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and Flanking Thermal/Mineral Waters at
Popocatépetl Volcano, Mexico*

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Cover Photo: Popocatepetl (smoking mountain) is surrounded by 30 million people living in the Mexico City and Puebla Basin regions. Historically active in Hispanic and pre-Hispanic times, Popocatepetl inspires the art and psychology of the Mexican people.

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ABSTRACT

Popocatépetl Volcano is potentially devastating to populations living in the greater Mexico City area. Systematic monitoring of fumarole gases and flanking thermal/mineral springs began in early 1994 after increased fumarolic and seismic activity were noticed in 1991. These investigations had two major objectives: 1) to determine if changes in magmatic conditions beneath Popocatépetl might be reflected by chemical changes in fumarolic discharges and 2) to determine if thermal/mineral spring waters in the vicinity of Popocatépetl are geochemically related to or influenced by the magmatic system. This report summarizes results from these two discrete studies.

Chemical and isotopic compositions of gases were monitored by placing alkaline traps containing 4N KOH around the crater and by collecting the trap solutions at near-monthly intervals until the volcano erupted on December 21, 1994. Absolute abundances of volatile constituents (ppm/day of Cl, S_{total}, F, CO₂, Hg, and As) show general increases during the June–July 1994 and Oct.–Dec. 1994 time periods. These increases correlated with increased SO₂ output measured by correlation spectrometry (COSPEC). The full range of sulfur isotope compositions measured during this study is 1.5 to 6.4‰; the lower values generally occurred in the Oct.–Dec. samples. These values are very close to that of mantle sulfur (~0‰). The higher values occurred in samples from the June–July period, suggesting possible incorporation of hydrothermal sulfate or underlying Cretaceous evaporitic rocks (roughly 16 to 19‰) into the magma during that time. Carbon isotope compositions measured on the trap solutions were not as useful because of contamination with atmospheric CO₂. Bulk chemistry and sulfur isotope variations of the volatiles can be explained by injection of mafic magma into a silicic magma chamber beneath the volcano, ascent of magma in the conduit or chamber, and incorporation of small volumes of altered rocks or older strata into the evolving melts.

The flanking thermal/mineral waters, which were collected periodically from May 1994 until June 1995, show no apparent geochemical changes with time, indicating that increased volcanic activity did not affect these springs. These fluids are relatively low in SiO₂, B, Br, Cs, Li, and Rb compared with those from known geothermal systems, indicating that Popocatépetl springs are not derived from a high-temperature reservoir. Chemical geothermometry of the waters and feeble gas emissions suggest equilibration temperatures of ≤60°C. The waters show chemical equilibrium with carbonate and evaporite minerals (calcite and gypsum), which are known to occur in regional Cretaceous strata. Limited stable isotope data on the waters indicate recharge at elevations considerably lower than Popocatépetl summit, whereas tritium contents indicate that the waters have maximum mean residence times of approximately 1000 years.

I. INTRODUCTION

Popocatépetl (5450 m) is an andesitic stratovolcano located in the eastern half of the Trans-Mexican Volcanic Belt, 70 km SE of downtown Mexico City (Fig. 1). The last major Plinian eruption occurred ca. 1200 years B.P., and a recent eruption (1920–27) built a dacitic dome in the crater (Siebe et al., 1996). After noting increased seismicity and fumarolic activity in 1991–1994, we began to monitor the fumarolic emissions around the crater and thermal/mineral springs flanking the southern side of the volcano. Fumarolic emissions were studied using alkaline traps placed around the crater rim. These traps contained a solution of 4N KOH, which dissolved volatile acids and volatile metals from the surrounding air. Alkaline traps were sampled monthly beginning February 1994 until the ash eruption on 21 December 1994. Since this date, collection of alkaline trap solutions has not been possible due to unpredictable eruptive activity. Four COSPEC determinations of SO_2 flux in the plume were made before the eruption began, and four measurements were obtained in late December 1994. Subsequent COSPEC determinations of Popocatépetl SO_2 emission rates are not included in this report.

Monitoring of springs located on the southern flank of Popocatépetl commenced in April 1994 and continued through June 1995. Spring samples were collected to determine if fluids are partially derived from a hydrothermal system within the volcano and to determine if temporal changes due to recent eruptive activity affect the fluid chemistry.

The purpose of this report is to present and analyze data collected during the fumarole and spring monitoring efforts on Popocatépetl. Each effort is discussed separately. We consider if observed changes in volatile discharges are related to injections of mafic magmas into an existing silicic magma chamber and if monitoring of volatiles and trace metals is useful for forecasting eruptions. In addition, we investigate possible relations between the spring waters and the magmatic system and determine if the spring waters originate from a high-temperature ($\geq 200^\circ\text{C}$) hydrothermal system.

II. REGIONAL GEOLOGY AND BACKGROUND ON POPOCATÉPETL

Popocatépetl (“smoking mountain” in Náhuatl language) lies in the eastern half of the Trans-Mexi-

Fig. 1: Regional map of the Trans-Mexican Volcanic Belt with a detailed map (insert) of the area near Popocatépetl (modified from Robin and Boudal, 1987).

can Volcanic Belt (TMVB). The TMVB runs approximately west-east from the Pacific Coast to the Gulf of Mexico (Fig. 1). The belt averages 900 km in length and 100 km in width. The Middle America Trench lies south of the TMVB, varying in distance from 350–450 km in the east to 200 km in the west (Robin, 1982).

Popocatepetl is located in the southern portion of the Sierra Nevada, which borders the southeast margin of the Valley of Mexico (Fig. 1). Other volcanoes in the Sierra Nevada include Iztaccíhuatl (5,286 m) located 15 km north of Popocatepetl. The Valley of Mexico is an enclosed basin located in the central portion of the TMVB and is about 100 km long by 30–60 km wide (Mooser et al., 1974). Nixon and co-workers (Nixon et al., 1987; Nixon, 1988a, 1988b, 1989) described the geology around the Valley of Mexico and Iztaccíhuatl and proposed that the earliest volcanism in the area began about 1.7 Ma. Based on K-Ar dating of lavas, Nixon determined that eruptive activity at Iztaccíhuatl began before 0.9 Ma and continued until approximately 10 ka. Rock types found at Iztaccíhuatl are predominantly calc-alkaline andesite and dacite that display mineralogical and chemical evidence for mixing of a dacitic magma with a mafic end-member.

Initial work on the evolution, petrology, and dating of Popocatepetl was completed mainly by Robin, Boudal, and Negendank in the 1970s and 1980s. Eruptive history of Popocatepetl has been divided into two periods: (1) the birth (probably <0.78 Ma; Delgado et al., 1988) and construction of an ancient stratovolcano, Nexpayantla, and (2) the most recent volcanism creating the modern volcano. Nexpayantla differed from the modern cone in that it had a large (30-km) base, was mainly effusive, and was active for several hundred thousand years (Robin, 1984). Peak elevations reached about 5000 m before collapse and crater formation. The primitive cone is exposed on the north-west and west flanks of the volcano and is marked by a change in slope (Boudal, 1985; Negendank, 1972; Robin and Boudal, 1987).

We now know that the present cone is not the first huge volcanic edifice that evolved at this site. At least three successive debris-avalanche deposits that fan out towards the south are evidence for the previous existence of large cones that were destroyed by gravitational collapse. Dates on debris-avalanche deposits related to the last collapse range between 24,000 and 19,000 years B.P. (Siebe et al., 1995a, 1995b). Explosive and effusive activity continued for 20,000 to 10,000 years with explosive activity occurring in cycles of 1000 to 3000 years, as determined by C-14 dating of pyroclastic deposits on the modern cone (Cantagrel et al., 1984; Boudal and Robin, 1988; Siebe et al., 1996). Major eruptions occurred between 3195 to 2830 BC, 800 to 215 BC, and 675 to 1095 AD (Siebe et al., 1996). The only post-European historic activity took place between 1920 and 1927, emplacing a dacitic dome (215 m) in the present crater during 1920–21 (Waitz, 1921). Explosive activity commencing in December 1994 did not erupt significant volumes of juvenile magma (Delgado et al., 1995a) but caused the temporary evacuation of 75,000 people when the first major explosions occurred.

The Sierra Nevada is known to overlie Tertiary sedimentary and volcanic terrain (Mooser, 1974) and Cretaceous carbonate and evaporitic rocks. These deposits are not exposed in the Valley of Mexico but are found 2,000 m below the surface. Cretaceous strata are exposed as isolated outcrops related to horst and graben fault structures at distances more than 20 km south of Popocatepetl summit. These deposits are surrounded mostly by lahars and debris-avalanche deposits from Popocatepetl.

III. ALKALINE TRAPS AND FUMAROLE MONITORING

Methods and Procedures for Collection and Analysis of Alkaline Trap Samples

Fumarolic emissions at Popocatepetl were monitored from February to December 1994 using alkaline traps and remote COSPEC. Alkaline traps

were sampled monthly and COSPEC flux measurements of the SO_2 content of the plume were made in February, May, July, and November before the 21 December eruption. Additional COSPEC measurements were made on 23 to 29 December 1994.

The alkaline trap method was initially used to collect wind-dispersed volcanic vapors by Noguchi and Kamiya (1963) and was further employed by Williams et al. (1990) and Italiano et al. (1991). Traps are used to monitor fumarolic emissions over a sampling interval, allowing for indirect observation of absolute concentration and flux changes with time when direct sampling is not feasible. Italiano et al. (1991) presented a generalized function showing that the concentration of any volatile species fixed in the trap solution is dependent on six factors: sampling interval, volatile flux from the fumarolic source, meteorological conditions, geometry of the trap, surface area of the trap solution, and absorbance efficiency of the trap solution. Volatile concentrations in the trap are also affected by exponential dilution of fumarole gas by air with increasing distance from the source (La Guern and Faivre-Pierret, 1982). Furthermore, some gas components undergo reactions after fumarole discharge. For example, sulfur gases react with oxygen in air or react in the large temperature gradient between the fumarole vent and ambient air to form new gas compounds and sublimates. HCl is very water soluble and can be "rained out" before reaching the trap solution. In spite of these limitations, the flux of volatile species from the volcano may be so large ($>1,000$ t/d) that the alkaline traps collect representative samples when direct fumarole sampling is too dangerous.

Seven alkaline traps were placed around the crater of Popocatépetl: two just inside the lower crater rim, three on the crater rim, and two just outside the crater (Fig. 2). Major, high-temperature fumaroles are only found inside the crater and were considered too dangerous to sample directly (Fig. 3). Sampling of the gas plume rising from the crater was complicated by regional wind directions, generally trending to the east in the fall-winter and to the west in the spring-summer (Delgado et al.,

Fig. 2: Map of Popocatépetl crater rim showing positions of alkaline traps (filled circles) around the lower crater rim and on the southeast side of the summit.

Fig. 3: Photograph of Popocatépetl crater. Due to the extreme danger in 1994 related to direct sampling of fumaroles (located on the floor and walls of the crater), alkaline traps were placed around the crater rim. Vertical walls are approximately 250 m deep, and the crater diameter is approximately 1 km (photo by J.A. Stimac).

Fig. 4: Photograph of Hugo Delgado collecting an alkaline trap sample on the crater rim of Popocatepetl.

1995b). The alkaline traps consisted of a plastic beaker approximately 20 cm high by 15 cm in diameter containing 500 ml of 4N KOH (Fig. 4). The trap was placed beneath an inverted, ventilated bucket, which allowed gases to contact the caustic solution, yet protected the trap from precipitation and large particle contamination. The caustic solution absorbed reactive gases (CO_2 , SO_2 , H_2S , HCl , and HF) and volatile metals (As, Hg, etc.). Other fumarolic components such as He, H_2 , O_2 , Ar, N_2 , CO, and CH_4 , however, were not absorbed by the caustic solution and were thus lost to the atmosphere. Some CO may have reacted with KOH to produce formaldehyde, but this constituent was not analyzed. The loss of these various gases is one disadvantage of alkaline trap sampling compared to direct sampling in which all fumarolic gas species are captured.

Methods of chemical analysis and detection limits for species analyzed in trap samples are listed in Table 1. Samples were analyzed for Cl, CO_3 , F, SO_4 (reported as total S), As, and Hg concentrations (Table 2). Aliquots of the trap solutions were prepared and analyzed for carbon and sulfur isotope compositions using methods described in Fahlquist and Janik (1992). Active volcanoes which have been closely monitored during eruptive episodes usually show short-term variations (Tedesco, 1995), which were evident in chemical and isotopic components of fumarolic emissions. Because alkaline trap data reflect emissions over the sampling interval, variations due to very short

term intervals are averaged. High-frequency variations in activity are not recorded.

An atmospheric blank was set out away from the volcano to estimate background levels of the measured constituents. This blank absorbed negligible amounts of all constituents except CO_2 . Gerlach et al. (in press) found that the CO_2 background concentration at 6000 m elevation in the vicinity of Popocatepetl was 5% higher than typical atmospheric levels, probably due to air pollution from Mexico City and Puebla.

Gas Geochemistry of Alkaline Trap Samples

Chemical analyses of the alkaline trap solutions are listed in Table 2 according to sample number and date of collection. Also listed are ratios of Cl, CO_3 , F, As, and Hg with respect to SO_2 calculated from the total S content in the caustic solutions. The collection time intervals vary among sampling sites due to difficulties in obtaining the samples. Also, absolute abundances vary with location around the crater rim for any one collection period due to complicated wind patterns, as well as changing flux rates. In some cases, concentrations behave erratically among stations suggesting winds have blown dust and sublimates with variable chemical composition into some traps but not others. Such phenomena may explain why in June Sta. 2 has much higher F and S (from wind dispersed volatiles) but Sta. 5 has higher Cl and Hg (from dust?).

Plotting the total concentrations per day for all stations versus time reveals a complex data set (Fig. 5); general trends in chemistry, however, demonstrate a pattern of degassing throughout the sampling period. High total concentrations of S, F, and Hg (Figs. 5a, b, c) are observed for one or more stations in June and July. The plot of As/day versus time (Fig. 5f) shows higher concentration in the earlier months of the year with lowering values toward mid- to late 1994. Cl/day is also highest in the earlier months, but a second peak is observed in the July collection (Fig. 5d). The plot of CO_3 /day versus time (Fig. 5e) shows variability

TABLE 1. Methods of chemical analysis and detection limits (ppm) for alkaline trap and spring samples.

Analyte	Method	Detection Limit	Analyte	Method	Detection Limit
<i>Alkaline Trap Constituents</i>			<i>Spring Waters</i>		
As	Hydride AA	0.002	Ag	GFAA	0.0005
Cl	IC	1	Al	ICP-AES	0.01
CO ₃	Titration	5	As	Hydride-AA	0.001
F	IC	0.1	B	ICP-AES	0.01
Hg	Cold Vapor AA	0.0002	Ba	ICP-AES	0.01
S	IC	1	Be	ICP-AES	0.002
<i>Methods Acronyms</i>			Br	IC	0.02
AA - Atomic Absorption Spectroscopy			Ca	ICP-AES	0.01
GFAA - Graphite Furnace AA			Cd	GFAA	0.0002
IC - Ion Chromatography			Cl	IC	0.01
ICP-AES - Inductively Coupled Plasma			Co	GFAA	0.002
Atomic Emission Spectroscopy			CO ₃ /HCO ₃	Titration	0.5
			Conductivity	Electrode	0.5
			Cr	GFAA	0.002
			Cs	GFAA	0.002
			Cu	GFAA	0.002
			F	IC	0.01
			Fe	ICP-AES	0.01
			Hg	Cold Vapor AA	0.0002
			I	IC	0.01
			K	ICP-AES	0.2
			Li	ICP-AES	0.01
			Mg	ICP-AES	0.01
			Mn	ICP-AES	0.01
			Mo	GFAA	0.002
			Na	ICP-AES	0.05
			NH ₄	Electrode	0.02
			Ni	GFAA	0.002
			NO ₂	IC	0.02
			NO ₃	IC	0.02
			Pb	GFAA	0.002
			pH	Electrode	0.01
			PO ₄	IC	0.05
			Pb	GFAA	0.002
			Sb	Hydride AA	0.001
			Se	Hydride AA	0.001
			Si	ICP-AES	0.02
			SO ₄	IC	0.02
			S ₂ O ₃	IC	0.01
			Sr	ICP-AES	0.01
			Ti	ICP-AES	0.002
			V	ICP-AES	0.002
			Zn	ICP-AES	0.005

for all stations, which probably reflects contamination with CO₂ in the air as well as absorption of magmatic CO₂. A general decreasing trend in CO₃/day is observed, however, from March through May, and a peak is evident for several stations in June–July. The lowest CO₂/day values are seen in the August through October collections. All plots except As/day and F/day show an increase in species abundance during the last sampling period, probably marking the onset of eruptive activity that began in December 1994.

Ratios of S/Cl and F/Cl have been used to forecast tentative eruptive activity (Noguchi and Kamiya, 1963; Italiano, 1991). Cl ratio diagrams were completed for this study (Fig. 6) using the highest ratio of all stations for a certain collection period, thus reducing the noise of the lower values on each plot. Highest values for S/Cl and F/Cl correspond with highs in SO₂ flux measured by COSPEC in July. CO₂/Cl, As/Cl, and Hg/Cl show respective highs in July. These highs correspond to a significant change in Cl concentration during these months as seen in Figure 5.

TABLE 2. Absolute concentrations of Cl, CO₂, F, S, As, and Hg (in ppm) for all Popocatepetl alkaline trap samples listed by sample and date of collection, ratios of Cl, CO₂, F, As, and Hg/SO₂ calculated from the S concentrations in the caustic samples, and sulfur-34 and carbon-13 data for May through December.

Sample Number	Date Out	Days Used	Cl	CO ₂	F	S	As	Hg	Cl/SO ₂	CO ₂ /SO ₂	F/SO ₂	As/SO ₂	Hg/SO ₂	δ ³⁴ S ‰ CDT	δ ¹³ C ‰ PDB
PCJ-1	02/20/94	21	373	67060	94.4	1271	0.15	0.0008	0.147	26.37	0.037	0.000058992	0.000000315	-	-
PCJ-1	03/13/94	21	223	51270	61.0	777	0.079	0.0006	0.143	32.99	0.039	0.000050834	0.000000386	-	-
PCJ-1	04/10/94	28	318	58390	112	1319	0.16	0.0008	0.121	22.13	0.042	0.000060648	0.000000303	-	-
PCJ-1	05/29/94	29	119	13844	48.9	676	0.003	0.0030	0.088	10.24	0.036	0.000002218	0.000000218	3.1	-18.24
PCJ-1	06/19/94	21	31.7	34820	103	1127	0.005	0.0032	0.014	15.45	0.046	0.000002218	0.000001419	2.7	-
PCJ-1	07/18/94	29	123	10795	70.5	752	0.003	0.0024	0.082	7.18	0.047	0.000001995	0.000001596	3	-21.72
PCJ-1	09/17/94	61	155	42030	370	1255	0.002	0.0006	0.062	16.74	0.147	0.000000797	0.000000239	3.5	-18.94
PCJ-1	10/09/94	22	31	18120	37	576	0.002	0.0003	0.027	15.74	0.032	0.000001737	0.000000261	2.7	-21.49
PCJ-1	10/28/94	19	135	39680	53	1225	0.003	0.0003	0.055	16.20	0.022	0.000001225	0.000000122	2.3	-20.86
PCJ-1	11/22/94	25	284	83840	138	2483	0.006	0.0019	0.057	16.88	0.028	0.000001208	0.000000383	1.5	-19.84
PCJ-2	02/20/94	21	114	38950	340	3302	0.20	0.0012	0.017	5.90	0.051	0.000030287	0.000000182	-	-
PCJ-2	03/13/94	21	1716	247350	490	6605	0.31	0.0022	0.130	18.72	0.037	0.000023465	0.000000167	-	-
PCJ-2	04/30/94	27	1432	239450	462	5340	0.41	0.0012	0.134	22.42	0.043	0.000038386	0.000000112	-	-14.11
PCJ-2	05/21/94	21	130	157697	423	4909	0.029	0.0040	0.013	16.06	0.043	0.000002954	0.000000407	2.5	-22.21
PCJ-2	06/19/94	29	106	218631	1958	22626	0.055	0.0056	0.002	4.83	0.043	0.000001215	0.000000124	3	-22.09
PCJ-2	07/18/94	29	399	101693	333	3074	0.015	0.0032	0.065	16.54	0.054	0.000002439	0.000000520	6.5	-21.93
PCJ-2	08/28/94	41	220	91510	104	1782	0.011	0.0040	0.062	25.68	0.029	0.000003086	0.000001122	3.4	-21.59
PCJ-2	09/17/94	20	64	54110	35	851	0.002	0.0003	0.038	31.79	0.021	0.000001175	0.000000176	3.9	-20
PCJ-2	10/09/94	22	82	69300	44	1068	0.002	0.0004	0.038	32.44	0.021	0.000000936	0.000000187	3.4	-20.11
PCJ-2	10/28/94	19	150	70220	42	1479	0.003	0.0003	0.051	23.74	0.014	0.000001014	0.000000101	2.9	-19.89
PCJ-2	11/22/94	25	450	176180	180	3815	0.002	0.0009	0.059	23.09	0.024	0.000000262	0.000000118	2.3	-21.36
PCJ-3	04/01/94	19	56.7	198600	96.4	224	0.008	0.0002	0.127	444.03	0.216	0.000017887	0.000000447	-	-
PCJ-3	04/30/94	29	33.8	166090	23.0	179	0.006	0.0002	0.095	465.05	0.064	0.000016800	0.000000560	-	-
PCJ-3	05/21/94	21	29.1	150765	21.2	205	0.001	0.0040	0.071	368.43	0.052	0.000002444	0.000000775	3.7	-18.39
PCJ-3	06/19/94	29	46.4	112512	36.0	302	0.002	0.0036	0.077	186.03	0.060	0.000003307	0.000000592	4.2	-
PCJ-3	07/18/94	29	2.0	73758	2.0	14.3	0.005	0.0024	0.070	2587.58	0.070	0.000175410	0.0000084197	2.3	-15.5
PCJ-3	10/09/94	42	2.4	12330	0.6	21	0.002	0.0002	0.057	293.18	0.014	0.000047556	0.000004756	5.1	-13.79
PCJ-3	10/28/94	19	17	124770	8	134	0.003	0.0003	0.064	467.26	0.030	0.000011235	0.000001124	3.8	-17.87
PCJ-3	12/02/94	35	34	262120	5	250	0.007	0.0003	0.068	523.54	0.010	0.000013981	0.000000599	3.1	-14.86
PCJ-4	04/01/94	19	156	126900	50.5	415	0.11	0.0006	0.188	152.81	0.061	0.000132460	0.000000723	-	-
PCJ-4	04/30/94	29	128	178500	55.4	442	0.038	0.0004	0.145	201.96	0.063	0.000042994	0.000000453	-	-
PCJ-4	05/21/94	21	14.4	99313	51.6	577	0.008	0.0026	0.012	86.09	0.045	0.000006935	0.000002254	3.5	-14.37
PCJ-4	06/19/94	29	117	89698	44.2	573	0.004	0.0016	0.102	78.21	0.039	0.000003488	0.000001395	3.3	-20.07
PCJ-4	07/18/94	29	49	103435	30	359	0.009	0.0007	0.068	143.87	0.042	0.000012518	0.000000974	3.2	-14.21
PCJ-4	08/28/94	41	19.1	9809	11.5	89	0.005	0.0005	0.107	55.03	0.065	0.000028052	0.000002805	5	-12.69
PCJ-4	10/09/94	42	11.1	14200	4.6	61	0.002	0.0002	0.091	116.24	0.038	0.000016372	0.000001637	5.4	-9.35
PCJ-4	10/28/94	19	19.8	8110	5.5	79	0.003	0.0002	0.125	51.26	0.035	0.000018962	0.000001264	4.9	-12.28
PCJ-4	12/02/94	35	14.7	15020	4.9	57	0.006	0.0002	0.130	132.35	0.043	0.000052871	0.000001762	3.2	-12.78
PCJ-5	04/01/94	19	980	69000	299	3184	0.28	0.0008	0.154	10.83	0.047	0.000043966	0.000000126	-	-
PCJ-5	05/21/94	21	213	47090	277	2359	0.022	0.0032	0.045	9.98	0.059	0.000004663	0.000000678	3.4	-
PCJ-5	06/19/94	29	222	76279	727	4939	0.044	0.0092	0.022	7.72	0.074	0.000004454	0.000000931	3.4	-
PCJ-5	07/18/94	29	1464	112072	1080	8275	0.024	0.0022	0.088	6.77	0.065	0.000001450	0.000000133	3.2	-22.33
PCJ-5	08/28/94	41	587	60625	532	5093	0.012	0.0005	0.058	5.95	0.052	0.000001178	0.000000049	4	-22.25
PCJ-6	04/01/94	19	1024	98500	327	3395	0.40	0.0008	0.151	14.51	0.048	0.000058907	0.000000118	-	-
PCJ-6	04/30/94	29	848	88050	371	3856	0.32	0.0004	0.110	11.42	0.048	0.000041496	0.000000052	-	-
PCJ-6	05/21/94	21	232	39780	212	1641	0.007	0.0022	0.071	12.12	0.065	0.000002133	0.000000670	2.9	-24.32
PCJ-6	06/19/94	29	486	64709	633	5104	0.026	0.0026	0.048	6.34	0.062	0.000002547	0.000000255	3.2	-
PCJ-6	07/18/94	29	67	89956	53.2	565	0.004	0.0028	0.059	79.59	0.047	0.000003539	0.000002477	3.5	-23.86
PCJ-6	08/28/94	41	300	44275	361	3597	0.009	0.0018	0.042	6.15	0.050	0.000001251	0.000000250	3.3	-24.14
PCJ-6	10/09/94	42	442	63700	353	3621	0.002	0.0007	0.061	8.79	0.049	0.000000276	0.000000097	3.4	-23.91
PCJ-6	10/28/94	19	375	72760	114	2353	0.002	0.0007	0.080	15.46	0.024	0.000000425	0.000000149	2.8	-22.26
PCJ-6	12/02/94	35	2230	278900	748	11295	0.004	0.0015	0.099	12.35	0.033	0.000000177	0.000000066	2.3	-25.14
PCJ-7	10/09/94	42	220	72700	118	1235	0.002	0.0004	0.089	29.43	0.048	0.000000810	0.000000162	-	-22.39
PCJ-7	10/28/94	19	154	73430	71	1429	0.002	0.0007	0.054	25.70	0.025	0.000000700	0.000000245	2.7	-21.73
PCJ-7	12/02/94	35	963	220690	350	4346	0.006	0.0008	0.111	25.39	0.040	0.000000690	0.000000092	2.1	-25.81
Blank	02/28/95	30	2.0	25450	0.1	6.1	0.007	0.0002	0.163	2088.99	0.008	0.000574575	0.000016416	-	-24.4

a> Chemical analyses by Dale Counce.

b> Isotopic analyses by L. Doug White, M. Huebner, and W.C. Pat Shanks, U.S. Geological Survey.

COSPEC measurements obtained in 1994 (Table 3) yield an average SO₂ flux of about 2000 tons/day (t/d), presently placing Popocatepetl as one of the largest current producers of SO₂ in the world (Delgado et al., 1995a). Analyses of gas samples taken directly from fumaroles are often combined with SO₂ COSPEC measurements of the volcanic plume to calculate fluxes of other gas components (e.g., Rose et al. 1986; Goff et al., 1994). It is assumed that direct samples are representative of

the overall composition of the gas released from the volcano and that the sulfur species remain constant after entering the atmosphere. Also, diffuse emissions of gas (mostly CO₂) sometimes found on the flanks of volcanoes (Baubron et al., 1990) are assumed to be minimal compared to the cumulative volatile budget. The flux calculation for this study was modified for alkaline trap sampling. First the ratios of absolute abundances per day of Cl, CO₂, F, As, and Hg versus SO₂ were calculated

Figs. 5a through f: Absolute abundances (ppm) per day of constituents measured from the seven alkaline trap stations located around the crater of Popocatépetl. Note the three pulses of degassing: The first pulse produced a general trend of broad highs in Cl, CO₂, and As during early 1994. The second produced peaks in S, F, and Hg during June 1994. The third produced increases in all components except As and F before the eruption in December 1994.

(listed in Table 2) using S_{total} concentrations from the alkaline trap solutions. The values were then multiplied by the SO₂ emission rates determined from COSPEC measurements. CO₃ concentrations in caustic solutions were converted to CO₂ for the flux calculation; however, these values are not reliable due to contamination of the trap solutions by CO₂ from the atmosphere.

Because only four COSPEC determinations were made during the time that the traps were in place, only the alkaline trap data for concurrent periods could be utilized. Four COSPEC measurements were obtained a few days after the eruption of December 21 and, for comparative purposes, the highest of these measurements (Dec. 24) is correlated with trap data from December 2. Calculated

Figs. 6a through f: a) SO₂ flux measured by COSPEC in 1994; b through f) Cl ratio diagrams using the highest value for a particular month from all alkaline trap stations. Highs in S/Cl and F/Cl occur before the high SO₂ flux measured on July 2, 1994. CO₃/Cl, As/Cl, and Hg/Cl show respective highs after July 2. These highs are caused by a significant decrease in Cl concentration that began in May 1994.

maximum and minimum fluxes of five components from February, May, July, and November COSPEC measurements are listed in Table 3. Highest calculated flux values are observed during July and December when SO₂ flux was highest. To our knowledge, these are the first flux measurements for As and Hg reported from alkaline trap data.

Maximum flux levels greater than 10⁶ t/d for CO₂ are highly suspect because of atmospheric contamination as mentioned above. Using a LiCor gas analyzer mounted in an airplane, Gerlach et al. (in press) state that the average CO₂ flux from January to June 1995 was at least 6400 t/d (CO₂/SO₂ = 2). Williams (private communication) reports CO₂/

TABLE 3. SO₂ emission rates from COSPEC compared with calculated flux of CO₂, Cl, F, As, and Hg ratioed from alkaline trap analyses and the COSPEC data, Popocatepetl Volcano, Mexico (values in t/d). The "max" and "min" values correspond to maximum and minimum values determined from the trap analyses on dates closest to COSPEC date. These calculations yield the probable range of flux values during 1994, except for CO₂, which is too high due to atmospheric contamination. The average SO₂ flux for 1994 was about 2000 t/d.

COSPEC Date	SO ₂	Trap Date	All Stations	CO ₂	Cl	F	As	Hg
2/19/94	1200	2/20/94	max	<2.2x10 ⁴	176	61	0.071	0.0004
			min	<5.1x10 ³	21	44	0.036	0.0002
5/04/94	900	4/30/94	max	<4.2x10 ⁵	131	57	0.039	0.0005
			min	<1.0x10 ⁴	86	39	0.015	<0.0001
7/02/94	3100	7/18/94	max	<8.0x10 ⁶	273	217	0.544	0.2610
			min	<2.1x10 ⁴	183	130	0.004	0.0004
11/05/94	1260	10/28/94	max	<5.9x10 ⁵	158	44	0.024	0.0016
			min	<1.9x10 ⁴	64	18	0.001	0.0001
12/23/94	2170							
12/24/94	3960	12/02/94	max	<2.1x10 ⁶	515	170	0.209	0.0070
			min	<4.9x10 ⁴	269	40	0.001	0.0003
12/27/94	1170							
12/29/94	1240							

SO₂ of 4 to 8 using ground-based GASPEC measurements taken in May 1996. These ratios indicate that CO₂ flux during 1994 probably never exceeded 25,000 t/d.

Except for CO₂, the relative proportions of the major acidic components determined from trap samples are similar to those found at many other active and passively degassing volcanoes. For example, our flux values for Popocatepetl (using about 4000 t/d SO₂ on December 24, 1994) can be compared with published flux data from other calc-alkaline volcanoes (Table 4) to get a rough estimate of the range of values expected during passive degassing events. Each constituent shows order of magnitude variations depending on the vigor of the volcano and its unique volatile composition. More detailed comparisons are beyond the scope of this report.

Sulfur and Carbon Isotope Geochemistry of Trap Samples

Despite irregular sampling intervals and seasonal variations in meteorological conditions, the data clearly indicate major changes in fumarolic discharges (Figs. 5 and 6). S_{total} and F increased five-

fold in the June sample from the NW crater rim location. Smaller peaks in S_{total}, CO₂, F, and Cl concentrations are seen in other June–July samples, particularly from the SE. Extremes in δ³⁴S (Fig. 7) occurred in July samples from the NW (overall maximum 6.5‰) and the SE (minimum 2.3‰), followed by a steady increase through October in δ³⁴S from the SE (to 5.4‰). Coupled with increased seismicity and high SO₂ flux (3100 t/d) reported in July, these data may indicate that mafic magma was injected into a reservoir of more silicic magma (discussed below). The higher δ³⁴S values could also indicate a contribution of heavy sulfur derived from secondary sources (Fig. 8). δ³⁴S analyses of native sulfur deposited near the crater, SO₄ dissolved in the crater lake water, and gypsum from a regional evaporite deposit yielded values of 1.3, 18.6, and 16.4‰, respectively. Between October and early December, all locations had decreasing δ³⁴S values (to an overall minimum of 1.5‰), along with increasing S_{total}, CO₂, F, and Cl concentrations. These combined trends probably reflect gases released from magma prior to the eruption and a more primordial origin for the sulfur gases (mantle-derived sulfur δ³⁴S = 0 ± 3‰, Rollinson, 1993; upper mantle ≈ +1.3‰, Ohmoto and Rye, 1979).

TABLE 4. Flux comparisons (t/d) among Popocatépetl and some other calc-alkaline, passively degassing volcanoes.¹

Volcano	Popo. Mexico	Galeras Colombia	Satsuma Japan	White Is. New Zealand
Method	Alk. Trap	Direct	Direct	Direct
Date	12/94	1/93	10/93	5/96
H ₂ O	(200,000) ²	10,000	13,200	38,000
SO ₂ ³	3,960	500	450	250
H ₂ S	-----	115	8.3	215
CO ₂	16,000 ⁴	2,100	120	530
HCl	390 ⁵	89	120	275
HF	100 ⁵	5.3	12	<1
As	0.10 ⁵	1.89?	0.007	0.22
Hg	0.0036 ⁵	0.0004	0.0001	0.040
S (wt-%)	(0.9) ²	2.8	1.7	0.8

¹ Data from this study and Goff et al. (1994; unpub. data).

² Values very approximate; assume 90% of total flux is H₂O.

³ SO₂ flux by COSPEC; other values ratioed to SO₂ flux.

⁴ CO₂ flux is based on CO₂/SO₂ = 4:1 (see text).

⁵ Value is average of maximum and minimum values shown in Table 3.

Figs. 7a and b: a) Sulfur-34 isotope compositions (in per mil relative to CDT) of total sulfur from alkaline trap solutions versus collection date. The extreme $\delta^{34}\text{S}$ values observed in July follow the pronounced S pulse of 19 June 1994 shown in Figure 5a. Most $\delta^{34}\text{S}$ values steadily increase between July and October, and all values decrease sharply in late Fall prior to the December eruption, corresponding to the increased flux of SO₂. b) Carbon-13 isotope compositions (in per mil relative to PDB) of total carbon in alkaline trap solutions versus collection date. All values are anomalously depleted relative to air or mantle carbon due to contamination by atmospheric CO₂ (see text). Heavier values reported for some stations may reflect a magmatic influence, but these data are not as useful as Sulfur-34 for tracking volcanic eruptions.

Experiments on kinetic sulfur isotope fractionation for SO₂ in air indicate that about a $\leq 1\text{‰}$ shift can be expected as gas leaves the volcanic vents and absorbs into the trap solutions (P. M. Nuccio, private communication). Thus, our sulfur isotope results could be about 1‰ more depleted than ac-

tual bulk values. If so, the corrected values would imply that there is a slightly larger contribution of sulfur from non-mantle sources than indicated. Our average value for 41 sulfur isotope measurements at Popocatépetl is $+3.35 \pm 0.92\text{‰}$, indicating that the sulfur is mostly of mantle origin. In the only

Figs. 8a and b: a) Sulfur isotope compositions of natural sources compared with data from this study (adapted from Rollinson, 1993). $\delta^{34}\text{S}$ values for trap samples range from 1.5 to 6.5‰. Values for sublimed sulfur in crater fumaroles, sulfate dissolved in the crater lake, and gypsum from underlying Cretaceous evaporites are 1.3, 18.6 and 16.4‰, respectively. b) Carbon isotope compositions of natural sources compared with data from this study (adapted from Rollinson, 1993). $\delta^{13}\text{C}$ values for trap samples range from -25.8 to -9.3‰. A blank located outside the range of fumaroles (to measure atmospheric CO_2 contamination) yielded -24.4‰.

other published study of sulfur isotopes from alkaline trap samples, Williams et al. (1990) obtained an average value of $+1.9 \pm 1.2$ ‰ ($n=5$) for Nevado del Ruiz Volcano, Colombia.

$\delta^{13}\text{C}$ values ranged from -25.8 to -9.3‰ (Fig. 7), and generally decreased with increasing CO_3 contents, opposite of the expected trend for higher contributions of volcanic CO_2 (mantle $\delta^{13}\text{C} \approx -8$ to -3‰ and a mean value ≈ -6 ‰, Rollinson, 1993) (Fig. 8). As the KOH solution trapped both atmospheric and volcanic CO_2 , reaction kinetics apparently favored the light isotope (Craig, 1953; Rollinson, 1993). CO_2 evolved from a blank placed on the flank of Popocatepetl, outside the influence of fumarolic activity yielded $\delta^{13}\text{C}$ -24.4‰, much lower than the value expected for atmospheric CO_2 (-7‰; Craig, 1953; Ohmoto and Rye, 1979). Although the air around Popocatepetl is polluted with a 5% addition of CO_2 from urban combustion of fossil fuels, it is unlikely that the value obtained from the blank represents the $\delta^{13}\text{C}$ of local atmospheric CO_2 . Kinetic fractionation by preferential absorption of isotopically lighter CO_2 is the dominant process in collecting CO_2 using alkaline solutions (see Craig, 1953, p. 71–72). A set of

KOH blank solutions placed on the lab bench at the USGS in Menlo Park during analyses of the trap samples yielded an average $\delta^{13}\text{C}$ value of -16‰.

In spite of these kinetic effects, the heaviest carbon values from the trap samples correspond to the October maximum in $\delta^{34}\text{S}$ for the SE traps. This peak in $\delta^{13}\text{C}$ is consistent with an increase in magmatic carbon but may indicate a contribution of carbon from regional limestone deposits being incorporated into the magma. Two locations show a trend towards higher $\delta^{13}\text{C}$ values (more volcanic in origin) in the two months prior to the eruption on December 1994. We conclude, however, that $\delta^{34}\text{S}$ is more useful than $\delta^{13}\text{C}$ as an indicator of increasing of volcanic activity when monitoring fumarolic acid-gas emissions using alkaline-solution traps.

Volatile Variations and Evidence for Magma Mixing, Assimilation, or Shallow Degassing

Degassing trends during 1994 (Fig. 5) showed early release of CO_2 , Cl, and As with later release of S, F, and Hg in June–July. Also, decreasing $\delta^{34}\text{S}$ in

SO₂ and increased emission of CO₂ and Cl relative to S, F, and Hg occurred prior to the eruption in December 1994. These observed variations of volatile components could be caused by an injection of mafic magma into a silicic chamber (Anderson, 1974), ascent of magma where gases are released due to pressure changes (Gerlach, 1986), or volatile addition from interaction of magma with secondary sources such as underlying evaporite and carbonate strata or altered volcanic rocks. These processes are not mutually exclusive and are discussed in more detail below.

Magma Mixing: Petrologic studies of lavas and ash deposits (≤ 10 ka) from Popocatepetl give both chemical and textural evidence for mixing of relatively shallow dacite with deeper, more mafic, primitive magma (Boudal, 1985; Kolisnik, 1990). Kolisnik provides the most comprehensive listing of magma mixing evidence which includes (a) rare resorbed, forsteritic olivine crystals (Fo 90–71) in many samples, (b) reverse zoning in both clinopyroxene and orthopyroxene crystals with increases in ΔEn of 10 to 18%, respectively, (c) plagioclase phenocrysts (An 71–21) showing normal and oscillatory zoning and evidence of resorption and regrowth with sharp calcic enrichments of 10 to 37%, (d) the occurrence of quartz and olivine together in single samples, (e) fritted plagioclase textures, and (f) orthopyroxene reaction rims on olivines. One Popocatepetl lava shows evidence of magma mingling with light and dark magma interspersed throughout hand samples. Other samples show microscopic streaks of different groundmass colors indicating that mixing was relatively efficient.

These features are classic magma mixing textures (Eichelberger, 1975; Bacon, 1986; Stimac and Pearce, 1992). As volatile-rich mafic magmas are injected into a more silicic and cooler host, the basalt is quenched, forcing crystallization and consequent volatile exsolution. Therefore, increases in total volatile output, increased concentration ratios, and decreasing $\delta^{34}\text{S}$ of released gases observed during June–July and prior to the eruption in December 1994, could indicate injection of mafic magma into the existing silicic reservoir. In

addition, increased seismic activity observed during June 1994 could correlate with the upward movement and decompression of magma and the increased output of S, F, and Hg. Unfortunately, seismic data for the period are quite limited because only one station was located near the volcano, and no deformation information is available.

Although the absolute abundance of Cl is not high, the Cl/SO₂ data are particularly interesting because values are highest during the beginning of 1994 and before the December 1994 eruption. In a pioneering study on melt inclusions in arc basalts (high-alumina tholeiites), Anderson (1974) found that inclusions in forsteritic olivine phenocrysts have considerably higher Cl values than in more ferric olivine crystallized after eruption. Anderson also proposed that undegassed mafic magmas are generally higher in Cl and S relative to water than more silicic magmas and that Cl preferentially degasses over S at higher pressures (greater depth; e.g., Gerlach, 1986). Similar findings were reported by Metrich et al. (1993) for melt inclusions in olivines from very young alkali basalts at Mt. Etna. Thus, relative increases in Cl in the trap samples could be signaling periods of mafic injection.

Assimilation: Minor assimilation of volatile components from strata underlying the volcano is also a viable process. Some recent Popocatepetl lavas, particularly the ca. 2300 year old basaltic andesite flow east of the mountain, contain a variety of xenoliths ≤ 20 cm diameter. Among these xenoliths are metamorphosed limestone and siliciclastic rocks partially converted to skarns (mineral assemblages of quartz+green hornblende+tremolite+diopside+sphene±garnet with residual carbonate and sedimentary layering). Since Cretaceous carbonates and evaporites underlie the volcano, their assimilation can provide additional C and S to the Popocatepetl magma chamber.

Because S from gypsum in this source is highly enriched in $\delta^{34}\text{S}$ (+16‰) relative to mantle S, the decrease in $\delta^{34}\text{S}$ observed in alkaline trap samples over time could be explained by injection of mafic

(relatively $\delta^{34}\text{S}$ depleted) magma into an existing, more silicic reservoir slightly pre-contaminated by Cretaceous sulfur. For example, if the magma initially contained only mantle S (at about 1‰ $\delta^{34}\text{S}$), raising the observed S-isotope value to 3.5‰ by digestion of gypsum requires that 16% of the total S comes from Cretaceous sources. If an average of 2000 t/d of SO_2 is released during 1994, then 320 t/d could originate from digestion of rocks containing gypsum. Pure gypsum contains about 19% S by weight, but gypsum-bearing strata might average only 10% S by weight, which is at least two orders of magnitude more S than contained in most basalt to dacite magmas (Metrich et al., 1993; Wallace and Gerlach, 1994); thus, a relatively small amount of gypsum assimilation ($\leq 1\%$) could profoundly influence the bulk S content and isotopic composition of Popo magma.

In their S-isotope study of coexisting anhydrite and sulfides in pumice from the June 1991 Pinatubo eruption, McKibben et al. (1992) showed that 23 anhydrite crystals varied in isotope composition from +3 to +16‰ $\delta^{34}\text{S}$. It was the conclusion of these authors that not all S in Pinatubo magma was of primary origin and that some S originated from hydrothermal anhydrite or from deep degassing of earlier magma batches.

Contamination of magma by hydrothermally altered ($\delta^{34}\text{S}$ enriched) volcanics in the edifice or from sulfur dissolved as sulfate in the summit crater lake is not considered to be a realistic mechanism for isotopic enrichment of the gases. Xenoliths in previous eruptive products indicate that the magma chamber resides at depths well below levels of shallow alteration, and the crater lake was too small to make a significant contribution (50 m diameter by 3 m deep). As opposed to Pinatubo and many other arc volcanoes which display extensive hydrothermal alteration and have well-developed hydrothermal systems, Popocatepetl apparently has neither. Exposed alteration is restricted to the summit area.

Shallow Degassing: Many experimental studies of silicate melts show that reduced pressures (and

depths) allow volatile components to be released as free gas. A natural example of the process for mantle basalt was described by Gerlach (1986) who compared shallow degassing behavior of several volatile components with magma emplacement depth and structural position of magma within conduits and dike systems at Kilauea volcano. Although shallow emplacement of magma in the conduit of Popocatepetl will facilitate volatile degassing, COSPEC data indicate that more volatiles have been released than can be contained in a reasonably sized volume of near-surface magma.

Eruptions since 1994 reveal that Popocatepetl tephra and extrusions contain 62–64 wt-% SiO_2 , very similar to Mount St. Helens dacite (Rutherford et al., 1985; Shevenell and Goff, 1993). If Popocatepetl magma contains about 4 wt-% volatiles, also like St. Helens dacite, then a 0.25-km-thick plug of magma ($\rho=2.3 \text{ g/cm}^3$) in a 0.25-km-diameter conduit contains about 1×10^6 tons of volatiles of which 90% is probably water (Tedesco, 1995; Table 3). On the other hand, Popo released a rough average of 2000 t/d SO_2 for a period of at least 300 days in 1994. Because SO_2 comprises no more than 5% of the total volatile content released from most silicic volcanoes (e.g., Table 3), Popo released roughly $1\text{--}5 \times 10^7$ tons of volatiles during 1994. Thus, it seems unreasonable that shallow plug degassing would produce the large volatile flux observed at Popo during 1994 and/or during events later than 1994. Most volatiles must come from a larger, convecting chamber, circulating at depth.

Implications for Eruption Forecasting

The alkaline trap method was not effective for eruption forecasting during recent events at Popocatepetl due to logistical and analytical limitations. Servicing the traps required periodic trips by scientists who had to be trained in high-altitude mountaineering because the summit is over 5000 m elevation. After the volcano erupted in December 1994, servicing the traps on a regular basis was considered too dangerous. The samples were analyzed in the United States because appropriate ana-

lytical capabilities were not available in Mexico. Time between sample collection and data acquisition was several weeks at best. Once acquired, however, the data showed significant changes in volatile chemistry that correlated with increased SO_2 emissions and provided insight for magmatic processes. The alkaline trap method for monitoring volcanic activity is very useful in situations where direct fumarole samples are impossible to obtain and should be considered an important part of a monitoring program. Timely results could contribute significantly to the integrated data sets used in eruption forecasting.

IV. GEOCHEMISTRY OF FLANKING THERMAL/MINERAL SPRINGS

Methods and Procedures for Collection and Analysis of Spring Waters

Weather in Central Mexico is characterized by a rainy season with almost daily precipitation during the months June–September, followed by a dry season that reaches its peak in March–April. Popocatepetl has low-volume runoff and a few ephemeral springs on its upper slopes and more abundant springs with relatively high-volume discharge near its base. Discharge rates of these lower-elevation springs vary little over the year despite the strong seasonal variations in precipitation. These characteristics are easily explained by the high permeability of the young pyroclastic deposits that mantle the volcano. In contrast, Iztaccíhuatl, to the north, has an abundance of small springs that feed small perennial streams on its upper slopes, and it lacks large-volume springs at its base.

Samples were collected from 13 springs at 10 locations around Popocatepetl between April 1994 and June 1995. Ten springs were sampled periodically, and three springs were sampled only once. All spring locations are shown in Figure 9, and photographs of two of the more renowned springs are shown in Figures 10a and 10b. Springs are located as close as ~6 km from the summit of Popocatepetl Volcano (Atlamaya) to as far as ~60

km (Amatitlanes). Sampling methods varied for all collections through May 1995. Many samples for chemical analysis were collected without filtering or acidification for cation preservation, and many samples were stored for several months before analysis. For these reasons, some of the data reported in Tables 5 and 6 may not be reliable. Unstable constituents affected by inconsistent sampling and storage procedures include HCO_3 , Ca, Mg, and Sr. However, standardized methods for collection and analysis (Trujillo et al., 1987) were used for the last sampling effort (labeled as MVT-# in both tables) completed in June 1995, and data on these samples are probably the most accurate for both major and trace constituents. Methods of analysis and detection limits for all constituents measured on spring samples are given in Table 1. No tritium or stable isotope analyses were performed on spring samples collected between April 1994 and May 1995.

Ten springs were sampled in June 1995. Collection procedures for these samples were as follows. A set of four samples was taken at each site. Two chemistry samples, both in 125-ml low-density polyethylene bottles and sealed with Polyseal caps, were filtered through 0.45- μm -pore-diameter filter membranes using a hand-operated vacuum pump. One sample for cation, silica, and trace constituent analysis was acidified with high-purity HNO_3 to $\text{pH} < 2$, and the other for anion analysis was left unacidified. Two isotope samples were left unfiltered and unacidified: one was collected in a 500-ml polyethylene bottle for tritium analysis and the other in a 30-ml glass bottle for δD and $\delta^{18}\text{O}$ analyses. Both were sealed with Polyseal caps. Data recorded in the field included pH (using indicator strips), temperature, flow rate (estimated), and rock type from which the spring issues.

Major Cation/Anion Analyses for Warm and Cold Springs

One objective for sampling springs was to monitor variations in spring chemistry potentially due to changes in eruptive behavior of Popocatepetl.

Spring Monitoring at Popocatépetl Volcano

Fig. 9: Map showing spring sampling sites in the vicinity of Popocatépetl Volcano, Mexico.

Figs. 10a and b: a) Photograph of Claus Siebe sampling diffuse gases discharging from the large spring at Oaxtepec; b) photograph of the large spring at Agua Hedionda, which also discharges very little gas.

TABLE 5. Major cation/anion analysis for warm and cold spring waters in the region of Popocatepetl, Mexico (values in ppm).²⁴

Sample Number	Description	Date	Temp (°C)	SiO ₂	Ca	Mg	Sr	Na	K	Li	HCO ₃	SO ₄	Cl	F	Br	B	CO ₃	TDS (ppm)	Cation Meq	Anion Meq	Balance (%)
MX94-51	Agua Hedionda	05/14/94	---	68.3	308	125	4.66	106	10.20	0.47	10.2*	1018	84.2	1.12	0.21	3.10	0	2071.90	30.71	29.30	0.05
MX94-54	Agua Hedionda	07/11/94	26.8	71.5	511	133	5.49	109	10.30	0.44	10.3*	1027	84.0	1.22	0.25	3.06	0	2608.40	41.68	34.51	0.19
MX94-70	Agua Hedionda	08/19/94	26.4	67.2	490	131	5.13	105	10.70	0.43	10.7*	1027	80.6	0.90	0.27	3.20	0	2496.20	40.30	33.14	0.20
MX94-74	Agua Hedionda	10/11/94	26.6	70.6	476	125	5.03	101	9.50	0.44	9.5*	1065	84.2	0.91	0.24	3.24	0	2464.20	38.92	33.19	0.16
MX94-10	Agua Hedionda	11/18/94	26.7	71.9	489	126	4.95	102	10.50	0.49	870.0	1095	85.6	1.35	0.26	2.97	0	2864.03	39.68	39.59	0.00
MX94-26	Agua Hedionda	12/28/94	26.5	65.7	481	128	5.10	99	9.48	0.31	865.0	1098	87.2	1.45	0.29	3.41	0	2845.01	39.21	39.61	-0.01
MX95-33	Agua Hedionda	01/28/95	26.5	70.2	475	116	5.27	104	9.84	0.45	861.0	1005	85.1	1.77	0.28	3.13	0	2606.28	38.20	37.57	0.02
MX95-41	Agua Hedionda	02/13/95	33.4	71.3	512	125	5.36	102	9.70	0.48	864.0	1087	84.2	1.57	0.27	3.14	0	2641.48	40.70	39.28	0.04
MX95-49	Agua Hedionda	03/06/95	33.1	71.7	508	123	5.46	107	9.58	0.50	863.0	1106	84.2	1.66	0.27	3.00	0	2652.72	40.55	39.66	0.02
MX95-80	Agua Hedionda	03/25/95	26.9	73.6	509	128	5.36	105	10.60	0.45	10.6*	1023	70.2	1.05	0.21	3.03	0	2796.90	40.98	37.55	0.09
MX95-88	Agua Hedionda	04/30/95	27.1	63.1	499	127	4.94	104	10.20	0.40	861.0	1098	81.5	1.81	0.24	3.28	0	2855.90	40.29	39.40	0.02
MVT-6	Agua Hedionda	06/26/95	25.8	73.0	496	125	5.25	107	8.70	0.41	868.0	1130	87.3	1.21	0.26	3.30	0	2906.00	40.04	40.31	-0.01
MX94-17	Amatitlanes	7/13/94	24.9	67.8	110	36.5	4.53	45.5	5.35	0.11	291	265	16.3	1.80	0.05	0.21	0	851.62	10.74	10.96	-0.02
MX94-64	Amatitlanes	08/18/94	25.2	71.5	146	42.6	5.16	53.2	6.00	0.15	279	248	15.2	1.99	0.02	0.23	14.3	890.80	13.43	10.86	0.21
MX94-8	Amatitlanes	11/17/94	25.4	71.5	149	37.2	5.13	46.4	5.96	0.14	388	271	17.6	1.76	0.05	0.21	0	1002.30	12.83	12.71	0.01
MX94-24	Amatitlanes	12/20/94	25.5	66.3	137	39.3	4.60	43.1	5.33	0.13	391	249	16.4	1.97	0.04	0.21	0	964.08	12.27	12.29	0.00
MX95-32	Amatitlanes	01/23/95	25.2	67.4	136	40.3	4.59	45.1	5.48	0.12	393	255	17.3	2.08	0.06	0.21	0	1098.50	12.33	12.45	-0.01
MX95-86	Atlamaya	04/25/95	21.7	47.7	4.3	2.3	0.05	7.3	3.24	0.04	42.7	2.4	1.1	0.20	<0.02	0.01	0	111.90	0.83	0.79	0.05
MX94-52	Atotonilco I	05/15/94	---	60.3	233	57.9	3.02	56.2	4.50	0.06	243	607	21.7	1.00	0.02	0.23	0	1291.90	19.05	17.32	0.10
MX94-55	Atotonilco I	07/13/94	32.9	61.0	235	58.6	2.93	52.2	4.30	0.05	245	647	21.4	1.00	<0.02	0.22	0	1331.20	19.02	18.15	0.05
MX94-61	Atotonilco I	08/17/94	32.8	62.3	242	59.2	3.00	55.5	4.70	0.05	204	635	22.4	0.89	<0.02	0.24	14.1	1309.80	19.60	17.80	0.10
MX94-71	Atotonilco I	10/11/94	34.4	56.3	229	54.7	2.88	49.4	4.20	0.05	212	606	21.6	0.87	<0.02	0.22	16.4	1260.90	18.28	17.38	0.05
MX94-1	Atotonilco I	11/18/94	32.7	62.1	225	54.1	2.89	50.4	4.32	0.07	243	626	20.7	0.78	<0.02	0.21	0	1297.04	18.09	17.73	0.02
MX94-18	Atotonilco I	12/20/94	33.0	58.4	232	54.5	2.97	47.0	4.26	0.05	240	665	22.8	0.98	<0.02	0.22	0	1335.43	18.31	18.56	-0.01
MX95-27	Atotonilco I	01/23/95	33.1	62.9	228	54.0	2.93	51.6	4.50	0.05	241	615	21.0	0.76	0.03	0.21	0	1271.25	18.27	17.43	0.05
MX95-34	Atotonilco I	02/13/95	33.4	59.1	231	55.6	2.88	52.4	5.41	0.06	247	616	21.0	0.79	<0.02	0.23	0	1471.31	18.61	17.50	0.06
MX95-42	Atotonilco I	03/05/95	33.2	61.2	240	57.3	2.96	51.5	4.35	0.06	242	642	21.4	0.79	<0.02	0.20	0	1435.37	19.14	18.00	0.06
MX95-78	Atotonilco I	03/25/95	33.0	63.1	234	56.6	2.91	53.5	4.40	0.04	244	655	22.5	1.02	<0.02	0.23	0	1343.40	18.87	18.39	0.03
MX95-89	Atotonilco I	05/04/95	33.1	56.9	235	55.2	2.8	51.3	4.68	0.05	242	631	20.2	1.12	<0.02	0.27	0	1304.10	18.72	17.76	0.05
MX94-53	Atotonilco II	05/15/94	---	58.6	344	74.6	4.55	61.3	4.80	0.08	214	1020	26.1	1.55	<0.02	0.29	0	1810.80	26.22	25.52	0.03
MX94-15	Atotonilco II	7/13/94	36.3	55.2	345	68.5	4.53	51.4	4.48	0.40	194	1002	27.1	1.25	<0.02	0.29	0	1754.76	25.36	24.83	0.02
MX94-62	Atotonilco II	08/17/94	35.6	57.4	344	71.4	4.43	55.4	4.00	0.06	159	965	26.2	1.49	<0.02	0.30	0	1690.60	25.68	23.49	0.09
MX94-72	Atotonilco II	10/11/94	34.4	58.9	342	73.3	4.54	58.8	4.50	0.07	171	1004	26.0	1.42	<0.02	0.30	0	1746.30	25.90	24.48	0.06
MX94-2	Atotonilco II	11/18/94	35.8	58.2	349	75.8	4.33	58.4	2.25	0.07	209	1001	25.8	1.14	<0.02	0.29	0	1787.45	26.38	25.03	0.05
MX94-19	Atotonilco II	12/20/94	35.0	52.6	326	68.4	4.23	56.0	4.96	0.06	210	940	29.9	1.27	<0.02	0.30	0	1698.16	24.61	23.93	0.03
MX95-85	Axocopan	04/03/94	19.4	101.0	36.2	43.0	0.24	55.5	5.50	0.05	391	36.8	16.2	0.40	<0.02	0.28	0	690.00	7.93	7.73	0.00
MX94-14	Axocopan	7/13/94	19.1	94.8	34.2	40.4	0.24	51.5	5.72	0.06	387	35.7	16.6	0.35	0.05	0.27	0	669.06	7.44	7.62	-0.02
MX94-63	Axocopan	08/18/94	19.1	98.7	33.5	42.5	0.23	59.0	5.90	0.08	324	36.3	15.9	0.43	<0.02	0.27	31.1	651.80	7.92	7.65	0.04
MX94-7	Axocopan	11/17/94	19.5	97.8	34.7	38.2	0.24	57.6	5.75	0.09	390	36.0	16.4	0.30	0.04	0.26	0	681.62	7.55	7.69	-0.02
MX94-23	Axocopan	12/10/94	19.4	97.2	36.4	39.8	0.22	53.5	5.63	0.05	386	35.8	16.6	0.36	<0.02	0.28	0	676.44	7.58	7.64	-0.01
MX95-76	Axocopan	01/14/95	19.3	97.2	35.1	40.3	0.23	55.1	5.20	0.05	376	34.1	14.4	0.63	<0.02	0.27	0	661.80	7.62	7.37	0.03
MX95-77	Axocopan	01/14/95	19.3	93.5	33.8	40.9	0.22	55.5	5.50	0.05	357	37.5	16.5	0.42	<0.02	0.28	18.2	663.60	7.63	7.80	-0.02
MX95-39	Axocopan	02/12/95	19.4	96.5	39.5	41.3	0.22	54.2	5.90	0.07	390	37.0	18.9	0.34	0.03	0.28	0	873.57	7.90	7.79	0.01
MX95-47	Axocopan	03/03/95	17.6	101.4	37.1	40.4	0.25	52.6	5.85	0.09	390	37.2	17.0	0.35	0.04	0.26	0	871.99	7.64	7.74	-0.01
MX95-94	Axocopan	05/04/95	19.3	95.0	35.8	41.2	0.30	54.5	5.94	0.05	390	35.3	17.0	0.37	0.03	0.29	0	679.80	7.72	7.70	0.00
MVT-11	Axocopan	06/26/95	18.6	98.0	36.2	41.4	0.24	58.4	5.30	0.07	395	37.6	17.1	0.44	0.04	0.28	0	694.00	7.91	7.84	0.01
MX94-12	El Recreo near Oaxtepec	7/11/94	22.2	67.6	324	74.7	3.97	37.4	5.43	0.12	373	825.0	32.3	0.64	0.10	1.00	0	1750.47	24.19	24.30	0.00

TABLE 5 (Continued).

Sample Number	Description	Date	Temp (°C)	SiO ₂	Ca	Mg	Sr	Na	K	Li	HCO ₃	SO ₄	Cl	F	Br	B	CO ₃	TDS (ppm)	Cation Meq	Anion Meq	Balance (%)
MX95-81	Ixtatlala A	04/03/94	50.1	53.7	533	83.2	9.80	335	21.20	0.56	219	1339	504	2.86	0.33	1.46	0	3104.80	48.85	45.74	0.07
MX94-66	Ixtatlala A	08/19/94	49.6	56.5	531	89.0	9.60	372	21.50	0.65	148	1260	491	2.56	0.35	1.42	0	2989.70	50.87	42.63	0.18
MX94-3	Ixtatlala A	11/17/94	50.1	62.9	512	86.2	9.9	303	20.60	0.57	217	1364	552	2.47	0.27	1.43	0	3135.73	46.66	47.57	-0.02
MX95-28	Ixtatlala A	01/23/95	49.8	57.6	561	83.9	9.34	300	20.60	0.51	217	1381	564	2.77	0.24	1.41	0	3234.42	48.67	48.25	0.01
MX95-35	Ixtatlala A	02/12/95	49.8	57.4	566	91.4	9.15	337	20.30	0.51	220	1410	567	2.87	0.30	1.46	0	3228.51	51.13	48.99	0.04
MX95-43	Ixtatlala A	03/05/95	49.6	54.1	552	90.5	9.57	304	20.20	0.51	220	1387	557	2.37	0.27	1.51	0	3203.54	48.97	48.21	0.02
MX95-90	Ixtatlala A	05/04/95	48.9	53.5	542	86.1	8.91	330	21.10	0.57	215	1440	525	2.79	0.22	1.49	0	3227.80	49.23	48.35	0.02
MVT-7	Ixtatlala A	06/26/95	49.7	60.8	563	86.9	9.73	352	18.30	0.60	218	1457	556	2.84	0.25	1.43	0	3329.00	51.24	49.62	0.03
MX95-82	Ixtatlala B	04/03/94	46.0	56.5	548	89.1	10.0	344	20.20	0.57	215	1403	534	2.80	0.32	1.42	0	3226.50	50.43	47.83	0.05
MX94-16	Ixtatlala	7/13/94	45.5	53.9	507	84.0	9.76	319	20.10	0.49	176	1398	581	2.70	0.27	1.53	0	3156.70	46.88	48.42	-0.03
MX94-67	Ixtatlala B	08/19/94	44.6	56.3	522	90.8	9.78	377	21.90	0.69	150	1389	525	2.73	0.37	1.41	0	3151.70	50.76	46.28	0.09
MX94-4	Ixtatlala B	11/17/94	44.1	58.0	528	92.1	9.6	327	21.10	0.62	213	1400	569	2.53	0.30	1.41	0	3224.54	48.94	48.71	0.00
MX94-20	Ixtatlala B larger pond	12/20/94	44.4	58.9	546	89.7	9.86	337	20.50	0.52	217	1357	571	2.80	0.29	1.50	0	3213.93	50.06	47.96	0.04
MX95-29	Ixtatlala B	01/23/95	45.0	53.1	564	84.1	9.20	321	20.70	0.60	215	1404	566	2.85	0.26	1.42	0	3349.29	49.74	48.75	0.02
MX95-36	Ixtatlala B	02/12/95	45.5	56.5	564	88.5	9.06	335	20.40	0.64	216	1411	570	2.74	0.25	1.53	0	3276.71	50.72	49.03	0.03
MX95-44	Ixtatlala B	03/05/95	45.1	58.9	559	89.6	9.70	316	20.30	0.57	214	1418	575	2.92	0.25	1.47	0	3361.80	49.75	49.28	0.01
MX95-91	Ixtatlala B	05/04/95	44.9	25.0	557	87.0	8.49	344	21.00	0.56	215	1430	518	2.75	0.24	1.48	0	3240.20	50.65	47.94	0.05
MVT-8	Ixtatlala B	06/26/95	43.0	25.9	582	89.3	9.47	352	20.40	0.60	214	1447	539	2.69	0.24	1.50	0	3315.00	52.44	48.87	0.07
MX94-13	Iztamatitlan near Oaxtepec	7/11/94	25.4	65.1	547	133	8.42	59.0	7.12	0.22	486	1583	52.4	1.25	0.18	1.67	0	2945.23	41.17	42.40	-0.03
MX94-50	Oaxtepec	05/13/94	---	68.3	513	138	5.77	111	10.70	0.49	903	1163	87.6	1.70	0.40	3.11	0	3008.30	42.20	41.61	0.01
MX94-11	Oaxtepec	07/11/94	26.4	66.1	497	119	5.79	99.3	10.10	0.42	798	1153	86.9	1.09	0.27	3.47	0	2842.25	39.36	39.63	-0.01
MX94-65	Oaxtepec	08/18/94	26.3	70.4	491	137	6.10	120	10.90	0.53	619	1099	87.0	1.20	0.31	3.02	0	2649.80	41.52	35.63	0.15
MX94-73	Oaxtepec	10/11/94	26.5	67.6	502	130	5.57	106	10.20	0.45	575	1075	86.6	1.02	0.28	3.28	0	2566.60	40.88	34.37	0.17
MX94-9	Oaxtepec	11/18/94	26.2	72.5	497	130	6.26	121	10.60	0.57	897	1128	87.1	1.61	0.27	3.12	0	2956.69	41.25	40.74	0.01
MX94-25	Oaxtepec	12/28/94	26.6	64.2	499	135	5.30	103	9.84	0.32	900	1110	88.0	1.55	0.24	3.43	0	2920.97	40.87	40.45	0.01
MX95-75	Oaxtepec	01/14/95	26.3	71.7	520	134	5.78	115	9.90	0.46	762	1097	82.5	1.26	0.25	3.15	0	2804.90	42.46	37.75	0.12
MX95-40	Oaxtepec	02/13/95	26.8	74.0	510	132	5.57	100	10.00	0.38	893	1044	84.6	1.74	0.25	3.07	0	2667.90	41.07	38.88	0.05
MX95-48	Oaxtepec	03/05/95	26.7	73.4	519	135	5.76	95.8	10.00	0.43	891	1149	87.4	1.76	0.28	3.17	0	2973.22	41.58	41.10	0.01
MX95-79	Oaxtepec	03/25/95	26.5	71.9	515	137	5.33	103	9.90	0.44	896	1120	84.5	1.59	0.28	3.31	0	2950.00	41.91	40.49	0.03
MX95-87	Oaxtepec	04/30/95	26.7	62.7	520	135	5.24	103	10.40	0.44	893	1142	86.8	1.58	0.25	3.23	0	2965.00	41.97	40.96	0.02
MVT-5	Oaxtepec	06/25/95	25.9	73.2	510	131	5.95	111	9.70	0.45	896	1200	87.8	1.40	0.25	3.33	0	3031.00	41.46	42.23	-0.02
MX95-83	Ojo del Carbon A	04/03/94	22.6	74.0	509	101	5.24	39.0	3.90	0.03	314	1426	17.8	1.89	<0.02	0.26	0	2493.20	35.64	35.34	0.01
MX94-68	Ojo del Carbon A	08/19/94	22.4	75.1	507	106	5.03	41.6	3.90	0.04	227	1399	17.9	1.81	<0.02	0.24	0	2385.50	36.05	33.35	0.08
MX94-5	Ojo de Carbon A	11/17/94	22.6	95.7	527	104	4.66	42.0	4.25	0.07	312	1425	17.7	1.32	0.05	0.22	0	2534.75	36.88	35.25	0.05
MX94-21	Ojo de Carbon A	12/20/94	22.6	86.0	502	95.9	4.91	40.1	4.19	0.07	312	1384	18.7	1.51	0.05	0.27	0	2451.67	34.96	34.44	0.01
MX95-30	Ojo de Carbon A	01/23/95	22.6	68.3	522	98.4	4.97	42.6	4.19	0.06	312	1441	17.7	1.64	<0.02	0.21	0	2513.39	36.16	35.60	0.02
MX95-37	Ojo de Carbon A	02/12/95	22.5	77.0	526	99.1	4.94	41.6	4.16	0.05	313	1455	17.8	1.75	0.03	0.22	0	2541.18	36.39	35.91	0.01
MX95-45	Ojo de Carbon A	03/05/95	22.4	79.0	509	100.0	5.07	37.4	4.10	0.08	313	1322	17.9	1.60	0.03	0.20	0	2389.88	35.46	33.15	0.07
MX95-92	Ojo de Carbon A	05/04/95	22.8	74.7	529	101.0	4.94	39.4	4.30	0.04	313	1360	17.4	1.40	0.02	0.22	0	2446.00	36.63	33.91	0.08
MVT-9	Ojo de Carbon A	06/26/95	21.8	75.3	522	95.2	4.96	43.4	3.60	0.06	313	1384	17.9	1.26	0.03	0.24	0	2462.00	35.95	34.42	0.04
MX95-84	Ojo del Carbon B	04/03/94	19.9	71.0	298	61.9	2.87	31.7	3.00	0.02	216	717	15.0	1.17	<0.02	0.19	18.6	1439.80	21.53	19.58	0.09
MX94-69	Ojo del Carbon B	08/19/94	21.3	71.7	290	65.5	2.80	35.0	3.10	0.03	191	777	15.1	1.07	<0.02	0.18	0	1454.60	21.56	19.78	0.09
MX94-6	Ojo de Carbon B	11/17/94	21.3	75.5	287	56.1	2.78	36.0	3.75	0.06	255	783	17.1	0.87	0.04	0.18	0	1518.06	20.69	20.97	-0.01
MX94-22	Ojo de Carbon B	11/20/94	21.3	66.8	283	58.3	2.60	31.7	3.45	0.05	252	756	16.1	1.14	<0.02	0.17	0	1474.75	20.49	20.39	0.00
MX95-31	Ojo de Carbon B	01/23/95	21.3	71.9	275	56.4	2.87	30.4	3.70	0.05	252	709	16.5	0.92	0.02	0.16	0	1462.11	19.87	19.42	0.02
MX95-38	Ojo de Carbon B	02/12/95	21.3	77.7	305	61.2	2.84	32.9	3.71	0.06	256	775	17.1	1.27	0.03	0.16	0	1536.08	21.86	20.89	0.05
MX95-46	Ojo de Carbon B	03/05/95	21.1	79.4	282	55.8	2.65	31.9	3.55	0.05	251	752	17.0	1.00	<0.02	0.16	0	1622.36	20.21	20.30	0.00
MX95-93	Ojo de Carbon B	05/04/95	21.3	67.6	280	58.3	2.90	31.2	3.65	0.03	251	747	15.9	1.41	0.02	0.17	0	1462.50	20.31	20.20	0.01
MVT-10	Ojo de Carbon B	06/26/95	20.1	79.4	283	65.2	2.97	36.6	3.30	0.05	256	765	15.4	0.86	0.02	0.18	0	1511.0	21.24	20.61	0.03
PLC-01	Crater Lake	02/20/94	21.3	295.0	781	2520	8.56	1835	329	3.31	0	23660	14200	1150	20.2	54	0	50882.3	868.25	907.41	-0.04

<a Analyses by Dale Counce

* Values lower than expected due to carbonate precipitation during storage.

TABLE 6. Trace element analyses for waters in the region of Popocatepetl, Mexico (values in ppm). ^{a-d}

Sample Number	Description	Date	Temp (°C)	Al	As	Ba	Cs	Cu	Fe	Mn	Mo	NH ₄	NO ₂	NO ₃	Pb	PO ₄	Rb	Zn
MX94-51	Agua Hedionda	05/14/94	---	0.67	0.005	---	---	---	---	---	---	---	<0.02	<0.02	---	<0.01	---	---
MX94-54	Agua Hedionda	07/11/94	26.8	0.81	0.004	---	---	---	---	---	---	1.13	<0.02	1.22	---	<0.01	---	---
MX94-70	Agua Hedionda	08/19/94	26.4	0.65	0.005	---	---	---	---	---	---	1.43	<0.02	1.88	---	<0.01	---	---
MX94-74	Agua Hedionda	10/11/94	26.6	0.80	0.004	---	---	---	---	---	---	1.23	0.95	<0.02	---	<0.01	---	---
MX94-10	Agua Hedionda	11/18/94	26.7	0.92	0.003	0.02	0.022	<0.002	0.03	0.02	<0.002	0.56	<0.02	2.26	0.008	0.09	0.040	0.03
MX94-26	Agua Hedionda	12/28/94	26.5	0.49	0.004	<0.01	0.029	<0.002	0.03	<0.01	<0.002	0.48	<0.02	<0.02	<0.002	0.10	0.041	<0.01
MX95-33	Agua Hedionda	01/28/95	26.5	0.48	0.004	0.02	---	---	0.02	0.01	---	0.71	<0.02	<0.02	---	<0.05	---	<0.01
MX95-41	Agua Hedionda	02/13/95	33.4	0.44	0.004	0.02	---	---	0.02	0.01	---	0.87	<0.02	<0.02	---	0.13	---	<0.01
MX95-49	Agua Hedionda	03/06/95	33.1	0.28	0.003	0.02	---	---	0.03	<0.01	---	0.96	<0.02	<0.02	---	0.07	---	<0.01
MX95-80	Agua Hedionda	03/25/95	26.9	0.78	0.004	---	---	---	---	---	---	0.92	<0.02	0.64	---	0.07	---	---
MX95-88	Agua Hedionda	04/30/95	27.1	0.47	0.003	0.01	---	---	---	---	---	0.81	<0.02	<0.02	---	0.08	---	0.02
MVT-6	Agua Hedionda	06/26/95	25.8	0.32	0.003	0.02	0.042	<0.002	0.04	0.01	0.002	0.42	<0.02	0.06	0.002	0.09	0.045	0.01
MX94-17	Amatitlanes	7/13/94	24.9	0.16	0.038	0.02	0.012	<0.002	<0.01	<0.01	0.010	0.05	<0.02	7.13	<0.002	<0.05	0.014	<0.01
MX94-64	Amatitlanes	08/18/94	25.2	0.34	0.052	---	---	---	---	---	---	0.12	<0.02	6.95	---	<0.05	---	---
MX94-8	Amatitlanes	11/17/94	25.4	0.33	0.048	0.03	0.005	0.003	<0.01	<0.01	0.004	0.05	<0.02	7.76	<0.002	<0.05	0.015	<0.01
MX94-24	Amatitlanes	12/20/94	25.5	0.42	0.053	0.03	0.010	0.007	0.27	0.12	0.011	0.06	<0.02	8.44	<0.002	<0.05	0.014	0.22
MX95-32	Amatitlanes	01/23/95	25.2	0.14	0.045	0.03	---	---	<0.01	<0.01	---	0.04	<0.02	6.59	---	<0.05	---	<0.01
MX95-86	Atlamaya	04/25/95	21.7	0.04	<0.001	0.01	---	---	---	0.03	---	0.11	<0.02	0.07	---	<0.05	---	0.02
MX94-52	Atotonilco I	05/15/94	---	0.39	0.032	---	---	---	---	---	---	---	<0.02	3.5	---	<0.05	---	---
MX94-55	Atotonilco I	07/13/94	32.9	0.38	0.034	---	---	---	---	---	---	---	<0.02	2.09	---	<0.05	---	---
MX94-61	Atotonilco I	08/17/94	32.8	0.39	0.034	---	---	---	---	---	---	0.21	<0.02	5.79	---	<0.05	---	---
MX94-71	Atotonilco I	10/11/94	34.4	0.34	0.038	---	---	---	---	---	---	0.26	<0.02	6.64	---	<0.05	---	---
MX94-1	Atotonilco I	11/18/94	32.7	0.39	0.034	0.02	<0.002	0.002	<0.01	<0.01	0.006	0.10	0.64	6.12	0.004	0.16	0.013	0.02
MX94-18	Atotonilco I	12/20/94	33.0	0.37	0.034	0.02	<0.002	0.002	<0.01	<0.01	0.008	0.05	<0.02	6.61	<0.002	0.11	0.015	0.01
MX95-27	Atotonilco I	01/23/95	33.1	0.32	0.034	0.03	---	---	<0.01	<0.01	---	0.04	<0.02	3.81	---	<0.05	---	0.02
MX95-34	Atotonilco I	02/13/95	33.4	0.37	0.033	0.03	---	---	0.02	<0.01	---	0.07	<0.02	1.33	---	<0.05	---	0.02
MX95-42	Atotonilco I	03/05/95	33.2	0.36	0.030	0.03	---	---	<0.01	<0.01	---	0.07	<0.02	3.10	---	<0.05	---	0.02
MX95-78	Atotonilco I	03/25/95	33.0	0.35	0.035	---	---	---	---	---	---	0.19	<0.02	5.5	---	<0.05	---	---
MX95-89	Atotonilco I	05/04/95	33.1	0.42	0.028	0.02	---	---	<0.01	<0.01	---	0.10	<0.02	2.9	---	<0.1	---	<0.01
MX94-53	Atotonilco II	05/15/94	---	0.51	0.023	---	---	---	---	---	---	---	<0.02	0.39	---	<0.1	---	---
MX94-15	Atotonilco II	7/13/94	36.3	0.31	0.021	<0.01	<0.002	<0.002	<0.01	<0.01	0.010	0.05	<0.02	0.15	<0.002	0.04	0.013	<0.01
MX94-62	Atotonilco II	08/17/94	35.6	0.44	0.024	---	---	---	---	---	---	0.18	<0.02	1.29	---	<0.1	---	---
MX94-72	Atotonilco II	10/11/94	34.4	0.47	0.028	---	---	---	---	---	---	0.22	<0.02	0.82	---	<0.1	---	---
MX94-2	Atotonilco II	11/18/94	35.8	0.58	0.022	0.02	0.002	0.002	<0.01	0.04	0.006	0.08	<0.02	1.31	0.007	0.06	0.016	0.02
MX94-19	Atotonilco II	12/20/94	35.0	0.69	0.024	0.01	0.010	0.006	0.05	0.08	0.008	0.08	<0.02	3.21	<0.002	0.07	0.019	0.14
MX95-85	Axocopan	04/03/94	19.4	0.10	0.001	---	---	---	---	---	---	0.12	<0.02	3.38	---	0.6	---	---
MX94-14	Axocopan	7/13/94	19.1	0.04	0.001	0.02	<0.002	0.009	<0.01	<0.01	0.004	0.06	<0.02	1.44	0.005	0.57	0.017	<0.01
MX94-63	Axocopan	08/18/94	19.1	0.11	0.001	---	---	---	---	---	---	0.13	<0.02	3.13	---	0.61	---	---
MX94-7	Axocopan	11/17/94	19.5	0.08	0.002	0.02	<0.002	0.011	<0.01	<0.01	0.003	0.05	<0.02	3.33	<0.002	0.72	0.022	<0.01
MX94-23	Axocopan	12/10/94	19.4	0.08	0.002	0.01	<0.002	<0.002	<0.01	<0.01	0.004	0.04	<0.02	3.72	<0.002	0.77	0.021	<0.01
MX95-76	Axocopan	01/14/95	19.3	0.10	0.001	---	---	---	---	---	---	0.14	<0.02	2.36	---	0.62	---	---
MX95-77	Axocopan	01/14/95	19.3	0.08	0.001	---	---	---	---	0.2	---	0.12	<0.02	3.44	---	0.59	---	---
MX95-39	Axocopan	02/12/95	19.4	0.04	0.001	0.02	---	---	<0.01	<0.01	---	0.06	<0.02	3.61	---	0.58	---	<0.01
MX95-47	Axocopan	03/03/95	17.6	0.09	0.002	0.03	---	---	<0.01	<0.01	---	0.06	<0.02	3.66	---	0.57	---	<0.01
MX95-94	Axocopan	05/04/95	19.3	0.08	0.002	0.02	---	---	<0.01	<0.01	---	0.07	<0.02	3.28	---	0.53	---	<0.01
MVT-11	Axocopan	06/26/95	18.6	0.05	0.001	0.02	0.002	<0.002	<0.01	<0.01	0.002	0.07	<0.02	3.2	<0.002	0.69	0.022	0.01
MX94-12	El Recreo near Oaxtepec	7/11/94	22.2	0.37	0.011	0.02	0.011	<0.002	<0.01	<0.01	0.002	0.04	<0.02	4.64	<0.002	0.08	0.016	<0.01

TABLE 6 (Continued).

Sample Number	Description	Date	Temp (°C)	Al	As	Ba	Cs	Cu	Fe	Mn	Mo	NH ₄	NO ₂	NO ₃	Pb	PO ₄	Rb	Zn
MX95-81	Ixtatlala A	04/03/94	50.1	0.77	0.044	---	---	---	---	---	---	0.86	<0.02	<0.02	---	<0.1	---	---
MX94-66	Ixtatlala A	08/19/94	49.6	0.94	0.048	---	---	---	---	---	---	0.89	<0.02	4.26	---	<0.1	---	---
MX94-3	Ixtatlala A	11/17/94	50.1	0.98	0.046	0.02	0.10	<0.002	0.05	0.09	<0.002	0.47	<0.05	1.48	0.012	<0.1	0.097	0.02
MX95-28	Ixtatlala A	01/23/95	49.8	0.31	0.045	0.04	---	---	<0.01	0.07	---	0.57	<0.05	0.05	---	<0.1	---	<0.01
MX95-35	Ixtatlala A	02/12/95	49.8	0.32	0.044	0.03	---	---	0.01	0.07	---	0.62	<0.05	0.07	---	<0.1	---	<0.01
MX95-43	Ixtatlala A	03/05/95	49.6	0.56	0.043	0.04	---	---	0.01	0.07	---	0.66	<0.05	0.08	---	<0.1	---	<0.01
MX95-90	Ixtatlala A	05/04/95	48.9	0.45	0.045	0.04	---	---	---	0.07	---	0.49	<0.02	0.05	---	<0.1	---	<0.01
MVT-7	Ixtatlala A	06/26/95	49.7	0.3	0.044	0.03	0.21	<0.002	0.04	0.09	0.003	0.63	<0.02	0.1	<0.002	0.09	0.1	0.02
MX95-82	Ixtatlala B	04/03/94	46.0	0.84	0.042	---	---	---	---	---	---	0.54	<0.02	0.19	---	<0.1	---	---
MX94-16	Ixtatlala B	7/13/94	45.5	0.59	0.039	0.03	0.089	<0.002	0.08	1.27	0.003	0.27	<0.02	0.19	<0.002	0.22	0.094	0.05
MX94-67	Ixtatlala B	08/19/94	44.6	0.74	0.048	---	---	---	---	---	---	0.54	<0.02	3.4	---	<0.1	---	---
MX94-4	Ixtatlala B	11/17/94	44.1	0.62	0.045	0.03	0.10	0.002	0.03	0.06	<0.002	0.34	<0.05	0.34	0.014	0.19	0.097	0.01
MX94-20	Ixtatlala B larger pond	12/20/94	44.4	0.74	0.049	0.02	0.11	<0.002	0.04	0.16	0.002	0.23	<0.02	0.44	0.002	<0.1	0.11	0.01
MX95-29	Ixtatlala B	01/23/95	45.0	0.27	0.045	0.04	---	---	<0.01	0.06	---	0.35	<0.05	0.32	---	<0.1	---	<0.01
MX95-36	Ixtatlala B	02/12/95	45.5	0.34	0.041	0.04	---	---	<0.01	0.06	---	0.40	<0.05	0.21	---	<0.1	---	<0.01
MX95-44	Ixtatlala B	03/05/95	45.1	0.47	0.042	0.03	---	---	<0.01	0.06	---	0.38	<0.05	0.16	---	<0.1	---	<0.01
MX95-91	Ixtatlala B	05/04/95	44.9	0.51	0.044	0.03	---	---	---	0.06	---	0.37	<0.02	0.14	---	<0.1	---	<0.01
MVT-8	Ixtatlala B	06/26/95	43.0	0.55	0.042	0.03	0.12	<0.002	<0.01	0.05	0.003	0.35	<0.02	0.34	<0.002	<0.1	0.09	<0.01
MX94-13	Iztamatitlan near Oaxtepec	7/11/94	25.4	0.65	0.022	0.01	0.013	<0.002	0.06	0.03	0.002	0.04	<0.02	<0.02	0.002	<0.2	0.020	0.06
MX94-50	Oaxtepec	05/13/94	---	0.64	0.004	---	---	---	---	---	---	---	1.35	0.23	---	<0.1	---	---
MX94-11	Oaxtepec	7/11/94	26.4	0.52	0.005	0.01	0.025	0.005	0.02	0.04	0.003	0.79	<0.02	0.66	0.003	0.17	0.033	<0.01
MX94-65	Oaxtepec	08/18/94	26.3	0.74	0.005	---	---	---	---	---	---	1.05	1.61	0.89	---	<0.1	---	---
MX94-73	Oaxtepec	10/11/94	26.5	0.78	0.005	---	---	---	---	---	---	1.5	<0.02	1.34	---	<0.1	---	---
MX94-9	Oaxtepec	11/18/94	26.2	0.73	0.004	0.02	0.023	<0.002	0.01	0.02	<0.002	0.53	<0.02	0.05	0.008	0.10	0.038	0.07
MX94-25	Oaxtepec	12/28/94	26.6	0.49	0.005	0.01	0.027	<0.002	<0.01	<0.01	<0.002	0.51	<0.02	<0.02	0.002	<0.1	0.042	<0.01
MX95-75	Oaxtepec	01/14/95	26.3	0.76	0.005	---	---	---	---	---	---	1.1	<0.02	<0.02	---	<0.1	---	---
MX95-40	Oaxtepec	02/13/95	26.8	0.33	0.005	0.02	---	---	<0.01	<0.01	---	0.83	<0.02	<0.02	---	0.06	---	<0.01
MX95-48	Oaxtepec	03/05/95	26.7	0.29	0.004	0.02	---	---	<0.01	<0.01	---	0.90	<0.02	<0.02	---	<0.05	---	<0.01
MX95-79	Oaxtepec	03/25/95	26.5	0.82	0.005	---	---	---	---	---	---	0.96	<0.02	<0.02	---	<0.1	---	---
MX95-87	Oaxtepec	04/30/95	26.7	0.53	0.005	0.02	---	---	---	0.02	---	0.8	<0.02	0.02	---	<0.1	---	<0.01
MVT-5	Oaxtepec	06/25/95	25.9	0.35	0.004	0.02	0.038	<0.002	0.03	0.01	<0.002	0.62	<0.02	0.04	<0.002	<0.05	0.039	0.01
MX95-83	Ojo del Carbon A	04/03/94	22.6	0.85	0.017	---	---	---	---	---	---	0.13	<0.02	<0.02	---	<0.1	---	---
MX94-68	Ojo del Carbon A	08/19/94	22.4	0.71	0.018	---	---	---	---	---	---	0.14	<0.02	<0.02	---	<0.1	---	---
MX94-5	Ojo de Carbon A	11/17/94	22.6	0.51	0.016	0.01	<0.002	<0.002	0.09	<0.01	0.012	0.07	<0.02	0.07	0.011	<0.1	0.011	0.02
MX94-21	Ojo de Carbon A	12/20/94	22.6	0.82	0.017	0.02	<0.002	<0.002	0.32	0.29	0.028	0.03	<0.02	0.10	<0.002	<0.2	0.013	0.30
MX95-30	Ojo de Carbon A	01/23/95	22.6	0.21	0.018	0.02	---	---	0.02	<0.01	---	0.05	<0.02	0.04	---	<0.05	---	<0.01
MX95-37	Ojo de Carbon A	02/12/95	22.5	0.32	0.016	0.02	---	---	0.01	<0.01	---	0.07	<0.02	0.05	---	<0.05	---	<0.01
MX95-45	Ojo de Carbon A	03/05/95	22.4	0.43	0.016	0.01	---	---	0.01	<0.01	---	0.07	<0.02	<0.02	---	<0.05	---	<0.01
MX95-92	Ojo de Carbon A	05/04/95	22.8	0.53	0.018	<0.01	---	---	---	<0.01	---	0.07	<0.02	<0.02	---	<0.1	---	<0.01
MVT-9	Ojo de Carbon A	06/26/95	21.8	0.47	0.015	0.01	0.008	<0.002	0.03	<0.01	0.034	0.08	<0.02	0.09	0.002	<0.05	0.011	0.01
MX95-84	Ojo del Carbon B	04/03/94	19.9	0.56	0.010	---	---	---	---	---	---	0.13	<0.02	2.57	---	<0.05	---	---
MX94-69	Ojo del Carbon B	08/19/94	21.3	0.47	0.010	---	---	---	---	---	---	0.12	<0.02	1.57	---	<0.1	---	---
MX94-6	Ojo de Carbon B	11/17/94	21.3	0.45	0.009	0.02	<0.002	0.002	<0.01	<0.01	0.008	0.06	<0.02	<0.02	0.004	0.07	0.011	<0.01
MX94-22	Ojo de Carbon B	11/20/94	21.3	0.60	0.009	0.01	<0.002	<0.002	<0.01	<0.01	0.018	0.04	<0.02	2.68	<0.002	0.10	0.011	<0.01
MX95-31	Ojo de Carbon B	01/23/95	21.3	0.37	0.009	0.02	---	---	<0.01	<0.01	---	0.05	<0.02	2.64	---	0.10	---	<0.01
MX95-38	Ojo de Carbon B	02/12/95	21.3	0.35	0.008	0.02	---	---	<0.01	<0.01	---	0.06	<0.02	2.60	---	0.09	---	<0.01
MX95-46	Ojo de Carbon B	03/05/95	21.1	0.28	0.008	0.02	---	---	<0.01	<0.01	---	0.06	<0.02	2.49	---	<0.05	---	<0.01
MX95-93	Ojo de Carbon B	05/04/95	21.3	0.43	0.010	0.01	---	---	---	<0.01	---	0.07	<0.02	2.65	---	0.09	---	<0.01
MVT-10	Ojo de Carbon B	06/26/95	20.1	0.26	0.009	0.01	0.003	<0.002	<0.01	<0.01	0.003	0.07	<0.02	2.48	<0.002	<0.05	0.01	0.01
PLC-01	Crater Lake	02/20/94	---	2110	1.2	0.1	0.27	0.09	3770	95.5	<0.02	11.3	<1	<0.5	1.63	17.8	1.23	8.9

<a Analyses by Dale Counce

<b The following constituents were analysed but not included due to low concentrations: Ag, Be, Cd, Co, Cr, Hg, I, Ni, Sb, Se, S₂O₃.

Results of major and trace constituent analyses of warm and cold spring waters in the region of Popocatepetl are listed in Tables 5 and 6, according to spring name and date of collection. No data trends or chemical changes were observed over the sampling period, indicating that recent eruptive behavior did not have immediate impact on spring chemistry.

The springs sampled in this study are all near neutral (pH 6–8), range in temperature from 17 to 49°C, and show a variety of compositions. The data are used to divide the waters into three basic groups: 1) cold, dilute (low-Cl group), 2) higher temperature, relatively high-Cl (high-Cl group), and 3) mid-range Cl water that displays higher B concentrations than either of the other two groups (high-B group).

Of the cold, dilute waters, two springs (Axocopan and Atlamaya) are most representative of background compositions. These springs are located closest to the summit (6 and 20 km, respectively) and issue from volcanic or volcanoclastic deposits. Atlamaya is very low in total dissolved solids and is likely shallow, local meteoric water. This spring contains very low concentrations of SiO_2 , Na, and K, indicating short residence time underground. Values for Axocopan are higher, suggesting more time for water to react with the glassy volcanic rocks from which it issues.

Three other springs belong to the low-Cl group. Although all are relatively dilute and display similar chemistry, they have distinct characteristics. Amatitlanes has similar chemistry to Axocopan except for lower SiO_2 values, higher Ca and SO_4 , and slightly higher TDS. Ojo de Carbon A is a large spring, and Ojo de Carbon B is a smaller nearby spring; both issue from Cretaceous limestone. Ojo de Carbon A contains higher Ca, Mg, HCO_3 and SO_4 than Ojo de Carbon B, and both contain more of these constituents than Amatitlanes. TDS for these two springs are increased two- to three-fold over that of Axocopan.

The high-Cl group (Ixtatlala A and B) consists of a spring and a holding tank next to the spring. The

spring issues two meters from the holding tank, and the waters vary in temperature by five degrees Celsius (50 and 45°C, respectively). These are the warmest waters sampled and are among the furthest from the volcano (46 km south). These waters have the highest Cl, Na, K, Sr and F concentrations. Ixtatlala has nearly equal amounts of Ca and SO_4 as Ojo de Carbon A (low-Cl group) and contains about the same Li and Br concentrations as Oaxtepec (high-B group).

The high-B group of springs (Oaxtepec and Agua Hedionda), located approximately 35–40 southwest of the Popocatepetl summit, is chemically unique compared to the other spring waters. High-B concentrations suggest these waters have interacted with borates associated with evaporitic sulfates and carbonates or with marine sediments. This group has mid-range values for Cl, F, and SO_4 . Next to Ixtatlala A and B, these waters and similar high-B waters have the highest TDS. El Recreo and Iztamatitlán, two springs sampled once near Oaxtepec, generally show chemistry between this group and the low-Cl group.

The similarities and differences mentioned above are also demonstrated by Cl variation diagrams (Figs. 11a–e). All graphs show the three distinct chemical groupings, although the differences are less pronounced in the SO_4/Cl plot (Fig. 11e). The transitional chemistries of the two springs near Oaxtepec indicate mixing between the high-B and the low-Cl waters flanking Popocatepetl, particularly in the B/Cl, Li/Cl, and Br/Cl diagrams (Figs. 11a, b, and c, respectively). These mixing relations are less obvious in the F/Cl plot (Fig. 11d). The SO_4/Cl diagram separates all of the individual spring chemistries. We note that Ojo de Carbon A and B, which issue less than a kilometer apart, are strikingly different in SO_4 content, indicating different flow paths and degrees of rock-water interaction. The high-Cl waters at Ixtatlala are unique in all of the plots of Figure 11.

Because it is known from regional geology that carbonate and evaporite strata probably underlie Popocatepetl Volcano, all waters were plotted on molar diagrams to evaluate equilibrium relations

Figs. 11a through e: Cl variation diagrams for spring waters. Three types of waters are highlighted in all graphs except SO₄/Cl (11e). Br, Li, and B show mixing trends between the low-Cl waters and the high-B waters. Ixtatlala A and B are the most mineralized of all waters sampled and comprise a high-Cl group.

with gypsum and gypsum + carbonate (Figs. 12a and b, respectively). Both plots show basically the same results; all waters contain an excess of divalent cations relative to HCO₃ and SO₄. This indicates that there is another source of Ca, Mg, and Sr other than interaction with carbonate and sulfate minerals (e.g., calc-alkaline volcanic rocks or older crystalline rocks). However, the plots also show that evaporites and carbonates supply most or all of the dissolved HCO₃ and SO₄. Low-Cl

waters fall on equilibration trends in both plots. These waters indicate varying amounts of equilibration with regional strata underlying the Tertiary to Quaternary volcanoes. Although Ixtatlala A and B fluids plot near the same trend as other regional waters in Figure 12, Ixtatlala waters are uniquely high in Cl (Fig. 11). The Cl-rich water probably has a deeper source than other regional waters, possibly obtaining its Cl from pre-Cretaceous metamorphic rocks.

Figs. 12a and b: a) Gypsum and b) gypsum plus carbonate equilibrium diagrams. All waters contain an excess of divalent cations relative to HCO_3 and SO_4 . All waters except the high-B group plot along an equilibrium trend with comparable slopes in both diagrams. Agua Hedionda and Oaxtepec are more affected by interaction with carbonate rocks than other springs.

The high-B group of waters (Agua Hedionda, Oaxtepec, etc.) does not display the same geochemical characteristics as Ixtatlala. For example, the other springs near Oaxtepec discharge mixtures of high-B and low-Cl fluids (Fig. 11), and the high-B waters contain more HCO_3 relative to SO_4 than other fluids in Fig. 12b. Therefore, a unique high-B aquifer exists in the Oaxtepec area.

Trace Element Chemistry of Spring Waters

Spring waters will again be approached in groups for analysis of trace component data. The low-Cl springs show the most variability, whereas high-Cl and high-B groups seem to be more consistent.

Local inhabitants of the area consider Axocopan to be pure, uncontaminated water. Axocopan contains, however, elevated PO_4 (~0.6 ppm) and NO_3 relative to most other springs, suggesting contamination from detergents, fertilizer, or organic waste along the fluid flow path to the spring. Other possible sources of nitrate include waters circulating through limestone caves where bats might live and guano accumulates. Although elevated in NO_3 and PO_4 , this water is dilute and potable; NO_3 is considered toxic at levels over 44 ppm (Hem, 1992).

Compared with the other spring waters, Amatitlanes contains much higher NO_3 (~7.25 ppm) and also relatively high As (~0.045 ppm). Arsenic is toxic in small amounts; US drinking standards place limits of 0.050 ppm for humans and 0.2 ppm for livestock (Hem, 1992). Arsenic is present in pesticides, which might enter the groundwater system through runoff or waste disposal. Arsenic is also present in most high-temperature geothermal waters at concentrations ≥ 1 ppm and in many waters circulating in S-rich sedimentary rocks.

Ojo de Carbon A and B show similar trace element chemistry to one another and are fairly dilute. Atotonilco 1 has somewhat elevated NO_3 (~4 ppm) compared with Atotonilco 2 (~1 ppm). Both springs contain moderate Al (~0.40 ppm) and As (~0.032 ppm) levels.

Aluminum in concentrations over 1 ppm is believed to represent particulate matter in the form of aluminum hydroxide or aluminosilicate. Gibbsite crystals down to $0.1\mu\text{m}$ have been found to have chemical and physical stability in neutral waters (Hem, 1992). Because the waters were collected either unfiltered or filtered with $0.45\mu\text{m}$ filter paper, elevated Al in these samples could represent particulate matter. Elevated Al can also be found in thermal waters due to increased reactivity of the fluids.

Compared with the rest of the springs, the high-Cl group contains the highest levels of Al, As, and

Mn, and relatively high NH_4 ; otherwise, its trace element contents are low. High-B springs contain elevated Al and NH_4 but otherwise are also low in trace components.

Stable Isotopes and Recharge Elevations

Stable isotope and tritium data for all springs sampled in June 1995 are listed in Table 7, and results are compared in Figs. 13 and 14. Although this is a rather small data set, the results are interesting. Three cold low-Cl springs (Axocopan, Ojo de Carbon A, and Ojo de Carbon B) plot very close to the world meteoric water line (WMWL) defined by Craig (1961). Axocopan water issues from volcanic rocks, as noted previously, and is probably recharged on the middle to lower flank of the volcano. One sample from a cold spring near the summit of Popocatepetl yielded very depleted isotope values ($\delta\text{D} = -125\text{‰}$ and $\delta^{18}\text{O} = -20.2\text{‰}$), indicating that the summit area is not a viable recharge zone for the other waters of this study.

The high-B and high-Cl waters are considerably more enriched in deuterium than the cold waters, indicating that the former are recharged at lower elevations than the latter. As noted before, chemical similarities exist between spring waters like Ojo de Carbon A and Ixtatlala, which appear to interact with regional carbonate and evaporite rocks. However, these springs have very different isotopic signatures. Ixtatlala has considerably more

enriched isotopic composition, which indicates that a major component of Ixtatlala water is recharged at a much lower elevation.

Based on δD /elevation gradient relations observed at other volcanic areas ($\sim 2\text{‰}/100\text{m}$, Vuataz and Goff, 1986; Janik et al., 1992), the high-B and high-Cl waters are recharged at about 500 m lower elevation than the cold waters. The high-B and high-Cl waters also show small $\delta^{18}\text{O}$ enrichments of $\leq 1.5\text{‰}$ relative to the WMWL, indicating some rock-water isotopic exchange, which occurs more easily at lower temperatures ($\leq 100^\circ\text{C}$) in carbonate-rich rocks than in silicate rocks.

Tritium and Relative Age

Tritium contents for the samples analyzed range from 0.15 to 0.6 TU, which is less tritium than typical concentrations (2 to 4 TU) measured in recent Central American rain (Janik et al., 1992). This indicates that the spring waters are probably older than about 50 years based on tritium-age relations presented in Goff et al. (1991). Ixtatlala, whose water type appears to be the most geothermal in character, has an apparent maximum mean residence time of about 400 years. No relation between any of the three water types is observed in a plot of tritium vs. Cl (Fig. 14a). Water from Ojo de Carbon B has slightly lower salinity and higher tritium than water from the nearby site A. Even though Axocopan is recharged from the flank of

TABLE 7. Stable isotope analyses of springs and gases emitted from springs around Popocatepetl Volcano, Mexico; all samples collected in June 1995.*

Description	Sample Number	Approx. Elev. (m)	Temp. ($^\circ\text{C}$)	δD (‰)	$\delta^{18}\text{O}$ (‰)	Tritium (T.U.)	$^{13}\text{C-CO}_2$ (‰)
Oaxtepec	MVT-5	1400	25.9	-75.5	-10.03	0.25	-9.80
Agua Hedionda	MVT-6	1350	25.8	-76.1	-10.24	0.31	-9.60
Ixtatlala A	MVT-7	1150	49.7	-78.3	-10.01	0.33	---
Ixtatlala B	MVT-8	1150	43	-74.3	-9.68	---	-15.6
Ojo de Carbon A	MVT-9	1500	21.8	-83.6	-11.41	0.15	---
Ojo de Carbon B	MVT-10	1500	20.1	-84.2	-11.48	0.6	---
Axocopan	MVT-11	1900	18.6	-84.5	-11.99	0.44	---

*Oxygen-18 and deuterium analyses were performed by Mike Fergeson at the Stable Isotope Laboratory, Southern Methodist University, Dallas, Texas. Tritium analyses were completed by H. Gote Ostlund at the Tritium Laboratory, University of Miami, Florida.

Fig. 13: Plot of δD versus $\delta^{18}O$ (both in per mil VSMOW) for water samples collected in June 1995. The shaded area indicates possible divergence off the World Meteoric Water Line due to rock-water interactions. A sample from a cold spring near the summit of Popocatepetl yielded very depleted isotope values indicating that the summit area is not a viable recharge area flanking gthermal/mineral waters (see text).

Figs. 14a and b: a) Tritium contents (TU) versus chloride concentration showing no correlation for spring waters sampled in June 1995; b) tritium versus SO_4 concentration showing mixing between low-Cl and high-B waters interacting with regional Cretaceous rocks.

the volcano, this spring also shows relatively low tritium. A plot of tritium vs. SO_4 (Fig. 14b) shows probable mixing relations between Ojo de Carbon A and B and the high-B waters (Oaxtepec and Agua Hedionda). Axocopan has very low SO_4 because this water has little to no interaction with underlying sedimentary rocks. Ojo de Carbon A and Ixtatlala have different tritium values, but comparable SO_4 , indicating that these waters have undergone similar rock-water interaction (Fig. 14) but are not on the same mixing trend as other regional waters.

Obviously, regional waters interact with carbonate and evaporite rocks and mix with other fluids to yield the high-B derivatives as observed in Figs. 11 and 12. The maximum mean residence time of some regional waters is rather long. Based on a well-mixed reservoir model (Goff et al., 1991), tritium indicates an average age (or mean residence time) of at least 1000 years for some fluids in this region.

Gas Geochemistry

Three springs discharge visible but diffuse gases (Fig. 10). Weak discharges usually suggest that the gases are in equilibrium with spring waters at their discharge temperature and do not represent deep equilibration. Although the gases at these sites contain substantial CO_2 (≥ 50 mol-%) and smell of H_2S , they contain relatively little H_2S and contain significant quantities of the air components (N_2 , O_2 , and Ar, Table 8). The $\delta^{13}C$ - CO_2 values for the gas samples (Table 7) are $\leq -10\text{‰}$, indicating that much of the CO_2 is probably derived from organic sources or mixtures of organic carbon and air carbon. Calculation of subsurface reservoir temperatures using the gas geothermometer (Table 8) of D'Amore and Panichi (1980) yields values of $\leq 52^\circ C$. Clearly these gases are not in equilibrium with a deep, high-temperature geothermal reservoir.

Spring Geothermometry

Estimated subsurface equilibration temperatures for the different spring waters are listed in Table 9.

TABLE 8. Analyses and calculated equilibrium temperatures of gases.^{>1}

Sample Number	Description	Date	CO ₂	H ₂ S	H ₂	CH ₄	N ₂	NH ₃	O ₂	Ar	He	Total	Gas Temp. ^{>2}
MVT-5	Oaxtepec	6/26/95	67.1	<0.0003	<0.007	0.16429	31.446	0.017	1.0219	0.4009	<0.007	100.53	45.43
MVT-6	Agua Hedionda	6/26/95	56.79	<0.0004	<0.009	0.24609	39.633	0.017	3.0264	0.5656	<0.009	100.69	50.37
MVT-8	Ixtalala	6/26/95	50.71	<0.0005	<0.01	0.44804	47.216	0.024	1.2259	0.4086	<0.01	100.13	52.02

1> Analyses by Dale Counce.

2> D'Amore and Panichi (1980); using pCO₂=0.1, and assuming H₂S and H₂ concentrations are at the reported detection limit.TABLE 9. Calculated equilibrium temperatures of waters in the Popocatepetl region using a standard suite of chemical geothermometers (values in °C). Underlined values indicate our best estimate. Number of analyses used in calculation (n) shown in parentheses.^{>1}

Field Location	Temperature (°C)	Silica Geothermometers ^{>2}			Na/K (T)	Na/K/Ca Geothermometers ^{>3}			Mg-Corr	Mg/Li ^{>5}	K/Mg ^{>6}
		Amorphous	Chalcedony	Quartz		1/3	4/3	R			
Agua Hedionda (n=11)	28.0 ± 2.6	-0.2 ± 1.9	88.9 ± 2.4	117.8 ± 2.2	183.9 ± 4.1	144.3 ± 2.1	<u>36.1 ± 2.8</u>	30.3 ± 3.0	<u>36.1 ± 2.8</u>	<u>39.5 ± 2.9</u>	<u>40.8 ± 0.7</u>
Amatitlanes (n=5)	25.2 ± 0.2	-0.6 ± 1.4	88.4 ± 1.7	117.4 ± 1.6	208.8 ± 5.2	152.0 ± 1.2	<u>35.8 ± 1.6</u>	31.9 ± 1.9	<u>35.8 ± 1.6</u>	<u>25.8 ± 2.0</u>	<u>40.9 ± 1.0</u>
Atotonilco I (n=11)	33.2 ± 0.5	-6.3 ± 1.6	81.2 ± 2.0	110.8 ± 1.8	172.9 ± 6.9	134.4 ± 2.8	<u>22.5 ± 1.7</u>	28.2 ± 0.4	<u>22.5 ± 1.7</u>	<u>5.5 ± 2.6</u>	<u>33.3 ± 1.3</u>
Atotonilco II (n=11)	35.4 ± 0.7	-8.8 ± 1.6	78.0 ± 2.1	107.8 ± 1.9	154.9 ± 24.0	124.8 ± 11.2	<u>15.2 ± 5.9</u>	25.7 ± 0.6	<u>15.2 ± 5.9</u>	<u>13.6 ± 13.8</u>	<u>29.1 ± 4.9</u>
El Recreo near Oaxtepec	22.2	-1.4	87.4	116.4	231.5	150.4	<u>19.3</u>	27.4	<u>19.3</u>	<u>17.9</u>	<u>34.1</u>
Ixtatlala A (n=7)	49.7 ± 0.4	-9.1 ± 2.2	77.7 ± 2.8	107.6 ± 2.6	144.0 ± 5.2	141.8 ± 1.7	<u>64.0 ± 1.6</u>	20.6 ± 0.6	<u>64.0 ± 1.6</u>	<u>49.0 ± 2.0</u>	<u>59.6 ± 0.7</u>
Ixtatlala B (n=9)	45.0 ± 0.6	-12.4 ± 9.5	73.6 ± 12.0	103.6 ± 11.3	140.8 ± 3.2	140.6 ± 1.1	<u>64.2 ± 1.5</u>	20.8 ± 0.8	<u>64.2 ± 1.5</u>	<u>50.1 ± 2.2</u>	<u>59.3 ± 0.5</u>
Iztamatitlan near Oaxtepec	25.4	-3.1	85.2	114.5	208.7	144.8	<u>21.0</u>	28.5	<u>21.0</u>	<u>24.2</u>	<u>33.8</u>
Oaxtepec (n=11)	26.5 ± 0.2	-0.3 ± 2.4	88.7 ± 2.9	117.7 ± 2.7	183.1 ± 6.2	143.8 ± 1.7	<u>35.6 ± 1.5</u>	29.9 ± 0.8	<u>35.6 ± 1.5</u>	<u>39.1 ± 3.3</u>	<u>40.6 ± 0.7</u>
Ojo de Carbon A (n=8)	22.6 ± 0.1	5.3 ± 4.5	95.7 ± 5.6	124.1 ± 5.1	189.7 ± 5.4	132.0 ± 1.7	<u>7.2 ± 0.7</u>	24.2 ± 0.6	<u>7.2 ± 0.7</u>	<u>0.2 ± 5.5</u>	<u>26.4 ± 0.7</u>
Ojo de Carbon B (n=8)	21.1 ± 0.5	1.8 ± 2.6	91.3 ± 3.3	120.1 ± 3.0	195.0 ± 11.0	135.2 ± 4.1	<u>10.3 ± 1.9</u>	25.2 ± 0.8	<u>10.3 ± 1.9</u>	<u>0.7 ± 6.6</u>	<u>28.1 ± 1.8</u>

1> Temperatures calculated using GATHERM code of Urbani (1986).

2> Quartz solubility data from Fournier and Potter (1982).

Other silica data from Fournier (1981).

3> Na/K (T) from Truesdell (1976).

4> Na/K/Ca using Beta=1/3 and 4/3 from Fournier and Truesdell (1973).

Mg-Corr from Fournier and Potter (1982).

5> Mg/Li from Kharaka and Mariner (1989).

6> K/Mg from Giggenbach et al. (1983); Giggenbach (1988).

(See a review by Fournier (1981) for further information on geothermometry.) Cold water sites with TDS less than about 800 mg/kg are not listed because they are not considered to have any substantial thermal/mineral component. Consistent temperatures are given by the Na-K-Ca ($\beta = 4/3$), Mg/Li, and K/Mg geothermometers, which best estimate low-temperature equilibrium or low temperatures due to reequilibration. Based on these calculations, it is our opinion that all spring waters of this study equilibrated at temperatures $\leq 60^\circ\text{C}$. Mixed waters discharging at Ixtatlala (highest temperature and Cl) seem to partially evolve from a small, relatively Cl-rich reservoir having the highest equilibration temperatures. This reservoir probably circulates within the Paleozoic metamorphic rocks shown schematically in Figure 15.

Comparison with High-Temperature Geothermal Fluids

Spring waters and gases from the Oaxtepec area and Ixtatlala, although having thermal/mineral

components, are distinctly different from waters and gases derived from high-temperature geothermal systems ($\geq 200^\circ\text{C}$). In Table 10 we compare these water and gas compositions with typical high-temperature fluids from Guatemala (Zunil), Costa Rica (Miravalles), and New Mexico (Valles caldera). Generally, high-temperature waters tend to have high contents of SiO_2 and "key" trace components (As, B, Br, Li, Rb, Cs), low Na/K ratios (typically <10 by weight, but sometimes <5), low Ca + Mg + Sr concentrations, and Cl as the major anion (see Goff and Gardner, 1994). Compared with the three high-temperature systems, the Mexico waters have low SiO_2 and trace element concentrations, Na/K ratios >10 , high Ca + Mg + Sr contents, and much lower Cl values. Thus, they are probably not related to a high-temperature hydrothermal system in the Popocatépetl region, if one exists (see discussion below). The same is true for the feeble gas emissions collected from the springs, which are high in air components and have very low concentrations of H_2S and H_2 , unlike typical higher-temperature geothermal gases.

Fig. 15: Schematic north-south cross section of the Popocatépetl region, Mexico. No precise contact can be drawn between Cretaceous marine rocks and Paleozoic metamorphic basement due to lack of deep borehole data. Variably mineralized waters up to 1000 yr in age circulate throughout Cretaceous strata. No geochemical evidence was found that indicates a connection between a possible ("blind") hydrothermal system beneath Popocatepetl and low-temperature thermal/mineral waters in surrounding areas. The Ixtatlala fluids ($\leq 60^\circ\text{C}$) probably circulate along a fault cutting Cretaceous and Paleozoic units.

TABLE 10. Comparison of spring and gas data from Oaxtepec and Ixtatlala with hydrothermal systems from Guatemala, Costa Rica, and New Mexico. #

	Oaxtepec	Ixtatlala A	Zunil	Miravalles	Valles
Temp (°C)	~26	~49	258	239	295
<i>Waters</i>					
SiO ₂	70	57	460	490	882
Ca	508	545	8.10	59	78.5
Mg	133	87.2	0.35	0.14	0.76
Sr	5.7	9.5	0.15	1.6	1.22
Na	107	329	653	1650	2350
K	10.2	20.5	122	210	700
Li	0.45	0.56	4.48	5.71	32.8
SO ₄	1123	1380	28.1	37.9	7.8
Cl	86.4	540	1065	2806	4150
F	1.46	2.69	2.49	1.1	5.67
Br	0.28	0.28	4.00	16.2	13.6
B	3.22	1.45	23.9	47	29.6
HCO ₃	827	209	62.2	84.2	105
CO ₃	0	0	0	-	5720*
Rb	0.036	0.098	0.77	0.96	11.5
Cs	0.027	0.16	0.58	0.8	5.45
As	0.045	0.58	6.18	6.2	~5.0
<i>Gases (mole % dry gas)</i>					
CO ₂	67.1	50.71	87.74	96.63	99.00
H ₂ S	<0.0003	<0.0005	9.48	0.345	0.66
H ₂	<0.007	<0.01	0.68	0.8089	0.06
CH ₄	0.16429	0.44804	0.043	0.042	0.056
N ₂	31.4455	47.2162	2.58	1.754	0.108
NH ₃	0.016716	0.023646	0	0.0044	0.107
O ₂	1.0219	1.2259	0.0081	0.0094	0.0005
Ar	0.4009	0.4086	0.0337	0.0269	0.0017
He	<0.007	<0.01	0.068	0	0.0069

Data from this study, Adams et al. (1991), Grigsby et al. (1989), and Goff and Gardner (1994).

* Total carbon species.

Hydrothermal Model

A schematic north-south cross section through the highest temperature spring (Ixtatlala) and the summits of Popocatepetl and Iztaccíhuatl is shown in Figure 15. Little is known about the detailed subsurface geology of this region because few deep wells have been drilled. The true extent and thickness of the carbonate strata are unknown as well as the characteristics of Paleozoic rocks beneath the carbonates. Cretaceous carbonates and other marine rocks are visible throughout the southern flank region of the volcano as isolated exposures deformed by earlier tectonic events. Commonly, carbonate strata are surrounded by late Tertiary and Quaternary volcanoclastic units. Such is the case with the carbonates exposed near Ixtatlala spring. High regional heat flow within the Trans-Mexican Volcanic Belt, possible residual heat from mid-Tertiary intrusive rocks (Urretia-Fucugauchi, 1992), fault circulation in Paleozoic rocks, and contact with carbonate strata are plausible explanations for the weak thermal/mineral character of the Ixtatlala waters. If this reservoir is equilibrated

at 60°C, its depth can be no more than 1–2 km based on expected geothermal gradients, thermal conductivities, and hydrologic conditions for this type of geothermal region (Goff and Decker, 1983).

We show a hypothetical (in this case, “blind”) hydrothermal system beneath Popocatepetl, recognizing that such systems frequently circulate in large, active stratovolcanoes (Goff et al., 1994; Rowe et al., 1995). However, there is no direct evidence that a hydrothermal system exists beneath Popocatepetl, other than the presence of hydrothermally altered limestone xenoliths in some Popocatepetl lavas. The geochemistry of the thermal/mineral waters in the surrounding region indicates no connection with a central volcanic-hosted, hydrothermal system, if such a system exists.

V. CONCLUSIONS

Monitoring of gas emissions at Popocatepetl during the year of the onset of new eruptive activity shows major variations in fumarolic discharges. Preferential degassing of CO₂, Cl, and As, seen in alkaline trap data for the early months of 1994, is followed by significant increases in S, F, and Hg flux by mid-year. Data from the June–July sampling periods show highs for all measured components relative to Cl and corresponding highs in the SO₂ flux measured by COSPEC. These highs also correlate with increased seismicity and with $\delta^{34}\text{S}$ values of 1.5 to 6.5‰, which are consistent with “normal” volcanic $\delta^{34}\text{S}$ -SO₂ of 0 to 10‰. For two months prior to the eruption on December 21, 1994, samples had increasing S_{total}, CO₃, F, and Cl concentrations along with decreasing $\delta^{34}\text{S}$ values (toward mantle composition).

The combined chemical and isotope trends probably reflect accelerated release of volatiles from rising magma and a more primordial origin for the sulfur gases. We suggest that the trends could result from injection of volatile-rich mafic magma into an existing, more silicic chamber beneath Popocatepetl. Such injections are consistent with chemical and textural evidence of magma mixing

observed in previous eruptive products. This injection could be a precursor to the onset of eruptive activity that began in December 1994. However, the sulfur isotope results do not preclude a small contribution of heavy sulfur derived from regional Cretaceous evaporite deposits ($\delta^{34}\text{S} = +16.4\text{‰}$ for local gypsum). Some Popocatepetl eruptions (e.g., the andesite flow of about 2100 B.P.) contain abundant xenoliths of Cretaceous sedimentary rocks.

Regional spring waters sampled between May 1994 and June 1995 show no immediate impact from renewed volcanic activity at Popocatepetl, and each spring maintains reasonably constant composition throughout the time period. Waters were found to fit in three distinct chemical categories: low Cl, high B, and high Cl. Mixing relations are evident between the high-B and low-Cl waters. The data show that all thermal/mineral spring waters interact with a widespread unit of Cretaceous marine rocks exposed south of the volcano. High-B waters from the Oaxtepec area mix with regional waters in Cretaceous rocks. High-Cl waters at Ixtatlala interact with Cretaceous strata but probably originate from underlying crystalline rocks. Deuterium and ^{18}O relations show that most mineralized fluids are recharged at elevations significantly lower than the higher flanks of Popocatepetl. Tritium contents indicate that mineralized fluids have maximum mean residence times as great as 1000 years. Chemical geothermometers for liquid and gas samples indicate subsurface equilibration temperatures of $\leq 60^\circ\text{C}$. The major and trace element chemistry of mineralized waters shows no resemblance to typical, high-temperature geothermal fluids. The high-B and high-Cl fluids are not derived from a high-temperature geothermal system associated with Popocatepetl, if one actually exists.

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