



Application of the Chlorine-36 isotopic system to the tracing of hydrothermal fluids at Valles Caldera, New Mexico

Usha Rao, Udo Fehn, Ray T. D. Teng, and Fraser Goff
1996, pp. 463-468. <https://doi.org/10.56577/FFC-47.463>

in:

Jemez Mountains Region, Goff, F.; Kues, B. S.; Rogers, M. A.; McFadden, L. S.; Gardner, J. N.; [eds.], New Mexico Geological Society 47th Annual Fall Field Conference Guidebook, 484 p. <https://doi.org/10.56577/FFC-47>

This is one of many related papers that were included in the 1996 NMGS Fall Field Conference Guidebook.

Annual NMGS Fall Field Conference Guidebooks

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

Free Downloads

NMGS has decided to make peer-reviewed papers from our Fall Field Conference guidebooks available for free download. This is in keeping with our mission of promoting interest, research, and cooperation regarding geology in New Mexico. However, guidebook sales represent a significant proportion of our operating budget. Therefore, only *research papers* are available for download. *Road logs*, *mini-papers*, and other selected content are available only in print for recent guidebooks.

Copyright Information

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

One printed copy of any materials from the NMGS website or our print and electronic publications may be made for individual use without our permission. Teachers and students may make unlimited copies for educational use. Any other use of these materials requires explicit permission.

This page is intentionally left blank to maintain order of facing pages.

APPLICATION OF THE ^{36}Cl ISOTOPIC SYSTEM TO THE TRACING OF HYDROTHERMAL FLUIDS AT VALLES CALDERA, NEW MEXICO

USHA RAO¹, UDO FEHN¹, RAY TENG¹ and FRASER GOFF²

¹Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627; ²Los Alamos National Laboratory, Los Alamos, NM 87545

Abstract—Valles caldera hosts a high-temperature geothermal system (220–300°C), which has surface expression in hot springs, fumaroles and other features in the area. In order to trace the sources of solutes in the hydrothermal fluids, we analyzed springs and well waters in the region for ^{36}Cl and chloride. The fluids sampled are of two types, one characterized by relative high $^{36}\text{Cl}/\text{Cl}$ ratios and low Cl concentrations, and the other with low $^{36}\text{Cl}/\text{Cl}$ ratios and high Cl concentrations. The results for the first group (Cl < 10 mg/L; $^{36}\text{Cl}/\text{Cl}$ of $300\text{--}1000 \times 10^{-15}$) are typical of rainwater, whereas the second group of samples (Cl, 800 to 9400 mg/L; $^{36}\text{Cl}/\text{Cl}$, $11\text{--}26 \times 10^{-15}$) are geothermal brines reflecting longer residence times in the subsurface, with associated leaching of solutes from subsurface sources. The history of the first group of samples is fairly uncomplicated, reflecting the recent meteoric nature of the waters with perhaps some anthropogenic addition, but the second group must derive its salts from non-meteorite sources which are assessed here. We calculated $^{36}\text{Cl}/\text{Cl}$ ratios in the major formations in the region, based on estimated subsurface neutron fluxes for these formations. A comparison of calculated $^{36}\text{Cl}/\text{Cl}$ ratios with measured $^{36}\text{Cl}/\text{Cl}$ ratios in the hydrothermal brines eliminates the Quaternary volcanic rocks that the waters currently reside in as a likely source for chloride in the waters. More likely sources are formations at depth, such as the Precambrian basement and Paleozoic rocks, especially the Madera and Abo Formations. A likely scenario is that meteoric waters penetrate to depths of 2–3 km, and leach solutes from rocks there before coming to reside in near-surface volcanics (residence time < 0.1 Ma) after convective upwelling.

INTRODUCTION

Valles caldera is the location of hot springs that result from the interaction between recent volcanic activity and groundwater. As such, this hydrothermal system has attracted considerable interest (e.g., Goff and Grigsby, 1982; Goff et al., 1988) as an active example of such interaction and as a potential source for geothermal power. Although stable isotope studies have shown convincingly that waters in the system are predominantly of meteoric origin (Vuataz and Goff, 1986), fluids collected from wells and hot springs within the region are often characterized by high solute content, indicating non-meteorite sources for salts in the hydrothermal fluids. Here we describe the use of the long-lived radioisotope of chlorine, ^{36}Cl ($T_{1/2} = 0.3$ Ma) as an isotopic tool to constrain sources of chloride within the hydrothermal system, and thus expand understanding of fluid pathways and fluid/rock interaction within the system. This paper summarizes results reported in greater detail elsewhere (Rao et al., in press), and describes the application of the ^{36}Cl system to an active hydrothermal system.

THE VALLES HYDROTHERMAL SYSTEM AND SAMPLE COLLECTION

The medium-sized hydrothermal system associated with Valles caldera has been a focus of recent interest (Nielson and Hulen, 1984; Goff et al., 1988). The high temperatures beneath the caldera are manifested at the surface in hot springs such as Soda Dam, Jemez Hot Springs, and Sulphur Springs that discharge in and around the caldera. Recharge to the hydrothermal system is primarily by meteoric waters (Vuataz and Goff, 1986). Thermal investigations suggest that relatively recent meteoric waters penetrate to depths of 2 to 3 km in the caldera, are heated, and reach temperatures of 200–300°C. These hot fluids take part in convective upflow along faults and fractures to reach depths of 500–600 m, where they flow laterally toward the southwest wall of the caldera (Goff and Grigsby, 1982; Swanberg, 1983). At the caldera wall, the waters flow along the Jemez fault zone, which serves as a lateral conduit for waters discharging from the caldera. Outflow along the Jemez fault zone has produced hot springs and other manifestations of derivative hydrothermal fluids outside the caldera. Although some discharge of hydrothermal waters from the caldera occurs through lateral flow in Paleozoic strata, much of the discharge is confined to the Jemez fault zone at Soda Dam and Jemez Springs, in San Diego Canyon along the Jemez River (Trainer, 1974; Goff and Grigsby, 1982; Goff et al., 1988).

The onset of the hydrothermal system (1 Ma; Goff and Shevenell, 1987) rapidly succeeded the eruptions that produced the Bandelier Tuff and created Valles caldera (1.2 Ma; Gardner et al., 1986). Waters en-

countered during drilling into the caldera generally reach temperatures of 200–300°C and chloride concentrations of several thousand mg/L. Stable isotope analyses of these fluids (Vuataz and Goff, 1986) show a characteristic $\delta^{18}\text{O}$ shift, reflecting the hydrothermal alteration of these fluids since meteoric recharge. In contrast, fluids from hot and cold springs in the western moat zone of the caldera have temperatures of 42°C and much lower chloride concentrations, generally 2 to 7 mg/L. These are relatively recent meteoric waters, some of which have been heated by shallow circulation in the ring fracture zone of the caldera (Goff and Grigsby, 1982).

We measured $^{36}\text{Cl}/\text{Cl}$ ratios and chloride concentrations in 15 samples from 13 different locations, of meteoric waters, thermal waters from drill-holes and springs within the caldera, and springs issuing outside the caldera (Fig. 1). Samples from two hot springs (Spence and San Antonio springs), one cold spring (Sino spring), and six high-temperature well samples collected from four drill-holes (VC-1, VC2A, VC-2B and HDR) were made available to us for ^{36}Cl analysis. In addition, four samples (Jemez spring, Soda Dam spring, Travertine Mound and Hidden warm springs) were collected from the Jemez fault zone, and are thought to be related to fluids within the caldera. Two samples (Zia Hot Well and Near "C" spring) from the Nacimiento fault zone southwest of the caldera are probably not related to the Valles hydrothermal system. The samples we measured could be divided into two groups based on their chloride and ^{36}Cl concentrations. One group has low chloride concentrations (2–7 mg/L) and high $^{36}\text{Cl}/\text{Cl}$ ratios ($307\text{--}1013 \times 10^{-15}$), whereas the second group has high chloride concentrations (910–9440 mg/L) and low $^{36}\text{Cl}/\text{Cl}$ ratios ($11\text{--}26 \times 10^{-15}$). This grouping is consistent with stable isotopic data (Vuataz and Goff, 1986).

THE ^{36}Cl ISOTOPIC SYSTEM

Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl , and one long-lived radioisotope, ^{36}Cl , with a half-life of 0.3 Ma. Concentrations of ^{36}Cl are expressed relative to total chloride. ^{36}Cl has cosmogenic, fissiogenic and anthropogenic modes of production.

Cosmogenic production of ^{36}Cl primarily occurs by cosmic ray spallation of argon atoms in the atmosphere, or by spallation of calcium and potassium atoms and neutron activation of ^{35}Cl atoms at the surface of the earth. Secular equilibrium ratios for surface rocks vary largely, depending on rock type (Fabryka-Martin, 1988). Fissiogenic production occurs in the subsurface from the thermal neutron activation of ^{35}Cl atoms in the rock and in groundwater. The neutrons result both from the direct fission of ^{235}U and from the reaction of α -particles (released from the decay of uranium- and thorium-group elements) on light elements.

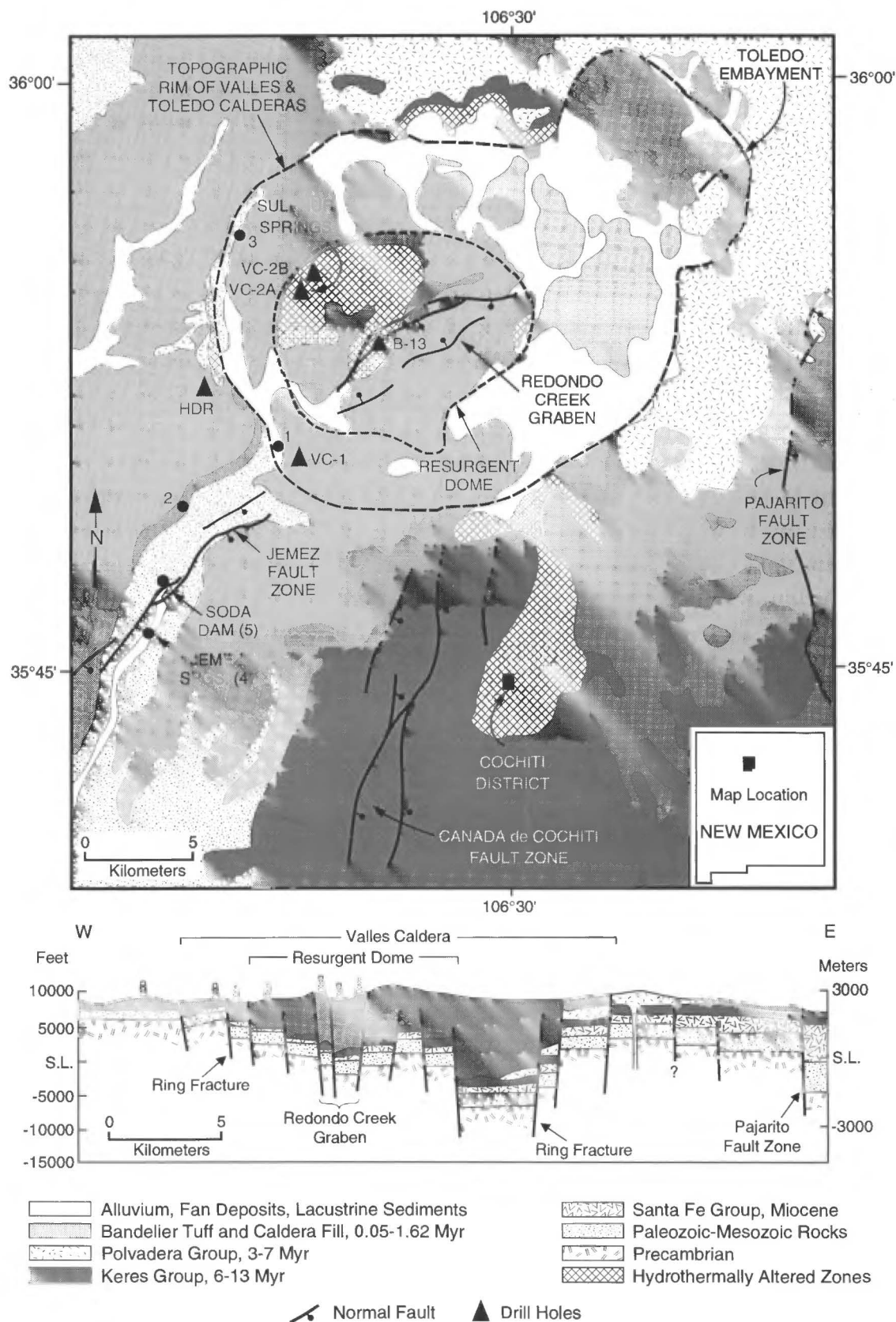


FIGURE 1. Geologic map and schematic cross-section (trending approximately WNW-ESE through the center of the resurgent dome of the caldera) of the Valles caldera region, New Mexico; numbered and/or named sample locations listed in Table 1. Two sites (Zia Well and near C spring) are located on the edge of the San Juan Basin approximately 20 km southwest of Jemez Springs and are not shown on the map (modified from Goff et al., 1989, and WoldeGabriel and Goff, 1992).

³⁶Cl/Cl ratios at secular equilibrium are therefore a product of the presence of uranium and thorium, and of neutron producing and absorbing light elements in the subsurface. Recent additions of ³⁶Cl to the environment have resulted mainly from nuclear weapons testing with minor releases from nuclear reprocessing facilities such as INEL, Idaho (Beasley et al., 1993). Atmospheric nuclear tests during the 1950s and 60s initially raised ³⁶Cl/Cl levels in the atmosphere by two to three orders of magnitude (Elmore et al., 1982; Bentley et al., 1982), but these levels have since returned to pre-nuclear values (Suter et al., 1987). Releases from nuclear fuel reprocessing facilities are generally minor and localized. A major factor responsible for the dilution of anthropogenic ³⁶Cl in the environment is the presence of large amounts of stable chlorine, in the form of chloride, in the atmosphere.

The ultimate source of atmospheric ³⁶Cl is the oceans, where ³⁶Cl/Cl ratios are below the detection limit of accelerator mass spectrometry (AMS), the method of choice for the measurement of this isotope. Another important effect of sea-spray derived chlorine in the atmosphere is that meteoric ³⁶Cl/Cl ratios reflect elevation as well as distance from the coasts, being highest inland and lowest near the coasts. Bentley et al. (1986) predicted ratios of between 100–1000 × 10⁻¹⁵ for the continental USA, which are in good agreement with measured values. The expected ratio for our study region is about 700 × 10⁻¹⁵, which agrees well with a ³⁶Cl/Cl ratio of 704 × 10⁻¹⁵ measured for soil water near Socorro, New Mexico (Phillips et al., 1984).

ANALYTICAL METHODS

Samples were prepared for ³⁶Cl analysis by standard procedure (Conard et al., 1986). As little as 25–40 mL of water were used to prepare samples in which chloride concentrations were relatively high, as was the case for the hydrothermal waters. In meteoric water samples (Sino spring, San Antonio hot spring and Spence hot spring), low levels of chloride (<7 mg/L) necessitated the use of larger volumes of starting material. Large samples were concentrated by vacuum distillation using a Brinkmann rotary evaporator.

Sample preparation essentially involves the precipitation of chlorine in the form of silver chloride and removal of any sulfur present, to avoid isobaric interference from ³⁶S during measurement. Samples were prepared by filtering through 0.2 μm Millipore filters and silver nitrate was added to each sample to precipitate out chlorine in the form of silver chloride. The precipitate was subsequently dissolved in 30% NH₄OH, which precipitates out sulfur compounds and any impurities present, which were filtered out of the solution. Addition of BaSO₄ with heating of the sample for an hour further caused the settling out of sulfur compounds. At the time, AgCl was reprecipitated with the addition of nitric acid. The steps of precipitating AgCl and sulfo-compounds alternately were repeated until no more sulfur precipitated out of solution. Silver chloride samples finally obtained were washed with ultrapure deionized water and dried under a heat lamp. Sample size obtained for measurement varied between 2 and 10 mg of silver chloride, depending on volume and chloride content of sample.

³⁶Cl/Cl ratios in the silver chloride samples were measured by accelerator mass spectrometry (AMS) at the Nuclear Structure Research Laboratory of the University of Rochester (see Kubik et al., 1987, for a description of the AMS system at Rochester). The detection limit of the AMS system at Rochester is <5 × 10⁻¹⁵, which is below ratios measured in the samples. Measured ratios were normalized to a known standard, and blank corrections were made by comparison to Weeks Island halite with a ³⁶Cl/Cl ratio of <5 × 10⁻¹⁵, following the usual procedure. Chloride concentrations in the water samples were detected by ion chromatography at Los Alamos National Laboratory, with errors of ±5%.

RESULTS

Measured ³⁶Cl/Cl ratios, chloride and ³⁶Cl concentrations for the water samples are shown in Table 1. On the basis of their Cl content and ³⁶Cl/Cl ratios, samples can be separated into two groups, which were previously identified as meteoric and thermal waters on the basis of stable isotope data (Vuataz and Goff, 1986) and major ion chemistry (Shevenell et al., 1987). Water samples known to be of meteoric origin have low chloride

concentrations of <3 mg/L and high ³⁶Cl/Cl ratios (>300 × 10⁻¹⁵). ³⁶Cl concentrations in the first group of samples are low, 36–37 atoms/μL, even though ³⁶Cl/Cl are high, reflecting low concentrations of stable chloride in these meteoric waters. The δD and δ¹⁸O compositions of these samples plot along the Jemez Mountains meteoric water line of Vuataz and Goff (1986).

Samples previously classified as hydrothermal waters, based on their δ¹⁸O-shift (Vuataz and Goff, 1986) have chloride concentrations ranging from 910 to 5150 mg/L, with one drill-hole sample reaching a concentration of 9440 mg/L. Samples in this group have ³⁶Cl/Cl ratios of 11.8–25.8 × 10⁻¹⁵, and ³⁶Cl concentrations ranging from 180 to 2085 atoms/μL. The observed high concentrations of chloride in these waters, along with low ³⁶Cl/Cl ratios, suggest that sources of chloride and other salts are non-meteoric.

This second group of samples includes both water from within the Valles caldera region itself, and water circulating in the Jemez and Nacimiento fault zones. Dondanville (unpubl. report for Union Oil Co., 1971), Trainer (1974), and Goff et al. (1988) reported that ratios of conservative ions, especially of B/Cl, Br/Cl and Li/Cl are similar between the reservoir fluids and those issuing from the Jemez fault zone, reflecting the chemical similarity of these groups of waters. The chemical and isotopic similarities reflect the fact that the 20-km Jemez fault zone acts as a conduit for waters discharging from the caldera. Because all deeply circulating hydrothermal waters within and outside the caldera group closely, we treat them as having a common source for ³⁶Cl, and consequently a common source for chloride and possibly other salts. However, minor differences within this group may result from slightly different residence times for each of these samples in the various source formations.

DISCUSSION OF ³⁶CL RESULTS

Figure 2 shows ³⁶Cl/Cl ratios in the samples vs. 1/Cl concentrations, along with a mixing line between pre-anthropogenic rainwater (estimated) and the sample with the lowest measured ³⁶Cl/Cl ratio, a drill-hole sample collected within the caldera (VC-2B 93). Possible sources for observed chloride and ³⁶Cl levels in the water samples discussed below, are meteoric recharge (addition of cosmogenic ³⁶Cl via recharge to the system), anthropogenic addition (added either via recent recharge, or during sampling/sample handling), fissiogenic subsurface production of ³⁶Cl (from

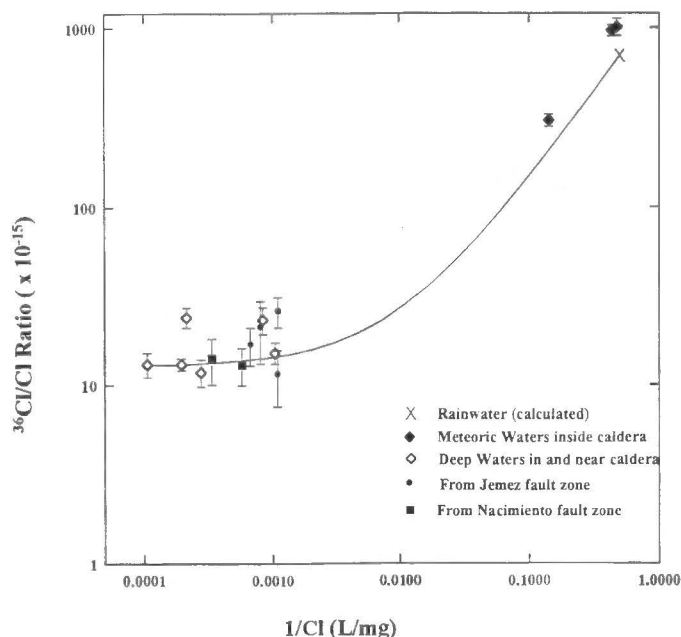


FIGURE 2. Plot of ³⁶Cl/Cl ratio vs. 1/Cl in the waters. The solid line indicates mixing between a rainwater endmember (calculated; 2 mg/L Cl; 700 × 10⁻¹⁵ ³⁶Cl/Cl) and VC-2B 93, the deeply circulating water sample with the highest chloride concentration (9400 mg/L Cl; 13 × 10⁻¹⁵ ³⁶Cl/Cl).

TABLE 1: Chloride concentrations, $^{36}\text{Cl}/\text{Cl}$ ratios and ^{36}Cl concentrations in samples from the Valles area (Sample locations on Fig. 1).

Location from Fig. 1	Sample	Cl^- (mg/L)	$^{36}\text{Cl}/\text{Cl}$ ($\times 10^{-15}$)	^{36}Cl (atoms/mL)	Production Formation
	Cold meteoric water (estimated)	2	700	23	
	METEORIC WATERS:				
1	Spence hot spring	7	307 \pm 25	36	Caldera Fill Rhyolite
2	Sino spring (cold)	2.3	967 \pm 64	37	Keres Group Volcanics
3	San Antonio hot spring.	2.1	1013 \pm 107	36	Caldera Fill Rhyolite
	DRILL-HOLE FLUIDS:				
VC-2A	VC-2A	3650	12 \pm 2	718	Bandelier Tuff
VC-2B	VC-2B 109	4700	24 \pm 3	1870	Bandelier Tuff and Santa Fe Grp.
VC-2B	VC-2B 93	9440	13 \pm 2	2085	Precambrian
VC-2B	VC-2B 94	5150	13 \pm 1	1137	Precambrian
VC-1	VC- 1 209	960	15 \pm 2	245	PA. Madera Ls.
HDR	HDR 92-124, Fenton Hill	1200	23 \pm 4	469	Precambrian
B-13	Baca-13 (Phillips et al., 1984)	1910	35 \pm 6	1146	Bandelier Tuff
	JEMEZ FAULT ZONE HOT SPRINGS:				
4	Jemez Well/Spring	920	11 \pm 4	180	PA. Madera Ls.
4	Travertine Mound Spring	910	26 \pm 5	390	PA. Madera Ls.
5	Soda Dam spring	1500	17 \pm 4	413	PA. Madera Ls. & Precambrian
5	Hidden Warm spring	1250	21 \pm 8	440	PA. Madera Ls.
	NACIMIENTO FAULT ZONE:				
off map	Zia Hot Well	3000	14 \pm 4	700	Triassic Chinle Fm.
off map	Near "C" spring	1750	13 \pm 3	380	Triassic Chinle Fm.

^{35}Cl present in the water or production in the rock with subsequent leaching into water), and magmatic or connate sources (Rao et al., in press).

Meteoric recharge

Using the pre-anthropogenic $^{36}\text{Cl}/\text{Cl}$ ratio of 700×10^{-15} (Bentley et al., 1986) and a typical rainwater chloride concentration of 2 mg/L, we calculated ^{36}Cl concentrations in rain in the region to be 24 atoms/ μL . Spence hot spring, San Antonio hot spring and Sino spring (diamonds, on Fig. 2) have concentrations of 36–37 atoms/ μL , which are slightly higher than this value. This indicates that these waters are primarily meteoric in origin, with some anthropogenic ^{36}Cl addition (<30%). This is reflected also in the fact that all three spring waters plot just slightly above the mixing line (Fig. 2), and also supports an anthropogenic component in these waters. Although ^{36}Cl concentrations in these springs are almost identical, a closer examination of $^{36}\text{Cl}/\text{Cl}$ ratios and chloride concentrations reveals differences in the history of these samples. While Sino spring and San Antonio hot spring reflect simply a meteoric origin with some anthropogenic addition, Spence hot spring appears to have had a more complicated history. A $^{36}\text{Cl}/\text{Cl}$ ratio lower than that for estimated pre-anthropogenic rain in the region suggests that this sample has a small component derived from deep chloride fluids. However, the sample plots above the mixing line between deep chloride samples and pre-anthropogenic rainwater in Figure 2, indicating that some anthropogenic addition of ^{36}Cl is also present, in addition to mixing with deep chloride fluids. Because meteoric sources with some anthropogenic ^{36}Cl addition are clearly responsible for observed $^{36}\text{Cl}/\text{Cl}$ ratios in the three meteoric water samples, these sample will not be discussed further.

Hydrothermal fluids, both within and outside the caldera, have chloride concentrations 500–2500 times those found in meteoric waters, and

^{36}Cl levels that are one to two orders of magnitude higher than estimated levels for unaltered meteoric waters. Clearly, while meteoric sources may contribute some chloride to the hydrothermal fluids, a large component of the salts must be non-meteoric.

Anthropogenic addition

While anthropogenic addition is clearly a factor in the meteoric samples it does not appear to influence chloride in the deep hydrothermal fluids. Although ^{36}Cl concentrations from anthropogenic sources are generally 100 to 1000 atoms/mL, chloride concentrations in such sources are typically low, about 1–2 mg/L on average. Hence, such additions cannot account for significantly higher chloride concentrations (910–9440 mg/L) or ^{36}Cl concentrations (180–2085 atoms/ μL) in the deep hydrothermal waters. The fact that anthropogenic addition is insignificant in deeply circulating hydrothermal fluids is supported by tritium data that shows low T.U. levels, indicating that post-nuclear waters do not form a significant component of recharge to the hydrothermal system (Shevenell and Goff, 1995; Shevenell and Goff, this volume).

Since meteoric and anthropogenic sources do not appear to be responsible for much of the ^{36}Cl and chloride in the system, fissiogenic sources and magmatic input are the most likely sources for chloride present in the deeply circulating waters.

Subsurface fissiogenic production

^{35}Cl has a large thermal neutron capture cross-section (44 barn), making the production of ^{36}Cl by this mechanism in the subsurface a fairly efficient process. Due to high levels of chloride present in most deep waters, production is equally viable in the water as in the rock. At secular equilibrium, reached at about 1.5 Ma, $^{36}\text{Cl}/\text{Cl}$ ratios are a factor of host

rock composition, reflecting primarily U and Th concentrations as well as light neutron producing and absorbing elements in the rock. Since production of ³⁶Cl at secular equilibrium is primarily dependent on neutron flux, which in turn depends on the presence of uranium and thorium series elements, ratios are independent of production in the rock or in the water. In both cases, subsurface production is described by the equation $N_{36} = \sigma \Phi N_{35} (1 - \exp(-\lambda_{36} t)) / \lambda_{36}$, where N_{36} and N_{35} refer to the concentrations of ³⁶Cl and ³⁵Cl respectively, σ is the thermal neutron capture cross-section of ³⁵Cl (44 barn), Φ the subsurface neutron flux, λ_{36} the decay constant for ³⁶Cl ($2.3 \times 10^{-6} \text{ a}^{-1}$) and t the time of exposure to neutrons (Andrews et al., 1986). Since subsurface neutrons result from α -particles (from the decay of U-Th series elements) impinging on light elements in the rocks, subsurface neutron fluxes can be estimated if concentrations of uranium, thorium and neutron producing and absorbing elements are known. These can be calculated if the exact chemical composition of the rock is known, or estimated based on typical chemical composition of various rock types using the approach given by Fabryka-Martin (1988) and Andrews et al. (1989). Estimated ratios for subsurface formations in the Valles area are expected to range from 4000–6600 neutrons $\text{cm}^{-2} \text{ sec}^{-1}$ in fresh volcanics such as the Bandelier Tuff, to 200–2000 neutrons $\text{cm}^{-2} \text{ sec}^{-1}$ in Paleozoic strata such as the Pennsylvanian Madera and Permian Abo Formations. Secular equilibrium ratios for potential formations were calculated using the equation above on the basis of these estimated neutron fluxes (Table 2; Fig. 3).

Altered and unaltered volcanics in the region have ratios in excess of 40×10^{-15} , due to high concentrations of uranium and thorium in these formations. Although calculations were made using the actual ages of the volcanics rather than assuming secular equilibrium, ratios are similar to secular equilibrium values for these rocks. Since these ratios are significantly higher than ratios in the hydrothermal waters ($11\text{--}25 \times 10^{-15}$), the volcanics cannot be a major source of chloride in the hydrothermal waters. Calculated residence times for fluids in the volcanic formations are $<0.1 \text{ Ma}$. A pilot study of the Valles system by Phillips et al. (1984) detected a ³⁶Cl/Cl ratio of 35×10^{-15} for Baca #13 drill-hole sample, which is notably higher than samples measured as part of our study. This higher ratio, although still lower than calculated ratios for fresh and altered volcanics, approaches these calculated ratios for the volcanics more closely than do the ratios for samples from the present study. It is quite likely that the Baca #13 sample reflects a larger contribution from the volcanics, and consequently a longer residence time there, than do other deep waters. This observation is supported by the fact that the Baca #13 drill-hole penetrates mainly a thick pile of volcanics and to a smaller extent Paleozoic rocks at the center of the resurgent dome of the caldera.

Since the volcanics are unlikely to be a large source of chloride in the deep waters, other formations, such as the Paleozoic and Precambrian formations that underlie the volcanics, must be considered. Lower ura-

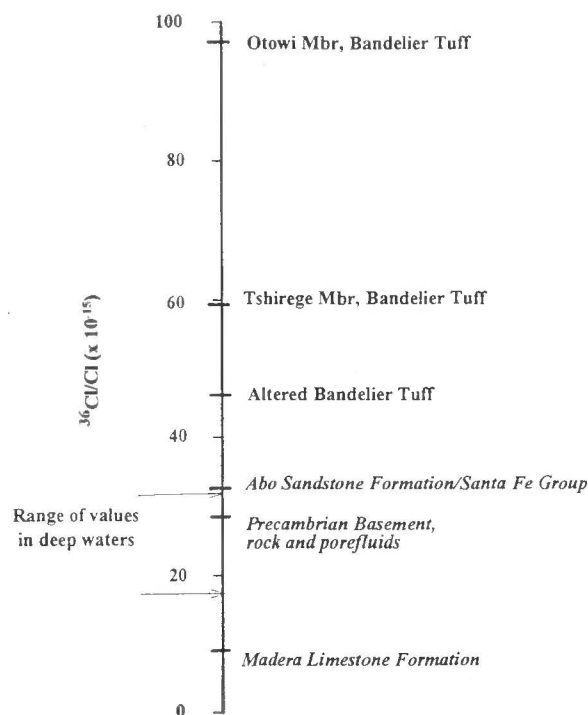


FIGURE 3. Comparison of ³⁶Cl/Cl ratios in deep waters and possible wide-spread source formations (likely sources are indicated in italics).

nium and thorium concentrations in these formations result in lower neutron fluxes and hence lower secular equilibrium ³⁶Cl/Cl ratios there. Based on U and Th concentrations of 4 and 11 mg/kg respectively, the Precambrian basement and trapped connate fluids within it are calculated to have ³⁶Cl/Cl ratios of $20\text{--}30 \times 10^{-15}$, which are on the higher end of ratios measured for the water samples. The Permian Abo Formation has a ratio of 26×10^{-15} , whereas the Pennsylvanian Madera Formation has a ratio of 5×10^{-15} . Since the Madera is the only formation that has a ³⁶Cl/Cl ratio that is not higher than the lowest ratio detected in the waters, mixing between Madera-derived chloride and one or more other sources best explains the ratios measured in the hydrothermal water samples (Rao et al., in press). Carbon isotope data, with $\delta^{13}\text{C}$ values of -3.1 to -5.6 per mil in the Madera Formation and $\delta^{13}\text{C}$ values of -3.8 to -4.8 per mil in the hydrothermal waters (Goff et al., 1986), further supports the idea that the Madera is one of the sources of salts in the hydrothermal fluids. Although the data indicate that the salts in the fluids represent a mixture from various sources, estimates of relative contributions or residence times in spe-

TABLE 2: Estimated neutron fluxes and equilibrium ³⁶Cl/Cl ratios in formations of the Valles area; calculations used analyses from core samples in wells VC-1, VC-2A, and VC-2B. Neutron fluxes for major formations are calculated on the basis of average uranium and thorium concentrations and on estimated concentrations of neutron absorbing light elements such as Na, Al, Si, and O, based on concentrations of these elements measured for other rocks in the Valles region. The calculations were made using the approach described by Fabryka-Martin (1988) and Andrews et al. (1989).

Production Formation	Cl (mg/kg)	U (mg/kg)	Th (mg/kg)	Neutron flux* ($\text{n cm}^{-2} \text{ s}^{-1}$)	³⁶ Cl/Cl ($\times 10^{-15}$)
Otowi Mbr, Bandelier Tuff (Quaternary)	2800	16	43	6600	91
Tshirege Mbr, Bandelier Tuff (Quaternary)	890	11	31	4000	53
Altered Volcanics (Quaternary)	80	9	20	3000	40
Abo SS Fm. (Paleozoic)	92	4	15	1750	26
Madera Ls. Fm. (Paleozoic)	130	2	<1	200	3
Precambrian complex	110	4	11	1500	22

cific formations are not likely to be meaningful due to the large number of mixing scenarios possible.

Magmatic sources

Volatile magmatic components have been cited as the source of some elements in hydrothermal settings, but as data are limited on $^{36}\text{Cl}/\text{Cl}$ ratios in magmatic sources, it is difficult to assess the contribution from such sources to chloride in the fluids in the present study. Some preliminary work by Goff and McMurtry however suggests that $^{36}\text{Cl}/\text{Cl}$ ratios in magmatic condensates from high-temperature fumaroles are generally low ($<15 \times 10^{-15}$; 10 samples from 4 active volcanoes). These ratios are within the range of some of the lower ratios measured in Valles hydrothermal fluids, so magmatic source contributions cannot be ruled out entirely. However, since a sole magmatic source cannot account for ratios $>15 \times 10^{-15}$, which are observed in some of the hydrothermal fluids, rock leaching must be a factor even with a magmatic source. In any case, high chloride concentrations in the hydrothermal fluids can easily be explained by the relatively high chloride concentrations in the reservoir rocks as well as brine pockets within the Precambrian rocks, and it is not necessary to call upon a volatile magmatic component to explain the observations, although it cannot be entirely ruled out.

CONCLUSIONS

Two groups of samples were encountered during our study of Valles waters: meteoric waters and deeply circulating hydrothermal waters. Meteoric waters, whose δD and $\delta^{18}\text{O}$ compositions plot along the Jemez Mountains meteoric water line, have temperatures $<40^\circ\text{C}$, chloride concentrations $<7\text{ mg/L}$, and $^{36}\text{Cl}/\text{Cl}$ ratios $>300 \times 10^{-15}$. Of the three samples from this group, two show anthropogenic addition of ^{36}Cl ($<30\%$), while the third shows a more complicated history, reflecting both mixing with deep chloride fluids and anthropogenic addition. The hydrothermal waters collected from springs and drill-holes within the caldera and springs outside the caldera, have high temperatures (up to 300°C), high chloride concentrations between 910 to 9440 mg/L , and relatively low $^{36}\text{Cl}/\text{Cl}$ ratios of 11 – 25×10^{-15} . Potential source formations, assessed on the basis of estimated neutron fluxes for the major rock units in the region, are Precambrian and Paleozoic formations which underlie the Quaternary volcanics that the fluids currently reside in. $^{36}\text{Cl}/\text{Cl}$ ratios for the fresh as well as altered volcanics that the fluids currently reside in are in excess of 40×10^{-15} . Ratios for the Precambrian basement and the saline porefluids trapped there, and for the Permian Abo Formation are between 20 and 30×10^{-15} , whereas ratios for the Madera Formation are $<5 \times 10^{-15}$. Although all of these sources have $^{36}\text{Cl}/\text{Cl}$ ratios consistent with ratios measured in the hydrothermal waters, no one source of chloride best accounts for chloride in the waters. Complex mixing of fluids from more than one source rock for chloride is indicated. Although all the ratios for the hydrothermal samples group closely, differences in relative contributions from the different formations may account for differences in $^{36}\text{Cl}/\text{Cl}$ ratios and chloride concentrations observed.

On the basis of ^{36}Cl and Cl data, the following fluid pathway, consistent with thermal data, is suggested. Cold, relatively recent meteoric waters recharge the hydrothermal system mainly in the caldera moat region, and penetrate to depths of 2 to 3 km , where they encounter Precambrian basement. At these greater depths, fluids are heated to temperatures of 200 – 300°C before flowing convectively upward to depths of 0.5 – 0.6 km via fractures and faults in the strata. Once fluids reach these shallower depths, they flow laterally southwest through permeable Paleozoic strata toward the southwest wall of the caldera before discharging via the Jemez fault zone (Swanberg, 1983; Goff and Grigsby, 1982). On the basis of ^{36}Cl data, it is clear that hot fluids leach solutes from these deeper sources before discharging outside the caldera. Residence time for the fluids in the volcanics is $<0.1\text{ Ma}$, during which time insignificant amounts of chloride have been leached from these surficial formations.

REFERENCES

- Andrews, J. N., Fontes, J.-Ch., Michelot, J.-L. and Elmore, D., 1986, In-situ neutron flux, ^{36}Cl production and groundwater evolution in crystalline rocks at Stripa: *Earth and Planetary Science Letters*, v. 77, p. 49–58.
- Andrews, J. N., Davis, S. N., Fabryka-Martin, J., Fontes, J.-Ch., Lehmann, B. E., Loosli, H. H., Michelot, J.-L., Moser, H., Smith, B. and Wolf, M., 1989, The in situ production of radioisotopes in rock matrices with particular reference to the Stripa granite: *Geochemica et Cosmochimica Acta*, v. 53, p. 1803–1815.
- Beasley, T. M., Cecil, L. D., Sharma, P., Kubik, P. W., Fehn, U., Mann, L. J. and Gove, H. E., 1993, Chlorine-36 in the Snake River Plain aquifer at the Idaho National Engineering Laboratory: origin and implications: *Ground Water*, v. 31, 302–310.
- Bentley, H. W., Phillips, F. M., Davis, S. N., Gifford, S., Elmore, D., Tubbs, L. and Gove, H. E., 1982, The thermonuclear ^{36}Cl pulse in natural water: *Nature*, v. 300, p. 737–740.
- Bentley, H. W., Phillips, F. M. and Davis, S. N., 1986, Chlorine-36 in the terrestrial environment; in Fritz, P. and Foutès, J.-Ch., eds., *Handbook of environmental isotopes*, 2B: the terrestrial environment: Elsevier, p. 420–480.
- Conard, N. J., Elmore, D., Kubik, P. W., Gove, H. E., Tubbs, L. E., Chrunyk, B. A. and Wahlen, M., 1986, The chemical preparation of AgCl for measuring ^{36}Cl in polar ice with accelerator mass spectrometry: *Radiocarbon*, v. 28, p. 556–560.
- Elmore, D., Tubbs, L. E., Newman, D., Ma, X. Z., Finkel, R., Nishiizumi, K., Beer, J., Oeschger, H. and Andree, M., 1982, The ^{36}Cl pulse measured in a shallow ice core from Dye 3, Greenland: *Nature*, v. 300, p. 735–737.
- Fabryka-Martin, J. T., 1988, Production of radionuclides in the earth and their hydrogeologic significance, with emphasis on chlorine-36 and iodine-129 [Ph.D. thesis]: Tucson, University of Arizona.
- Gardner, J. N., Goff, F., Garcia, S. and Hagan, R. C., 1986, Stratigraphic relations and lithologic variations in the Jemez volcanic field, New Mexico: *Journal of Geophysical Research*, v. 91, p. 1763–1778.
- Goff, F., Gardner, J. N., Baldrige, W. S., Hulen, J. B., Nielson, D. L., Zaniman, D., Heiken, G., Dungan, M. A. and Broxton, D., 1989, Excursion 17B: volcanic and hydrothermal evolution of Valles caldera and Jemez volcanic field: New Mexico Bureau of Mines and Mineral Resources, Memoir 46, p. 381–434.
- Goff, F. and Grigsby, C. O., 1982, Valles caldera geothermal system, New Mexico, USA: *Journal of Hydrology*, v. 56, p. 119–136.
- Goff, F., Rowley, J., Gardner, J. N., Hawkins, W., Goff, S., Charles, R., Wachs, D., Maassen, L. and Heiken, G., 1986, Initial results from VC-1, first Continental Scientific Drilling Program core hole in Valles caldera, New Mexico: *Journal of Geophysical Research*, v. 91, p. 1742–1752.
- Goff, F. and Shevenell, L., 1987, Travertine deposits of Soda Dam, New Mexico, and their implications for the age and evolution of the Valles caldera hydrothermal system: *Geological Society of America Bulletin*, v. 99, p. 292–302.
- Goff, F., Shevenell, L., Gardner, J. N., Vuataz, F. D. and Grigsby, C. O., 1988, The hydrothermal outflow plume of Valles caldera, New Mexico, and a comparison with other outflow plumes: *Journal of Geophysical Research*, v. 93 (B6), p. 6041–6058.
- Kubik, P. W., Elmore, D., Hemmick, T. K., Gove, H. E., Fehn, U., Teng, R. T. D., Jiang, S. and Tullai, S., 1987, Accelerator mass spectrometry at the University of Rochester: *Nuclear Instruments and Methods*, v. B29, p. 138–142.
- Nielson, D. L. and Hulen, J. B., 1984, Internal geology and evolution of the Redondo Dome, Valles caldera, New Mexico: *Journal of Geophysical Research*, v. 89, p. 8695–8711.
- Phillips, F. M., Goff, F., Vuataz, F., Bentley, H. W., Elmore, D. and Gove, H. E., 1984, ^{36}Cl as a tracer in geothermal systems: example from Valles caldera, New Mexico: *Geophysical Research Letters*, v. 11, p. 1227–1230.
- Rao, U., Fehn, U., Teng, R. T. D. and Goff, F., in press, Sources of chloride in hydrothermal fluids from the Valles caldera, New Mexico: a ^{36}Cl study: *Journal of Volcanology and Geothermal Research*.
- Shevenell, L. and Goff, F., 1995, The use of tritium in groundwater to determine fluid mean residence times of Valles caldera hydrothermal fluids, New Mexico, USA: *Journal of Volcanology and Geothermal Research*, v. 67, p. 187–193.
- Shevenell, L., Goff, F., Vuataz, F. D., Trujillo, P., Counce, D., Evans, B. and Janik, C., 1987, Hydrochemical data for thermal and nonthermal waters and gases of the Valles caldera-southern Jemez Mountains region, New Mexico: Los Alamos National Laboratory Report, LA 10923-OBES, 60 p.
- Suter, M., Beer, J., Bonani, G., Hofmann, H. J., Michel, D., Oeschger, H., Synal, H. A. and Wolfli, W., 1987, ^{36}Cl studies at the ETH/SIN-AMS Facility: *Nuclear Instruments and Methods in Physics Research*, v. 00, p. 211–215.
- Swanberg, C. A., 1983, Geothermal resources of rifts: a comparison of the Rio Grande rift and the Salton trough: *Tectonophysics*, v. 94, p. 659–678.
- Trainer, F. W., 1974, Groundwater in the southern part of the Jemez Mountains volcanic region, New Mexico: New Mexico Geological Society, Guidebook 25, p. 337–345.
- Vuataz, F. D. and Goff, F., 1986, Isotope geochemistry of thermal and nonthermal waters in the Valles caldera, Jemez Mountains, northern New Mexico: *Journal of Geophysical Research*, v. 91, p. 1835–1853.
- WoldeGabriel, G. and Goff, F., 1992, K/Ar dates of hydrothermal clays from core holes VC-2B, Valles caldera, New Mexico and their relation to alteration in a large hydrothermal system: *Journal of Volcanology and Geothermal Research*, v. 50, p. 207–230.