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The chemical and hydrologic structure of Poás Volcano, Costa Rica *

Gary L. Rowe Jr.^{a,1}, Susan L. Brantley^a, Jose F. Fernandez^b, Andrea Borgia^c

^aDepartment of Geosciences, The Pennnsylvania State University, University Park, PA 16802, USA ^bDepartment Estudios Basicos, Seccion Laboratorio Quimíco, Instituto de Costarricense de Electricidad, San Jose, Costa Rica

^cDeparment of Earth Sciences, The Open University, Milton Keynes, MK7 6AA, UK

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Abstract

Comparison of the chemical characteristics of spring and river water draining the flanks of Poás Volcano, Costa Rica indicates that acid chloride sulfate springs of the northwestern flank of the volcano are derived by leakage and mixing of acid brines formed in the summit hydrothermal system with dilute flank groundwater. Acid chloride sulfate waters of the Rio Agrio drainage basin on the northwestern flank are the only waters on Poás that are affected by leakage of acid brines from the summit hydrothermal system. Acid sulfate waters found on the northwestern flank are produced by the interaction of surface and shallow groundwater with dry and wet acid deposition of SO₂ and H_2SO_4 aerosols, respectively. The acid deposition is caused by a plume of acid gases that is released by a shallow magma body located beneath the active crater of Poás.

No evidence for a deep reservoir of neutral pH sodium chloride brine is found at Poás. The lack of discharge of sodium chloride waters at Poás is attributed to two factors: (1) the presence of a relatively volatile-rich magma body degassing at shallow depths (< 1 km) into a high level summit groundwater system; and (2) the hydrologic structure of the volcano in which high rates of recharge combine with rapid lateral flow of shallow groundwater to prevent deep-seated sodium chloride fluids from ascending to the surface. The shallow depth of the volatile-rich magma results in the degassing of large quantities of SO₂ and HCl. These gases are readily hydrolyzed and quickly mix with meteoric water to form a reservoir of acid chloride-sulfate brine in the summit hydrothermal system. High recharge rates and steep hydraulic gradients associated with elevated topographic features of the summit region promote lateral flow of acid brines generated in the summit hydrothermal system. However, the same high recharge rates and steep hydraulic gradients diverse. However, the reserves and steep hydraulic gradients prevent lateral flow of deep-seated fluids, thereby masking the presence of any sodium chloride brines that may exist in deeper parts of the volcanic edifice.

Structural, stratigraphic, and topographic features of Poás Volcano are critical in restricting flow of acid brines to the northwestern flank of the volcano. A permeable lava-lahar sequence that outcrops in the Rio Agrio drainage basin forms a hydraulic conduit between the crater lake and acid chloride sulfate springs. Spring water residence times are estimated from tritium data and indicate that flow of acid brines from the active crater to the Rio Agrio source springs is relatively rapid (3 to 17 years). Hydraulic conductivity values of the lava-lahar sequence calculated from residence time estimates range from 10^{-5} to 10^{-7} m/s. These values are consistent with hydraulic conductivity values determined by aquifer tests of fractured and porous lava/pyroclastic sequences at the base of the northwestern flank of the volcano.

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¹Present address: Water Resources Division, U.S. Geological Survey, 975 West Third Avenue, Columbus, OH 43235-3192, USA.

Fluxes of dissolved rock-forming elements in Rio Agrio indicate that approximately 4300 and 1650 m³ of rock are removed annually from the northwest flank aquifer and the active crater hydrothermal system, respectively. Over the lifetime of the hydrothermal system (100's to 1000's of years), significant increases in aquifer porosity and permeability should occur, in marked contrast to the reduction in permeability that often accompanies hydrothermal alteration in less acidic systems. Average fluxes of fluoride, chloride and sulfur calculated from discharge and compositional data collected in the Rio Agrio drainage basin over the period 1988–1990 are approximately 2, 38 and 30 metric tons/day. These fluxes should be representative of minimum volatile release rates at Poás in the last 10 to 20 years.

1. Introduction

Research into the chemical and hydrologic structure of hydrothermal systems located in active volcanos is driven by a combination of commercial, scientific and hazard mitigation concerns. For instance, interest in assessing the geothermal potential of hydrothermal systems in active or recently active volcanos has motivated several recent studies (e.g., Da Silva, 1985; Fitterman, 1988; Traineau et al., 1989). Knowledge of fluid flow patterns in volcanos is essential in gauging the impact of volcanic activity on surface- and groundwater supplies in volcanic terrains. The effect of volcanic and hydrothermal activity on flank agricultural activity and on volcanic ecosystems has also received attention (e.g., Parnell and Burke, 1990; Pringle et al., 1993). High-level hydrothermal systems in active volcanos, and the geochemical processes operating in such systems, are consider to be modern analogs for ore-depositing environments associated with the formation of epithermal precious metal deposits and the upper portions of porphyry copper deposits (Henley and Ellis, 1983; Sillitoe and Bonham, 1984; Henley, 1985). Finally, the goal of developing more reliable techniques for forecasting future eruptive activity has led to increased monitoring of fumaroles, hot springs, crater lakes and other manifestations of volcano-hosted hydrothermal systems (Sturchio and Williams, 1990; Brown et al., 1991; Rowe et al., 1992a,b).

2. Poás Volcano

Poás Volcano, located in central Costa Rica, has several features that make it an excellent place to study fluid-volcano interactions (Fig. 1). The summit area of Poás contains at least three nested calderas and an active crater bordered by two composite cones: Von Frantzius to the north (E=2639 m), and Botos cone to the south (E = 2708 m). Of these, Botos has a 400m-diameter cold freshwater lake in its crater whereas the active crater hosts a small but active hydrothermal system (Casertano et al., 1987) (Fig. 1). There are two main features of the active crater and its associated magmatic-hydrothermal system: (1) a 300-m-diameter pit crater occupied by a hot, acidic crater lake whose volume, temperature and water chemistry vary sharply in response to changing rainfall and volcanic activity (Brown et al., 1989; Rowe et al., 1992a,b); and (2) a 30-m-high pyroclastic cone formed during the last phreatomagmatic eruption at Poás in 1953-1954; this cone, located on the southern edge of the crater lake is the site of subaerial fumarolic activity of variable temperature and intensity (Casertano et al., 1985, 1987; Rowe et al., 1992a). The crater-lake brines are among the most acidic natural waters ever sampled; pH of the acid chloride sulfate brine is usually near zero. The heat source for the hydrothermal system is a small, shallow magma body whose upper margin may be less than 500 m below the floor of the active crater (Rymer and Brown, 1987, 1989). Rainfall in the vicinity of the active crater averages approximately 4 m a year (Rowe et al., 1992a).

Another important hydrologic feature of Poás is the presence of acid chloride sulfate springs and streams on the northwestern flank of the volcano. These springs are located 2–3 km from the active crater and are restricted to the Rio Agrio drainage basin (Fig. 1). A link between Rio Agrio and the acid crater lake was proposed in 1861 by Alexander Von Frantzius (Von Frantzius, 1861 in Vargas, 1979). The hypothesis of Von Frantzius was supported by heat and water mass balance calculations made by Brantley et al. (1987) that showed that downward-directed seepage of acid lake brine is an important component of the crater lake's hydrologic budget. Evaluation of data collected at Poás over the period 1978–1989 indicated average seepage rates on the order of several hundred kilograms



Fig. 1. Topographic map of Poás Volcano. Compositional data for numbered sites are given in Table 3. Shaded area on the northwest flank marks the approximate area of the Rio Agrio drainage basin. The line A-A' marks the linear transect used to draw the schematic cross-section given in Fig. 11. Inset-Map showing location of Poás Volcano in relation to other volcanic centers of Costa Rica.

per second. However, leakage of lake brine at a rate of only 20 to 25 kg/s into the Rio Agrio drainage basin is required to explain the fluxes of F, Cl and S observed in Rio Agrio. These results indicate that most brine seeping out of the lake is stored beneath the active crater and does not leak into flank aquifers (Rowe et al., 1992a)

Numerical modelling of groundwater transport on a regional scale by Sanford et al. (1995, this issue) also indicates that the crater lake and summit hydrothermal system are hydraulically connected to acid chloride sulfate springs of the northwestern flank of Poás. Numerical simulations of the summit groundwater system indicate that seepage of lake brines should be limited to the northwestern flank. The critical factors that controlled the direction and quantity of lake brine seepage were the density of the lake brine, height of the water table around the lake, and the permeability of volcanic deposits in the vicinity of the active crater. Results of Sanford et al. (1995, this issue) indicate that the most important factor affecting brine discharge to the northwestern flank is the permeability distribution of the summit area.

This paper presents geochemical and geologic data collected over four years to develop an accurate chemical and hydrogeologic model of Poás Volcano. The data are used to advance and constrain the hypothesis that acid groundwater of the Rio Agrio drainage basin on the northwestern flank of Poás is related to leakage of acid chloride sulfate brine from the crater lake and underlying hydrothermal system. Chemical characteristics of the various water types are compared with potential source fluids to identify brine flow paths in the volcano. Tritium-based residence times are combined with flow equations to estimate several hydrogeologic properties of the aquifer linking the summit hydrothermal system to the acid source springs of the Rio Agrio drainage basin. Finally, dissolved solute fluxes of Rio Agrio are utilized to estimate bulk dissolution rates in the flank aguifer and the minimum rates of volatile release from the summit hydrothermal/ magmatic system.

3. Sampling and analytical methods

Sampling of spring and river waters at Poás began in February 1987 with an initial survey of the rivers draining the northwestern quadrant of Poás. Sampling was expanded to include the southern and eastern flanks of the volcano in late 1987 and early 1988 (Fig. 1). Sampling of water at these sites continued through early

1989 with the number of samples taken at each site ranging from one to six. After 1989, major streams and rivers of the northwestern flank were sampled at approximately monthly intervals through early 1991. Rain water samples were collected at several sites by use of plastic rain gauges that were open to the atmosphere. Total acidity and anion concentrations of these samples represent the sum of both wet and dry acid deposition. At the summit, rain gauges were placed at the base of the crater floor (top of 1953–1954 cone), and at the top of the eastern and western rim of the active crater for one or two week periods. Rain water was also collected on the northwestern flank between July 1989 and December 1990. Sampling sites were chosen to minimize contamination by windblown dust and organic debris. All rainwater samples were filtered in the field with a 0.45 μ m polycarbonate filter and were then analyzed for pH, F, Cl and SO₄. Major cations (Na, K, Ca, Mg and Si) were determined on a sample set collected in August 1989. All river, spring and rain water samples were stored in acid-rinsed polypropylene bottles; all samples were analyzed within one to three weeks of collection.

Routine analysis of spring and river waters included determination of pH, Na, K, Ca, Mg, Fe_T, Al, HCO₃, F, Cl, SO₄ and SiO₂. On selected samples Mn, Zn, Cu, B and Br⁻ and ferrous/ferric iron ratios were determined. Analytical methods, detection limits and relative accuracy of the methods are summarized in Table 1. Sample pH and total alkalinity determinations were made on unfiltered samples. Water samples used for analysis of the other cations and anions were filtered through a 0.45- μ m polycarbonate filter. Water analyses that had charge balance errors greater than ten percent were not used in this study.

 δD and $\delta^{18}O$ data from Rowe (1994) for Poás waters are reported relative to Standard Mean Ocean Water (SMOW). Analytical reproducibility of the delta values is $\pm 0.1\%$ for oxygen and $\pm 2\%$ for deuterium. Tritium analyses were performed by Dr. Robert Michel at the U.S. Geological Survey Tritium Laboratory in Reston, Virginia. Sulfur isotope data for dissolved sulfate and various sulfur-bearing phases (SO₂ gas, gypsum, native sulfur) discussed later in this paper is taken from Rowe (1994). Bulk oxide and trace-element concentrations of lava and altered rock samples that were collected during reconnaissance mapping of the northwestern flank were determined by use of standard X-

Table 1 Analytical methods, detection limits, and relative accuracy

Element/Analysis	Method	Detection limit	Relative accuracy
рН	Combination electrode	_	± 0.05 pH units
Eh	Platinum electrode	_	30mV
Na, K, Ca, Mg, Fe _r	AA - Air Acetylene ¹	0.05 mg/kg	±5%
Mn, Zn, Cu	AA - Air Acetylene	0.02 mg/kg	±5%
Fe ²⁺	Spectrophotometic	0.005 mg/kg	± 5%
Al	AA - Nitrous oxide-Air ²	0.05 mg/kg	± 5%
Si	AA - Nitrous oxide-Air	0.50 mg/kg	±5%
F, Cl, SO₄	Ion chromatography	0.01 mg/kg	±5%
Br	Ion chromatography	0.01 mg/kg	±10%
В	Spectrophotometic	0.01 mg/kg	±5%
Total alkalinity ³	Potentiometric titration	0.50 mg/kg	$\pm 5\%^{4}$

 $^{1}AA = Atomic absorption spectroscopy - air-acetylene flame.$

 $^{2}AA = Atomic absorption spectroscopy - nitrous oxide-air flame.$

³Total alkalinity assumed equal to bicarbonate alkalinity.

⁴Observed reproducibility on analysis of duplicate samples.

ray fluorescence techniques. Mineralogy of the rocks was determined by use of X-ray diffraction, optical microscopy, and scanning electron microscopy.

Discharge of selected rivers, streams, and springs was measured with a portable electronic flow meter. An average velocity profile was obtained by making point velocity measurements at six-tenths depth below the stream surface at intervals not greater than 10% of the total stream width. Discharge was then calculated by multiplying the cross-sectional area of the stream by the average velocity profile. For low-flow springs (total discharge <10 liters per second), visual estimates of discharge were made.

4. Results

4.1. Flank spring and river waters

River and spring water compositions divide into two broad groups based on pH and total dissolved solids (TDS) concentrations: (1) near-neutral to slightly alkaline waters displaying low TDS concentrations and pH values between 5.0 and 8.0; and (2) acid waters displaying moderate to high TDS concentrations and pH values between 1.4 to 5.0. The division between acidic and non-acidic waters follows that of Galloway et al. (1982) who defined a pH value of 5.0 as the lower pH limit for natural rainfall unaffected by anthropogenic (or volcanic) emissions. Further subdivision of the acid and non-acid waters is based on the relative concentrations of major anions in the water following the classification schemes developed for geothermal waters by White (1957) and Ellis and Mahon (1977) (Table 2). Non-acid waters divide into neutral bicarbonate and neutral sulfate waters. Neutral sulfate waters are characterized by HCO₃/SO₄ ratios less than one. Acid springs and rivers are divided into acid chloride sulfate and acid sulfate waters. Acid chloride sulfate waters have low pH (1.4-2.5), above ambient temperature (19-56°C), high TDS concentrations (500-22,000 mg/L) and SO₄/Cl concentration ratios that are between 2 and 3. Acid sulfate waters have pH values between 3.0 and 5.0, ambient temperatures, moderate TDS concentrations (90-350 mg/L) and SO_4/Cl ratios greater than 3.5 (Table 2). Analytical data collected during this study for the sites shown on Fig. 1 are summarized in Table 3.

Neutral bicarbonate waters collected from springs, streams and small rivers are found on the southern, northern, and eastern flanks of Poás Volcano (Fig. 1). Springs and rivers containing acidic waters (pH < 5.0) are restricted to areas immediately adjacent to the active crater and to the northwestern flank of the volcano. An exception is Quebrada Azufre (Site 5, Table 3), a slightly warm, acid sulfate spring located on the topo-

Water type ¹	pH range	HCO ₃ /SO ₄	SO4/Cl	Site # ²
Neutral bicarbonate (NC)	5.0-8.0	> 1.0	Variable	1.2.4.7–16
Neutral sulfate (NS)	5.0-8.0	< 1.0	> 3.5	3.17.23.30–33
Acid sulfate (AS)	3.0-5.0	NA^3	> 3.5	5.18-22.29.AC ³
Acid chloride culfate (ACS)	1.4-3.0	NA ³	2.0-3.5	24–28,34,AC ³

 Table 2

 Chemical classification of Poás Volcano water types

¹Water type abbreviations to be used throughout text are given in parentheses.

²Site # refers to numbers given on Fig. 1.

 ${}^{3}NA = not applicable; AC = active crater.$

graphic saddle separating Poás from neighboring Barva Volcano (Fig. 1). This spring possesses a distinct odor of H₂S in the dry season; its location and acid sulfate composition indicate that the origin of this spring is related to low-level degassing of the magma body associated with the summit of Barva Volcano. Low-temperature, H₂S-bearing fumaroles have been reported in an old crater located west of the summit of Barva at a location a few kilometers south of Quebrada Azufre (Arce, 1980). Also monitored was Rio Segundo (Site 18). Rio Segundo, which is also an acid sulfate water, drains Volcan Viejo, an old composite cone that is part of the Platanar-Porvenir volcanic center northwestern of Poás. Although it is unlikely that these two waters are directly related to summit volcanic activity at Poás, data concerning these waters is used for comparative purposes in this paper.

At Poás, the most acidic waters are the acid sulfate chloride waters of springs and streams draining the Rio Agrio drainage basin (Fig. 1). The hottest (56°C) and most concentrated acid chloride sulfate water (TDS = 22,000 mg/L) on the northwestern flank of Poás is the source spring of the Affluente de Rio Agrio (Site 24), the northern tributary of Rio Agrio. The Affluente hot spring is located approximately 2 km northwest of the active crater at an elevation of about 2000 m. It is the only known spring on the flanks of Poás whose temperature greatly exceeds ambient groundwater temperature (14-17°C). Source springs for the southern tributary of Rio Agrio (Sites 25-26) display temperatures 1 to 5°C above those recorded for ambient temperature waters at similar elevations. Four acid chloride sulfate springs were found in the vicinity of Site 25 whereas only one spring was found at Site 26. The Site 25 springs are located approximately 3 km from the active crater at elevations between 1780 and

1830 m. The Site 26 spring is located at an elevation of approximately 1520 m and is about 5 km northwest of the active crater (Fig. 1).

Less acidic, acid sulfate waters are found north and south of the Rio Agrio drainage basin in the Quebrada Pilas (Site 29) and Rio Desagüe (Sites 19–22) drainage basins, respectively. Rio Desagüe, whose headwaters originate at the base of the south rim of the active crater, is directly downwind of the plume of acid gases released by the active crater and consequently, is severely affected by acid rain (Fig. 2). Rivers and streams north of Quebrada Pilas (Sites 30–33) and to the south of Rio Desagüe (Site 17) contain neutral sulfate waters that have SO_4/Cl concentration ratios greater than four. The only other neutral sulfate river is Rio Angel (Sites 3, 23) whose headwaters originate at the fresh, cold water lake at the top of Botos Cone (Fig. 1).

4.2. Acid rain

Interaction of rain water with the plume of acid gases and aerosols emitted by the crater lake and adjacent fumaroles results in intense acid rain, which, due to prevailing wind conditions and topographic effects, is confined to the summit region and the western flank of Poás (Fig. 2). Average pH and anion concentrations differ markedly between the three summit sites (Tables 4, 5). These differences are attributed to the location of the three sites relative to plume of acidic gases and vapors issuing from the crater lake and adjacent fumaroles. The gas plume is typically directed west-southwest due to prevailing winds and local topographic features (Fig. 2). Thus, samples from the west rim site, which is directly downwind of the acid gas plume, are extremely acid (pH_{avg} ≈ 0.99) whereas the crater floor site (beneath the plume) and the east rim site (upwind of the plume) are much less acidic ($pH_{avg} = 2.93$, and 4.55, respectively). Acid rain collected at the three summit sites is enriched in chloride relative to sulfate; all three active crater sites have average SO₄/Cl ratios that are less than one (Table 4).

Rain samples collected on the west flank of Poás have pH and solute compositions that are quite similar to those recorded for the east rim samples (Tables 4 and 5). Flank stations experienced acid precipitation (rain with $pH \leq 5.0$) over sixty percent of the time with the Rio Desagüe site (#19) receiving the most acidic rainfall ($pH_{avg} = 4.35$) during the sampling period. The distribution of acid rain on the northwestern flank is related to a 400-m scarp which extends westward from Botos Cone to the base of the northwest flank. This scarp, known locally as Cerro Pelon, acts as a topographic barrier to the relatively dense gas plume redirecting a significant part of the plume westward along the southern edge of the Rio Desague drainage basin (Fig. 2). However, the gas plume occasionally affects the cultivated southwest flank. During the recent disappearance of the crater lake, gas emissions from the active crater affected both human health and agricultural production on the southwest flank of the volcano (Smithsonian Institution, 1990).

4.3. Waters of the active crater

Waters of the active crater include extremely acidic chloride sulfate brines of the crater lake, acid condensates collected from subaerial fumaroles issuing from the eroded pyroclastic cone, and calcium-rich, acid sulfate seeps issuing from the walls of the pit crater which hosts the crater lake (Table 6). Compositions of the lake brine and the fumarole condensates vary sharply with time. Such variations have been correlated with changing temperature, rainfall, and subsurface volcanic activity (Rowe et al., 1992a,b). Acid sulfate waters found in the active crater are unusually enriched in calcium relative to flank acid sulfate waters. These calcium-rich waters are associated with small springs and seeps issuing from the walls of the pit crater that hosts the crater lake (Table 6). The pit crater springs were only recently exposed by the drop in lake level; temperatures of these springs and seeps are only a few degrees above ambient and the spring waters are actively depositing gypsum.

4.4. Oxygen and hydrogen stable isotope data

 δD and $\delta^{18}O$ values for acid spring and river waters plot on the meteoric water line of Craig (1961) indicating that these waters are predominantly of meteoric origin (Fig. 3). An exception is the Affluente de Rio Agrio hot spring (Site 24), which is shifted approximately 3‰ in δ^{18} O to the right of the meteoric water line. This shift is probably caused by dilution of the isotopically heavy lake brine by meteoric water but could also be due to isotopic exchange with wallrock during flow through the flank aquifer (Rowe, 1994). Also shown is the average isotopic composition of crater lake brine which is almost 18% heavier than average meteoric water. The extreme $\delta^{18}O$ shift observed in the lake brine is related to a kinetic isotope effect associated with steady-state evaporation of the lake brine at elevated temperatures (40-70°C), not brine-rock interaction at elevated temperatures (Craig, 1963; Giggenbach, 1982; Rowe, 1994).

4.5. River precipitates and alteration mineralogy

Progressive neutralization of acidic river waters due to mixing with dilute, neutral pH waters at lower elevations produces marked color changes in the river waters draining the northwestern flank. River waters with pH's less than three are clear, rivers whose waters have a pH between three and five have greenish tinge and their channel bottoms are colored bright orangered by Fe(OH)₃ precipitates. River waters with nearneutral pH's are a translucent whitish-blue color due to suspension of an amorphous milky-white precipitate. Qualitative SEM-EDS results indicate that the precipitate is composed of aluminum, silica, and oxygen with minor sulfur and iron. The translucent blue coloration is best observed in the waters of Quebrada Gata (Sites 30-31) whose name in Spanish refers to the opalescent blue color seen in a cat's eyes.

Alteration minerals associated with the acid chloride sulfate waters of the Rio Agrio springs include amorphous silica, potassium jarosite (K/Na ratio ≥ 20 , ≤ 0.05 wt.% Al₂O₃), Fe-oxyhydroxides, and rare gypsum (Sites 25–26). These minerals occur as coatings, fillings and vug linings in vesicles and fractures in the lava and lahar that outcrop near the spring outlets. Amorphous silica occurs as layered white coatings in vugs and fractures whereas gypsum was noted only

Site	Location	Water type ¹	Elev. (m)	Temp. ² (°C)	рН (20°С)	Eh (mV)	{ Na] (mg/kg)	[K] (mg/kg)	[Ca] (mg/kg)	(Mg) (mg/kg)	[Fe] _T (mg/kg)	Fe ³ ' /Fe ² ' (mg/mg)
1#	Rio Maria Aguilar	NC	016	18.0±0.0	6.97 ± 0.46	QN	3.7+1.1	2.3 ± 0.5	06+20	29+06		CIN
	•			NA ³	6.45-7.56	٩N	2.5-5.6	1.9-3.0	7.3-12.0	2.1-3.6	NA U	AN
				N = 3	N=3	NA	N = 3	N=3	N=3	N=3	N = 3	NA
#1	Rio Cariblanco	NC	820	17.7 ± 1.2	7.12 ± 0.20	QN	3.8 ± 0.7	2.8 ± 0.8	0.1±0.9	2.3 ± 0.2	0.02 ± 0.02	QN
				16.0-19.5	6.90-7.66	NA	2.5-4.4	2.0-3.8	8.8-11.2	2.1-3.4	0.0-0.06	NA
				N=5	N=5	٨A	N = 5	N=5	N = 5	N=5	N=5	NA
#3	Rio Angel	NS	860	18.0 ± 1.1	7.10 ± 0.16	QN	4.7 ± 0.6	2.3 ± 0.5	9.8 ± 1.7	2.7 ± 0.5	0.03 ± 0.04	(IN
				17.0-19.5	6.90-7.28	NA	4.0-5.6	1.9-3.0	7.4-11.0	2.1-3.2	0.0 - 0.08	NA
				N=3	N=3	VA	N=3	N=3	N=3	N = 3	N=3	VV
#4	Rio La Paz Grande	NC	1480	16.1 ± 0.5	7.21 ± 10.38	ND	3.2 ± 0.4	1.9 ± 0.3	8.0 ± 0.8	3.4 ± 0.3	LD	CIN
				15.5-17.0	6.80-7.76	NA	2.6-3.8	1.6-2.3	7.1-9.0	3.1-3.7	NA	NA
				N = 4	N = 4	NA	N = 4	N = 4	N = 4	N = 4	N=4	NA
#C	Quebrada Azufre	AS	1860	19.5 ± 0.9	3.92 ± 0.34	QN	6.3 ± 0.7	3.4 ± 0.6	17.1 ± 0.6	5.2 ± 0.1	1.9 ± 2.9	CIN
				19.0-21.0	3,66-4,50	NA	5.1-7.0	2.4-4.0	16.4-18.0	5.0-5.3	0.13-6.9	NA
				N = 4	N = 4	NA	N=4	N = 4	N ∞ 4	$N \approx 4$	N = 4	NA
#6	Río Prendas	NC	1160	18.3 ± 0.03	7.37 ± 0.17	QN	3.7±1.1	3.1 ± 0.1	11.0 ± 0.1	4.8±0.1	0.03 ± 0.03	(IN
				18.0-18.5	7.20-7.53	AA	2.6-4.8	3.1-3.2	11.0-11.1	4.6-4.9	0.0-0.06	NA
		1		N=2	N = 2	NA	N=2	N = 2	N=2	N=2	N = 2	NA
L#	Rio Cabuyo	NC	1080	18.0	7.05	QN	1.5	3.3	5.6	2.9	0.10	(IN
8#	Rio Tacares	NC	1040	17.5 ± 1.5	6.97 ± 0.06	QN	2.2 ± 0.3	1.6 ± 0.7	6.0 ± 0.4	3.3 ± 0.05	0.03 ± 0.03	CIN
				16.0-19.0	6.90-7.03	NA	1.9-2.5	0.9-2.5	5.6-6.5	3.2–3.3	0.0-0.06	NA
				N=2	N = 2	NA	N = 2	N = 2	N = 2	N = 2	N = 2	NA
6#	Rio Achiote	NC	1080	17.0	7.69	QN	3.3	1.3	0.0	4.5	LI)	CIN
#10	Rio Rosales	NC	0011	19.1 ± 1.0	7.20 ± 0.19	QN	4.3 ± 0.5	3.3 ± 0.3	12.3 ± 1.9	5.7 ± 1.0		ND
				19.0-21.5	7.0-7.41	٧A	3.5-4.9	2.9-3.6	10.0-15.0	4.56.8	NA	NA
				N 4	N-4	AN	N = 4	N = 4	N = 4	N = 4	N = 4	NA
#11	Rio Vigia	S	1220	19.3 ± 1.7	7.16 ± 0.32	QN	2.7 ± 0.5	1.9 ± 0.5	8.6 ± 1.4	4.0 ± 0.3	0.03 ± 0.05	QN
				17.0-21.0	6.80-7.58	NA	2.2-3.4	1.2-2.4	6.6-9.6	3.6-4.4	0.0-0.08	NA
				N=3	N = 3	NA	N=3	N=3	N=3	N=3	N=3	NA NA
#12	Rio San Juan	vc	1140	20.7 ± 1.9	7.05 ± 0.17	QN	3.3 ± 0.9	2.7 ± 0.8	9.0 ± 0.7	4.0±0.1	0.05 ± 0.04	CIN
				18.0-22.0	6.85-7.26	٨A	2.4-4.5	1.83.8	8.1-9.9	4.0-4.1	0.0-0.10	NA
				N=3	N=3	٧N	N=3	N=3	N=3	N=3	N=3	NA
#13	Rio Sarchi	NC	1400	21.0 ± 1.6	7.27 ± 0.20	QN	3.7 ± 1.0	2.2 ± 0.7	10.5 ± 1.1	4.2 ± 0.2	0.02 ± 0.02	QN
				19.0-23.0	7.00-7.47	NA	2,4-4.4	1.7-3.2	9.6-12.0	4.0-4.5	0.0-0.04	NA
	; ;			N=3	N=3	NA	N≖3	N=3	N=3	N=3	N=3	NA
#14	Rio Trojas	S	1040	$19.5 \pm 0A$	7.21 ± 0.23	Q	4.5 ± 0.8	2.7 ± 0.8	11.0 ± 2.3	4.6 ± 1.4	0.02 - 0.03	QN
				19.0-20.0	6.95-7.51	NA	3.7-5.6	1.8-3.8	8.3-14.0	2.8-6.3	0.0-0.07	NA
				N=3	N=3	V A	N=3	N=3	N = 3	N=3	N=3	NA
#15	Rio Toro	UU	1440	17.4 ± 1.0	7.37 ± 0.28	QN	3.5 ± 0.7	1.8 ± 0.5	7.1 ± 0.7	2.7 ± 0.2	0.02 ± 0.02	QN
				16.0-19.5	6.75-7.90	NA	2.1-4.7	0.8 - 3.1	5.8-8.2	2.3-3.0	0.0-0.09	NA
				N=17	N = 17	NA	N=17	N = 17	N = 17	N=17	N= 17	NA
#16	Rio Gorrion	Ŋ	1440	17.3 ± 1.0	7.22 ± 0.28	CIN	2.9 ± 0.5	1.4 ± 0.4	8.1 ± 0.6	2.4 ± 0.2	0.04 ± 0.04	CIN
				15.0-19.5	6.70-7.85	NA	1.7-4.0	0.6-2.2	7.2-9.7	2.2-3.2	0.0-0.14	NA
				N = 20	N = 28	NA	N = 28	N = 28	N = 28	N = 28	N = 28	NA
#17	Rio Anonos	NC	1420	17.9±1.1	6.96 ± 0.34	Ŋ	4.2 ± 0.7	2.0 ± 0.9	15.4 ± 3.9	3.9 ± 0.5	0.04 ± 0.04	CIN
				16.0-20.5	6.16-7.50	NA	2.1-6.2	0.9-5.1	1.9-32.5	3.1-5.6	0.0-0.18	NA
				N-20	N-28	۲N	N - 28	N = 28	N = 28	N = 28	N = 28	NA

Table 3 Selected compositional data for springs and rivers of Pods Volcano

Site	{Mn]-	[A]	[24]	[Cu]	[F]	[CI]	[30,1	(HCO,1	[SiO-]	[8]	TDS
ĺ	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
#1	LD	LD	ND	QN	0.21 ± 0.10	3.8 ±1.0	15.8±5.0	35.5±4.6	40.6±9.5	n	115±24
	NA	NA	NA	NA	0.10-0.35	2.4-4.9	9.1-21.2	29.0-39.4	28.2-51.3	NA	83-141
	N=1	N=3	N = 0	N = 0	<i>N</i> =1	N=3	N=3	N=3	N=3	N = 1	N=3
#2	E E	E E	9 :	ED :	0.15 ± 0.03	2.7 ± 0.4	16.6 ± 2.2	32.6±3.4	38.7±6.0	0.05	110 ± 12
	NA M-1	NA N - N	N-1	NA M-1	0.12-0.19	2.1-5.2 M-5	13.5-19.5 V-E	29.6-39.0	28.2-46.0	NA N J	91-123 ve
۲۳ ۲	1-2		1-4		N = 4 0.24 ± 0.01	74+06	N=5 767468	v=v	N=5 1 + 4 0	1=2	V = 5
C#	NA	NA	NA	NA	1.22-0.25	1.5-2.9	20.7 ± 0.8 18-34.7	18.8–27.9	25.7-42.6	NA	89-121
	<i>N</i> = 1	N=3	N = 1	<i>N</i> =1	N=1	<i>N</i> =1	N=3	N=3	N=3	L=1	N=3
#4	LD	E	LD	LD	0.09 ± 0.05	1.7 ± 0.3	5.0±0.7	43.3 ±4.2	36.8 ± 3.9	LD	103 ± 10
	NA	NA	NA	NA	1.03-0.14	1.2-2.1	3.8-5.7	8.7-48.5	30.4-40.6	NA	91-114
	N= {	N = 4	N=1	N=1	N=1	<i>N</i> = 1	N = 1	N=4	N=4	N = 1	N-4
#5	гD	0.86 ± 0.24	QN	QN	0.48 ± 0.04	5.6±0.6	82.8 ± 2.7	1.3±2.5	67.1±4.7	QN	192 ± 8
	NA	0.47 - 1.10	NA	NA	0.44-0.55	5.0-6.5	78.4-85.7	0.0-4.9	61.6-73.2	NA	184-203
	N= 1	N = 1	N=()	N=0	N= 1	N = 1	N=4	N=4	N=4	N=0	N = 4
#6	QN	LD	QN	QN	0.06 ± 0.05	2.2 ± 0.2	7.4±1.1	59.4±1.4	48.5 ± 1.4	ND	140 ± 2
	NA	NA	NA	NA	0.06-0.07	2.0-2.4	6.2-8.5	58.0-60.7	47.1-49.0	NA	138-142
	N=0	N=2	N=0	N=0	N=2	N=2	N=2	N=2	N=2	N=0	N=2
L#	QN	ED	QN	QN	0.06	1.8	3.1	27.7	32.7	QN	79
#8	QN	ΓD	DN	QN	0.03 ± 0.02	1.6±0.5	3.2 ± 0.7	35.6 ± 5.0	31.8 ± 0.3	QN	85 ± 5
	NA	NA	NA	NA	0.0-0.5	1.1-2.1	2.5-4.0	30.6-40.6	31.4-32.0	NA	16-08
	N=0	N=2	N=0	N=0	N=2	N=2	N=2	N=2	N=2	N=0	N=2
6#	QN	8	DN	QN	0.09	3.1	5.7	46.9	40.6	DN	114
#10	Q	P	QN	QN	0.05 ± 0.07	4.9±2.0	13.3±4.3	55.4±5.5	42.5±4.1	QN	142±8
	NA	NA	NA	NA	0.0-0.16	3,1-8,1	9.2-20.5	50.7-64.6	37.6-49.0	NA	129-152
	N=0	N=4	N=0	N=0	N=4	N=4	N=4	N=4	N=4	N=0	N=4
#11	QN	LD	QN	Ð	0.10 ± 0.03	4.10±0.7	11.2±1.7	39.5±8.3	41.3 ± 11.0	QN	113 ± 23
	NA	NA	NA	NA	0.06-0.14	3.2-5.0	8.8-12.5	29.0-49.4	25.9-51.1	NA	83-136
	N=0	N=3	N=0	N=0	N=3	N=3	N=3	N=3	N=3	N=0	N=3
#12	CN	rD	ON N	Q	0.13 ± 0.02	3.9 ± 0.6	15.0±2.5	31.1±1.5	46.7 ± 7.0	QN	116±12
	NA	ANA	NA	NA .	0.12-0.16	3.4-4.7	11.8-17.9	29.0-32.6	37.0-53.3	NA	99–127
	0=N	N=3	N=0	N=0	N=3	N=3	N=3	N=3	N=3	N=0	N=3
#13		9 :		ŪN ;;	0.12±0.09	3.6 ± 0.4	16.3 ± 6.5	36.7 ± 4.0	51.3 ± 4.6		129±7
	NA V D	NA V J		NA M_0	د2.0-0.0	3.1-4.0	5.C2-C.UI	51.1-59.5	45.0-26.0	NA S	121-139
					V=0 0.00+0.00	N=3 30107	N=3 152175	N=5 101	N=3	V=U	N = 5
±.#			AN	NN N	00.0 I 5	7.0 T 0.5	0.7 1 5 5 1	1.41 I 7.64	17 I / 1764		00 T 701
		M= 2	0-2	0-M	N-3	C.C-1.4	U.21-2.01	0.10-1-61 M - 2	20.00-0.00	N-0	91-102 11-102
214				0-4	A - 2	19405	V=5	70 4 4 6 6	N=3 26 4 4 2	0 = V	N = 5
	NA	NA	A N	NA	0.08_0.18	08-30	111101	77 6 46 0	C+TC+CC	5070 ± 7070	11 E C C
	N= 11	N= 17	N-11	N=11	N-17	N= 17	N-17	N=17	N = 17	N=6	N=17
#16	3	9	a	LD LD	0.13 ± 0.05	2.9 ± 0.8	8.8±1.8	31.4 ± 6.0	32.4+2.5	0.05 ± 0.04	90+7
	NA	NA	NA	NA	0.05-0.31	1.7-4.3	5.4-14.0	22.0-44.5	27.0-39.9	0.0-0.12	80-109
	N=11	N=28	N= 11	N=11	N=26	N = 28	N = 28	<i>N</i> = 28	N = 28	N=6	N = 28
#17	0.03 ± 0.02	ГD	rD	ĽD	0.43 ± 0.12	8.4±1.5	36.0±13.7	20.6±6.3	43.6±4.1	0.02 ± 0.03	133 ± 20
	0.01-0.06	NA	NA	NA	0.13-0.78	5.9-12.8	27.0-91.6	10.5-30.1	35.1-51.3	0.0-0.08	90-199
	N=5	N = 28	N=13	N=13	N=25	N=28	N = 28	<i>N</i> = 28	N=27	N=6	N = 28

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Site	Location	Water type ¹	Elev. (m)	Temp. (°C)	рН (20°С)	Eh (mV)	[Na] (mg/kg)	{K] (mg/kg)	[Ca] (mg/kg)	[Mg] (mg/kg)	[Fe] ^T (mg/kg)	Fe ³⁺ /Fe ²⁺ (mg/mg)
#18	Rio Segundo	AS	1440	17.3±0.4	4.24 ± 0.20	(IN	2.5 ± 0.4	1.8±0.4	7.0±0.6	1.4±0.1	0.07 ± 0.07	QN
	•			17.0-18.0	3.80-4.55	NA	1.7-3.1	1.0-2.4	6.0-8.4	1.3-1.6	0.0-0.19	NA
				N == 7	N= 14	NA	N= 14	N = 14	N = 14	<i>N</i> = 14	<i>N</i> =14	NA
#19	Rio Desague	AS	1320	17.6 ± 1.6	4.67 ± 0.47	QN	6.8 ± 1.6	2.4 ± 0.6	23.0 ± 4.4	5.5±1.1	0.07 ± 0.06	ND
				15.5-20.0	4.10-5.83	CIN	2.5-9.7	1.1-3.6	14.2-29.7	3.4-7.4	0.0-0.20	NA
				N = 16	N = 21	QN	N = 21	N = 21	N=21	N = 21	N = 21	NA
#20	Rio Desague	AS	1720	15.3 ± 1.2	3.73 ± 0.13	664	10.5 ± 2.9	3.6 ± 0.8	37.7 ± 1.9	7.1±1.5	0.44 ± 0.02	4.19
				14.5-17.0	3.55–3.82	NA	6.5-13.3	2.5-4.2	35.0-39.0	5.0-8.2	0.41-0.46	NA
				N=3	N=3	N = 1	N=3	N=3	N = 3	N=3	N = 3	N = 1
12#	Rio Desague	AS	2300	13.0 ± 2.0	3.43 ± 0.17	CIN	6.9 ± 1.4	2.1 ± 0.2	27.7 ± 5.3	5.8 ± 1.1	1.04 ± 0.86	ND
				11.0-15.0	3.30-3.60	NA	5.5-8.3	1.9-2.3	2,4-33.0	4.6-6.9	0.18-1.90	NA
				N=2	N = 2	NA	N = 2	N = 2	N = 2	N=2	N = 2	NA
#22	Naciente de	AS	2390	14.7 ± 0.9	3.92 ± 0.38	UN	8.2 ± 0.8	3.9 ± 1.3	22.5 ± 1.7	4.3 ± 0.2	0.05 ± 0.01	CIN
	Mirador			12.9-15.6	3.50-4.35	NA	7.3-9.4	2.3-5.9	19.5-24.0	4.0-4.7	0.03-0.06	NA
				N=5	N = 5	NA	N = 5	N = 5	N = 5	N = 5	N = 5	NA
#23	Rio Angel Spring #1	NS	2300	13.9	6.40	(IN	6.3	3.4	16.5	3.0	ED)	CIN
#24	Naciente de Affluente	ACS	2000	56.0	1.46	614	460	120	425	820	1020	0.17
#25	Naciente de Agrio #1	ACS	1800	21.3 ± 0.5	2.24 ± 0.09	823 ± 30	49.6 ±6.2	14.5 ± 1.9	110 ± 19.3	60.5 ± 7.5	47.3 ± 7.1	75.4 ± 25.4
				20.7-22.0	2.10-2.35	790-858	38.7-56.7	11.8-17.1	82.7-140	50.0-70.4	37.9-58.8	33.8-101.4
				N = 6	N = 1	N = 4	N = 6	N = 6	N = 6	N = 6	N = 6	N = 4
#26	Naciente de Agrio #2	ACS	1520	20.0	2.46	854	55.0	14.8	85.0	52.0	6.61	105
#27	Rio Agrio	ACS	1290	19.6 ± 0.5	2.34 ± 0.08	819	48.0 ± 12.3	16.3 ± 3.0	79.1 ± 9.4	61.5 ± 6.9	47.0 ± 6.3	52.0
				19.0-20.0	2.20-2.55	NA	33.2-58.6	11.0-21.5	60.0-95.0	50.7-71.8	35.8-57.8	NA
				N = 12	N = 19	N == 1	N= 19	N = 19	N = 19	N = 19	N = 19	N = 1
#28	Agrio/Toro Confluence	ACS	1280	17.8	2.95	377	14.3	5.3	27.5	16.4	10.9	24.2
#29	Quebrada Pilas	AS	1410	16.7 ± 2.3	3.93 ± 0.03	499	9.3 ± 0.1	4.5 ± 0.6	29.8 ± 0.9	7.8 ± 0.1	0.82 ± 0.29	0.66
				14.4-19.0	3.9(-3.96	NA	9.2-9.4	3.9-5.0	29.0-30.8	9.7-7.T	0.53-1.11	NA
				N=2	N = 2	N = 1	N = 2	N=2	N = 2	N = 2	N = 2	N = 1
#30	Quebrada Gata	NS	1570	14.9	6.80	ND	3.3	2.3	9.9	2.1	0.07	ND
#31	Quebrada Gata	NS	0801	18.3 ± 1.0	6.69 ± 0.47	ND	6.7 ± 1.7	2.8 ± 0.7	17.9 ± 3.8	5.7 ± 1.2	0.02 ± 0.04	ND
				16.0-21.0	5.40-7.30	V N	1.8-9.3	0.9 - 3.9	11.5-24.0	3.6-7.7	0.0-0.19	NA
				N = 17	N = 25	NA	N = 25	N= 25	N = 25	N = 25	N = 25	NA
#32	Quebrada Latas	NS	1040	18.3 ± 1.0	6.89 ± 0.38	QN	4.4 ± 0.8	2.1 ± 0.9	11.5 ± 2.4	3.0 ± 0.6	0.02 ± 0.04	QN
	(=Rio Claro)			17.0-21.0	5.70-7.50	٧N	3.2-7.5	1.0-5.3	7.7-22.0	2.0-5.3	0.0-0.19	NA
				<i>N</i> = 19	N = 29	VV	N = 29	N = 29	N = 29	N = 29	N = 29	NA
#33	Rio Pozo Azul	SN	066	18.4 ± 1.0	7.04 ± 0.30	QN	7.0 ± 1.6	2.6 ± 0.9	18.0 ± 5.0	5.0 ± 1.3	0.03 ± 0.07	CIN
				17.0-20.0	6.35-7.45	٩z	3.5-9.6	0.7-4.5	9.4-26.7	2.5-7.1	0.0-0.27	NA
				N = 14	N = 18	AN	N = 11	N= 18	N = 18	N = 18	N = 18	NA
¥.3	Rio Toro	ACS	700	18.8 ± 1.3	3.57 ± 0.33	667	8.8 ± 2.6	3.1 ± 1.0	22.1 ± 5.5	9.5 ± 2.5	1.10 ± 1.42	2.45
				17.0-21.0	2.75-4.25	٩N	2.6-12.4	13-5.0	11.5-33.4	4.3-13.3	0.08-5.67	NA
				N = 13	N = 1.5	N = 1	N = 15	N=15	N=15	N=15	N = 15	N = 1

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Table 3 (continued)

Site	[Mn]T (mg/kg)	{Al] (mg/kg)	{Zn] (mg/kg)	[Cu] (mg/kg)	[F] (mg/kg)	[C] (mg/kg)	[S04] (mg/kg)	[HC0,] (mg/kg)	[SiO ₂] (mg/kg)	[B] (mg/kg)	TDS mg/kg
#18	0.03 ± 0.02	2.36±0.69	E I	l di	0.10 ± 0.3	1.1±0.7	45.0±7.0	0.7 ± 1.7	41.9±4.4	0.02 ± 0.03	104±11
	0.0-06	1.12-3.17	NA	AN	0.0-0.12	0.3-3.2	33.5-57.0	0.0-6.3	29.0-48.4	0.0-0.10	121-121
	N = 10	N=]4	N=9	N=9	N = 13	<i>N</i> = 14	N = 14	<i>N</i> = 14	N= 14	N=11	N = 14
#19	0.15 ± 0.04	2.4 ± 0.9	ГD	ΓD	1.05 ± 0.39	17.2 ± 3.5	82.3 ± 14.4	1.2 ± 1.6	56.9 ± 8.4	0.02 ± 0.03	199 ± 32
	0.10-0.20	0.60-4.3	NA	NA	0.56-2.33	11.4-23.3	60.5-112	0.0-5.4	40.9-73.1	0.0-0.12	139-255
	N=12	N = 20	N=9	N=9	N = 20	N=21	N = 21	N = 21	N = 21	N = 12	N = 21
#20	0.49	10.5 ± 0.8	0.04	0.02	1.81 ± 0.22	30.1 ± 2.3	161 ± 6.3	LD	80.0 ± 11.8	QN	344 ± 28
	NA	9.5-11.3	NA	NA	1.50-1.96	26.8-31.7	153-166	NA	63.3-88.4	V N	304-364
	N=1	N=3	N=1	N = 1	N=3	N=3	N=3	N=3	N=3	N=0	N=3
#21	0.18	15.3 ± 9.2	0.02	0.04	1.87 ± 1.05	42.6 ± 17.1	152 ± 52	P	86.0 ± 12.1	Q	342±100
	NA	6.1-24.4	NA	AN	0.82-2.92	25.5-59.6	100-242	Q	73.8-98.1	NA	242-442
	N=1	N=2	N=1	N=1	N=2	N=2	N=2	N=2	N=2	N=2	N=2
#22	9 :	2.37 ± 0.75	9 :	0.07	$0.75 \pm .06$	10.5 ± 1.0	89.8±4.4	E	70.8 ± 3.5	0.08 ± 0.04	212 ± 10
	NA S	1.30-2.90	NA .	NA	0.64-0.80	8.9-12.0	86.0-97.5	AN	67.5-77.2	0.04-0.11	200-226
	N=2	N=3	N=2	N=1	N=5	N=5	N=5	N = 5	N=5	N=2	N=5
#23	9	8	P	ED	0.30	3.5	56.2	10.5	56.2	9	157
#24	ON 200	1740	2.7	0.07	152	5930	12000	AN 1	150	2.2	22680
* 22	2.63 ± 0.42	135±18	0.17 ± 0.02	3	19.1 ± 4.2	410 ± 74	1170±103	â	90.3 ± 13.1	0.25 ± 0.03	2113±214
	2.21-3.05	112-160	0.15-0.20	NA	11.5-24.0	340-560	1030-1300	N A	73.3-108	0.22-0.28	1831-2384
	N-2	N=6	N=4	N-4	N=6	N=6	N-6	N=0	N=6	N=2	6V - 6
97#	UN DU COL	131	UN 101	n :	10.9	330	1030	AN 1			1862
#27	2.23 ± 0.56	157±19.7	0.18 ± 0.04	9 3	25.3±5.5	460±60 350 550	1180 ± 160	Q :	93.4±5.8	0.33 ± 0.05	2179 ± 272
	N-2-201	110-104	0.10-0.20 M - 10	NA 10	V 10. / 20.2	005-065	890-1490 N - 10	N-0	81.4-104 M - 10	0.27-0.42 M = 0	1607-0601
¥78		33.0	N = 10		11=11	N = 19 116	61 = V		v = 12	2 - 2 - 2 	V= 19
#29	0.04	16.2 + 1.4	0.04	9 9	0.56 ± 0.40	42.4 + 5.2	227 168 + 121	3 3	59.7+3.5	0.03	340+26
	AN	14.8-17.6	NA	NA	0.16-0.96	37.2-47.5	147-189	NA	56.2-63.1	NA	314-366
	<i>N</i> = 1	N=2	N = 1	N= 1	N = 2	N=2	N=2	N=2	N = 2	N = 1	N=2
06#	ED	ΓD	LD LD	ED	0.37	5.2	27.3	9.11	42.1	P	105
#31	0.05 ± 0.05	0.37 ± 0.74	LD LD	ΓD	0.67 ± 0.15	13.3 ± 3.4	54.8 ± 14.4	14.5 ± 5.1	43.5 ± 6.6	$0.02 \pm .02$	158 ± 30
	0.0-0.13	0.0-3.4	NA	AN	0.37-0.95	6.8-19.4	29.1-80.1	5.7-24.6	27.3-56.0	0.0-0.07	106-202
	N=13	N=25	N=12	N=12	N = 22	N = 25	N = 25	N = 25	N = 24	N=11	N=25
# 27	NA U	0114 ± 0.15			0.25±0.04	6.6±1.8 4.0-14.1	50.5±7.8	15.8±2.9	34.8±4.9 220.424	0.05±0.05	109±15 26,152
	N= 11	N=70	N=11	N=11	V = V = V	N=20	N=79	0.02-C.0	N = 70	N = 14	701-0/ N= 70
#33	: : 1	0.07 + 0.16	. 9	:	0.38 ± 0.16	11.2+3.2	51.3 + 14.3	16.9+4.4	32.2+5.9	0.02 ± 0.04	143+35
	NA	0.0-0.66	NA	AN	0.24-0.99	5.4-17.3	24.1-74.3	8.8-31.3	18.3-41.9	0.0-0.15	74-196
	N= 12	N=18	N = 11	N=1]	N=18	<i>N</i> = 18	N = 18	N = 18	N=17	N = 15	N= 18
¥;¥	0.29 ± 0.08	15.2 ± 3	8	ED	2.59 ± 1.16	43.3±11.4	144±54	8	44.4 ± 6.7	0.04 ± 0.04	290±91
	0.20-0.45	5.2-23.0	NA	NA	0.34-4.32	20.4-68.7	44.9-229	NA	24.4-51.3	0.0-0.14	125-424
	N = 10	<i>N</i> = 11	<i>N</i> = 11	N = 4	N=11	N= 15	N = 15	N= 15	N = 14	N= 11	N=15
¹ ACS = at ² Analytics	cid chloride sulfate v il data given include	water; AS = acid sulfate es: Average concentratic	water; NC = neutral bi on ± one σ, Concentrat	icarbonate water, N ion range (min-ma	S = neutral sulfate wate x value); N = number	er. of samples collected.					
NA = no	t applicable; ND = n	not determined; LD = bei	low detection limit.								

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Table 4 Compositional data for summit and northwest flank acid rain

Location ¹	Date	Elev. (m)	Temp. (°C)	рН (20°С)	Na (mg/kg)	K] (mg/kg)	Ca] (mg/kg)	[Mg] (mg/kg)
Top of cinder cone	1/10/88	2330	ND^2	3.05	0.40	0.10	0.40	0.09
Top of cinder cone	1/19/88	2330	ND	2.90	1.30	1.17	1.00	0.20
Top of cinder cone	6/26/88	2330	ND	2.80	0.18	0.97	3.05	0.58
Top of cinder cone	1/27/89	2330	ND	3.05	0.49	2.39	4.67	0.16
Top of cinder cone	2/7/89	2330	ND	2.85	0.69	6.53	0.50	0.14
Top of cinder cone	9/13/90	2330	ND	2.90	0.42	0.36	12.9	0.21
$Avg \pm std$		2330	ND	2.9 ± 0.1	0.6 ± 0.4	1.9 ± 2.2	3.8 ± 4.4	0.2 ± 0.2
Range			NA	2.9-3.1	0.2-1.3	0.1-6.5	0.4-12.9	0.1-0.6
# samples			NA	N = 6	N = 6	N=6	N = 6	N = 6
East rim	6/26/88	2400	ND	4.25	0.40	0.80	3.00	0.55
East rim	1/27/89	2400	ND	7.75	2.14	3.41	1.87	0.15
East rim	2/7/89	2400	ND	4.85	0.49	6.72	0.13	0.20
East rim	8/8/89	2400	ND	3.85	0.18	LD	1.12	0.04
East rim	3/17/90	2400	ND	3.35	0.09	0.17	LD	0.02
East rim	9/13/90	2400	ND	3.30	0.09	0.05	1.13	0.04
$Avg \pm std$		2400	ND	4.6 ± 1.7	0.6 ± 0.7	1.9 ± 2.5	1.2 ± 1.0	0.2 ± 0.2
Range			NA	3.3-5.1	0.1-2.1	0.0-6.7	0.1-1.9	0.02-0.55
# samples			NA	N = 6	N = 6	N=6	N=6	N=6
West rim	6/26/88	2400	ND	1.00	3.20	5.40	52.50	2.88
West rim	1/27/89	2400	ND	0.40	1.73	4.39	1.51	0.55
West rim	2/7/89	2400	ND	0.20	1.42	3.39	1.49	0.36
West rim	8/8/89	2400	ND	2.45	0.40	LD	9.11	0.19
West rim	3/17/90	2400	ND	0.90	0.21	0.20	1.75	0.23
$Avg \pm std$		2400	ND	1.0 ± 0.8	1.4 <u>+</u> 1.1	2.7 ± 2.2	13.3 ± 19.8	0.8 ± 1.0
Range			NA	0.2 - 2.5	0.2-3.2	0.0-5.4	1.5-52.5	0.2-2.9
# samples			NA	N = 5	N = 5	N=5	N=5	N=5
NW flank transect						_		
16.8 km S of Site #19	8/6/89	1580	24.1	4.68	0.25	0.77	0.18	0.09
13.2 km S of Site #19	8/6/89	1760	23.7	4.02	0.59	0.40	0.14	0.03
9.9 km S of Site #19	8/6/89	2000	20.7	4.41	0.18	0.30	0.39	0.06
7.7 km S of Site #19	8/6/89	1760	19.4	4.48	0.18	0.08	0.30	0.06
5.6 km S of Site #19	8/6/89	1560	22.4	4.45	0.26	0.25	0.14	0.05
2.5 km S of Site #19	8/6/89	1420	23.4	4.68	0.38	0.12	0.14	0.07
Site #19	8/6/89	1320	21.4	5.36	0.46	0.46	0.34	0.08
Site #27	8/6/89	1280	21.2	5.01	0.32	LD	0.10	0.05
Site #30	8/6/89	1080	21.6	5.37	0.35	LD	0.22	0.04
Site #32	8/6/89	1040	21.3	5.23	0.28	LD	0.14	0.04
$Avg \pm std$		NA	21.9 ± 1.4	4.8 ± 0.4	0.3 ± 0.1	2.0 ± 0.2	0.2 ± 0.1	0.06 ± 0.02
Range		NA	19.4-24.1	4.0-5.5	0.2-0.6	0.0-0.8	0.1-0.4	0.03-0.09
# samples		NA	N = 10	N = 10	N = 10	N = 10	N = 10	N = 10

[Fe] _T (mg/kg)	[Al] (mg/kg)	[F] (mg/kg)	[Cl] (mg/kg)	[SO4]T (mg/kg)	[HCO ₃] (mg/kg)	[SiO ₂] (mg/kg)	TDS [mg/kg]	SO₄/Cl
0.12	LD	0.37	26.0	11.9	LD	LD	40.3	0.46
0.38	LD	0.32	40.8	16.0	LD	3.29	65.8	0.39
0.35	LD	0.41	53.7	13.6	LD	1.65	76.1	0.25
ND	ND	0.28	28.4	19.9	LD	2.55	59.7	0.70
ND	ND	0.39	49.0	11.6	LD	2.55	72.8	0.24
ND	ND	4.21	28.3	46	LD	LD	93.8	1.63
0.14 ± 0.16	LD	1.0 ± 1.4	37.7 ± 10.8	19.8 ± 12.0	LD	2.51 ± 0.58	68.1 ± 16.3	0.61 ± 0.48
0.0-0.38	NA	0.3-4.2	26.0-53.7	11.6-19.9	NA	1.65-3.29	40-94	0.25-1.63
N=3	N=3	N=6	N=6	N=6	N=6	N=6	N=6	N=6
0.17	LD	LD	4.1	7.8	LD	1.65	18.5	1.89
ND	ND	0.06	5.1	6.8	1.3	2.55	23.4	1.32
ND	ND	0.03	7.7	1.7	LD	0.79	17.8	0.22
ND	ND	0.11	3.1	3.4	3.0	LD	11.1	1.08
ND	ND	0.13	12.7	3.45	LD	LD	17.0	0.27
ND	ND	1.03	10.2	9.13	LD	LD	22.2	0.89
0.03 ± 0.06	LD	0.23 ± 0.36	7.2 ± 3.4	5.4 ± 2.7	1.4 ± 1.2	0.83 ± 0.97	18.3 ± 4.0	0.95 ± 0.58
0.0-0.17	NA	0.0-1.03	3.1-12.7	1.7-9.1	0.0 ± 3.0	0.0-2.55	11-23	0.27-1.89
N = 1	N = 1	N = 5	N=6	N=6	N=6	N=6	N = 6	N=6
10.60	LD	10	3250	590	LD	31.2	4056	0.18
ND	ND	53	13100	220	LD	32.6	13812	0.02
ND	ND	112	20600	228	LD	48.5	21626	0.01
ND	ND	2.67	107	53.1	LD	9.36	185	0.50
LD	1.18	19.4	4140	166	LD	ND	4455	0.04
NA	NA	39.4 ± 40.1	8240 ± 7540	251 ± 201	LD	30.4 ± 14.0	8830±7810	0.15 ± 0.19
NA	NA	2.7-112	107-20600	53-590	NA	9.4-48.5	185-21626	0.04-0.50
N = 2	N=2	N=5	N=5	N=5	N=5	N=5	N=5	N=5
ND	ND	0.07	0.59	2.54	LD	6.00	11	4.31
ND	ND	LD	1.47	4.36	LD	3.00	10	2.97
ND	ND	LD	1.34	2.54	LD	4.50	9	1.90
ND	ND	LD	0.76	2.04	LD	4.50	8	2.68
ND	ND	LD	0.98	2.24	LD	7.50	11	2.29
ND	ND	LD	0.76	1.23	LD	6.00	9	1.62
ND	ND	LD	0.60	0.82	1.45	10.50	15	1.37
ND	ND	LD	0.33	0.40	0.90	7.50	10	1.21
ND	ND	LD	0.29	0.33	1.15	9.00	11	1.14
ND	ND	0.05	0.24	0.38	0.70	6.75	9	1.58
ND	ND	NA	0.74 ± 0.40	1.69 ± 1.2	0.42 ± 0.3	6.5 ± 2.1	10.2 ± 1.9	2.11 ± 0.94
NA	NA	NA	0.24-1.5	0.33-4.4	0.0-1.45	3.0-10.5	8.0-15.0	1.14-4.31
N = 0	N = 0	N = 10	N = 10	N = 10	N = 10	N = 10	N = 10	N = 10

¹Site #'s location are given on Fig. 1.

 $^{2}LD =$ below detection limit; ND = not determined; NA = not applicable.

once, occurring as small crystals in the dry vug of an altered sample of lahar. Comparison of fresh and altered lava samples collected at Site 25 (Table 7) indicates almost complete leaching of rock-forming

elements such as Na, Ca, Mg, Al and Si with concurrent enrichment in Fe, K, S, Cl, P, Pb and Ba.



Fig. 2. Areal distribution of acid precipitation at Poás Volcano. Light shaded areas of the western flank are affected by dilute acid rain (pH 3.0-5.0). The dark shaded area immediately west of the active crater marks the extent of the devegetated zone. The devegetated zones reflect the combined effects of the gas plume and intense acid rain (pH 1.0-3.0). Cerro Pelon is a 400-m-high fault scarp that redirects a significant portion of the gas plume westward, along the Rio Desagüe watershed.

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Table 5

Average pH, chloride and sulfate concentrations	for northwest flank acid rain for	r the period July 1989 to December 199)0'
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Location ²	Elevation (m)	pH (20°C)	[Cl ⁻] (mg/kg)	[SO ₄] _T (mg/kg)	SO₄/Cl (mg/mg)
2 km S of Site 16	1560	4.83 ± 0.87 4.10-5.95	2.97 ± 2.40 0.15-6.21	2.38 ± 1.46 0.30-3.91	1.46 ± 1.32 0.35-4.16
Site 16	1440	4.70 ± 0.77 3.70-6.02	3.07 ± 3.32 0.12 - 9.2	2.97 ± 3.95 0.36-13.5	N=0 1.40±1.18 0.25-3.86 N=0
Site 17	1420	4.88 ± 0.75 4.00-6.20	2.91 ± 3.12 0.09-10.5	1.69 ± 1.54 0.33-4.31	1.24 ± 1.23 0.13-3.67
Site 19	1320	4.35 ± 0.55 3.60-5.10	1.39 ± 0.75 0.35 - 3.01	N = 8 1.23 ± 1.06 0.40-2.93	N = 8 0.94 ± 0.70 0.34-2.50 N = 7
Site 27	1280	N = 7 4.63 ± 0.52 4.02–5.75	N = 7 0.91 ± 0.51 0.11-1.90	N = 7 1.21 ± 0.83 0.27 ± 2.54	N = 7 1.94 ± 1.92 0.36-6.58
Site 31	1080	N = 8 4.71 ± 0.59 3.80-5.50	N = 8 0.96 ± 0.57 0.25 ± 2.08	N=8 1.17 ± 1.10 0.33-4.02	N = 8 1.72 ± 1.75 0.39-5.15
Site 32	1040	N=9 5.22 ± 0.82 4.21-6.45	N=9 1.73 ± 1.43 0.10-4.31	N=9 0.40 ± 0.28 0.16-0.93	N=9 0.59±0.55 0.04-1.60
Site 33	990	N=5 5.14 ± 0.75 3.90-6.20	N=5 1.08 ± 0.76 0.12-2.27	N=5 0.85±0.51 0.16-1.51	N=5 0.97 \pm 0.46 0.55-1.70
All NW flank sites	NA	N=5 4.77 ± 0.74 3.60-6.45 N=57	N=5 1.90 ± 2.22 0.09-10.5 N=57	N=5 1.57 ± 2.02 0.16-13.5 N=57	N = 5 1.34 ± 1.37 0.04-6.58 N = 57

¹Analytical data given includes: average concentration \pm one σ ; Concentration range (min-max value); N=number of samples collected; NA=not applicable.

²Site #'s locations are given on Fig. 1.

4.6. Hydrogeology of the Rio Agrio watershed

Acid chloride sulfate spring waters of the Rio Agrio drainage basin are associated with lava-lahar sequences produced by the active crater and along contacts between active crater deposits and older deposits of Von Frantzius and pre-Von Frantzius age (Fig. 4). Source springs (Sites 25–26) for the southern tributary of Rio Agrio outcrop along a lava-lahar-lava sequence (total thickness 15–25 m) that is exposed in several small ravines at elevations between 1780 and 1830 m about 3 km from the active crater. The upper lava of the sequence is a dacitic andesite that can be traced back to the active crater in aerial photographs. Bulk chemical and petrographic characteristics of the dacitic flow are virtually indistinguishable from those of a lava flow exposed at the base of the northern wall of the active crater (Table 7). The age of the dacitic andesite is unknown; however ¹⁴C age-dating of a Botos tephra deposited just prior to the initiation of eruptive activity at the active crater by Prosser and Carr (1987) indicates that the flow is less than 7500 years old. The dacitic flow is underlain by a weathered lahar and a basaltic andesite lava that does not outcrop in the active crater.

Acid chloride sulfate springs of the southern tributary of Rio Agrio issue from the contact between the basal breccia of the dacitic andesite flow and the fractured, upper surface of the lahar. Attempts to correlate the lower lahar-basaltic andesite sequence with other flows on the northwestern flank were hampered by poor exposure. The sequence also did not correlate with lava-tephra-lahar sequences exposed by erosion and

Water type/ Sampling Interval	Temp. (°C)	ρ@20°C (g/cm³)	рН (20°С)	[Na] (mg/kg)	[K] (mg/kg)	[Ca] (mg/kg)	[Mg] (mg/kg)
Crater Lake	49.4 + 6.5	1.08 + 0.01	0.00 + 0.09	740 ± 460	260 + 110	1120+420	780 + 330
Brine	38-62	1.04-1.09	-0.03-0.36	420-2460	120-560	780-2340	490-1650
10/80 to 6/87	N = 48	N = 23	N = 30	N = 30	N = 30	N = 30	N = 30
Fumarole	360 ± 130	ND^2	1.06 ± 0.58	11.1 ± 17.2	9.2 + 9.8	29.6 + 49.9	3.0+3.5
Condensate	95603	NA	0.26-2.44	0.18-78.5	0.01-79.0	0.20-231	0.07-16.9
6/84 to 2/89	N = 23	NA	N = 23	N=23	N = 23	N = 23	N = 23
Active Crater	18.0 ± 3.9	ND	2.55 ± 0.34	49.7 ± 32.0	7.0 ± 31	587±66	55.6 + 26.6
Acid-SO₄ Seeps	14.0-23.8	NA	2.05-3.00	30.0-105	2.3-9.8	500-685	29.0-83.2
6/88 to 9/90	N = 4	NA	N = 4	N = 4	N = 4	N==4	N = 4

Table 6 Compositional data for Crater Lake Brine fumarole condensates and active crater acid sulfate waters¹

faulting in the canyon cut by Rio Desagüe. The dacitic andesite (Table 7) also outcrops about 2 km northeast of the active crater at an elevation of about 2200 m along Rio Angel (Fig. 4). However, no evidence of acid chloride sulfate waters were found in this area. Instead, several ambient temperature seeps of neutral sulfate composition (Site 23) were found flowing into Rio Angel.

The geology and stratigraphy of volcanic deposits associated with the Affluente de Agrio hot spring (Site 24) are uncertain due to poor exposure. The spring occurs at the head of a steep canyon that marks the contact between Von Frantzius and pre-Von Frantzius volcanic deposits. The presence of several faults and lineaments (inferred from aerial photographs) in the vicinity of this canyon (Fig. 4) indicates that some combination of structural and stratigraphic control is responsible for channeling hot brines of the summit hydrothermal system to this area of the northwestern flank.

The Rio Agrio drainage basin has the third highest flow per unit area $(0.115 \text{ m}^3/\text{km}^2)$ of all rivers draining the flanks of Poás despite having a hydraulic gradient (0.15 km/km) that is slightly below the average cal-



Fig. 3. $\delta D - \delta^{18}O$ data for Poás waters. Data from Rowe (1994).

[Fe] _T (mg/kg)	[A]] (mg/kg)	[Br] (mg/kg)	[F] (mg/kg)	[Cl] (mg/kg)	[SO₄] (mg/kg)	[SiO ₂] (mg/kg)	[B] (mg/kg)	TDS (mg/kg)
1240 ± 540 730-2600	2290±1550 10906700	63.8±5.8 59.0±75.1	1270±240 810–1820	22100 ± 4400 14200-35900	59500±12100 36900-82900	234±67 110-320	17.0±7.2 9.2-29.8	87700 ± 13600 59000 ± 126200
N = 30	N = 30	N = 5	N = 32	N = 48	N = 48	N = 10	N = 7	N = 48
12.5±15.1 0.44~76.0	21.8±24.5 0.58-116	5.6±4.8 0.50-17.0	114±180 0.60603	5760±5930 237-19100	3180±3930 65-11500	114±121 1.0-500	NA ND	9490±9990 580-31000
N = 23	N = 23	N = 21	N=23	N=23	N=23	N=23	ND	N = 23
97.1±84.3	146±65.6	0.47 ± 0.04	33.7 ± 12.9	366 ± 282	2760 ± 470	116±19.5	0.27 ± 0.04	4180 ± 960
32.6-239	91.3-252	0.42-0.51	20.6-46.5	142-837	2250-3310	98.6-144	0.23-0.31	32405330
N = 4	N=4	N=2	N=4	N = 4	N = 4	N=3	N=2	N = 4

¹Analytical data given includes: Average concentration \pm one σ ; Concentration range (min-max value); N = number of samples collected. ²NA = not applicable; ND = not determined.

culated for all flank drainage basins at Poás (0.16 km/ km) (Table 8). Analysis of discharge data as a function of elevation for Rio Agrio indicates that the river is a gaining stream until just before it reaches its confluence with Rio Toro at an elevation of 1280 m (Site 27). Source springs on the southern tributary of Rio Agrio (Site 25) possess an aggregate flow of approximately 116 L/s which increases to 462 L/s just below the confluence between Agrio and the Affluente de Agrio (1510 m) and 934 L/s near Site 27 (1280 m). Comparison of source spring chemistry (Site 25) for the southern Rio Agrio tributary with the solute composition of Rio Agrio at Site 27 reveals almost no dilution despite an eight-fold increase in stream discharge (Tables 3 and 8). This indicates that baseflow recharging the southern tributary is groundwater whose chemical characteristics closely match that of Rio Agrio at the base of the northwestern flank. It also indicates that mixing with lower-elevation, near-neutral pH surface waters is insignificant. In contrast, the northern tribu-

Table 7

Composition of the fresh and altered dacitic andesite for samples collected from both the active crater and northwest flank

Location:	Active crater	Site 25	Site 25	Enrichment factor C_{alt}/C_{unalt}^{1}	
Rock type:	Dacitic	Dacitic	Altered dacitic		
	andesite	andesite	andesite		
SiO_2 (wt.%)	64.57	64.20	22.60	0.35	
TiO_2 (wt.%)	0.50	0.53	0.57	1.29	
Al_2O_3 (wt.%)	15.80	16.20	2.63	0.16	
Fe_2O_3 (wt.%)	5.16	5.40	38.0	7.04	
MnO (wt.%)	0.10	0.13	0.04	0.31	
MgO (wt.%)	1.67	1.93	0.40	0.21	
CaO (wt.%)	4.38	4.91	0.04	0.01	
Na ₂ O (wt.%)	3.37	3.59	0.55	0.15	
K ₂ O (wt.%)	2.57	2.53	6.98	2.76	
P_2O_5 (wt.%)	0.16	0.16	1.27	7.94	
LOI (wt.%)	1.53	0.08	21.08	NA	
S (wt.%)	ND	0.09	5.92	65.8	
Cl (ppm)	ND	85	390	4.59	
Cu (ppm)	79	67	63	0.94	
Zn (ppm)	ND	51	66	1.29	
Pb (ppm)	ND	10	872	87.2	
Ba (ppm)	976	1050	2430	2.31	

 ${}^{1}C_{alt}$ = element concentration in altered sample. C_{unalt} = element concentration in unaltered sample.



Fig. 4. Schematic geologic map of the summit and upper flank portions of Poás Volcano showing major geomorphic contacts, faults, and lineaments as deduced from field reconnaissance mapping, interpretation of aerial photographs and the interpretation of summit geology and stratigraphy given by Prosser (1983) and Prosser and Carr (1987).

tary, the Affluente de Agrio (102 L/s) exhibits a 20fold increase in flow that is accompanied by a 10-fold decrease in solute concentration between the source spring (Site 24) and its confluence with the southern tributary of Rio Agrio (1510 m). This indicates that inputs of acid brine along the northern tributary of Rio Agrio are largely restricted to the Affluente hot spring at Site 24.

 Table 8

 Discharge and related physical data for major drainage basins of Poás Volcano

Location/Site # ¹	Elevation (m)	Discharge ² (L/s)	Flow error (L/s)	Basin area (km ²)	Flow/Area (m ³ /km ²)	Av. hydraul gradient (km/km)
Rio Mary Aguilar-Site #1	910	113	14	5.89	0.019	0.18
Rio Cariblanco-Site #2	820	1860	142	20.56	0.090	0.30
Rio Angel-Site #3	860	1380	112	20.81	0.066	0.21
Rio la Paz Grande-Site #4	1480	1390	109	22.52	0.062	0.16
Ouebrada Azufre-Site #5	1860	< 10 (est)	5	ND ⁴	ND	ND
Rio Prendas-above Site #6	1340	101	8	9.65	0.010	0.12
Rio Cabuyo-Site #7	1080	47	5	4.35	0.011	0.09
Rio Tacams-Site #8	1040	36	4	5.27	0.007	0.11
Rio Achiote-Site #9	1080	34	3	8.26	0.004	0.13
Rio Rosales-Site #10	1100	57	58	27.01	0.002	0.12
Rio Vigia-Site #11	1220	91	8	17.42	0.005	0.12
Rio San Juan-Site #12	1140	109	10	11.13	0.010	0.10
Rio Sarchi-Site #13	1400	627	58	15.86	0.040	0.09
Rio Trojas-Site #14	1040	200	27	19.09	0.010	0.09
Rio Toro-Site #15	1440	715	55	16.35	0.044	0.16
Rio Gorrion-Site #16 ($N=3$)	1440	397	37	7.45	0.053	0.11
Rio Anonos-Site #17	1420	332	28	9.65	0.034	0.16
Rio Desague-Site #19 ($N=4$)	1320	478	43	11.86	0.040	0.14
Rio Desague-Site #20	1720	71	6	ND	ND	ND
Rio Desague-Site #21	2300	<10 (est)	ND	ND	ND	ND
Naciente de Mirador-Site #22	2390	<5 (est)	ND	ND	ND	ND
Rio Angel Spring #1-Site #23	2300	<5 (est)	ND	ND	ND	ND
Naciente de Affluente-Site #24	2000	<5 (est)	ND	ND	ND	ND
Site 25-ACS-springs of Agrio	1800	116	20	ND	ND	ND
Agrio spring-Site #26	1510	< 10 (est)	ND	ND	ND	ND
Affluente de Agrio $(N=3)$	1510	102	16	2.02	0.050	0.18
Rio Agrio near Site #26 ($N=3$)	1515	374	56	2.85	0.131	0.16
Rio Agrio-Site #27	1290	934	81	8.14	0.115	0.16
Rio Agrio/Toro confl-Site #28	1280	4570	650	ND	ND	ND
Quebrada Pilas-below Site #29	1220	621	79	3.30	0.188	0.27
Rio Gata-Site #30	1370	586	46	11.86	0.049	0.22
Rio Gata-Site #31	1080	1470	400	11.86	0.124	0.14
Rio Claro-Site #32	1040	244	23	2.48	0.098	0.17
Rio Pozo Azul-Site #33	990	107	10	2.97	0.036	0.19

¹Flow measurements made between January 1988 and March 1990. Number of measurements in excess of one given in parentheses. ²(est) indicates visual flow estimate.

³Average hydraulic gradient over basin = $(\Delta L)/(\Delta H)$, where L is the length of the river basin and H is the vertical head drop over the the length of the basin.

 $^{4}ND = no data.$

5. Discussion

5.1. Origin of acid chloride sulfate waters

Comparison of the chemical characteristics of the various water types that occur at Poás indicates that acid chloride sulfate waters of the Rio Agrio drainage basin are genetically related to acid brines formed in the summit hydrothermal system (Table 9). A plot of sulfate versus chloride concentrations reveals a clear linear trend that is defined by acid chloride sulfate waters of the Rio Agrio drainage basin and the average composition of crater-lake brine (Fig. 5). The linear trend falls on a mixing line calculated by assuming progressive dilution of average crater-lake brine with dilute groundwater. The dilute groundwater has chloride and sulfate concentrations equivalent to the average chloride and sulfate concentration of neutral

Water type ¹	рН	[F] (mg/kg)	[Cl] (mg/kg)	SO4] (mg/kg)	F/Cl mg/mg	SO ₄ /Cl mg/mg	Cl/B mg/mg	Ca/SO ₄ mg/mg
Average Lake Brine ²	0.00	1270	22100	59500	0.057	2.69	1247	0.018
Fumarole Condensate ²	1.06	114	5670	3180	0.020	0.55	ND ⁶	0.009
Active Crater AS Seeps ²	2.55	33.7	366	2760	0.092	7.54	1355	0.210
Affluente ACS (Site 24) ³	1.46	152	5930	12000	0.026	2.02	2695	0.035
Rio Agrio ACS (Site 27) ³	2.34	25.3	460	1180	0.055	2.56	1394	0.067
West Rim Acid Rain ⁴	0.99	39.4	8240	251	0.005	0.03	ND	0.060
Northwest Flank AS ⁵	3.94	1.21	28.6	131	0.042	4.56	660	0.210
Northwest Flank NS ⁵	7.20	0.10	2.9	10.1	0.035	3.39	98	0.880
Neutral bicarbonate ⁵	6.85	0.37	7.1	41	0.049	5.86	311	0.350

Summary of key geochemical properties of Poás water types¹

¹Water type definitions are given in Table 2.

²Data from Table 6.

³Data from Table 3.

⁴Average values calculated from data in Table 4.

⁵Average values calculated from data in Table 3.

⁶ND = No data.

bicarbonate waters (Table 9). Similar mixing trends are indicated by other conservative solute ratios, such as F/Cl and Cl/B (Table 9).

Crater lake brine is used to represent the composition of acid brines in the summit hydrothermal system because heat and water mass balance calculations (Rowe et al., 1992a) indicate that lake brines are rapidly circulated through the uppermost, liquid-dominated zones of the summit hydrothermal system. Thus, brine leaking from the active crater into flank aquifers



Fig. 5. Plot of Log $[SO_4]_T$ vs Log [C1] for Poás waters. Mixing line calculated by assuming progressive dilution of average crater lake brine with water having 2.9 ppm Cl and 10.1 ppm sulfate (see text for details of calculations). High *T* fum refers to the average composition of 15 fumarole condensates collected by Gemmell (1987) and Prosser (1983) from near-magmatic temperature (700–850°C) fumaroles of the 1953– 1954 cinder cone over the period 1981–1983. Low *T* fum (200–550°C) refers to the average composition of fumarole condensates collected between June 1984 and February 1989 (Table 6).

Table 9

is likely to be compositionally similar to crater-lake brine. Direct derivation of Rio Agrio acid chloride sulfate waters by seepage and mixing of crater-lake brine with meteoric water along the Rio Agrio aquifer is strongly supported by the geologic evidence presented in the results section. Chloride and sulfate concentrations of neutral bicarbonate waters on the northwestern flank are considered to be representative of dilute flank groundwater. Sulfate and chloride concentrations of the neutral bicarbonate groundwater are also similar to the chloride and sulfate concentrations of acid rain samples collected at the east rim of the active crater and at the base of the northwest flank (Tables 4 and 5). The chloride and sulfate concentrations of neutral bicarbonate waters are less than those observed in west rim acid rain samples. However, these samples are unlikely to be representative of the composition of acid rain falling on the upper portions of the west flank (see below). Note that the slight upward bend of the mixing curve shown on Fig. 5 is caused by the difference between the SO_4/Cl ratio of the average lake brine (2.56) and average neutral bicarbonate water (3.39).

Most acid rain samples collected at both summit and flank sites plot below the calculated mixing line indicating enrichment in chloride over sulfate relative to the crater lake brines (Fig. 5). High chloride concentrations of the west rim acid rain waters reflect enhanced volatilization of HCl from the crater lake surface. Volatilization of HCl was caused by sharp increases in lake temperature and acidity that accompanied disappearances of the crater lake in April 1989 and 1990 (Rowe et al., 1992b). Release of HCl from the lake surface was minimal before mid-1988; prior to mid-1988 the composition of acid rain was controlled by the interaction of rain water with the plume of volcanic gas and steam issuing from the 1953–1954 pyroclastic cone.

The extreme composition of acid rain samples collected on the west rim is directly related to the location of the sample site. The rain gauge used to sample acid rain on the west rim was placed on the edge of the west wall of the active crater directly downwind of the acid vapor plume emitted by the lake. It is doubtful, however, that the extreme conditions which existed at the edge of the west rim existed more than a few hundred yards downwind of the collection site as prevailing winds rapidly dispersed the acid plume. More representative data on the long-term composition of acid rain falling on the area west of the active crater are given by Rosario-Alfaro et al. (1986). These workers report that 17 samples collected between May 1985 and June 1986 at a location 1 km southwest of the active crater had an average pH of 2.90, and average sulfate and chloride concentrations of 36 and 22 ppm, respectively. Acid rain samples collected at the base of the northwestern flank also plot below the mixing line shown on Fig. 5. In contrast to the chloride-enriched rain samples collected at the summit, these waters have SO_4/Cl ratios greater than one (Tables 4 and 5). Because HCl is more soluble in water than SO₂, it is partitioned into rain water faster than sulfur dioxide. Hence, the SO_4/Cl ratio of the gas plume will become greater as distance from the active crater increases. Similar trends have been observed at Masaya Volcano, Nicaragua (Johnson and Parnell, 1986) and Nevado del Ruiz Volcano, Columbia (Parnell and Burke, 1990). The data collected at Poás shows that acid rain that affects the summit and northwest flank is either too dilute or is too enriched in chloride to be a potential source fluid for the acid chloride sulfate springs of the Rio Agrio drainage basin.

Subaerial fumarole compositions at Poás are a mixture of magmatic gases (SO₂, H₂S, CO₂), and halogenrich vapor (HCl, HF) distilled from hydrothermal brine at depth (Rowe et al., 1992a). Low-temperature (200-550°C) fumaroles are extremely enriched in chloride and fluoride because boiling of brines at depth causes mobilization of highly volatile HCl and HF in preference to relatively non-volatile H₂SO₄. Thus, low-temperature fumaroles that contain a significant brine component will be enriched in chloride relative to sulfur and can not be primary source fluids for the acid chloride sulfate waters of the Rio Agrio drainage basin. In contrast, data reported by Gemmell (1987) and Prosser (1983) indicates that higher-temperature fumaroles are enriched in sulfur relative to chloride and have condensate sulfur to chloride weight ratios between 3 and 15. S_T/Cl and F/Cl weight ratios obtained by Delorme (1983) from magmatic temperature gas samples (960°C) collected in June, 1981 are 3.4 and 0.06 respectively, quite similar to the average lake ratios of 2.69 and 0.055 (Table 6). Geochemical modeling by Rowe (1991) indicates that acid brines similar to those found in the crater lake are readily formed by condensation of such high-temperature magmatic gas into dilute groundwater. It is therefore possible that Rio Agrio acid chloride sulfate waters are derived from degassing of magmatic gases directly into shallow parts of the Rio Agrio drainage basin. However, surface features indicative of shallow fumarolic activity such as steaming ground or boiling temperature hot springs are not found in the Rio Agrio drainage basin. This observation, combined with the near ambient temperatures exhibited by most of the Rio Agrio source springs suggests that direct input of magmatic gases into northwest flank aquifers is minimal.

5.2. Acid sulfate waters

Slightly thermal acid sulfate springs and seeps found in the active crater are enriched in sulfate over chloride and plot above the calculated mixing line shown on Fig. 5. These waters are saturated with respect to gypsum (see below) and have Ca/SO_4 concentration ratios that are an order of magnitude higher than crater lake and fumarole condensate waters (Table 9). Extremely high calcium concentrations are attributed to the dissolution of gypsum which is found in abundance in the fumarolic deposits of the 1953-1954 cone and in old lake sediments and weathered tephra sequences exposed in the walls of the active crater. However, the Ca/SO₄ ratio of these waters is significantly less than one indicating that most sulfate is not derived by the dissolution of gypsum. Instead, the majority of the sulfate in the crater acid sulfate waters is probably derived from the oxidation of sulfur gases or weathering of native sulfur and alunite $[(Na,K)Al_3(SO_4)_2(OH)_6]$. Native sulfur is abundant in zones of low temperature fumaroles and is a major constituent of recently formed lake sediments. Alunite is found in old lake sediments exposed in the walls of the active crater.

The origin of acid sulfate waters in the Rio Desagüe and Quebrada Pilas drainage basins is less certain. Flank acid sulfate waters may be formed by mixing crater acid sulfate waters with dilute meteoric water that has SO_4/Cl , F/Cl and Cl/B ratios less than those of the crater acid sulfate waters (neutral bicarbonate waters–Table 3, dilute acid rain–Table 4). However, simple two-component mixing calculations involving the dilution of crater acid sulfate waters with dilute acid rain or neutral bicarbonate waters does not yield consistent dilution factors for the conservative components considered (F, Cl, SO_4 and B). Subsurface oxidation of H₂S, native sulfur, or sulfides (e.g., pyrite) present

in altered volcanics is discounted on the basis of sulfur isotope data reported by Rowe (1994). The δ^{34} S values of sulfate in Rio Desagüe (Site 19) and Quebrada Pilas acid sulfate waters (Site 29) were 4.1 and 11.2%, respectively. The δ^{34} S values of native sulfur and low temperature (95°C) H₂S collected in the active crater ranged from -9 to -12% (Rowe, 1994). Low-temperature inorganic oxidation of H₂S, native sulfur, or metal sulfides is accompanied by minimal fractionation (Ohmoto, 1986); therefore, sulfate produced by oxidation of native sulfur or H₂S would be isotopically light. Instead, the observed δ^{34} S value of dissolved sulfate in Rio Desagüe river water is similar to the δ^{34} S value of sulfate in gypsum found coating canyon walls in the upper reaches of Rio Desagüe ($\delta^{34}S = 7.1\%$). The sulfur in this gypsum is hypothesized to be derived from SO₂ in the gas plume (Rowe, 1994). Note that the heavier δ^{34} S value of Quebrada Pilas sulfate is in the range of δ^{34} S values obtained for SO₂ gas samples (7.0 to 14.5%) collected from subaerial fumaroles in the active crater (Rowe, 1994).

The most reasonable hypothesis for sulfate enrichment in acid sulfate waters of the northwest flank of Poás is sulfate loading of soils and shallow groundwater in the upper reaches of the Anonos, Desagüe, Pilas, and Gata drainage basins (Fig. 2). The dominant fraction of sulfate loading is attributed to dry deposition of gaseous SO_2 . Because oxidation and hydration of SO_2 is slow relative to the lateral transport rate of plume SO₂ across the western flank, it is likely that some fraction of SO_2 is removed from the gas plume by adsorption of SO₂ onto plant and soil surfaces. Subsequent rain events convert this SO₂ to sulfuric acid and flush it into the soil horizon. Another mechanism for depositing SO₂ from the plume is gravitational settling of small dust particles and mineral fragments entrained in the plume. Such particles are almost always have a thin layer of water vapor that absorbs SO_2 (and HCl) producing a coating of sulfuric acid (cf. Casadevall et al., 1984). Because seasonal winds and topographic barriers direct the SO₂-rich plume west-northwest, acid and neutral sulfate waters are largely confined to the northwestern flank of Poás.

Sulfate loading by the above mechanisms will be reflected in the sulfate concentrations of soils collected near volcanic vents. Parnell and Burke (1990) have shown that soils downwind of the gas plume emitted by Nevado del Ruiz volcano are greatly enriched in sulfate. The enrichment is partially due to the affinity of sulfate for anionic exchange sites in allophanic clays under acidic soil conditions. During high pH rain events sulfate is displaced from the exchange sites into the soil solution. Pore waters collected from the Ruiz soils exhibited SO_4/Cl ratios that were a factor of seven greater than the SO_4/Cl ratio of the source acid rain. This enrichment was ascribed to dry deposition of SO_2 from the plume and preferential adsorption of SO_2 derived sulfate from acidic pore water. The results obtained at Nevado del Ruiz support the hypothesis that ambient temperature, acid sulfate waters of the northwest flank originate by flushing of sulfate-rich pore and groundwater into flank streams and rivers.

5.3. Neutral sulfate waters

Neutral sulfate waters, the majority of which are found on the northwestern flank, are readily derived by neutralization of acid sulfate waters. Neutralization can occur through water-rock reactions or by mixing of acid sulfate water with neutral bicarbonate water. Rio Angel river water is the only neutral sulfate water found on the east flank of Poás. The mouth of Rio Angel originates at Botos lake and its upper reaches are affected by acid rain generated in the active crater (Fig. 2) Further downstream, Rio Angel receives the input of several ambient temperature neutral sulfate springs and seeps (Site 23). The SO_4/Cl ratio of these springs (16.0 at Site 23; Table 3), is much higher than the average SO_4/Cl ratio (4.6) of acid and neutral sulfate waters of the northwestern flank. The SO_4/Cl ratio is however, very similar to the SO_4/Cl ratio exhibited by the Quebrada Azufre spring on the east flank of Poás (Site 5 $SO_4/Cl = 14.8$). Sulfate in water of the Quebrada Azufre spring results from the oxidation of H₂S derived from low-level degassing associated with Barva Volcano (as indicated by the strong smell of H₂S associated with the spring). The ratio data suggest that neutral sulfate waters of the upper Rio Angel springs are derived by neutralization of acid sulfate waters that were initially generated by the oxidation of H_2S .

5.4. Geochemical controls on flank acid water solute compositions

Saturation indices of both primary and secondary alteration minerals were evaluated by use of the aqueous speciation model WATEQ4F (Ball and Nordstrom, 1991) to check for possible mineralogic controls on spring and river water chemistry. The saturation index (SI) is defined by the following equation:

$$SI = \text{Log}\frac{IAP}{K_{\text{T}}}$$
(1)

where *IAP* is the ion activity product of the mineral, and K_T is the thermodynamic equilibrium constant evaluated at the collection temperature of the water sample (Nordstrom and Munoz, 1986). If the *SI* value is greater than zero, the water is supersaturated with respect to the particular mineral and precipitation of the mineral is possible. If the *SI* value is less than zero, the water is undersaturated and dissolution of the mineral is possible. *SI* values equal to zero indicate equilibrium between water and the mineral.

WATEO4F uses an ion association model to calculate the distribution of aqueous species used in evaluation of the ion activity product. Speciation is evaluated as a function of temperature and ionic strength. Calculations are constrained by relevant mass balance and mass action equations (Truesdell and Jones, 1974). Activity coefficients used to correct analytical concentrations for ionic strength effects are estimated with an ionic strength dependent form of the Debye-Hückel equation (Robinson and Stokes, 1965) and are considered to be reliable to ionic strengths approaching 1.0 molal. The most concentrated water considered in this study, the acid chloride sulfate water of the Affluente hot spring (Site 24), has an ionic strength approaching 0.5 molal after the activities of free and complexed ions are taken into account. Remaining acid chloride sulfate and crater acid sulfate waters have ionic strengths less than 0.2 molal, well within the accuracy of the modified Debye-Hückel equation used by the WATEO4F model.

Acid chloride sulfate waters of the Rio Agrio drainage basin are extremely undersaturated with respect to primary silicate phases such as feldspar, pyroxene, and olivine. Ferric iron concentrations of both acid chloride sulfate and acid sulfate waters appear to be regulated by equilibrium with colloidal iron hydroxide (Fox, 1988) (Fig. 6a). The predominant form of dissolved iron in the acid chloride sulfate waters is ferric iron and its complexes (Fe^{3+}/Fe^{2+} ratios 25 to > 100–Table 3). This is consistent with the low pH and high concentrations of dissolved oxygen (6.5–8.0 ppm)



Fig. 6. Plots of log IAP/K against pH for: (a) amorphous $Fe(OH)_{2,35}$; (b) amorphous silica; (c) potassium jarosite; and (d) gypsum for acid chloride sulfate waters (filled triangles), flank acid sulfate waters (filled circles), neutral sulfate and neutral bicarbonate waters (unfilled triangles), and crater acid sulfate waters (unfilled squares).

observed in these waters. An exception is the Affluente de Agrio hot spring (Site 24) which possesses an Fe^{3+}/Fe^{2+} ratio of 0.17 and a dissolved oxygen concentration of 1.4 ppm. Eh values measured with a platinum redox electrode (Table 3) are in good agreement with those predicted from the Fe^{3+}/Fe^{2+} activity ratio, similar to results reported for acid mine waters by Nordstrom et al. (1979).

Acid chloride sulfate waters are saturated to slightly undersaturated with respect to amorphous silica although silica undersaturation increases as pH values rise (Fig. 6b). This result is consistent with experimental data which indicates that the solubility of volcanic glass in water is approximately equivalent to that of amorphous silica (Fournier, 1985a). Acid chloride sulfate and acid sulfate waters also appear to be in equilibrium with potassium jarosite (Fig. 6c). Although earlier studies (e.g., Nordstrom et al., 1979) had shown low-pH waters to be highly supersaturated with respect to jarosite, recent work by Alpers et al. (1991) has shown that the high levels of supersaturation indicated by the previous studies were caused by an error in the thermodynamic equilibrium constant of potassium jarosite. Reevaluation of the previous data indicates that most acid waters have saturation index values near zero and hence, are close to saturation with respect to jarosite.

SI values for gypsum approach saturation with decreasing pH indicating that this mineral provides an upper limit for calcium concentrations in acid sulfate and acid chloride sulfate waters (Fig. 6d). Acid sulfate waters of the active crater are saturated with respect to gypsum, consistent with the observation of gypsum crystals growing on rocks in contact with these waters. Crater-lake brines are also saturated with respect to gypsum, which is a common constituent of crater lake sediments (Brantley et al., 1987; Rowe, 1991). Levels of dissolved barium (5-10 ppb), lead (7-20 ppb) and dissolved phosphate (400 ppb-Pringle et al., 1993), are within one log unit of saturation with respect to barite (BaSO₄), anglesite (PbSO₄), and amorphous ferric phosphate, suggesting that precipitation of these phases may be regulating concentrations of these trace elements in the Rio Agrio spring waters.

Dissolved aluminum concentrations of acid chloride sulfate and acid sulfate waters are at levels indicating saturation or slight supersaturation with respect to the aluminum-hydroxysulfate mineral jurbanite $(Al(OH)SO_4 \cdot 5H_2O)$ (Fig. 7a). This mineral has been identified in acid sulfate soil horizons and is also found in streams where aluminum-rich acid mine drainage mixes with neutral pH streams (Nordstrom, 1982). Equilibrium with an amorphous form of jurbanite may provide an upper limit on concentration of dissolved aluminum in low temperature, acidic, sulfate-rich waters although kinetic considerations may prevent the precipitation of jurbanite in systems with short residence times (Nordstrom, 1982; Nordstrom and Ball, 1986). With increasing pH, other secondary Al-bearing phases such as alunite (Fig. 7b), gibbsite (Fig. 7c), and kaolinite (Fig. 7d) become saturated or oversaturated. Neither jurbanite nor any other secondary aluminous phases were identified in the altered lava/lahar samples collected at Sites 24 and 25; however, the Xray diffraction techniques used by this study would not have detected any amorphous phases in the altered rocks). Energy-dispersive spectrum analysis (SEM-EDS) of the amorphous white precipitate found downstream mixing zones of acid and neutral pH waters indicates that the amorphous precipitate is composed of approximately equivalent amounts of Al and Si with only minor amounts of S. These data indicate that the white precipitate is not an aluminum sulfate phase and is probably a mixture of amorphous aluminum hydroxide and silica.

5.5. Evaluation of Rio Agrio aquifer properties

In this section, estimates of the hydrogeologic properties of the aquifer connecting the summit hydrothermal system to source springs of the southern tributary of Rio Agrio are made to provide constraints on numerical modeling of solute transport from the active crater area to flank springs by Sanford et al. (1995, this issue). One of the most important parameters in any hydrologic study of an aquifer is determination of the hydraulic conductivity of the aquifer. The hydraulic conductivity K (in m/s) can be estimated from the following equation if the mean residence time t (in seconds) of water in the aquifer can be estimated:

$$K = \frac{n_o \Delta L^2}{t \Delta H}$$
(2)

where n_o is the average active porosity (dimensionless), and ΔL and ΔH are the length and head drop of the flow path (in meters) respectively (Davis and Bentley, 1982). The residence time of acid chloride sulfate spring water in the Rio Agrio aquifer system was constrained by two techniques: (1) tritium dating; and (2) monitoring of SO₄/Cl ratios of Rio Agrio.

Two water samples for tritium analysis were collected from the same spring at Site 25. The first, collected in July 1989 had a tritium concentration of 5.0 ± 0.6 TU (TU = 1 tritium unit = 1 atom ³H per 10¹⁸ atoms H₂O). The second, collected in March 1990, possessed a tritium concentration of 2.34 ± 0.15 TU. Site 24 acid chloride sulfate water, also sampled in March 1990, had a similar tritium concentration



Fig. 7. Plots of log IAP/K against pH for: (a) jurbanite; (b) alunite; (c) gibbsite; and (d) kaolinite for acid chloride sulfate waters (filled triangles), flank acid sulfate (filled circles), and crater acid sulfate waters (unfilled squares).

 $(2.1 \pm 0.3 \text{ TU})$. A sample of rain water, collected in March 1990, possessed a tritium concentration of $1.77 \pm 0.15 \text{ TU}$. Two end-member models can be used to place limits on the mean residence time of the Poás spring water: the piston-flow model, and the wellmixed model (Pearson and Truesdell, 1978). The piston-flow model assumes that there is no mixing of the water along the flow path from the point of recharge to the point of discharge. The tritium concentration of discharge waters is controlled by the concentration of tritium in the input water and the radioactive decay of tritium along the flow path. The well-mixed model assumes that recharge to the aquifer is completely mixed with water already in the aquifer and that fluid



Fig. 8. (a) Piston-flow and well-mixed model curves for 1990 based on tritium input curves of Goff et al. (1987, 1988). Note that sample collected on 7/89 can only be modeled with the piston flow curve whereas the sample collected on 3/90 can be modeled by either end-member model. (b) Tritium input function derived from monthly precipitation samples collected at Howard Air Force Base, Panama. Vertical shaded areas indicate time intervals where a 2.6 TU decrease in the tritium input curve is observed over an eight month period (1973 and 1978–1979).

at the discharge point has the composition of the mixed fluid.

Both the piston-flow and the well-mixed model have been evaluated using Central American tritium data by Goff et al. (1987, 1988) in their studies of Honduran geothermal systems. Curves for the piston-flow and well-mixed models calculated from the tritium input functions estimated by Goff et al. (1987) for the year 1990 indicate that water samples that have a tritium concentration greater than 3.0 TU cannot be waters from a well-mixed reservoir (Fig. 8a). Thus, the July 1989 sample collected at Site 25 must possess a significant piston-flow component whose age is between 17 and 20 years. Age estimates for the March 1990 sample collected at Site 25 can however, be estimated by use of the well-mixed model (3 to 50 years). However, based on the tritium concentration of the July 1989 sample it appears that the well-mixed reservoir model is inappropriate for the Rio Agrio aquifer. Hence, these estimates are discarded. Instead, the 2.6 TU difference observed between the July 1989 and March 1990 samples probably reflects seasonal variations in the tritium



Fig. 9. Temporal variation of SO_4/Cl concentration ratios for crater-lake brine (unfilled circles) and Rio Agrio river waters (filled triangles) collected at Site 27. Lake brine data from Rowe et al. (1992b). Inverted triangles at top of figure mark disappearance of the crater lake in April 1989 and 1990.

concentration of rain water. The tritium concentration of rain water is known to vary seasonally; tritium levels are typically highest in the rainy season (May–November) and lowest during the dry winter months (December–April) (International Atomic Energy Agency, 1975, 1979, 1983). If piston flow conditions are assumed to apply to the Rio Agrio aquifer, the possibility exists that a more precise date can be obtained by examining Central American tritium data acquired on a monthly basis.

The most complete tritium data available for Central America is for rain-water samples collected at Howard Air Force base in Panama over the years 1969 to early 1988 (International Atomic Energy Agency 1973, 1975, 1979, 1983, 1986, 1989). The data set consists of tritium values measured on bulk precipitation samples collected over one month time periods. At least two intervals are noted (within the error of the data). where seasonal variations in the tritium concentration of Panamanian rain result in a 2.6 TU difference over an eight-month time interval as is observed for the Site 25 tritium data (Fig. 8b). These intervals occurred over 1973-1974 and 1978-1979 indicating mean residence times of approximately 17 and 12 years respectively. Extrapolation of tritium data for the last 5 months of 1987 (no data after 12/87) indicates that the Site 25 spring water could be as little as three years old. Note

that the multiple age estimates made from the pistonflow model are caused by seasonal and yearly variations in atmospheric tritium levels. Monthly variations were not accounted for by the piston flow model of Goff et al. (1987, 1988) (Fig. 8a) whose input function represented a smoothed fit to weighted-mean annual tritium values.

An additional constraint on the age of the Rio Agrio spring waters is provided by monitoring temporal trends in the SO_4/Cl ratio of Rio Agrio river water. Sharp increases in the crater lake SO_4/Cl ratio were observed prior to the recent disappearance of the lake (Rowe et al. 1992b). These changes should be reflected in Rio Agrio river and spring waters due to the hydraulic connection that exists between the summit hydrothermal system and the Rio Agrio drainage basin. However, comparison of temporal trends in crater lake brine and Rio Agrio SO_4/Cl ratios reveals no significant changes in the SO_4/Cl ratio of Rio Agrio through early 1991 indicating a minimum residence time of at least 3 years (Fig. 9). This result is consistent with the minimum age estimate provided by the tritium data.

Hydraulic conductivities of the Rio Agrio aquifer calculated with Equation One ranged from 10^{-5} to 10^{-7} m/s. These values are based on a mean residence time of 3 to 17 years, an active porosity of 5 to 25 percent, a horizontal flow distance of 3.25 km (distance

between the active crater and Site 25 springs) and a vertical head drop of approximately 450 m (elevation change from base of lake to Site 25 springs). The active porosity estimate is taken from porosity measurements made on fresh to moderately weathered lavas and ignimbrites of the southern flank of Barva Volcano by Foster et al. (1985). These porosity estimates should be representative of volcanic strata which comprise the Rio Agrio aquifer although the Rio Agrio rocks may be even more porous because of the intense dissolution that accompanies flow of acid chloride sulfate groundwater through these deposits. The hydraulic conductivities calculated above are similar to those reported for fractured and brecchiated lava and lahar units at the base of the northwestern flank that were determined during aquifer testing of wells drilled for a hydroelectric project involving Rio Toro (Sites 15, 28, 34-Fig. 1) (Estrada-Barrios et al., 1989).

The age estimates can also be used to derive a crude estimate of the quantity of acid groundwater in the Rio Agrio aquifer. If flow in the aquifer is assumed to be at steady state then the reservoir volume (V) will be equal to the steady-state discharge rate (q) times the mean residence time (t) of the fluid in the aquifer (e.g., V = qt; Pearson and Truesdell, 1978). Site 25 source springs have an aggregate discharge of approximately 116 L/s (Table 8). For residence times of 3 or 17 years the above equation yields fluid volumes between 0.01 to 0.06 km³ for the Rio Agrio aquifer.

5.6. Mass transfer rates and volatile fluxes of the Rio Agrio watershed

The hydrologic and chemical link between the Rio Agrio drainage basin and the crater lake can be used to estimate the amount of dissolution that occurs beneath the active crater, and in the Rio Agrio aquifer. Mass transfer rates are determined by taking the average discharge of Rio Agrio measured at the base of the northwest flank (Site 27) and multiplying it by the average concentrations of rock-forming elements in Rio Agrio (Table 3). The average baseflow discharge of Rio Agrio over the period 1987–1990 at Site 27 was $930 \pm 85 \text{ L/s}$ (Table 8). Multiplying this discharge by the average concentrations of Na, K, Ca, Mg, Fe, Al, and Si (as SiO₂) in Rio Agrio at Site 27 (Table 3) yields an aggregate flux of 42 ± 4.2 metric tons/day. This flux represents the dissolution flux that results from dissolution of rock beneath the active crater and in the Rio Agrio aquifer.

Estimates of the proportion of rock dissolving beneath the active crater to that dissolving during flow in the flank aquifer can be made by correcting the concentrations of rock-forming elements observed in Rio Agrio source springs by the concentrations of these elements in the initial mixture of meteoric water and acid brine. To estimate the amount of each element contributed by the hydrothermal brine component, an estimate of the amount of dilution occurring along the flow path must be made. This is accomplished by use of a chloride-based dilution factor. Chloride is chosen because it is assumed to behave conservatively along the flow path and negligible amounts of chloride are likely to be introduced into solution by dissolution of aquifer material (Rowe and Brantley, 1993). The chloride dilution factor is calculated by dividing the average concentration of chloride in the lake brine (22,000 ppm-Table 6) by the concentration of chloride in the Rio Agrio source springs (410 ppm-Table 3). The calculated dilution factor is 54; similar dilution factors are calculated from the concentrations of other conservative solutes such as boron, fluoride, and sulfate. To estimate the concentration of rock-forming elements in the initial solution, concentrations of rock-forming elements in the lake brine are divided by the chloridebased dilution factor. For example, dividing the average concentration of sodium in the lake brine (740 ppm-Table 6) by 54 indicates that 28 percent of the 49.6 ppm Na observed in the Rio Agrio source springs (13.7 ppm) was in the original brine-meteoric mixture whereas the remaining 72 percent (35.9 ppm) was derived from dissolution of flank aquifer wallrock (Rowe and Brantley, 1993).

The calculations described above indicate that about 28% of the flux of rock forming elements in the Rio Agrio source springs is derived from hydrothermal inputs while the remaining 72% is produced by dissolution and leaching in the Rio Agrio aquifer. This yields annual aggregate fluxes of rock-forming elements of approximately 4.3×10^3 t/yr from the summit hydrothermal system and 1.1×10^4 t/yr from dissolution along the flank aquifer. Assuming that the dissolving rock has a bulk density of 2600 kg/m³ (unfractured and non-vesiculated andesitic lava) results in the removal of approximately 1650 and 4300 m³ of rock-forming elements per year in the summit hydrothermal



Fig. 10. Rose diagram illustrating the chemical weathering fluxes at Poás Volcano. Units are metric tons of rock per day per km^2 of drainage basin.

system and flank aquifer, respectively. The mass transfer flux calculated for the Rio Agrio drainage basin, normalized to basin area, is about five times greater than the next highest flux (Quebrada Pilas), and is approximately one order of magnitude greater than fluxes observed in other major rivers draining the flanks of Poás. Note that structural and stratigraphic features of Poás that focus flow of acid brines towards the northwestern flank results in a narrow, tightly focused zone of intense chemical weathering and dissolution (Fig. 10).

The above fluxes provide only minimum estimates of the actual amount of rock material involved in the dissolution and alteration process. Summit and flank lava and tephras average approximately 2.2 wt.% Na (Prosser and Carr, 1987; Rowe, 1991). Given that 100 grams of rock must be completely leached to provide 2.2 grams of sodium (assuming no other significant sources of sodium), the observed Na flux in Rio Agrio (3.8 t/day) indicates leaching of unaltered rock at a rate of 170 metric t/day or approximately 60,000 t/yr. In terms of volume, this is almost 25,000 m³ or almost a factor of four greater than the volume indicated by the aggregate flux calculations. Thus, over a 100-year period about 2.5 million m³ of material would be altered on the northwestern flank of Poás. Over this same time interval about half a million cubic meters of material would be removed from the Rio Agrio drainage basin and approximately 160,000 m³ would be removed from the active crater area. The amount of flank material altered by the flow of acidic brines (0.025 km³) is rather insignificant when the total volume of Poás is considered ($V_{Poás} \approx 100 \text{ km}^3$). However, because about 20% of the volume of altered rock is removed from the aquifer, gradual increases in the porosity and permeability of the flank aquifer can be expected through time.

The increase in aquifer permeability is in sharp contrast to the reduction in permeability that accompanies mineral precipitation/alteration reactions in the upper portions of near neutral pH geothermal systems. Fieldwork on the northwestern flank revealed several areas near Site 25 where acid chloride sulfate water flowing on top of an altered tephra unit had produced dissolution features (including one small sinkhole) analogous to those observed in karstic terrains. The increase in permeability caused by flow of acid chloride sulfate water helps explain why the Rio Agrio drainage basin has the second highest baseflow discharge per unit area $(\approx 115 \text{ L/km}^2)$ despite the fact that the hydraulic gradient of the Rio Agrio basin is slightly above average relative to other major drainage basins of Poás (Table 8). Finally, removal of 160,000 m³ of material from beneath the crater lake would lower the lake floor (surface area = $60,000 \text{ m}^2$) by almost 2.5 m over 100 years. Thus, formation of small collapse craters could be caused by dissolution that accompanies circulation of acid brine. On a shorter time scale, dissolution of rock beneath the active crater may be important in interpreting small degreases in microgravity centered below the 1953-1954 cone that were recently recorded by Brown et al. (1991).

Fluxes of F, Cl, and S (as SO_4) measured in Rio Agrio provide a minimum estimate of the background volatile release rate from the hydrothermal/magmatic system of Poás Volcano. During periods of constant crater lake composition, volatile element inputs into the lake and associated hydrothermal system must equal volatile element losses through dome fumaroles and flank springs assuming minimal volatile release from the lake surface (Rowe et al., 1992a). Therefore, minimum volatile losses from the summit hydrothermal system will be given by fluxes observed in the Rio Agrio drainage basin. Average fluxes of F, Cl, and S



Fig. 11. Schematic cross-section through Poás Volcano along the linear transect A-A' of Fig. 1 illustrating the chemical and hydrologic structure of the volcano. Thick arrows show water flow paths. The stippled zone marks the inferred extent of two-phase conditions in the summit and associated zones of hydrothermal fluid convection. The vertically-striped layer represents the dacitic andesite–lahar sequence and associated strata that constitute the Rio Agrio aquifer.

calculated from compositional and discharge data collected over the period 1988–1990 (Tables 3 and 8) are 1.9 ± 0.2 , 38 ± 4 , and 30 ± 3 t/D. These fluxes should be representative of background volatile release rates at Poás within last 20 years. The fluxes are also roughly equivalent to background volatile fluxes of F, Cl, and S estimated by Rowe et al. (1992a) with a magma crystallization model.

5.7. Water-rock ratios in the flank and summit aquifer

The sodium concentration of Rio Agrio spring waters can also be utilized to estimate fluid-rock ratios in the flank aquifer and the summit hydrothermal system. According to Gislason and Eugster (1987) the water-rock ratio (WR) for complete dissolution of glassy and crystalline lavas is:

$$WR = \frac{C_{\rm r}^{\rm b}}{\Delta C_{\rm w}} \tag{3}$$

where WR is the water-rock ration; C_r^b is the conservative solute concentration in the rock before reaction; and ΔC_w is the change in conservative solute concentration in water caused by dissolution. Using the average value of ΔC_w derived from data in Table 3 for Site 25 acid chloride sulfate water $(1.5 \times 10^{-6} \text{ mol Na/} \text{ cm}^3 = 0.023 \text{ g Na/kg sol})$ and a value of C_r^b taken from Table 7 for the dacitic andesite (22 g Na/kg rock) results in an average water/rock ratio of 956. In other words, a little over one gram of rock reacts with 1000 grams of acid chloride sulfate water during flow through the flank aquifer. Average chloride concentration of the unaltered dacitic andesite is 85 ppm (Table 7) indicating that almost all chloride in the Rio Agrio spring waters is derived from summit hydrothermal fluids. Water-rock ratios calculated for the summit hydrothermal system using the average sodium content of the crater-lake brine are near 30 (33 grams rock/ 1000 grams brine) which is consistent with the more intense alteration associated with the extremely acidic brines of the active crater. The actual water-rock ratio is probably somewhat higher as an unknown amount of sodium in the crater-lake brine is derived from magmatic degassing.

5.8. Chemical and hydrologic model of Poás Volcano

The geochemical and geologic data summarized in this paper may be used to construct a generalized model of the chemical and hydrogeologic structure of Poás Volcano (Fig. 11). In the model, heat derived from the shallow, partially molten magma body drives convection in the summit hydrothermal system; interaction of ascending magmatic gases with infiltrating meteoric water produces a reservoir of extremely acidic chloride

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sulfate brine. The surface expression of this reservoir is the crater lake. Acid chloride sulfate brines mix with infiltrating meteoric water and flow laterally down the northwestern flank along the permeable contact between a lava-lahar sequence. Because the dip of these strata is shallower than the topographic slope of the northwestern flank, the lava-lahar sequence eventually intersects the northwestern flank producing a line of acid chloride sulfate springs near Site 25. The nearconstant chemical composition of Rio Agrio from its source springs to its confluence with Rio Toro indicates that laterally migrating acid waters also leak downward into older, deeper lava flows and pyroclastic units. Acid groundwater in the deeper aquifers is the source of acid baseflow that increases the flow of Rio Agrio at lower elevations. The result is relatively narrow band of acid chloride sulfate water with little compositional variation that discharges on the northwest flank of the volcano.

Ambient temperature acid sulfate waters of the northwestern flank do not reflect the effects of subsurface hydrothermal activity. Instead, these waters appear to be derived from sulfate-loading on the upper flanks of the volcano. The sulfate is derived from dry and wet acid deposition in the form of sulfur dioxide and sulfuric acid, respectively. Soil pore water and shallow groundwater are acidified; these acid waters also migrate laterally along short, shallow flow paths, eventually discharging to the surface as acid or neutral sulfate springs or streams. Other acid sulfate waters are formed by the oxidation of low temperature H₂S. Subsequent mixing, dilution, and water-rock interaction neutralize the acid sulfate waters to produce neutral sulfate waters. Neutral-bicarbonate waters draining the southern and eastern flanks of Poás appear to be largely unaffected by summit volcanic and hydrothermal activity.

The chemical and hydrologic structure of Poás is similar to the generalized model of volcano-hosted geothermal systems presented by Henley and Ellis (1983) and validates the hypothesis that seepage of crater-lake brines can affect the chemical composition of both surface and groundwater present on the flanks of active volcanos. Lacking however, are the near-neutral chloride thermal waters that are typically associated with the lower elevation parts of volcanic hydrothermal systems. The presence of a volatile-rich, near surface magma body degassing large quantities of acidic volatiles may preclude the development of a significant reservoir of near neutral sodium chloride fluids in the shallow parts of the volcanic edifice. Alternatively, such a reservoir may be present at deeper levels (3–4 km) in the volcanic edifice where pressure-temperature conditions favor the generation of a sodium chloride brine phase (c.f. Fournier, 1985b; Giggenbach, 1987). However, high rates of recharge in the summit area may limit flow of deep-seated brines (Traineau et al., 1989; Sanford et al., 1995, this issue).

The lack of hot spring activity at Poás (with the exception of the Affluente de Agrio hot spring–Site 24) is also notable given the relatively concentrated nature of the Rio Agrio acid chloride sulfate waters. However the chemical composition of the Rio Agrio springs is consistent with the relatively shallow nature of the flank aquifer, the extreme amounts of rainfall at the summit area, and the resulting high degree of dilution by cold meteoric waters. The lack of hot spring activity also implies that the heat source of the summit hydrothermal system does not extend much beyond the boundaries of the active crater, an observation that is consistent with narrow pipe-like structure of the current magma body (Thorpe et al., 1981; Rymer and Brown, 1987).

Analysis of the probable head distribution in the summit region by Sanford et al. (1995, this issue) indicates that the crater lake represents a closed basin with respect to the water table. Due to the presence of Von Frantzius cone to the north and Botos cone to the south-southeast, the water table in the vicinity of the active crater is saddle-like, with the water table divide lowest towards the northwestern (and northeastern) flank. Based on this water table configuration, the path of least resistance for brine seepage into the flank, will be towards the northwest, and to a lesser extent, the northeast. Numerical simulations of the Poás groundwater system by Konikow et al. (1989) and Sanford et al. (1990) that assumed homogeneous permeability distributions in the vicinity of the active crater indicated that density-driven flow of concentrated lake brines $(\rho_{\text{lake}} = 1.05 - 1.30 \text{ g/cm}^3, \text{ Table 6})$ was an important driving force for lateral seepage of acid brine towards the northwestern flank of the volcano.

However, results of later simulations (Sanford et al., 1995, this issue) indicate that when heterogeneous permeability distributions are considered, structural and stratigraphic controls are shown to be more important

than lake brine density in controlling the rate and direction of brine seepage from the active crater. Faults, fracture zones and the tongue-shaped geometry of recent eruptive deposits of the northwestern flank provide high-permeability conduits that facilitate the leakage of acid brines from the active crater. These high-permeability conduits allow the brine to migrate laterally from the active crater, despite the presence of an elevated water table that tends to focus groundwater flow towards the active crater. Solute-transport simulations by Sanford et al. (1995, this issue) indicate that a plume of laterally-migrating acid brine would intersect the northwestern flank at an elevation similar to that of the Site 25 springs in a little over 10 years. In contrast, the hydraulic head associated with the elevated water table of Botos cone prevented lateral migration of acid brine towards the southeast flank, even after simulation times exceed 1000 years. The model results are consistent with the fact that no evidence of brine seepage from the active crater is found on the southern and eastern flanks of Poás.

The most interesting attribute of the chemical and hydrologic model of Poás Volcano is the rapid circulation of highly acidic fluids through the volcanic edifice. Acid brines of the summit hydrothermal system are capable of dissolving significant quantities of volcanic rock and pyroclastic material. If these fluids are produced over the life span of the magmatic-hydrothermal system (100's to 1000's of years), significant changes in the morphology of the active crater would be expected to occur. Such changes could involve the formation and enlargement of collapse craters beneath zones of acid brine circulation. Geomorphic changes can also be expected in the flanks of the volcano in which flow of acid brines through transmissive fracture zones or permeable stratigraphic units produces localized zones of dissolution and alteration. The flux of acid brine flowing through such zones can be expected to increase with time because the permeability of these zones should increase as aquifer material is dissolved and transported out of the volcanic edifice. These increases could lead to significant changes in patterns of fluid flow in the volcano and could also affect the structural integrity of the volcano's flanks. Thus, the circulation of acid fluids may play a role in determining the location, type and magnitude of future eruptions at Poás Volcano.

6. Conclusions

Comparison of key chemical properties and conservative solute ratios of the various water types of Poás Volcano strongly supports the hypothesis that acid chloride sulfate springs of the Rio Agrio drainage basin are derived by leakage and mixing of crater lake brine with dilute groundwater. Acid chloride sulfate waters appear to be the only waters on Poás directly affected by the subsurface flow of hydrothermal brines generated in the summit. Structural, stratigraphic and topographic features of Poás volcano play a critical role in restricting flow of acidic brines to the NW flank of the volcano. A permeable lava-lahar sequence is the hydraulic link between crater lake brines and acid chloride sulfate springs of the Rio Agrio drainage basin. Acid sulfate and neutral sulfate waters found on the northwestern flank of the volcano reflect the effects of both dry and wet acid deposition from the plume of volcanic gases issuing from the active crater.

In contrast with other volcano-hosted hydrothermal systems no evidence for a reservoir of neutral pH sodium chloride water at depth is found at Poás. The lack of NaCl brines at Poás is attributed to two factors: the presence of a volatile-rich magma body degassing at very shallow depths into a complex, high-level aquifer system; and 2) the hydrogeologic structure of the volcano in which high rates of recharge combine with laterally-directed flow of acid brine along sub-horizontal flank aquifers to prevent deep reservoir fluids from ascending to the surface.

Tritium-based residence time estimates indicates that fluid flow from the active crater to the source springs of Rio Agrio is hydrologically rapid (3 to 17 yrs). The residence time data yielded hydraulic conductivity estimates (10^{-5} to 10^{-7} m/s) consistent with those obtained during aquifer testing of fractured and porous lava/pyroclastic sequences at the base of the northwestern flank. Fluxes of dissolved rock-forming elements in the Rio Agrio drainage basin indicate that approximately 4600 and 1600 m³ of rock is removed from the flank aquifer and summit hydrothermal system per year respectively. Over the lifetime of the hydrothermal system (100's to 1000's of years), significant increases in aquifer porosity and permeability are expected, in marked contrast to the sharp reduction of permeability that often accompanies hydrothermal alteration in less acidic geothermal systems.

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References

Alpers, C.N., Nordstrom, D.K. and Ball, J.W., 1991. Solubility of jarosite solid solutions precipitated from acid mine waters, Iron Mountain, California, U.S.A. Sci. Geol. Bull., 42(4): 281–298.

- Arce, Y.M., 1980. Actividad residual en el Barva. Bol. Vulcanol., Universidad Heredia, Costa Rica, 9: 5–8.
- Ball, J.W. and Nordstrom, D.K., 1991. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. Geol. Surv., Open-File Rep. 91-183, 189 pp.
- Brantley, S.L., Borgia, A., Rowe, G., Fernandez, J. and Reynolds, J.R., 1987. Poás Volcano acts as a condenser for acid metal-rich brine. Nature, 330: 470–472.
- Brown, G.C., Dowden, J., Kapadia, P., Stevenson, D., Barquero, J. and Morales, L.D., 1989. Energy budget analysis for Poás crater lake: implications for predicting volcanic activity. Nature, 339: 370–373.
- Brown, G.C., Rymer, H. and Stevenson, D., 1991. Volcano monitoring by microgravity and energy budget analysis. J. Geol. Soc. London, 148: 585–593.
- Casadevall, T.J., Rose Jr., W.I., Fuller, W.H., Hart, M.A., Moyers, J.L., Woods, D.C., Chuan, R.L. and Friend, J.P., 1984. Sulfur dioxide from Poás, Arenal, and Colima Volcanoes, Costa Rica and Mexico. J. Geophys. Res., 89: 9633–9641.
- Casertano, L., Borgia, A., Cigolini, C., Morales, L.D., Montero, W., Gomez, M. and Fernandez, J.F., 1985. Investigaciones geofisicas y caracterisiticas geoquimicas de las aguas hidrotermales: Volcan Poás, Costa Rica. Geofis. Int., 24(2): 315–332.
- Casertano, L., Borgia, A., Cigolini, C., Morales, L., Gomez, M. and Fernandez, J., 1987. An integrated dynamic model for the volcanic activity at Poás Volcano, Costa Rica. Bull. Volcanol., 49: 588–598.
- Craig, H., 1961. Isotopic variations in meteoric waters. Science 133: 1702–1703.
- Craig, H., 1963. The isotopic geochemistry of water and carbon in geothermal areas. In: E. Tongiori (Editor), Nuclear Geology of Geothermal Areas, Spoleta, Italy. Consiglio Nazionalle delle Ricerche, Pisa, pp. 53–92.
- Da Silva, A.R., Duffield, W.A. and Muffler, L.J.P., 1985. Geothermal studies of Agua de Pau Volcano, San Miguel, Azores. Geotherm. Res. Council Trans., 9: 395-399.
- Davis, S. and Bentley, H., 1982. Dating groundwater, a short review. In: L. Currie (Editor), Nuclear and Chemical Dating Techniques: Interpreting the Environmental Record. Am. Chem. Soc. Symp. Ser., 176: 187–222.
- Delorme, H., 1983. Composition chimique et isotopique de la phase gazeuse de volcans calcoalcalins: America Centrale et Soufrière de la Guadaloupe, Application à la surveillance volcanologique. Ph.D. dissert., University of Paris VII, 415 pp.
- Ellis, A.J. and Mahon, W.A.J., 1977. Chemistry and Geothermal Systems. Academic Press, New York, NY, 392 pp.
- Estrada-Barrios J., Ballar, M.A. and Fernandez, G.L., 1989. Informe hidroelectrico Toro I y II. Instituto de Costarricense de Electricidad, San Jose, Costa Rica. 55 pp. (unpubl.).
- Fitterman, D.V., 1988. Overview of the structure and geothermal potential of Newberry Volcano, Oregon. J. Geophys. Res., 93(B9): 10,059–10,066.
- Foster, S.S.D., Ellis, A.T., Losilla-Penon, M. and Rodriguez-Estrada, H.V., 1985. Role of volcanic tuffs in the ground-water regime of the Valle Central, Costa Rica. Ground Water, 23: 795–801.

- Fournier, R.O., 1985a. The behavior of silica in hydrothermal solutions. In: B.R. Berger and P.M. Bethke (Editors), Geology and Geochemistry of Epithermal Systems. Soc. Econ. Geol., Rev. Econ. Geol., 2: 45–61.
- Fournier, R.O., 1985b. Conceptual models of brine evolution in magmatic-hydrothermal systems. In: Volcanism in Hawaii. U.S. Geol. Surv., Prof. Pap., 1350 (Chpt 55): 1487–1506.
- Fox, L.E., 1988. The solubility of colloidal ferric hydroxide and its relevance to iron concentrations in river water. Geochim. Cosmochim. Acta, 52: 771–777.
- Galloway, J.N., Likens, G.E., Keene, W.C. and Miller, J.M., 1982. The composition of precipitation in remote areas of the world. J. Geophys. Res., 87(C11): 8771–8786.
- Gemmell, B., 1987. Geochemistry of metallic trace elements in fumarolic condensates from Nicaraguan and Costa Rica Volcanos. J. Volcanol. Geotherm. Res., 33: 161–181.
- Giggenbach, W.F., 1982. Processes controlling the isotopic composition of steam and water discharges from steam vents and steamheated pools in geothermal areas. Geothermics, 11(2): 71–80.
- Giggenbach, W.F., 1987. Redox processes governing the chemistry of fumarolic gas discharge from White Island, New Zealand. Appl. Geochem., 2: 143-161.
- Gislason, S.R. and Eugster, H.P., 1987. Meteoric water-basalt interactions I: A field study in Northeast Iceland. Geochim. Cosmochim. Acta, 51: 2827–2840.
- Goff, F., Truesdell, A., Grigsby, C., Janik, C., Shevenell, L., Parades, R., Gutierrez, J., Trujillo, P. and Counce, D., 1987. Hydrogeochemical investigation of six geothermal sites in Honduras, Central America. Los Alamos Nat. Lab. Rep., 179 pp. (unpubl.).
- Goff, F., Truesdell, A., Shevenell, L., Janik, C., Grigsby, C., Parades, R., Trujillo, P., Counce, D., Gutierrez, J., Adams, A., Urbani, F. and Perdomo, R., 1988. Hydrogeochemical report of the second Honduras sampling trip, January–February 1986. Los Alamos National Lab. Rep., 105 pp. (unpubl.).
- Henley, R.W., 1985. The geothermal framework of epithermal ore deposits. In: B.R. Berger and P.M. Bethke (Editors), Geology and Geochemistry of Epithermal Systems. Soc. Econ. Geol., Rev. Econ. Geol., 2: 1–23.
- Henley, R.W. and Ellis, A.J., 1983. Geothermal systems, ancient and modern. Earth-Sci. Rev., 19: 1–50.
- International Atomic Energy Agency, 1973. Environmental isotope data no. 4: World survey of isotope concentrations in precipitation (1968–1969). Tech. Rep. Ser. No. 147. IAEA, Vienna.
- International Atomic Energy Agency, 1975. Environmental isotope data no. 5: World survey of isotope concentrations in precipitation (1970–1971). Tech. Rep. Ser. No. 165. IAEA, Vienna.
- International Atomic Energy Agency, 1979. Environmental isotope data no. 6: World survey of isotope concentrations in precipitation (1972–1975). Tech. Rep. Ser. No. 192. IAEA, Vienna.
- International Atomic Energy Agency, 1983. Environmental isotope data no. 7: World survey of isotope concentrations in precipitation (1976–1979). Tech. Rep. Ser. No. 226. IAEA, Vienna.
- International Atomic Energy Agency, 1986. Environmental isotope data no. 8: World survey of isotope concentrations in precipitation (1980–1983). Tech. Rep. Ser. No. 264. IAEA, Vienna.

International Atomic Energy Agency, 1989. Environmental isotope data no. 9: World survey of isotope concentrations in precipitation (1984-1987). Tech. Rep. Ser. No. 311. IAEA, Vienna.

- Johnson, N. and Parnell, R.A. Jr., 1986. Composition, distribution and neutralization of "acid rain" derived from Masaya volcano, Nicaragua. Tellus, 38B: 106-117.
- Konikow, L.F., Sanford, W.E., Rowe, G.L. and Brantley, S.L., 1989. Ground-water flow around a hot acidic, brine lake in a volcanic crater. EOS, Trans. Am. Geophys. Union, 70:(43): 1101.
- Nordstrom, D.K., 1982. The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system Al₂O₃-SO₃-H₂O. Geochim. Cosmochim. Acta, 46: 681–692.
- Nordstrom, D.K. and Ball, J.W., 1986. The geochemical behavior of aluminum in acidified surface waters. Science, 232: 54–56.
- Nordstrom, D.K., Jenne, E.A. and Ball, J.W., 1979. Redox equilibria of acid mine waters. In: E. Jenne (Editor), Chemical Modelling of Aqueous Systems. Am. Chem. Soc., Symp. Ser., 93: 51–79.
- Ohmoto, H., 1986. Stable isotope geochemistry of ore deposits. In: J.W. Valley, H.P. Taylor Jr. and J.R. O'Neil (Editors), Stable Isotopes in High Temperature Geological Processes. Min. Soc. Am., Rev. Mineral., 16: 491–556.
- Parnell, R.A. and Burke, K., 1990. Impacts of acid emissions from Nevado del Ruiz volcano, Columbia, on selected terrestrial and aquatic ecosystems. J. Volcanol. Geotherm. Res., 42: 69–88.
- Pearson, F. and Truesdell, A., 1978. Tritium in waters of Yellowstone National Park. U.S. Geol. Surv., Open-file Rep., 78-701: 327– 329.
- Pringle, C.M., Rowe, G.L., Triska, F.J., Fernandez, J.F. and West, J., 1993. Landscape patterns in the chemistry of geothermallyimpacted streams draining Costa Rica's Atlantic slope: Geothermal processes and ecological response. Limnol. Oceanogr., 38(4): 753-774.
- Prosser, J.T., 1983. The geology of Poás Volcano, Costa Rica. Master's Thesis, Dartmouth College, Hanover, NH, 165 pp. (unpubl.).
- Prosser, J.T. and Carr, M., 1987. Poás Volcano, Costa Rica: Geology of the summit region and spatial and temporal variations among the most recent lavas. J. Volcanol. Geotherm. Res., 33: 131–146.
- Robinson, R.A. and Stokes, R.H., 1965. Electrolyte Solutions, 2nd ed. Butterworths Scientific Publications, London, 595 pp.
- Rosario-Alfaro, M., Fernandez, E., Barquero, J., Joaquín-Rodríguez, J. and Rodríguez, M., 1986. Lluvia acida del origen volcanico. Bol. Vulcanol., 16: 15–22 (in spanish).
- Rowe, G.L., 1991. The acid crater lake system of Poás Volcano, central Costa Rica: Geochemistry, hydrology and physical characteristics. Ph.D dissertation, The Pennsylvania State University, University Park, PA, 309 pp.
- Rowe, G.L., 1994. Oxygen, hydrogen, and sulfur isotope systematics of the crater lake system of Poas Volcano, Costa Rica. Geochem. J., 28(3): 263–287.
- Rowe, G.L. and Brantley, S.L., 1993. Estimation of the dissolution rates of andesitic glass, plagioclase, and pyroxene in a flank aquifer of Poás Volcano, Costa Rica. Chem. Geol., in press.
- Rowe, G.L., Brantley, S.L., Fernandez, M., Fernandez, J.F., Barquero, J. and Borgia, A., 1992a. Fluid-volcano interaction in an active stratovolcano: The crater lake system of Poás Volcano, Costa Rica. J. Volcanol. Geotherm. Res., 49: 23-51.
- Rowe, G.L., Ohsawa, S., Takano, B., Brantley, S.L., Fernandez, J.F. and Barquero, J., 1992b. Using crater lake chemistry to predict

volcanic activity at Poás Volcano, Costa Rica. Bull. Volcanol., 54: 494-503.

- Rymer H. and Brown, G.C., 1987. Causes of microgravity changes at Poás Volcano, Costa Rica: an active but non-erupting system. Bull. Volcanol., 49: 389–398.
- Rymer, H. and Brown, G.C., 1989. Gravity changes as a precusor to volcanic eruption at Poás Volcano, Costa Rica. Nature, 342: 902– 905.
- Sanford, W.E., Konikow, L., Rowe, G. and Brantley, S., 1990. Heat and solute transport in ground water at Poás Volcano, Costa Rica. EOS, Trans. Am. Geophys. Union, 71(43): 1687.
- Sanford, W.E., Konikow, L.F., Rowe, G.L. and Brantley, S.L., 1995. Ground-water transport of crater-lake brine at Poás Volcano, Costa Rica. J. Volcanol. Geotherm. Res., 64: 271–297.
- Sillitoe, R.H. and Bonham, H.F. Jr., 1984. Volcanic landforms and ore deposits. Econ. Geol., 79: 1286–1298.
- Smithsonian Institution, 1990. Bull. Global. Volcanism Network, 15(4): 6–9.

- Thorpe, R.W., Locke, C.A., Brown, G.C., Francis, P.W. and Randal, M., 1981. Magma chamber below Poás Volcano, Costa Rica. J. Geol. Soc. London, 138: 367–373.
- Traineau, H., Westercamp, D. and Benderitter, Y., 1989. Case study of a volcanic geothermal system, Mount Pelée, Martinique. J. Volcanol. Geotherm. Res., 38: 49-66.
- Truesdell, A.H. and Jones, B.F., 1974. WATEQ, a computer program for calculating chemical equilibria of natural waters. J. Res. U.S. Geol. Surv., 2(2): 233–248.
- Sturchio, N.C. and Williams, S.N., 1990. Variations in chemistry of acid sulfate-chloride springs at Nevado del Ruiz volcano, Columbia: November 1985 through December 1988. J. Volcanol. Geotherm. Res., 42: 203–210.
- Von Frantzius, A., 1861. A contribution of knowledge of the volcanos of Costa Rica. In: C.A. Vargas (Editor), 1979. Antologia el volcán Poás, Universidad de Estatal a Distancia, San Jose, Costa Rica, pp. 11–34 (in spanish).
- White, D.E., 1957. Thermal waters of volcanic origin. Geol. Soc. Am. Bull., 68: 1637–1658.