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Chemical characteristics of the crater lakes of Popocatetetl, El Chichon, and Nevado de Toluca volcanoes, Mexico

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Abstract

Three crater lakes from Mexican volcanoes were sampled and analyzed at various dates to determine their chemical characteristics. Strong differences were observed in the chemistry among the three lakes: Nevado de Toluca, considered as dormant, El Chichón at a post-eruptive stage, and Popocatépetl at a pre-eruptive stage. Not surprisingly, no influence of volcanic activity was found at the Nevado de Toluca volcano, while the other volcanoes showed a correlation between the changing level of activity and the evolution of chemical trends. Low pHs (<3.0) were measured in the water from the active volcanoes, while a pH of 5.6 was measured at the Nevado de Toluca Sun lake. Changes with time were observed at Popocatépetl and El Chichón. Concentrations of volcanic-gas derived species like Cl^-, SO_4^{2-} and F^- decreased irregularly at El Chichón from 1983 until 1997. Major cations concentrations also diminished at El Chichón. A 100% increase in the SO_4^{2-} content was measured at Popocatépetl between 1985 and 1994. An increase in the Mg/Cl ratio between 1992 (Mg/Cl = 0.085) and 1994 (Mg/Cl = 0.177) was observed at Popocatépetl, before the disappearance of the crater lake in 1994. It is concluded that chemical analysis of crater lakes may provide a useful additional tool for active-volcano monitoring.

Keywords: Mexican volcanoes; crater lakes; Popocatépetl; El Chichón; Nevado de Toluca; volcano monitoring

1. Introduction

Holocene volcanism in Mexico is varied and widespread. In the northwest of the country, recent volcanoes are associated with the spreading process that is currently opening the Gulf of Cortés, or due to remnants of the subduction of the Farallon plate. The Revillagigedo islands show some acid volcanism whose origin is difficult to explain. Most of the recent volcanism occurs along the Trans-Mexican Volcanic Belt (TMVB), which has an oblique position with respect to the trench in the Pacific coast that is believed to result from the varying-angle subduction of the Rivera and Cocos plates under the North American plate. Volcanism, in the southeast of México is parallel to the trench marking the subduction of the Cocos plate under the Caribbean plate (Fig. 1).

Thousands of volcanic structures have been formed by these processes. Of those, only a few have crater lakes. Three main types of crater lake may be recognized: those associated with Xalapasco or maars, inactive or long-time dormant volcanoes, and currently active volcanos. In this paper, chemical analyses of one lake of a dormant volcano and two of active volcanoes are discussed to relate the measured chemical features with their state of activity. The dormant volcanic crater lake is located at the summit caldera of Nevado de Toluca volcano. The other lakes discussed

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are at Popocatépetl and El Chichón, which were volcanoes in a pre-eruptive and a post-eruptive stage, respectively, at the time of this study.

2. Geological setting and volcanic history

2.1. Popocatépetl Volcano (19°N; 99°W; 5426 m.a.s.l.)

Popocatépetl Volcano is located 60 km southeast of Mexico City and 40 km west of the City of Puebla. The construction of the andesitic–dacitic stratovolcano started around 1 Myr ago (Demant, 1981; Robin and Boudal, 1987). The volcano is sitting upon a Mesozoic basement of limestone, evaporites, and sandstones of Cretaceous age.

Popocatépetl Volcano has a central elongated crater with an approximated dimension of 820 × 650 m and 100–300 m deep walls. Prior to its eruption on December 21, 1994, it contained an internal crater on its crater floor formed after its last historic activity that occurred between 1919 and 1927. The northern flank of the volcano is covered by a glacier of about 0.05 km^3.

The present cone of Popocatépetl volcano has been built upon the remains of older, destroyed craters, due to repetitive sector collapse of the edifice. At least three sector collapses of the volcanic edifice have been reported of which the most recent one occurred between 24,000 and 22,000 years ago (Siebe et al., 1995). Several geological studies of the volcano have dealt mainly with the geological record of the present cone (Heine and Heide-Weise 1973; Lambert and Valastro, 1976; Boudal, 1984; Miehlich, 1984; Robin, 1984; Boudal and Robin, 1989; Siebe et al., 1995; Siebe et al., 1996).

According to Siebe et al. (1997), Popocatépetl Volcano has had intense volcanic activity during the last 23,000 years, with at least eight cataclysmic eruptions dated at ca. 14,000, 10,700, 9100, 7100, 5000, 2150, 1700, and 1200 yr. BP. The last four eruptions have largely influenced the development of prehispanic cultures in this part of central Mexico. In addition, important historic activity has been observed at the volcano since prehispanic times (De la Cruz-Reyna et al., 1995).

In the 20th century, Popocatépetl has had two similar episodes of activity. The first one from 1919 to 1927 and the current one, which began with an increase in the fumarolic emissions in 1993, and was followed by ash emissions in 1995 and dome

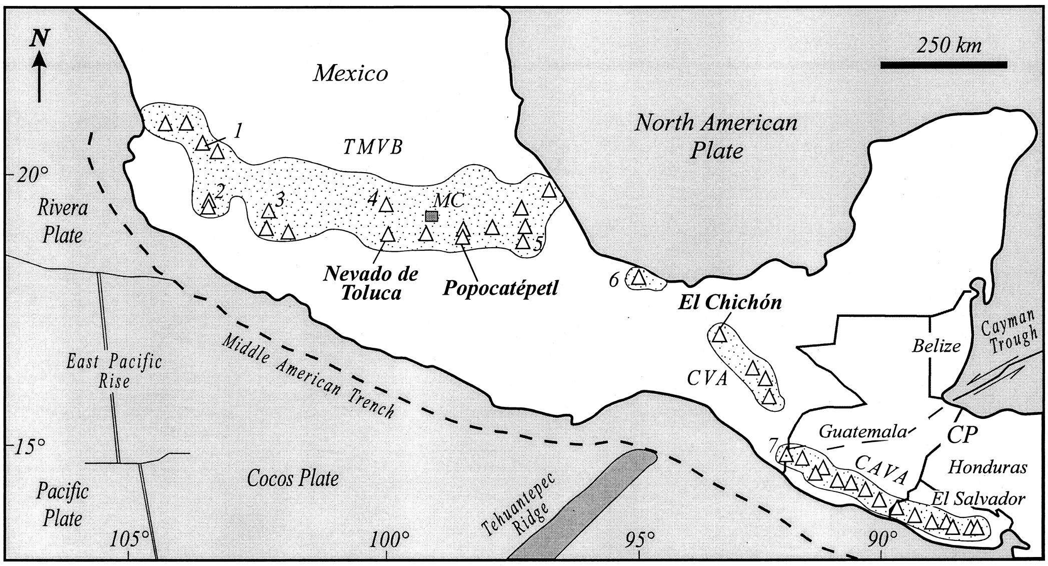


Fig. 1. Map of México showing the Trans-Mexican Volcanic Belt (TMVB), the Chiapas Volcanic Arc (CVA) and the Central-America Volcanic Arc (CAVA). Open triangles indicate Holocene volcanoes. (1) Ceboruco, (2) Colima, (3)Paricutín, (4) Jocotitlán, (5) Pico de Orizaba, (6) San Martín and (7),Tacaná. MC = México City.

growth that continues up to date. Currently, over one hundred thousand people live in an area that could be directly affected in the event of a major eruption, and nearly 20 million live within a radius of 80 km, where they may be affected by significant ash fall (De la Cruz-Reyna and Siebe, 1997).

Between the 1919–1927 and the 1993 episodes, a seasonal crater lake formed at the floor of Popocatépetl's crater. The presence of that lake was reported in 1986 (SEAN Bulletin, 1986). This report describes a small, clear, greenish, roughly circular lake, about 40 m in diameter and 10 m deep, with a temperature of 29°C. Increased fumarolic activity caused the total evaporation of the crater lake in 1994.

2.2. El Chichón Volcano (17°21′N; 93°41′W; 1100 m.a.s.l.)

El Chichón is an isolated volcano located in the northwestern edge of the state of Chiapas, in the middle of sedimentary province. It is the youngest active volcano SE–NW of Chiapas Volcanic Arc (Damon and Montesinos, 1978). El Chichón is located in the Chiapas anticlinorium, which dips towards the Gulf of Mexico with direction NW–SE and is buried by Post-Miocene sediments in the coastal plains (Macías et al., 1997a). The basement rocks of the volcano are early Cretaceous evaporites and limestones, dolomitic limestones of Middle to Late-Cretaceous age, with interbedding of epiclastic sandstones and limestones of Tertiary age. General geological features of the volcano can be found elsewhere (Canul and Rocha, 1981; Duffield et al., 1984).

El Chichón volcano has an older somma rim with dimensions of 1.5×2 km that before the eruption was closed by a forest-covered dome. The crater produced by the 1982 eruptions lies within the somma volcano. This crater is 1 km wide and about 200 m deep. The highest elevation of the crater is at 1100 m.a.s.l. with its floor placed at 860 m.a.s.l.

Before the 1982 eruption, little was known about the volcano and its eruptive history. Mülleried (1932) studied the region after some seismic unrest was reported, and concluded that El Chichón was an active volcano. Damon and Montesinos (1978), dated the somma crater at 0.209 ± 0.019 Ma Canul and Rocha (1981) while doing fieldwork for Comisión Federal de Electricidad (The National Power Bureau) identified El Chichón as potentially active. After the 1982 eruption, Duffield et al. (1984) analyzed drilled logs obtained from nearby exploration boreholes by PEMEX (the national oil company) and established the geological setting of El Chichón. Regarding its volcanic history, Rose et al. (1984) and Tilling et al. (1984) found at least three periods of volcanic activity during the last 2000 years. Recent stratigraphic studies suggest that El Chichón volcano has had at least 10 episodes of explosive volcanic activity which occurred at ca. 550, 850, 1250, 1400, 1700, 1800, 2000, 2400, 3100 and 3700 yr. BP (Macías et al., 1997a).

The most recent eruption of El Chichón developed as an episode having six pulses during the week 28 March–4 April, 1982. This episode had a relatively low magnitude (juvenile mass ejected $\sim 0.3\ km^3$ DRE) and a high intensity (maximum mass ejection rate $\sim 10^5$ ton/s,Yokoyama et al., 1982). The effects of these eruptions were disastrous, causing an almost total devastation in a radius 10 km around the volcano. About 2000 people were killed by pyroclastic flows and tephra falls, and about 20,000 lost their homes. Ashfalls extended over several hundred kilometers and rain-triggered lahars produced additional damage weeks after the end of the eruption.

On April 25, 1982, the first views of the crater floor after the 1982 eruption showed three small lakes. By November 1982, the level of the water rose forming one bigger lake with a surface area of $1.4 \times 10^5\ m^2$ (Casadevall et al., 1984). In January 1997, the area had decreased to approximately $0.5 \times 10^5\ m^2$. Variations in the level and shape of the lake have been observed since its appearance, as shown in Figs. 2 and 3.

2.3. Nevado de Toluca Volcano (19°09′N; 99°45′W; 4565 m.a.s.l.)

Nevado de Toluca volcano is located at 23 km SW of the City of Toluca, it is an andesitic–dacitic stratovolcano of Late Pleistocene age (Bloomfield and Valastro, 1974; Cantagrel et al., 1981). Nevado de Toluca is built upon a volcanosedimentary basement of Jurassic–Tertiary age, which has been affected by a complex set of three fault systems (García et al., 1996).

The crater has an E–W-elongated form (1–1.5 km

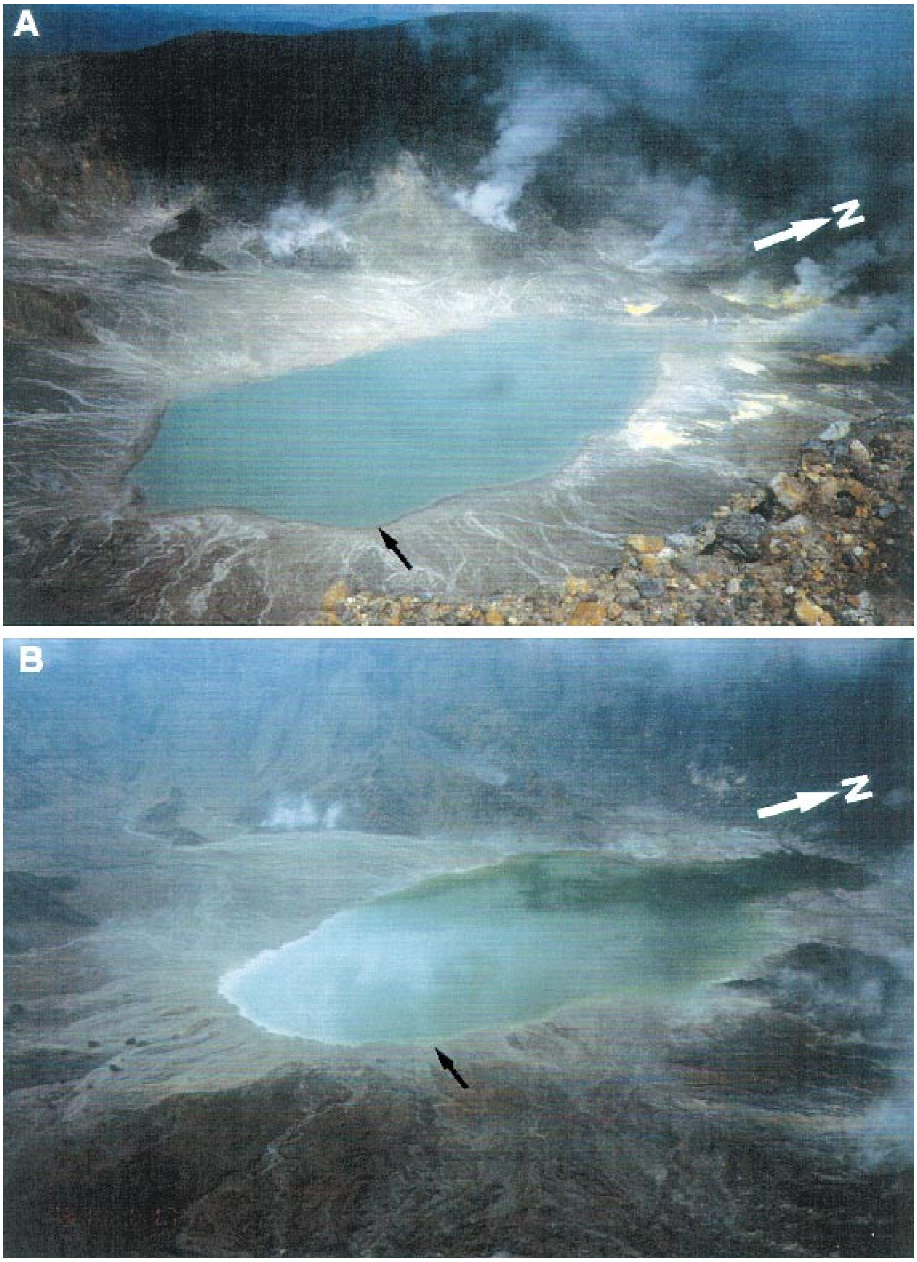


Fig. 2. Views of El Chichón crater lake from the southeastern rim. (A) August, 1985 (photo – S. De la Cruz-Reyna). Notice the intense fumarolic activity and sulfur sublimates. (B) January 1997 (photo – J.L. Macías). Arrows point to the sampling site.

in diameter) with a horseshoe-shaped opening towards the east. The oval central crater is emplaced on top of two older amphitheater-shaped craters whose remains are still visible on the SE and NE flanks of the volcano. Glacial advances occurring during the Holocene also affected the volcano's morphology (Heine, 1988).

The first studies of Nevado de Toluca described general geological features of the volcano (Ordoñez, 1902; Otis, 1902; Flores, 1906; Waitz, 1909).

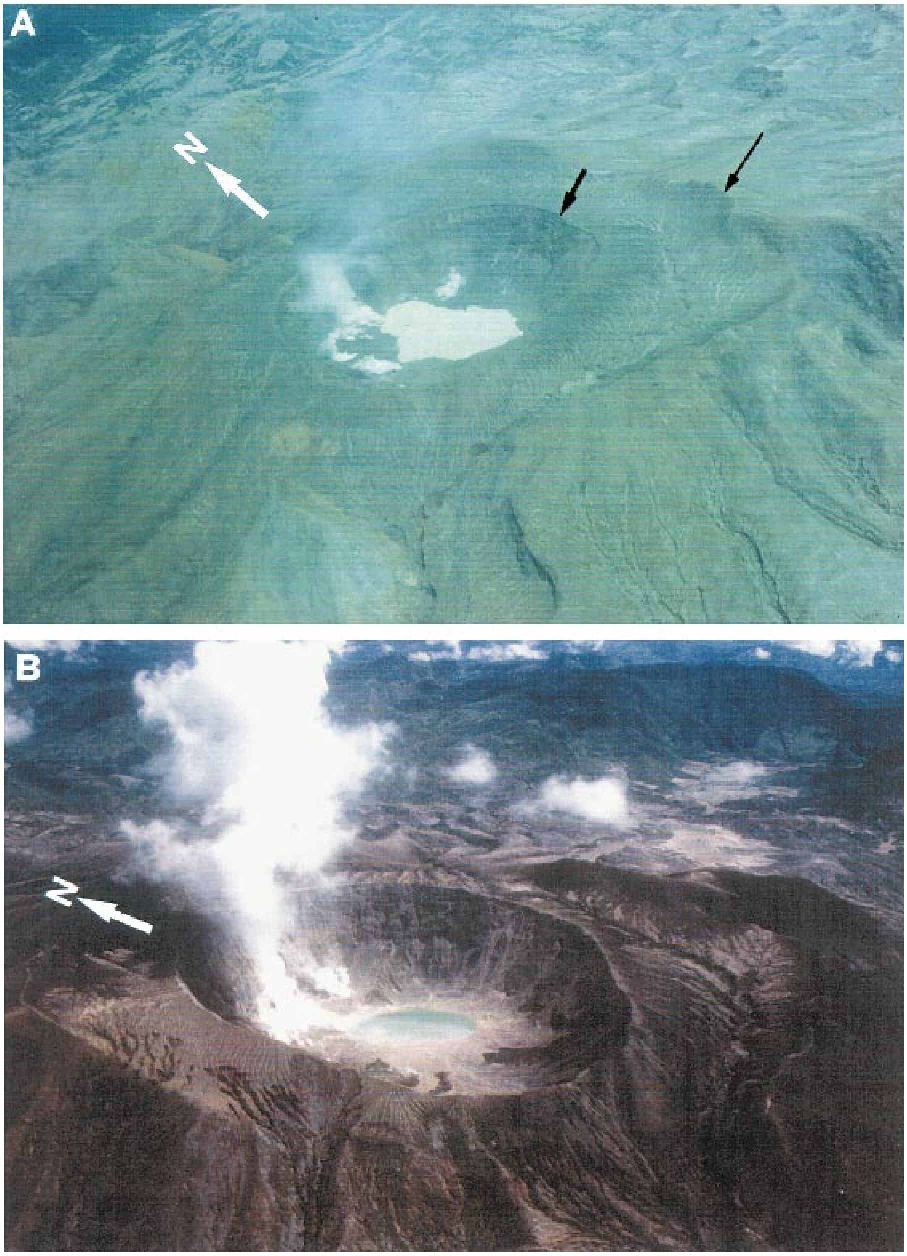


Fig. 3. Aerial views towards the northeast of El Chichón crater. (A) November, 1982. The lake area is about 1.4×10^5 m^2. The thick arrow shows the 1982 crater, and the thin arrow points to the somma crater. (B) September, 1986 (approximate lake area $= 0.5 \times 10^5$ m^2).

Bloomfield and Valastro (1974,1977) and Bloomfield et al. (1977) attempted for the first time to define the volcanic events that occurred at Nevado de Toluca, as well as its eruptive history. These authors concluded that the last cycle of activity occurred about 11,500 yr. BP, and for this reason Nevado de Toluca had been considered an extinct volcano. Recent studies, indicate that Nevado de Toluca has had at least two episodes of cone destruction by major sector collapse older than 40,000 yr. BP; several explosive episodes including

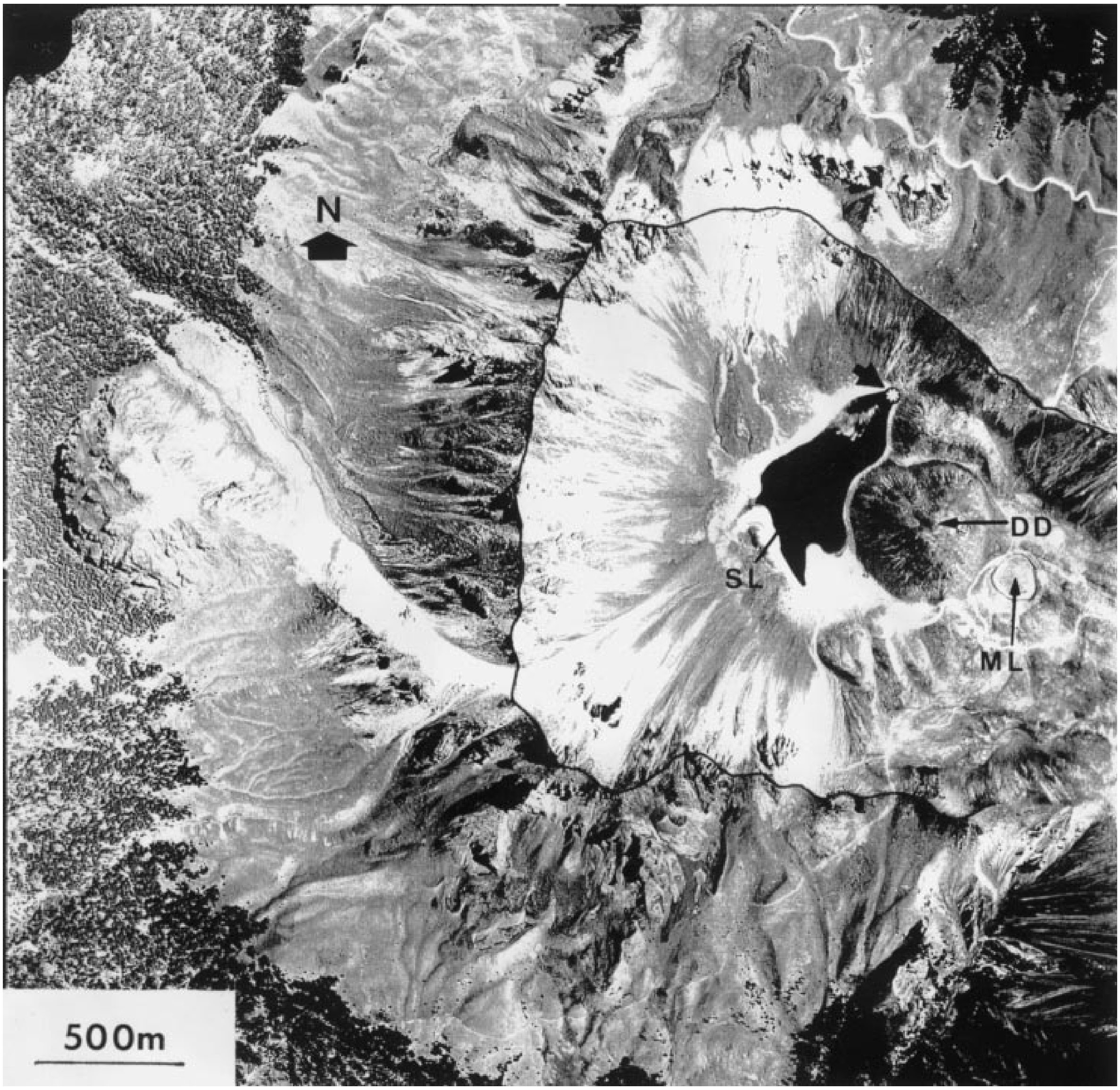


Fig. 4. Aerial photograph of Nevado de Toluca crater (INEGI, 1989). Simbols are: SL = Lago del Sol, ML = Lago de la Luna, and DD = Dacitic Dome "El Ombligo". The black line represents the present crater rim.

dome-destruction events at ca. 37,000 and 28,000 yr. BP; and two plinian eruptions recorded at 24,000 and 11,600 yr. BP. These eruptions occurred during the Pleistocene but a young eruption characterized by surge and ash flows occurred ca. 3300 yr. BP, and therefore Nevado de Toluca should be considered as dormant (Macías et al., 1997b).

Two lakes lie inside the crater "Lago de la Luna" and "Lago del Sol" which are separated by two dacitic dome intrusions (Fig. 4). Although their morphology changes with time, their areas are approximately 0.025 km^2 and about 0.175 km^2, respectively (Caballero-Miranda, 1996).

3. Methodology

Water samples were taken from the crater lakes at different dates, depending upon accessibility to the areas. At El Chichón, water sampling began in 1985 and continued with an irregular periodicity until 1997. Two samples from Popocatépetl Lake were taken in 1985 and in April, 1992. Finally, a sample from Nevado de Toluca was obtained in August, 1997. Temperature and pH were measured in the field. pH was determined potentiometrically, the pH-meter calibration was made with buffer solutions submerged in the lake to allow equilibrium with the water temperature. Water was directly poured in polyethylene bottles. One liter was used for the determination of alkalinity, conductivity, Cl^-, F^-, SiO_2, B and SO_4^{2-}. Another 500-ml aliquot of water was added to 1 ml of concentrated HNO_3 and used for the analyses of metals. Finally, a 125-ml aliquot with Na_2CO_3 and zinc acetate added, was also taken for sulfide determinations. All the bottles were refrigerated at 4°C after sampling.

Chemical analyses were performed by wet methods, basically following the procedures described in APHA (1989). Bicarbonates were measured by acid titration to pH 4.6, using a mixed indicator of methyl red and bromcresol green. Iron concentration was measured by colorimetry using the phenantroline method until 1990. After that year, Fe was determined by atomic absorption spectroscopy. Sulfates were determined by turbidimetry. Magnesium and calcium concentrations were obtained by complexometric titration with EDTA. Boron was colorimetrically measured through its reaction with carminic acid. Chloride was potentiometrically determined with an ion-selective electrode, adding a 5 M solution of $NaNO_3$ as ionic strength adjuster. Fluoride concentrations were determined also with an ion selective electrode, adding a TISAB solution for decomplexing and adjusting the ionic strength. Sodium, potassium and lithium were measured by atomic emission spectroscopy. Silica and sulfide were colorimetrically determined; using the molibdosilicate method for the former, and the methyl blue reaction for the latter. Detection limits were as follows: $B = 0.5$ mg/l, $SiO_2 = 2.5$ mg/l, $F^- = 0.05$ mg/l, $S^{2-} = 0.5$ mg/l, $Li = 0.05$ mg/l.

4. Results

Large differences were observed in the chemical composition of the three crater lakes. In order to emphasize the relevant differences and their time evolution, the results are presented comparatively.

4.1. Nevado de Toluca

The Nevado de Toluca crater lake showed stability when compared with a previous sample obtained by Caballero-Miranda (1996) in 1991. It presented a very low conductivity (18 μS/cm), and pH = 5.6 (Fig. 5). In August, 1997 the temperature in the crater lake water of Nevado de Toluca was 11.7°C. Nevado de Toluca water type was mixed in anions and calcium–magnesium in cations. Lithium, boron and fluoride were below the detection limits. Cl^- and SO_4^{2-} concentrations were also very low ($Cl^- = 1.5$ mg/l, $SO_4^{2-} = 3.3$ mg/l).

4.2. El Chichón and Popocatépetl

Regarding acidity, conductivity and temperature, El Chichón crater lake water showed an increasing pH from 1983 to 1986. Conductivity varied in the opposite direction. Dark and light triangles in Fig. 5 show those trends. Water temperatures varied from 56°C in 1983 to 35.4°C in 1997.

Popocatépetl crater lake water did not change its acidity much in the pre-eruptive phase, and the pH measured values were never as low as the immediate post-eruptive phase of El Chichón, but the conductivity of Popocatépetl water was 123,700 μS/cm in April 1992, higher than any measured value at El Chichón. Water temperature at Popocatepetl lake increased from 29°C in January 1986 (SEAN, 1986) to 65°C in 1994 (Smithsonian Institution, 1994).

Water-type evolved differently in both crater lakes: from analyses of Casadevall et al. (1984) the El Chichón water can be classified as acid, calcium-chloride in 1983, and in 1997, it was acid, sodium-chloride type.

Popocatépetl water was magnesium-sodium-chloride-sulfate in 1985, and acid, magnesium-chloride-sulfate in 1994 as may be inferred from the analyses of Werner et al. (1997). Fig. 6 shows these types along with water types of other crater lakes around the world.

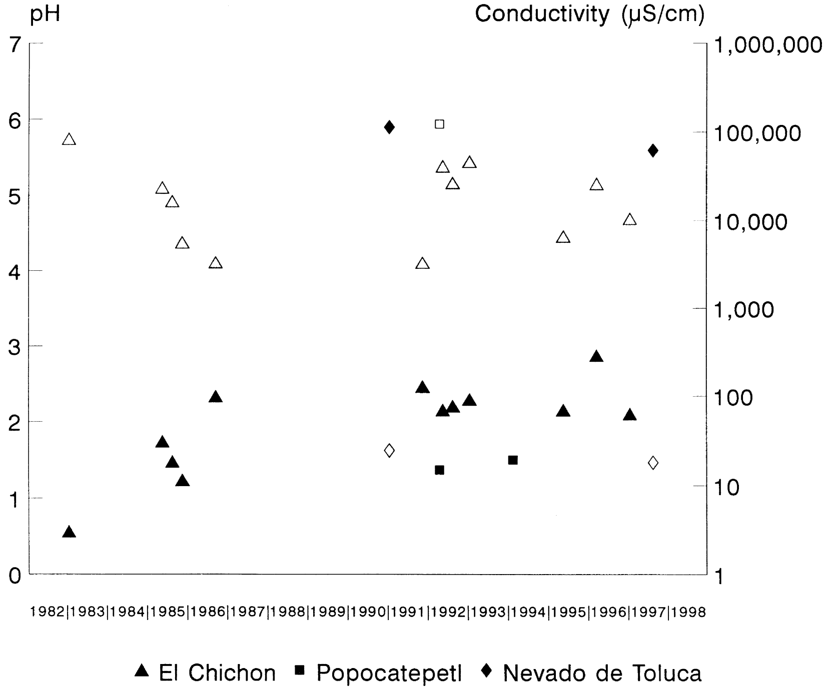


Fig. 5. Conductivity (light symbols) and pH (dark symbols) values of El Chichón, Popocatépetl, and Nevado de Toluca crater lakes at different dates. The 1983 conductivity was calculated from TDS vs. conductivity trends.

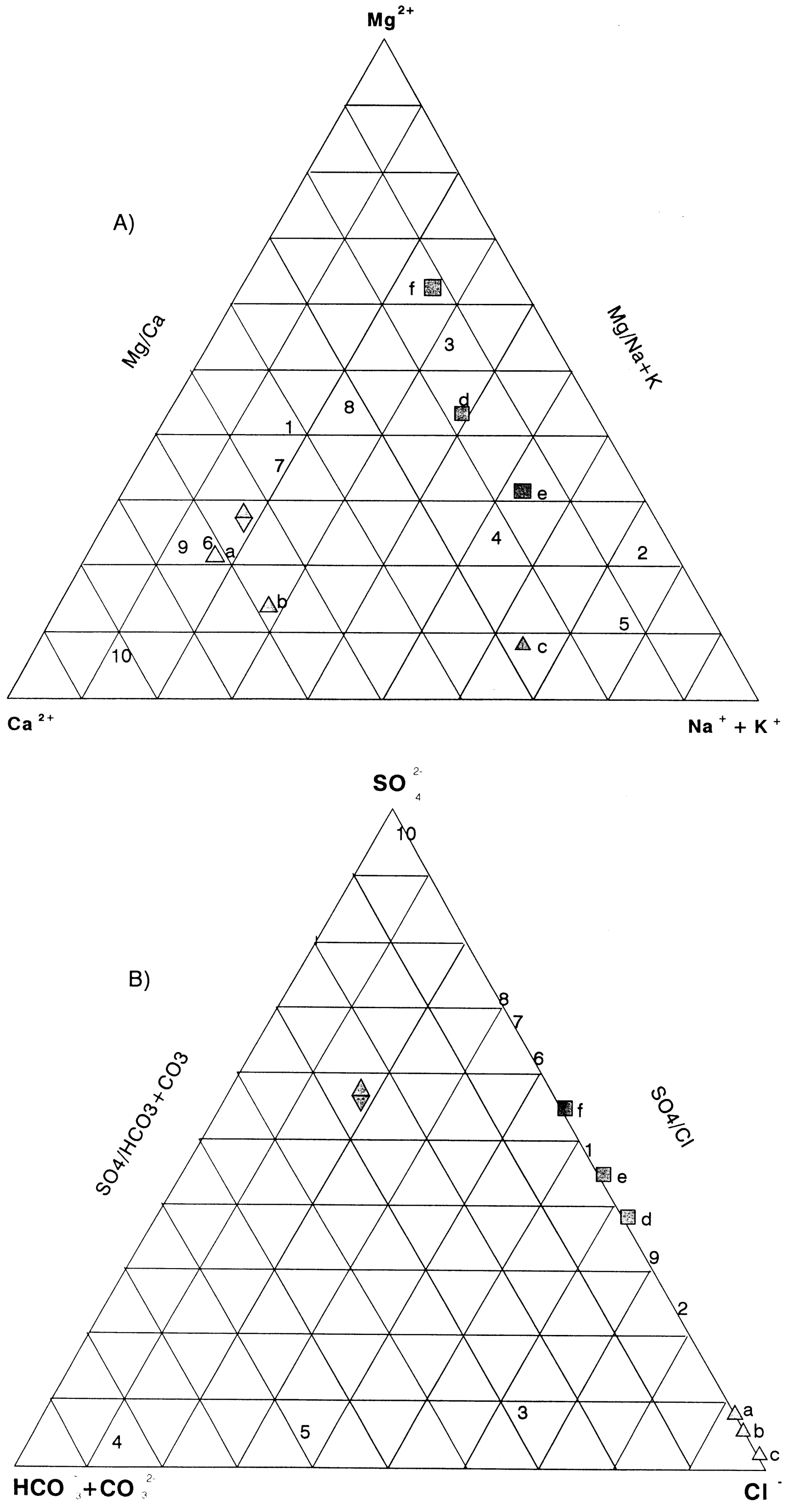
The major anions SO_4^{2-} and Cl^- varied over time at El Chichón and at Popocatépetl (Table 1).

A decreasing trend with time was observed for sulfate and chloride concentrations at El Chichón (Fig. 7). The chloride concentration decreased from 24,030 mg/l in 1983 to 3740 mg/l in 1997. The sulfate content diminished from 3550 mg/l in 1983 to 469 mg/l in 1997. Rock derived elements like Ca, Mg and Fe also showed a decreasing trend at El Chichón.

At Popocatépetl an increase in chloride was observed between 1985 and 1994 (from 12,400 mg/l to 14,200 mg/l), and a greater increase was detected in the sulfate content (from 11,100 mg/l in 1985 to 23,660 mg/l in 1994). The magnesium content at Popocatépetl diminished slightly between 1985 and 1992, but increased above 100% between 1992 and 1994 (1239 mg/l in 1992, and 2520 mg/l in 1994) (Fig. 8). Iron also increased from 2550 mg/l in 1992 to 3770 mg/l in 1994 (Table 1).

At El Chichón, boron diminished irregularly from 433 mg/l in 1983 to 37 mg/l in 1997. Lithium showed a decreasing trend until 1992 (0.76 mg/l in 1983 to 0.28 mg/l in August 1992), but increased in May 1995 to 1.64 mg/l, and has been keeping high values since. Fluoride increased between 1983 and 1985 (0.16 mg/l in 1983 to 4.5 mg/l in 1985), decreasing afterwards up to less than 0.05 mg/l in January, 1997 (Table 1).

Fig. 6. Triangular diagrams of (A) cations and (B) anions. The numbers correspond to: (1) Sirung Lake, 1984 (Poorter et al., 1989); (2) Anak Krakatau, 1933 (Poorter et al., 1989); (3) Soufrière, 1971 (Sigurdsson, 1977); (4) Albano (Martini et al., 1994); (5) Furnas (Martini et al., 1994); (6) Poás, 1987 (Rowe et al., 1992); (7) Ruapehu, 1988 (Christenson and Wood, 1993); (8) Kawah Ijen 1964 (Delmelle and Bernard, 1994); (9) Yugama, 1992 (Ohba et al., 1994); and (10) Kusatsu-Shirane, 1976 (Ossaka et al., 1980). (▼a) Chichón, January, 1983. (Casadevall et al., 1984). (▼b) Chichón, January, 1993. (▼c) Chichón, January, 1997. (■d) Popocatépetl, November, 1985. (■e) Popocatépetl, April, 1992. (■f) Popocatépetl February, 1994 (Werner et al., 1997). (◆) Nevado de Toluca, August, 1997.


A)
Mg2+
Ca 2+
Na + + K +
Mg/Ca
Mg/Na+K
f
d
e
a
b
c
1
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B)
SO 4 2-
HCO 3 - +CO 3 2-
Cl -
SO4/HCO3+CO3
SO4/Cl
f
e
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Table 1
Chemical composition of Popocatépetl, El Chichón and Nevado de Toluca Crater Lakes (concentrations in mg/l)

Date	pH	T (°C)	Λ (μS/cm)	HCO_3	CO_3	SO_4	Cl	Ca	Mg	Na	K	F	B	Li	Fe	SiO_2	Al
Popocatépetl >																	
Nov 1985	–	–	–	0	0	11,100	12,400	1020	1347	2280	141	2.12	38	–	–	–	–
Apr 1992	1.37	–	12,3700	0	0	17,000	14,500	997	1239	3438	575	0.48	73	–	2550	–	–
Feb 1994[a]	1.5	65	–	0	0	23,660	14,200	781	2520	1835	329	11.5	54	3.31	3770	295	2210
El Chichón																	
Jan 1983[b]	0.56	56	83,800	0	0	3550	24,030	2110	424	607	232	0.16	433	0.76	914	257	745
May 1985	1.74	–	23,560	0	0	345	4338	1368	684	–	–	2.00	–	0.16	190	330	–
Aug 1985	1.48	–	16,500	0	0	554	818	243	110	–	–	2.93	–	0.17	248	450	–
Nov 1985	1.24	29.5	5650	0	0	170	6092	1368	637	200	–	4.50	176	0.18	210	248	–
Sep 1986	2.33	–	3358	0	0	1577	9200	2019	775	–	–	–	146	–	146	–-	–
Nov 1991	2.46	–	3320	0	0	484	320	92	22	100	23	0.37	5	0.14	13.3	71	–
May 1992	2.15	32.1	41,100	0	0	420	12,250	2517	317	3400	670	0.52	165	0.46	–	273	–
Aug 1992	2.20	–	26,650	0	0	390	6900	1590	217	3000	410	0.36	115	0.28	17.7	550	–
Jan 1993	2.29	30.7	46,400	0	0	293	13,200	2660	363	1325	210	0.68	188	–	15.2	250	1.02
May 1995	2.15	33	6640	0	0	671	986	228	38	460	108	–	10	1.64	23	111	13.11
Mar 1996	2.87	28.3	25,850	0	0	529	4220	691	114	1839	262	$<$ 0.05	50	5.50	22	251	–
Jan 1997	2.10	35.4	10,450	0	0	469	3740	502	106	1189	184	$<$ 0.05	37	3.5	12	212	4.40
Nevado de Toluca																	
Jan 1991[c]	5.90	7	24.6	12.2	0	–	$<$ 1.0	$<$ 0.8	3.9	$<$ 1.0	$<$ 0.5	–	$<$ 0.5	–	–	$<$ 2.5	–
Aug 1997	5.59	11.7	18.0	2.3	0	3.3	1.5	1.6	0.7	0.6	0.5	$<$ 0.05	–	–	–	$<$ 2.5	–

[a] Werner et al., 1997.
[b] Casadevall et al., 1984.
[c] Caballero-Miranda, 1996.

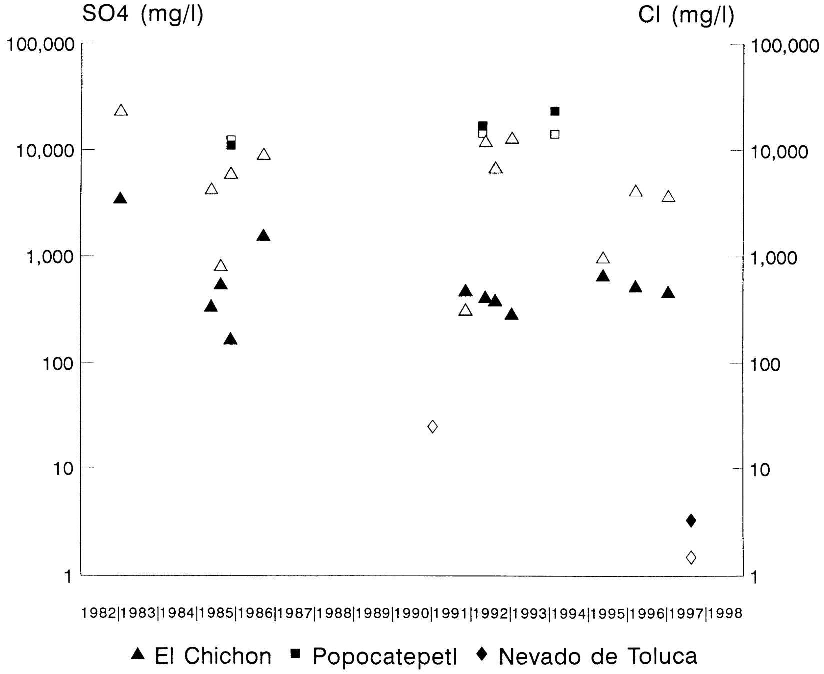


Fig. 7. Cl^- (light symbols) and SO_4^{2-} (dark symbols) concentrations (mg/l) at El Chichón, Popocatépetl and Nevado de Toluca crater lakes against time.

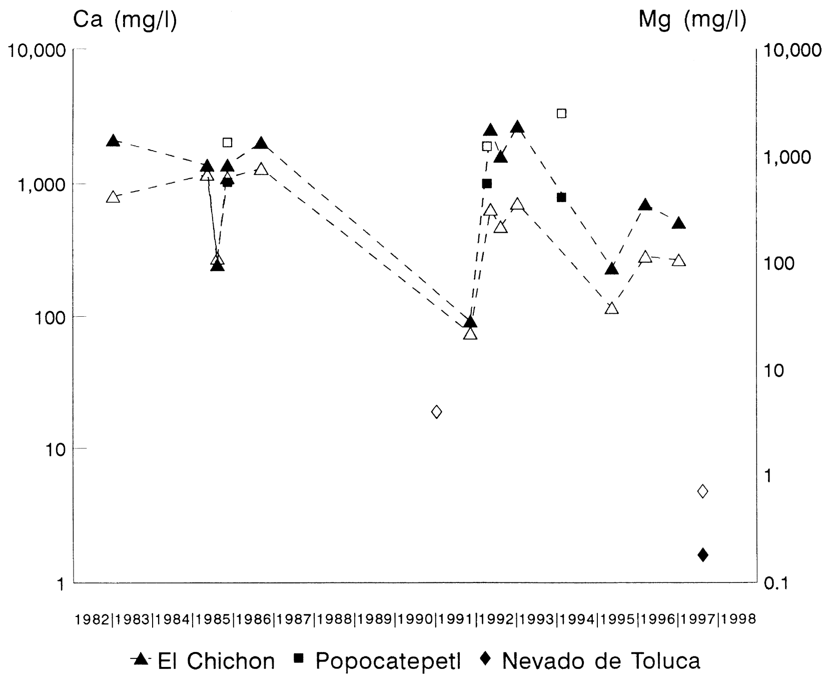


Fig. 8. Ca (dark symbols) and Mg (light symbols) concentrations (mg/l) at El Chichón, Popocatépetl and Nevado de Toluca crater lakes on various dates.

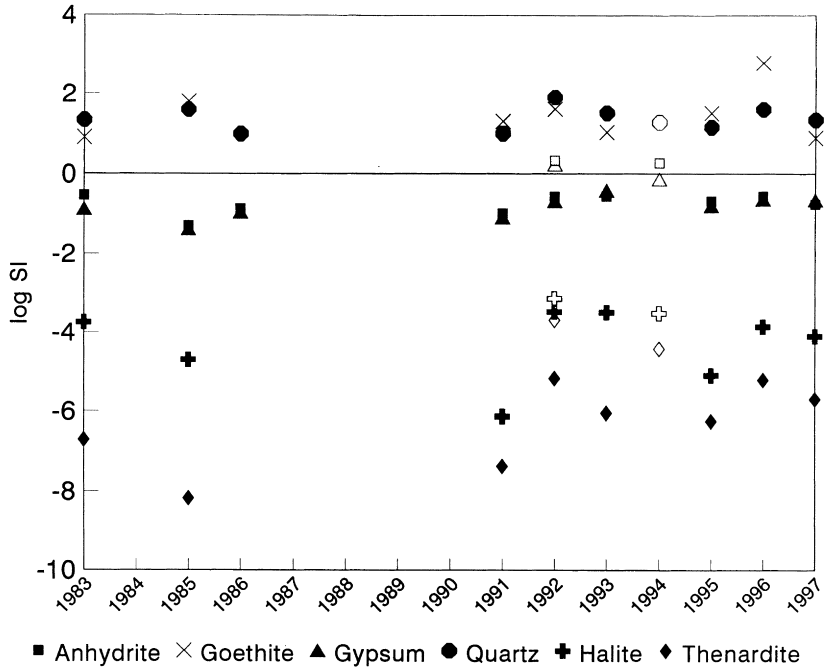


Fig. 9. Logarithm of Saturation Indexes (LSI) of quartz, gypsum, anhydrite, goethite, halite and thenardite at El Chichón (dark symbols) and Popocatépetl (light symbols) crater lakes against time.

At Popocatépetl, the boron concentration varied from 38 mg/l in 1985 to 73 mg/l in 1992, and to 54 mg/l in 1994. Fluoride increased almost 30 fold between 1992 and 1994 (0.48 mg/l in 1992 to 11.5 mg/l in 1994) (Table 1).

The geochemical modeling programs WATEQ4F (Ball and Nordstrom, 1991) and MINTEQA2 (1991) were used for calculating saturation indices and predominance of species. The results obtained at El Chichón since 1983 and at Popocatépetl in 1992 and 1994 are shown in Fig. 9.

Oversaturation of quartz was determined for all the samples at El Chichón and Popocatépetl. A logarithm of saturation index (LSI) of goethite greater than 0.9 was calculated for all the El Chichón samples except for the first one in 1983. El Chichón lake was saturated with anhydrite in 1983, and undersaturated, though near saturation with anydrite and gypsum since 1986. Anhydrite and gypsum were around the saturation values for the 1992 and 1994 Popocatépetl samples. At El Chichón, thenardite had a lower LSI in 1983 (-6.71) than in 1997 (-5.69). Popocatépetl lake showed undersaturation of thenardite in 1992 (LSI $= -3.69$) and in 1994 (LSI $= -4.44$). Gypsum precipitation at Popocatépetl was evidenced by its presence in the non-juvenile ashes erupted in 1994 and early 1995 (Martin-del Pozzo et al., 1995). The precipitation of anhydrite, gypsum and goethite at El Chichón was predicted by Casadevall et al. (1984). Nevertheless, no studies have been made on the sediment of the crater lake that may reveal the actual formation of those minerals at El Chichón.

Differences in the predominance of species were observed between 1983 and 1997 at El Chichón (Table 2). The most important change occurred in the sulfate distribution. In 1983 SO_4^{2-} was present mainly as HSO_4^-, while in 1997 the higher percentage was SO_4^{2-} followed by HSO_4^-.

At Popocatépetl the geochemical modeling, made without the input of the Al concentration, showed an increase on the percentage of HSO_4^- and a decrease of SO_4^{2-} in 1994 with respect to 1992 (Table 3). On the other hand, if the Al concentration (2210 mg/l) reported by Werner et al. (1997) is introduced in the input file, stronger differences in the species distribution of SO_4^{2-} are obtained between 1992 and

Table 2
Percentage distribution of components among species at El Chichón crater lake

Component	Species	Percentage (1983)	Percentage (1997)
SO_4^{2-}	SO_4^{2-}	4.0	52.0
	$CaSO_4$ aq	2.7	14.5
	$MgSO_4$ aq		4.4
	NaSO4		4.7
	HSO_4^-	91.3	23.4
H_4SiO_4	H_4SiO_4	100	100
H_3BO_3	H_3BO_3	100	100
Fe^{2+}	Fe^{2+}	97.8	94.5
	$FeSO_4$ aq	2.2	5.5
HF	HF	99.6	98.6
Cl^-	Cl^-	100	100
Ca^{2+}	Ca^{2+}	98.1	94.3
	$CaSO_4$ aq	1.9	5.7
Mg^{2+}	Mg^{2+}	98.3	95.0
	$MgSO_4$ aq	1.7	5.0
Na^+	Na^+	99.8	99.6
K^+	K^+	99.6	99.3

1994. The complexing of Al with SO_4^{2-} reduces even more the percentage of sulfate as SO_4^{2-}. Finally, Ca^{2+} and Mg^{2+} distributions increased their percentages as free ions in 1994 with respect to 1992.

The chemical geothermometers developed by Fournier and Truesdell (1973), Fouillac and Michard (1981) and Fournier and Potter (1982), were applied for the El Chichón and Popocatépetl lakes. The results are shown in Table 4. The Na/Li vs *T* equation for $Cl^- < 0.2$ M was used for the 1997 El Chichón sample, the equation for $Cl^- > 0.3$M was applied for the rest of the samples.

5. Discussion

Chemical changes in crater lake waters related to volcanic activity have been observed at several volcanoes of the world. Changes in inputs of magmatic heat and volatiles are generally reflected in the

Table 3
Distribution of components among species at Popocatépetl crater lake

Component	Species	Percentage (1992)	Percentage[a] (1994)	Percentage[b] (1994)
Fe^{2+}	Fe^{2+}	65.9	60.3	66.6
	$FeSO_4$ aq	34.1	39.7	33.4
SO_4^{2-}	SO_4^{2-}	28.3	16.3	11.2
	$MgSO_4$ aq	9.8	13.2	10.9
	$CaSO_4$ aq	5.2	2.7	2.3
	$NaSO_4^-$	5.3	1.9	1.4
	$FeSO_4$ aq	8.8	10.9	9.2
	HSO_4^-	41.9	54.6	39.5
	$AlSO_4^+$			10.9
	$Al(SO_4)_2^-$			14.4
Cl^-	Cl^-	100	100	100
Ca^{2+}	Ca^{2+}	62.8	65.4	71.2
	$CaSO_4$ aq	37.2	34.6	28.8
Mg^{2+}	Mg^{2+}	65.9	68.7	74.2
	$MgSO_4$ aq	34.1	31.3	25.8
Na^+	Na^+	93.8	94.2	95.7
	$NaSO_4^-$	6.2	5.8	4.3
K^+	K^+	91.5	88.7	91.4
	KSO_4^-	8.5	11.3	8.6
F^-	F^-	2.5	1.7	
	MgF^+	1.5	4.9	
	HF	95.9	93.1	
	AlF^{2+}			85.8
	AlF_2^+			14.1
H_3BO_3	H_3BO_3	100	100	100

[a] Werner et al., 1997. Calculations without Al concentration input.
[b] Werner et al., 1997. Calculations including Al concentration.

Table 4
Chemical geothermometers at El Chichón and Popocatépetl

Geothermometer	Chichón 1983 T(°C)	Chichón 1993 T(°C)	Chichón 1997 T(°C)	Popocatépetl 1985 T (°C)	Popocatépetl 1992 T (°C)	Popocatépetl 1994 T(°C)
T measured	56	31	35.4	–	–	65
Quartz[a]	179	177	181	–	–	189
Na/Li[b]	257	–	133	–	–	298
Na–K–Ca[c]	242	180	219	166	233	226

[a] Fournier and Truesdell (1973).
[b] Fouillac and Michard (1981).
[c] Fournier and Potter (1982).

temperature and chemistry of the lakes (Rowe et al., 1992). At Yugama crater lake, Takano and Watanuki (1990) found a decrease in the polythionate and an increase in the sulfate concentrations of the lake water before its 1982 eruption. During the 1971–1972 eruption of Soufrière volcano the concentration of Cl^- and SO_4^{2-} increased (Sigurdsson, 1977). Increases in the Mg/Cl ratio during and after eruptive periods have been observed at Ruapehu volcano (Giggenbach, 1983). Chemical changes in the lake water from Kusatsu-Shirane volcano were detected one year before its 1976 eruption (Ossaka et al., 1980).

The crater lakes act as condensers that trap the more soluble or reactive magmatic volatiles (mainly SO_2, H_2S, HCl, HF and HBO_2) (Delmelle and Bernard, 1994). Characteristics of crater lakes situated over actively degassing volcanoes are extreme acidity, a sulfur-rich chemistry and elevated concentrations of dissolved rock-forming elements (Rowe et al., 1992; Ohba et al., 1994).

The decreasing volcanic influence on the El Chichón crater lake water is mostly reflected in the increasing pH, and decreasing temperature. The overall concentration decrease from 1983 to 1997 of magma-related ions such as Cl^-, SO_4^{2-} and F^- also indicates that the dissolution of volcanic gases has diminished on average. Furthermore, fumarolic and bubbling gas isotopic and chemical measurements made by Taran et al. (1998) from May 1995, to January, 1997, suggested a transition from magmatic to hydrothermal conditions.

The similar trends observed for calcium and magnesium (Fig. 8) indicate the same source for both ions, probably related with trachyandesite dissolution in the lake water, as proposed by Casadevall et al. (1984). Sulfate variations with time could result from redox-reactions of sulfur or from dissolution–precipitation reactions, since gypsum and anhydrite were close to saturation over the sampled period. Precipitation of sulfate could take place through:

$$Ca^{2+} + SO_4^{2-} \leftrightarrow CaSO_4 \text{ (anhydrite)}$$

and

$$Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4{\cdot}2H_2O \text{ (gypsum)}$$

The presence of sulfur sublimates on the crater floor (Fig. 2) suggests that oxidation–reduction processes of sulfur occur within the lake.

Except for the large initial drop in concentrations, no correlation was found between sulfate and chloride at El Chichón since 1985. The predominance of Cl^- over SO_4^{2-} in the water samples is unexpected from the huge emission of SO_2 during the 1982 eruptions of El Chichón. Ash leachates from samples collected in April 1982 had a S/Cl weight ratio of 2.6 (Varekamp et al., 1984). Although the S/Cl ratio in the lake water varied with time, it has always been much lower than in the leachates. In January, 1983 the measured ratio in the water was S/Cl = 0.049 and in 1997, S/Cl = 0.042. The highest ratio was obtained in the November, 1991 sample (S/Cl = 0.504) which had the lowest conductivity of all the sampling period.

The lower, varying S/Cl ratios observed at El Chichón crater lake may result from different effects. The ash leachates reveal the conditions during the eruption. The water samples reveal a post-eruptive condition. The co-eruptive condition implies catastrophic degassing of large volumes of sulfur-rich magma. The post-eruptive condition implies a much lower, remanent degassing of a volatile-depleted magma through a system containing liquid water.

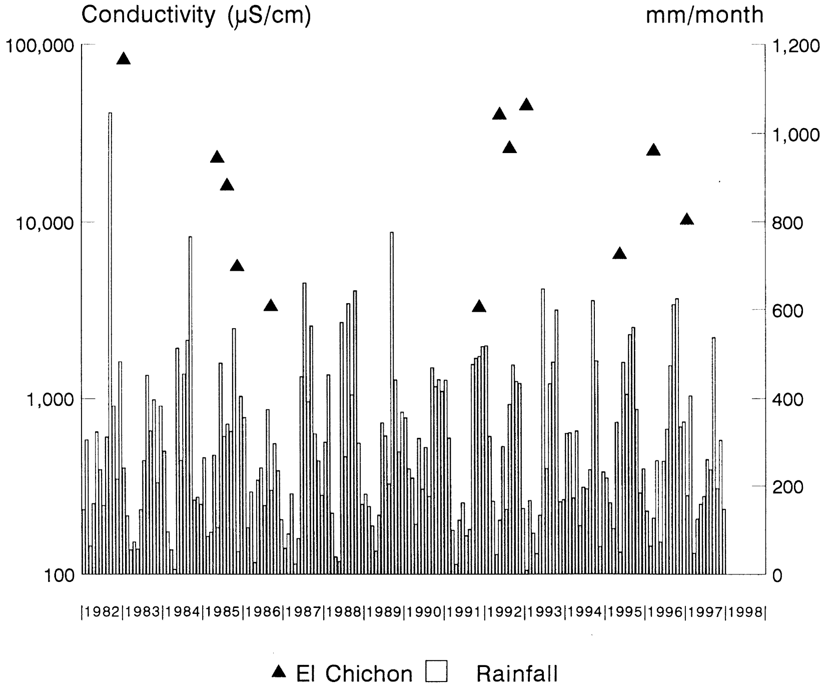


Fig. 10. Conductivity (μS/cm) and rainfall (mm/month) from 1983 to 1997 at El Chichón. Rainfall data corresponds to the Pichucalco metereological station (CNA, 1998) located about 20 km from El Chichón volcano.

Even gases having a relatively high S/Cl ratio may reduce their SO_2 concentration, when bubbling through a thick body of water. SO_2 may react in the deeper parts of the water body forming other sulfur compounds and the surface water may yield lower S/Cl ratios.

Additional effects producing variations in the S/Cl ratio may be the precipitation of gypsum, anhydrite and sulfur. As an example, the increase in that ratio in November 1991 may have been a result of a higher dilution of the lake water at the end of the rainy season, decreasing the formation of sulfate minerals, and allowing more sulfate with respect to chloride to be in solution.

The irregular behavior of the conductivity of El Chichón water could result from both changes in the magmatic influence on the lake, and variations in the amount of water in the crater as a result of seasonal and variable rainfall effects (Fig. 3). The decreasing of the conductivity from 1983 to 1985, despite the diminishing of the rainfall (Fig. 10) suggests a decrease of the magmatic influence. On the other hand, from 1991 higher conductivities were obtained in times of lower rainfall rates, indicating more influence of seasonal effects. Boron concentration behaved similarly to conductivity with a clear decreasing trend until 1985 (Fig. 11), and a minimum value in November 1991, after a heavy rain period.

Iron concentration at El Chichon (Fig. 11) is controlled by dissolution–precipitation reactions. This may be inferred from the oversaturation of goethite that was obtained for all the samples after 1983. The precipitation of goethite is pH-dependent through:

$$Fe^{3+} + 2H_2O \leftrightarrow FeOOH + 3H^+$$

besides, the E_h of the water influences the ratio Fe^{2+}/Fe^{3+}, and hence the extent of the goethite formation.

The changes observed at Popocatépetl crater lake might be related with the restart of its activity since 1993. A sulfate increase in spring water was observed prior to eruptive events at Tacaná, México (De la Cruz-Reyna et al., 1989), Poás crater lake, Costa

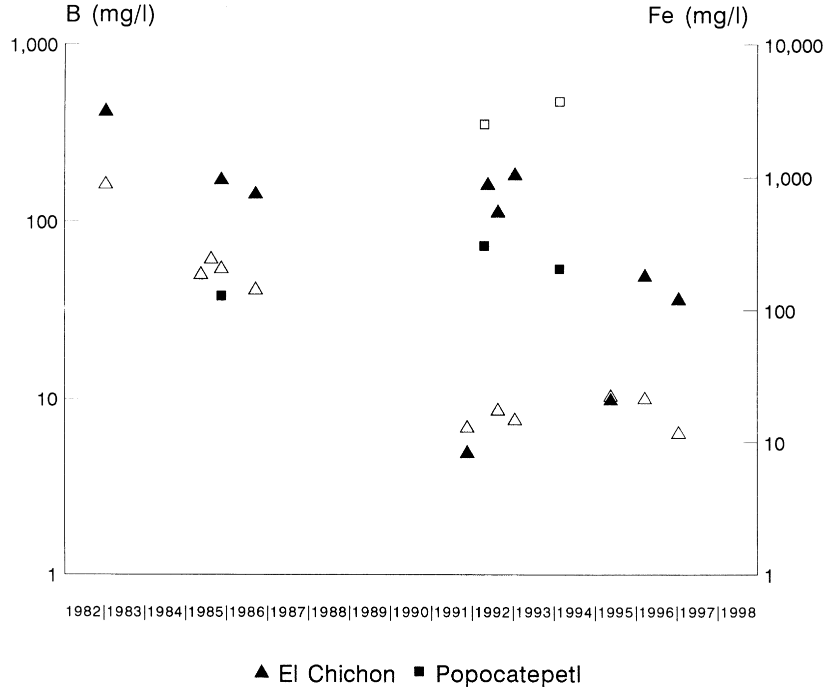


Fig. 11. B (dark symbols) and Fe (light symbols) in mg/l at El Chichón, Popocatépetl and Nevado de Toluca lakes against time.

Rica (Rowe et al., 1995), and Yugama crater lake, Japan (Takano and Watanuki, 1990). During the 1971–1972 eruption of Soufrière volcano on St. Vincent Island, the SO_4^{2-} concentration in the crater lake water also increased (Sigurdsson, 1977). At Popocatépetl, the sulfate was more than 100% higher in 1994 than in 1986. This increase preceded the December 21, 1994 ash eruption, which initiated the current activity. Besides, at Poás the SO_4/Cl ratio presented a peak prior to the disappearance of the crater lake (Rowe et al., 1995). An increment in this ratio was also observed at Popocatépetl, since the SO_4/Cl ratio was 1.17 in 1992 and 1.66 in 1994.

Variations in the Mg/Cl quotient in crater lake water have been correlated with the activity of Ruapehu volcano (Giggenbach, 1983). An increase in this ratio was detected just prior to ash eruptions. The magnesium content was related with the degree of interaction of lake waters with high-temperature andesitic material (Giggenbach, 1983).

In the crater lake water of Popocatépetl, the Mg/Cl also increased, varying from 0.085 in 1992 to 0.177 in 1994, before the ash emission which occurred in December. The magnesium input was also reflected in the water type change from sodium-chloride-sulphate in 1992 to magnesium-chloride-sulphate in 1994.

The variations in the predominance of SO_4^{2-} species at El Chichón between 1983 and 1997 are due mainly to the increase of the pH that allowed more SO_4^{2-} to form aqueous species with cations other than H^+. The same effect, but in the opposite sense, was observed at Popocatépetl, since the percentage of SO_4^{2-}, bound as HSO_4^-, shifted from 41.9 in 1992 to 54.6 in 1994 (without the Al concentration input). By including the data of Al concentration (probably resulting from Al-silicate dissolution due to the low pH) in the geochemical model, the formation of aluminium complexes with sulfate is evident; these complexes might also had been present in 1992, but could not be modelled for the lack of Al data.

Application of chemical geothermometers to the lake waters may give results far from the real temperature at depth. Both El Chichón and Popocatépetl were oversaturated in quartz, resulting in fairly constant calculated temperatures through time. Following the criteria given by Giggenbach (1988) on the degree of thermodynamic fluid–rock equilibrium of thermal waters, these lakes were placed in the field of immature waters (Fig. 12A). Fig. 12B shows that El Chichón in 1983 was close to the line of rock dissolution, but farther from that line ten years later. Popocatépetl in 1992 and 1994 was placed next to the Ruapehu water produced during an eruptive period (Giggenbach, 1988). The sample from Nevado de Toluca was below the full equilibrium line and very far from the volcanic waters depicted by Giggenbach (1988) in this diagram. Nevertheless, by applying the Na–K–Ca geothermometer, a decreasing trend in the temperature between 1983 and 1997 could be inferred at El Chichón. This trend agrees with the tendency of the measured temperatures and also with the results from the empirical Na/Li geothermometer (Foullac an Michard, 1981). At Popocatépetl, a temperature increase was obtained with the Na–K–Ca geothermometer between 1985 and 1994. The readings made in January 1986 (SEAN Bulletin, 1986), and in 1994 by Werner et al. (1997), showed also the same trend. The application of the three geothermometers to the 1994 Popocatépetl sample gave different temperatures. Probably the best temperature estimate is obtained from the Na/Li geothermometer (Foullac and Michard, 1981). Although it was developed including only data from springs and wells in geothermal areas, some of them were acid sulfate waters, like Popocatépetl lake water in 1994.

In contrast with Popocatépetl and El Chichón, minor changes were observed at Nevado de Toluca with time. The pH and conductivity measured in 1997 (pH $= 5.59$, $\Lambda = 18$ μS/cm) were slightly lower than the values measured by Caballero-Miranda (1996) in January, 1991 (pH $= 5.90$, $\Lambda = 24.6$ μS/cm). This difference might be due to seasonal effects, as the 1997 sample was obtained in the rainy season. The concentrations of boron and F^- below detection levels as well as the low concentrations of dissolved ions indicate no influence of volcanic products at Nevado de Toluca lake.

6. Conclusions

The chemical characteristics determined at El Chichón, Popocatépetl and Nevado de Toluca crater lakes, reflect the stage of their volcanic activity. Magmatic influence in active volcanoes such as Popocatépetl and El Chichón is reflected in the very low pH and high conductivity values of their crater lakes. Reduced magmatic influence in a post-eruptive stage allows fluctuations of the conductivity derived from external factors, such as rainfall. Higher measured temperatures corresponded to lake water more influenced by magmatic gases. The dormant stage of Nevado de Toluca was revealed by the chemical features of its crater lake water, with low conductivities and low concentrations of magma-related ions, as well as a water temperature close to the environment.

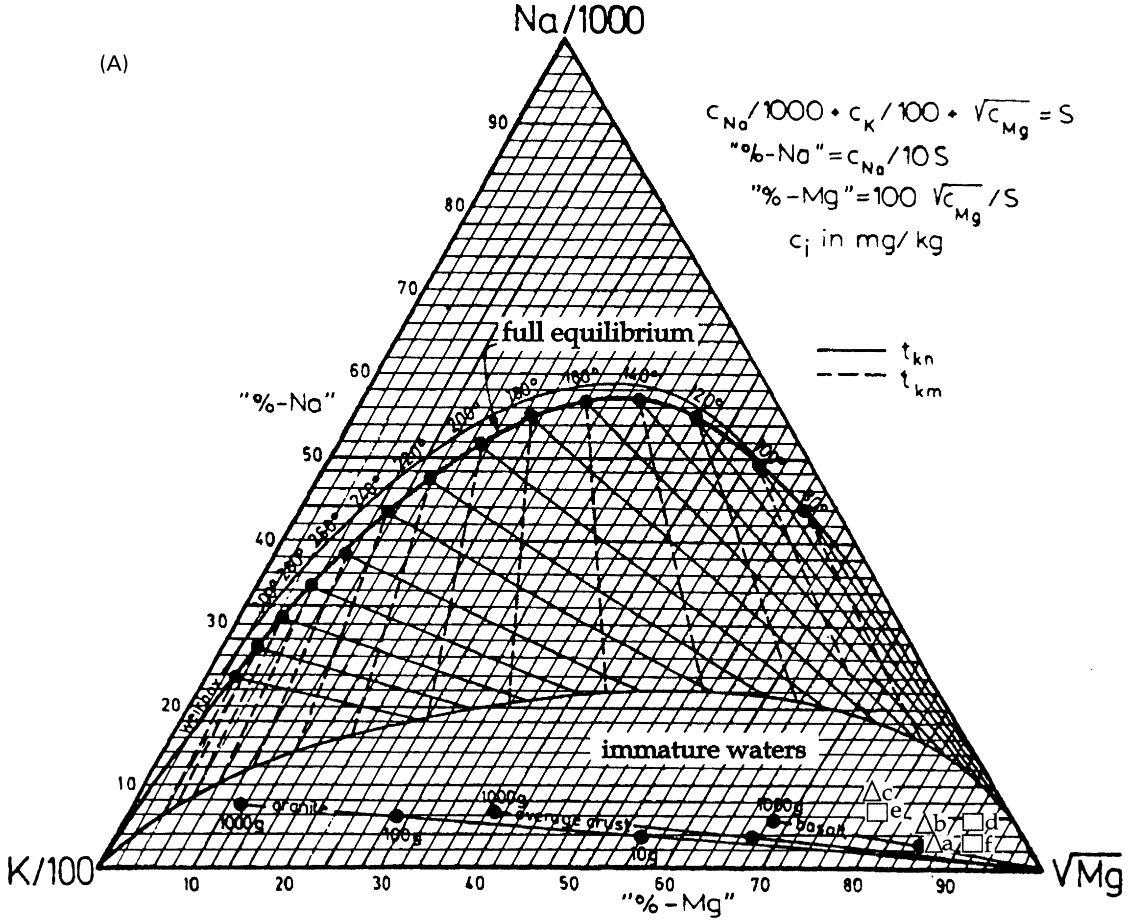
The decrease in the volcanic-related species like sulfate, chloride, boron and fluoride since 1983 at El Chichón indicates a lowering of the magmatic contribution in the crater lake, though its current general chemistry reflects that such contribution is still present.

At Popocatépetl, its reawakening was evident from the chemical changes observed in the crater lake that preceded the ash eruption occurred in December, 1994. Sulfate was the anion showing more correlation with volcanic activity at Popocatépetl. The ratio S/Cl rised mainly as an effect of sulfate increase, since Cl^- concentrations varied erratically and in a lower proportion. The evolution of major cations represented in Giggenbach diagrams also reflected the changes of the magmatic influence at El Chichón and Popocatépetl.

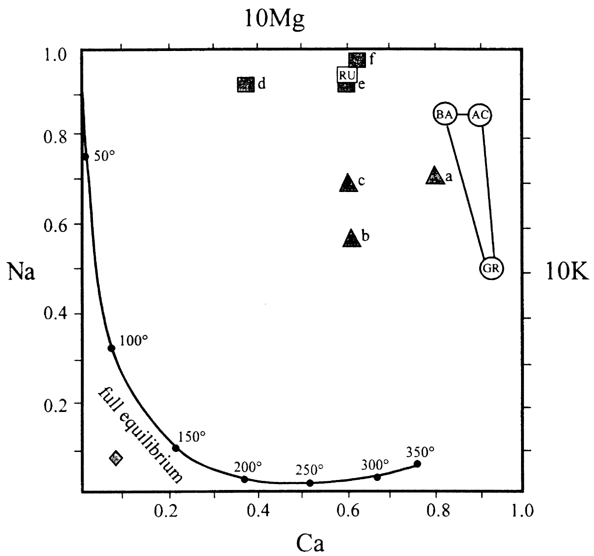
The Mg/Cl quotient revealed to be an important ratio in the assessment of the level of volcanic activity. At El Chichón, this value decreased persistently between 1985 and 1991 from 0.157 to 0.068, and then kept a low value. Magnesium content has been related with interactions of lake-water with high-temperature andesitic material (Giggenbach, 1983). However, at Popocatépetl, the crater lake evaporated months before solid andesitic ash was emitted. The higher contribution of magnesium was probably derived from heating of the andesitic lake basin at the crater bottom by hot fumarolic gases.

Two other factors frequently used to measure the level of magmatic influence in crater lake waters, S/Cl ratio and water type, poorly reflected the decrease in the magmatic influence at El Chichón, while they showed a better correlation with the increasing activity of Popocatépetl. Water type change at El Chichón

(A)


Na/1000
c_Na/1000 + c_K/100 + √c_Mg = S
"%-Na" = c_Na/10S
"%-Mg" = 100 √c_Mg /S
c_i in mg/kg
full equilibrium
t_kn
t_km
"%-Na"
immature waters
granite
average crust
basalt
K/100
√Mg
"%-Mg"
c
e
b
d
a
f

(B)


10Mg
Na
10K
Ca
full equilibrium
50°
100°
150°
200°
250°
300°
350°
d
f
RU
e
BA
AC
GR
c
a
b

crater lake water has been controlled by a relative increase of Na with respect to other cations. Since this increase occurs along with a clear decrease of the magmatic influence, this effect ought to be increasingly hydrothermal. In contrast, water type at Popocatépetl has been controlled by higher dissolution of magmatic sulfur gases and increased temperatures enhancing the dissolution of magnesium.

Even though Popocatépetl and El Chichón lakes can be classified as immature waters, the Na–K–Ca geothermal thermometer reflected the same trends of the surface measured temperatures, suggesting that it can render useful results in active volcanoes.

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Fig. 12. (A) Giggenbach (1988) diagram for the evaluation of Na–K and K–Mg equilibration temperatures. Symbols are the same as those of Fig. 6. (B) Plot of $10C_{Mg}/(10C_{Mg} + C_{Ca})$ vs. $10C_K/10C_K + C_{Na}$) of Popocatépetl, El Chichón and Nevado de Toluca Volcanoes. (◆) Nevado de Toluca. El Chichón and Popocatépetl symbols are the same as those of Fig. 6 (after Giggenbach, 1988).

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