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## Geochemistry of the volcano-hydrothermal system of El Chichón Volcano, Chiapas, Mexico

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**Abstract** The 1982 eruption of El Chichón volcano ejected more than 1 km<sup>3</sup> of anhydrite-bearing trachyan-desite pyroclastic material to form a new 1-km-wide and 300-m-deep crater and uncovered the upper 500 m of an active volcano-hydrothermal system. Instead of the weak boiling-point temperature fumaroles of the former lava dome, a vigorously boiling crater spring now discharges >20 kg/s of Cl-rich (~15 000 mg/kg) and sulphur-poor (>200 mg/kg of SO<sub>4</sub>), almost neutral (pH up to 6.7) water with an isotopic composition close to that of subduction-type magmatic water ( $\delta D = -15\%$ ,  $\delta^{18}O = +6.5\%$ ). This spring, as well as numerous Cl-free boiling springs discharging a mixture of meteoric water with fumarolic condensates, feed the crater lake, which, compared with values in 1983, is now much more diluted (~3000 mg/kg of Cl vs 24 030 mg/kg), less acidic (pH=2.6 vs 0.56) and contains much lower amounts of S (>200 mg/kg of SO<sub>4</sub>, vs 3550 mg/kg) with  $\delta^{34}S = 0.5-4.2\%$  (+17‰ in 1983). Agua Caliente thermal waters, on the southeast slope of the volcano, have an outflow rate of approximately 100 kg/s of 71 °C

Na–Ca–Cl water and are five times more concentrated than before the eruption (B. R. Molina, unpublished data). Relative N<sub>2</sub>, Ar and He gas concentrations suggest extensional tectonics for the El Chichón volcanic centre. The <sup>3</sup>He/<sup>4</sup>He and <sup>4</sup>He/<sup>20</sup>Ne ratios in gases from the crater fumaroles (7.3R<sub>a</sub>, 2560) and Agua Caliente hot springs (5.3R<sub>a</sub>, 44) indicate a strong magmatic contribution. However, relative concentrations of reactive species are typical of equilibrium in a two-phase boiling aquifer. Sulphur and C isotopic data indicate highly reducing conditions within the system, probably associated with the presence of buried vegetation resulting from the 1982 eruption. All Cl-rich waters at El Chichón have a common source. This water has the appearance of a “partially matured” magmatic fluid: condensed magmatic vapour neutralized by interaction with fresh volcanoclastic deposits and depleted in S due to anhydrite precipitation. Shallow ground waters emerging around the volcano from the thick cover of fresh pumice deposits (Red waters) are Ca–SO<sub>4</sub>-rich and have a negative oxygen isotopic shift, probably due to ongoing formation of clay at low temperatures.

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### Introduction

El Chichón Volcano erupted violently in 1982, forming a new 1-km-wide summit crater. Now, 15 years after the eruption, a typical volcano-hydrothermal system has developed within the volcanic edifice, with all possible manifestations of such a system: acid crater lake, boiling-point-temperature fumaroles, boiling pools, thermal springs and steaming ground. Precipitation (averaging over 4000 mm/a) drains through the cover of fresh and old pumice deposits and forms numerous cold springs around the volcano that precipitate Fe-hydroxides and discharge a slightly acidic water, rich in

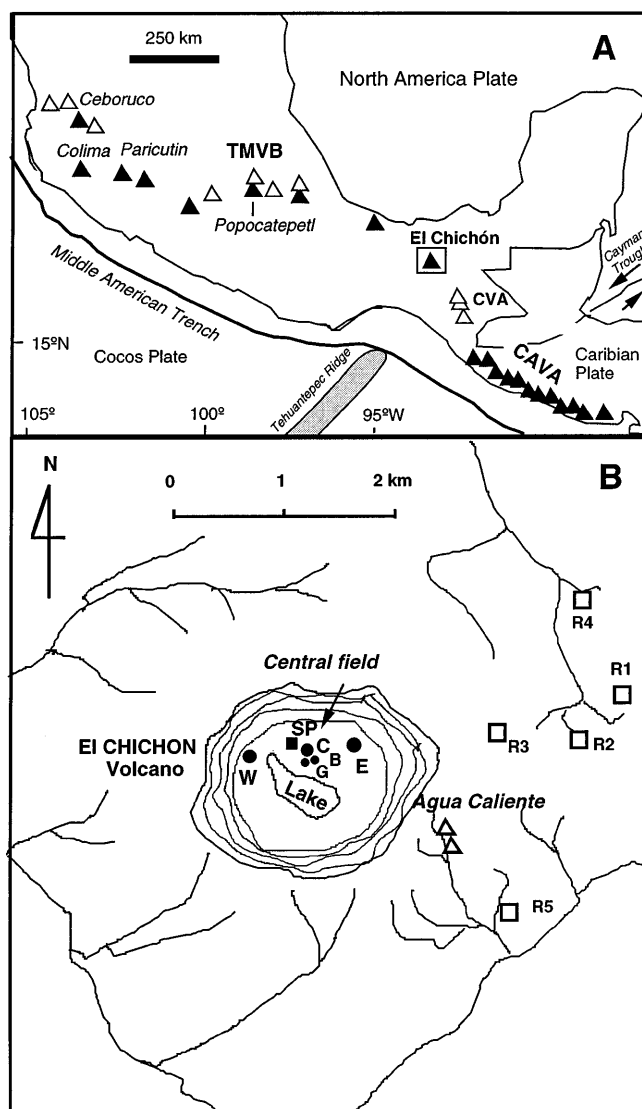
Ca-SO<sub>4</sub>, with TDS up to 3000 mg/kg. On the outer southeast slope of the volcano, 1.5 km from the top, is a group of thermal springs (Agua Caliente) that has a total outflow of more than 100 kg/s of a 71 °C neutral Na/Cl-type water.

This paper presents the results of a chemical and isotopic study of gases and waters from the crater lake, crater fumaroles, boiling pools, and thermal and cold springs at El Chichón. Samples were obtained from May 1995 through January 1997. The volcano-hydrothermal system is strongly affected by dilution with ground water, evaporation and near-surface rock-water interaction, as well as by processes within the interface between the magmatic body and overlying rocks. A specific feature of the present system is the very low sulphur content of waters and gases discharging in the crater, as compared with the huge amount of sulphur emitted during the eruption and in older deposits (Luhr et al. 1984; Rose et al. 1984; Varekamp et al. 1984).

### Geological background

El Chichón Volcano (1100 m a.s.l.) is in the state of Chiapas, southern Mexico. It lies in the northern margin of the highlands of Chiapas and Guatemala, part of a 450-km-long volcanic gap between the eastern end of the Trans-Mexican volcanic belt to the northwest and the northwestern end of the narrow Central American volcanic arc to the southeast (Fig. 1), with both chains composed primarily of calc-alkaline volcanic rocks. El Chichón Volcano, however, has produced potassic alkaline magmas (e.g. Luhr et al. 1984). Nixon (1982) proposed that this alkaline volcanism is related to extensional tectonism associated with the triple junction between the North American, Caribbean and Cocos plates. Other authors suggest, however, an association between El Chichón volcanism and the subduction of the Cocos plate under the North American plate (Stoiber and Carr 1973; Burbach et al. 1984, and references therein).

The basement rocks in the vicinity of El Chichón range in age from Middle Cretaceous to Miocene. Massive dolomitic limestone from the middle and upper Cretaceous crops out 6 km east of the volcano, on the crest of the Caimba anticline. These rocks are overlain by a sequence of Tertiary rocks that includes Paleocene, Eocene and Miocene formations, predominantly interbedded epiclastic sandstone and siltstone. Lower Cretaceous rocks were found at a depth of approximately 2200 m.b.s.l. in a PEMEX Caimba borehole, 7 km east of the volcano. They consist of evaporites, mostly anhydrite and halite, and limestone. Evaporites have a wide distribution in the uppermost 4 km of the Chiapas crust and adjacent areas, a fact that may have an effect on the composition of the hydrothermal fluids of El Chichón.



**Fig. 1** **A** Tectonic setting of southern Mexico. *TMVB* Trans-Mexican volcanic belt; *CAVA* Central America volcanic arc; *CVA* Chiapanecan volcanic arc. *Solid triangles* show historically active volcanoes, and *open triangles* show extinct or dormant volcanoes in Mexico. **B** Sketch map of the area around the El Chichón Volcano and sample sites (see the text)

### Previous work

Prior to the 1982 eruption, El Chichón consisted of a 2-km-wide somma crater housing two nested domes with heights of approximately 1260 m. The moat, a narrow low area between the inner somma crater walls and the central domes, was the focus of intense fumarolic activity (Müllerried 1933; Damon and Montesinos 1978; R.F. Cañul and V. L. Rocha, unpublished data). According to B. R. Molina (unpublished data), the maximum recorded temperature of thermal springs on the southeast slope of the volcano (Agua Caliente hot springs; Fig. 1) was 71 °C, and maximum Cl concentration was 456 mg/kg. L. A. Templos et al. (unpublished

data) do not give the temperature of Agua Caliente hot springs but present an almost identical chemical composition. No other data on the chemistry of waters near El Chichón were reported.

According to Casadevall et al. (1984), the January 1983 fumarole gas emissions in the crater were water rich (more than 99 mol%), with temperatures in the range 99–115 °C. The water in the lake was hot (52–58 °C), acidic (pH=0.56) and of high salinity (TDS=34000 mg/kg). Sulphur isotopic ratios were measured for native sulphur suspended in the lake water ( $\delta^{34}\text{S} = +0.8\text{‰}$ ) and for  $\text{SO}_4$  dissolved in lake ( $\delta^{34}\text{S} = +17\text{‰}$ ). The isotopic composition of magmatic S from anhydrite phenocrysts ( $\delta^{34}\text{S} = +9\text{‰}$ ) and magmatic pyrrhotite (+2.7‰) was measured by Rye et al. (1984). No data have been reported on the isotopic composition of water and carbon.

### Sampling and analysis

Gases from fumaroles and bubbling pools were collected and analysed according to the procedure of Giggenbach and Goguel (1989). The acidic gases and anions in the waters were determined by ion chromatography ( $\text{SO}_4$ , Cl), selective ion electrodes (F), potentiometry ( $\text{HCO}_3$ ,  $\text{CO}_2$ ) and alkaline iodine titration ( $\text{H}_2\text{S}$ ). The non-absorbed gases were analysed by gas chromatography with Ar and He/or  $\text{H}_2$  as carrier gases, and the cations in waters by AAS and flame spectrophotometry. Concentrations of trace metals (Ba, Sr, Li, Rb, Cs) were measured using ICP-MS techniques.

Two traps cooled by ice were used to condense the fumarolic steam for H and O isotopic analysis. Isotopic data for H, O, S and C were obtained by mass spectrometry.  $\text{CO}_2$  for C isotope analysis was extracted from an oxidized alkaline solution by 2N  $\text{H}_2\text{SO}_4$  and then purified in a vacuum line. Sulphate for S and O isotopes was precipitated from an oxidized alkaline solution as  $\text{BaSO}_4$ . Isotopic results for  $\text{H}_2\text{O}$ , S and C are expressed in the  $\delta$ -notation relative to V-SMOW, CDT and PDB, respectively. The reproducibility of  $\delta$ -values for D is  $\pm 2\text{‰}$ , and  $\pm 0.3\text{‰}$ ,  $\pm 0.2\text{‰}$  and  $\pm 0.2\text{‰}$  for O, S and C, respectively.

Samples for He isotopes were obtained from vacuum line gas splits of the caustic samples. In the laboratory, after purification using hot Ti–Zr getters and activated charcoal traps held at liquid nitrogen temperature, the  $^3\text{He}/^4\text{He}$ ,  $^4\text{He}/^{20}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios were measured by use of a noble gas mass spectrometer (Sano and Wakita 1985). The observed  $^3\text{He}/^4\text{He}$  ratios were calibrated against atmospheric standard gas and are expressed in the  $R_a$  notation where  $R_a$  is the atmospheric  $^3\text{He}/^4\text{He}$  ratio of  $1.39 \times 10^{-6}$ . The error of the ratio is approximately 3%. The error of the  $^4\text{He}/^{20}\text{Ne}$  ratio is approximately 10%.

## Results

### Composition of volcanic and geothermal gases

Chemical compositions of volcanic gases from the crater and of gases from the Agua Caliente (AC) hot spring are presented in Table 1. Currently, there are three main fumarolic fields: the Central, Western and Eastern (Fig. 1). A few small but “whistling” fumaroles of the central field discharged a 101 °C gas in 1996 (samples C1, C2) with low water, high  $\text{CO}_2$  and low S and Cl content. Sulphur is present mainly as  $\text{H}_2\text{S}$  at very low concentrations of  $\text{SO}_2$  (Table 1). They were calculated from the difference between total sulphur and sulphur after the alkaline iodine titration (Giggenbach and Goguel 1989), with 5% accuracy. Western fumaroles are located at the base of the northwest crater wall. The flow rate here was higher than at the central field, but they discharge a steam–water mixture from under blocks of a recent landslide (98 °C,  $\text{H}_2\text{O} > 98\text{ mol}\%$ , sample W) with similar ratios of major species as from the central site. The eastern field is a small spot of weak and wet boiling-point-temperature fumaroles (sample E) with virtually the same chemical composition as fumaroles from the western field. In 1996 and 1997 only fumaroles from the central field were sampled (samples C3, C4).

The hydrological conditions in the volcano crater varied significantly during the year. In January 1997 the crater-lake level rose by more than 0.5 m, and a large

**Table 1** Composition of fumarolic and bubbling gases in mmol/mol  
n.a. – not analysed; n.d. – not detected

Date	Site	T (°C)	$\text{H}_2\text{O}$	$\text{H}_2$	$\text{CO}_2$	CO	$\text{H}_2\text{S}$	$\text{SO}_2$	HCl	HF	$\text{N}_2$	Ar	Ne	He	$\text{CH}_4$
0183	*	115	992.4	0.14	7.1	n.a.	0.024	0.17	0.25	n.a.	0.042	0.00002	n.a.	n.a.	0.0033
0595	C1	101	841.6	1.04	142.6	0.0002	2.2	0.4	0.40	0.0064	0.37	0.0011	n.a.	0.00094	0.0038
0595	C2	101	872.1	0.90	119.4	n.d.	1.4	0.2	0.36	0.0050	0.18	0.0004	n.a.	0.00032	0.0009
0595	W	98	985.1	0.05	13.2	n.d.	0.16	0.04	0.006	0.0005	0.14	0.0012	n.a.	0.0001	0.0005
0496	E	98	986.5	0.06	11.7	n.d.	0.12	0.02	0.018	0.004	0.16	0.0011	n.a.	n.d.	0.0012
0197	C3	97	967.8	0.081	32.2	0.00014	1.29	0.17	n.d.	n.d.	0.023	0.00012	$5.2 \times 10^{-8}$	0.00006	0.0005
0197	C4	97	971.9	0.16	27.5	0.00014	0.82	0.01	n.d.	n.d.	0.028	0.0001	$3.5 \times 10^{-8}$	0.00009	0.0002
0197	A1	71		0.00076	982.1	n.d.	n.d.				16.94	0.426	0.00034	0.0151	0.489
0197	A2	71		0.0010	977.6	n.d.	n.d.				21.24	0.516	n.a.	0.0172	0.612

C1–C4 – Central fumarolic field; W – Western field; E – Eastern field; A1–A2 – Agua Caliente bubbling gas

shore area with steaming ground and numerous small boiling pools was flooded. Bubbling gas from the Agua Caliente hot springs was collected from a 70 °C pool, 20 m below the main vent. Results are shown in Table 1.

#### Composition of waters discharging in the crater

Principal features within the crater are a few powerful boiling pools and springs in the central fumarolic field (Fig. 1). One of them, Soap Pool (SP), discharges clear, highly saline (TDS > 20000 mg/kg), vigorously boiling Na–Ca–Cl water with a total outflow rate of more than 20 kg/s in 1996 and not less than 15 kg/s in 1997. This water varies in pH from slightly acidic (3.3 in 1995) to neutral (6.7 in 1997). It is high in Mg, independent of the pH. The drainless Black Pool, located closer to the lake shore, at a distance of approximately 50 m from the SP spring, contains very diluted, slightly acidic muddy water. The water from the drainless Grey Pool, which was located between SP and Black Pool and which disappeared in 1996, is high in SiO<sub>2</sub> (306 mg/kg) and has Na, K, Mg and Ca contents which are approximately half of those of the SP water. Numerous small boiling pools in the crater discharge slightly acidic

steam-heated water with low salinity, similar in composition to the Black Pool water.

Compositions of all types of water collected in the crater are shown in Tables 2 and 3. The lake water is cooler, more diluted and not so acidic as in 1983. The long-time monitoring of lake-water chemistry (Armienta and De la Cruz Reyna 1995) shows a general trend in dilution by ground water, and irregular annual fluctuations of salinity, and nearly constant ratios of dissolved components. There are no visible traces of convecting plumes on the lake surface, but a narrow (2–5 m wide) linear zone of bubbling gas extends from the central fumarolic field across the lake approximately to the middle of the lake.

#### Agua Caliente thermal waters

Numerous hot springs are at the southeast slope of the volcano, at elevations near 800 m a.s.l. along a 200 m cliff on the eastern side of a deep, overgrown valley, aligned approximately in a NW–SE direction. Their maximum temperature is 71 °C (the same value measured by B. R. Molina, unpublished data), and they discharge neutral Na–Ca–Cl water with a total outflow rate not less than 0.1 m<sup>3</sup>/s. The chemical composition of

**Table 2** Chemical compositions of thermal and cold waters at El Chichon volcano (mg/L)  
n.d. – not detected; n.a. – not analyzed

Site	Date	T °C	pH <sub>lab</sub>	SiO <sub>2</sub>	Na	K	Ca	Mg	Al	Fe	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	F	B
<b>Crater</b>															
L0	1983	55	0.56	257	607	232	2110	424	745	914	24030	3550	n.d.	0.16	433
L1	05.95	33	2.25	111	400	115	228	38	7.2	26	980	671	n.d.	0.5	10
L2	03.96	29	2.36	238	1735	257	675	79	3.9	21	3900	502	n.d.	0.03	49.7
L3	01.97	36	2.61	212	1189	184	502	106	4.4	12	3740	469	n.d.	0.025	36.8
L4	01.97	32	2.63	264	1414	233	577	112	5.5	11.5	4430	403	n.d.	0.021	41.7
S1	05.95	99	3.30	439	4450	1200	1994	348	7.4	0.1	11780	1272	n.d.	0.44	143
S2	03.96	99	5.18	104	5780	777	2014	208	n.a.	n.a.	13100	131	16	0.26	152
S3	01.97	99	6.68	128	4291	699	1741	381	2.9	0.31	13550	169	39	0.27	n.a.
G	05.97	99	3.09	306	2263	317	886	122	4.3	24	5200	386	n.d.	0.03	62
B1	05.95	99	5.50	132	19	15	48	39	n.a.	n.a.	4.2	228	n.d.	0.2	4.7
B2	03.96	99	3.86	136	17.3	8.2	40.3	41	n.a.	n.a.	4.1	204	n.d.	0.06	34.7
B3	01.97	99	4.97	95	12.3	7.2	26.3	11	4.0	1.53	5.23	225	n.d.	0.07	14.1
<b>Agua Caliente</b>															
1974 <sup>a</sup>	1974	71	7.6	132	140	21	205	50	n.a.	n.a.	456	276	71	n.a.	3.0
A1	05.95	70	6.42	196	790	140	604	88	2.1	0.1	1976	385	262	0.6	27
A2	03.96	46	7.62	131	444	56	373	22	n.a.	n.d.	1055	396	105	0.41	19.8
A3	01.97	69	6.72	135	715	95	562	60	0.93	0.25	2040	442	191	0.47	19.1
A1	01.97	71	6.42	172	816	109	623	70	1.1	5.01	2330	451	228	0.52	31.3
<b>Red waters</b>															
R1	05.95	25.1	3.52	58	20.0	21.0	568	34	n.a.	n.a.	6.3	2234	n.d.	n.a.	1.5
R2	05.95	24.0	3.58	63	20.1	26.9	334	34	0.15	4.6	13.7	1403	n.d.	n.a.	1.3
R3	05.95	23.2	4.48	48	33.8	27.5	556	23	1.7	0.05	8.1	1475	83	0.71	n.d.
R1	01.97	24.0	6.07	32	13.7	11.7	151	18	0.48	0.08	3.7	387	12.3	0.12	0.61
R3	01.97	23.5	3.70	43	16.3	12.7	277	16	1.2	0.33	3.7	710	n.d.	0.16	n.d.
R4	01.97	27.5	3.67	56	36.3	34.3	397	39	3.2	0.5	8.3	1251	n.d.	0.02	0.52
R5	01.97	23.5	3.54	42	28.0	23.0	507	23	20	1.1	5.7	1598	n.d.	0.04	n.a.
R2	01.97	24.0	3.24	48	28.0	25.0	435	33	3.0	4.4	5.6	1277	n.d.	0.05	0.51

NOTE: For location see Fig. 1

<sup>a</sup> Data of Molina (unpublished data)

**Table 3** Li, Rb, Cs, Sr and Ba in thermal and cold waters at El Chichón (mg/kg) and in El Chichón rocks (in mg/kg, Luhr et al., 1984)

Sample	Li	Rb	Cs	Sr	Ba
L0	0.76	0.90	0.55	15.60	17.80
L2	2.87	0.76		7.14	0.31
L3	3.53	1.35	0.29	6.13	0.49
S2	10.1	2.48		22.8	3.68
S3	11.2	4.46	0.92	18.6	3.75
G	3.50	0.95		7.85	0.30
A1	1.72	0.80	0.25	5.31	0.21
A2	1.35	0.67	0.21	5.15	0.19
A3	0.67	0.25		4.33	0.12
R1	0.006	0.028	<0.001	0.92	0.015
R2	0.009	0.039	<0.001	1.58	0.026
R3	0.032	0.071	0.001	3.57	0.028
R4	0.010	0.039	0.001	3.63	0.039
R5	0.067	0.135	0.002	3.48	0.026
Pumice		87		1080	755
Glass			8.7	200	1320
Whole rock		84	4.2	1000	824
Lake sediments		110		632	

the most saline water collected in 1995–1997 (Table 2) differs from that given by B. R. Molina (unpublished data) and L. A. Templos et al. (unpublished data); the 1995–1997 samples are five times higher in Cl. It is not clear whether this effect reflects post-eruption changes or water samples from other vents. The observed difference is unlikely to be the result of seasonal variations in the hydrological regime of the area.

#### Red waters

The main visible shallow ground-water drainage around the volcano at elevations of 500–600 m consists of numerous springs of ambient temperature emerging from the 1982 pumice deposits. These so-called Red waters are slightly acidic (pH=3–6), precipitate iron hydroxides, and are essentially Ca–SO<sub>4</sub> in composition, with TDS up to 3000 mg/kg (Table 2). These waters vary in composition depending on the season and have shifting discharge sites along the base of pumice cliffs.

#### Isotopic data

##### *Isotopic composition of He*

Helium isotope ratios (Table 4) in fumarolic gases are typical for volcanic and geothermal gases above subduction zones (Sano and Wakita 1985; Poreda and Craig 1989) and, in combination with very high <sup>4</sup>He/<sup>20</sup>Ne ratios, suggest a strong magmatic contribution to the volcano-hydrothermal system of El Chichón Volcano. The lower <sup>3</sup>He/<sup>4</sup>He value in the bubbling gas of AC thermal water, but with a high <sup>4</sup>He/<sup>20</sup>Ne ratio (44), may indicate that He in this gas contains a high fraction of crustal, radiogenic He. Assuming all Ne in gases has an atmospheric origin, and that <sup>3</sup>He/<sup>4</sup>He values for depleted mantle and crust are  $1.2 \times 10^{-5}$  and  $2 \times 10^{-8}$  re-

spectively (Ozima and Podochek 1983; Rozhkov and Verkhovsky 1990), the fraction of atmospheric He in AC gases is only 1%; in fumarolic gases it is much lower. The fractions of crustal (radiogenic) He are 40% in AC gases and 17% in fumarolic gases.

##### *Isotopic composition of waters*

Isotopic data for all types of water are listed in Table 4 and plotted in Fig. 2A. The average isotopic composition is  $\delta D = -23$  to  $21\text{‰}$  and  $\delta^{18}O = -4.5$  to  $-4.1\text{‰}$  for local ground waters collected from cold springs discharging from the basement rocks at elevation close to 500 m a.s.l. The isotopic composition of rain waters ranges more, from  $\delta D = -19$  to  $-31\text{‰}$ . The isotopic composition of the hot AC water is close to these values, suggesting that magmatic contributions are negligible. Red waters have unusual isotopic compositions, with a negative oxygen isotopic shift. Red waters collected in January 1997 are enriched in light isotopes (except the R3 spring) but still have a negative oxygen shift. Both trends are subparallel to the meteoric water line.

Crater lake water is highly enriched in both D and <sup>18</sup>O, with positive or close to zero  $\delta D$  values. The isotopic composition of water from boiling pools in the central fumarolic field ranges from values close to the “andesitic water” isotopic signature (Taran et al. 1989; Giggenbach 1992) for the SP nearly to meteoric water values for Black Pool. The  $\delta D$  values of fumarolic condensates are similar to, or below, those of local meteoric water; however, the condensates are enriched (several per mil) in <sup>18</sup>O relative to meteoric water values. Apart from the SP and AC spring waters, all waters collected during the cold and rainy period in January 1997 are depleted in D (Table 4).

**Table 4** Isotopic composition of H, O (V-SMOW), S (CDT), C (PDB),  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  ratios in El Chichon water and gas discharges

Site	Date	$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta^{16}\text{O}$ SO <sub>4</sub>	$\delta^{13}\text{C}_{\text{CO}_2}$	$\delta^{34}\text{S}_{\text{SO}_4}$	R/Ra	$^4\text{He}/^{20}\text{Ne}$
L0	1983	—	—	—	—	+17	—	—
L1	05.95	- 3.0	+0.4	+3.2	—	+ 0.5	—	—
L2	03.96	+ 7.0	+3.5	—	—	+ 2.7	—	—
L3	01.97	+ 6.1	+1.0	+1.9	—	+ 4.2	—	—
S1	05.95	-15	+6.5	—	—	+ 5.0	—	—
S3	01.97	-17	+6.4	—	—	—	—	—
G	05.95	+ 1.0	+3.4	—	—	+ 1.1	—	—
G	03.96	- 6.0	+6.0	—	—	—	—	—
B1	05.95	-22	-1.5	—	—	—	—	—
B3	01.97	-25	+1.0	—	—	+ 2.9	—	—
A1	05.95	-22	-4.7	+2.2	—	+ 4.5	—	—
A1	03.96	-19	-4.5	+2.6	-10.5	+ 6.2	5.1	44
A2	01.97	-27	-4.6	—	—	—	—	—
R1	05.95	- 4.0	-3.5	—	—	+ 8.1	—	—
R1	01.97	-21	-5.0	—	—	+ 8.9	—	—
R2	05.95	-12	-5.9	—	—	—	—	—
R2	01.97	-13	-5.5	—	—	+ 8.5	—	—
R3	05.95	- 7.0	-4.0	—	—	+ 8.3	—	—
R4	03.96	- 5.0	-3.6	—	—	—	—	—
R4	01.97	-22	-5.4	—	—	+ 8.8	—	—
R5	01.97	-32	-7.2	+6.4	—	+ 8.1	—	—
Cold spring	05.95	-21	-4.1	—	—	—	—	—
Cold spring	05.95	-23	-4.5	—	—	—	—	—
Rain	05.95	-19	-3.9	—	—	—	—	—
Rain	01.97	-32	-5.3	—	—	—	—	—
C3	01.97	-30	-4.5	—	—	—	7.1	1160
C4	01.97	-29	-4.0	—	-8.1	+ 4.5 (H <sub>2</sub> S)	7.3	2560
C1	05.95	-17	-2.2	—	—	—	—	—
W	05.95	-25	-4.1	—	-9.0	—	—	—
E	05.95	-23	-3.9	—	-8.7	—	—	—
S <sup>o</sup> , crater		—	—	—	—	+ 4.6	—	—
Gypsum RW		—	—	—	—	+11.7	—	—

NOTE: S<sup>o</sup> from the C site; gypsum from secondary depositions (incrustations) near the R3 site

### Isotopic composition of S and C

The isotopic composition of S ( $\delta^{34}\text{S} = +0.5$  to  $+4.2\%$ ; Table 4) from dissolved sulphate of the lake water in 1995–1996 drastically differs from the  $+17\%$  measured in 1983 by Casadevall et al. (1984). The value of  $\delta^{34}\text{S} = +4.5\%$  of H<sub>2</sub>S from the central fumarolic field is quite high for such gases and is similar to those from New Zealand geothermal systems (Robinson 1987) and Satsuma-Iwojima Volcano, Japan (Shinohara et al. 1993). Sulphate from the SP spring and AC thermal waters is similar in sulphur isotopic composition ( $\delta^{34}\text{S} +5\%$  and  $+4.6$  to  $+6.2\%$ , respectively). Such a low value is unusual for neutral NaCl waters. Sulphate from the Red waters has  $\delta^{34}\text{S}$  values of  $+8$  to  $+9\%$ , close to those measured for anhydrite phenocrysts and absorbed SO<sub>4</sub> from the 1982 pumice deposits (Rye et al. 1984).

Carbon from CO<sub>2</sub> in fumarolic and AC waters is enriched in light isotope ( $\delta^{13}\text{C} = -10$  to  $-8\%$ ), when compared with “magmatic” values of  $-5$  to  $-3\%$  (Taylor 1986).

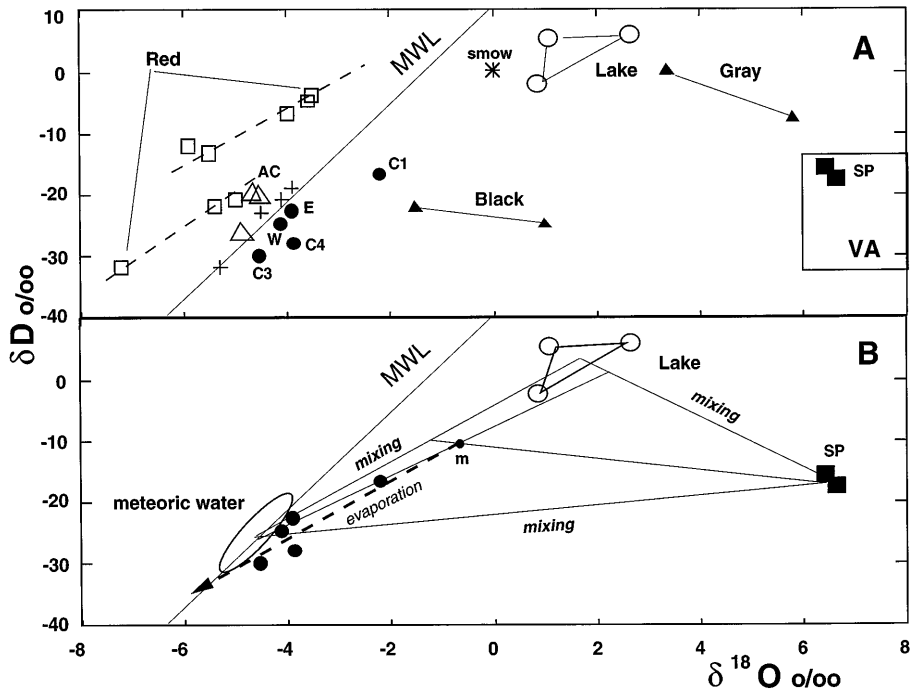
### Oxygen isotopes in dissolved sulphate

Dissolved SO<sub>4</sub> in the lake water has  $\delta^{18}\text{O}$  values in the same range as  $\delta^{18}\text{O}$  of the lake water itself (Table 4). This indicates the lack of fractionation between water and dissolved SO<sub>4</sub> and is typical for steam-heated pools, where SO<sub>4</sub> is formed through the oxidation of H<sub>2</sub>S by dissolved O<sub>2</sub>. Fractionation of O isotopes between dissolved SO<sub>4</sub> and H<sub>2</sub>O in Agua Caliente hot springs is near  $7\%$  and corresponds to an isotope equilibrium temperature of approximately  $240^\circ\text{C}$ . Dissolved SO<sub>4</sub> from Red waters (sample R5) has  $\delta^{18}\text{O}$  value  $+6.4\%$ , which is close to, but somewhat lower than,  $\delta^{18}\text{O}$  of anhydrite phenocrysts or SO<sub>4</sub> absorbed by the ash and measured just after the 1982 eruption ( $+8\%$ ; Rye et al. 1984).

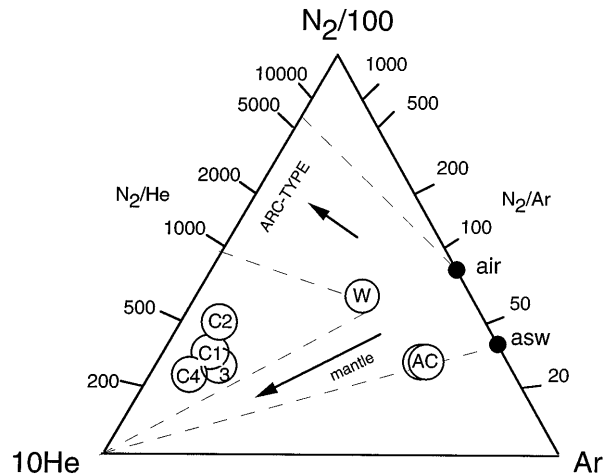
### Discussion

#### Chemical composition of gases

Relative concentrations of N<sub>2</sub>, Ar and He are shown in Fig. 3. N<sub>2</sub>/Ar ratios vary from ASW (air-saturated wa-



**Fig. 2** **A** Variations of  $\delta D$  with  $\delta^{18}O$  for all types of waters collected at El Chichón. The maximum and minimum data points for meteoric waters (*crosses*) correspond to rain waters collected in March 1995 (maximum) and in January 1997 (minimum). Other sampling sites are shown on the plot. Segments connect data points from the same site. All samples collected in January 1997 are depleted in deuterium. Compositions of Red waters form two trends subparallel to the meteoric water line (MWL). The lower trend corresponds to the January 1997 samples. **B** The three-end-member mixing plot for isotopic compositions of fumarolic condensates (see discussion below). Evaporation line (*dashed line*) has a slope corresponding to the equilibrium fractionation of H and O isotopes for steam separation at 100 °C from a boiling mixture of the lake water, meteoric water and the SP (magmatic?) water. A hypothetical point *m* corresponds to the isotopic composition of this steam–water mixture. Fraction of each end member can be determined as shown. The steam fraction in the boiling aquifer can be estimated from the isotopic compositions of fumarolic vapour (see Taran et al. 1997)



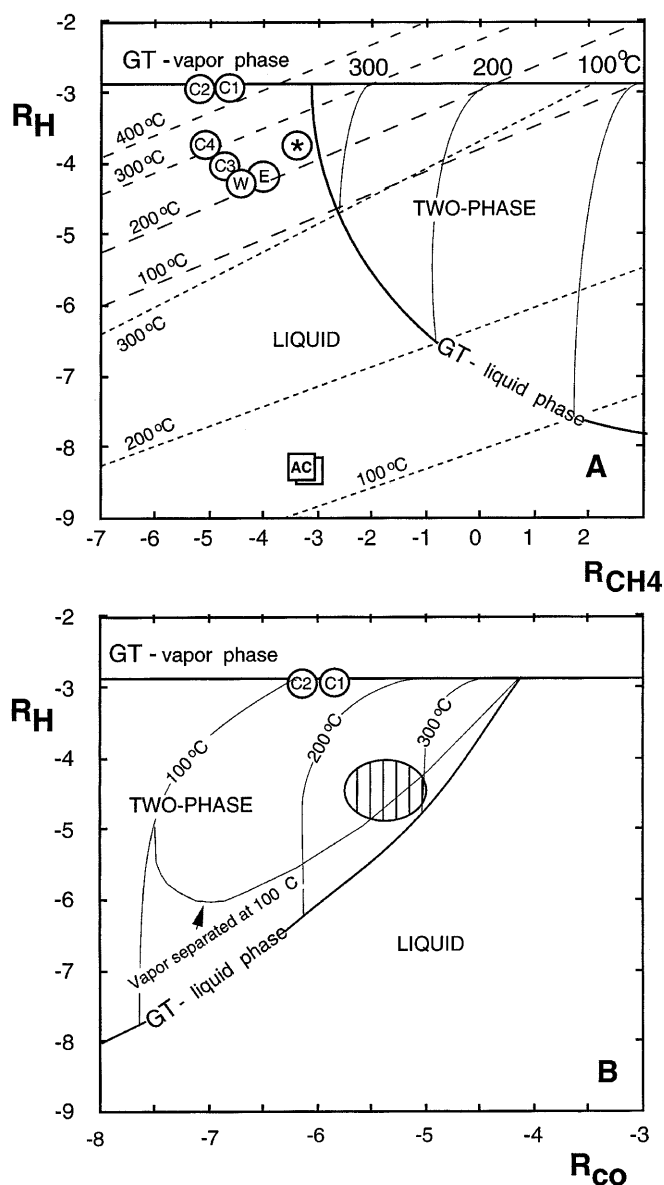
**Fig. 3** Relative  $N_2$ –Ar–He concentrations in fumarolic gases and gases from Agua Caliente hot springs. The arc-type and mantle trends are shown according to Giggenbach (1992a)

ter) values for the AC springs to 480 for the central fumarole in the crater. The Ar/Ne ratio for the AC springs (1250) is in the range of atmospheric values (500–1900). Values >2000 (2700 and 2300) for fumarolic gases might be caused by a partial depletion of Ne due to steam loss (Mazor and Truesdell 1984). Despite the scattering of data points, there is a clear difference between gases of El Chichón and “typical” volcanic and geothermal gases from volcanic arcs, such as Japan, Kuriles, New Zealand, etc. (Sano and Wakita 1985; Sano et al. 1987; Rozhkov and Verkhovsky 1990; Fischer et al., in press). The much higher relative He concentration, combined with a large proportion of magmatic He (high  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  ratios), make these gases similar to “rift”-type gases (Giggenbach 1995). This may be the result of the unusual tectonic position of the volcano and supports ideas of Nixon (1982) about al-

kaline volcanism in this area being associated with extensional tectonics.

The redox diagrams for El Chichón gases in terms of  $R_H = \log(x_{H_2}/x_{H_2O})$ ,  $R_{CH_4} = \log(x_{CH_4}/x_{CO_2})$  and  $R_{CO} = \log(x_{CO}/x_{CO_2})$  are shown in Fig. 4. The dashed area corresponds to the detection limit for CO in gas chromatography analysis. Theoretical lines on this diagram correspond to equilibrium in vapour and liquid phases, with  $R_H$  ratios controlled by “geothermal” (GT)  $\text{FeO}_{1.5}$  rock–water buffer (solid lines; Giggenbach et al. 1986) or by gas equilibria in single gas or liquid phases (dashed line isotherms).

For  $\text{CH}_4/\text{CO}_2$ – $\text{H}_2/\text{H}_2\text{O}$  pairs (Fig. 4A), neither the data points for fumarolic gases from the crater nor



**Fig. 4A,B** Redox diagrams for fumarolic and AC gases.  $R_H$   $\log(x_{H_2}/x_{H_2O})$ ,  $R_{CH_4}$   $\log(x_{CH_4}/x_{CO_2})$  and  $R_{CO}$   $\log(x_{CO}/x_{CO_2})$ . Both diagrams according to Chiodini et al. (1996). Solid lines correspond to equilibria with GT (geothermal)  $FeO_{1.5}$  redox buffer (Giggenbach et al. 1986) in vapour, liquid or two-phase system. Dashed-line isotherms correspond to equilibrium in a single vapour phase (upper isotherms) or in a single liquid phase (lower isotherms). **A** The  $R_H$ – $R_{CH_4}$  diagram shows that neither data points for fumarolic gases nor those for AC gases lie in the area of the steam–water equilibrium. **B** CO was detectable in only two fumarolic gas samples. The ruled area corresponds to the detection limit of the gas chromatograph analysis for CO in other samples. The points and the ruled area plot within the area corresponding to chemical equilibrium in a steam–water mixture controlled by the rock buffer

those for AC hot springs lie within the steam–water coexistence area. The composition of fumarolic gases corresponds to equilibrium in a single gas phase at temperatures between 200 and 500 °C, whereas AC gases apparently have equilibrated in a single water phase around 120 °C.

The data points for the AC bubbling gas are based on an assumption about the total gas content,  $x_g$ , in the spring water and a semi-empirical expression (Taran 1988):

$$x_g \text{ (mmol/mol)} = 0.3/x_{Ar,g},$$

where  $x_{Ar,g}$  is the Ar concentration in dry gas (mmol/mol), based on simple calculations of a single-step gas separation from initially non-degassed deep water, saturated by argon from air. Observed data from water-dominated hydrothermal systems can be fitted to this expression with an accuracy of approximately 0.3 order of magnitude for a wide range of the total gas contents (Y. Taran, unpublished data). This approach is almost equivalent to the application of the  $H_2/Ar$  ratio as a geothermometer (Giggenbach and Gougel 1989; Giggenbach et al. 1993), but it is useful in cases when it is necessary to know, at least approximately, absolute concentrations of the gas species in deep water.

Another source of uncertainty for AC gases, as for any  $CO_2$ -rich warm waters, is underestimating the initial  $CO_2$  content in the deep water, which is actually much higher and should be corrected by taking into account carbonate equilibrium in the aquifer. But even if we know how to correct these data, the points for AC will be shifted no more than one order of magnitude for both  $H_2$  (up) and  $CO_2$  (left) concentrations and will still lie within the area of equilibrium in a single liquid water phase at relatively low temperature.

In contrast to the “slow”  $CH_4$  equilibrium, a few available  $CO/CO_2$  data points for fumarolic gases (Fig. 4B is a diagram for the “fast” equilibrating species) lie within the steam–water mixture field at reasonable temperatures 100–300 °C. This corresponds to the present-day situation in the El Chichón crater, where the main discharge of thermal waters and vapours is situated within a limited area, suggesting the presence of a boiling aquifer beneath the crater floor.

It seems, therefore, that  $CH_4$  in gases and waters of the El Chichón hydrothermal system, as for the majority of terrestrial hydrothermal systems, is not equilibrated (Taran 1986, 1988; Ohmoto 1986). At hydrothermal temperatures its concentrations depend only on the productivity of the source region, which is sedimentary organic material.

But there is still a problem explaining why “hydrothermally” equilibrated fumarolic gas contains noticeable “magmatic” HCl (100–200 mg/kg in condensates) and  $SO_2$ . The HCl content of the vapour, separated from an acidic Cl-rich solution, may be high enough, as reported by Truesdell et al. (1989) and experimentally shown by Simonson and Palmer (1993). To have a measurable HCl concentration in separated vapour, the



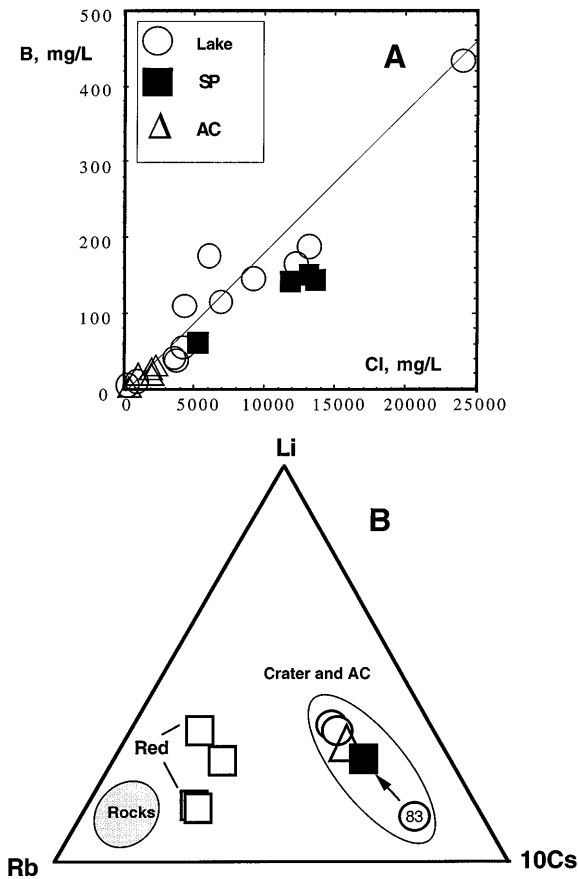
liquid water solution in equilibrium must have high concentration of molecular HCl and has to be highly acidic. This is not the case for the El Chichón discharging waters. The lake water contains between 1000 and 4000 mg/kg of Cl with  $\text{pH} > 2$ , and the SP water is almost neutral ( $\text{pH} = 6.7$ ). It may be suggested that the main source of Cl, as well as of the high oxidized sulphur species in fumarolic gas, is droplets of saline waters in the collecting bottles. In this case, the El Chichón volcanic gas has a typical “hydrothermal” appearance.

Chemical composition of thermal waters

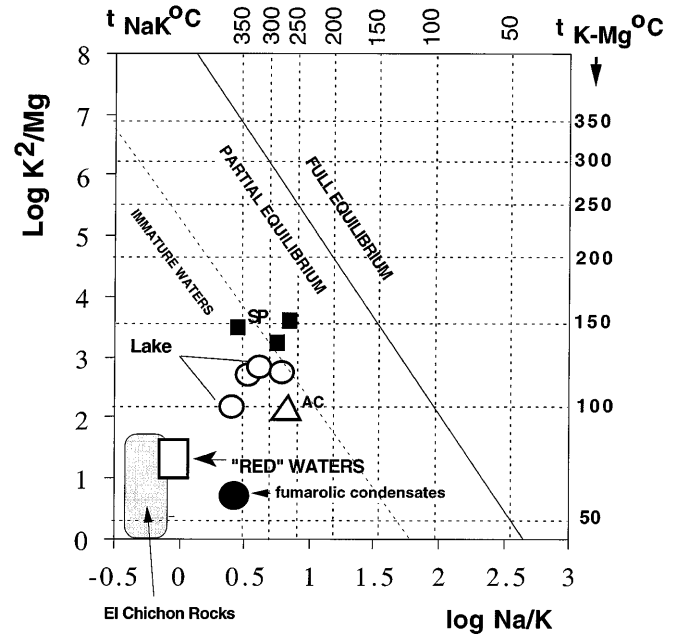
Correlation of Cl-B and relative concentrations of Li, Rb and Cs (Table 3) for the lake water, SP water and AC water (shown in Fig. 5) suggest a common primary source for all chloride waters discharging at El Chichón. The Na-K-Mg “rectangle” in Fig. 6 (modified after Giggenbach 1988) for the SP and AC waters shows that the high-Cl crater waters are even more “mature” than water from the long-lived Agua Caliente thermal

field. The water-rock (Na-K) equilibrium temperatures suggested by Fig. 6 are in the range 250–350 °C and are likely to reflect conditions at a depth where “brine”, already partially neutralized but still not diluted by ground water, is located. This brine may be formed by the condensation and subsequent neutralization of pure magmatic vapour (the SP water contains more than 10000 mg/kg of Cl, as do most high-temperature volcanic gas condensates (Symonds et al. 1994). A “shield” protecting mixing of this partially neutralized magmatic condensate with ground waters may be precipitates of anhydrite, as in sea-floor hydrothermal systems (e.g. Taran et al. 1992). SOLVEQ (Reed 1982) calculations show that the SP2 water becomes oversaturated with anhydrite near 200 °C.

The outflow rate of the SP spring is approximately 20 kg/s or 600 kt/a. Assuming the AC hot springs are supplied from the same aquifer, and taking into account a fivefold dilution of these waters when compared with the SP water, the total outflow rate of saline water is ~ 1 Mt/a. It corresponds to the complete dissolution of 50000 m<sup>3</sup>/a of fresh rock (or 1/20 of the “effective” rock/water ratio) close in composition to the El Chichón erupted products (4 wt.% of Na<sub>2</sub>O; Luhr et al. 1984). Accepting that 250 °C is the minimum for the “last” equilibrium rock-water temperature, and that temperature-with-depth conditions are close to the BPD curve (Haas 1971), the upper level of the aquifer with partially neutralized water is located 400–500 m beneath the crater floor. The high efficiency of the water-rock interaction is probably related to the large amount of fresh, fine-grained ejected material, which



**Fig. 5** Correlation between **A** B and Cl concentrations in Cl-rich waters, and **B** relative Li-Rb-Cs concentrations, demonstrating a common source of solutes for Cl-rich waters discharging into the crater (SP and lake) and from AC hot springs. Average rock composition of the El Chichón erupted products is from Luhr et al. (1984)



**Fig. 6** Log K<sup>2</sup>/Mg vs log Na/K plot for water samples collected at El Chichón. The *Full Equilibrium* line, and Na-K and K-Mg temperatures, are according to Giggenbach (1988). Average rock composition of the El Chichón erupted products is from Luhr et al. (1984)

**Table 5** Chemical composition of the El Chichon Crater Lake from 1983 to 1997 (mg/kg)

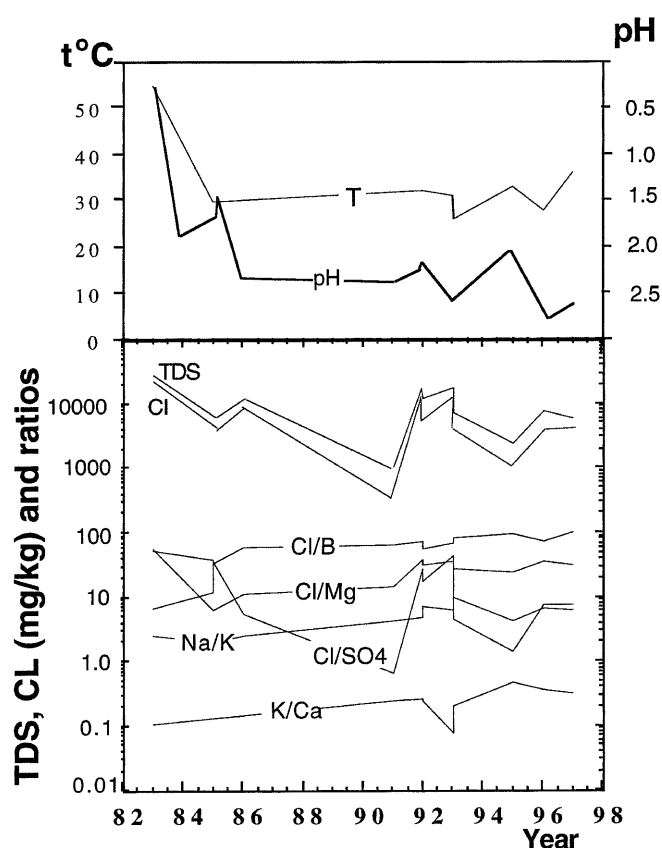
Date	T °C	pH	Na	K	Ca	Mg	Al	Fe	Sr	Li	Cl	SO <sub>4</sub>	F	B	SiO <sub>2</sub>
0183	55	0.56	607	232	2110	424	745	914	15.6	232	24030	3550	0.16	433	257
1083	42	1.90													
0585		1.74			1368	684		190			4338	345	2.0		330
1185	29.5	1.48									6092	170	4.5	176	250
0986		2.33			2019	775		146			9200	1577		146	
1191		2.46	100	23	92	22		13.3		0.14	320	484	0.37	5	71
0592		2.32	3400	670	2517	317				0.46	12250	420	0.52	165	273
0892	32.1	2.20	3000	410	1590	217		17.7		0.28	6900	390	0.36	115	550
0193	30.7	2.29	1325	210	2660	363	1.0	15.2		13.5	13200	293	0.68	188	250
0493	26.1	2.58	1850	185	858	127		24.0		3.88	3600	772	0.29	41	285
0595	33	2.15	460	108	226	39	7.2	23.4	6.6	1.20	986	671	0.15	10	111
0396	28.3	2.87	1850	262	691	114	3.9	21.0	7.2	3.90	4220	529	0.02	55	251
0197	36.2	2.61	1189	184	577	112	5.5	11.5	5.2	3.00	3740	469	0.02	37	240

accumulated in the newly formed crater following the eruption.

All available data on the chemical composition of the lake water after the 1982 eruption are shown in Table 5 (see also Armienta and De la Cruz Reyna 1995). After a period of 3 years, the temperature and pH of the lake stabilized at approximately 30°C and 2.5, respectively, but the salinity of the water has experienced large fluctuations with nearly the same ratios of major species (except Cl/SO<sub>4</sub>, which repeats the TDS trend; Fig. 7), suggesting the strong effect of dilution by ground and rain waters.

It is reasonably safe to suggest that the lake and other high-Cl waters in the crater have a common source. The SP spring puts approximately 20 kg/s into the lake. Approximately the same amount flows into the lake from numerous boiling springs whose water is represented by a Cl-free condensed fumarolic vapour with pH near 3.5. This adds up to approximately 10<sup>6</sup> m<sup>3</sup>/a of superficial "volcanic" water. A large area of the lake bottom, adjacent to the central fumarolic field, is covered with numerous small gas vents, suggesting that a considerable amount of the steam condensate may contribute to the lake. The acidity of the lake water (pH > 2.3) may, to a great extent, result from shallow oxidation of H<sub>2</sub>S: 400–600 mg/kg of sulphate (4–6 mmol/kg), corresponding to 8–12 mg-eq of H<sup>+</sup>, or pH of approximately 2. The isotopic data (see below) support this suggestion. Unfortunately, no data exist about the depth profile of the lake, and therefore it is not possible to estimate, even approximately, the total heat and mass budget of the system. But it seems likely that approximately 0.5 Mt of saline water per year are supplied from the SP spring, and that when combined with 4000 mm/a of precipitation (3 Mt/a to the 1-km-wide crater), it is enough to provide the observed variations in chemical composition of the El Chichón crater lake.

The next problem is to understand why there is such a low amount of sulphur in the waters and gases in the present-day El Chichón discharging system, considering the huge amount of sulphur in the erupted material. The 1982 pumice contains up to 2 wt.% anhydrite mi-



**Fig. 7** Variations in time of temperature, pH, TDS (mg/kg) and concentration ratios for water from El Chichón crater lake from 1983 to 1997

crophenocrysts (Luhr et al. 1984), and the leachates from the fresh ash were also rich in sulphate (Varekamp et al. 1984). The S species currently discharging from the hydrothermal system are H<sub>2</sub>S and products of its oxidation, mostly sulphate and a very low amount of native sulphur. This indicates that the loss of sulphur occurs at some depth, most probably due to the precipitation of newly formed anhydrite (see above) and/or alunite.

### Isotopic composition of waters and gases

In the  $\delta D$  vs  $\delta^{18}O$  diagram (Fig. 2A), the composition of AC waters plots very close to the meteoric water line, without a significant positive O-shift. Data points for high-saline SP water lie in the volcanic arcs (VA) field for isotopic compositions of subduction-type magmatic waters (Taran et al. 1989; Giggenbach 1992). This supports the assumption of a pure magmatic condensate as the main source of the SP water. Lake water is enriched in D; its isotopic composition is the result of low-temperature (30°C) evaporation of water initially similar to local meteoric water,  $\delta D \sim -20\text{‰}$ , and  $\delta^{18}O \sim -4\text{‰}$  (Gonfiantini 1986). Compositions of fumarolic condensates show a trend from meteoric water values to the mixing line between lake water and SP water. This trend can be explained in terms of a single-step steam separation from a shallow boiling water mixture (Fig. 2B) and the involvement of at least three components: meteoric water, lake water and SP (magmatic?) water (Taran et al. 1997).

Sulphate from the lake water is isotopically light, with  $\delta^{34}S$  values from close to zero (+0.5‰ in 1995) to  $\delta^{34}S = +4.2$  in 1997. This may be direct evidence for oxidation of  $H_2S$  by air dissolved in the lake water. The  $\delta^{18}O$  data for the dissolved  $SO_4$  from the lake water support this assumption. At least, we can say that there is no direct “magmatic” input into the lake and that the lake can be considered as a large, drainless reservoir of steam-heated water with a composition formed by mixing of SP, partially evaporated fumarolic condensate and meteoric waters. The  $\delta^{34}S$  value of +5‰ for sulphate from the SP spring is similar to  $\delta^{34}S$  of the lake  $SO_4$ , but too low for saline waters, and indicates some complex redox processes governing the budget of sulphur within the hydrothermal system. Almost the same value (+4.5 to +6.2‰) was measured for sulphate from the AC thermal water, supporting a common source for AC and SP waters.  $H_2S$  from the central field is enriched in heavy isotopes ( $\delta^{34}S = +4.5\text{‰}$ ). Elemental S from this site has the same value (Table 4). These data explain the isotopic composition of sulphur in the lake water; it is a mixture of  $SO_4$  from the SP spring and  $SO_4$  formed as the result of oxidation of  $H_2S$  from the lake bottom fumaroles. Sulphate from the SP spring, in turn, is probably the result of shallow subsurface oxidation of  $H_2S$ , and all S species on the surface of the El Chichón hydrothermal system are likely to be derived from a common magmatic source.

The isotopically light C of  $CO_2$  fumarolic gases with  $\delta^{13}C$  values from -8 to -9‰ may be “thermogenic”, formed from buried organic-rich material. Before the 1982 eruption, the dome of El Chichón was covered by a thick forest. Thousands of cubic meters of wood were buried together with old and new rocks in the new crater. This organic material may be involved in sulphur reduction.

The El Chichón volcano-hydrothermal system may be assumed to pass through a “magmatic-to-hydrother-

mal transition”. Several factors make this “transition” efficient: the unequivocal presence of a shallow hot magmatic body after the 1982 eruption beneath the new crater; the presence of fresh, fine-grained erupted products that collapsed into the crater, which in turn contained a considerable amount of organic material; the high level of the ground-water table; and the high amount of precipitation. Apart from acidic crater lakes, there are many examples of Cl- $SO_4$  acidic springs at volcanoes that are in steady-state fumarolic activity (e.g. Kiyosu and Kurahashi 1983; Hedenquist and Aoki 1991). Generally, these waters are associated with highly altered rocks. Therefore, the current situation within the El Chichón volcano-hydrothermal system probably is temporary and depends on the rate of alteration and the total “neutralizing” and “reducing” capacity of the newly erupted material collapsed into the crater.

The central fumarolic field and especially the SP spring can be considered as a “hot spot” in the crater – a permeable zone connected to the top of any future dome. It seems that the SP water with its isotopic composition and Cl content is an exotic example of condensed, almost completely neutralized water partially equilibrated with rocks – “partially mature magmatic water” in the terminology of Giggenbach (1988). One more example of such water, but strongly diluted, may be Loowit hot springs at Mount St. Helens, associated with the 1980 eruption and initiated soon after emplacement of shallow magma and pyroclastic deposits (Shevenell and Goff 1995).

### Possible influence of basement sedimentary rocks on the composition of hydrothermal solutions and gases

Massive evaporites and limestone underlying volcanic rocks of the El Chichón area might be an additional source of the alkali-enrichment, S, Cl and  $CO_2$  in erupted products of the volcano (Duffield et al. 1984; Luhr et al. 1984; Varekamp et al. 1984; Rose et al. 1984). There is, however, no evidence of assimilation or incorporation of evaporite and/or limestone constituents into El Chichón hydrothermal fluids, at least on the basis of isotopic data. The values of  $\delta^{34}S$  are too low in all S species, and isotopically light C of  $CO_2$  in fumarolic gases almost excludes a noticeable contamination of fluids by S from evaporite and C from limestone. In contrast to Vulcano, Italy (e.g. Tedesco 1995), where values close to 0‰ of the  $\delta^{13}C_{CO_2}$  are common and ascribed to crustal contamination of magma, the El Chichón plumbing system and adjacent hydrothermal system seem closed with respect to the basement rocks. Very high  $^3He/^4He$  ratios (7.3 $R_a$ ) in El Chichón fumarolic gases (again, in contrast to Vulcano with 5 $R_a$ ; Tedesco 1995) support this suggestion.

## Red waters and the negative oxygen isotopic shift

Red waters, with their distinct chemical (Table 2) and isotopic compositions (Fig. 2; Table 4), are another example of exotic waters discharging at El Chichón Volcano. There are a few published reports about waters with a negative oxygen isotopic shift (NOS). Fumarolic condensates from Galapagos volcanoes (W. Giggenbach, pers. commun.; Goff et al. 1995) and hydrothermal steam from Valles caldera (Vuataz and Goff 1986) and Ascension Island (Adams 1996) are isotopically shifted due to a relatively low-temperature isotopic exchange with CO<sub>2</sub>. Taran et al. (1986) reported a significant "left" shift from the Craig line for secondary steam from closed geothermal wells. Lawrence et al. (1975) observed an NOS in oceanic pore waters that participated extensively during the hydration of submarine volcanic ash and basalt. Saline ground waters from the Canadian shield (Fritz and Frapé 1982) are negatively O- and positively H-shifted and are also suggested to be due to low-temperature clay formation. The clays prefer heavy O isotopes, light H isotopes (e.g. Savin 1980) and consume much water to form hydroxyl groups.

Shallow ground waters, passing from the recharge area on the slopes of El Chichón Volcano through fresh pumice deposits, probably lose their heavy oxygen due to hydration of pumice and formation of low-temperature clay minerals. The chemical composition of the waters, and their sulphur isotopic composition, are due mainly to dissolution of anhydrite (up to 2 wt.% in fresh pumice; Luhr et al. 1984) with a contribution of the absorbed SO<sub>4</sub> (Varekamp et al. 1984). Slightly acidic reaction of the discharging Red waters may be the result of biogenic sulphate reduction (buried vegetation) and subsequent oxidation of the produced H<sub>2</sub>S. Lower pH values are the main reason for relatively high Fe concentrations and precipitation of Fe-hydroxides on the surface. The trends of δ<sup>18</sup>O and δD data points (Fig. 2) have slopes of approximately 5–6 that may be related to the subsurface low-temperature (25–40 °C, ambient temperature) evaporation (drying out).

## Conclusion

This discussion of available data on the El Chichón volcano-hydrothermal system provides some constraints on the origin of the El Chichón fluids and the hydrology of the crater system. The Cl-rich water discharging in the crater at SP spring receives its cations from below the crater floor as the result of the interaction of condensed magmatic vapour with volcanic rocks, as is indicated by elemental ratios in water and water isotopic composition. The flow path for this water is apparently "shielded" by anhydrite precipitates from dilution by ground water to the level of >200 °C, corresponding to >100 m of depth. The crater lake is fed by the SP

spring, as well as by the condensate of low-temperature hydrothermal steam and rain water.

The long-lived Agua Caliente vent system on the outer slope of the volcano was apparently only little affected by the 1982 eruption. The temperature of hot water of the main vent remained constant, but the salinity of the water increased almost five times when compared with the pre-eruption data. Isotopic composition of C, S and cation ratios of the Agua Caliente and Soap Pool waters and gases suggest a common deep source of the solutes.

Chemical and isotopic compositions of fumarolic and bubbling gases suggest a strong magmatic input into the system (high <sup>3</sup>He/<sup>4</sup>He and <sup>4</sup>He/<sup>20</sup>Ne ratios), associated with the extensional tectonics of the El Chichón area (deduced from the relative N<sub>2</sub>, Ar and He concentrations) and a high rate of transition from "magmatic-to-hydrothermal" conditions. Redox state and concentrations of reactive species are essentially "hydrothermal".

Sulphur and C isotopic compositions of S species and CO<sub>2</sub> from water and gas discharges of El Chichón indicate highly reducing conditions at depth and the presence of organic material. The current situation within the volcano-hydrothermal system is likely to be temporary and will change as the fresh rocks lose their "neutralizing" and "reducing" capacity.

There is no evidence in the chemical and isotopic compositions of hydrothermal fluid for interaction with the basement evaporites and/or limestone underlying the edifice of El Chichón Volcano. The magmatic-hydrothermal system of El Chichón is probably closed with respect to deep crustal rocks.

Shallow ground waters discharging on the slopes of the volcano dissolve anhydrite and absorbed salts from fresh pumice deposits and are negatively shifted in O-isotopes relative to the meteoric water line, most probably due to present-day, low-temperature clay formation.

The El Chichón magmatic-hydrothermal system is still very active even 15 years after the eruption in 1982. The chemical and isotopic compositions of fumarolic gases and thermal waters are useful indicators of the state of activity, and chemical surveillance of the crater lake water and fumarolic gases may provide valuable information for the assessment of future activity and hazards of the volcano.

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We dedicate this paper to the memory of a great geochemist, our colleague and friend, Werner Giggenbach, whose unprecedented scientific activity led him to his last volcano on 7th November, 1997.

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