over the hydrologic relationship of the Valles reservoir to the hot springs in San Diego Canyon southwest of the caldera (Erickson, 1977; All Indian Pueblo Council, 1979; State of New Mexico, 1980; Balleau, 1984). Native American groups and resort owners contended that development of the Valles geothermal resource would deplete or terminate water flow from the hot springs and hot aquifers in San Diego Canyon. This issue was never resolved in court because the cooperative geothermal project was terminated.

Erickson (1977) prepared a report for UNOCAL evaluating the hydrological effects of a 50 MWe power plant on water flow to the surrounding Jemez Mountains watershed. He predicted that there would be only a 1% reduction in total Jemez River water flow during 30 years of operation. In contrast, Faust et al. (1984) used a three-dimensional finite difference model to examine the depletion of the discharge rate of fluid to the Jemez River (depletion of the "hydrothermal plume"). Their analysis predicted that electricity production from a 50 MWe could be maintained for 30 years, but that there would be a decrease of about 75% of thermal water discharge to the river. Note the difference in terminology. The predicted difference was so large (1% versus 75%; Fig. 18) that the DOE funded an independent study beginning in 1980 to compare the results and parameters of the two water-impact models

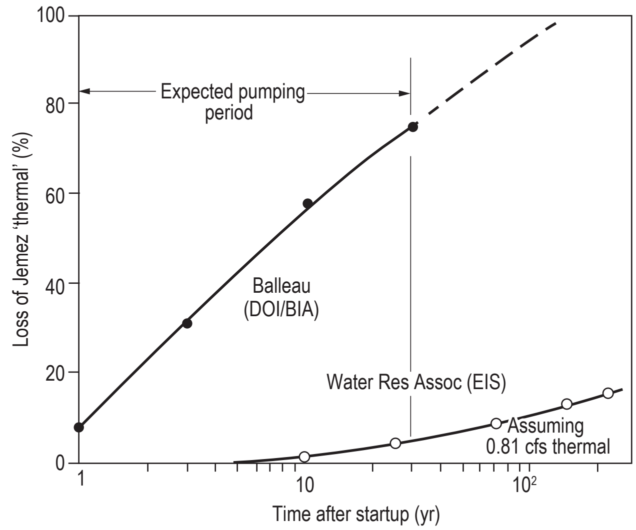


Figure 18. Predicted losses of thermal waters to the Jemez River after startup of a 50 MWe geothermal power plant assuming a 30-year pumping life (from Williams, 1986). "Balleau (DOI/BIA)" refers to the model of Balleau (1984) that predicts about 75% decrease of **thermal** water discharge to the river. "Water Res Assoc (EIS)" refers to the report of Erickson (1977) written for UNOCAL that predicts a 1% reduction in **total** Jemez River water flow during 30 years of operation. The two predictions are vastly different.

(Williams, 1986). The primary areas of disagreement were the total volume of water in the reservoir and the movement of reservoir fluid to the point of withdrawal.

Baca Project Summary

Although reservoir waters in the Baca geothermal field are 210 to >300°C and maximum measured temperatures in underlying rocks are 342°C at roughly 3,055 m depth, the fluids are extremely localized. There is little fluid continuity among successful wells. In addition, reservoir fluids are under-pressured because the depth to fluids is ≥500 m and rocks filled with low-pressure vapor overlie the reservoir. UNOCAL encountered many drilling problems. Wells displayed highly variable permeability and porosity along their courses. Permeable horizons in one well did not correlate with those in other nearby wells. Interconnectivity among the wells was extremely poor and bulk reservoir permeability was low. Permeability was restricted to fault zones and short lateral horizons cutting intracaldera Bandelier Tuff and associated rocks, and to zones in precaldera Tertiary volcanic rocks and sediments. Attempts to find better permeability in underlying Paleozoic and Precambrian rocks were unsuccessful. In the end, only six wells were suitable as production wells and legal battles over water depletion were ensuing. Thus, UNOCAL terminated their lease with Baca Land and Cattle Company in early 1984. In addition to WB-1 and Baca-4, all deep wells drilled and/or tested by UNOCAL were plugged and abandoned as per "California standards." A plug was set at 610 m (2,000 ft), cement was pumped in the casing to about 7 m (25 ft) from surface, the well head and casing above 7 m were cut off with a torch, and a green labeled standpipe was planted next to the decapitated well to show its location (Fig. 19A). The only Baca well that we know is still accessible is Baca-3 (see Table 1), although Baca-2 may also be accessible. The power plant site prepared by PNM is slowly decaying in a large flat area near Redondo Creek (Fig. 19B).

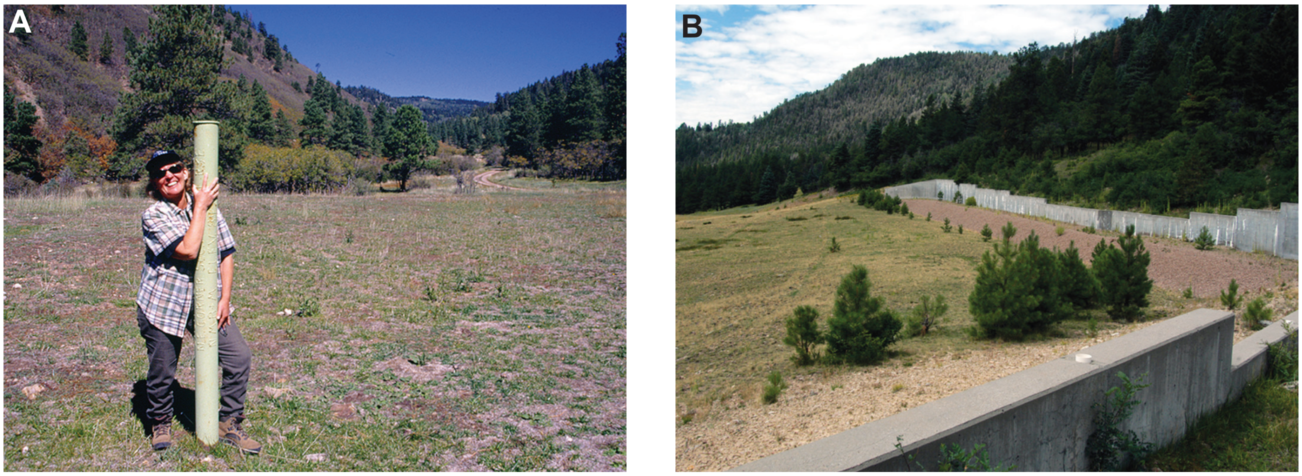


Figure 19. Remains of the Baca Geothermal Project. **A**—Photo looking northeast shows Cathy Goff embracing pipe that marks the buried location of Baca-12 (Fig. 6), once the hottest and deepest geothermal well drilled in Valles caldera (3,055 m and 342°C). This well was deepened by UNOCAL into Precambrian basement to search for better permeability, an endeavor that failed. All UNOCAL wells were plugged and abandoned and marked with similar pipes by 1984. Redondo Peak is to the right and Redondo Border is to the left. **B**—Photo looking southwest of retaining wall at the west side of the intended 50 MWe power plant site in Redondo Creek graben (blue square marked P in Fig. 6). Redondo Border is ridge to the right. *Photos by Fraser Goff.*

Universal 5000 rig, setting up to drill VC-2B, once the deepest and hottest corehole in the United States. *Photo by Jamie Gardner (LANL, deceased).*

Longyear 44 rig, setting up to drill VC-2A in Sulphur Springs. *Photo by Fraser Goff.*

VII. CONTINENTAL SCIENTIFIC DRILLING PROGRAM, VALLES CALDERA

Valles caldera was a high-priority site for investigation of fundamental processes in magmatism, hydrothermal systems, and ore deposit mechanisms from the earliest planning phases of the emerging Continental Scientific Drilling Program (CSDP) of the 1970s and 1980s (Shoemaker, 1974; U.S. Geodynamics Committee, 1979; Continental Scientific Drilling Committee, 1984a, 1984b). Consequently, the DOE Office of Basic Energy Sciences (OBES) began to sponsor scientific investigations, task groups, and workshops concerning the Valles caldera (and elsewhere) to identify data gaps, drilling objectives and targets (Luth and Hardee, 1980; Taschek, 1981). Five of the primary goals of the Valles caldera CSDP are described by Goff and Nielson (1986):

1. Study the origin, evolution, and physical-chemical character of the vapor-rich cap of the geothermal system; map the liquid-dominated portions of the geothermal system to understand recharge, heat transfer, convective upflow, and outflow.
2. Investigate the characteristics of caldera fill and mechanisms of caldera collapse and resurgence.
3. Study mechanisms of ore deposition within the caldera environment.
4. Develop and test high-temperature well-drilling techniques and logging tools.
5. Serve as a natural laboratory for testing and calibration of high-temperature geophysical techniques.

A unique feature of all CSDP drilling projects in Valles caldera was the use of coring rigs developed for mining exploration to obtain nearly continuous core. These drill rigs are relatively small and were adapted for high-temperature geothermal conditions by using blowout preventers, high-temperature drilling muds and additives, H_2S monitors, and other necessary equipment not utilized in mining exploration holes.

Core Hole VC-1

Not long after UNOCAL left the Baca area, the VC-1 hole was spudded in August 1984 in the southwest moat of Valles caldera (Fig. 5) on U.S. Forest Service land about 100 m south of the property boundary with Baca Land and Cattle Company (Goff et al., 1986; Rowley et al., 1987). The primary objective was to intersect the postulated hydrothermal outflow plume at a point roughly midway between the source reservoir and surface discharge of its diluted fluids from hot springs in San Diego Canyon. Secondary objectives were to core the youngest post-caldera eruption (Banco Bonito vitrophyre, about 70 ka), obtain structural and stratigraphic information in the southwest moat, and obtain information on past and present hydrothermal activity (Goff et al., 1986). Only information of geothermal significance is discussed herein.

VC-1 was a great success. Final depth was 856 m and BHT was 184°C with >95% core recovery. Detailed core logs and photos can be found in Gardner et al. (1987). The final string of coring rods was "planted" at the bottom of the hole to act as casing. After running a series of temperature logs to ascertain the temperature profile and gradient, the casing was perforated at several horizons ≥480 m to let hydrothermal fluids enter the well. These fluids are chemically similar to those previously identified as part of the hydrothermal outflow plume (Table 1; Goff et al., 1988). Paleozoic rocks and Precambrian breccias toward the bottom of the hole showed several episodes of faulting, hydrothermal disruption and mineralization (Hulen and Nielson, 1988; Keith, 1988). Moderate negative and positive inclination magnetizations measured in the core indicate that maximum temperatures in the hydrothermal plume at 400 to 856 m were once 300°C at about 1 Ma (Geissman, 1988). Alteration style is propylitic (calcite–quartz–illite–chlorite–albite) to phyllic (quartz–illite–pyrite). Identified sulfide minerals are molybdenite, sphalerite, galena, chalcopyrite, and arsenopyrite. Most fluid inclusions in hydrothermal vein minerals are ≤1 wt-% NaCl equivalent, approximately the same as those found in the active geothermal system (Sasada, 1988). VC-1 was plugged and abandoned, and the drill site restored to pre-drilling conditions in 1988 (Musgrave et al., 1989).

Core Hole VC-2A

This hole was drilled in September 1986 in the Sulphur Springs acid-sulfate hot spring area located near the intersection of the ring-fracture zone with the western margin of the resurgent dome (Figs. 5, 6). The major objective of VC-2A was to penetrate the interface between the vapor cap and the underlying liquid-dominated reservoir beneath the Sulphur Springs portion of the Valles geothermal system. Secondary objectives were to obtain information on hydrothermal and ore deposit processes and structural and stratigraphic information. As Sulphur Springs is private land, the landowners wanted to gain possession of the well to pursue their personal objectives after scientific tests were completed.

In spite of high-temperature acid conditions and constant concern with H_2S emissions, VC-2A exceeded all expectations (Goff et al., 1987; Hulen et al., 1987). Final depth was 528 m at 212°C with about 98% core recovery. As with VC-1, the final coring string was planted in the hole as casing and the hole was filled with cold surface water. Several temperature logs were run in the well over the next few months while the well returned to thermal equilibrium. A lost circulation zone at 490 m and 210°C corresponds with a rubble zone in the Bandelier Tuff. To determine if hydrothermal fluid would enter the hole at this horizon, a 3-m perforation of the casing centered at this depth was planned in May 1987. The first attempt to explode holes through the casing failed because high temperature water filling the casing caused the slim-hole perforating gun to malfunction. A tense hour ensued while the perforating gun was retrieved, repaired, rearmed, and rerun down hole; the second attempt was successful. Over the next few days, the well was purged of standing water with a bailer to lower the water level (lower the pressure) and encourage the well to flash (boil). Toward the end of this operation, fluid in the well began to geyser after each bailer run and finally the well "turned on" (Fig. 20A). Several flow tests were made of the 490 m zone over the following months. Chemical analyses (Tables 1 and 2) show that fluids

Figure 20. Continental Scientific Drilling Program core holes in Valles caldera. **A**—Photo looking south of VC-2A erupting flashed brine during initial flow tests at Sulphur Springs in May 1987. The producing interval is a single fracture in hydrothermally altered Bandelier Tuff at 490 m and 210°C. Note widespread near-surface advanced argillic alteration that consists of silica, kaolinite, sulfur, alunite, jarosite, pyrite and Fe-oxides. **B**—Photo of VC-2B erupting flashed brine during flow tests of November 1990; wellhead is 2.2 m tall for scale. Five zones were perforated in the casing and the combined flow had a mean formation temperature of 225°C, producing 1.4 MW of thermal energy (see text). *Figures 21A–D photos by Fraser Goff.*

from the 210°C horizon at Sulphur Springs are slightly more concentrated than fluids produced from the Redondo Creek graben, which led Goff et al. (1988) to postulate that there was a third fluid in the Valles geothermal system.

From the drilling and well testing, a model was developed defining the structure of the Sulphur Springs system (Goff et al., 1987; Goff and Gardner, 1994). The top of the system consists of an acid condensation zone only 5 m thick overlying a vapor zone that is about 175 m thick. Within the vapor zone, open fractures are filled with steam rich in CO_2 and H_2S. The model predicts the vapor- and liquid-dominated zones are separated from each other by a 310-m-thick region of tightly sealed, hydrothermally altered, intracaldera Bandelier Tuff and minor interlayered sediments. This zone is rich in illite–smectite–chlorite and corresponds to the "clay cap" typically found at the top of liquid-dominated geothermal reservoirs (Stimac et al., 2015, p. 799 and fig. 46.2A). No sharp interface was discovered between zones as per White et al. (1971). The first appearance of the liquid-dominated, Cl-rich reservoir fluid occurs at 490 m as described above.

An interesting discovery in VC-2A is a shallow zone of molybdenite mineralization, or "moly," at 25 to 125 m depth in a stockwork breccia of quartz–sericitized Bandelier Tuff (Hulen et al., 1987; Fig. 21A). The moly occurs as jordisite, a black, powdery colloidal form of molybdenum sulfide. MoS_2 concentrations run as high as 0.56 wt-% and the moly is associated with quartz, pyrite, fluorite, illite, sphalerite, chalcopyrite, and rhodochrosite. There is no calcite in this moly-rich horizon. Fluid inclusion work indicates temperatures of moly deposition at 175–240°C from fluids with apparent salinities of 0–2.0 wt-% NaCl equivalent (Sasada and Goff, 1995). Generally, fluid salinity has decreased with time. Because the moly mineral assemblage was deposited from liquid water but resides in an interval where fractures are now filled with low-pressure vapor, the top of the liquid-dominated zone has descended with time. Dating of the hydrothermal illite indicates that the vapor zone is ≤0.66 Ma (WoldeGabriel and Goff, 1989). Phyllic alteration dominates to a depth of 300 m in VC-2A whereas propylitic alteration dominates below 300 m.

VC-2A was relinquished as a functioning geothermal well to the landowners of Sulphur Springs as per legal agreement in November 1988, about two years ahead of schedule (Musgrave et al., 1990). Nothing constructive or useful has been done since, but conceivably, VC-2A can be entered for future private, commercial, or scientific endeavors if desired.

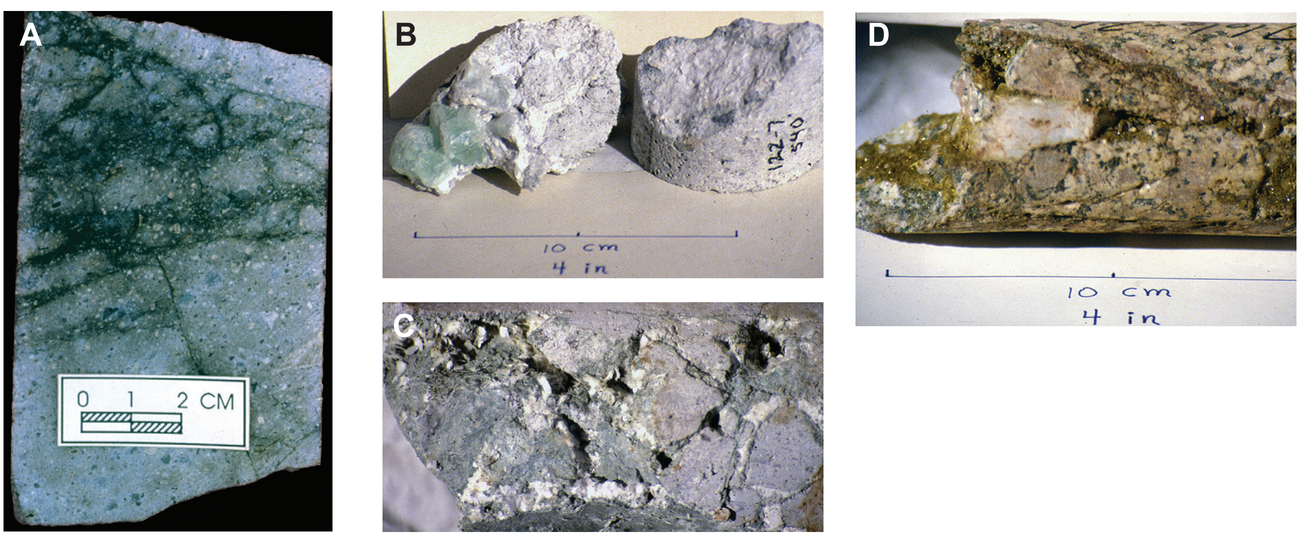


Figure 21. Photos of interesting core. **A**—Fractured, quartz-sericitized, intracaldera Bandelier Tuff with breccia cement of molybdenite (MoS_2), 30.5 m depth, VC-2A (Hulen et al., 1987). The moly is associated with pyrite-illite-quartz-fluorite and trace sphalerite-chalcopyrite-rhodochrosite. Maximum fluid inclusion homogenization temperature is 200°C but present temperature is about 90°C. Core diameter is 63.5 mm. **B**—Intensely altered, quartz-sericitized, intracaldera Bandelier Tuff with large vug filling of apple green fluorite with minor rhodochrosite, 168 m depth, VC-2A. Maximum fluid inclusion homogenization temperature is 220°C but present temperature is about 140°C. Core diameter is 63.5 mm. **C**—Breccia zone in intracaldera Bandelier Tuff partially healed with chlorite-illite-calcite-quartz-pyrite, 663 m depth, VC-2B. Present temperature is about 196°C. The casing in the well at this horizon was perforated and produced some of the fluid erupting during flow tests (Fig. 20B). Core diameter is 85 mm. **D**—Precambrian biotite quartz monzonite with open fractures containing epidote-quartz-calcite-illite-chlorite-pyrite-chalcopyrite, 1,755 m depth, VC-2B. Present temperature is 295°C. Fluid from this zone was extensively sampled during a series of in situ experiments (Goff et al., 1994). Core diameter is 47.6 mm. *Figure 21A photo by Jeff Hulen (University of Utah Research Institute, retired). Figures 21B–D photos by Fraser Goff.*

Core Hole VC-2B

VC-2B was located on land owned by Baca Land and Cattle Company; thus roughly 1.5 years were required to negotiate, prepare, and sign the mutually acceptable legal agreements. This hole was drilled from July to October 1988 about 0.5 km northeast of Sulphur Springs in a stabilized landslide complex where Baca-1 and -3 were previously drilled (Fig. 6). A companion to VC-2A, the primary objective of VC-2B was to penetrate the roots of the Sulphur Springs hydrothermal system and reach Precambrian rocks beneath the caldera floor. Based on drilling in Baca-2 about 1 km northeast of VC-2B, the estimated depth to top of Precambrian was about 1,525 m (5,000 ft) and the expected temperature was ≥250°C. To accomplish this task, VC-2B was drilled with a Universal 5000, one of the biggest wireline diamond drills available at the time. Heavy-duty drill rods were used (see Gardner et al., 1989 for drilling details). The entire drilling effort, including mobilization and demobilization, took 100 days. The drilling operation and surrounding site were monitored to ensure that no detrimental environmental impacts had occurred (Meeker et al., 1990).

VC-2B was a third fabulous success and at the time of completion was the deepest and hottest continuously cored hole drilled in the United States. The Precambrian interval, which is a moderately to severely altered biotite quartz monzonite, was encountered at 1,558 m (5,110 ft). Coring continued to a final depth of 1,762 m (5,780 ft). Drill rods were cemented at 1,697 m (5,567 ft) leaving the bottom of the hole open for fluid sampling. Core recovery was 99.2% with most losses occurring in friable landslide debris in the upper 30–40 m of the hole. Final BHT was 295°C (Fig. 22). The hole was flushed with cold water and allowed to thermally equilibrate. During the final days of coring, the mud returns showed spikes in concentrations of silica, chloride, and calcium that were interpreted to be hydrothermal fluids entering and mixing with mud from the Precambrian interval (Gardner et al., 1989). This fluid was originating in part from a fracture zone at 1,755 m (Fig. 21D).

Alteration intensity was most pronounced in the landslide, caldera fill sediments, Bandelier Tuff, Santa Fe Group, Sandia Formation, and Precambrian. As noted elsewhere in the geothermal system, the alteration assemblage changed from argillic to propylitic with depth. The principal alteration minerals in the bottom 300 m are quartz–calcite–illite–chlorite–epidote–albite–adularia–pyrite (see Stimac et al., 2015, fig. 46.5 for a chart comparing alteration mineral assemblages with temperature stabilities). Fluid inclusion studies (Goff and Gardner, 1994; Sasada and Goff, 1995) show that hydrothermal fluids in the geothermal system were originally hotter, especially in the shallow parts of the system, as well as more saline. These studies also show that the boiling point curve was once much higher than today, which is attributed to draining of intracaldera lakes, loss of hydraulic head, and formation of the vapor cap in the system.

One of the objectives of VC-2B was to obtain uncontaminated hydrothermal fluid from the Precambrian interval. In May 1989, an in situ sample was obtained from 1,753 m that contained roughly 750 mg/kg Cl. Thus, hydrothermal fluid was entering

Table 5. Production characteristics of geothermal wells in Redondo Creek graben. Wells in bold type were considered commercial.[a]

Well	Total Mass Flow (kg/hr)	Wellhead Press (MPa gauge)	Wellhead Flash (%)	Perm-Thickness (mD-m)	Skin Factor	Prod Enthalpy (KJ/kg)	Prod Temp[e] (°C)	Comments
B-4	75,800	0.965	27	1280	15	1160	291	L-D reservoir
B-6 [b]	68,000	0.655	22	1950	10	1110	280	L-D reservoir; well bridged off
B-10	57,200	0.110	34	1550	43	nr	<250	Subcommercial; damaged
B-11	120,000	0.965	44	1050	-4	1550	(356) [c]	Two-phase, excess enthalpy
B-13	90,700	0.965	27	616	4	1170	292	L-D reservoir
B-15	79,400	0.965	60	>1680	-3	1810	(374) [d]	Two-phase, excess enthalpy
B-19	54,400	0.152	25	732	9	950	223	Subcommercial
B-20	25,400	0.172	nr	305	-4.9	nr	282	Subcommercial; stimulated
B-23	33,100	0.255	nr	762	-3.9	nr	232	Subcommercial; stimulated
B-24	56,900	1.048	19	nr	nr	1100	247	L-D reservoir
Tot (n=6)	490,800	≥0.655	Ave = 33	---	---	1150 f	287 [f]	

[a] Data from Atkinson (1980), Morris and Bunyak (1982) and White et al.(1984). Wells B-5A, B-12, B-14 and B-16 were considered to be injector wells. Wells B-9, B-17, B-18, B-21, and B-22 were considered subcommercial but no production data are available; nr = data not reported.

[b] Well B-6 was marginally commercial because of lower wellhead pressure; [c] Maximum measured temperature was 331°C; [d] Maximum measured temperature was 281°C;

[c] Temperature calculated from the enthalpy; [f] Average enthalpy from liquid dominated reservoir; average temperature uses measured values for B-11 and B-15.

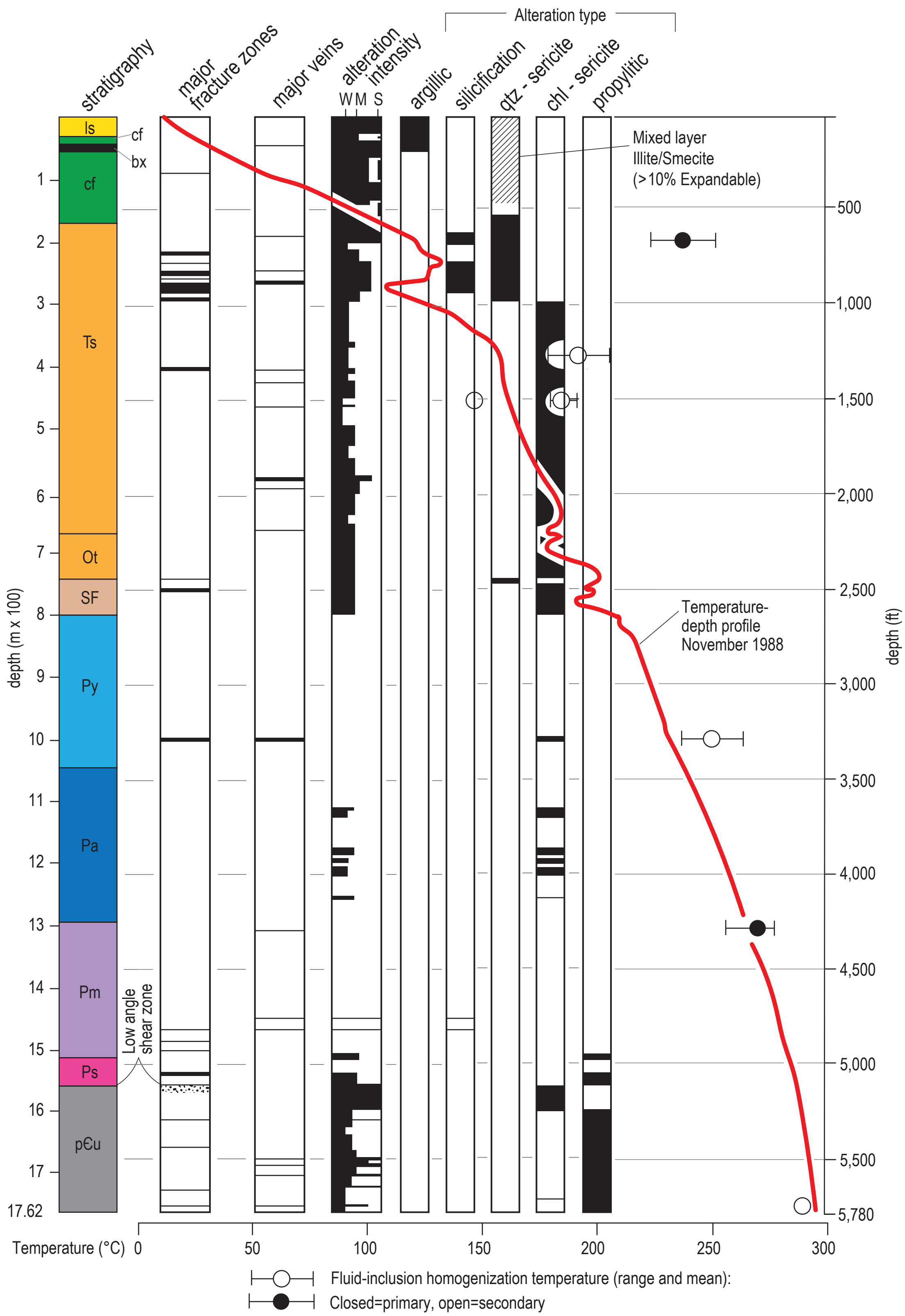


Figure 22. Generalized lithologic, structural, alteration, and vein mineralization log for core hole VC-2B. Stratigraphic designations: ls = landslide debris, cf = caldera-fill deposits, bx = hydrothermal breccia, Ts = Tshirege Member Bandelier Tuff, 1.25 Ma, Ot = Otowi Member Bandelier Tuff, 1.62 Ma, SF = Miocene Santa Fe Group, Py = Permian Yeso Group, Pa = Permian Abo Formation, Pm = Pennsylvanian rocks, Ps = Pennsylvanian Sandia Formation, p€u = Precambrian rocks, undivided (from Hulen et al., 1989 with Bandelier stratigraphy revised according to Warren et al., 2007). W = weak, M = moderate, S - severe alteration intensity. qtz = quartz. chl = chloride.

the hole and mixing with the water that had been introduced the previous October. In June 1989, a liquid nitrogen lift was conducted on VC-2B to purge it of all residual drilling fluids and to stimulate flow. Although the hole dramatically unloaded and was successfully purged, the Precambrian interval could not sustain flow after 36 hours. Over the next days and weeks, the hole slowly filled with formation fluid to a depth of 204 ± 7 m from surface and a shut-in pressure of roughly 2.52 MPa (360 psi).

From October 1989 to late August 1990, several in situ experiments were conducted in VC-2B using three different (and relatively expensive) in situ sampling tools and a custom gas extraction system (Goff et al., 1994). Obtaining representative in situ fluid and gas samples from the Precambrian proved to be exceedingly difficult and costly because of various problems (see details in Goff et al., 1994). Tables 1 and 2 list the water and gas composition of hydrothermal fluid from the Precambrian beneath the Sulphur Springs area. This water is substantially more concentrated than the Redondo Creek graben samples (Baca-13 and Baca-15) and indicates that yet another fluid exists in the Valles caldera geothermal system, bringing the total number of geochemically unique fluids in the system to four. Interestingly, gas compositions of all Valles wells are approximately the same (Table 2).

After the in situ experiments were completed, the Precambrian interval was plugged. By examination of temperature logs and fractures in the core, five horizons were perforated up hole on October 3, 1990, to allow hydrothermal fluids from upper horizons to enter the well:

Zone 1: 1,454 m, 282°C in Madera Group (Pennsylvanian limestone)

Zone 2: 989 m, 232°C in Yeso Group (Permian sandstone)

Zone 3: 777 m, 207°C in Santa Fe Group (Miocene sandstone)

Zone 4: 686 m, 199°C in Bandelier Tuff (Quaternary)

Zone 5: 663 m, 196°C in Bandelier Tuff (Quaternary)

Each perforating gun was 3 m long and fired 20 shots at 180° phasing. At the time, the lowermost zone (Zone 1) was the hottest slim-hole perforation ever accomplished. When Zone 2 was perforated, 5 x 10^4 L of water in the casing was "sucked" into the interval suggesting that the "Yeso zone" would ultimately contribute substantial amounts of fluid.

On November 1, 1990, VC-2B was prepared for flow tests by adding a flow line with sampling ports and a weir box. Initial shut-in pressure was 2.34 MPa gauge (340 psi). The hole was opened rapidly at the gate valve, depressurized noisily while geysering 12 m high, and then erupted continuously to heights of 30–40 m for 45 min (Fig. 20B). Major flow tests of VC-2B were conducted on November 6–9, 1990 and in May 1991. Many samples were collected and analyzed. The weighted mean average temperature of the produced fluid from the five perforated zones is about 225°C (Janik and Goff, 1996) (Tables 1 and 2). The TDS of fluids is higher than those in Redondo Creek although bulk temperature is lower. Gas compositions are about the same.

The power output of VC-2B was calculated during the November flow tests. The flow rate on November 9 was about 1.13 ±0.2 L/sec at the weir box. Using a steam fraction of 0.25 from steam tables (225 versus 95°C, ΔH = 925 KJ/kg), the total flow was 1.51 ±0.2 L/sec producing 1.40 MWt of thermal energy. Assuming steam separation at 170°C, the steam produced for electricity would amount to 0.45 MW, which is not bad for a hole only 7.6–10.2 cm in diameter (3–4 in). Final shut-in pressure at the end this test was 0.75 MPa gauge (110 psi). Scaling this up to a 20.3 cm (8 in) production well would amount to 2.3 MW of electrical energy. However, no long-term flow tests were conducted in VC-2B to determine if it could sustain this flow for extended periods of time. The average geothermal production well produces around 4 MW of energy (Grant, 1996).

By 1992, scientific and technical studies in VC-2B were complete and the well was plugged and abandoned. A summary of the scientific results of Continental Scientific Drilling Program efforts in the Valles geothermal system can be found in Goff and Gardner (1994), Gardner and Hulen (1995), and references therein. Due to continually falling costs of oil and gas during this time, the focus of the U.S. DOE/OBES changed from scientific drilling of magma hydrothermal systems to environmental cleanup issues. Thus, no more scientific core holes were drilled in the Valles caldera, which effectively stopped further deep geothermal and scientific investigations. A few small geothermal companies looked at the Baca after 1994 as a possible geothermal "play," but shied away because of past difficulties and the cost of the lease payment required by Baca Land and Cattle Company ($100,000 per year).

VIII. VALLES CALDERA NATIONAL PRESERVE

After two years of negotiations, the White House reached an agreement to buy and permanently protect the 95,000-acre Baca ranch as a national preserve. The ranch and the caldera are roughly coincident in aerial extent; the west and southwest margins of the caldera consist mostly of U.S. Forest Service lands. A bill appropriating the money ($101 million) was passed by the U.S. Congress and signed by President Clinton late in 1999. Authorizing legislation, called the Valles Caldera Preservation Act, H.R. 3288/S. 1892, passed the House and Senate, and was signed by President Clinton on July 25, 2000.

The recently created Valles Caldera National Preserve was managed by a board of trustees appointed by the U.S. President. Members of the Valles Caldera Trust held regular board meetings to share information with the public as they formulated plans for the Preserve. Before the Valles Preserve was opened to the general public in 2003–2004, the archeology, geology, animal and plant ecology, grazing potential, and Native American heritage underwent intensive investigation and re-evaluation. Elk hunting and limited cattle grazing are income-producing activities allowed since 2002. Turkey hunting has been added in subsequent years. Limited hiking commenced in 2003 and this was expanded to include skiing, snowshoeing, mountain biking, wildlife tours, and other tours. The Valles Caldera National Preserve successfully became part of the U.S. National Park system in 2014. This move changed jurisdiction from the Department of Agriculture to the Department of Interior and management of the Vales Caldera Trust ended in September 2015. For more information on the Valles Caldera National Preserve and available public activities, see www.nps.gov/vall/index.htm.

The former Baca Land and Cattle Company actually consisted of four companies with different commercial interests (grazing, mineral development, etc.). One of the companies was partly owned by Joe Harrell and his heirs (Joe was a colleague of Pat Dunigan); he refused to sell his 12.5% interest in geothermal and mineral rights. A chess game ensued in the early years after the U.S. government purchased the “Baca” and established the Valles Caldera National Preserve, in which Harrell wanted to either redevelop the geothermal field or obtain a more lucrative price for his interest. Details are not public information, but by 2006, the government had retired the geothermal resource from development and the value of the 12.5% interest was being argued in court. According to R. Parmenter of Valles Caldera National Preserve, the Preserve can still use geothermal energy in the caldera for local facilities if it chooses, but no commercial leases or development are permitted without an Act of Congress.

All that remains of the Westates-Bond #1 Well drilled in 1960 in Alamo Canyon, first geothermal well in the Valles. View is looking south. *Photo by Fraser Goff.*

IX. THERMAL REGIME AND GEOTHERMAL MODEL

Geothermal wells drilled inside the caldera show that the Valles geothermal system is highly compartmentalized. Geochemically, separate subsystems apparently underlie the Sulphur Springs and Redondo Creek areas of the caldera. Wildcat wells and the Fenton Hill Hot Dry Rock wells show that the thermal footprint of the underlying magma body decreases rapidly outside the structural margin of the caldera (ring-fracture zone) and the topographic wall (Fig. 23).

An idealized model of the deep geothermal system and the hydrothermal outflow plume is shown in the southwest-northeast cross section of Figure 24. Meteoric precipitation slowly percolates to depth and recharges the system, primarily from the northeastern resurgent dome and intracaldera basins to the east and north (see Fig. 2). This recharge water eventually equilibrates at depths of 2–3 km and temperatures exceeding 300°C within intracaldera tuffs and precaldera volcanic and sedimentary rocks. Thermal waters

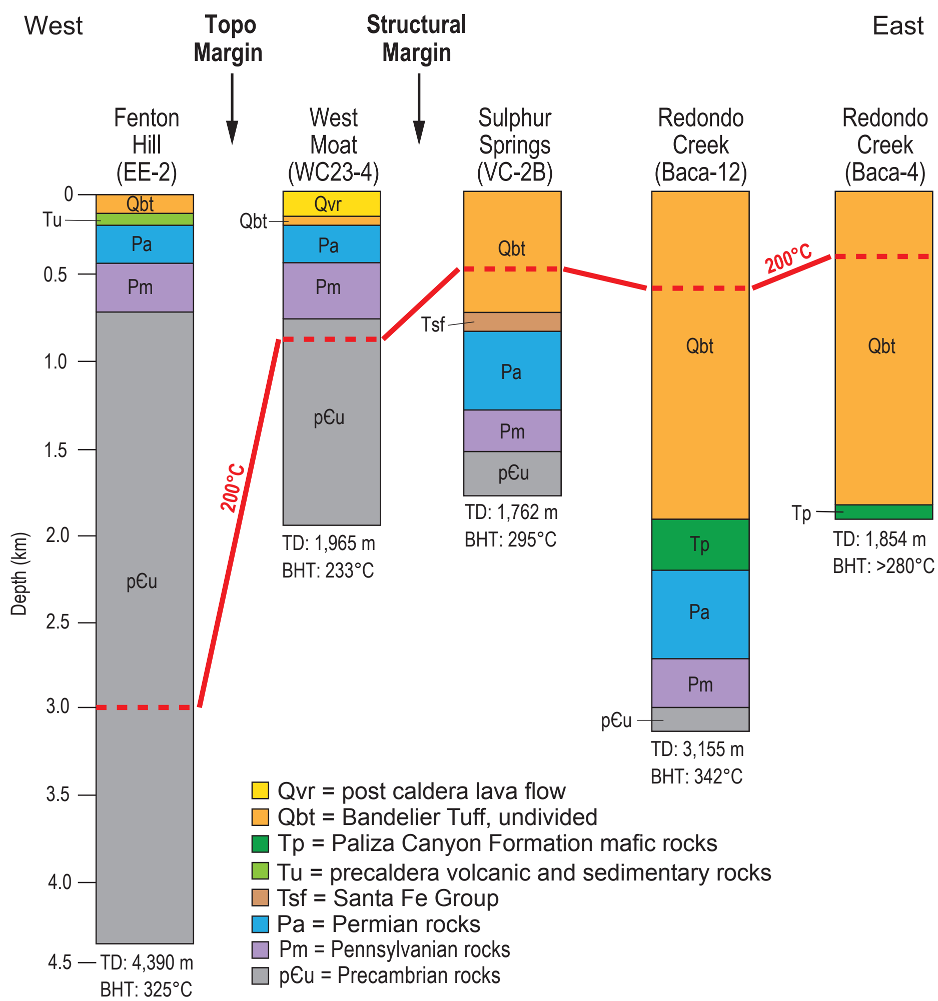


Figure 23. Side-by-side comparison of important Valles geothermal wells shows dramatic difference in thickness of Bandelier Tuff, and deepening of the 200°C isotherm between intracaldera environment and caldera exterior. The caldera depression and thick tuff infill act as crude trap for the geothermal reservoir.

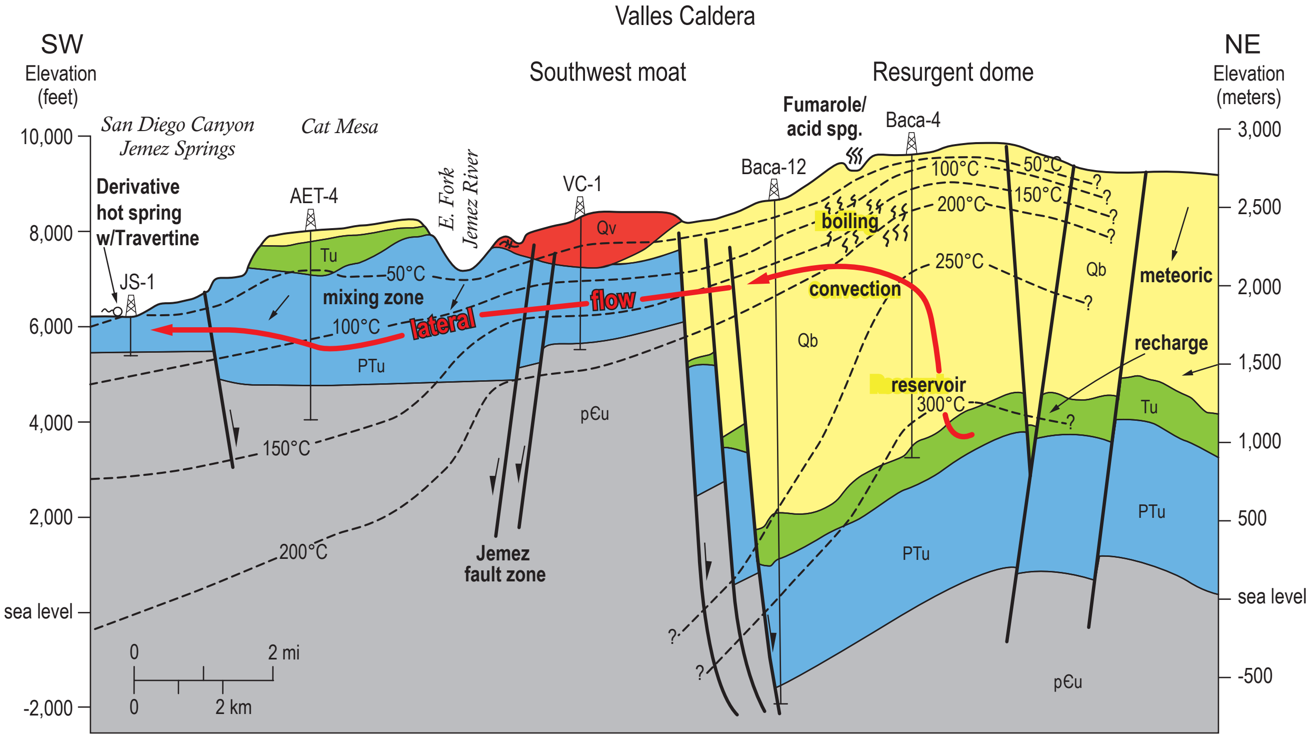


Figure 24. Idealized cross section of southwest margin of the Valles Caldera shows general configuration of the geothermal system. The line of the section can be ascertained by examining Figures 4, 5, and 6. The JS-1 well is located in Jemez Springs (Figs. 5 and 7K). Subsurface geology, well bore data, geophysics, and fluid geochemistry place tight constraints on this model (from Goff and Gardner, 1994; vertical exaggeration is about 4:1). The Jemez fault zone is highlighted because it is the principal channel of geothermal fluids in the lateral flow system. This model has been adapted by several recent studies to highlight other aspects of the geothermal system (see Tafoya, 2012, p. 3). Colors: Red (Qv) = moat volcanics and associated sediments, yellow (Qb) = intracaldera flows, tuffs and minor associated sediments, green (Tu) = Tertiary volcanics and sediments, blue (PTu) = Paleozoic and minor Triassic rocks, and gray (p€u) = Precambrian rocks, undivided.

rise convectively to depths of roughly 500–600 m before boiling and flowing laterally toward the southwest caldera wall. A vapor zone containing steam, CO_2, H_2S, and other volatile components forms above the top of a liquid-dominated zone at a temperature of roughly 200°C. Acid springs, mud pots, and fumaroles form in a surface condensation zone only a few meters thick. The lateral flow system (hydrothermal outflow plume) crosses the southwest caldera wall above Precambrian basement through the Jemez fault zone and semipermeable Paleozoic strata. Mixing of reservoir water and other groundwaters occurs along the lateral flow path forming derivative fluids that issue as hot springs or flow in subsurface aquifers adjacent to the Jemez fault zone.

The Jemez fault zone strikes northeast toward the Redondo Creek graben and the geothermal reservoir (Fig. 5). This fault or a related splay was intersected by core hole VC-1, which encountered several fractures producing derivative geothermal fluids (Goff et al., 1986; 1988). Other faults (e.g., Cat Mesa fault zone east of Jemez fault zone) trend southeast to south from the caldera margin but do not host known hot springs, gas vents, or related hot aquifers. Instead of a conduit for thermal fluid flow, the Cat Mesa fault zone probably acts as a barrier confining fluids of the hydrothermal outflow plume to the San Diego Canyon area to the west.

The model shown in Figure 24 is relatively simple and resembles general models of volcanic-hosted hydrothermal systems presented in Henley and Ellis (1983), Goff and Janik (2000), and Stimac et al. (2015). Differences between models exist primarily in structural setting and direction of lateral flow caused by differences in tectonics and hydrology. We know that the hydrothermal system is more complex when examined in detail (Grant et al., 1984; Smith and Kennedy, 1985; Truesdell and Janik, 1986).

X. CONCLUSIONS

With the above facts in mind, several conclusions can be stated about the Valles geothermal system:

1. A partially molten magma body underlies the southwest sector of the caldera at depths of 7–15 km. This magma provides significant heat and some volatiles (He, N_2, S, etc.) to the overlying geothermal reservoir.
2. Deep fluids in the geothermal reservoir are typical for liquid-dominated systems, consisting of relatively dilute Na-K-Cl-HCO_3 brines (3.8–9 x 103 mg/kg TDS) with significant amounts of B, Br, Li, and As. Intracaldera gases are typical for geothermal systems hosted in volcanic rocks and the gases consist of about 98 mol-% CO_2, 1 mol-% H_2S, and 1 mol-% other components on a water free basis.
3. The deep reservoir discharges Cl-rich fluids into the Jemez fault zone and San Diego Canyon forming a hydrothermal outflow plume. Waters at Soda Dam and Jemez Springs are diluted with cooler groundwaters that cool conductively before emerging as springs. These waters dissolve considerable amounts of Paleozoic limestone along their flow paths. Gas associated with these waters is depleted in H_2S. About 1,600 L/min of mixed fluids emerge at Soda Dam and perhaps another 200 L/min discharges from the smaller system at Jemez Springs.
4. Within the caldera, the geothermal reservoir is overlain by localized fumaroles, gas vents, and acid-sulfate springs. Natural sulfuric acid is formed by oxidation of H_2S gas emitted from the underlying geothermal system.
5. Dilute thermal meteoric waters acquire their heat by conduction and issue from hot springs in the caldera moat. These waters are not chemically derived from the deep reservoir.
6. It is our contention that brines in the Jemez Pueblo-San Juan Basin area are not part of the Valles geothermal system because their chemical and isotopic compositions are different from Valles deep reservoir fluids and derivative fluids in San Diego Canyon. Fluids analyzed from the Hot Dry Rock geothermal experiment are also unique from those in the Valles geothermal system.
7. The basic structure of the geothermal system (top down) consists of a thin acid-sulfate condensation zone roughly 5 m thick, a vapor-zone as much as 300 m thick, a zone of tightly sealed impermeable rock as much as 300 m thick (i.e., the cap zone), and the underlying reservoir, which is highly compartmentalized.
8. The most voluminous fluid production comes from faulted and fractured zones within intracaldera Bandelier Tuff, Paliza Canyon Formation mafic rocks, and sandstone of the Santa Fe Group. Commonly, good fluid production comes from or near contacts of tuff with these other two units.
9. Small amounts of geothermal fluid circulate in localized fractures within Paleozoic and Precambrian rocks beneath the Valles geothermal reservoir, but these zones are not capable of sustained flow.
10. The hydrothermal alteration structure of the reservoir consists of advanced argillic to argillic assemblages around the acidic cover, argillic to weak propylitic alteration down to about 300 m, and moderate to strong propylitic alteration at the bottom. At 300°C the prevailing mineral assemblage is quartz–calcite–albite–chlorite–illite–adularia–epidote–pyrite. Wairakite, anhydrite, and fluorite are also common. Production zones are commonly associated with phyllic alteration (quartz–illite–pyrite). Hydrothermal alteration is associated with "moly" (MoS_2) and minor sulfide mineralization anomalies of economic interest.
11. The Redondo Creek graben and fault zones are the only known area within Valles where

successful production wells were drilled. Even there, most wells were sub-commercial. Ten more wells were drilled in western sectors of the caldera near Sulphur Springs and Alamo Graben, but none proved to be useable production wells in these supposedly favorable locations.

12. The sustainability of the geothermal resource is unproven. Because the Valles geothermal reservoir displays poor hydraulic connectivity, it is not known if the reservoir will produce sufficient volume of fluids at pressures sufficient to keep a geothermal plant operational for 30 years. Computer simulations concluded that the reservoir flow rate and pressure would drop quickly in the first few years of operation.

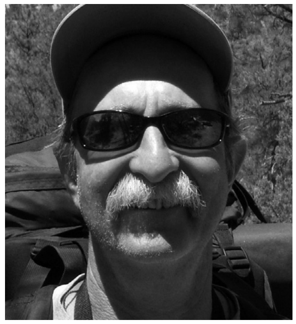
13. Exploitation of the Valles reservoir will have an unknown impact on the hot springs and aquifers in San Diego Canyon (Williams, 1986; Trainer et al., 2000). Past experience at many other geothermal systems shows that production of reservoir fluids can have dramatic detrimental impacts on surface thermal features (e.g. Hunt and Scott, 1998). The local Pueblos revere the hot springs and some spring waters in the Jemez Springs area are used by resorts and religious institutions for recreational purposes. Unless those groups share in the development scheme, any new geothermal project will probably be subject to litigation. As an example, seismic projects conducted in the Jemez Mountains in the late 1990s were delayed by threats of litigation from Native American groups (Baldridge et al., 1997). This project included some shallow drilling. It is highly likely that a new Valles geothermal project would face similar obstacles.

14. The geothermal wells drilled by Baca Land and Cattle Company and by UNOCAL are probably not reusable, contrary to what is suggested by some geothermal developers. They were plugged and abandoned to California standards. Few rational developers would want to reopen high temperature wells that have unknown casing problems and that are now 30–40 years old.

15. After years of drilling and considerable expense, only 20 MW of geothermal reservoir capacity is proven at Valles caldera. Perhaps this could be doubled by up-to-date drilling and completion methods and binary power plants. Geothermal developers occasionally state that Valles contains as much as 1,000 MW of undiscovered power but these claims are unsubstantiated. The shallow heat contained within Valles rocks is immense, but extracting large quantities of hot fluids from these rocks has been exceptionally difficult.

16. Now that Valles caldera is largely controlled by the Federal Government and the geothermal resource is “retired,” it is unlikely that the known geothermal reservoir will be exploited, much like those in Yellowstone or Lassen Volcanic National Parks. The Federal Government received nine lease applications in 2011 to develop geothermal resources on the north and west sides of the Valles Caldera National Preserve, but as of this date, these applications have not been approved. Nonetheless, this shows that the desire to develop high-temperature resources in the Valles caldera region remains.

AUTHORS



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Fraser Goff received a B.S. in chemistry from San Jose State University (1971) and his Ph.D. in Earth Science from University of California Santa Cruz (1977), where his thesis dealt with igneous petrology and geochemistry of basalt. During this period he worked at the U.S. Geological Survey in Menlo Park, California (1969–1977) on geothermal and volcano projects. From 1978–2004 Fraser was employed by Los Alamos National Laboratory, New Mexico working on a series of geothermal, volcano, and environmental projects. He was Chief Scientist and Principal Investigator on three high-temperature scientific wells in the Valles Caldera (1983–1991). He was head geochemist during drilling of four exploration wells in Central America for U.S. AID (1985–1992). Since 2004 Fraser has been adjunct professor at University of New Mexico and New Mexico Institute of Technology, a member of the StateMap Program (NMBGMR), and a private consultant. Fraser led or co-led long-term projects to investigate the chemical and isotopic composition of magmatic and geothermal fluids, and to develop remote sensing techniques to analyze gas compositions from active volcano plumes. He has worked on about 40 geothermal systems and 15 active volcanoes worldwide during his career and has been author or co-author on more than 100 refereed journal publications. Since 2004 Fraser has been author or co-author on 15 geologic maps. In 2009 he published Valles Caldera—A Geologic History (114 p., University of New Mexico Press). Fraser is now completing a geologic map and report on Mount Taylor, New Mexico's "other" famous volcano.

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Cathy J. Goff (formerly Janik) obtained her B.S. in Geology from San Jose State University (1983, magna cume laude). From 1978 to 2002, Cathy was employed by the U.S. Geological Survey, Menlo Park, California and became a specialist on the fluid geochemistry of geothermal and volcanic systems. She conducted major projects at Los Azufres and Cerro Prieto (Mexico), Klamath Falls (Oregon), Valles caldera (New Mexico), Makushin Volcano (Alaska), Yellowstone National Park (Wyoming), Salton Sea, Long Valley Caldera, The Geysers-Clear Lake (California), and Lassen Volcanic National Park (California), geothermal systems in Guatemala, and Honduras. In 1986–1987, Cathy attended Stanford University under the USGS Geologic Division Graduate School Training Scholarship (competitive award), where she studied physical and fluid geochemistry of geothermal and ore-depositing systems; determined the stable isotope properties of epidote in active and fossil hydrothermal systems; and investigated fluid-mineral equilibrium in the State 2-14 well, Salton Sea geothermal system. In 1990 she became Chief of the Chemical Processes in Geothermal Systems Project and performed several special assignments on the Kilauea Volcano geothermal system (Hawaii), the Alid geothermal system (Eritrea) and the Dixie Valley geothermal system (Nevada). From 1995 to 2002, Cathy managed the Gas and Stable Isotope Laboratory for the USGS Volcano Hazards Team, worked on the Magmatic Volatiles and Hydrothermal Systems Project with special emphasis on the Cascades and Aleutian volcanic arcs, and a project at Popocatépetl volcano (Mexico). In 2002, Cathy retired from the USGS and moved to New Mexico where she is a consultant and part-time contributor to the New Mexico Statemap Program (2003–present).

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GLOSSARY

Acid springs—Geothermal springs discharging waters that have pH ≤3, often ≤2; generally such waters have sulfate as the major anion, in which case the waters are commonly called acid-sulfate waters. Springs of this type are found near the top or cap of geothermal systems.

Alluvium—A general term for clay, silt, sand, gravel or similar unconsolidated detrital material, deposited during comparatively recent geologic time by a stream or other body of running water.

Andesite—A dark-colored igneous extrusive rock usually forming lava flows, domes and stratovolcanoes (e.g., Mount Shasta, CA; Mount Fuji, Japan); chiefly composed of the minerals plagioclase, pyroxene ± olivine ± hornblende ± biotite, and glass. Commonly has a fine-grained porphyritic texture.

Anions—Atoms that have acquired a negative charge by virtue of gaining one or more electrons.

Arc—As in "island arc" or "volcanic arc" is a curved linear belt of volcanoes above a subduction zone.

Argillic—Pertaining to clay or clay minerals as in "argillic alteration" in which certain minerals of an original rock are converted to clay minerals such as illite, smectite, kaolinite, chlorite, etc.

Basalt—A general term for a dark colored extrusive igneous rock usually forming lava flows and scoria cones; chiefly composed of the minerals clinopyroxene, plagioclase, olivine, and glass. It is the fine-grained igneous equivalent of gabbro.

Breccia—A coarse-grained rock composed of angular broken rock fragments held together by a fine-grained matrix and/or by a mineral cement. It differs from conglomerate in that the fragments have sharp edges and unworn corners. There are many types of breccias usually discriminated by how they form: fault breccia, lava breccia, talus breccia, explosion breccia, etc.

Calc-alkaline—A term used for a magma series of basalt, andesite, dacite and rhyolite that has relatively high calcium but low silica relative to sodium + potassium. Calc-alkaline magmas are most common along and near volcanic arcs near subduction zones and plate boundaries but can occur in other tectonic settings.

Cations—Atoms that have acquired a positive charge by virtue of having lost one or more electrons.

Connate—A term applied to water entrapped in the interstices (open spaces) of a sedimentary rock at the time of deposition; generally speaking, such a water has been out of contact with the atmosphere for at least an appreciable part of geologic time.

Dacite—A light-colored igneous extrusive rock usually forming lava flows, lava breccias, domes and dome complexes; chiefly composed of plagioclase and potassium feldspar and usually with quartz ± pyroxene ± hornblende ± biotite. Commonly has a fine-grained porphyritic texture and often flow banded.

Dike—A tabular igneous intrusion of any composition that cuts across the bedding or foliation of country rocks. If the country rocks are relatively soft, the dike will form a linear ridge or wall tens of meters to kilometers in length.

Dome—In volcanology, a large magmatic extrusion of highly viscous lava that piles up on itself forming a hill or small mountain (see also resurgent dome).

Evaporite—A sedimentary rock composed primarily of minerals produced from a saline solution as a result of extensive or total evaporation of the solvent water. The minerals in such a rock are commonly gypsum, anhydrite, halite, etc. Thick deposits form an evaporite sequence.

Flow(s)—Lava flow(s)

Fossil—As in seawater; another name for connate water trapped in rocks that were originally of marine origin.

Frac job—Hydraulic fracturing designed to create fractures in an otherwise solid or impermeable rock mass to encourage flow of water, oil, gas, etc.; usually stimulated by high-pressure water containing chemicals and/or small solid grains of sand or other proppants.

Friable—A term applied to a rock, soil or mineral that crumbles naturally or is easily broken, pulverized or reduced to powder.

Fumaroles—A vent, usually volcanic, from which gases and vapors are emitted; fumaroles occur near the summit and flanks of active volcanoes, and in clusters of vents or along faults resulting from geothermal activity.

Gneiss—A layered or foliated rock formed by regional metamorphism in bands or lenses of granular minerals alternating with bands of flaky or elongate minerals.

Graben—An elongate trough or basin, bounded on both sides by high-angle normal faults that dip toward one another.

Half graben—An elongate, asymmetric trough or basin bounded on one side by a normal fault.

Horst—An elongate structural block, usually uplifted, that is bounded on both sides by normal faults that dip away from each other.

Intraplate (magmatism)—Igneous activity far away from any plate boundary and therefore considered unrelated to subduction or sea floor spreading processes.

Laccolith—A concordant igneous intrusion with a convex-up roof and a flat floor; the size of the intrusion is usually >1 km.

Lacustrine—Fine-grained, laminated sedimentary rocks formed at the bottom of a lake.

Mafic—Igneous rocks chiefly composed of dark-colored ferromagnesian (Fe, Mg, Ca-rich) minerals; loosely equivalent to areas or regions in which basalt and andesite dominate.

Meteoric (water)—Water of recent or relatively recent atmospheric origin (rain, snow, ice).

Moat (zone)—A valley-like depression around the inner wall of a caldera, between the rim and the resurgent dome or eruptive dome or cone in the center.

Mud pot—A type of hot spring containing bubbling mud, usually acidic and sulfurous, often boiling from discharge of steam and acidic gases; such springs are often multi-colored (paint pots).

Petrology—The branch of geology dealing specifically with the origin, occurrence, structure, mineralogy and history of rocks.

Phyllic—Hydrothermal alteration resulting from replacement of original (often volcanic) rock minerals with high-temperature micas and other secondary minerals. The typical mineral assemblage is quartz-illite (sericite)-pyrite, the formation temperature is ≥180°C and the color is often pale gray to gray.

Plug—A vertical pipe-like body of a solidified magmatic intrusion representing the conduit of a volcano or volcanic vent. Because the plug is generally harder than the surrounding country rock, a plug often forms prominent geomorphic features (e.g. Devil's Tower, WY). A neck is a small volcanic plug.

Porphyritic—An igneous rock texture in which larger crystals (phenocrysts) are set in a finer-grained groundmass that may be crystalline, glassy or both. In volcanic rocks, the larger crystals typically grow in the magma before eruption.

Precipitate—An insoluble solid that emerges from a liquid, generally by evaporation or chemical reaction.

Proppant—A solid material, typically sand, treated sand, or man-made ceramic materials designed to keep an induced hydraulic fracture open.

Propylitic—Hydrothermal alteration resulting from replacement of original (often igneous) rock minerals with high-temperature, low-pressure secondary minerals. The typical assemblage is chlorite-calcite-epidote-albite-adularia and usually quartz, the formation temperature is ≥220°C, and the color is often green (from chlorite and epidote).

Pyroclastic—Clastic rocks formed by volcanic explosions or aerial expulsion from a volcanic vent; commonly refers to a volcanic rock texture of explosive origin.

Resurgent (caldera, dome)—A caldera in which the down-dropped (subsided) block is uplifted by underlying rising magma (resurgence) following crater formation; the uplifted block is a structural dome (resurgent dome) that may or may not be intruded by later magma and volcanic eruptions.

Rhyodacite—A volcanic rock intermediate between dacite and rhyolite; commonly used by geologists/volcanologists working in calc-alkaline volcanic areas. Typically light colored, porphyritic, and flow banded forming lava flows, lava breccias, and lava domes.

Rhyolite—A light-colored igneous extrusive rock usually forming lava flows, lava breccias, lava domes and dome complexes; chiefly composed of potassium feldspar and quartz ± plagioclase ± hornblende ± biotite. Commonly has a fine-grained porphyritic texture and always flow-banded. Rhyolites are usually so viscous that lava domes are the normal landform. Rhyolite is the extrusive equivalent of granite.

Silicic—Silica-rich (SiO_2 ≥65 wt%) igneous rocks or magmas such as dacites, rhyodacites and rhyolites.

Silicic (alteration)—Hydrothermal alteration in which a given area or zone is "flooded" with silica (SiO_2) usually in the form of pervasive secondary quartz, quartz veins, and chalcedony. Silicic alteration is usually light colored and forms at temperatures ≥125°C.

Sinter—Hot spring deposits or precipitates composed primarily of SiO_2. Springs that deposit sinter are usually at or near boiling temperatures. A similar term is geyserite.

Soda (springs)—Hot or mineral spring waters rich in bicarbonate anions (HCO_3^-); soda springs commonly form travertine deposits. Most have temperatures ≤80°C.

Subduction zone—A long, narrow belt along which one tectonic (or lithospheric) plate descends beneath another at a convergent plate boundary. The absolute boundary between plates occurs below sea level; thus most subduction zones contain an assortment of marine rocks as well as igneous rocks.

Sublimates—Solids that have been deposited from volcanic gases, often around the mouths of fumaroles.

Travertine—Hot or mineral spring deposits or precipitates composed primarily of calcium carbonate as calcite and/or aragonite. Springs that deposit copious amounts of travertine are nearly always ≤80°C, usually cooler.

Vug—Small cavity in a rock or vein usually lined with secondary minerals of a different composition than the enclosing rock.

Wildcat (well)—An exploratory well drilled for oil, gas, or geothermal resources on a geologic feature not yet proven to be productive, or in an unproven territory.

ABBREVIATIONS

Ag—silver
A-S—acid-sulfate
ASMW—air saturated meteoric water
Au—gold
Be—beryllium
Bbls—barrels
BBO—billion bbls oil
BCF—billion cubic feet (ft^3)
BHP—Broken Hill Proprietary or bottom hole pressure if one is discussing geothermal, oil and gas wells
BHT—Bottom hole temperature (in a well)
BLM—U.S. Bureau of Land Management
Btu/lb—British thermal units per pound of fluid
CPD—Carlsbad potash district
CSDP—Continental Scientific Drilling Program
CO_2—Carbon dioxide
Cu—copper
D—Derivative waters (geothermal)
DPA—Designated Potash Area
DG—Deep geothermal waters
EMNRD—Energy, Mineral, and Natural Resources Department (New Mexico)
GCC—Grupo Cementos de Chihuahua (cement)
GPM—Great Plains Margin
HDR—hot dry rock (geothermal)
I/S—illite/smectite clays
JPSB—Jemez Pueblo-San Juan Basin type
ka—thousand years ago
KCl—potassium chloride
km—kilometers
LANL—Los Alamos National Laboratory
LBL—Lawrence Berkeley Laboratory
lbs—pounds
Li—lithium
m—meters
Ma—million years ago
Myr—Million years old
MBO—thousand bbls oil
mi—miles
MOP—muriate of potash
MORB—mid-ocean ridge basalt
MRI—Magnetic resonance imaging
MVT—Mississippi Valley-type
MWe—Megawatts (electrical)
NMBMMR—New Mexico Bureau of Mines and Mineral Resources
NMBGMR—New Mexico Bureau of Geology and Mineral Resources
NMMMD—New Mexico Mining and Mineral Division
NMIMT—New Mexico Institute of Mining and Technology
NURE—National Uranium Resource and Evaluation
OSHA—Occupational Safety and Health Administration
oz—ounces
oz/short ton—ounces per short ton
P & A'd—plugged and abandoned (well)
PGE—platinum group elements (platinum, Pt; palladium, Pl; osmium, Os; ruthenium, R; iridium, I; and rhodium, Rh)
Pb—lead
PNM—Public Service Company of New Mexico
ppb—parts per billion
ppm—parts per million
REE—rare earth elements
RGR—Rio Grande Rift
SMCRA—Surface Mine Control and Reclamation Act
SMOW—Standard Mean Ocean Water
TDS—Total dissolved solids
Th—thorium
TCF—trillion cubic feet (ft^3)
U—uranium
µm—micrometers
UNOCAL—Union Oil Company of California
USDOE—U.S. Department of Energy
USGS—U.S. Geological Survey
USBM—U.S. Bureau of Mines
VCNP—Valles Caldera National Preserve
VMS—Volcanogenic massive sulfide
WIPP—Waste Isolation Pilot Plant
Wt%—weight per cent
Y—yttrium
Zn—zinc
Zr—zirconium
δ—delta value used in isotope measurements
°C—degrees centigrade

INDEX

APPENDIX 1: Chemical geothermometers used in this report; the catagories “high-temperature” and “intermediate- to low-temperature” are guidelines used in the geothermal industry. See Fournier, 1981 or Goff and Janik, 2000 for discussions of limitations.

Geothermometer	Original Equation Source	Temperature Equation (°C unless otherwise noted)	Units	Error[a]	Restrictions and Rules
		High-temperature (≥150°C)			
Quartz (no steam loss)	Fournier and Rowe (1966)	T=[1309/(5.19-logC)]-273.15	C=SiO_2 in mg/kg	±2 (lcf)	Valid from T= 0-250°C
Na/Kf	Fournier and Truesdell (1973)	T=[1217/ (log{Na/K}+1.483)]-273.15	Na, K in mg/kg	±30 (ecf)	Valid if T>150°C
Na/Kt	Truesdell (1976)	T=[855.6/ (log{Na/K}+0.8573)]-273.15	Na, K in mg/kg	±30 (ecf)	Valid if T>150°C
Na-K-Ca (1/3)	Fournier and Truesdell (1973)	T=[1647/(log{Na/K}+1/3(log{$Ca^{1/2}$/ Na}+2.06)+2.47)]-273.15	Na, K, Ca in mg/kg	±30 (ecf)	Use only if the 4/3 Eq below is >100°C
Na/Li	Fouillac and Michard (1981)	T=[1000/(log{Na/Li}+0.389)]-273.15	Na, Li in molal units	±25 (ecf)	Valid only if Cl concentration is <0.3m[b]
Oxygen-18 (SO_4-H_2O)	McKenzie and Truesdell (1977)	1000 ln a=2.88[10^6{T^2}]-4.1 where a={1000+del^{18}O-HSO_4}/ {1000+del^{18}O-H_2O}; T=°K	del-values in permil	±20 (lcf)	Valid if T>150°C
		Intermediate- to low-temperature (≤150°C)			
Chalcedony	Fournier (1973)	T=[1032/(4.69-logC)]-273.15	C=SiO_2 in mg/kg	±2 (ecf)	Valid from T=0-250°C
Na-K-Ca (4/3)	Fournier and Truesdell (1973)	T=[1647/(log{Na/K}+4/3(log {$Ca^{1/2}$/Na}+2.06)+2.47)]-273.15	Na, K, Ca in mg/kg	±30 (ecf)	Valid only if result is ≤100°C
Na-K-Ca-Mg	Fournier and Potter (1979)	**Step 1:** Calculate R=[Mg/ (Mg+Ca+K)] x 100 **Step 2:** Use graph (Fig. 4) to obtain deltaT; subtract deltaT from *correct Na-K-Ca estimate*	Mg, Ca, K in equivalents	±30 or more	Use if R>5 to R<50; if R>50, water is “cool”
K/Mg	Giggenbach et al. (1983)	T=[4410/{14.0-log{K^2/Mg})]-273.15	K, Mg in mg/kg	±25 (ecf)	Valid from T= 30–300°C
Li/Mg	Kharaka and Mariner (1989)	T=[2200/{log($Mg^{1/2}$/Li)+5.47}]-273.15	Mg, Li in mg/kg	±25 (ecf)	Valid from T= 30–350°C
		Ternary plot evaluations with Mg			
Na-K-$Mg^{1/2}$	Giggenbach (1988)	See original reference for logic and interpretation of this plot	Na, K, Mg in mg/kg	n.a.	Valid from T= 30–300°C (?)
Na-K-$Mg^{1/2}$	Fournier (1990)	See original reference for logic and interpretation of this plot	Na, K, Mg in mg/kg	n.a.	Valid from T= 30–300°C (?)

[a]lcf=laboratory calibrated experiments with curve-fitting equation; the SiO_2 equations break down above 250°C; ecf=empirical, least-squares curve fit of “selected” data; not all reaserchers report the error but it can be estimated from their plots.
[b]The Na/Li geothermometer has a different equation for waters with Cl>0.3 molal (e.g. true brines and seawater, Foulliac and Michard, 1981).

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