

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

3
4 Dmitri Rouwet¹, Sergio Bellomo¹, Lorenzo Brusca¹, Salvatore Inguaggiato¹, Martin
5 Jutzeler^{2,3}, Raúl Mora⁴, Agnes Mazot⁵, Ruben Bernard⁵, Michael Cassidy³, Yuri Taran⁵

6
7 ¹*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italy*

8 ²*Centre for Ore Deposit Research (CODES), University of Tasmania, Australia*

9 ³*Centre of Exchange and Research in Volcanology, Universidad de Colima, Colima, Mexico*

10 ⁴*RSN-Universidad de Costa Rica, San José, Costa Rica*

11 ⁵*Instituto de Geofísica, UNAM, México D.F., Mexico*

12
13 **RESUMEN**

14 Se presenta un estudio detallado de la composición isotópica y química (elementos
15 mayores y traza) del lago cratérico, Soap Pool y de los manantiales termales en el Volcán
16 Chichón para el período noviembre 2006-octubre 2007. Después de dos décadas de
17 estudios del lago cratérico, se confirma la relación compleja entre la distribución anual de
18 la precipitación y el volumen y la química del lago cratérico: durante tres años (2001,
19 2004 and 2007) un volumen grande del lago rico en Cl se relaciona con la reactivación de
20 la descarga alta (>10 kg/s) hacia el lago de aguas salinas con un pH cerca de la
21 neutralidad de los manantiales hirvientes Soap Pool, únicamente algunos meses (~enero)
22 después del final de la temporada de lluvias (junio-octubre). El volumen más grande
23 jamás observado ocurrió en marzo 2007 (~6x10⁵ m³).

24 No obstante el hecho que los manantiales termales de Agua Tibia 2 descargan al pie del
25 domo SO, su química indica un regimen de temperaturas más bajas, una interacción agua-
26 roca y una contribución del basamento (evaporitas y carbonatos) más avanzada y una

27 lixiviación de anhidrita de los depósitos piroclásticos de 1982; el domo SO no demuestra
28 actividad. Existen nuevas evidencias sobre una posible infiltración del lago cratérico
29 hacia el manantial de Agua Caliente. Los modelos existentes del sistema “lago cratérico-
30 Soap Pool” y el sistema hidrotermal más profundo se justifican y se detallan. Creemos
31 que los cambios químicos en el acuífero geothermal profundo alimentando los
32 manantiales termales, podrían anticipar el crecimiento futuro de un domo. El monitoreo
33 volcánico futuro se tendría que enfocar en los cambios en la química de los manantiales,
34 aparte del monitoreo del lago cratérico.

35

36 **PALABRAS CLAVE:** El Chichón, geoquímica de fluidos, monitoreo volcánico.

37

38 **ABSTRACT**

39 We report a detailed study of isotopic, major and trace element composition in the
40 crater lake, Soap Pool and thermal springs at El Chichón volcano for the period
41 November 2006-October 2007. After two decades of studying the crater lake, it is
42 possible to confirm the complex relationship between the annual rainfall distribution and
43 the crater lake volume and chemistry: during three years (2001, 2004 and 2007) a large
44 volume high-Cl lake can be related to the reactivation of high discharge (>10 kg/s) of
45 saline near-neutral water from the Soap Pool boiling springs towards the lake, only a few
46 months (~January) after the end of the rainy season (June-October). The highest lake
47 volume ever observed occurred in March 2007 ($\sim 6 \times 10^5$ m³).

48 Despite the fact that the Agua Tibia 2 thermal springs discharge at the foot of the SW
49 dome, their chemistry indicates a lower temperature regime, an enhanced water-rock
50 interaction and basement contribution (evaporites and carbonates), and anhydrite leaching
51 from the 1982 pyroclastic deposits, rather than dome activity. New suggestions on crater
52 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 justified and detailed. We believe that chemical changes in the deep geothermal aquifer feeding the thermal springs will anticipate dome rise. Future volcanic surveillance should focus on the changes in spring chemistry, besides crater lake monitoring.

KEY WORDS: El Chichón, fluid geochemistry, volcanic surveillance.

1. Introduction

El Chichón volcano is located in northwest Chiapas, southern Mexico, in between two major volcanic regions, the Transmexican Volcanic Belt and the Central American Volcanic Arc (Fig. 1(a)). Dome destroying eruptions are frequent at El Chichón: each 100-600 years during the past 8,000 years (Espíndola *et al.*, 2000). In fact, 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) (Fig. 1(b)); moreover, the two centrally nested domes were blasted away in 1982 (Luhr *et al.*, 1984; Varekamp *et al.*, 1984).

During 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, 2007; Rouwet *et al.*, 2008; Taran *et al.*, 2008). As for 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 in predicting volcanic crisis at El Chichón. Surprisingly, the 1982 Plinian eruptions were not followed by dome growth in the 1 km wide-200 m deep explosion crater. Although changes in chemistry of thermal springs at active volcanoes have scarcely proven to be efficient precursors before magmatic crisis, we

79 believe that the El Chichón spring network is adapted to start up volcanic surveillance.
80 Before this, one needs to know the baseline behaviour of the springs during quiescent
81 degassing periods; the main goal of this study.

82 Taran *et al.* (2008) reported for the first time the chemistry of the Agua Tibia 2 springs
83 (AT2 thereafter), discharging from beneath the SW dome. Since April 1998, the AT2
84 springs have been revisited only twice: in November 2006 and March 2007. This study
85 could be the missing link to shed light on (1) the relationship of the AT2 springs with the
86 state of activity of the volcano, and (2) the connection between the crater manifestations
87 and the thermal springs. Crater lake seepage, is a common feature at crater lake hosting
88 volcanoes, justified by similarities in major element contents, Cl/SO₄ ratios and pH (e.g.
89 Poás, Copahue, Kawah Ijen, Patuha, Keli Mutu, Rincón de la Vieja, Ruapehu; Pasternack
90 and Varekamp, 1994; Rowe *et al.*, 1995; Sanford *et al.*, 1995; Deely and Sheppard, 1996;
91 Sriwana *et al.*, 1998; Delmelle and Bernard, 2000, Kempter and Rowe, 2000, Varekamp
92 *et al.*, 2001, Löhr *et al.*, 2005). This process was suggested for the highly saline Agua
93 Salada acidic springs discharging at the NW dome (Taran *et al.*, 2008), but these springs
94 are not necessarily the only direct output of crater lake water at El Chichón.

95 We propose new ideas on the southern parts of the El Chichón volcano-hydrothermal
96 system, by adding chemical and isotopic data on Agua Caliente (AC thereafter) and the
97 AT2 thermal waters. The existing model for the “lake-Soap Pool spring” system in the
98 crater (Rouwet *et al.*, 2004; Taran and Rouwet, 2007; Rouwet *et al.*, 2008) is tested by
99 introducing recent data on crater lake volume, and lake and Soap Pool geyser-like boiling
100 spring chemistry.

101

102

103

104

2. 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 largest part of the crater floor at ~850 m a.s.l (Fig. 2(a)). 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” by Taran *et al.* (1998) (SP thereafter). The SP alternates periods of high discharge of near neutral, saline and Cl-rich waters towards to lake with periods of exhalation of only vapour. Based on a chemical and isotope balance approach, the total heat output from the crater is estimated to be 35-60 MW, and the diffuse CO₂ flux from the crater is not lower than 140 g/m²day (Taran and Rouwet, 2007). This last value coincides with the minimum values obtained by direct CO₂ flux measurements from the crater lake surface (March 2007; Mazot and Taran, this volume).

Besides the crater manifestations, El Chichón is known for its 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 sedimentary basement. All thermal springs finish into Río Magdalena, finally draining towards the Gulf of Mexico (Fig. 1(b)). The total thermal heat output through the springs is estimated to be ~100 MW (Rouwet, 2006). Despite the fact that pre-1982 reports (Molina Berbeyser, 1974; Templos *et al.*, 1981) already mention thermal springs at El Chichón, up until now, the springs have not been targeted during volcanic surveillance, mainly because they are located in remote and densely vegetated canyons. The “fresh looking” domes (Fig. 2(a-b)), outside the 1982 crater, may still be rooted by a cooling magma body, possibly remaining the principal heat source at the present hydrothermal system.

130 The AC springs discharge in the southeastern horseshoe-shaped canyon (Guyabal Tuff
131 cone, <10 ka; Layer *et al.*, this volume), testifying Holocene explosive activity (Fig. 1(b)
132 and 2(c)-(d)). Based on the Cl content of Río Tuspac, Taran *et al.* (1998) estimated the
133 total outflow rate of the AC springs to be >100 kg/s. The temperature of the slightly
134 acidic to near-neutral AC waters (pH 5.7-7.6) remained stable at ~71°C since before 1982
135 (Molina Berbeyrer, 1974; Templos *et al.*, 1981). The conductivity varies from 4.3 to 5.9
136 mS/cm (2004-2007), representing similar salinities than the present crater lake (Table 1).
137 The AC springs form numerous cascades and hot water spurts discharging into densely
138 vegetated swampy pools (Fig. 2(d)). Weak bubbling degassing can be observed at AC,
139 and coinciding with negative Eh values, this indicates a H₂S input (Taran *et al.*, 1998).
140 The AC springs discharge at less than 1.5 km distance from the 1982 crater with a vertical
141 difference of only 200 m.

142 Some 2.5 km west of AC, the AT2 springs discharge east of the SW dome (Fig. 1(b)
143 and 2(b)). This dome shows surface alteration, the result of past fumarolic activity (dome
144 age 217 ± 10 ka; Layer *et al.*, this volume); active fumaroles cannot be distinguished. A
145 total discharge of 80 kg/s of the AT2 thermal springs is estimated (Taran *et al.*, 2008). In
146 April 1998, discharge temperatures of AT2 waters of 51-49°C were detected, similar to
147 the pre-1982 temperature reported by Templos *et al.* (1981). We measured lower
148 discharge temperatures for various AT2 springs in November 2006 and March 2007 (35.4
149 to 46.5°C, Table 1). The AT2 spring mainly discharges from beneath rocks in the river
150 bed, forming numerous pools downstream of 10-20 meters of translucent whitish-
151 turquoise water (Fig. 2(e)). Abundant amorphous milky-white precipitates can be
152 observed at the bottom of the pools. More downstream, Fe-oxy-hydroxides colour the
153 river bed orange, such as at AC. The horizontal distance of the AT2 springs from the
154 crater lake is ~1.6 km, with a height difference of ~150 m. Besides temperature, the
155 conductivity is also lower than for AC waters, varying from 1.8 to 4.2 mS/cm (Table 1).

156 Eh values are negative, which might indicate an H₂S input, although no strong evidence
157 on bubbling degassing exists. The pH of AT2 waters is slightly lower than at AC: 5.15 to
158 5.85 (2006-2007).

159 The most acidic and saline waters of the entire volcano-hydrothermal system discharge at
160 the northwestern ends of El Chichón (Agua Salada, pH ~2.2-5.6, 79°C), north of the
161 younger NW dome (age 90 ± 18 ka; Layer *et al.*, this volume) (Fig. 1(b)). The Agua Tibia
162 1 springs (68°C) are similar to AC waters (Taran *et al.*, 2008) (Fig. 1(b)). The Agua
163 Salada and Agua Tibia 1 springs were not revisited since 2005. Nevertheless, the head of
164 the Agua Salada canyon was visited in March 2007. The Agua Suerte cold spring
165 discharges here at <1km distance from the crater at an elevation of ~800 m (Fig. 1(b)).
166

167 **3. Sampling and analytical methods**

168 The crater lake was sampled in November 2006, and January, March, September
169 and October 2007. The SP water was collected during the March 2007 campaign. In
170 November 2006 and September-October 2007, the SP geyser only emitted vapour, so no
171 water sample could be collected. The AC springs were sampled in November 2006 (Fig.
172 2(d)); the AT2 springs in November 2006 and March 2007. Temperature, pH,
173 conductivity and Eh were directly measured at the lake surface or spring outlet. Waters
174 were stored in polyethylene bottles after passing through 0.45 µm filters. Samples for
175 cation analyses were acidified in the field with a 60% HNO₃ solution. Anion analyses
176 were elaborated from non-acidified filtered samples. Water samples for minor and trace
177 element analyses were stored in ultra-pure HDPE Nalgene flasks and acidified by a 60%
178 HNO₃ and 60% HCl solution in 4/1 proportions.

179 Major element contents (Na, K, Ca, Mg and F, Cl, SO₄) were obtained by Liquid
180 Chromatography (Dionex) with an accuracy of 3%. HCO₃ concentrations were detected
181 by means of titration with a 0.01N HCl solution of 10 ml of a non-filtered non-acidified

182 sample aliquot. SiO₂ concentrations were measured by colorimetric photospectrometric
183 methods on diluted samples. Trace element concentrations were determined by ICP-MS
184 (Agilent 7500 CE). All determinations were performed with the external standard
185 calibration method, using Re and In as internal standards. The accuracy of the results
186 ($\pm 5\%$) was obtained by analyzing certified reference materials (NRCCLR-4, SPS-SW1
187 and NIST-1643e). The water samples were analyzed for their oxygen and hydrogen
188 isotopic composition, using Analytical Precision AP 2003 and Finnigan MAT Delta Plus
189 spectrometers, respectively. The isotope ratios are expressed as the deviation per mil ($\delta\%$)
190 from the reference V-SMOW. The uncertainties are $\pm 0.1\%$ for $\delta^{18}\text{O}$ and $\pm 1\%$ for δD (one
191 standard deviation).

192

193 **4. Results and discussion**

194 4.1 Stable isotopes and major ion species

195 4.1.1 *Isotopic composition of thermal waters: δD and $\delta^{18}\text{O}$*

196 The stable isotopic composition (δD and $\delta^{18}\text{O}$) of thermal and cold spring waters
197 at El Chichón are presented in Table 1, and plotted in Fig. 3. Considering δD and $\delta^{18}\text{O}$ of
198 crater lake and SP waters, the same tendency as observed in earlier years is repeated: (1)
199 in November 2006 the SP did not discharge water towards the crater lake, and
200 consequently, δD and $\delta^{18}\text{O}$ of the crater lake water clearly follow the evaporation trend
201 originating from the local meteoric water, and (2) in March 2007, the SP water discharge
202 towards the lake was high, and the δD and $\delta^{18}\text{O}$ of lake and SP waters plot near each
203 other in Fig. 3, although the evaporation effect for the lake water is not excluded. The δD
204 and $\delta^{18}\text{O}$ for the March 2007 SP water plot near the range established in Rouwet *et al.*
205 (2008) of $-8\pm 2\text{‰}$ and $+1.5\pm 0.7\text{‰}$, respectively. River and cold spring waters (i.e. Agua
206 Suerte) determine the correct isotopic composition of local meteoric water, slightly

207 shifted to the left off the meteoric water line (MWL in Fig. 3). The isotopic composition
208 of AC and AT2 thermal spring waters plot near the values for the local meteoric waters
209 (Fig. 3).

210

211 *4.1.2 Major ion species*

212 The major element composition of the 2006-2007 thermal waters at El Chichón
213 are shown in Table 1. All thermal waters at El Chichón, flank springs, as well as crater
214 fluids, are of a Na-Ca-Cl-SO₄ type. As Cl behaves as a conservative element, the cation
215 vs Cl plots (mixing plots) serve to distinguish main ion sources. Cationic species roughly
216 have a common source for all waters (Fig. 4(a), i.e. the trachy-andesitic rock, see section
217 4.2.1), nevertheless, the data of AC and AT2 spring waters sometimes scatter along the
218 general mixing trends between the meteoric and hydrothermal end-member (Fig. 4). The
219 AT2 springs have significantly lower discharge temperatures compared to AC. Lower
220 temperatures result in lower relative K contents (Fig. 4(b)). El Chichón thermal waters are
221 less “immature” than conventional solute geochemistry suggests (Giggenbach, 1988;
222 Henley *et al.*, 1984); a partial equilibrium between waters and an Al-silicate alteration
223 mineral assemblage is attained, and the equilibrium temperatures coincide well with the
224 chalcedony equilibrium temperature (Taran *et al.*, 2008). The AT2 springs are fed by a
225 colder water source than the neighbouring AC springs, the chalcedony geothermometers
226 result in (Henley *et al.*, 1984): 100-130°C for AT2 springs against 160-180°C for AC
227 springs. The latter temperatures are even higher than for SP (~115°C) and lake waters
228 (115-130°C). AT2 waters are enriched in Ca and are less rich in K, with respect to AC
229 waters (Fig. 4(b)-(c)), so AT2 waters cannot be considered just diluted AC waters, but
230 indicate re-equilibration processes to lower temperatures of a same source as AC.

231 We show evidence on a contribution of the evaporite basement for the thermal waters at
232 El Chichón (Fig. 4(d)). The AT2 and AC springs seem to be affected by a non-volcanic

233 halogen source. The AC and AT2 waters plot towards the line of Cl/Br~289, the ratio
234 representative for “seawater” (\approx evaporite) (Böhlke and Irwin, 1992). The January 2007
235 crater lake water plots more towards the “volcanic Cl/Br line” (Cl/Br >1,450; Taran *et al.*,
236 1995; Fig. 4(d)). During this period, the SP geyser had returned to its high water
237 discharge. The March 2007 SP and lake water plot along the same mixing trend,
238 confirming the strong influence of SP waters on the crater lake chemistry. This mixing
239 trend has a Cl/Br concentration ratio of \sim 500, meaning that Cl and Br at El Chichón in
240 any way can be considered a mixture of “seawater” and “volcanic” originating fluids (Fig.
241 4(d)). In any case, all observed Cl/Br ratios for El Chichón fluids are common in volcanic
242 waters produced in the magmatic-hydrothermal environment.

243

244 *4.1.3 The crater lake-Soap Pool system in 2006-2007*

245 Within the scope of continuing the monitoring of the current activity of the crater
246 lake-Soap Pool volcano-hydrothermal system, we present the updates for 2007, on: (1)
247 the crater lake volume (Table 2, Fig. 5), and (2) the Cl content in the crater lake and SP
248 spring waters (Table 1, Fig. 5).

249 Since a large lake has been observed for the first time in January-April 2001, and a
250 second time in March-April 2004, the lake has entered a large volume situation for the
251 third time by March 2007. Since January 2007, water has been discharging from the SP
252 site (no sample), and the lake volume has consequently been increasing (January 2007,
253 pers. comm. Protección Civil Chapultenango staff). In March 2007, El Chichón crater
254 lake reached its largest volume ever observed ($\sim 6 \times 10^5$ m³, Table 2). The SP discharge
255 was estimated in the field, resulting in ~ 10 kg/s. Assuming we did not miss any
256 significant volume changes of the lake with our observation frequency, for the first time,
257 three real trends can be observed in the alternation between a small and a large volume
258 lake: (1) a large volume lake occurs each three years (2001, 2004 and 2007) starting a few

259 months (~January) after the rainy season (June-October), (2) the maximum volume
 260 slightly increased from 2001 to 2007 (white dotted arrow in Fig. 5) and (3) intermediate
 261 volume lakes were observed in 2002 and 2006, probably coinciding with shorter periods
 262 of SP water discharges (black arrows, Fig. 5).

263 The Cl content in the lake increased from 135 mg/l in November 2006 to 1,256 mg/l in
 264 September 2007. In March 2007 the Cl content was 1,149 mg/l. In November 2006 and
 265 September 2007 the SP geyser emitted only vapour, while in March 2007 SP water
 266 discharge was high (~10 kg/s). This sequence probably indicates that in the summer of
 267 2007, the Cl content in the lake, and probably the lake volume, was even higher than
 268 detected in March 2007, and that the relatively high Cl content in September 2007 is the
 269 remnant Cl shortly after the ceasing of SP water discharge towards the lake. Because the
 270 estimated seepage flux (>17 kgm⁻¹d⁻¹; Rouwet *et al.*, 2004) is higher than the yearly
 271 average precipitation flux (<12 kgm⁻²d⁻¹; Rouwet *et al.*, 2004), the lack of SP water
 272 feeding the lake results in a rapid decrease in lake volume, although no decrease in Cl
 273 concentration. Lake water residence times were calculated to be extremely short (~2
 274 months; Taran and Rouwet, 2007). The El Chichón crater lake is probably the best
 275 example in the world to demonstrate the delicate balance between input and output of
 276 heat, water and chemical species, to actually make a crater lake exist.

277 Rouwet *et al.* (2008) deduced an empirical equation to quantify the linear trend of
 278 diminishing Cl content in the SP waters for the period 1983-2005:

$$279 \quad Cl_L = -79.221x t + 25,628 \quad (1)$$

280 Where Cl_L is the Cl content in the SP water and t the number of months since January
 281 1983 (t = 1). Applying this equation, the SP springs and crater lake should theoretically
 282 be Cl-free by 2009±1; instead, for March 2007 a Cl content in SP waters of ~1,600 mg/l
 283 should be reached. Despite this trend, the Cl content in the March 2007 SP waters is as
 284 high as 3,028 mg/l. For the first time since 1995, a non-linear though diminishing Cl trend

285 for SP water is shown (Fig. 5). These higher than expected Cl contents in SP waters could
286 imply the presence (or appearance) of an additional Cl-source feeding the shallow boiling
287 aquifer beneath the El Chichón crater. At present it is difficult to rule out the origin of this
288 Cl-enrichment, though different scenarios can be proposed. The first probable source of
289 Cl-rich waters feeding the shallow aquifer is the crater lake itself, due to an efficient
290 recycling of lake water through infiltration at the lake bottom. Consecutive boiling in the
291 shallow aquifer, enriches the liquid phase (SP geyser water) in Cl (Ohba *et al.*, 2000). If
292 so, steam separation has become more efficient recently. Secondly, the SP geyser and the
293 shallow aquifer can be fed by the main hydrothermal aquifer, probably the same as the
294 one feeding the flank thermal springs (Cl ~2,000 mg/l), through upward fluid migration.
295 Until now, a linear dilution of the remains of the 1982 ultra-acidic brine-like
296 hydrothermal fluid (24,000 mg/l of Cl, Casadevall *et al.*, 1984; Rouwet *et al.*, 2004) could
297 clearly be observed. In the near future (2009±1) it will become clear if all original Cl will
298 be flushed out off the crater hydrothermal system (zero-Cl in SP and lake water) or if Cl
299 content in the SP and lake water remains constant. If not, the regime of fluid flow inside
300 the volcanic edifice should be more complex, and existing models should be revised.

301

302 4.2 Trace element geochemistry

303 4.2.1 Relative mobility of trace metals

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

311 1982 deposits, while Cl can enter thermal waters by water-basement interaction
312 (evaporites). The correlation between these two variables is generally rather good in all
313 graphs (Fig. 6(a)-(d)), stating that the rock composition plays a major role in the
314 distribution of RFE in thermal waters. Considering the main RFE, the alkalis and alkaline
315 earths (Na, K, Ca, Mg, Sr, Rb), it can be noticed that these have a strong tendency to
316 concentrate in solution. The water-rock ratios, marked by full diagonal lines in Fig. 6,
317 demonstrate that 100 to 1,000 l of water is needed to leach out 1 kg of the main RFEs
318 from the deposits. Especially Ca and S are more concentrated in the thermal springs,
319 supporting the hypothesis of anhydrite leaching from the 1982 deposits. Also Sr, Mg, and
320 Rb are slightly more mobile in the spring waters with respect to the lake water. This can
321 be due to the high state of alteration of sediments at the lake bottom by the acidic crater
322 lake water: the most mobile major elements are already exhausted in the lake sediments.
323 Additionally, Sr, Mg and Rb are also more abundant in carbonate rocks, present in the
324 basement. Sulphur, and especially Cl, show lower water-rock ratios (100 to <10) than the
325 main RFEs, indicating that the rock (trachy-andesite and its available anhydrite) is
326 obviously not the only source. Chlorine and sulphur might enter by magmatic degassing,
327 or even magmas and its resulted eruptive products are initially influenced by the Cl-SO₄-
328 rich basement rocks. All elements but S are more mobile in the March 2007 crater lake
329 with respect to November 2006. This indicates that besides direct leaching by crater lake
330 water of lake sediments, the SP springs are an additional source of metals: in November
331 2006 the crater lake was not fed by SP waters. Aluminium behaves differently if
332 comparing the crater lake waters (Fig. 6(a)-(b)) with the AC (Fig. 6(c)) and AT2 waters
333 (Fig. 6(d)). Aluminium generally has a strong tendency to concentrate in weathering
334 minerals such as oxides and clays (e.g. Aiuppa *et al.*, 2000). Under acidic conditions clay
335 minerals are not stable, thus Al remains in solution (crater lake with pH <2.7). In the less

336 acidic spring waters (pH 5.15-5.85) Al is lost by secondary mineral precipitation (Fig.
337 6(c)-(d)).

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

346

347 4.2.2 log-log plots and crater lake seepage

348 We already detected some differences in the major element chemistry between the
349 AT2 and AC springs. Nevertheless, we would like to rule out whether AT2 is fed by an
350 independent aquifer near the SW dome, or if it is part of a large S-SW deep geothermal
351 aquifer. If plotting the trace element content of the November 2006 AT2 waters (46.5°C)
352 against this of AC, the good correlation ($R^2 \sim 0.95$) infers that the AT2 springs are fed by
353 the same large aquifer as AC (Fig. 7).

354 Going beyond the application proposed by Taran *et al.* (2008), the log-log plots could be
355 used to detect possible lake seepage of crater lake water towards the deep geothermal
356 aquifer, if plotting data sets of earlier samples of the crater lake against more recent data
357 sets for spring waters. An extremely good correlation exists for the November 2006 AC
358 and June 2004 crater lake waters ($R^2 \sim 0.98$; Fig. 8(a)). Correlation coefficients for later
359 dates (lake in March 2005 and November 2006) are near 0.90. If crater lake seepage
360 towards the flank springs takes place, the changes in chemistry in the lake water thus
361 seem to be transmitted into the deep geothermal aquifer. With these observations, it

362 would take ~30 months -the period between June 2004 and November 2006- for the lake
 363 water to reach the deep geothermal aquifer and come out through the AC springs. The
 364 same trend can be noticed for the AT2 spring (46.5°C, November 2006), although
 365 correlation coefficients are lower (Fig. 8(b)). At Poás volcano a tritium-based residence
 366 time of seeping crater lake water of 3 to 17 years was deduced (Rowe *et al.*, 1995). Our
 367 estimate of 30 months seems reasonable considering that the Poás fluids need to travel a
 368 larger horizontal distance (3.25 km vs 1.5 km at El Chichón). The only tritium value for
 369 the Agua Caliente spring at El Chichón (2.4 T.U. in 1998) corresponds well with the
 370 values for Central America in the 1970's (2.6 T.U., as reported in Rowe *et al.*, 1995),
 371 suggesting that in 1998 the aquifer feeding the AC spring had an age of 20-25 years in
 372 1998. Crater lake water in 1998 showed lower tritium isotopic values (1.3 T.U.)
 373 corresponding with meteoric waters (1.1 T.U. for Agua Roja cold spring water).

374

375 4.2.3 Chemical distribution of rock forming elements

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

380

$$381 \quad (RFE/Mg)_w / (RFE/Mg)_r \quad (2)$$

382

383 With RFE each rock forming element (including S and Cl); subscript w stands for water, r
 384 for rock. We choose Mg to normalize because it is well-reserved in acidic sulphate-rich
 385 solutions (Giggenbach, 1974; Delmelle and Bernard, 1994; Pasternack and Varekamp,
 386 1994; Takano *et al.*, 2004). The crater lake, AC and AT2 waters roughly follow the same
 387 element distribution (Fig. 9). Sulphur is relatively enriched with respect to the other

388 RFEs, confirming anhydrite leaching. The acidic crater lake water is more efficient in
389 leaching Cu, Co, and V from rocks or sediments.

390 A remarkable difference exists in the distribution of Cu and Zn between the AC and AT2
391 spring waters (Fig. 9): Cu and Zn are depleted in AC waters, with respect to AT2. At AC
392 bubbling degassing takes place, accompanied by an H₂S smell, features absent at AT2.
393 The entrance of H₂S creates reduced environments adapted to sink Cu and Zn as sulfides.
394 The turquoise colour at the head of the AT2 spring might be due to a Cu enrichment. At
395 the AC, and more downstream at the AT2 stream, massive Fe-oxy-hydroxides form,
396 indicating strongly oxidized conditions, responsible for the Fe depletion. This effect is
397 stronger at AT2.

398 It is highlighted in Fig. 9 that As is depleted in the AC spring with respect to the crater
399 lake water. Under acidic oxidized conditions (\approx crater lake) As is stable as H₃AsO_{4(a)}, and
400 thus remains in solution. On the other hand, under near-neutral reduced conditions (\approx AC
401 spring outlet) As will precipitate as As₃S₃ (Aiuppa *et al.*, 2000). Moreover, As co-
402 precipitates with or adsorbs on Fe-oxy-hydroxides (Fig. 9) (Ballantyne and Moore, 1988;
403 Aiuppa *et al.*, 2003).

404

405 **5. Conceptual models: present and future state of the El Chichón volcano-** 406 **hydrothermal system**

407 5.1 The crater lake-Soap Pool system

408 For the first time since the observations started in 1995 (Taran *et al.*, 1998), a
409 relationship with the annual rainfall distribution is noticed. In January-April 2001, March-
410 June 2004 and March 2007 a large volume lake was observed. It is a fact that since 2001,
411 every three years, a few months after the rainy season (June-October), the SP spring
412 enters in a high water discharge activity, responsible for the lake growth and consecutive
413 increase in Cl content in the lake water. Considering an average rainfall flux of 1.34×10^{-4}

414 $\text{kgm}^{-2}\text{s}^{-1}$ (Rouwet *et al.*, 2004), the total volume of rainwater accumulated during a time
415 span of three years beneath the crater floor ($\sim 8 \times 10^5 \text{ m}^3$) is in the order of 10^7 m^3 . This can
416 be considered the maximum volume of the shallow boiling aquifer beneath the 1982
417 crater floor, because part of the infiltrating rainwater dissipates in the volcanic edifice.

418 Geothermometry suggests boiling processes at shallow depth beneath the crater floor
419 ($115\text{-}130^\circ\text{C}$). Fluid migration takes place inside the heterogeneous shallow aquifer,
420 testified by rumbling and low frequency noise. Such rumbling has been observed at other
421 active volcano-hydrothermal systems such as e.g. Kusatsu-Shirane volcano, the host of
422 the Yugama crater lake, where steam-driven explosive activity was common in the 1970's
423 and 80's (Ohba *et al.*, 2008). Thus, these features at El Chichón can be interpreted as
424 small steam-driven phreatic explosions inside the shallow aquifer. Considering that the
425 lake volume strongly depends on the SP water input, the slight increase of the maximum
426 lake volume observed through 2001, 2004 and 2007 (Fig. 5) could demonstrate an
427 increase in volume of the shallow aquifer feeding the SP geyser.

428

429 5.2 The deep geothermal aquifer

430 We found arguments in favour of a small degree of crater lake seepage into the S-SE deep
431 geothermal aquifer ($\sim 200 \text{ m}$) reaching the AC and, in probably lower proportion, the AT2
432 springs. Crater lake seepage towards the S of the volcano might be enhanced by the
433 morphology of the southern rim of the Somma crater, opening into a big "barranca"
434 ending into the AT2 canyon. The horse-shoe shaped explosion crater at AC could be
435 another morphological weakness, enhancing lateral and downward fluid flow. The seeped
436 crater lake water is thought to reach the AC springs in ~ 30 months, a reasonable residence
437 time to migrate along a distance of $\sim 1.5 \text{ km}$ for a height difference of $\sim 200 \text{ m}$. This effect
438 has been seen for the June 2004 crater lake infiltration, when lake volume was high
439 ($\sim 5 \times 10^5 \text{ m}^3$, Table 2). When the crater lake level is high, more permeable parts of the

440 crater floor are flooded than at low crater lake level: the constantly covered lake bottom is
441 composed of sealing clays, while near the coast of the lake, the lake bottom floor is
442 composed of pumiceous permeable sediments (Fig. 11). High level lakes thus tend to
443 infiltrate preferentially (Fig. 11). If this mechanism is a fact, the March 2007 crater lake
444 will have reached the AC springs by the autumn of 2009. Trace element contents in a
445 large volume lake are generally higher than in a small volume lake. A monitoring with
446 time of the RFE patterns between the lake and spring waters will contradict or affirm the
447 here proposed lake seepage. The Cl/SO₄ ratio in both lake and AC waters has shown to be
448 variable with time and tracing this parameter will be less efficient to detect possible lake
449 seepage. Moreover, estimates of important parameters of the physical properties (i.e.
450 hydraulic conductivity, active porosity, permeability, etc.) of the volcanic edifice still
451 lack, and are necessary to establish a hydrogeochemical modelling of the entire El
452 Chichón volcano-hydrothermal system. The AT2 springs, at the foot of the SW dome, are
453 fed by the same deep geothermal aquifer. This aquifer is formed as the result of the
454 permeability decrease at the contact between the volcanic edifice and the basement rocks.
455 The main heat source beneath El Chichón is probably long-lived and stable, as spring
456 temperatures have not changed since the late 1970's. The remains of the 1982 magma is
457 an additional heat source. No chemical evidence exists on the location of any heat source
458 or a high temperature degassing magma body. Moreover, the normal faults could serve as
459 upward migration pathways for deep Cl-rich fluids, frequently present at hydrothermal
460 systems (e.g. Pinatubo volcano; Stimac *et al.*, 2004). The Cl from the deep geothermal
461 aquifer probably originates partly from the same evaporites (~Cl/Br ratios). The current
462 uncertainty on an additional Cl input at the crater system still points to a possible masking
463 effect of the deep geothermal aquifer to absorb all rising (magmatic?) Cl before reaching
464 the crater area. That is the reason why we believe dome intrusion will probably be

465 anticipated by chemical changes in the thermal springs, even before modifying crater lake
466 dynamics and chemistry of gas emissions.

467

468 **6. Conclusions**

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

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

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

491 **ACKNOWLEDGEMENTS**

492 We thank the “*Belgische Stichting Roeping*” (<http://www.stichtingroeping.be/>) for their
493 moral and financial support. F. Sanchez and family for logistic support. Protección Civil
494 and the Gobierno Municipal of Chapultenango (Chiapas) for their support and additional
495 sampling (January 2007). M. Iorio and D. Polgovsky for support in the field.

496

497 **BIBLIOGRAPHY**

498

499 AIUPPA, A., P. ALLARD, W. D’ALESSANDRO, A. MICHEL, F. PARELLO, M.
500 TREUIL and M. VALENZA, 2000. Mobility and fluxes of major, minor and trace metals
501 during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily).
502 *Geochim. Cosmochim. Acta*, 64, 1827-1841.

503

504 AIUPPA, A., W. D’ALESSANDRO, C. FEDERICO, B. PALUMBO and M. VALENZA,
505 2003. The aquatic geochemistry of arsenic in volcanic groundwaters from southern Italy.
506 *Appl. Geochem.* 18, 1283-1296.

507

508 BALLANTYNE, J. M. and J. N. MOORE, 1988. Arsenic geochemistry in geothermal
509 systems. *Geochim. Cosmochim. Acta*, 52, 475-483.

510

511 BÖHLKE, J. K. and J. J. IRWIN, 1992. Laser microprobe analyses of Cl, Br, I and K in
512 fluid inclusions: implications for sources of salinity in some ancient hydrothermal fluids.
513 *Geochim. Cosmochim. Acta*, 56, 203-225.

514

515 CAPACCIONI, B., Y. TARAN, F. TASSI, O. VASELLI, G. MANGANI and J. L.
516 MACIAS, 2004. Source conditions and degradation processes of light hydrocarbons in
517 volcanic gases: an example from El Chichón volcano (Chiapas State, Mexico). *Chem.*
518 *Geol.*, 206, 81-96.

519

520 CASADEVALL, T. J., S. DE LA CRUZ-REYNA, W. I. ROSE, S. BAGLEY, D. L.
521 FINNEGAN, and W. H. ZOLLER, 1984. Crater lake and post-eruption hydrothermal
522 activity, El Chichón volcano, Mexico. *J. Volcanol. Geotherm. Res.*, 23, 169-191.

523

524 CHRISTENSON, B. W., 2000. Geochemistry of fluids associated with the 1995-1996
525 eruption of Mt. Ruapehu, New Zealand: signatures and processes in the magmatic
526 hydrothermal system. *J. Volcanol. Geotherm. Res.*, 97, 1-30.

527

528 DAMON, P. and E. MONTESINOS, 1978. Late Cenozoic Volcanism and metallogenesis
529 over an active Benioff Zone in Chiapas, Mexico. *Arizona Geol. Soc. Digest.*, 11, 155-168.

530

531 DEELY, J. M. and D. S. SHEPPARD, 1996. Whangaehu River, New Zealand:
532 geochemistry of a river discharging from an active crater lake. *Appl. Geochem.*, 11, 447-
533 460.

534

535 DELMELLE, P. and A. BERNARD, 1994. Geochemistry, mineralogy, and chemical
536 modeling of the acid crater lake of Kawah Ijen Volcano, Indonesia. *Geochim.
537 Cosmochim. Acta*, 58, 2445-2460.

538

539 DELMELLE, P. and A. BERNARD, 2000. Downstream composition changes of acidic
540 volcanic waters discharged into the Banyupahit stream, Ijen Caldera, Indonesia. *J.
541 Volcanol. Geotherm. Res.*, 97, 55-75.

542

543 DUFFIELD, W. A., R. I. TILLING and R. CANUL, 1984. Geology of El Chichón
544 Volcano, Chiapas, Mexico. *J. Volcanol. Geotherm. Res.*, 20, 117-132.

545

546 ESPÍNDOLA, J. M., J. L. MACÍAS, R. I. TILLING and M. F. SHERIDAN, 2000.
547 Volcanic history of El Chichón Volcano (Chiapas, Mexico) during the Holocene, and its
548 impact on human activity. *Bull. Volcanol.*, 62, 90-104.

549 GIGGENBACH, W. F., 1974. The chemistry of Crater Lake, Mt. Ruapehu (New
550 Zealand) during and after the 1971 active period. *N. Z. J. Sci.*, 17, 33-45.

551

552 GIGGENBACH, W. F., 1988. Geothermal solute equilibria. Derivation of Na-K-Mg-Ca
553 geoindicators. *Geochim. Cosmochim. Acta*, 52, 2749-2765.

554

555 HENLEY, R. W., A. H. TRUESDELL, P. B. BARTON and J. A. WHITNEY, 1984.
556 Fluid-mineral equilibria in hydrothermal systems. *Reviews in economic geology Vol.1.*

557

558 KEMPTER, K. A. and G. L. ROWE, 2000. Leakage of Active Crater Lake brine through
559 the north flank at Rincón de la Vieja volcano, northwest Costa Rica, and implications for
560 crater collapse. *J. Volcanol. Geotherm. Res.*, 97, 143-159.

561

562 LÖHR, A. J., T. A. BOGAARD, A. HEIKENS, M. R. HENDRIKS, S. SUMARTI, M. J.
563 VAN BERGEN, C. A. M. VAN GESTEL, N. M. VAN STRAALEN, P. Z. VROON and
564 B. WIDIANARKO, 2005. Natural Pollution Caused by the Extremely Acidic Crater Lake
565 Kawah Ijen, East Java, Indonesia. *Environ. Sci. & Pollut. Res.*, 12, 89-95.

566

567 LUHR, J. F., I. S. E. CARMICHAEL and J. C. VAREKAMP, 1984. The 1982 eruptions
568 of El Chichón volcano, Chiapas, Mexico: Mineralogy and petrology of the anhydrite-
569 bearing pumices. *J. Volcanol. Geotherm. Res.*, 23, 69-108.

570

571 LAYER, P. W., J. L. MACIAS, D. JONES, A. GARCIA-PALOMO, J. L. ARCE and J.
572 C. MORA, 2008. El Chichón Volcanic Complex, Chiapas, Mexico: stages of evolution
573 based on field mapping and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. *Geofís. Int.*, this volume.

574

575 MAZOT, A. and Y. TARAN, 2008. CO₂ flux from the crater lake of El Chichón volcano
576 (México). *Geofís. Int.*, this volume.

577

578 MOLINA BERBEYER, R., 1974. Informe preliminary geoquímico de los fluidos
579 geotérmicos del volcán del Chichonal, Chiapas. *Comisión Federal de Electricidad*,
580 *Internal report*, pp. 5.

581

582 OHBA, T., J. HIRABAYASHI and K. NOGAMI, 1994. Water, heat and chlorine budgets
583 of the crater lake, Yugama at Kusatsu-Shirane volcano, Japan. *Geochem. J.*, 28, 217-231.

584

585 OHBA, T., J. HIRABAYASHI and K. NOGAMI, 2000. D/H and $^{18}\text{O}/^{16}\text{O}$ ratios of water
586 in the crater lake at Kusatsu-Shirane volcano, Japan. *J. Volcanol. Geotherm. Res.*, 97,
587 329-346.

588

589 OHBA, T., J. HIRABAYASHI and K. NOGAMI, 2008. Temporal changes in the
590 chemistry of lake water within Yugama Crater, Kusatsu-Shirane Volcano, Japan:

- 591 Implications for the evolution of the magmatic hydrothermal system. *J. Volcanol.*
592 *Geotherm. Res., Special volume on Crater Lakes ed. Varekamp and van Bergen.*
593
- 594 PASTERNAK, G. B. and J. C. VAREKAMP, 1994. The geochemistry of the Keli Mutu
595 crater lakes, Flores, Indonesia. *Geochem. J.*, 28, 243-262.
596
- 597 ROUWET, D., 2006. Estudio geoquímico comparativo de los sistemas hidrotermales de
598 los volcanes activos en Chiapas: El Chichón y Tacaná. *PhD. Dissertation, IGF-UNAM,*
599 pp. 218.
600
- 601 ROUWET, D., Y. A. TARAN and N. R. VARLEY, 2004. Dynamics and mass balance of
602 El Chichón crater lake, Mexico. *Geofis. Int.*, 43, 427-434.
603
- 604 ROUWET, D., Y. TARAN, S. INGUAGGIATO, N. VARLEY and J. A. SANTIAGO S.,
605 2008. Hydrochemical dynamics of the “lake-spring” system in the crater of El Chichón
606 volcano (Chiapas, Mexico). *J. Volcanol. Geotherm. Res., Special volume on Crater Lakes*
607 *ed. Varekamp and van Bergen.*
608
- 609 ROWE JR., G. L., S. L. BRANTLEY, J. F. FERNANDEZ and A. BORGIA, 1995. The
610 chemical and hydrologic structure of Poás Volcano, Costa Rica. *J. Volcanol. Geotherm.*
611 *Res.*, 64, 233-267.
612
- 613 SANFORD, W. E., L. KONIKOW, G. ROWE and S. BRANTLEY, 1995. Ground-water
614 transport of crater-lake brine at Poás Volcano, Costa Rica. *J. Volcanol. Geotherm. Res.*,
615 64, 271-297.
616
- 617 SRIWANA, T., M. J. VAN BERGEN, S. SUMARTI, J. C. M. DE HOOG, B. J. H. VAN
618 OS, R. WAHYUNINGSIH and M. A. C. DAM, 1998. Volcanogenic pollution by acid
619 water discharges along Ciwidey River, West Java (Indonesia). *J. Geochem. Explor.*, 62,
620 161-182.
621
- 622 STIMAC, J. A., F. GOFF, D. COUNCE, A. C. L. LAROCQUE, D. R. HILTON and U.
623 MORGENSTERN, 2004. The crater lake and hydrothermal system of Mount Pinatubo,
624 Philippines: evolution in the decade after eruption. *Bull. Volcanol.*, 66, 149-167.

- 625 SYMONDS, R. B., W. I. ROSE, M. H. REED, F. E. LICHTER and D. L. FINNEGAN,
626 1987. Volatilization, transport and sublimation of metallic and non-metallic elements in
627 high temperature gases at Merapi Volcano, Indonesia. *Geochim. Cosmochim. Acta*, 51,
628 2038-2101.
- 629
- 630 TAKANO, B., 1987. Correlation of volcanic activity with sulfur oxy-anion speciation in a
631 crater lake. *Science*, 235, 1633-1635.
- 632
- 633 TAKANO, B., K. SUZUKI, K. SUGIMORI, T. OHBA, S. M. FAZLULLIN, A.
634 BERNARD, S. SUMARTI, R. SUKHYAR and M. HIRABAYASHI, 2004. Bathymetric
635 and geochemical investigation of Kawah Ijen Crater Lake, East Java, Indonesia. *J.*
636 *Volcanol. Geotherm. Res.*, 135, 299-329.
- 637
- 638 TARAN, Y., T. P. FISCHER, B. POKROVSKY, Y. SANO, M. A. ARMIENTA and J. L.
639 MACIAS, 1998. Geochemistry of the volcano-hydrothermal system of El Chichón
640 Volcano, Chiapas, Mexico. *Bull. Volcanol.*, 59, 436-449.
- 641
- 642 TARAN, Y. A., J. W. HEDENQUIST, M. A. KORZHINSKY, S. I. TKACHENKO and
643 K. I. SHMULOVICH, 1995. Geochemistry of magmatic gases from Kudriavy Volcano,
644 Iturup, Kuril Islands. *Geochim. Cosmochim. Acta*, 59, 1749-1761.
- 645
- 646 TARAN, Y.A., and D. ROUWET, 2007. Energy-budget and mass balance estimations of the
647 thermal input to El Chichón crater lake, Mexico. In: *Water-Rock Interaction-12*, 947-951.
- 648
- 649 TARAN, Y., D. ROUWET, S. INGUAGGIATO and A. AIUPPA, 2008. Major and trace
650 element geochemistry of neutral and acidic thermal springs at El Chichón volcano,
651 Mexico. Implications for monitoring of the volcanic activity. *J. Volcanol. Geotherm. Res.*,
652 *Special volume on Crater Lakes ed. Varekamp and van Bergen*.
- 653
- 654 TASSI, F., O. VASELLI, B. CAPACCIONI, J. L. MACÍAS, A. NENCETTI, G.
655 MONTEGROSSI and G. MAGRO, 2003. Chemical composition of fumarolic gases and
656 spring discharges from El Chichón volcano, Mexico: causes and implications of the
657 changes detected over the period 1998-2000. *J. Volcanol. Geotherm. Res.*, 123, 105-121.
- 658

659 TEMPLOS M., L. A., F. MUNGUÍA B. and V. M. BARRERA G., 1981. Observaciones
660 geoquímicas en la zona geotérmica del Chichonal, Chiapas, Mexico. *Comisión Federal de*
661 *Electricidad, Internal report*, pp. 12.

662

663 VAREKAMP, J. C., J. F. LUHR and K. L. PRESTEGAARD, 1984. The 1982 eruptions
664 of El Chichón Volcano (Chiapas, Mexico): Character of the eruptions, ash-fall deposits,
665 and gasphase. *J. Volcanol. Geotherm. Res.*, 23, 39-68.

666

667 VAREKAMP, J. C., A. P. OIUMETTE, S. W. HERMAN, A. BERMUDEZ and D.
668 DELPINO, 2001. Hydrothermal element fluxes from Copahue, Argentina: A “beehive”
669 volcano in turmoil. *Geology*, 29, 1059-1062.

670

671

672

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 (x10⁴ m²)	d (m)	V (x10⁴ m³)	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	3.9	1.0	3.9	-
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	-

1
2
3**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	-	-	-	-	-	-	-

4

5 **FIGURE CAPTIONS**

6

7 Fig. 1

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

16

17 Fig. 2

18 (a) Panoramic view of the 1982 crater from the NE rim, showing the largest lake
 19 ever observed (27/03/2007). The top part of the SW dome peeps over the crater rim.
 20 Soap Pool (SP) site is also indicated. (b) Panoramic view from the southern Somma
 21 crater rim, showing the SW dome and the canyon where AT2 springs discharge. To
 22 the right of the picture, the outside rim of the 1982 crater is shown. (c) The AC
 23 thermal springs and Río Tuspac seen from the Somma crater rim, towards the SE
 24 (27/11/2006). (d) Sampling at the main AC thermal spring (23/11/2006). (e) The
 25 AT2 thermal spring (27/11/2006) discharging at the foot of the SW dome. (Pictures
 26 by M. Jutzeler).

27

28 Fig. 3.

29 $\delta^{18}\text{O}$ vs δD plot for El Chichón thermal spring, cold spring, crater lake and Soap
 30 Pool waters for the period November 2006-October 2007. MWL: Meteoric water

31 line, M: meteoric water at El Chichón. SP: range for Soap Pool spring waters taken
32 from Rouwet *et al.* (2008).

33

34 Fig. 4.

35 Mixing plots for El Chichón thermal waters for the period November 2006-October
36 2007. (a) Cl vs Na, (b) Cl vs K, (c) Cl vs Ca, (d) Cl vs Br.

37

38 Fig. 5.

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

42

43 Fig. 6.

44 Ion concentrations in thermal waters at El Chichón vs the average concentrations in
45 the 1982 trachy-andesitic rocks (taken from Luhr *et al.*, 1984; and Varekamp *et al.*,
46 1984), for (a) the November 2006 crater lake, (b) the March 2007 crater lake, (c)
47 the November 2006 Agua Caliente springs, and (d) the November 2006 Agua Tibia
48 2 springs.

49

50 Fig. 7.

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

54

55

56

57 Fig. 8.

58 Log-log scatter plots for ion contents in thermal waters, showing changes of R^2 with
59 time. (a) November 2006 Agua Caliente spring waters vs the June 2004, March
60 2005 and November 2006 crater lake waters, (b) November 2006 ($T= 46.5^\circ\text{C}$) AT2
61 spring waters vs the June 2004, March 2005 and November 2006 crater lake waters.
62 Pre-2006 data are taken from Rouwet *et al.* (2008).

63

64 Fig. 9.

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

69

70 Fig. 10.

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

75

76 Fig. 11.

77 Model to explain enhanced crater lake seepage during high volume lake situations
78 (2001, 2004 and 2007).

79

80

81

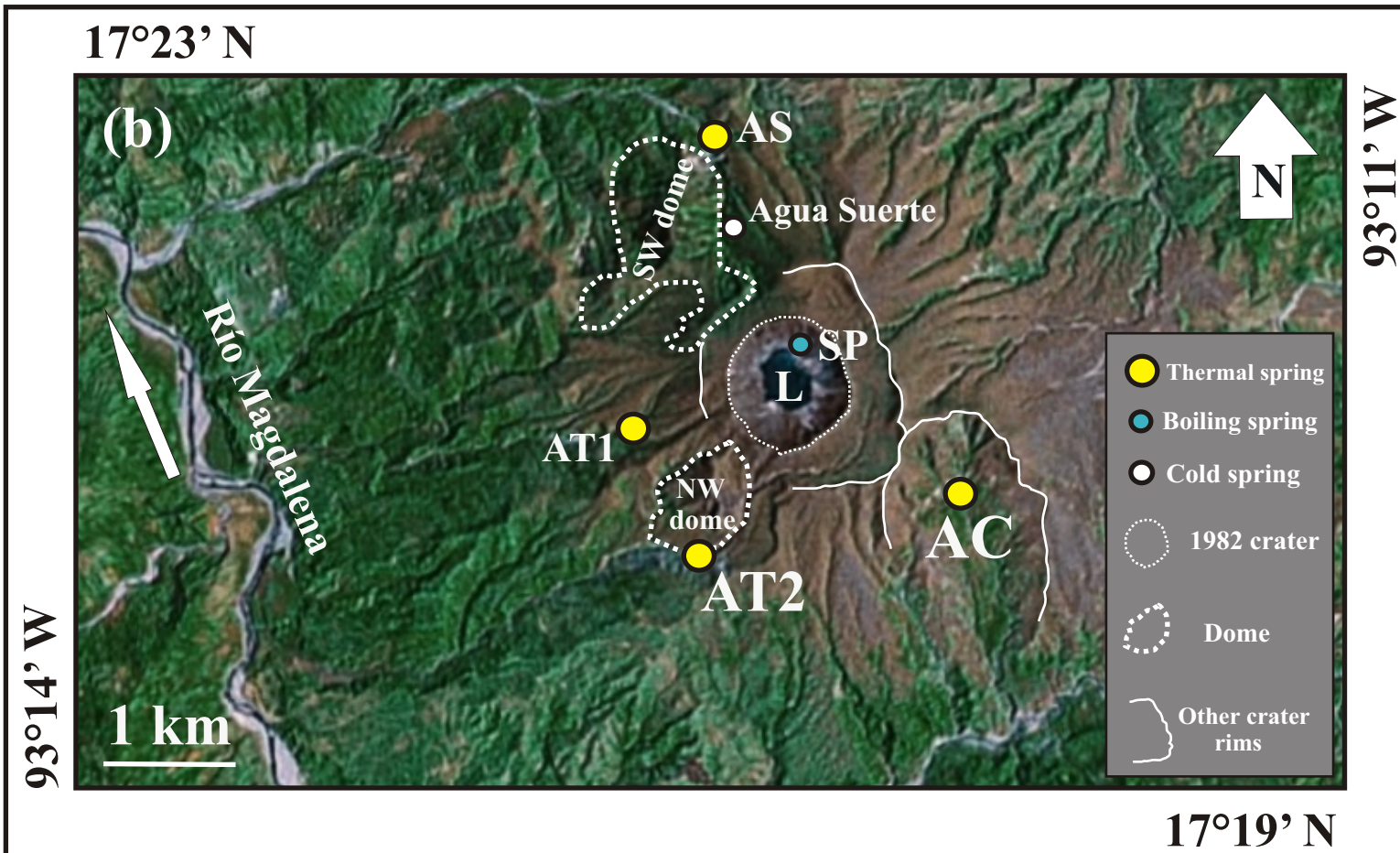
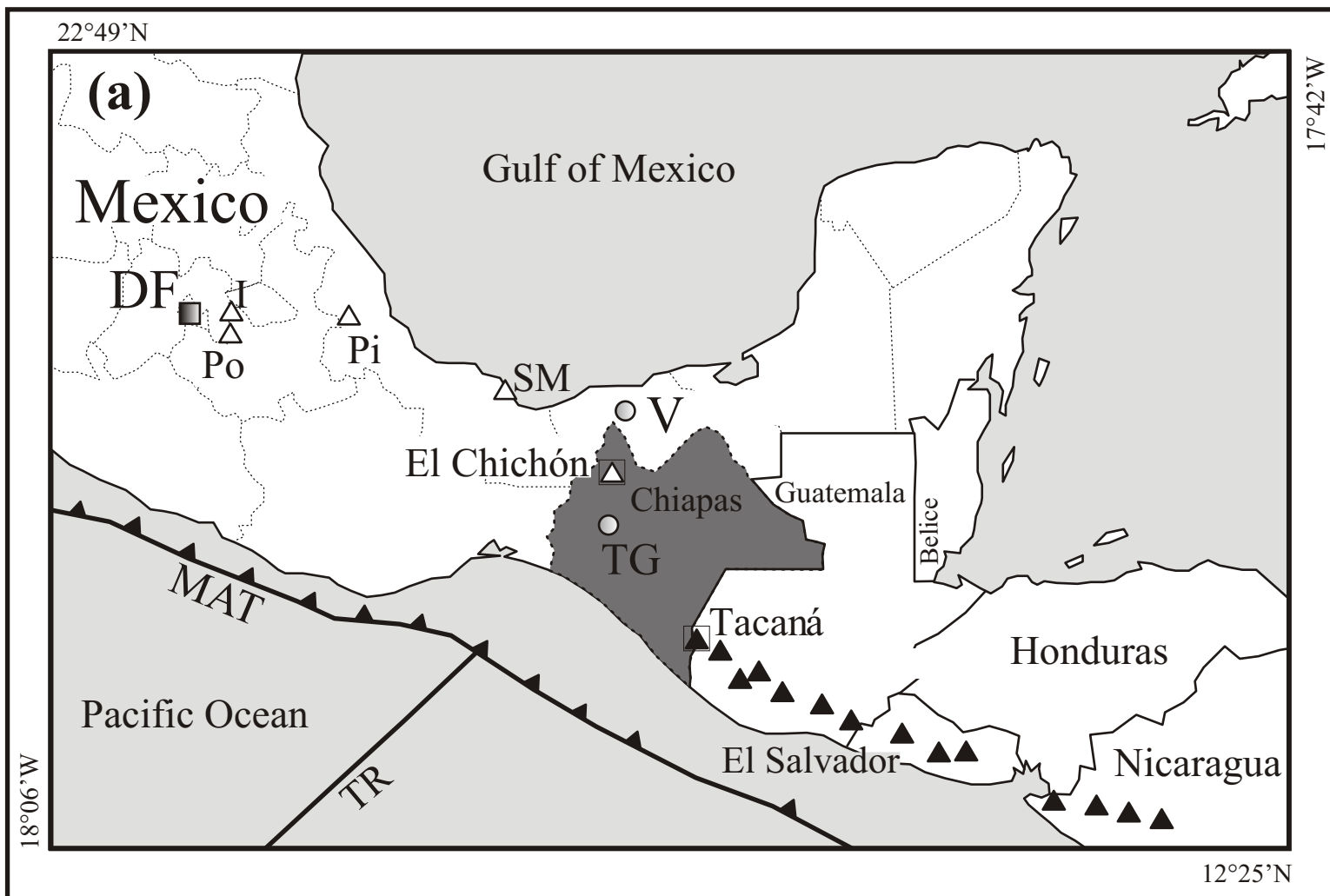


Figure 1. Rouwet et al.



Figure 2. Rouwet et al.

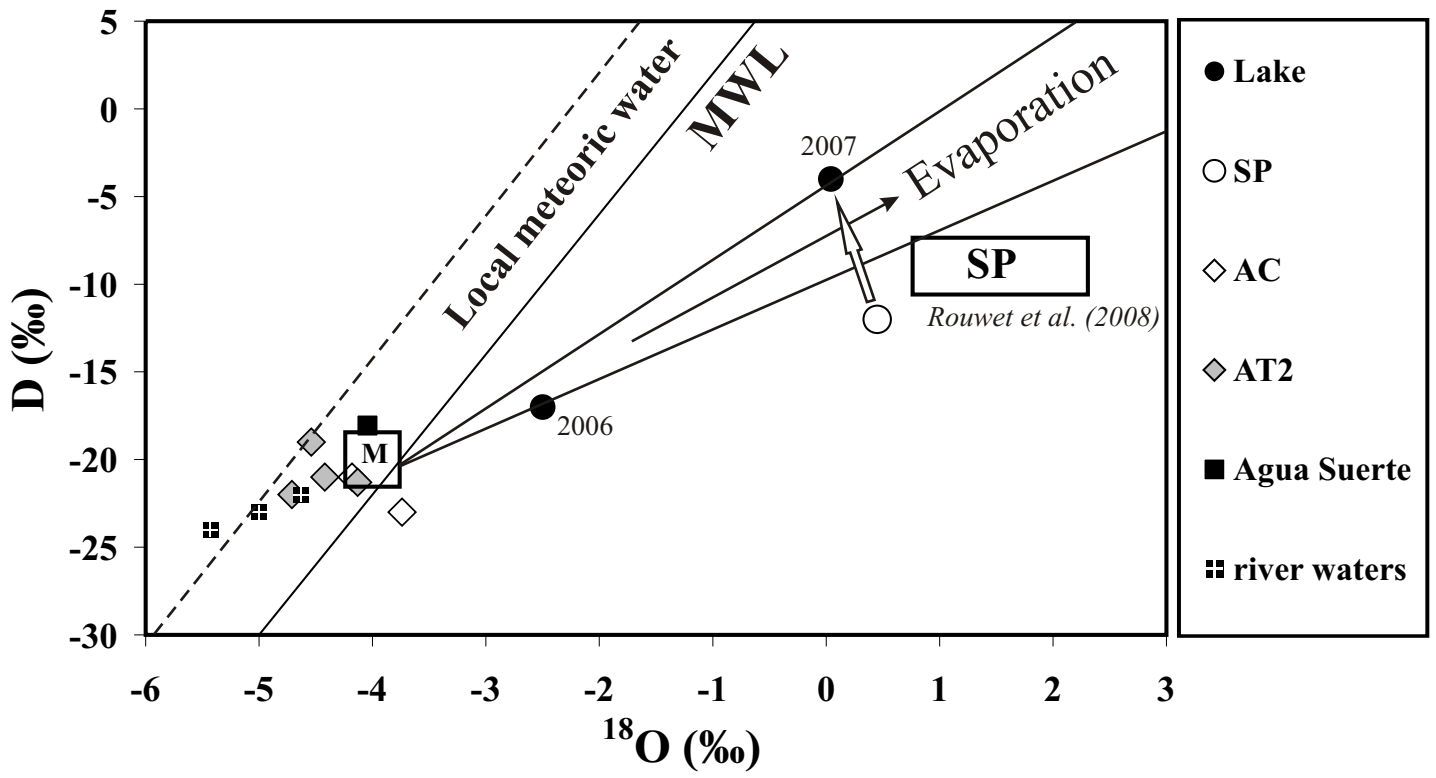


Fig. 3. Rouwet et al.

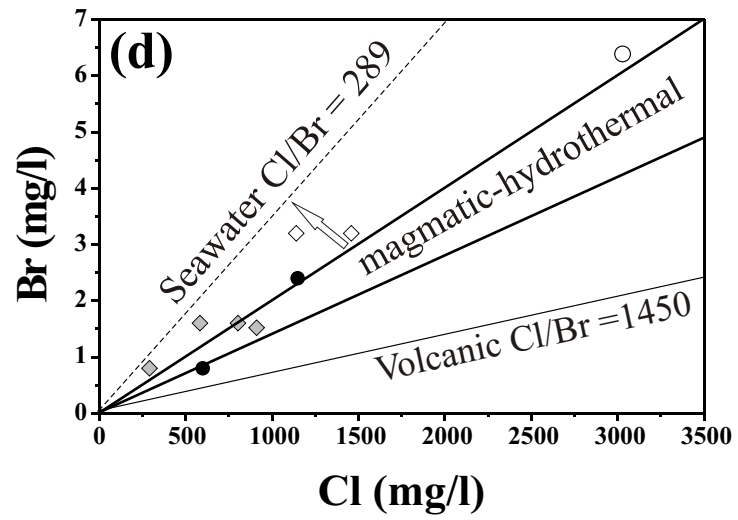
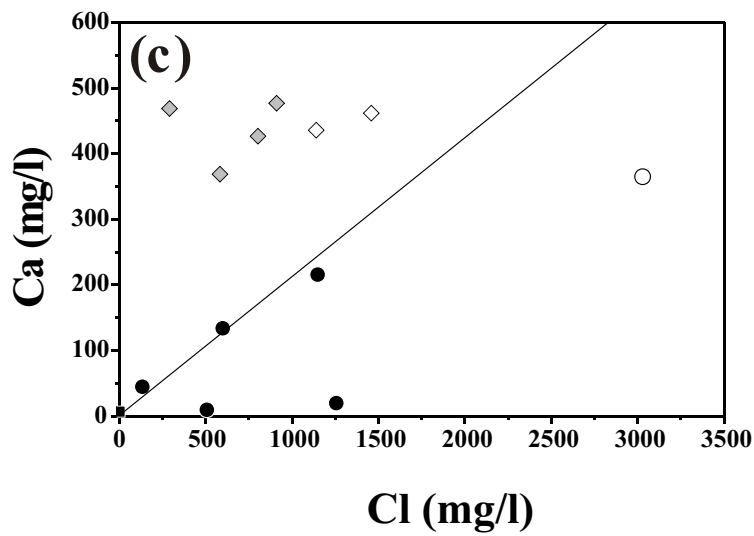
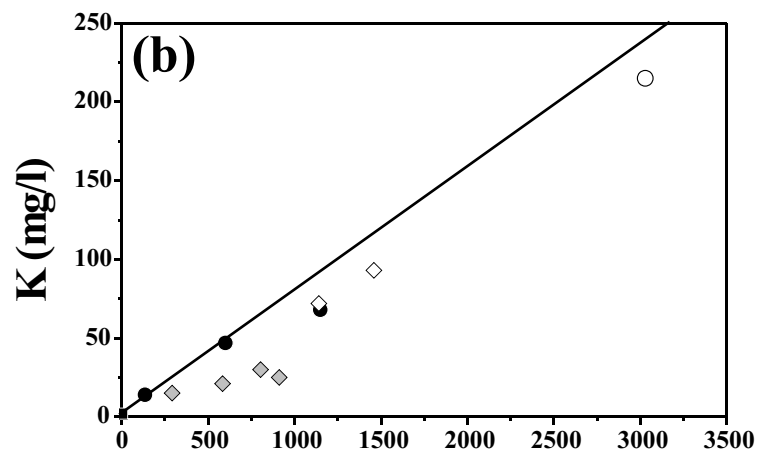
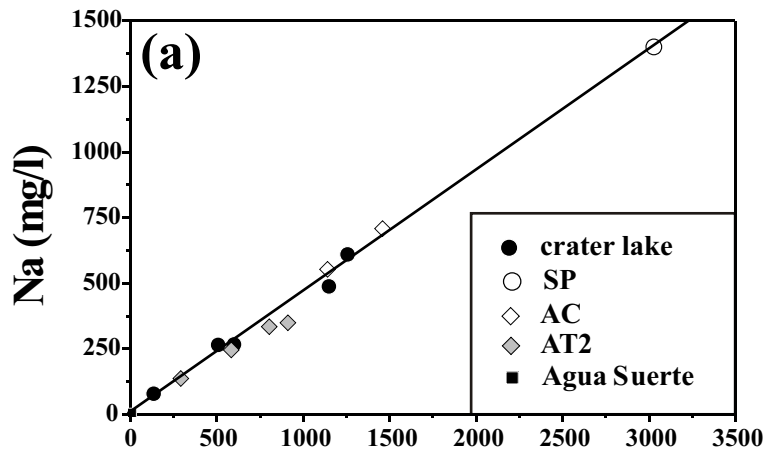
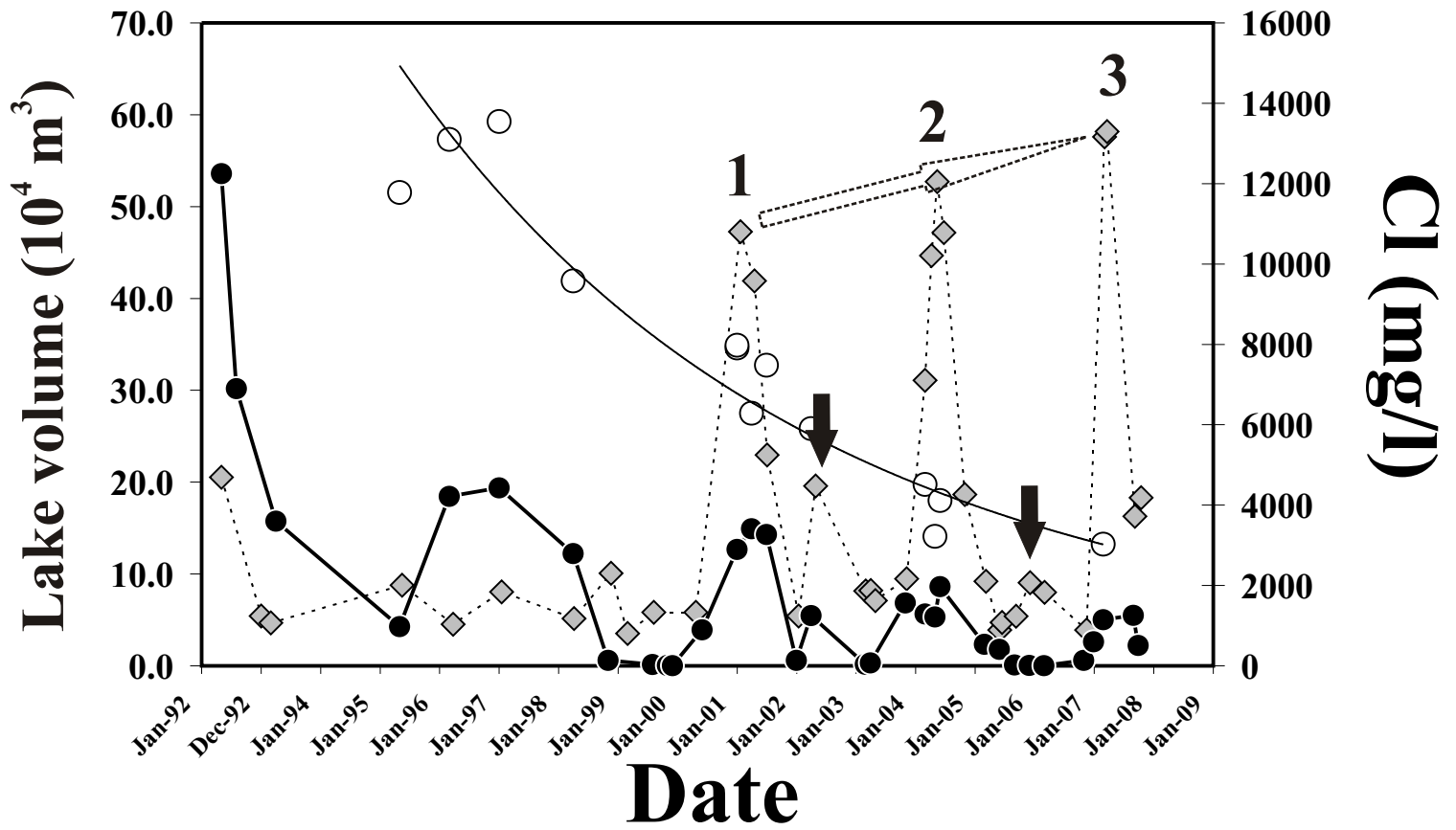


Fig. 4. Rouwet et al.



- Crater lake Cl content
- SP Cl content
- ◇ Crater lake volume

Fig. 5. Rouwet et al.

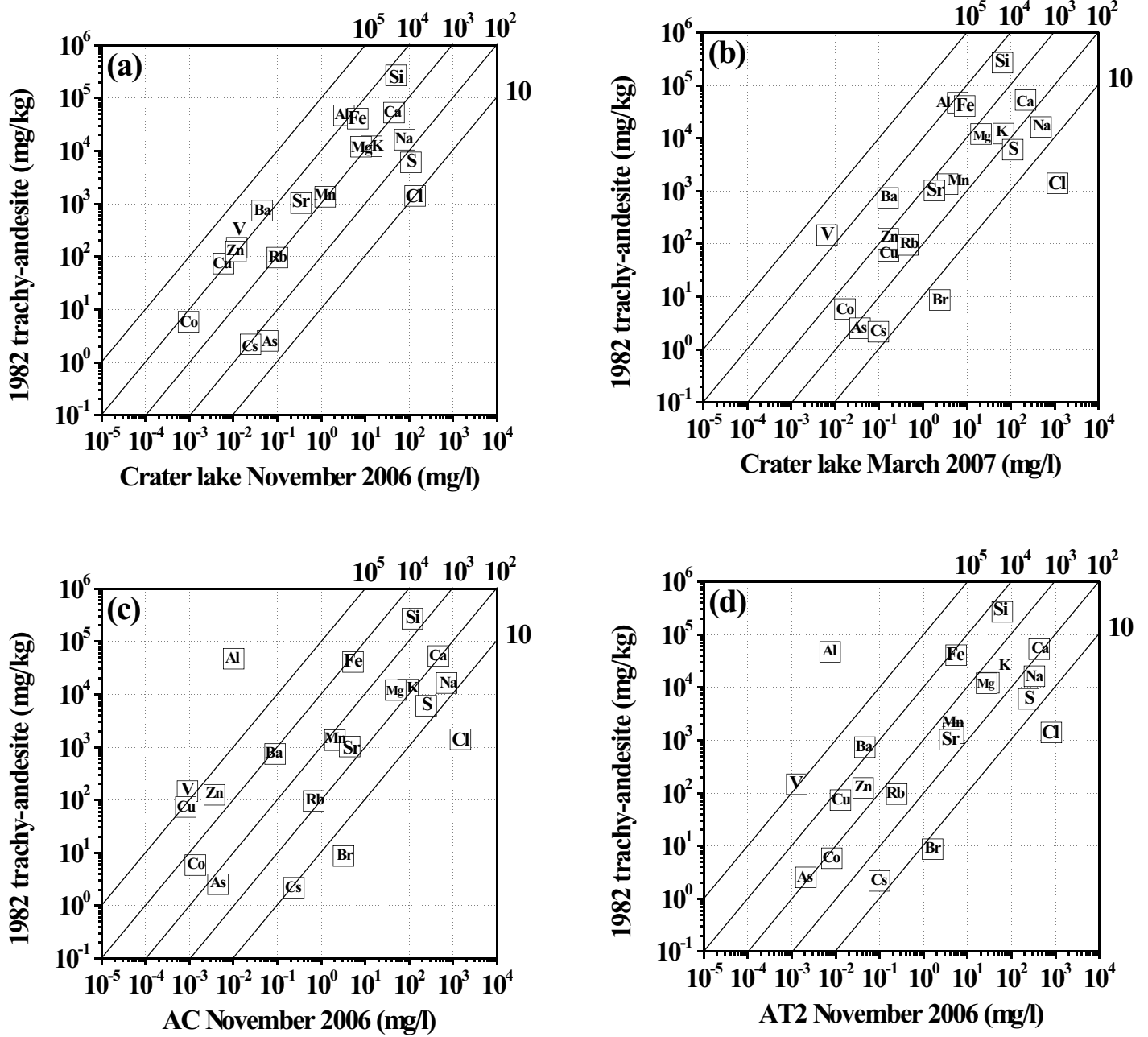


Fig. 6. Rouwet et al.

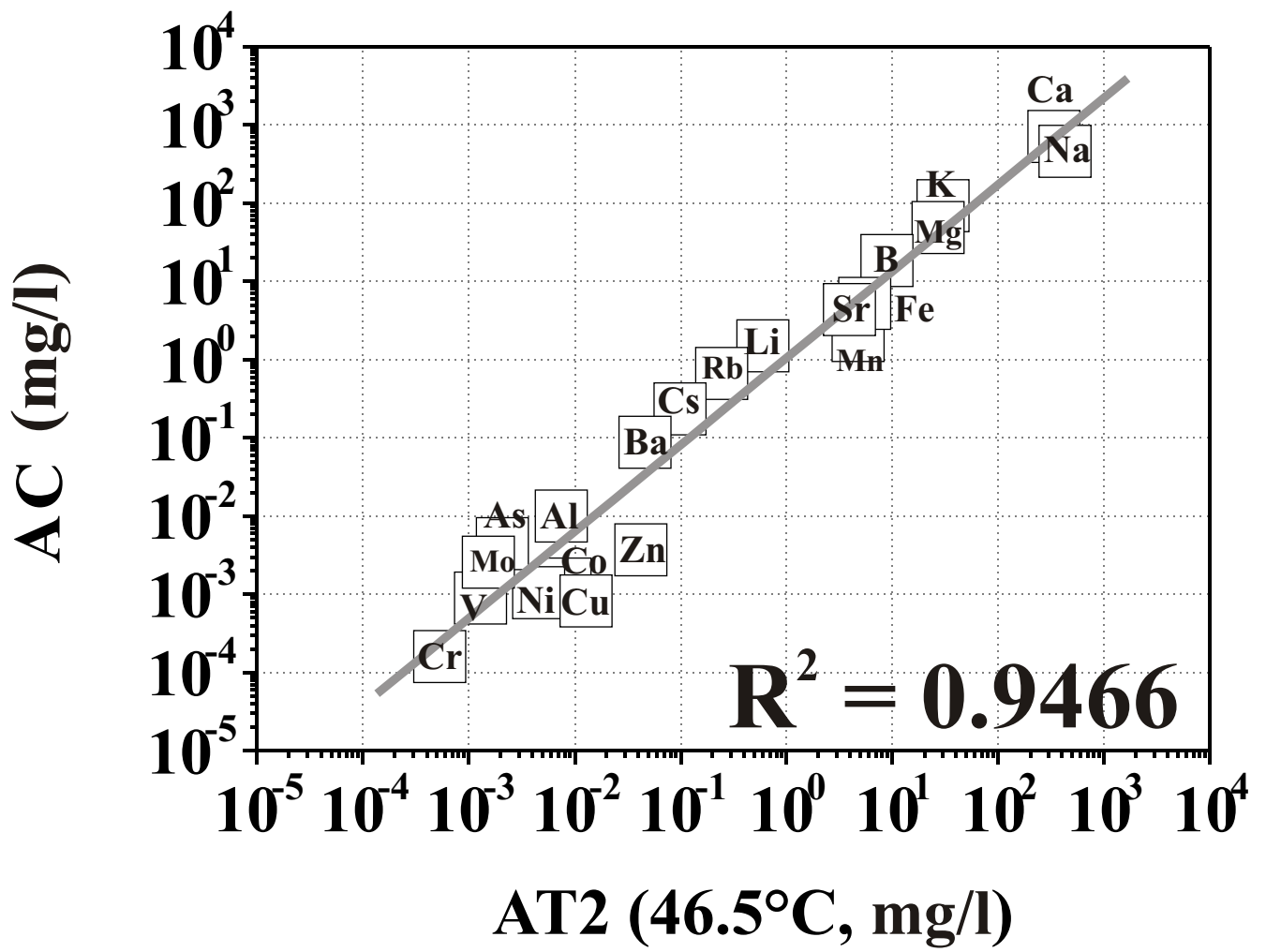


Fig. 7. Rouwet et al.

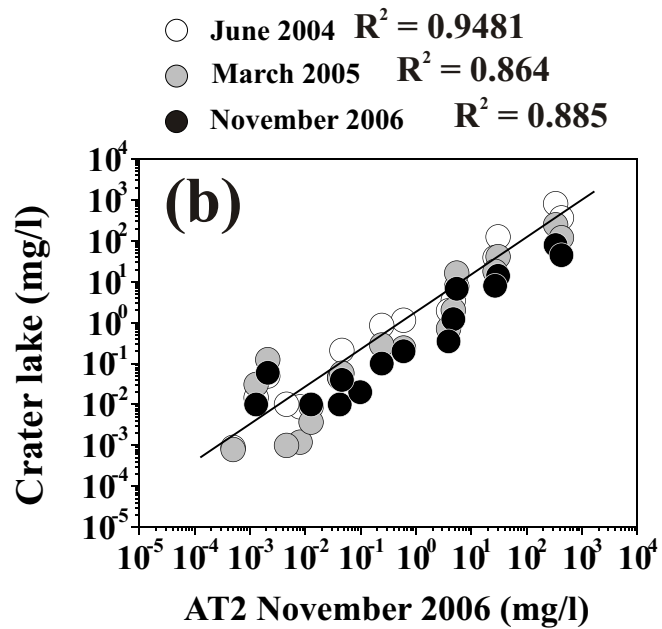
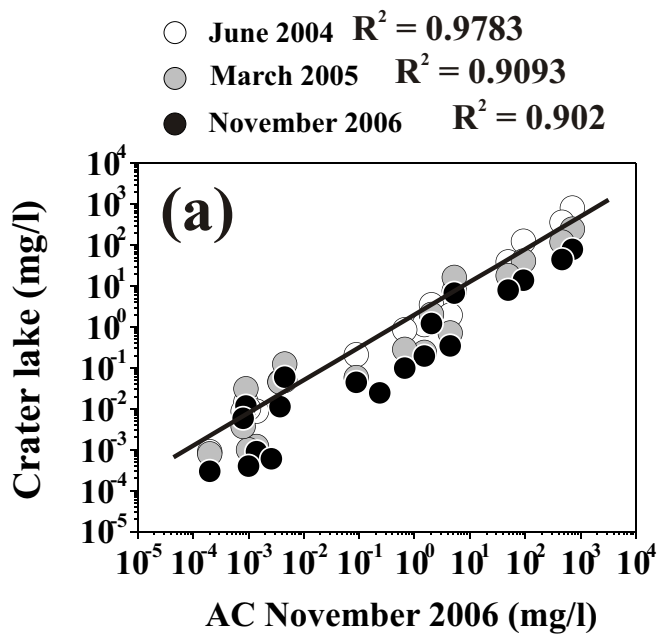


Fig. 8. Rouwet et al.

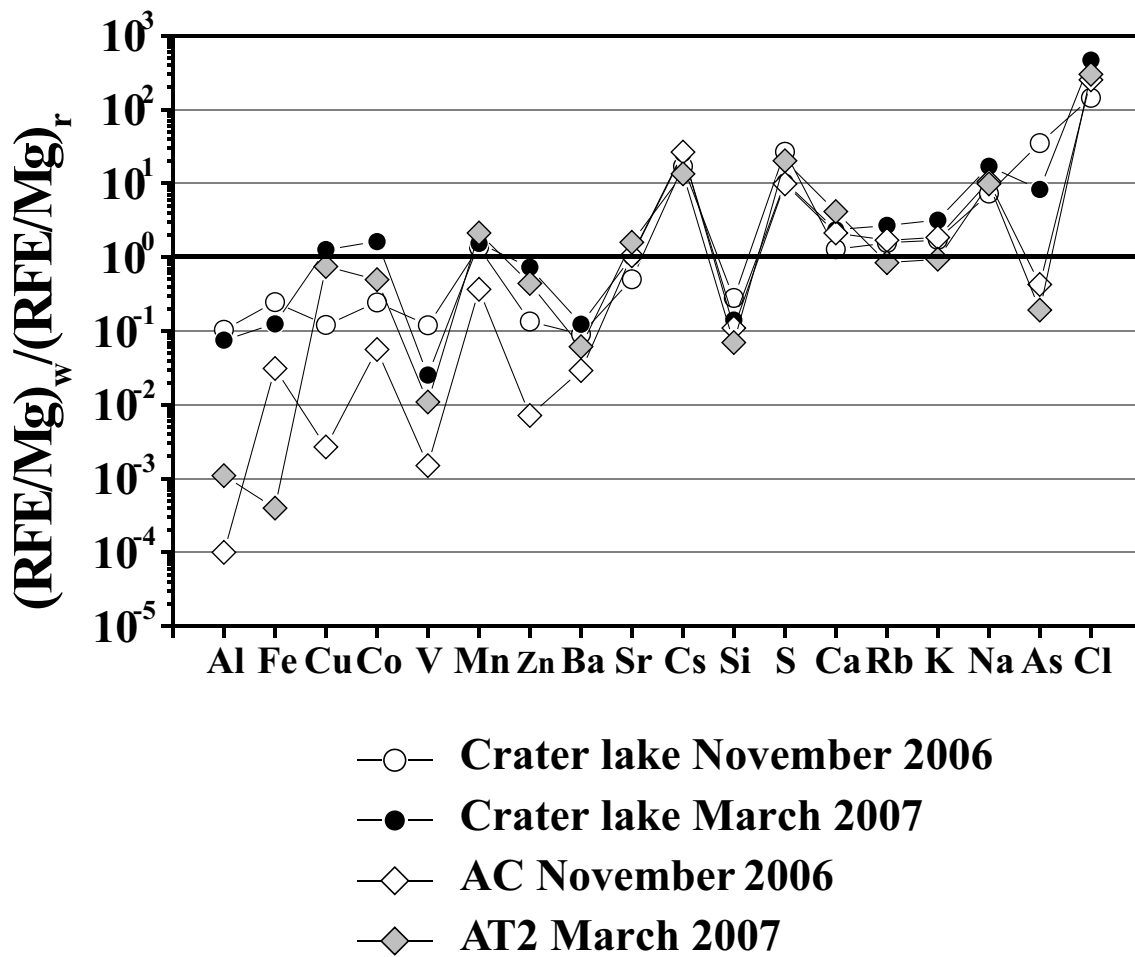


Fig. 9. Rouwet et al.

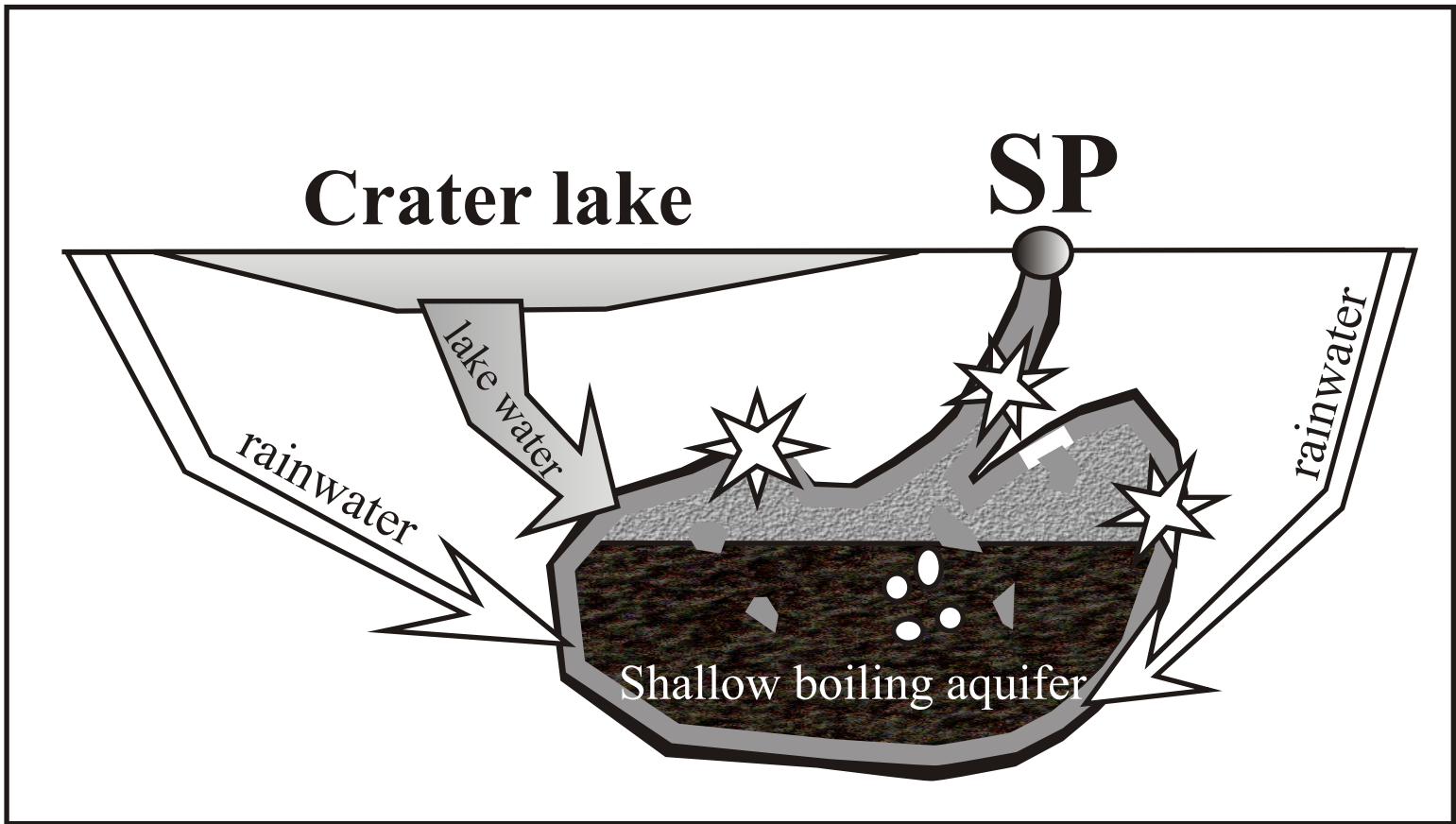


Fig. 10. Rouwet et al.

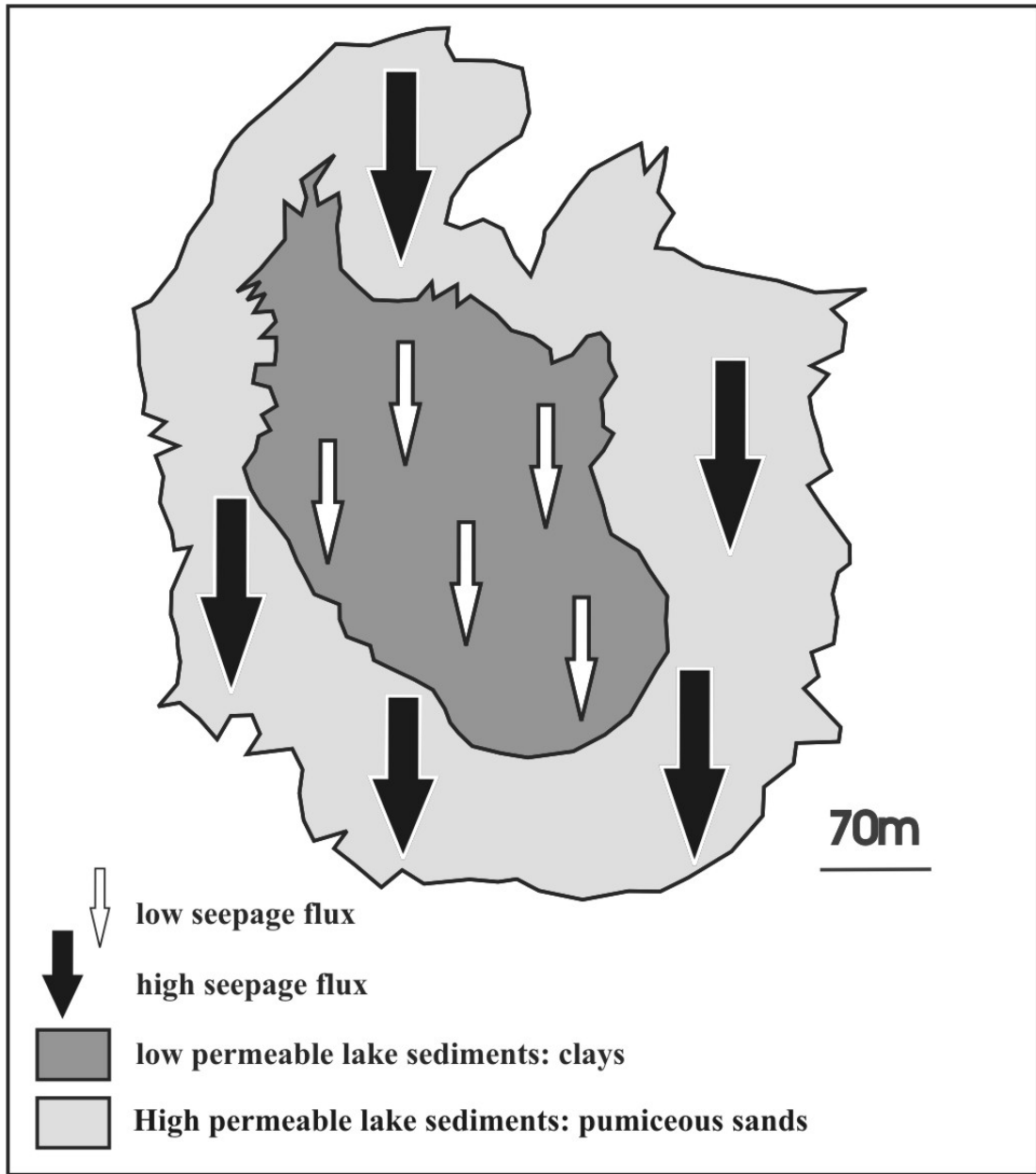


Fig. 11. Rouwet et al.