

Mixing of magmatic volatiles with groundwater and interaction with basalt on the summit of Kilauea Volcano, Hawaii

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[1] We interpret new chemical and isotopic data from samples collected between October 1998 and March 2002 from the NSF well (also called the Keller well), the only deep well on the summit of Kilauea Volcano, Hawaii. Sample collection followed cleaning of the well, which renewed access to the hydrothermal system very close to the loci of magmatic and fumarolic activity. The chemical and isotopic compositions of the new samples differ remarkably from data published previously. On the basis of the S/Cl ratio and carbon and helium isotopes we conclude that the thermal fluids formed by condensation of magmatic gas into shallow meteoric groundwater. Gas condensation was followed by a complex pattern of basalt dissolution accompanied by an increase of fluid pH and precipitation of secondary minerals. Geochemical modeling and geothermometry imply that the fluids equilibrated with an assemblage of secondary minerals at temperatures between 90 and 140°C. The significantly different chemical composition of the NSF well fluids from that of springs along the southern coast of the island indicates that mass transport from the summit region toward the lower flanks of the volcano is limited.

INDEX TERMS: 1040 Geochemistry: Isotopic composition/chemistry; 1832 Hydrology: Groundwater transport; 1829 Hydrology: Groundwater hydrology; 8424 Volcanology: Hydrothermal systems (8135); *KEYWORDS:* Kilauea Volcano, magmatic volatiles, groundwater chemistry, water-rock interaction, hydrothermal system, mass transport

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1. Introduction

[2] Previous studies of hydrothermal systems have demonstrated that the chemical composition of circulating fluids within active volcanoes reflects a mixture of meteoric water with volatiles degassed from the underlying magma [White, 1957; Henley and Jones, 1964; Holland, 1965; Henley and Ellis, 1983; Giggenbach, 1988; Hedenquist and Aoki, 1991; Shevenell and Goff, 1993; Hedenquist et al., 1994; Taylor, 1997]. Dissociation of magma-derived volatiles upon condensation in circulating meteoric groundwater acidifies the fluids and promotes extensive cation leaching of host rocks. As the fluid cools and neutralizes, secondary minerals begin to form. The complex transition from rock dissolution to fluid-rock equilibrium results in highly variable fluid compositions within the hydrothermal system, controlled by gas composition, rock lithology, rock/water ratio, residence time, and the thermal regime [Reed, 1982; Giggenbach, 1988; Symonds et al., 2001].

[3] The evolution of hydrothermal systems in oceanic volcanoes begins at the seafloor with seawater circulation in the system. Entrapment of highly saline brines, and deposition of sulfide deposits, may mask the “mantle” signature of magmatic volatiles [Fournier, 1987]. After an island forms, volatiles and heat are transported into relatively cold meteoric water circulating in a hydrothermal system [Fournier, 1987]. The reduced hydrostatic pressure may permit boiling of circulating water at shallow depths. In these evolving systems the boundaries between dilute water, saline water, sulfate-bicarbonate-rich water, and steam are likely to be complex and highly transient, changing in response to pulses of magmatic activity and uplift rates [Henley and Ellis, 1983; Fournier, 1987; Giggenbach, 1988].

[4] Kilauea, on the Island of Hawaii (Figure 1a), is one of the world’s most active and best studied volcanoes [Tilling and Dvorak, 1993]. It has been proposed that magma degassing in Kilauea occurs in two ways [Gerlach and Graeber, 1985; Gerlach, 1986]. First, during sustained summit eruptions CO₂-rich volcanic gases are emitted. The second type of degassing follows the equilibration of magma in the summit chamber, and occurs in two stages: as quiescent degassing of CO₂-rich fumarole gases from the shallow summit chamber and, during subaerial eruptions, by eruptive degassing of CO₂-poor volcanic gases along the volcano’s rift zones.

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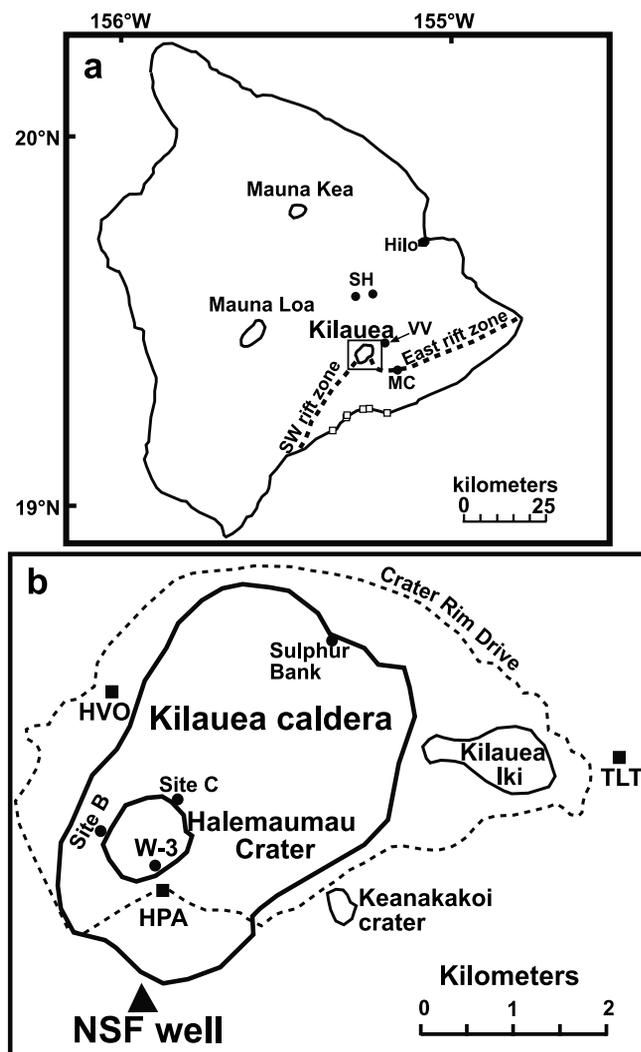


Figure 1. (a) Location of the study area showing: a. Kilauea Volcano on the Island of Hawaii. VV (Volcano Village), SH (Stainback Highway), and MC (Makaopuhi Crater) are locations of rain collectors [Scholl *et al.*, 1996], and open squares along the southern coast represent springs analyzed by Janik *et al.* [1994]. (b) Kilauea caldera and the NSF well, Halemaumau pit crater, and the fumaroles mentioned in the text. HVO (Hawaiian Volcano Observatory), HPA (Halemaumau Parking Area), and TLT (Thurston lava tube) are locations of rain collectors [Scholl *et al.*, 1996]. Sites B, C, and W-3 are locations of high-temperature fumaroles.

[5] Studies of fluid-rock interactions along Kilauea's east rift zone revealed that deep fluids there are highly affected by mixing with seawater and that the contribution of magmatic fluids to the hydrothermal system is negligible [McMurtry *et al.*, 1977; Thomas, 1987; Janik *et al.*, 1994; Conrad *et al.*, 1997]. We concentrate instead on gas-groundwater-basalt interactions in the summit region where thermal gradients are highest [Kauahikaua, 1993] and where most magma degassing of CO₂ occurs [Gerlach and Graeber, 1985]. In 1998 the U.S. Geological Survey cleaned and began to sample the only deep well in Kilauea's summit region, which provides access to the hydrothermal

system very close to the loci of magmatic and fumarolic activity ("NSF well" in Figure 1b and hereinafter in text; locally referred to as "Keller well"). We compare the well water chemical and isotopic compositions with new and existing fumarole chemistry data to characterize the sources of dissolved constituents. The chemical database will serve as a reference for future monitoring of the volcano and may enable identification of temporal trends caused by magma-hydrothermal interaction.

2. Geology of Kilauea

[6] Kilauea is a large, basaltic shield volcano located above a mantle "hot spot" underlying the Pacific plate and is the youngest of five subaerial volcanoes on the Island of Hawaii [Decker, 1987; Clague and Dalrymple, 1989; Tilling and Dvorak, 1993]. Magma rises from the mantle through a conduit located below Kilauea summit to a plexus of magma bodies underlying the southern part of the caldera [Dawson *et al.*, 1999; Haslinger *et al.*, 2001]. The top of this magma reservoir is ~2 km beneath the summit and extends to a depth of roughly 7 km [Ryan *et al.*, 1981]. The magma enters the chamber at an average rate of 0.10 km³/yr [Dzurisin *et al.*, 1984] or 0.18 km³/yr [Cayol *et al.*, 2000] and is then partitioned upward to feed summit eruptions or laterally into east and southwest rift zones where intrusive and/or eruptive activity occurs. Kilauea has frequent and usually nonexplosive eruptions; however, several explosive phreatic or phreatomagmatic eruptions have occurred within the past 1200 years [Swanson *et al.*, 1998]. Sustained eruptions from the summit caldera, through Halemaumau pit crater (Figure 1b), were nearly continuous for more than a century prior to 1924 [Holcomb, 1987]. The current volcanic activity along Kilauea's east rift zone began in 1983 and is the longest Hawaiian rift eruption in historical times [Heliker *et al.*, 1998]. Approximately 90% of Kilauea's surface is covered by lava flows less than 1100 years old [Holcomb, 1987]. The lavas are olivine tholeiites with a glassy to microcrystalline groundmass and a variable degree of vesicularity. Olivine (Fo₇₈₋₈₉) is the main phenocryst, and most lavas also contain microphenocrysts of clinopyroxene and plagioclase [Wright and Fiske, 1971; Pietruszka and Garcia, 1999].

3. Characteristics of Summit Fumaroles

[7] Most fumaroles in the summit region have temperatures <96°C which are boiling point temperatures for their respective elevations [Casadevall and Hazlett, 1983]. In 1990 a few high temperature fumaroles (110°–300°C) were discovered on the bottom of Halemaumau pit crater (Figure 1b) [Gerlach *et al.*, 1991]. Sampling of major summit fumaroles shows large temporal and spatial variations in flux and chemical and isotopic composition [Gerlach, 1980; Casadevall and Hazlett, 1983; Greenland *et al.*, 1985; Gerlach and Thomas, 1986; Hinkley *et al.*, 1995; Hilton *et al.*, 1997; Giggenbach, 1997; Elias *et al.*, 1998; Goff and McMurtry, 2000].

[8] Halemaumau pit crater is currently the major locus of fumarolic discharge, producing an average of ~8500 and 100–250 tons per day of CO₂ and SO₂, respectively [Sutton

et al., 2001; *Gerlach et al.*, 2002]. The temperature of Halemaumau fumaroles ranges from 72°C to ~300°C. Other boiling, or subboiling point fumaroles ($\leq 96^\circ\text{C}$) are widely distributed around Kilauea and are associated with eruptive fissures, caldera boundary faults, and lava ponds such as Kilauea Iki. Summit fumaroles are characterized by high CO_2 concentrations [*Gerlach et al.*, 2002], relatively low chloride concentrations [*Gerlach*, 1980; *Gerlach and Taylor*, 1990; *Goff and McMurtry*, 2000], high $^3\text{He}/^4\text{He}$ ratios [*Hilton et al.*, 1997], carbon and sulfur isotopes showing magmatic signatures [*Gerlach and Thomas*, 1986], and oxygen and deuterium isotopes characteristic of local meteoric water [*Hinkley et al.*, 1995; *Goff and McMurtry*, 2000]. Fumarole condensates collected in Halemaumau since 1991 are consistently acidic ($\text{pH} \leq 2$), and relatively rich in sulfur compounds. The S/Cl and F/Cl ratios in these condensates are similar to the coexisting gases [*Goff and McMurtry*, 2000]. In contrast, low-temperature fumaroles from surrounding locations contain substantial air components (high N_2 , O_2 , and Ar) and less steam and CO_2 and are relatively stripped of Cl, F, and S [*Goff and McMurtry*, 2000]. Condensates from such vents are relatively dilute and not very acidic.

4. The Deep Well at the Summit of Kilauea Volcano

[9] A research well funded by the National Science Foundation (the NSF well) was drilled in 1973 to a total depth of 1262 m from an elevation of 1103 m above sea level (msl) [*Zablocki et al.*, 1974; *Keller et al.*, 1979] (Figure 2). The well is located on the southwest rim of the caldera, 1.2 km south of Halemaumau crater (Figure 1b), and has been sampled intermittently since 1973 [*McMurtry et al.*, 1977; *Janik et al.*, 1994; *Tilling and Jones*, 1996; *Goff and McMurtry*, 2000]. The water table in the well was encountered at a depth of 488 m, indicating a steep hydraulic gradient between Kilauea caldera and the coast (a drop of ~600 m along a lateral distance of 14 km). Resistivity cross sections indicate that the water level within the borehole coincides with the regional high-level water table in the summit region [*Kauahikaua*, 1993]. The bottom hole temperature measured after drilling was 137°C.

[10] During drilling, 47 m of core was recovered at nearly evenly spaced intervals throughout the borehole. Petrographic analysis of these cores indicates a sharp transition from unaltered olivine basalt with high permeability above the water table to altered, low-permeability basalt below the water table [*Keller et al.*, 1979]. The unaltered basalt consists mostly of flows, and less commonly sills of olivine tholeite, generally similar to the composition of the Puna basalt [*Wright and Fiske*, 1971; *Dzurisin et al.*, 1995; *Clague et al.*, 1999; *Pietruszka and Garcia*, 1999], and contains phenocrysts and microphenocrysts of olivine, augite, plagioclase (mainly labradorite), and abundant iron oxides. Below the water table, vesicles are filled with secondary minerals, most olivine has been altered to serpentine, pyroxene is altered less extensively, and plagioclase has remained practically unaltered. Deposition of secondary minerals increases with depth. In cores from the bottom parts of the hole, the vesicles are nearly

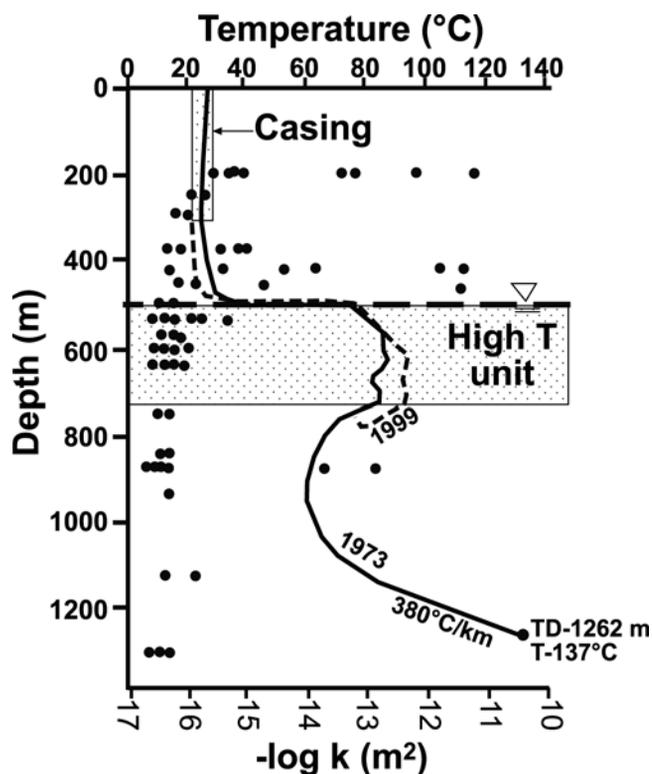


Figure 2. Data from the NSF well showing the temperature profiles measured in 1973 (solid line; after *Keller et al.* [1979]) and 1999 (dashed line), core permeability (dots; after *Keller et al.* [1979]), thickness of the proposed aquifer (stippled area), cased interval of hole, and the water table (dashed line at a depth of 488 m).

filled. Secondary minerals include silica, calcite, smectite, zeolite, and some chlorite and hydrous calcium silicates [*Keller et al.*, 1979].

[11] After completion of drilling, the NSF well became largely plugged by inflow of drilling mud, and access to the hydrothermal fluids was restricted. In the fall of 1998, the USGS conducted bailing and drilling operations to clear mud out of the hole to a depth of about 690 m. This cleaning removed a “mud-cake” that had been supporting a perched water layer above the deeper saturated zone. As a result, the water table declined by 12 m in the first 6 months and dropped by almost 8 m in the following 2 years. Since November 2000 water levels have remained at a level of 493.0 ± 0.4 m (S. Hurwitz, unpublished data, 2002).

[12] The major element and isotopic compositions presented in this study, collected after access to the hydrothermal system was restored, differ drastically from compositions published previously [*McMurtry et al.*, 1977; *Janik et al.*, 1994; *Tilling and Jones*, 1996; *Goff and McMurtry*, 2000]. Most of the previously published data from the NSF well probably represent interaction of the relatively cold, perched water body with the surrounding basalt [*Tilling and Jones*, 1996]. The tritium concentration in a sample obtained from above the mud cake in 1993 was 5 TU, about 3 TU above the rainwater concentration at that time [*Goff and McMurtry*, 2000], suggesting

Table 1. Major Element Chemistry of NSF Well Fluids and Fumarole Condensates^a

Sample	Date	Depth, m	T, °C	Al	Ca	Mg	Fe	Sr	Na	K	Li	Rb	B	Alk	S _t ^b	Cl	F	SiO ₂	pH	Bal, %	TDS
KW98-01	5 Oct. 1998	518	77	<0.02	162	673	<0.01	0.87	739	224	0.20	0.64	1.27	1004	3866	91.9	0.27	107	7.11	1.04	6877
KW99-01	13 May 1999	507	76	0.017	149	639	<0.02	0.83	834	235	0.23	0.62	1.66	985	4310	99	<0.05	171	7.18	-3.00	7238
KW99-02	13 May 1999	616	92	0.015	150	737	<0.02	0.83	834	245	0.23	0.62	1.52	954	3998	90.3	0.05	166	6.85	3.46	7071
KW99-03	13 May 1999	556	84	0.008	145	713	0.06	0.81	838	239	0.23	0.62	1.59	960	4251	93.5	0.09	166	6.77	-0.13	7576
KW00-02	8 June 2000	518	77	0.015	114	559	<0.02	0.70	807	236	0.20	0.62	1.40	997	3510	85.0	<0.05	171	7.28	0.56	6564
KW00-03	8 June 2000	503	76	0.005	114	569	<0.02	0.69	803	236	0.20	0.60	1.42	998	3500	84.0	<0.05	172	6.72	1.03	6552
KW00-04	8 June 2000	625	92	0.009	117	588	0.41	0.72	810	236	0.21	0.62	1.43	988	3749	89.7	<0.04	173	8.04	-1.54	6388
KW00-05	9 June 2000	550	83	0.017	103	549	0.15	0.67	763	220	0.19	0.55	1.60	721	3567	86.9	0.19	119	8.30	-0.17	6136
KW01-01	17 Jan. 2001	625	92	0.034	100	488	0.02	0.41	722	217	0.18	0.50	1.18	967	3215	78.3	0.06	158	7.99	-2.21	5951
KW01-02	17 Jan. 2001	550	83	0.045	108	527	0.16	0.52	789	237	0.20	0.53	1.27	944	3076	76.5	0.04	172	8.07	3.93	5935
KW01-04	18 Jan. 2001	625	92	0.017	82.2	335	0.37	0.36	525	151	0.14	0.35	0.93	633	2012	49.1	0.06	134	8.07	7.30	3928
KW01-08	11 Sept. 2001	550	83	0.074	89.3	399	0.47	0.64	656	214	0.15	0.48	1.00	869	2625	72.6	1.60	165	8.70	0.44	5096
KW01-09	31 Oct. 2001	550	83	0.011	83.3	373	0.39	0.48	604	197	0.16	0.44	0.85	938	2429	56.6	0.11	163	8.74	1.92	4848
KW02-02	12 March 2002	550	83	0.007	80.8	371	0.07	0.43	576	200	0.15	0.40	2.10	979	2107	50.9	3.19	168	8.33	1.6	4538
KW02-03	12 March 2002	496	73	0.005	77.4	366	0.02	0.40	548	190	0.15	0.39	0.88	1014	2025	49.2	1.18	171	8.41	1.6	4443
KW00-WH ^c	13 June 2000	-	23	<0.01	91	4.54	<0.01	1.19	29.6	8.37	<0.10	0.01	0.16	49	265	3.7	<0.01	20	7.29	0.04	473
HV93-45 ^d	Oct. 1993	490	34.5	<0.1	100	108	0.03	0.57	72.1	9.04	0.02	0.04	0.59	900	102	2.66	0.63	94	6.84	1.41	1390
HV91-41 ^c	Dec. 1991	-	260	3.80	5.7	2.04	358	0.12	0.89	0.74	<0.01	-	0.32	0	21200	633	175	55	1.54	-	-
KV97-3 ^e	May 1997	-	308	0.16	0.77	0.06	0.08	0.03	0.30	0.08	<0.01	<0.01	0.72	0	4673	112	78.9	19	1.46	-	-

^aUnits of mg/L.^bTotal sulfur. In NSF well waters, all sulfur is in the form of sulfate.^cSample from the cistern located at the wellhead.^dSample collected from the NSF well by F. Goff and G. M. McMurtry (unpublished data, 1993).^eThe 300°C fumarole condensates from W-3 (Figure 1b).

that the well might have plugged shortly after drilling (M. Scholl, USGS, written communication, 2001).

5. Sampling and Analytical Techniques

[13] After cleaning the NSF well, samples were obtained between October 1998 and March 2002 (Table 1). The samples were recovered from various depths between the water table (~493 m depth) and the current bottom of the hole (~670 m depth). Samples were also collected from a subsurface cistern located adjacent to the wellhead (samples KW-WH in Tables 1 and 2). The samples from 1998, 2001, and 2002 were collected with a stainless steel bailer. The samples from 1999 and samples KW00-04 and KW00-05 were collected with a stainless steel Kuster sampler, and samples KW00-02 and KW00-03 were collected into a preevacuated, gas-tight, stainless steel cylinder with a unidirectional pressure valve at the bottom. For samples collected with the Kuster tool the gas was split into a preevacuated, sealed stainless steel cylinder in the field, after which the liquid was released to plastic and glass bottles. For the two samples collected with the stainless steel cylinders, gas was extracted in the laboratory, followed by the release of liquids. In situ fluid temperature was determined either by a maximum temperature thermometer installed in the bailer or according to the temperature-depth profile obtained in 1999 (Figure 2), and field pH values were measured with pH-sensitive papers.

[14] Water samples were filtered into 125 mL polypropylene bottles through 0.45 μm pore diameter filter. Cation samples were acidified with spectrographically pure nitric acid to pH ≤ 2, whereas anion samples were left unreserved. A 30 mL bottle was filled with a 1:10 sample dilution for silica analysis. Major and trace element analyses were performed at the Los Alamos National Laboratory using methods described by Goff *et al.* [2001]. Raw (unfiltered, unreserved) samples for oxygen

18 and deuterium isotope analyses were stored in 30 mL glass bottles and analyzed at the USGS laboratories in Menlo Park, California, or Reston, Virginia. In both laboratories the analysis of oxygen isotopes was according to the methods of Epstein and Mayeda [1953] with a precision of ±0.1‰, and the hydrogen isotopes were analyzed according to the method described in Kendall and Coplen [1985] and Coplen *et al.* [1991] with a precision of ±1.5‰. Tritium samples were collected from the well in 100 to 500 mL plastic bottles and were analyzed at the University of Miami tritium laboratory by the electrolytic enrichment method using gas proportional counters. The tritium values were compared to tritium levels in rainfall at Hilo according to procedures described by Scholl *et al.* [1996].

[15] Alkalinities for all but three samples were determined by potentiometric titration with H₂SO₄. For selected samples, the concentration of the dissolved inorganic carbon (DIC) was determined by transferring the water into a vacuum bottle and acidifying it to pH 2, converting all carbonate species to CO₂. The amount of CO₂ that was extracted on a high vacuum line and the weight of extracted water were used to derive the DIC concentration [Evans *et al.*, 2002]. For sample KW00-03 the CO₂ was then dried and purified and the δ¹³C-DIC was analyzed by mass spectrometry at the USGS. Analytical uncertainty of the mass spectrometry is 0.1‰. Samples for sulfate isotope analysis were preserved in 60 mL plastic bottles with 1 ml formaldehyde and were prepared for isotopic analysis at the USGS using methods described by Nehring *et al.* [1977].

[16] Gases were analyzed for bulk composition using a gas chromatograph (GC) equipped with a thermal conductivity detector and using helium and argon as carrier gases. Analytical uncertainty is ±2%. Following the GC analysis, a split of the CO₂ was dried and purified and its δ¹³C value was determined by mass spectrometry. For a single gas

sample, $^3\text{He}/^4\text{He}$ isotopes were measured at the University of Rochester, using methods described by *Poreda and Farley* [1992] and corrections for atmospheric contamination described by *Craig et al.* [1978].

6. Composition of Borehole Waters

[17] Water samples were obtained from the NSF well between October 1998 (immediately after cleaning the “mud cake”) and March 2002. Samples were obtained from the depth interval between 507 and 625 m at in situ temperatures ranging between about 65°C and 92°C (Figure 2). The chemical and isotopic data (Tables 1–3) suggest some progressive dilution by local meteoric waters (Figure 3). Three discrete events may have contributed to the pronounced variations observed after 1 January 2001: (1) On 10 September 2000, the well was cleaned for installation of a downhole strainmeter; between 15 and 20 m³ of water from a reservoir located at the National Park headquarters was flushed down the hole (M. Johnston, U.S. Geological Survey, personal communication, 2001). (2) An intense storm occurred on 2 November 2000, with 59 cm of rain measured at a gauge near Halemaumau; during the storm the cistern at the wellhead filled with water, some of which probably drained into the well. (3) During a slug test on 18 January 2001, approximately 3 m³ of water from the cistern was siphoned into the well. In much of our interpretation we will emphasize the NSF well samples selected prior to these three large external disturbances.

6.1. Major and Trace Element Composition

[18] During a single sampling period the concentrations of most ions show no more than 10% variation with depth (Table 1). The major element composition of all the water sampled after cleaning of the well differs significantly from the samples obtained during 1973–1993 [*McMurtry et al.*, 1977; *Janik et al.*, 1994; *Tilling and Jones*, 1996; F. Goff and G. M. McMurtry, unpublished data] as depicted in Table 1 and Figures 4 and 5.

[19] The water in the NSF well is steam heated [*Giggenbach*, 1997] and has a near-neutral pH. All the dissolved sulfur is in the form of sulfate, and nearly all of the alkalinity is in the form of carbonate species. The anion composition differs significantly from that of seawater, or seawater-derived hydrothermal fluids from Kilauea’s east rift zone (Figure 4). There is a shift toward the HCO_3^- apex along the $\text{SO}_4\text{-HCO}_3^-$ line between May 1999 and March 2002. This trend is similar to the 1973–1993 trend [*Tilling and Jones*, 1996] (Figure 4). The water has a low chloride concentration relative to typical magmatic hydrothermal fluids and a high $\text{SO}_4/\text{HCO}_3^-$ ratio ($\sim 4:1$). The mean S/Cl mass ratio in the well water (14.1; Table 1) is similar to the ratio in gas condensate samples from the high-temperature Halemaumau fumarole (12.9–14.9 [*Goff and McMurtry*, 2000]) and to the calculated ratio of S/Cl dissolved in the parental Kilauea magma (14.9 [*Gerlach and Graeber*, 1985]). In contrast, the F/Cl mass ratio in the well samples (<0.001) is orders of magnitude lower than the ratio in fumarole condensates (0.3 [*Goff and McMurtry*, 2000]) and in the parental Kilauea magma (4.1 [*Gerlach and Graeber*, 1985]). The F/Cl data suggest either relatively weak volatilization of fluoride (as HF) from magma into depressurized

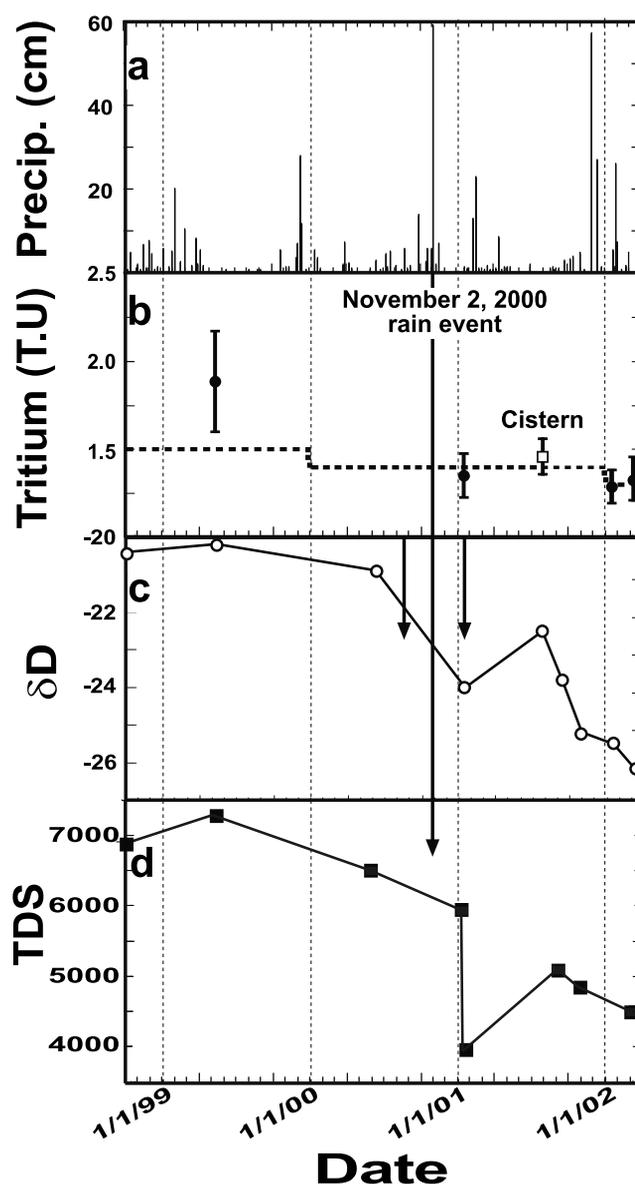


Figure 3. (a) Diagram showing time variation of a. Mean daily precipitation at a station located near Halemaumau Crater (data from the National Climatic Data center), (b) tritium concentration of samples from the well (solid circles), the cistern at the wellhead (open square), and in precipitation (bold dashed line; data from M. Scholl (USGS, written communication, 2001), (c) averaged δD of samples from the well, and (d) averaged total dissolved solids of samples from the well. The arrows show the timing of the big storm on 2 November 2000 and the two dates when water from surficial reservoirs was flushed to the well (see text for details).

vapor, or fluorite precipitation along the flow path, or both. The C/S mass ratio in the only well sample where the DIC was measured (0.25 in KW00-03; Table 1) is lower than the ratio in the Halemaumau fumarole gas (~ 2 [*Goff and McMurtry*, 2000]), the entire caldera gas plume (20–70) [*Sutton et al.*, 2001; *Gerlach et al.*, 2002] and the ratio in the parental Kilauea magma (1.4; *Gerlach and Graeber*

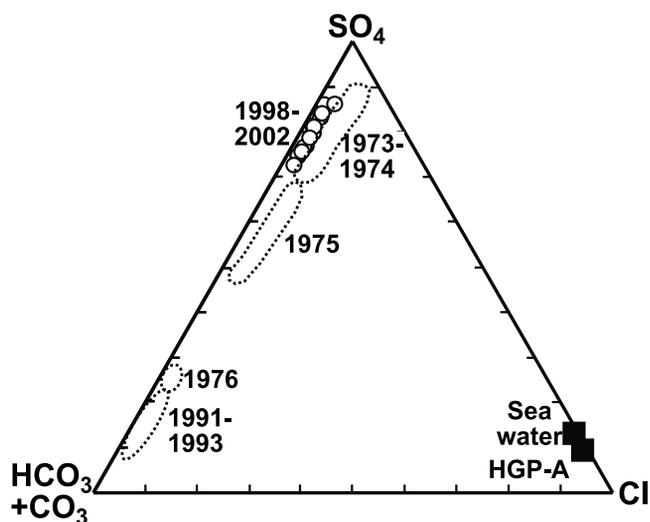


Figure 4. Ternary diagram showing the anion composition of samples collected from the NSF well. Open circles represent postcleaning NSF well samples from this study (1998–2002). Areas bounded by dashed lines represent precleaning samples from the well in 1973–1976 [Tilling and Jones, 1996], 1991 [Janik et al., 1994], and 1993 (F. Goff and G. M. McMurtry, unpublished data, 1993). Squares represent the compositions of seawater and water from geothermal well HGP-A on Kilauea's lower east rift zone [Janik et al., 1994].

[1985]). This indicates that, relative to CO_2 , sulfur compounds are dissolved more efficiently by the circulating groundwater.

[20] The cation composition of 1998–2002 NSF well waters (Figure 5) is characterized by enrichment in alkali elements and high Mg/Ca ratios relative to typical mature magmatic hydrothermal fluids [Giggenbach, 1997], fluids from wells in Kilauea's lower east rift zone [Thomas, 1987], or nonthermal waters from the Island of Hawaii [McMurtry et al., 1977; Janik et al., 1994; Tilling and Jones, 1996]. Relative to high temperature fumarole condensates from Halemaumau (Table 1), the NSF well waters are depleted in aluminum, but enriched in all other cations. The cation composition of the well waters differs significantly from the compositions of seawater and of typical Kilauea summit basalt [Wright and Fiske, 1971; Dzurisin et al., 1995; Clague et al., 1999; Pietruszka and Garcia, 1999], the NSF well fluids are depleted in calcium and enriched in the alkali elements.

6.2. Isotopic Composition

[21] The oxygen and deuterium isotopic values of the postcleaning NSF well samples fall in two ranges near the local meteoric water line (Figure 6). The $\delta^{18}\text{O}$ and δD content of samples collected between October 1998 and June 2000, prior to the three external dilution events, is in the range of -4.19 to -4.32 and -19.6 to -22.0 , respectively, and shows little time dependence (Figure 3c). The isotopic composition of samples collected between January 2001 and March 2002 is significantly more depleted. The $\delta^{18}\text{O}$ and δD values vary from -4.43 and -22.8 , respec-

tively, in July 2001 to -4.81 and -26.5 in March 2002 (Table 2). The isotopic composition of the samples collected in 2002 is similar to the isotopic composition of samples collected from the NSF well in 1973 [Tilling and Jones, 1996] (Figure 6).

[22] The isotopic compositions of the well waters were compared with those of mean annual precipitation at several sites on and near Kilauea [Scholl et al., 1996]. The pre-1998 isotopic compositions of the well waters are consistent with the inferred ponding of local precipitation above a mudcake, prior to cleaning of the borehole. The isotopic values of well waters sampled between 1998 and June 2000 are similar to those of precipitation at Thurston lava tube on the eastern margin of Kilauea's caldera (Figure 1b, TLT), Makaopuhi Crater on the upper part of the east rift zone (Figure 1a, MC), and Stainback Highway, north of Kilauea (Figure 1a, SH). These well waters are significantly heavier than precipitation from the eastern flanks of Mauna Loa, the Hawaiian Volcano Observatory (Figure 1b, HVO) or south of Halemaumau (Figure 1b, HPA), just 500 m from the well. The isotopic values of well waters sampled between January 2001 and March 2002 are similar to the composition of samples collected from the well in 1973–1993 [Tilling and Jones, 1996; Scholl et al., 1996; Goff and McMurtry, 2000], and to the composition of precipitation at HVO and south of Halemaumau (Figure 6).

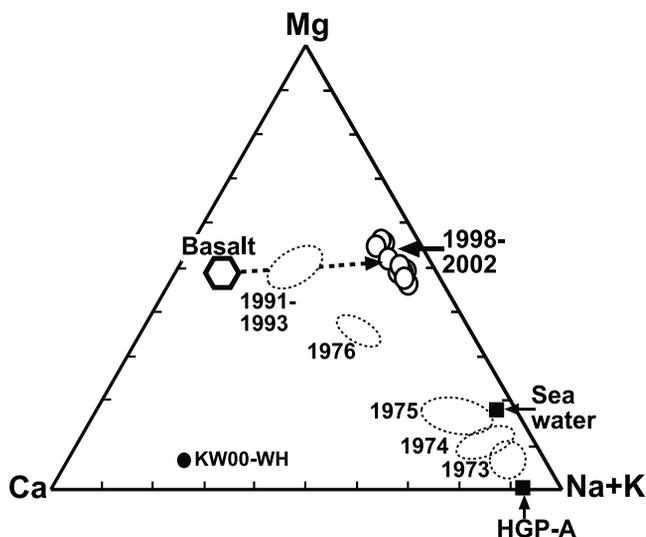


Figure 5. Ternary diagram showing the cation composition of samples collected from the NSF well. Open circles represent postcleaning NSF well samples from this study (1998–2002). Solid circle represents a sample from the cistern at the wellhead. Areas bounded by dashed lines represent precleaning samples from the well; 1973–1976 from Tilling and Jones [1996], 1991 from Janik et al. [1994], and 1993 from F. Goff and G. M. McMurtry (unpublished data). Squares represent the compositions of seawater and water from geothermal well HGP-A on Kilauea's lower east rift zone [Thomas, 1987]. The hexagon represents the composition of Kilauea basalt [Wright and Fiske, 1971; Dzurisin et al., 1995; Clague et al., 1999; Pietruszka and Garcia, 1999]. The dashed line shows the inferred shift in composition due to precipitation of secondary minerals.

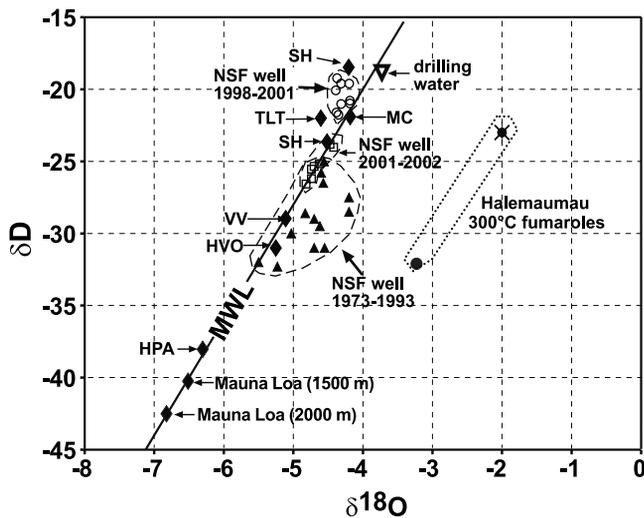


Figure 6. The oxygen-deuterium isotopic composition of samples collected from the NSF well after cleaning in 1998 (open circles and squares) and before cleaning (triangles, 1973–1975 [Tilling and Jones, 1996], 1991 [Scholl et al., 1996], and 1993 [Goff and McMurtry, 2000]). Also shown are the composition of drilling water from well PSM-1 south of Hilo [Tilling and Jones, 1996] and high-temperature (W-3) fumaroles [Hinkley et al., 1995; Goff and McMurtry, 2000], the local meteoric water line (MWL [Scholl et al., 1996]), and values for the mean annual precipitation on and near Kilauea (diamonds; Scholl et al. [1996]); SH, Stainback Highway; MC, Makaopuhi Crater; TLT, Thurston Lava Tube; VV, Volcano Village; HVO, Hawaiian Volcano Observatory; HPA, Halemaumau parking area.

[23] The isotopic content of sample KW01-WH3, collected from the cistern at the wellhead on 17 January 2001, is significantly lighter than both precleaning and postcleaning samples from the NSF well (Figure 6). It was collected 2 months after the large storm event in November 2000, during which the cistern was flooded by local runoff and shallow flow. Its extremely depleted isotopic composition is consistent with previous inferences that the isotopic composition of precipitation from large storms differs significantly from mean precipitation values in the summit area [Scholl et al., 1996].

[24] The tritium data from January 2001 on (Table 2 and Figure 3b) are consistent with the presence of recent precipitation in the well. The tritium concentration in sample KW99-02, including the 1σ analytical error, was higher than the tritium concentration in precipitation of that year, which was ~ 1.5 TU (M. Scholl, USGS, written communication, 2001). In contrast, the tritium concentrations in three samples collected in 2001–2002 are similar to those of current precipitation, and to water in the cistern at the wellhead (Figure 3b).

[25] The $\delta^{18}\text{O}$ of the high-temperature fumarole condensates in Halemaumau is shifted by 2.5‰ from the local meteoric line (Figure 6) [Hinkley et al., 1995; Goff and McMurtry, 2000]. It has been suggested that this shift might be due to water-rock interaction, exchange with CO_2 , or a mixture of meteoric water and 10–15% magmatic water [Hinkley et al., 1995].

[26] The $\delta^{13}\text{C}$ on DIC from the NSF well (-3.6‰) falls in the same narrow range as the $\delta^{13}\text{C}$ - CO_2 from the summit area and that calculated for CO_2 in the parental magma (-3.4‰ to -3.6‰) [Gerlach and Thomas, 1986; Friedman

Table 2. Isotopic Composition of NSF Well Waters and Summit Fumaroles^a

Sample	Date	δD (SMOW)	$\delta^{18}\text{O}$ (SMOW)	$\delta^{13}\text{C}$ (CO_2)	$\delta^{13}\text{C}$ (DIC)	$\delta^{34}\text{S}$	Tritium (TU)
KW98-02	5 Oct. 1998	-20.4	-4.19				
KW99-01	13 May 1999	-20.1	-4.39			6.5	
KW99-02	13 May 1999	-19.6	-4.20			6.4	1.9 ± 0.3^b
KW99-03	13 May 1999	-20.8	-4.19			6.4	
KW00-02	8 June 2000	-22.0	-4.36				
KW00-03	8 June 2000	-21.0	-4.32		-3.59		
KW00-04	8 June 2000	-19.6	-4.32				
KW01-01	17 Jan. 2001	-24.0	-4.40				1.35 ± 0.12
KW01-06	26 July 2001	-22.8	-4.43				
KW01-07	30 July 2001	-22.2	-4.53				
KW01-08	11 Sept. 2001	-23.8	-4.52				
KW01-09	31 Oct. 2001	-25.2	-4.59				
KW02-01	17 Jan. 2002	-25.4	-4.76				1.30 ± 0.24
KW02-02	17 Jan. 2002	-25.7	-4.78				1.29 ± 0.09
KW02-03	12 March 2002	-25.9	-4.75				1.33 ± 0.12
KW02-04	12 March 2002	-26.5	-4.81				
KW00-WH1 ^f	13 June 2000	-19.2	-3.63				
KW01-WH2 ^f	30 July 2001	-19.9	-4.18				1.46 ± 0.10
KW01-WH3 ^f	17 Jan. 2001	-55.4	-8.26				
KW01-SHV ^g	30 July 2001						1.43 ± 0.10
W-3	Dec. 1991	-32.1 ^c	-3.23 ^c	-3.5 ^d		0.3 ^c	0.25 ± 0.09^e
Site C		-30.1 ^c	-11.20 ^c	-3.5 ^d			1.81 ± 0.01^e
Sulphur Bank		-46.4 ^c	-5.46 ^c	-3.4 ^d		10.0 ^e	

^aSee Figure 1b.

^bMeasured on two duplicates from a sample that contained 90 cm^3 .

^cGoff and McMurtry [2000].

^dHilton et al. [1997].

^eSakai et al. [1982].

^fSamples from the cistern at the wellhead.

^gPrecipitation sample from Volcano Village (Figure 1a).

Table 3. Gas Chemistry of Samples From the NSF Well and Summit Fumaroles^a

	KW99-02	KW99-03	KW00-03	KW00-04	KW00-05	KV97-3 ^b	KV97-2 ^b	Site B
T (°C)	92	84	76	92	83	308	260	96
CO ₂	3.360	4.498	24.700	48.230	2.944	77.7	77.9	84.1
S _t ^c	<5 × 10 ⁻⁴	22.0	21.9	14.8				
HCl	-	-	-	-	-	0.04	<0.02	<0.03
HF	-	-	-	-	-	0.08	<0.02	<0.03
H ₂	0.003	0.045	0.236	0.197	0.017	0.0013	0.0349	0.020
CH ₄	0.0005	0.0005	0.0009	0.0026	0.0009	<5 × 10 ⁻⁴	<0.0005	<2 × 10 ⁻⁴
N ₂	76.251	76.089	59.385	39.694	74.787	0.174	0.192	0.880
Ar	0.8727	0.8914	0.5026	0.4078	0.8235	0.0024	0.0037	0.0125
O ₂	19.405	19.778	12.015	8.221	19.860	0.000	0.013	0.016
He	5 × 10 ⁻⁴	<4 × 10 ⁻⁴	<4 × 10 ⁻⁴	<4 × 10 ⁻⁴	<4 × 10 ⁻⁴	2 × 10 ⁻⁴	0.0005	0.0008
Sum	99.896	99.896	96.840	96.752	98.433	100.0	101.18	99.83
N ₂ /Ar	87.4	85.4	118.2	97.3	90.8	72.5	51.9	70.4
³ He/ ⁴ He			12.0				14.9–15.7 ^d	13.7 ^d

^aSee Figure 1b. Units of mol %.

^bFrom W-3 fumaroles in Halemauau [Goff and McMurtry, 2000].

^cTotal sulfur gas.

^dHilton et al. [1997].

et al., 1987; Hilton et al., 1997] and dissolved carbon in the parental magma (−3.1 to −3.6‰) [Gerlach and Thomas, 1986], probably indicating a magmatic source for the carbon. If all the carbon is of magmatic origin, it implies that all the dissolved CO₂ transformed into HCO₃, or that very little isotopic fractionation occurs between CO₂ and HCO₃. Experimental and theoretical data indicate that at temperatures of 120°C to 160°C such fractionation should be minimal [Mook et al., 1974; Friedman and O'Neil, 1977]. This consistency also implies that there are no major sources or sinks of carbon along the flow path.

[27] The δ³⁴S of sulfate from the NSF well (6.4 to 6.5‰ relative to Canyon Diablo troilite) (Table 2) is higher than that of SO₂ from summit fumaroles (+0.3 to +1.2‰ [Sakai et al., 1982]), that of δ³⁴S-S_t in high temperature fumaroles (+0.3‰ [Goff and McMurtry, 2000]) or that calculated for sulfur gas in equilibrium with melt in the magma chamber (+1.1‰ [Gerlach and Thomas, 1986]). It is within the range of values for δ³⁴S-S_t in gas from Sulphur Bank (Figure 1b) fumaroles (+6‰ Goff and McMurtry, 2000), but lower than δ³⁴S-SO₂ in Sulphur Bank fumaroles (+10‰) [Sakai et al., 1982]. In light of the consistent S/Cl ratio, which suggests no major sources or sinks of sulfur along the flow path, the relatively high δ³⁴S values at the NSF well may result from isotopic fractionation associated with redox reactions involving SO₂, H₂S, and SO₄ at temperatures above ~300°C [Friedman and O'Neil, 1977; Sakai et al., 1982; Ohmoto and Goldhaber, 1997] or with some deposition of isotopically lighter native sulfur (−8 to −12‰) [Sakai et al., 1982].

6.3. Dissolved Gas Composition

[28] The composition of gases extracted from groundwater in the NSF well indicates that most samples were heavily contaminated with air (Table 3 and Figure 7). Detectable amounts of H₂ and CH₄ in the gas argue that the well fluid is anoxic at depth. The gases have a low He content and an N₂/Ar ratio between 85 and 118 (Table 3), which is slightly above the atmospheric ratio of 84. The gas compositions of the summit fumarole samples lie on a mixing line connecting air or air-equilibrated groundwater with a helium enriched component typical of mantle gases [Giggenbach, 1997; Goff and McMurtry, 2000]. The large variation in the exsolved CO₂ concentration (Table 3) is

probably due air contamination associated with the different sampling methods used.

[29] The ratio of ³He/⁴He in a dissolved gas sample extracted from well water and corrected for air contamination (R_C) is 12.0 times that of air-derived helium (R_A). This value is slightly lower than the R_C/R_A value in the high temperature and boiling point fumaroles (Table 3) [Hilton et al., 1997] but is clearly indicative of a mantle plume-magmatic source for the helium [Ballentine et al., 2001].

7. Fluid Equilibrium

[30] To examine the equilibrium conditions of fluids from the NSF well we applied the computer code SOLMINEQ88 [Kharaka et al., 1988], which models speciation, saturation, dissolution/precipitation and ion exchange between solution and minerals at specified conditions. As input to the model we inserted the average composition of the NSF well fluids

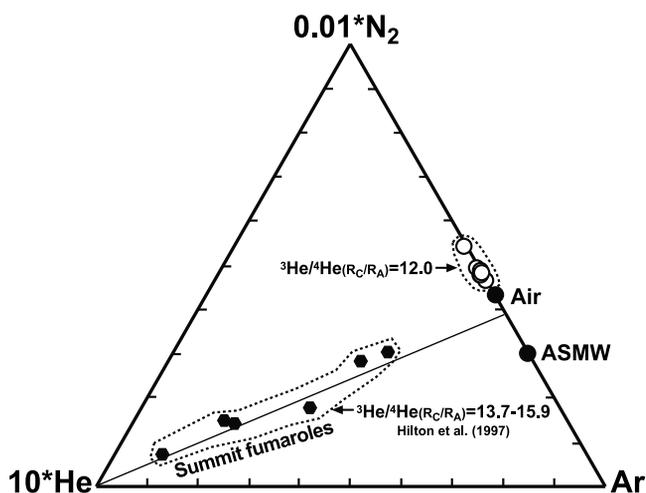


Figure 7. Ternary diagram showing the composition of dissolved gas extracted from well samples (open circles) and of summit fumarolic gas (fumarole data from Goff and McMurtry [2000]). Also shown are the composition of air and air-saturated meteoric water (ASMW).

from October 1998 to June 2000, and examined the saturation of a large suite of minerals at 10°C temperature increments between 90°C and 150°C and pH between 4.0 and 7.0. Pressure was varied in the range of 0.1 to 2 MPa (1 to 20 bars). The degree of saturation in the program is defined by the Gibbs free energy difference between the actual and equilibrium states of a mineral for a given fluid composition and specified conditions.

[31] Results indicate that at 90°C and pH between 6.0 and 7.0 (the conditions measured in the well), the fluid is highly undersaturated with respect to all mineral phases present in fresh Hawaiian basalt in the summit region. The fluid is slightly supersaturated with quartz, and highly supersaturated with all smectites (Figure 8). Calcite and chlorite are supersaturated above a pH value of ~6.5. Calcite saturation is highly pH sensitive, and occurs at a pH value greater than 6.8, and quartz saturation occurs at temperatures below 100°C. All of these secondary minerals are abundant in core from the NSF well [Keller *et al.*, 1979]. Chalcedony and amorphous silica, which were also described as secondary minerals in the core [Keller *et al.*, 1979], are undersaturated over the simulated range. Pressure has a minor effect on the results. At temperatures greater than ~130°C all the smectite minerals become undersaturated. Calcite and chlorite are supersaturated in the entire temperature range, but only at pH values greater than 6 and 6.5, respectively. The calculated results indicate that the fluid in the well is close to equilibrium with the secondary mineral assemblage in the rock as described from core samples [Keller *et al.*, 1979].

8. Geothermometry

[32] The maximum temperature of the accessible well waters is presently 92°C (Figure 2). The alteration mineral assemblage and mineral equilibria calculations indicate that temperatures in the high-temperature unit below the water table (Figure 2) may have been a few tens of degrees higher in the past but have probably not exceeded 150°C.

[33] Most chemical geothermometers, particularly cation geothermometers designed for estimating the “reservoir” temperature of the fluids, are not considered reliable for sulfate-rich waters [Fournier, 1981; Giggenbach, 1988; Kharaka and Mariner, 1989]. However, the K-Mg [Giggenbach, 1988] and Na-Li [Fouillac and Michard, 1981] geothermometers result in fluid temperatures of 94°C and 92°C, respectively, similar to the maximum temperature of the current fluids in the well. On the basis of the SiO₂ concentration in samples from October 1998 to June 2000, the quartz conductive and chalcedony geothermometers yield average temperatures of 164°C and 140°C, respectively. These geothermometer values are near the upper temperature limit permitted by the alteration mineral assemblage and suggest that the well waters may be derived from a higher temperature fluid.

9. Discussion

[34] The new chemical and isotopic data from the NSF well, combined with chemical and isotopic data from Kilauea’s summit fumaroles, enables us to examine possible sources of water and solutes in the well, as well as the major

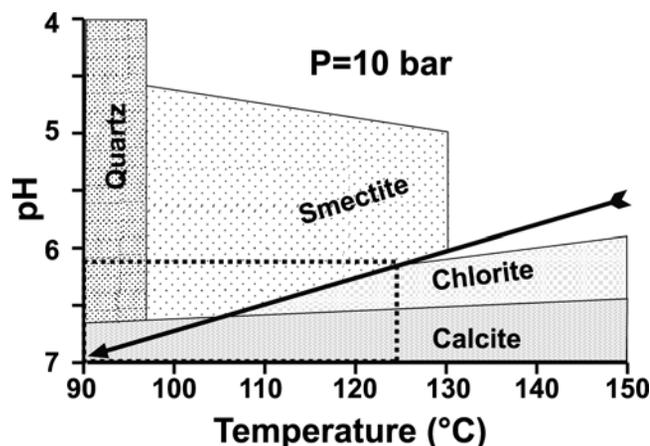


Figure 8. Calculated results of mineral saturation at 10 bars, using the computer code SOLMINEQ88 [Kharaka *et al.*, 1988]. The stippled areas denote supersaturation for the indicated minerals. The dashed rectangle represents the area where the secondary mineral assemblage may have formed. The arrow represents a hypothetical evolution of the fluid as it cooled and pH increased.

processes occurring along the flow path toward the NSF well. The new data presented in this study differs from previously published data [McMurtry *et al.*, 1977; Janik *et al.*, 1994; Tilling and Jones, 1996; Goff and McMurtry, 2000], which probably represented a perched water body above the regional water table that slowly equilibrated with the surrounding basalt and hosted secondary minerals by progressive silicate hydrolysis. Such equilibration is suggested by the progressive water composition shift toward basalt composition (Figure 5) and away from the meteoric water line (Figure 6). Although our new data show some temporal trends (mainly dilution by local waters, Figure 3), these trends are distinct from those observed between 1973 and 1991 [Tilling and Jones, 1996].

[35] Waters in the NSF well are of meteoric origin. On the basis of the oxygen and deuterium isotopic composition of samples from the NSF well collected between October 1998 and June 2000 (after cleaning of the well, but before any discrete dilution event), water recharged into the system either along the rainy, eastern margin of the caldera, or north of Kilauea. The water may recharge along caldera bounding faults, acquire exsolved, superheated steam from underlying magma near Halemaumau, and then flow further down-gradient toward the well.

[36] The tritium concentrations in the well waters do not constrain the flow rates or flow paths to the well. Although the concentration in samples collected from the well during 2001 and 2002 are consistent with addition of recent waters from the discrete dilution events, interpretation of the tritium concentration in sample KW99-02 (1.9 ± 0.3 TU) is complicated. The tritium concentration in this 1999 sample is significantly higher than the tritium concentration in precipitation of that year. A simple decay piston flow model and the tritium history of Hawaiian precipitation would indicate recharge between 1976 and 1980, or 1993 and 1996. During drilling in 1973, 5000 to 10,000 m³ of water were transported to the well from a well south of Hilo

[Murray, 1974], but the oxygen and deuterium isotope signature of these waters is distinct from that observed in the well (Figure 6). If a mixing model is invoked [Shevenell, 1991; Shevenell and Goff, 1995], then the tritium concentration in the 1999 sample may represent a small component of waters recharged in the early 1960s diluted by older or younger water, consistent with recharge along the eastern or northern margins of the caldera and lateral flow. The detectable tritium concentrations in all the analyzed samples from the well cannot be attributed to in situ production by cold fusion processes in the magma or rocks, as it has been demonstrated that this contribution is negligible [Quick et al., 1991; Goff and McMurtry, 2000].

[37] The major element composition of the NSF well waters does not resemble that of seawater or altered seawater in Kilauea's east rift zone [Conrad et al., 1997] (Figures 4 and 5). Rather, the S/Cl ratio of the water, as well as the carbon and helium isotope values of the dissolved gas, are similar to values calculated for parental magma [Gerlach and Graeber, 1985; Gerlach and Thomas, 1986] and those expected for gas exsolving from a mantle plume [Hilton et al., 1997; Ballentine et al., 2001], thus indicating a magmatic origin of S, C, Cl and He. The magmatic gas-meteoritic water mixture is initially acidic (pH = 1.5 in sample HV91-41; Table 1) and magma-derived chloride and sulfur dominate the steam condensate composition. The high content of magmatic volatiles dissolved in the groundwater may be due to shallow magma degassing below Halemaumau. Recent analysis of long-period seismic events [Almendros et al., 2001] suggested that gas condensation (phase transition) occurs at 200 to 400 m depths below the northeastern and central parts of Halemaumau Crater.

[38] Following condensation of magmatic volatiles, dissolution of cations from the host basalt and formation of HCO₃ (at pH > 5) causes progressive neutralization of the fluid, transforming it into a Na-Mg-SO₄-HCO₃ water. Upon cooling to below ~130°C, fluid composition is modified by precipitation of secondary minerals (Figure 8). This decreases calcium and increases the sodium and potassium in the solution (dashed arrow in Figure 5). The low mean C/S mass ratio in the NSF well waters (0.25) relative to the ratio in the parental magma (1.4 [Gerlach and Graeber, 1985]), the high-temperature fumaroles (2.0 [Goff and McMurtry, 2000]), or the gas plume emanating from Kilauea caldera (20–70 [Gerlach et al., 2001]), demonstrates the effects of preferential scrubbing of sulfur relative to CO₂ from the gas plume [Symonds et al., 2001]. The similar S/Cl ratios in Kilauea's parental magma, fumarole gas condensates and water in the NSF well indicate that there are no significant dissolution-precipitation reactions involving these elements along the flow path, so that large subsurface deposits of native sulfur, sulfides, or gypsum are not expected.

[39] To estimate the significance of mass transport toward the lower flanks of the volcano, we compared the major element composition of the NSF well waters with those in a series of coastal springs located ~14 km downgradient, along the southern coast of the island (Figure 1a) [Janik et al., 1994]. The concentration of total dissolved solids (TDS) in the coastal springs indicates that they represent a mixture of 10–50% seawater with dilute meteoric water [Janik et al., 1994]. The ratios among major ions in the spring waters

are similar to those in seawater (except for higher HCO₃/Cl and lower Mg/Ca in all springs) and generally differ by 1 or 2 orders of magnitude from those in the NSF well water. For example, the SO₄/Cl and Mg/Cl (equivalent ratios) are 0.1–0.2 and 0.2, respectively, in the springs, and 31.3 and 20.3 in the NSF well waters. This suggests that the coastal springs do not represent mixing of seawater with “NSF well type” water, and that the rate of mass transport from the summit region toward the lower flanks of the volcano is limited.

10. Conclusions

[40] The hydrothermal fluids sampled from the NSF well in the Kilauea summit area formed by the condensation of high-temperature magmatic gas into shallow meteoric groundwater. The resulting highly acidic, sulfate-rich mixture was progressively neutralized by reaction with the host basalt. Dissolution of cations from the basalt was balanced mainly by an increase of fluid pH and transformation of dissolved CO₂ to HCO₃. Upon cooling of the fluid, secondary minerals were precipitated, mainly calcite, Fe-Ti oxides, and Ca-Mg smectites. Alteration mineralogy and thermal modeling [Hurwitz et al., 2002] suggest that waters sampled at the well have probably never been equilibrated at a temperature higher than 150°C. The significantly different chemical composition of the NSF well waters from that of springs along the southern coast of the island indicates that mass transport toward the lower flanks of the volcano is limited.

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