

Major and trace element geochemistry of El Chichón volcano-hydrothermal system (Chiapas, México) in 2006-2007: implications for future geochemical monitoring

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Resumen

Se presenta un estudio detallado de la composición isotópica y química (elementos mayores y traza) del lago cratérico, *Soap Pool* y de los manantiales termales del Volcán Chichón para el período comprendido entre noviembre de 2006 y octubre de 2007. Después de dos décadas de estudio del lago se confirma una relación compleja entre la distribución anual de la precipitación y el volumen y química del lago. Durante los años 2001, 2004 y 2007 se pueden correlacionar concentraciones importantes de Cl en el lago con la descarga alta (>10 kg/s) de aguas salinas con un pH casi neutro desde los manantiales hirvientes *Soap Pool*. Este proceso ocurrió generalmente durante el mes de enero después de la temporada de lluvias que tiene lugar de junio a octubre. El volumen más grande del lago jamás observado ocurrió en marzo de 2007 ($\sim 6 \times 10^5 \text{ m}^3$).

A pesar de que los manantiales termales de Agua Tibia 2 descargan al pie del domo SO, su química indica un régimen de temperaturas más bajas, una interacción agua-roca y una contribución del basamento (evaporitas y carbonatos) más avanzada y una lixiviación de anhidrita de los depósitos piroclásticos de 1982, más que actividad magmática asociada al domo. Además se presentan datos que apuntan nuevas evidencias sobre la posible filtración del agua del lago cratérico hacia el manantial de Agua Caliente.

Finalmente, se justifican y se detallan los modelos existentes del sistema “lago cratérico-*Soap Pool*” y el sistema hidrotermal más profundo. Creemos que los cambios químicos en el acuífero geotérmico profundo que alimenta los manantiales termales, podrían anticipar el crecimiento de un domo en el futuro. Por lo tanto, el monitoreo volcánico futuro se tendría que enfocar en los cambios en la química de los manantiales, además del monitoreo del lago cratérico.

Palabras clave: El Chichón, geoquímica de fluidos, monitoreo volcánico.

Abstract

Isotopic, major and trace element composition studies for the crater lake, the Soap Pool and thermal springs at El Chichón volcano in November 2006-October 2007 confirm the complex relationship between annual rainfall distribution and crater lake volume and chemistry. In 2001, 2004 and 2007 high volume high-Cl lake may be related to reactivation of high discharge (>10 kg/s) saline near-neutral water from the Soap Pool boiling springs into the lake, a few months ($\sim$ January) after the end of the rainy season (June-October). The peak lake volume occurred in March 2007 ($\sim 6 \times 10^5 \text{ m}^3$).

Agua Tibia 2 thermal springs discharge near the foot of the SW dome but their chemistry suggests a lower temperature regime, an enhanced water-rock interaction and basement contribution (evaporites and carbonates), anhydrite leaching from the 1982 pyroclastic deposits, rather than dome activity. New suggestions of crater lake seepage are evidenced by the Agua Caliente thermal springs.

Existing models on the “crater lake-Soap Pool spring” and the deep hydrothermal system are discussed. Chemical changes in the deep geothermal aquifer feeding the thermal springs may predict dome rise. Future volcanic surveillance should focus on spring chemistry variations, as well as crater lake monitoring.

Key words: El Chichón, fluid geochemistry, volcanic surveillance.

Introduction

El Chichón volcano is located in northwest Chiapas, southern Mexico, between the Transmexican Volcanic Belt and the Central American Volcanic Arc (Fig. 1a). Dome destroying eruptions at El Chichón have occurred every 100-600 years over the past 8,000 years (Espíndola *et al.*, 2000). El Chichón is a dome complex volcano: two “fresh looking” domes (NW and SW) are the main morphological features of the volcanic edifice formed by the 2 km wide Somma crater (~0.2 Ma, Damon and Montesinos, 1978; Duffield *et al.*, 1984; Layer *et al.*, this volume). The two centrally nested domes (Fig. 1b) were blasted away in 1982 (Luhr *et al.*, 1984; Varekamp *et al.*, 1984).

In the last two decades, the El Chichón volcano-hydrothermal system has been extensively studied (Taran

et al., 1998; Tassi *et al.*, 2003; Capaccioni *et al.*, 2004; Rouwet *et al.*, 2004; Rouwet, 2006; Taran and Rouwet, 2008; Rouwet *et al.*, 2008; Taran *et al.*, 2008; Tassi *et al.*, this volume; Mazot and Taran, this volume). As in other crater lake bearing volcanoes (Giggenbach, 1974; Takano, 1987; Ohba *et al.*, 1994; Christenson, 2000), crater lake dynamics and chemistry seems to be an adequate monitoring tool for predicting a volcanic crisis at El Chichón. However, the 1982 Plinian eruptions were not followed by dome growth in the 1 km wide-200 m deep explosion crater. Changes in chemistry of thermal springs at active volcanoes have scarcely proven to be efficient precursors before a magmatic crisis, but the El Chichón spring network may be well adapted for volcanic surveillance. To this effect, the baseline behaviour of the springs during quiescent degassing periods must be better understood. This represents the main goal of the present study.

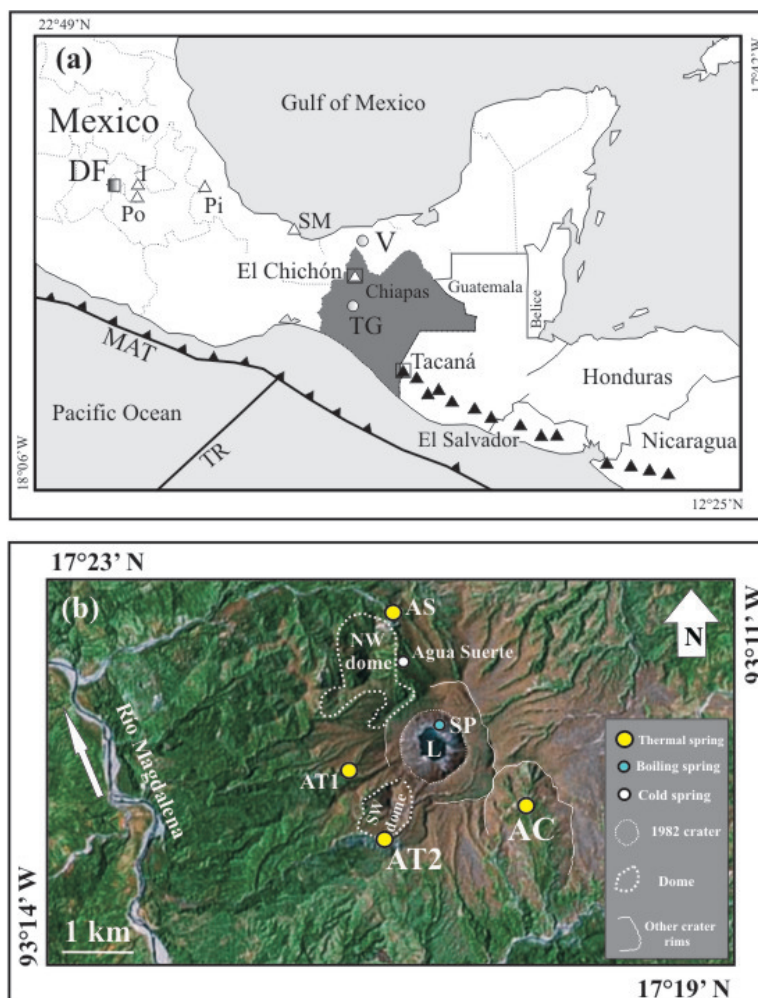


Fig. 1. (a) Location map of El Chichón volcano. TR: Tehuantepec Ridge, MAT: Middle America Trench. Triangles are volcanoes. Po: Popocatepetl, I: Iztaccíhuatl, Pi: Pico de Orizaba, SM: San Martín. Black triangles indicate volcanoes of the Central American Volcanic Arc, white triangles are Mexican volcanoes (Transmexican Volcanic Belt, besides El Chichón and San Martín). Cities, DF: Distrito Federal, V: Villahermosa, TG: Tuxtla Gutiérrez. (b) Location map of the hydrothermal manifestations at El Chichón. Thermal manifestations, AC: Agua Caliente, AT1: Agua Tibia 1, AT2: Agua Tibia 2, AS: Agua Salada, SP: Soap Pool, L: crater lake.

Taran *et al.* (2008) reported the chemistry of the Agua Tibia 2 springs (AT2 thereafter), discharging from beneath the SW dome. Since April 1998, the AT2 springs were revisited: in November 2006 and March 2007. Here we discuss (1) the relationship of the AT2 springs with the state of activity of the volcano, and (2) the connection between the crater manifestations and the thermal springs. Crater lake seepage is a common feature of crater lake hosting volcanoes, as justified by similarities in major element content, Cl/SO₄ ratio and pH (as in Poás, Copahue, Kawah Ijen, Patuha, Keli Mutu, Rincón de la Vieja and Ruapehu (Pasternack and Varekamp, 1994; Rowe *et al.*, 1995; Sanford *et al.*, 1995; Deely and Sheppard, 1996; Sriwana *et al.*, 1998; Delmelle and Bernard, 2000; Kempter and Rowe, 2000; Varekamp *et al.*, 2001; Löhr *et al.*, 2005). Such a process has been suggested for the highly saline Agua Salada acidic springs discharging at the NW dome (Taran *et al.*, 2008), but these springs are not necessarily the only direct output of crater lake water at El Chichón.

New ideas on the southern parts of the El Chichón volcano-hydrothermal system will be discussed on the strength of chemical and isotopic data on Agua Caliente (AC thereafter) and AT2 thermal waters. The earlier model of the “lake-Soap Pool spring” system in the crater (Rouwet *et al.*, 2004; Taran and Rouwet, 2008; Rouwet *et al.*, 2008) is tested by using new data on crater lake volume, and lake and Soap Pool geyser-like boiling spring chemistry.

Hydrothermal manifestations at the El Chichón dome complex

El Chichón is an actively degassing volcano, as manifested by boiling temperature fumaroles, abundant bubbling degassing through the lake bottom, and diffuse degassing inside the 1982 crater. An acidic (pH = 2.2–2.7), warm (T ~30°C) and shallow crater lake (1 to 3.3 m deep) covers the main part of the crater floor at ~850 m a.s.l (Fig. 2a). This lake changes dynamically in chemistry and volume, due to its direct connection with a group of geyser-like boiling springs on the northern shore of the lake, called “Soap Pools” (SP) by Taran *et al.* (1998). SP alternating discharges near neutral, saline and Cl-rich waters and vapour exhalations. From a chemical and isotope balance approach, the total heat output of the crater is estimated to be 35–60 MW, and the diffuse CO₂ flux from the crater is not higher than 150 g/m²day (Taran and Rouwet, 2008). These values are lower than the values obtained by direct CO₂ flux measurements from the crater lake surface (March 2007; Mazot and Taran, this volume).

El Chichón is also known for extremely high discharge of thermal waters (>300 kg/s), through

numerous springs near domes outside the 1982 crater, at the contact between the permeable volcanic edifice and the sedimentary basement. All thermal springs discharge into the Magdalena River that drains towards the Gulf of Mexico (Fig. 1b). The total thermal heat output through the springs is estimated at ~100 MW (Rouwet, 2006). Pre-1982 reports (Molina-Berbey, 1974; Templos *et al.*, 1981) mention thermal springs at El Chichón; yet, the springs have not been targeted for volcanic surveillance, mainly because they are located in remote areas of dense vegetation. The “fresh looking” domes (Fig. 2a–b), outside the 1982 crater, may still grow from a cooling magma body, possibly the principal heat source of the present hydrothermal system.

The AC springs discharge in a south-eastern horseshoe-shaped canyon (Guayabal Tuff cone, <10 ka; Layer *et al.*, this volume), with Holocene explosive activity (Fig. 1b and 2c–d). Based on the Cl content of the Tuspac River, Taran *et al.* (1998) estimated the total outflow rate of the AC springs at be >100 kg/s. The slightly acidic to near-neutral AC waters (pH 5.7–7.6) have remained stable at a temperature of ~71°C since before 1982 (Molina-Berbey, 1974; Templos *et al.*, 1981). The conductivity varied from 4.3 to 5.9 mS/cm (2004–2007), as in the present Crater Lake (Table 1). The AC springs form numerous cascades and hot water spurts discharging into densely vegetated swampy pools (Fig. 2b). Weak bubbling degassing can be observed at AC that coincides with negative Eh values indicating a H₂S input (Taran *et al.*, 1998). The AC springs discharge a less than 1.5 km distance from the 1982 crater with a vertical difference of only 200 m.

Some 2.5 km west of AC, the AT2 springs discharge east of the SW dome (Fig. 1b and 2b). This dome shows surface alterations, due to past fumarolic activity (dome age 217 ± 10 ka; Layer *et al.*, this volume), but active fumaroles are not present. A total discharge of 80 kg/s of the AT2 thermal springs is estimated (Taran *et al.*, 2008). In April 1998, discharge temperatures of AT2 waters of 51–49°C were detected, similar to the pre-1982 temperature reported by Templos *et al.* (1981). We measured lower discharge temperatures for various AT2 springs in November 2006 and March 2007 (35.4 to 46.5°C, Table 1). The AT2 spring mainly discharges from beneath rocks in the river bed, forming numerous pools downstream of 10–20 meters of translucent whitish-turquoise water (Fig. 2e). Abundant amorphous milky-white precipitates can be observed at the bottom of the pools. More downstream, Fe-oxy-hydroxides colour the river bed orange, such as at AC. The horizontal distance of the AT2 springs from the crater lake is ~1.6 km, with a height difference of ~150 m. Both temperature, and conductivity from 1.8 to 4.2 mS/cm are lower than for AC waters (table 1). Eh values are negative, which might indicate H₂S input, although

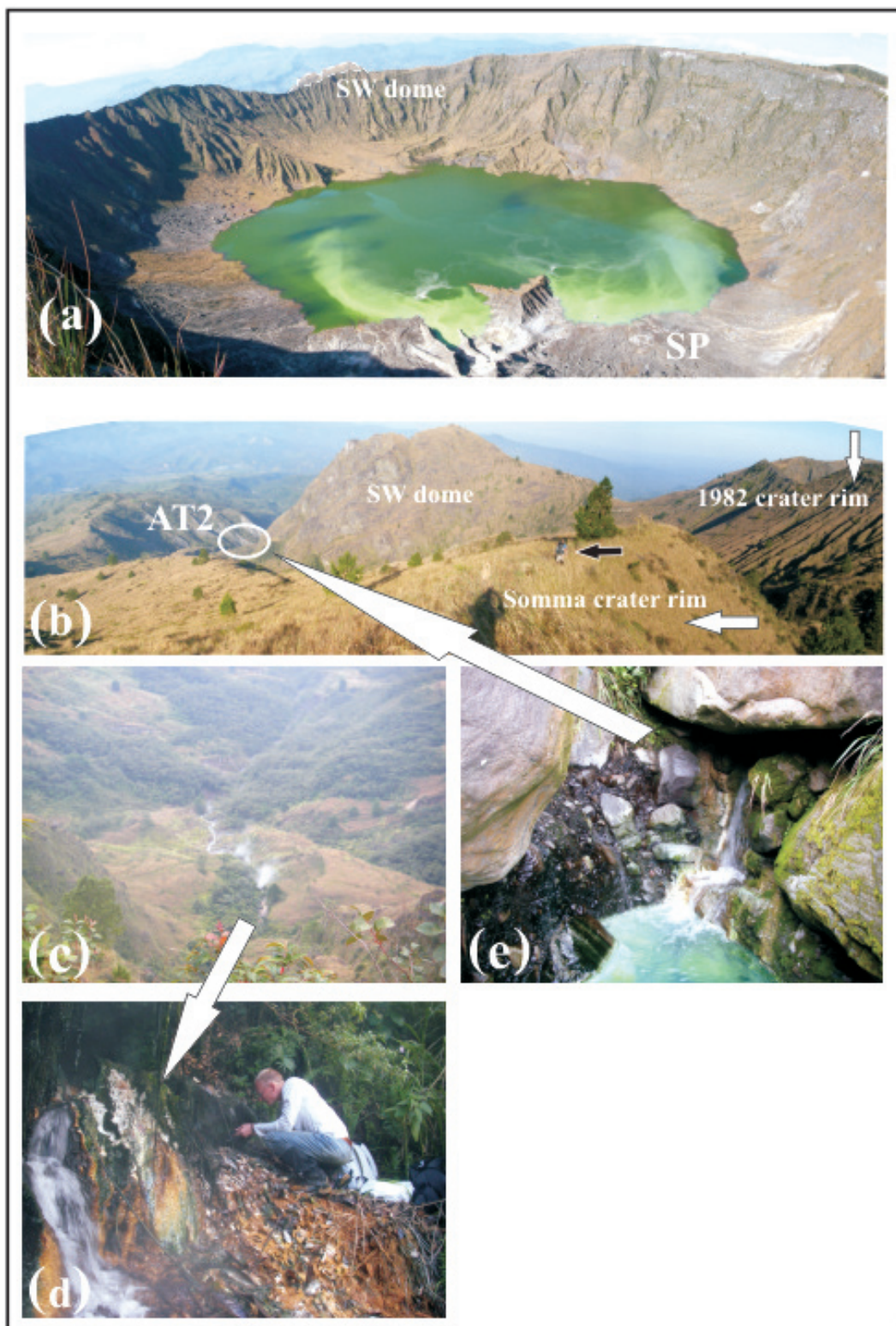


Fig. 2. (a) Panoramic view of the 1982 crater from the NE rim, showing the largest lake ever observed (27/03/2007). The top part of the SW dome peeps over the crater rim. Soap Pool (SP) site is also indicated. (b) Panoramic view from the southern Somma crater rim, showing the SW dome and the canyon where AT2 springs discharge. To the right of the picture, the outside rim of the 1982 crater is shown. (c) The AC thermal springs and Tuspac River seen from the Somma crater rim, towards the SE (27/11/2006). (d) Sampling at the main AC thermal spring (23/11/2006). (e) The AT2 thermal spring (27/11/2006) discharging at the foot of the SW dome. (Pictures by M. Jutzeler).

Table 1

Chemical and isotopic composition of thermal waters at El Chichón volcano. Concentrations are expressed in mg/l, isotopic composition in ‰ vs V-SMOW, Conductivity in mS/cm, Eh in mV. nm: not measured.

Sample	Date	T(°C)	pH	Cond.	Eh	δD	δ ¹⁸ O	SiO ₂	Na	K	Mg	Ca	F	Cl	Br	SO ₄	HCO ₃
LE	19/11/2006	26	2.48	2.4	nm	-17	-2.5	108	79	14	8	45	-	135	-	327	-
LE	23/01/2007	nm	2.70	3.4	nm	-	-	-	267	47	17	134	-	600	0.80	381	-
LE	10/03/2007	29.2	2.57	5.0	525	-4	0.0	138	488	68	21	216	0.95	1149	2.40	332	-
LE	12/09/2007	nm	nm	nm	nm	-	-	-	610	-	34	20	0.30	1256	-	619	-
LE	19/10/2007	nm	nm	nm	nm	-	-	-	265	-	12	10	-	508	-	431	-
SP	10/03/2007	98	7.07	9.9	-319	-12	0.5	105	1401	215	64	365	0.00	3028	6.39	264	43
AC1	23/11/2006	70.6	5.77	5.2	9	-23	-3.7	251	708	93	49	462	0.57	1459	3.20	733	293
AC2	23/11/2006	58.8	5.85	4.3	-27	-21	-4.2	205	553	72	51	436	0.38	1141	3.20	624	271
AT2.1	27/11/2006	36.4	5.75	1.8	-131	-22	-4.7	83	137	15	17	469	1.14	292	0.80	984	52
AT2.2	27/11/2006	46.5	5.85	3.4	-67	-21	-4.4	133	334	30	27	427	1.14	803	1.60	738	122
AT2.TOP	27/11/2006	36	5.35	2.6	3	-19	-4.5	99	246	21	22	369	0.38	583	1.60	618	76
AT2.TOP	28/03/2007	35.4	5.15	4.2	-120	-21	-4.1	93	349	25	26	477	0.30	911	1.52	797	49
Agua Suerte	27/03/2007	22.5	6.28	nm	16	-18	-4.0	54	3	2	1	7	0.08	2	-	17	12
river water AC	23/11/2006	nm	nm	nm	nm	-24	-5.4	-	-	-	-	-	-	-	-	-	-
river water AC	23/11/2006	nm	nm	nm	nm	-22	-4.6	-	-	-	-	-	-	-	-	-	-
river water AT2	27/11/2006	nm	nm	nm	nm	-23	-5.0	-	-	-	-	-	-	-	-	-	-

no strong evidence on bubbling degassing exists. The pH of AT2 waters is slightly lower than at AC: 5.15 to 5.85 (2006-2007).

The most acidic and saline waters of the entire volcano-hydrothermal system discharge at the northwestern ends of El Chichón (Agua Salada, pH ~2.2-5.6, 79°C), north of the younger NW dome (age 90 ± 18 ka; Layer *et al.*, this volume) (Fig. 1b). The Agua Tibia 1 springs (68°C) are similar to AC waters (Taran *et al.*, 2008) (Fig. 1b). Agua Salada and Agua Tibia 1 were not revisited since 2005, but nevertheless, the head of Agua Salada canyon was visited in March 2007. The Agua Suerte cold spring discharges here at <1km distance from the crater at an elevation of ~800 m (Fig. 1b).

Sampling and analytical methods

The crater lake was sampled in November 2006, and in January, March, September and October 2007. SP water was collected during the March 2007 campaign. In November 2006 and September-October 2007, the SP geyser only emitted vapour, and no water sample could be collected. The AC springs were sampled in November 2006 (Fig. 2b); the AT2 springs in November 2006 and March 2007. Temperature, pH, conductivity and Eh were directly measured at the lake surface or spring outlet. Waters were stored in polyethylene bottles after passing

through 0.45 µm filters. Samples for cation analyses were acidified in the field with a 60% HNO₃ solution. Anion analyses were elaborated from non-acidified filtered samples. Water samples for minor and trace element analyses were stored in ultra-pure HDPE Nalgene flasks and acidified by a 60% HNO₃ and 60% HCl solution in 4/1 proportions.

Major element contents (Na, K, Ca, Mg and F, Cl, SO₄) were obtained by Liquid Chromatography (Dionex) with an accuracy of 3%. HCO₃ concentrations were detected by means of titration with a 0.01N HCl solution of 10 ml of a non-filtered non-acidified sample aliquot. SiO₂ concentrations were measured by colorimetric photometric methods on diluted samples. Trace element concentrations were determined by ICP-MS (Agilent 7500 CE). All determinations were performed with the external standard calibration method, using Re and In as internal standards. The accuracy of the results (±5%) was obtained by analyzing certified reference materials (NRC SLR-4, SPS-SW1 and NIST-1643e). The water samples were analyzed for their oxygen and hydrogen isotopic composition, using Analytical Precision AP 2003 and Finnigan MAT Delta Plus spectrometers, respectively. The isotope ratios are expressed as the deviation per mil (‰) from the reference V-SMOW. The uncertainties are ±0.1‰ for δ¹⁸O and ±1‰ for δD (one standard deviation).

Results and discussion

Stable isotopes and major ion species

Isotopic composition of thermal waters: δD and $\delta^{18}O$

The stable isotopic composition (δD and $\delta^{18}O$) of thermal and cold spring waters at El Chichón are presented in Table 1, and plotted in Fig. 3. Considering δD and $\delta^{18}O$ of crater lake and SP waters, the same tendency as observed in earlier years is repeated: (1) in November 2006 the SP did not discharge water towards the crater lake, and consequently, δD and $\delta^{18}O$ of the crater lake water clearly follow the evaporation trend originating from the local meteoric water, and (2) in March 2007, the SP water discharge towards the lake was high, and the δD and $\delta^{18}O$ of lake and SP waters plot near each other in Fig. 3, although the evaporation effect for the lake water is not excluded. The δD and $\delta^{18}O$ for the March 2007 SP water plot near the range established in Rouwet *et al.* (2008) of -8 ± 2 ‰ and $+1.5 \pm 0.7$ ‰, respectively. River and cold spring waters (i.e. Agua Suerte) determine the correct isotopic composition of local meteoric water, slightly shifted to the left off the meteoric water line (MWL in Fig. 3). The isotopic composition of AC and AT2 thermal spring waters plot near the values for the local meteoric waters (Fig. 3).

Major ion species

The major element composition of the 2006-2007 thermal waters at El Chichón is shown in Table 1. All

thermal waters at El Chichón, flank springs as well as crater fluids, are of Na-Ca-Cl-SO₄ type. As Cl behaves as a conservative element, the cation vs. Cl plots (mixing plots) serves to distinguish main ion sources. Cationic species roughly have a common source for all waters (Fig. 4a), i.e. the trachy-andesitic rock, see section 4.2.1), nevertheless, the data of AC and AT2 spring waters sometimes scatter along the general mixing trends between the meteoric and hydrothermal end-member (Fig. 4). The AT2 springs have significantly lower discharge temperatures compared to AC. Lower temperatures result in lower relative K contents (Fig. 4b). El Chichón thermal waters are less “immature” than conventional solute geochemistry suggests (Giggenbach, 1988; Henley *et al.*, 1984); a partial equilibrium between waters and an Al-silicate alteration mineral assemblage is attained, and the equilibrium temperatures coincide well with the chalcedony equilibrium temperature (Taran *et al.*, 2008). The AT2 springs are fed by a colder source than the neighbouring AC springs, the chalcedony geothermometers result in (Henley *et al.*, 1984): 100-130°C for AT2 springs against 160-180°C for AC springs. The latter temperatures are even higher than for SP (~115°C) and lake waters (115-130°C). AT2 waters are enriched in Ca and are less rich in K, with respect to AC waters (Fig. 4b-c), so AT2 waters cannot be considered diluted AC waters, but indicate re-equilibration processes to lower temperatures of the same source as AC.

We show evidence of a contribution of the evaporite basement to the thermal waters at El Chichón (Fig. 4d).

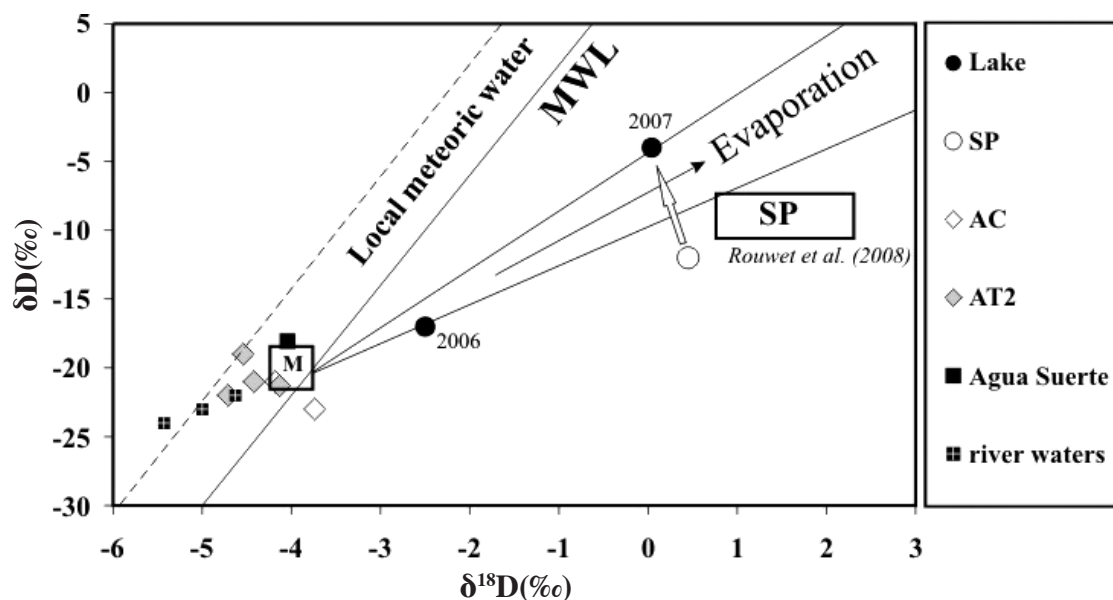


Fig. 3. $\delta^{18}O$ vs δD plot for El Chichón thermal spring, cold spring, crater lake and Soap Pool waters for the period November 2006-October 2007. MWL: Meteoric water line, M: meteoric water at El Chichón. SP: range for Soap Pool spring waters taken from Rouwet *et al.* (2008).

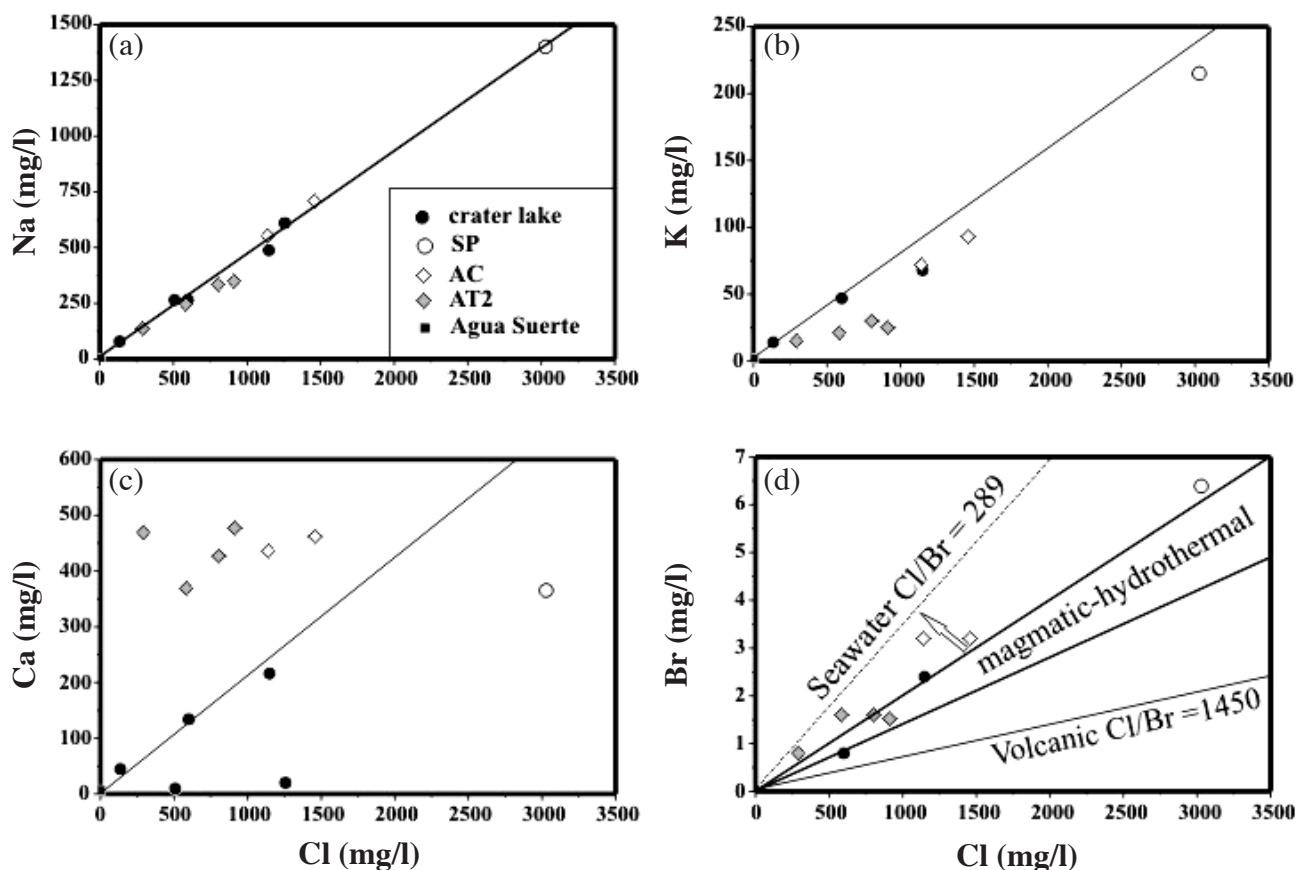


Fig. 4. Mixing plots for El Chichón thermal waters for the period November 2006–October 2007. (a) Cl vs Na, (b) Cl vs K, (c) Cl vs Ca, (d) Cl vs Br.

The AT2 and AC springs seem to be affected by a non-volcanic halogen source. The AC and AT2 waters plot towards the line of $\text{Cl}/\text{Br} \sim 289$, the ratio representative for “seawater” ($\approx$ evaporite) (Böhlke and Irwin, 1992). The January 2007 crater lake water plots more towards the “volcanic Cl/Br line” ($\text{Cl}/\text{Br} > 1,450$; Taran *et al.*, 1995; Fig. 4d). During this period, the SP geyser had again a high water discharge level. The March 2007 SP and lake water plot along the same mixing trend, thus confirming the strong influence of SP waters on crater lake chemistry. This mixing trend has a Cl/Br concentration ratio of ~ 500 , meaning that Cl and Br at El Chichón in any way can be considered a mixture of “seawater” and “volcanic” originating fluids (Fig. 4d). In any case, all observed Cl/Br ratios for El Chichón fluids are common in volcanic waters produced in the magmatic-hydrothermal environment.

The crater lake-Soap Pool system in 2006–2007

Within the scope of continuing monitoring of the current activity of the crater lake-Soap Pool volcano-hydrothermal system, we present updates for 2007 of (1)

the crater lake volume (Table 2, Fig. 5), and (2) the Cl content in the crater lake and SP spring waters (Table 1, Fig. 5).

A large lake was observed for the first time in January–April 2001, and later in March–April 2004 and in March 2007. Since January 2007, water has been discharging from the SP site (no sample), and the lake volume has been increasing (January 2007, pers. comm. Protección Civil Chapultenango staff). In March 2007, El Chichón crater lake reached its largest volume ever observed ($\sim 6 \times 10^5 \text{ m}^3$, Table 2). The SP discharge was estimated in the field, at $\sim 10 \text{ kg/s}$. Unless we missed a significant volume change of the lake, three real trends can be observed in the alternation between small and large volume of the lake: (1) a large volume lake occurs every three years (2001, 2004 and 2007) starting a few months ($\sim$ January) after the rainy season (June–October), (2) the maximum volume slightly increased from 2001 to 2007 (white dotted arrow in Fig. 5) and (3) intermediate volume lakes were observed in 2002 and 2006, probably coinciding with shorter periods of SP water discharges (black arrows, Fig. 5).

Table 2

The changes in crater lake surface area, depth and volume. The estimates were obtained applying the methods evolved by Rouwet *et al.* (2008). The lake depth was calculated by the equation: $d = -0.913 + 0.0097.S^{1/2}$ (Rouwet *et al.*, 2004; 2008), the lake volume by the multiplication S.d. References: ¹Rouwet *et al.* (2008), *: direct measurement of the lake depth during bathymetric surveys.

Date	S (x10 ⁴ m ²)	d (m)	V (x10 ⁴ m ³)	Ref.
May-92	9.7	2.1	20.5	1
Jan-93	4.6	1.2	5.4	1
Mar-93	4.3	1.1	4.7	1
16/05/95	6.0	1.5	8.8	-
24/03/96	4.2	1.1	4.5	1
16/01/97	5.7	1.4	8.0	1
07/04/98	4.0	1.3*	5.1	1
20/11/98	4.8	2.1*	10.1	1
01/03/99	3.7	1.0	3.5	1
10/08/99	4.8	1.2	5.8	1
24/04/00	4.8	1.2	5.8	-
22/01/01	14.3	3.3*	47.3	1
19/04/01	14.8	2.8	41.9	1
05/07/01	10.4	2.2	23.0	1
15/01/02	4.6	1.2	5.4	1
29/04/02	8.2	2.4*	19.6	1
03/03/03	5.8	1.4	8.2	1
03/04/03	5.8	1.4	8.2	1
01/05/03	5.3	1.3	7.1	1
10/11/03	6.3	1.5	9.5	1
01/03/04	12.4	2.5*	31.1	1
10/04/04	15.4	2.9	44.7	1
15/05/04	17.1	3.1	52.7	1
25/06/04	15.9	3.0	47.2	1
31/10/04	9.2	2.0	18.7	-
10/03/05	6.2	1.5	9.2	1
04/06/05	3.9	1.0	3.9	1
18/06/05	4.3	1.1	4.7	1
12/09/05	4.6	1.2	5.4	1
06/12/05	6.1	1.5	9.0	1
05/03/06	5.7	1.4	8.0	-
19/11/06	9.1	2.0	18.3	-
09/03/07	18.0	3.2	57.6	-
25/03/07	18.1	3.2	58.2	-
12/09/07	8.5	1.9	16.3	-
19/10/07	9.1	2.0	18.3	-

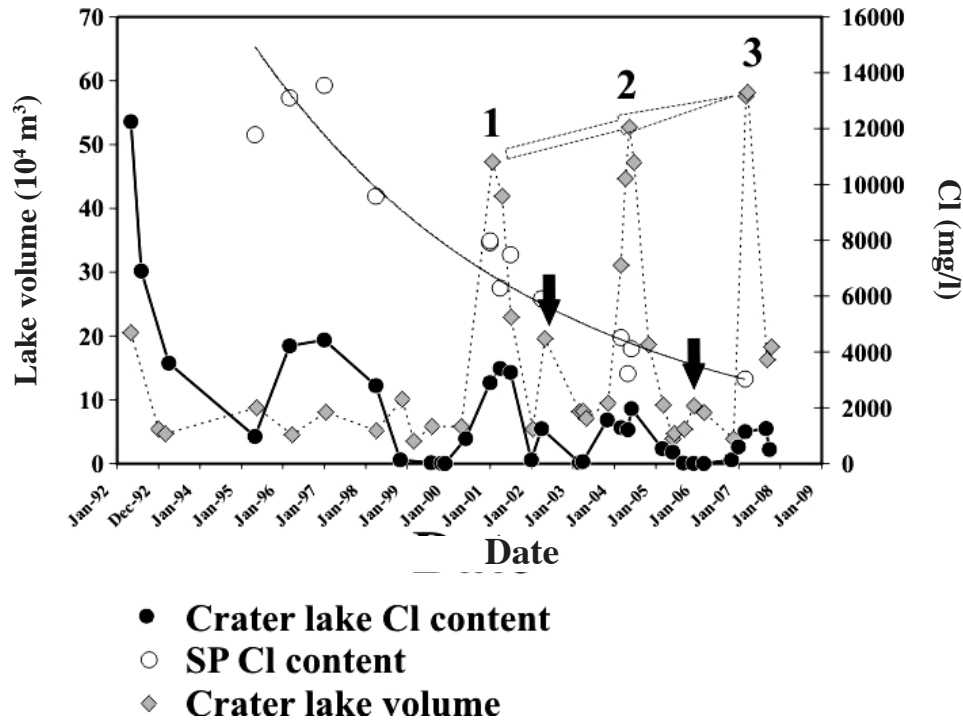


Fig. 5. Changes with time for the Cl content in the crater lake and Soap Pool waters (right-hand scale), and the crater lake volume (left-hand scale). Pre-November 2006 data are compiled from Rouwet *et al.* (2008).

The Cl content in the lake increased from 135 mg/l in November 2006 to 1,256 mg/l in September 2007. In March 2007 the Cl content was 1,149 mg/l. In November 2006 and September 2007 the SP geyser emitted only vapour, while in March 2007 SP water discharge was high (~10 kg/s). This sequence probably indicates that in the summer of 2007, the Cl content in the lake, and probably the lake volume, was even higher than detected in March 2007, and that the relatively high Cl content in September 2007 is the remnant Cl shortly after the ceasing of SP water discharge towards the lake. Because the estimated seepage flux (>17 kgm⁻¹d⁻¹; Rouwet *et al.*, 2004) is higher than the yearly average precipitation flux (<12 kgm⁻²d⁻¹; Rouwet *et al.*, 2004), the lack of SP water feeding the lake results in a rapid decrease in lake volume, although no decrease in Cl concentration. Lake water residence times were calculated to be extremely short (~2 months; Taran and Rouwet, 2008). The El Chichón crater lake may be the best example in the world to demonstrate the delicate balance between input and output of heat, water and chemical species, causing a crater lake to exist.

Rouwet *et al.* (2008) deduced an empirical linear equation for diminishing Cl content in SP waters over 1983-2005:

$$Cl_L = -79.221x t + 25,628 \quad (1)$$

Where Cl_L is the Cl content in the SP water and t the number of months since January 1983 ($t = 1$). From this equation, the SP springs and crater lake should theoretically be Cl-free by 2009±1; instead, for March 2007 a Cl content in SP waters of ~1,600 mg/l should be reached. However, the Cl content in the March 2007 SP waters is as high as 3,028 mg/l. For the first time since 1995, a non-linear though diminishing Cl trend for SP water is shown (Fig. 5). These higher than expected Cl contents in SP waters could imply the presence (or appearance) of an additional Cl-source feeding the shallow boiling aquifer beneath the El Chichón crater. At present it is difficult to determine the origin of this Cl-enrichment, though different scenarios can be proposed. The most probable source of Cl-rich waters feeding the shallow aquifer is the crater lake itself, due to efficient recycling of lake water through infiltration at the lake bottom. Consecutive boiling in the shallow aquifer, enriches the liquid phase (SP geyser water) in Cl (Ohba *et al.*, 2000). If so, steam separation has become more efficient recently. Secondly, the SP geyser and the shallow aquifer can be fed by the main hydrothermal aquifer, probably the same as the one feeding the flank thermal springs (Cl ~2,000 mg/l), through upward fluid migration. Until now, a linear dilution of the remains of the 1982 ultra-acidic brine-like hydrothermal fluid (24,000 mg/l of Cl, Casadevall *et al.*, 1984; Rouwet *et al.*, 2004) could clearly be observed. In

the near future (2009±1) it will become clear whether all original Cl will be flushed out off the crater hydrothermal system (zero-Cl in SP and lake water) or if Cl content in the SP and lake water remains constant. Otherwise, the regime of fluid flow inside the volcanic edifice should be more complex, and existing models should be revised.

Trace element geochemistry

Relative mobility of trace metals

Trace element compositions of thermal waters at El Chichón are presented in Table 3. Fig. 6 is a scatter plot of the concentration of a large amount of metals in the crater lake and AC and AT2 spring waters, with respect to the 1982 trachy-andesitic rock (Luhr *et al.*, 1984). Besides the major rock forming elements (thereafter RFEs), Cl and S are plotted as well, because both can originate from the basement rock. The 1982 deposits are renowned for their exceptionally high content of microphenocrystic anhydrite (2.6 wt% as SO₃, Varekamp *et al.*, 1984). Thus, S can be an abundant leaching product of the 1982 deposits, while Cl can enter thermal waters by water-basement interaction (evaporites). The correlation between these

two variables is generally rather good in all graphs (Fig. 6a-d), stating that the rock composition plays a major role in the distribution of RFE in thermal waters. Considering the main RFE, the alkalis and alkaline earths (Na, K, Ca, Mg, Sr, Rb), it can be noticed that these have a strong tendency to concentrate in solution. The water-rock ratios, marked by full diagonal lines in Fig. 6, demonstrate that 100 to 1,000 kg of water is needed to leach out 1 kg of the main RFEs from the deposits. Especially Ca and S are more concentrated in the thermal springs, supporting the hypothesis of anhydrite leaching from the 1982 deposits. Also Sr, Mg, and Rb are slightly more mobile in the spring waters with respect to the lake water. This can be due to the high state of alteration of sediments at the lake bottom by the acidic crater lake water: the most mobile major elements are already exhausted in the lake sediments. Additionally, Sr, Mg and Rb are also more abundant in carbonate rocks, present in the basement. Sulphur, and especially Cl, show lower water-rock ratios (100 to <10) than the main RFEs, indicating that the rock (trachy-andesite and its available anhydrite) is obviously not the only source. Chlorine and sulphur might enter by magmatic degassing, or even magmas and its resulted

Table 3

Trace element content in thermal and cold spring waters at El Chichón for the period 2006-2007. Concentrations are expressed in µg/l.

Sample	LE	LE	AC1	AC2	AT2.1	AT2.2	AT2.TOP	AT2.TOP	Agua Suerte
Date	19/11/06	10/03/07	23/11/06	23/11/06	27/11/06	27/11/06	27/11/06	28/03/07	27/03/07
Li	196	815	1505	1107	211	596	392	516	1
B	4421	16410	18370	14000	3521	8895	6728	8943	210
Al	3250	6167	10.1	5.0	374	7.4	28.1	116	17.6
V	11.8	6.5	0.90	0.99	0.59	1.3	4.8	3.5	3.6
Cr	0.34	<0.1	0.16	0.20	0.07	0.53	0.08	<0.1	<0.1
Mn	1217	3654	2030	2223	3580	4754	3518	6224	4.6
Fe	6738	8931	5233	1223	202	5486	7.4	31.6	4.7
Co	0.95	16.7	1.4	1.9	6.9	8.1	1.9	6.3	<0.1
Ni	0.41	6.2	1.0	4.2	14.4	4.6	6.9	12.0	<0.1
Cu	5.9	163.0	0.82	5.1	61.4	12.8	60.3	119	0.68
Zn	11.3	162	3.7	5.9	116	41.9	68.5	120	0.61
As	59.8	36.8	4.5	2.6	0.81	2.1	1.3	1.1	0.41
Se	0.19	0.32	-	-	0.25	-	-	-	0.14
Rb	99	452	666	501	97.9	243	163	175	12.8
Sr	346	1828	4394	3602	3289	3907	3138	3536	83.5
Mo	0.64	0.23	2.6	2.0	0.38	1.5	0.56	0.33	0.41
Cd	<0.1	1.7	<0.1	<0.1	0.49	<0.1	0.40	0.84	<0.1
Sb	0.38	0.23	<0.1	0.17	<0.1	<0.1	0.15	<0.1	<0.1
Cs	24.6	96.1	236	158	26.9	99.0	57.9	63.3	0.3
Ba	44.6	159	88.2	92.0	34.2	45.9	75.0	98.7	6.0
Hg	<0.05	0.08	0.06	<0.05	<0.05	<0.05	<0.05	0.06	0.07
Pb	<0.1	<0.1	0.24	0.18	<0.1	<0.1	<0.1	<0.1	<0.1
Th	-	<0.05	-	-	-	-	-	<0.05	<0.05
U	-	0.13	-	-	-	-	-	0.55	<0.05
Be	-	0.13	-	-	-	-	-	-	-

eruptive products are initially influenced by the Cl-SO_4 -rich basement rocks. All elements but S are more mobile in the March 2007 crater lake with respect to November 2006. This indicates that besides direct leaching by crater lake water of lake sediments, the SP springs are an additional source of metals: in November 2006 the crater lake was not fed by SP waters. Aluminium behaves differently if comparing the crater lake waters (Fig. 6a-b) with the AC (Fig. 6c) and AT2 waters (Fig. 6d). Aluminium generally has a strong tendency to concentrate in weathering minerals such as oxides and clays (e.g. Aiuppa *et al.*, 2000). Under acidic conditions clay minerals are not stable, thus Al remains in solution (crater lake with $\text{pH} < 2.7$). In the less acidic spring waters ($\text{pH} 5.15\text{--}5.85$) Al is

lost by secondary mineral precipitation (Fig. 6c-d).

Generally, As, Zn, and Cu enter as highly volatile compounds in high-temperature magmatic gases (Symonds *et al.*, 1987; Taran *et al.*, 1995). No strong enrichment in waters of any of these metals can be detected, not surprisingly indicating the absence of a near-surface high temperature degassing magma batch. Comparing these metal abundances in the lake water with respect to the spring waters, the crater lake water is enriched by one order of magnitude with respect to the springs, probably due to the higher acidity enhanced leaching capacity. Cu and Zn in AC waters are less mobile than in AT2 waters by two orders of magnitude of water-rock ratio (Fig. 6c-d).

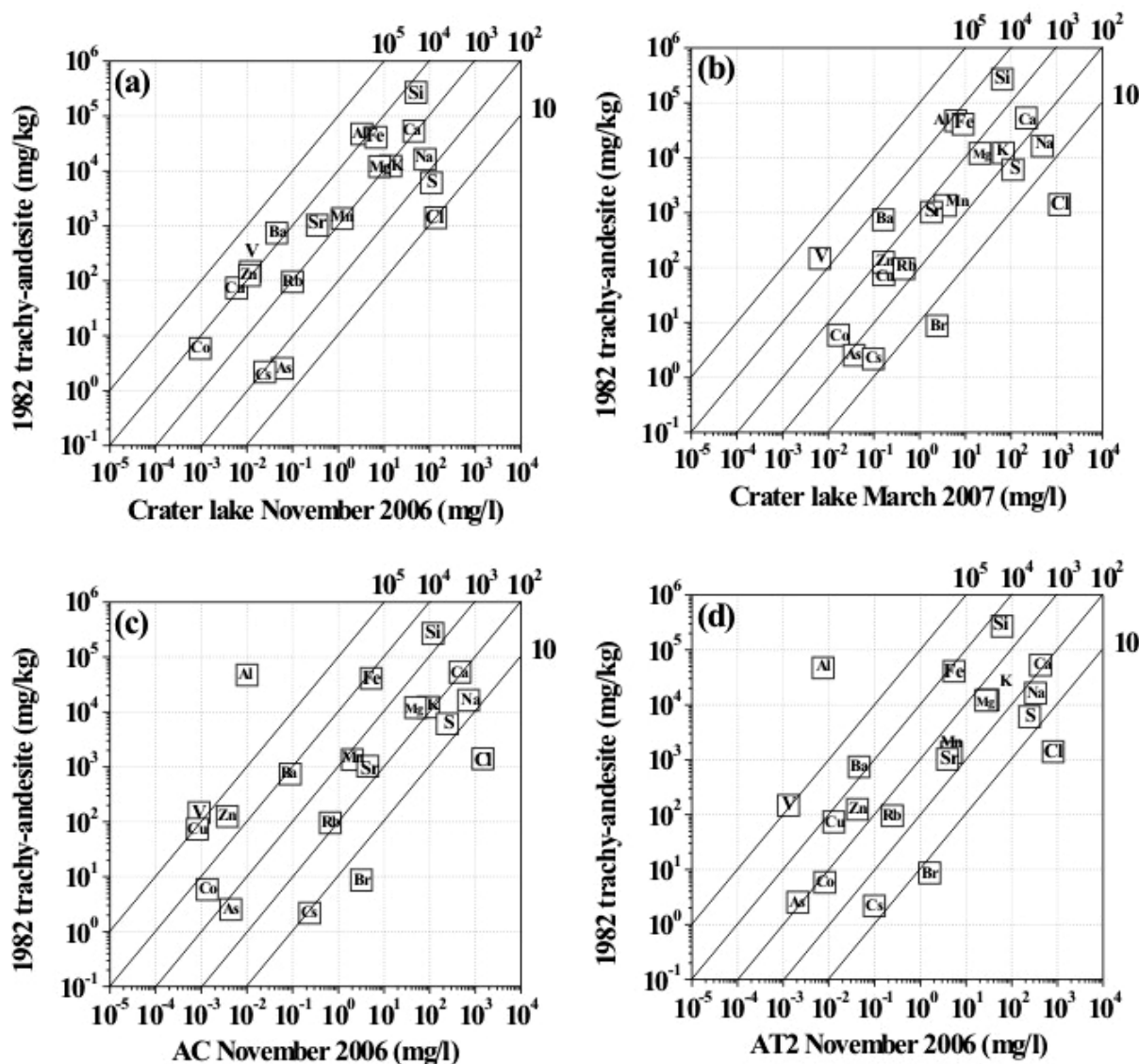


Fig. 6. Ion concentrations in thermal waters at El Chichón vs the average concentrations in the 1982 trachy-andesitic rocks (taken from Luhr et al., 1984; and Varekamp et al., 1984), for (a) the November 2006 crater lake, (b) the March 2007 crater lake, (c) the November 2006 Agua Caliente springs, and (d) the November 2006 Agua Tibia 2 springs.

log-log plots and crater lake seepage

We already detected some differences in the major element chemistry between the AT2 and AC springs, but, we should determine whether AT2 is fed by an independent aquifer near the SW dome, or if it is part of a large S-SW deep geothermal aquifer. Plotting the trace element content of the November 2006 AT2 waters (46.5°C) against that of AC, a good correlation ($R^2 \sim 0.95$) means that the AT2 springs are fed by the same large aquifer as AC (Fig. 7).

Beyond the application proposed by Taran *et al.* (2008), log-log plots could be used to detect possible lake seepage of crater lake water towards the deep geothermal aquifer, if plotting data sets of earlier samples of the crater lake against more recent data sets for spring waters. An extremely good correlation exists for the November 2006 AC and June 2004 crater lake waters ($R^2 \sim 0.98$; Fig. 8a). Correlation coefficients for later dates (lake in March 2005 and November 2006) are near 0.90. If crater lake seepage towards the flank springs takes place, the changes in chemistry in the lake water thus seem to be transmitted into the deep geothermal aquifer. With these observations, it would take ~ 30 months -the period between June 2004 and November 2006- for the lake water to reach the deep geothermal aquifer and come out through the AC springs. The same trend can be noticed for the AT2 spring (46.5°C, November 2006), although correlation coefficients are

lower (Fig. 8b). At Poás volcano a tritium-based residence time of seeping crater lake water of 3 to 17 years was deduced (Rowe *et al.*, 1995). Our estimate of 30 months seems reasonable considering that the Poás fluids need to travel a larger horizontal distance (3.25 km vs 1.5 km at El Chichón). The only tritium value for the Agua Caliente spring at El Chichón (2.4 T.U. in 1998) corresponds well with the values for Central America in the 1970's (2.6 T.U., as reported in Rowe *et al.*, 1995), suggesting that in 1998 the aquifer feeding the AC spring had an age of 20-25 years in 1998. Crater lake water in 1998 showed lower tritium isotopic values (1.3 T.U.) corresponding with meteoric waters (1.1 T.U. for Agua Roja cold spring water).

Chemical distribution of rock forming elements

Incongruent dissolution of volcanic rocks is the major, but not the only source of RFEs in acidic volcano-hydrothermal systems and crater lakes. Fig. 9 shows the chemical distribution of RFEs with respect to the 1982 trachy-andesitic rock (Luhr *et al.*, 1984, Varekamp *et al.*, 1984), defined as follows:

$$(RFE/Mg)_w / (RFE/Mg)_r \quad (2)$$

With RFE each rock forming element (including S and Cl); subscript w stands for water, r for rock. We choose

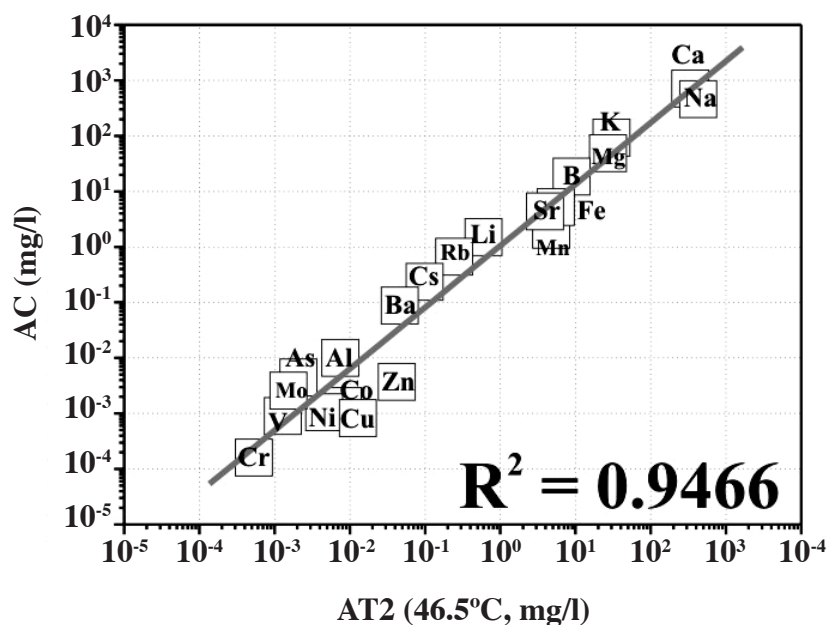


Fig. 7. Log-log scatter plots: metal concentrations in AT2 (November 2006, T= 46.5°C) thermal spring water vs metal concentrations in November 2006 Agua Caliente spring water. R^2 represents the correlation coefficient.

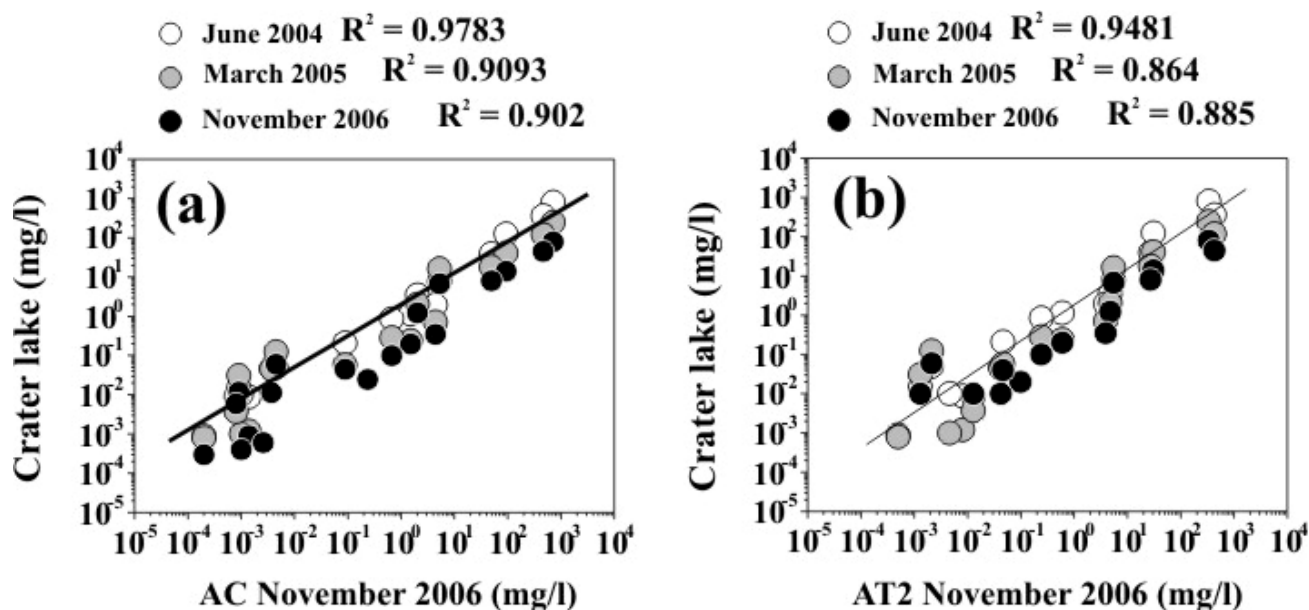


Fig. 8. Log-log scatter plots for ion contents in thermal waters, showing changes of R^2 with time. (a) November 2006 Agua Caliente spring waters vs the June 2004, March 2005 and November 2006 crater lake waters, (b) November 2006 ($T= 46.5^\circ\text{C}$) AT2 spring waters vs the June 2004, March 2005 and November 2006 crater lake waters. Pre-2006 data are taken from Rouwet *et al.* (2008).

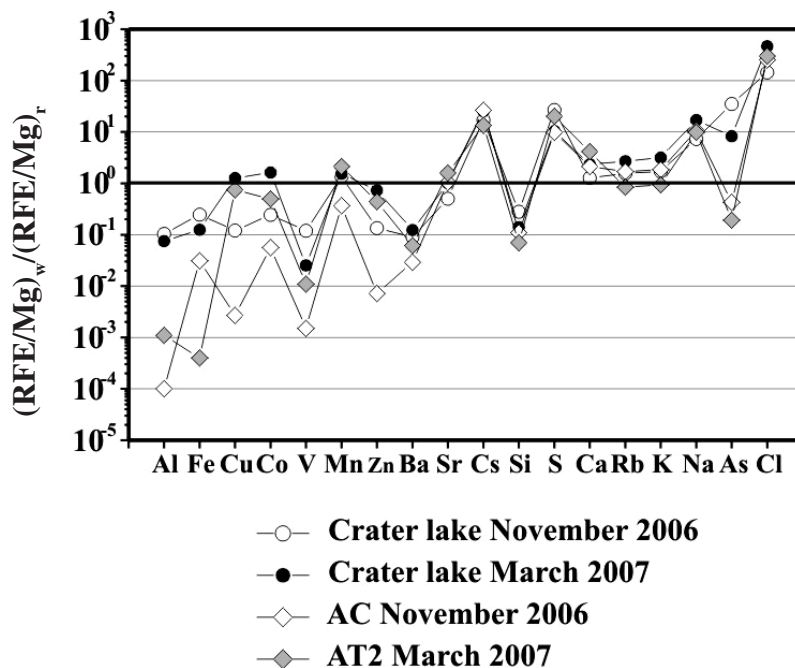


Fig. 9. Relative abundances of elements normalized against Mg in the crater lake waters (November 2006 and March 2007), AC (November 2006), AT2 (March 2007) and that in the average 1982 trachy-andesitic rocks (taken from Luhr *et al.*, 1984; and Varekamp *et al.*, 1984).

Mg to normalize because it is well-reserved in acidic sulphate-rich solutions (Giggenbach, 1974; Delmelle and Bernard, 1994; Pasternack and Varekamp, 1994; Takano *et al.*, 2004). The crater lake, AC and AT2 waters roughly follow the same element distribution (Fig. 9). Sulphur

is relatively enriched with respect to the other RFEs, confirming anhydrite leaching. The acidic crater lake water is more efficient in leaching Cu, Co, and V from rocks or sediments.

A remarkable difference exists in the distribution of Cu and Zn between the AC and AT2 spring waters (Fig. 9): Cu and Zn are depleted in AC waters, with respect to AT2. At AC bubbling degassing takes place, accompanied by an H_2S smell, features absent at AT2. The entrance of H_2S creates reduced environments adapted to sink Cu and Zn as sulfides. The turquoise colour at the head of the AT2 spring might be due to a Cu enrichment. At the AC, and more downstream at the AT2 stream, massive Fe-oxy-hydroxides form, indicating strongly oxidized conditions, responsible for the Fe depletion. This effect is stronger at AT2.

It is highlighted in Fig. 9 that As is depleted in the AC spring with respect to the crater lake water. Under acidic oxidized conditions ($\approx$ crater lake) As is stable as H_3AsO_4 (a), and thus remains in solution. On the other hand, under near-neutral reduced conditions ($\approx$ AC spring outlet) As will precipitate as As_3S_3 (Aiuppa *et al.*, 2000). Moreover, As co-precipitates with or adsorbs on Fe-oxy-hydroxides (Fig. 9) (Ballantyne and Moore, 1988; Aiuppa *et al.*, 2003).

Conceptual models: present and future state of the El Chichón volcano-hydrothermal system

The crater lake-Soap Pool system

For the first time since the observations started in 1995 (Taran *et al.*, 1998), a relationship with the annual rainfall distribution is noticed. In January-April 2001, March-June

2004 and March 2007 a large volume lake was observed. It is a fact that since 2001, every three years, a few months after the rainy season (June-October), the SP spring enters in a high water discharge activity, responsible for the lake growth and consecutive increase in Cl content in the lake water. Considering an average rainfall flux of $1.34 \times 10^{-4} \text{ kgm}^{-2}\text{s}^{-1}$ (Rouwet *et al.*, 2004), the total volume of rainwater accumulated during a time span of three years beneath the crater floor ($\sim 8 \times 10^5 \text{ m}^2$) is in the order of 10^7 m^3 . This can be considered the maximum volume of the shallow boiling aquifer beneath the 1982 crater floor, because part of the infiltrating rainwater dissipates in the volcanic edifice.

Geothermometry suggests boiling processes at shallow depth beneath the crater floor ($115\text{-}130^\circ\text{C}$). Fluid migration takes place inside the heterogeneous shallow aquifer, testified by rumbling and low frequency noise. Such rumbling has been observed at other active volcano-hydrothermal systems such as e.g. Kusatsu-Shirane volcano, the host of the Yugama crater lake, where steam-driven explosive activity was common in the 1970's and 80's (Ohba *et al.*, 2008). Thus, these features at El Chichón can be interpreted as small steam-driven phreatic explosions inside the shallow aquifer. Considering that the lake volume strongly depends on the SP water input, the slight increase of the maximum lake volume observed through 2001, 2004 and 2007 (Fig. 5) could demonstrate an increase in volume of the shallow aquifer feeding the SP geyser.

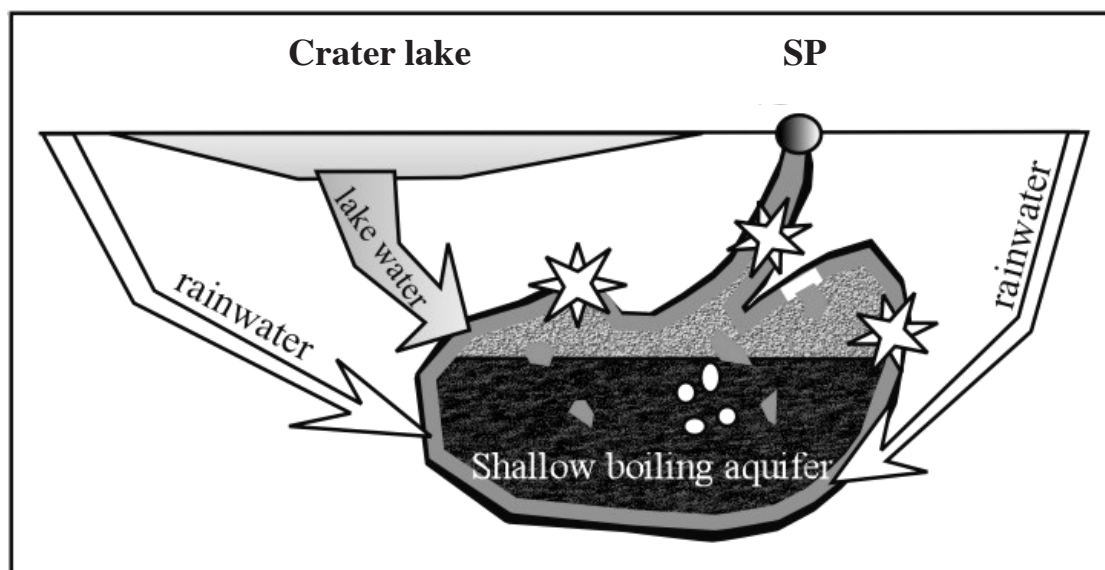


Fig. 10. Current dynamics of the “crater lake-Soap Pool spring” system. Phreatic explosions (stars) inside the shallow boiling aquifer breach through secondary sealing minerals, increasing on its turn the aquifer volume. The boiling aquifer is continuously filled by infiltrating rain and crater lake water.

The deep geothermal aquifer

We found arguments in favour of a small degree of crater lake seepage into the S-SE deep geothermal aquifer (~200 m) reaching the AC and, in probably lower proportion, the AT2 springs. Crater lake seepage towards the S of the volcano might be enhanced by the morphology of the southern rim of the Somma crater, opening into a big “barranca” ending into the AT2 canyon. The horse-shoe shaped explosion crater at AC could be another morphological weakness, enhancing lateral and downward fluid flow. The seeped crater lake water is thought to reach the AC springs in ~30 months, a reasonable residence time to migrate along a distance of ~1.5 km for a height difference of ~200 m. This effect has been seen for the June 2004 crater lake infiltration, when lake volume was high (~5 x 10⁵ m³, Table 2). When the crater lake level is high, more permeable parts of the crater floor are flooded than at low crater lake level: the constantly covered lake bottom is composed of sealing clays, while near the coast of the lake, the lake bottom floor is composed of pumiceous permeable sediments (Fig. 11). High level lakes thus tend to infiltrate preferentially (Fig. 11). If this mechanism is correct, the March 2007 crater lake will have reached the AC springs by the autumn of 2009. Trace element contents in a large volume lake are generally higher than in a small volume lake. A monitoring with time of the RFE patterns between the

lake and spring waters will contradict or affirm the here proposed lake seepage. The Cl/SO₄ ratio in both lake and AC waters has shown to be variable with time and tracing this parameter will be less efficient to detect possible lake seepage. Moreover, estimates of important parameters of the physical properties (i.e. hydraulic conductivity, active porosity, permeability, etc.) of the volcanic edifice still lack, and are necessary to establish a hydrogeochemical modelling of the entire El Chichón volcano-hydrothermal system. The AT2 springs, at the foot of the SW dome, are fed by the same deep geothermal aquifer. This aquifer is formed as the result of the permeability decrease at the contact between the volcanic edifice and the basement rocks.

The main heat source beneath El Chichón is probably long-lived and stable, as spring temperatures have not changed since the late 1970's. The remains of the 1982 magma is an additional heat source. No chemical evidence exists on the location of any heat source or a high temperature degassing magma body. Moreover, normal faults could serve as upward migration pathways for deep Cl-rich fluids, frequently present at hydrothermal systems (e.g. Pinatubo volcano; Stimac *et al.*, 2004). This is the case of El Chichón crater emplaced atop the main trace of the San Juan left-lateral fault (García-Palomo *et al.*, 2004). The Cl from the deep geothermal aquifer probably originates partly from the same evaporites (~Cl/Br ratios).

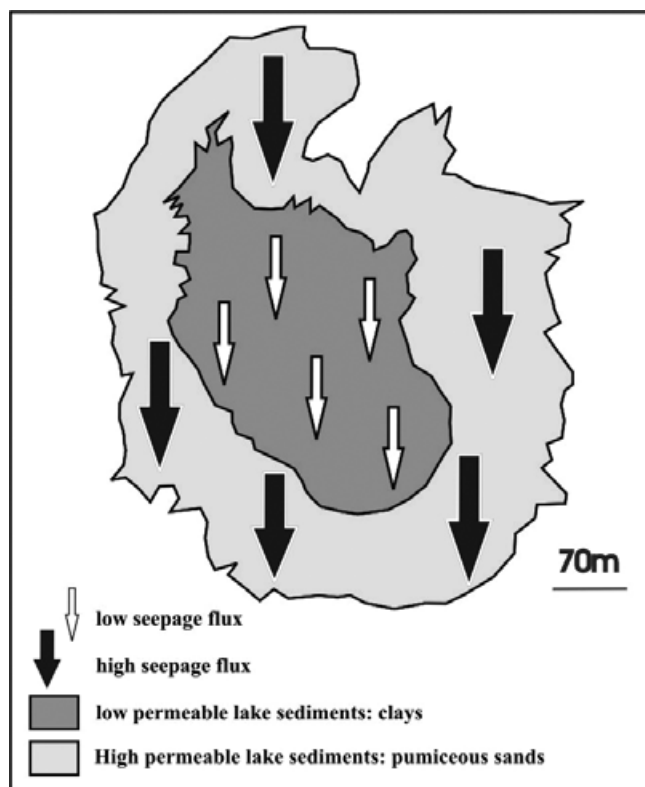


Fig. 11. Model to explain enhanced crater lake seepage during high volume lake situations (2001, 2004 and 2007).

The current uncertainty on an additional Cl input at the crater system still points to a possible masking effect of the deep geothermal aquifer to absorb all rising (magmatic?) Cl before reaching the crater area. That is the reason why we believe dome intrusion will probably be anticipated by chemical changes in the thermal springs, even before modifying crater lake dynamics and chemistry of gas emissions.

Conclusions

In this study, the results of the geochemical survey obtained during the period November 2006-October 2007 are integrated in the monitoring program of the crater lake-Soap Pool spring system at El Chichón volcano. Moreover, we propose new ideas for future volcanic surveillance of magmatic activity using the AT2 and AC thermal springs. New data on stable isotopes (δD and $\delta^{18}O$), major, minor and trace elements verify existing hydro-geochemical models (Taran and Rouwet, 2008; Rouwet *et al.*, 2008; Taran *et al.*, 2008).

In March 2007 the crater lake reached its largest volume ever observed ($\sim 6 \times 10^5 \text{ m}^3$). For the first time a trend between the lake volume and the annual rainfall distribution could be noticed: during three years (2001, 2004 and 2007), high water discharges from the Soap Pool spring result in a large lake, starting some months after the rainy season (June-October). The diminishing-Cl trend with time for Soap Pool and crater lake waters shows a non-linear behaviour for the first time; current Cl contents are higher than expected, though few evidence on a renewed Cl input exist.

Earlier suggestions on a strong basement-volcano interaction are confirmed. Cl has impure volcanic origin of thermal spring waters. The AT2 springs testify an enhanced water-rock interaction, anhydrite leaching, evaporite contribution, absence of degassing and lower temperature conditions. Thus, the SW dome does not seem to be active. A small portion of the deep geothermal aquifer seems to originate from the direct seepage of crater lake water. Strongest evidence is found for the AC springs. We suggest further research on the spring systems to ascertain the response of the thermal springs during increased volcanic activity (e.g. future dome growth).

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