# Water chemistry of Lake Quilotoa (Ecuador) and assessment of natural hazards

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## Abstract

A geochemical survey carried out in November 1993 revealed that Lake Quilotoa was composed by a thin ($\sim$14 m) oxic epilimnion overlying a $\sim$200 m-thick anoxic hypolimnion. Dissolved $CO_2$ concentrations reached 1000 mg/kg in the lower stratum. Loss of $CO_2$ from epilimnetic waters, followed by calcite precipitation and a consequent lowering in density, was the apparent cause of the stratification.

The Cl, $SO_4$ and $HCO_3$ contents of Lake Quilotoa are intermediate between those of acid–$SO_4$–Cl Crater lakes and those of neutral-$HCO_3$ Crater lakes, indicating that Lake Quilotoa has a 'memory' of the inflow and absorption of HC1- and S-bearing volcanic (magmatic) gases. The Mg/Ca ratios of the lake waters are governed by dissolution of local volcanic rocks or magmas, but K/Na ratios were likely modified by precipitation of alunite, a typical mineral in acid–$SO_4$–Cl Crater lakes.

The constant concentrations of several conservative chemical species from lake surface to lake bottom suggest that physical, chemical and biological processes did not have enough time, after the last overturn, to cause significant changes in the contents of these chemical species. This lapse of time might be relatively large, but it cannot be established on the basis of available data. Besides, the lake may not be close to steady state. Mixing of Lake Quilotoa waters could presently be triggered by either cooling epilimnetic waters by $\sim$4°C or providing heat to hypolimnetic waters or by seismic activity.

Although Quilotoa lake contains a huge amount of dissolved $CO_2$ ($\sim$3 $\times$ 10$^{11}$ g), at present the risk of a dangerous limnic eruption seems to be nil even though some gas exsolution might occur if deep lake waters were brought to the surface. Carbon dioxide could build up to higher levels in deep waters than at present without any volcanic re-awakening, due to either a large inflow of relatively cool $CO_2$-rich gases, or possibly a long interval between overturns. Periodical geochemical surveys of Lake Quilotoa are, therefore, recommended. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Crater lakes frequently contain large amounts of water that can come in contact with ascending magmas, thus causing destructive eruptions (e.g. pyroclastic surges and lahars).

In the late 1980s another danger posed by Crater lakes containing deep, $CO_2$-rich waters became evident. If deep lake waters are displaced towards the surface by an external cause (e.g. landslides, cold rains, strong winds, earthquakes), violent exsolution

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of $CO_2$ can take place. Such a phenomenon, termed limnic eruption (Sabroux et al., 1987) occurred on 21 August 1986 at Lake Nyos (Cameroon), producing a gas cloud that spread into nearby valleys resulting in over 1700 casualties. A similar gas cloud was discharged on 15 August 1984 from Lake Monoun (Cameroon), killing about 40 people (Sigurdsson et al., 1987).

Carbon dioxide might accumulate in deep waters of Lake Quilotoa as well. In fact, high fluxes of $CO_2$ have been measured in the Crater area (Fulvi, 1994) and an inflow of volcanic (magmatic) gases in hypolimnetic waters likely took place in the recent past, as indicated by chemical evidence discussed below. The amount of $CO_2$ potentially involved in the accumulation process is somewhat larger than for Lake Nyos, which has a similar depth but smaller area.

Carbon dioxide release from the lake may have been involved in one or more of the last four recorded events in 1725, 1740, 1759 and 1797 (Simkin and Siebert, 1994). In particular, on the morning of 4 February 1797 as a consequence of an earthquake centered underneath Tunguragua volcano, "flames and suffocating vapors escaped from Lake Quilotoa and killed all the cattle on its shores" (Lyell, 1830). Although the "flames" would seem to imply a volcanic (magmatic) eruption, the absence of deposits argues against such an explanation. Therefore, the 1797 event and possibly the other three 18th century events might have been $CO_2$-driven limnic eruptions.

The present paper is aimed at understanding the evolution of Lake Quilotoa and evaluating the risk of $CO_2$ accumulation in deep waters, using mainly geochemical evidence. This danger is in addition to the serious hazard posed the by interaction of magma with lake water upon possible renewal of volcanic (magmatic) activity.

## 2. Geological framework

Quilotoa volcano is located in the Cotopaxi province ~100 km SW of Quito at 0.85S and 78.90W (Fig. 1a). It is a stratovolcano truncated by a subcircular, 2.4–2.8-km-diameter caldera. Lava domes and thick pyroclastic deposits crop out along the caldera walls, which are generally steep, except in the southwestern sector. The caldera rim is highly irregular and reaches its maximum elevations (3810 m to the N, 3894 m to the NW and 3915 m to the SE) at three lava domes.

Most volcanic products are dacites rich in plagioclase (oligoclase and andesine) and hornblende, accompanied by less abundant biotite, quartz, K-feldspar and rare orthopyroxene (Barbieri, 1996).

Based on $^{14}C$ datings, the last five, highly explosive eruptions of Quilotoa volcano took place $0.8 \pm 0.05$, $14.7 \pm 0.1$, $24.0 \pm 0.3$, $33.7 \pm 0.56$ and $40.0 \pm 0.8$ ky BP (Hall and Mothes, 1992).

The volume of the pyroclastic fall, surge and flow deposits emitted during the last eruption totals 10–14 $km^3$ (Barbieri, 1996). This eruption was characterized by four distinct phases separated by relatively short periods of quiescence. The deposits related to the second phase are very rich of lithics, whose hydrothermal alteration suggests the presence of an active geothermal system. The fourth eruptive phase was phreatomagmatic, indicating that a Crater lake was already present at that time.

The present lake occupies much of the caldera depression and has no inlets or outlets. Its shoreline is elliptical and the two main axes, oriented ESE and NNE, are 1.9 and 1.7 km long. The bathymetric map of the lake (Fig. 1b) shows a series of irregularities as a result of several tectonic features. The lake bottom is made up of two plains separated by a NNE-trending fault escarpment. The northeastern plain has a maximum depth of 256 m, while the southeastern one has an average depth of ~220 m below lake surface, which is located at ~3500 m asl. The total volume of water stored in Lake Quilotoa is ~0.35 $km^3$. According to local inhabitants, the lake level has been slowly declining over the last 10 years. Lacustrine travertine deposits occur along the shore up to ~10 m above the present lake level.

Strong gas emissions in the form of bubble streams are visible near the coast in the southern portion of the Crater lake, along the NNE-trending fault that dissects the lake bottom and the caldera walls. A gas chromatographic analysis of one of these bubbles gave the following results (in $\mu mol/mol$): $CO_2 = 987\,000$; $N_2 = 7700$; $O_2 + Ar = 2700$; $H_2 = 1700$; $CH_4 = 126$; $CO = 3.3$.
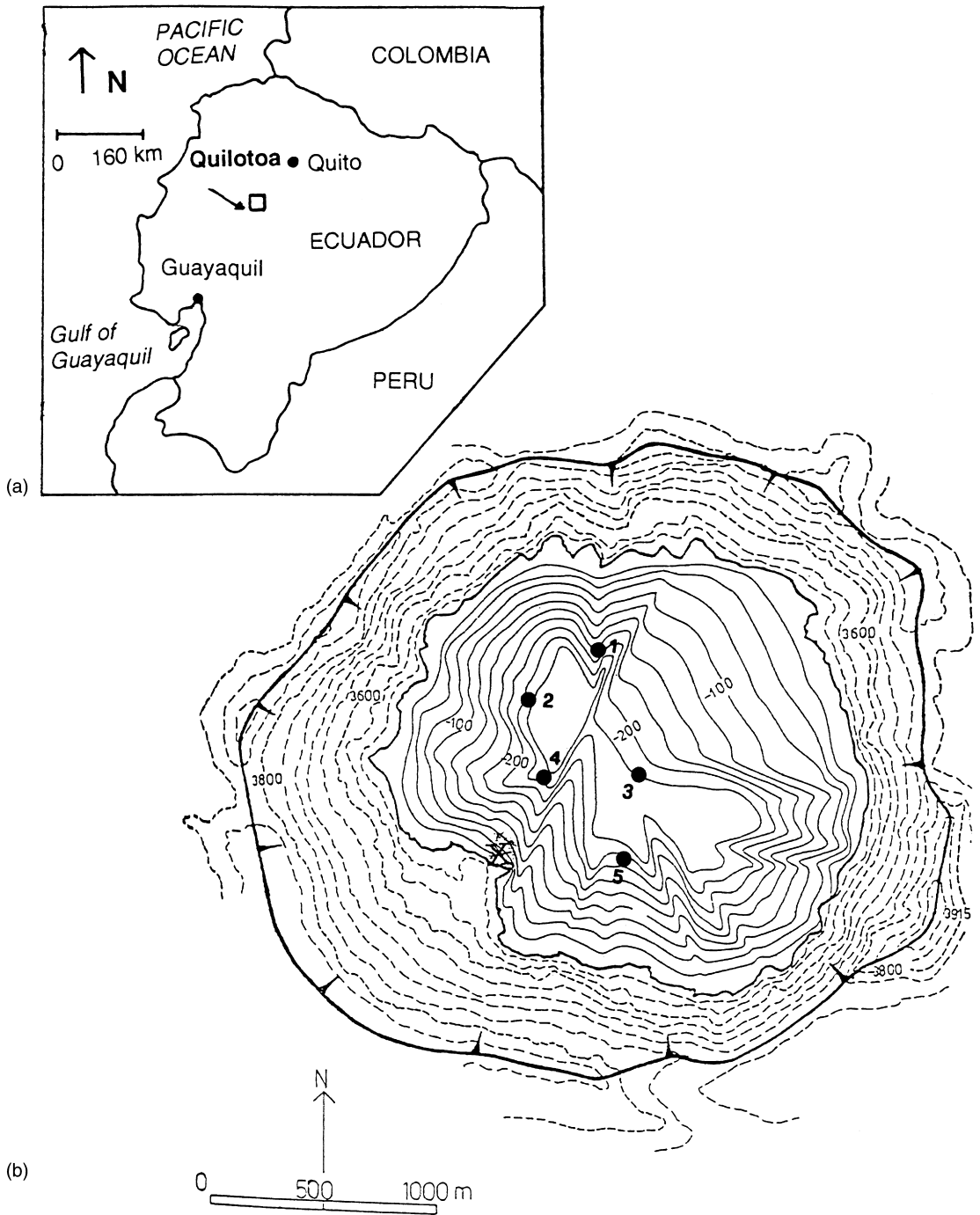
Fig. 1. (a) Location map; and (b) bathymetric map of Lake Quilotoa, also showing the location of vertical profiles (1–5) and the gas sampling point (X).
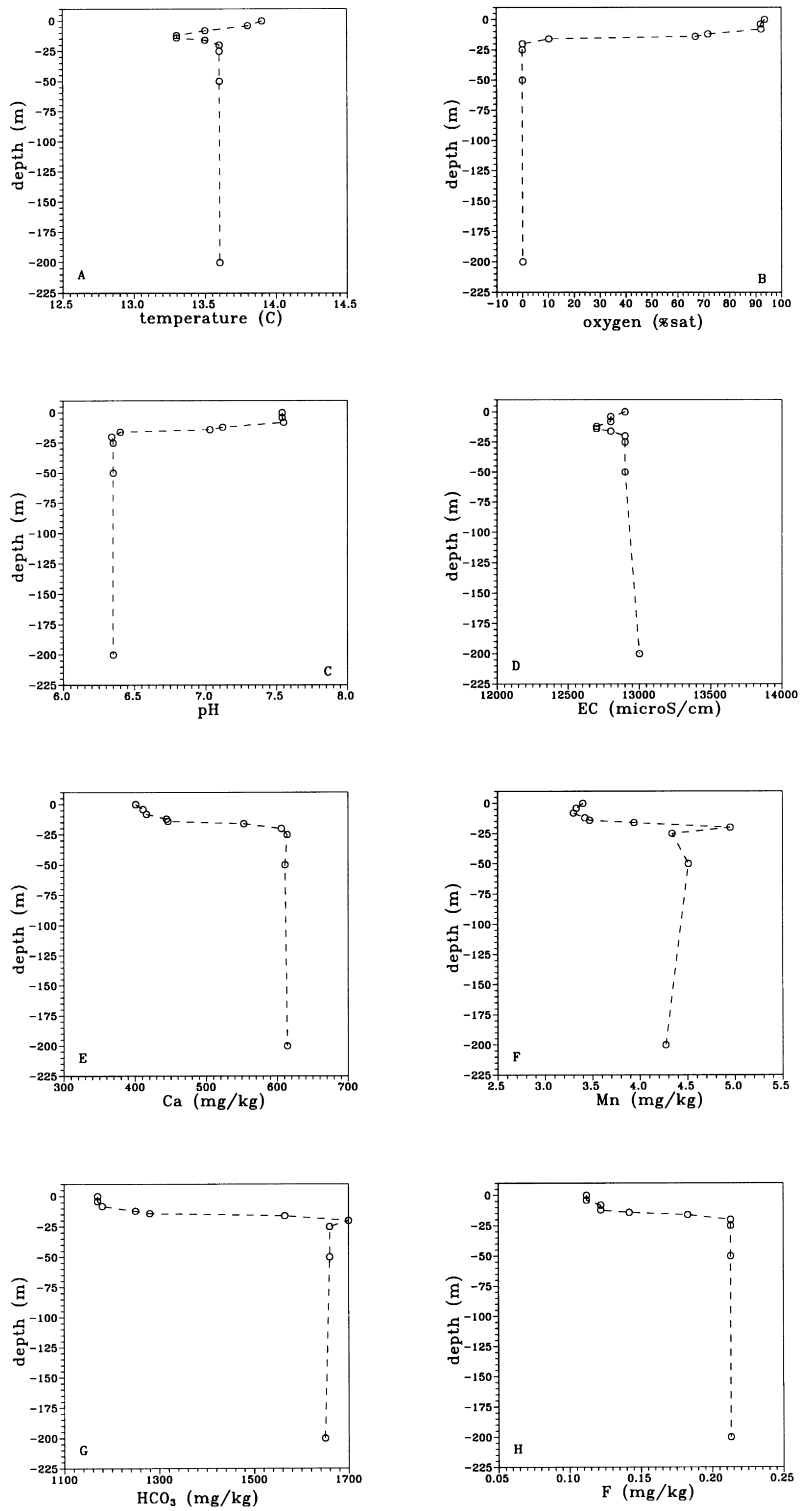
Fig. 2. Lake Quilotoa: vertical profiles of: (a) temperature; (b) dissolved $O_2$; (c) pH; (d) electric conductivity; (e) Ca; (f) Mn; (g) $HCO_3$; and (h) F in November 1993 at station 4.

## 3. Field and laboratory work

Lake waters were surveyed in November 1993, along five different vertical profiles (Fulvi, 1994). Profiles 1, 4 and 5 reached depths $\geq 200$ m, while profiles 2 and 3 were limited to depths $\leq 20$ m (Fig. 1b). Temperature, dissolved $O_2$, pH and electric conductivity (EC) were measured by means of an OCEAN SEVEN 401 instrument (Idronaut, Italy) equipped with a multi-sensor probe connected to a portable computer. The probe holds the sensors for the measurement of pressure (depth) and physico-chemical parameters. A microprocessor, built into the probe, electronically scans the parameters each 29 ms, transforms the analog signals into digital signals and transmits these to the computer through a mono-conductor cable. The nominal precisions are as follows: pressure $\sim 5$ mbar, i.e. 0.05 m in depth; temperature $\sim 0.02°C$; $O_2$ $\sim 0.2$ mg/kg; pH $\sim 0.05$ pH-units; EC $\sim 20$ mS/cm. The vertical profiles obtained at different locations in November 1993 do not show significant differences within the analytical uncertainties. Hence only the vertical profiles measured at station 4 are presented in Fig. 2.

For water sampling, a polyethylene pipe was lowered to the chosen depth maintaining its submerged end close to the T–$O_2$–pH–EC sensors. Water was pumped to the surface by means of a manual vacuum pump. Samples were collected after displacement of a water volume at least twice the inner volume of the pipe. Raw, filtered (0.45 μm) and filtered-acidified (with HCl 1:1) samples were collected and stored in polyethylene bottles. Alkalinity was measured immediately by acidimetric titration. Water samples were analyzed in the laboratory as follows: (1) Li, Na, K, Mg, Ca, Fe, Mn by AAS and/or AES; (2) Cl, $SO_4$, $NO_3$ by ion chromatography; (3) B, $SiO_2$ by visible spectrophotometry; and (4) F by ion-selective electrode. Analytical results are reported in Table 1.

## 4. Physical and chemical characteristics of Lake Quilotoa

Vertical profiles of T, $O_2$, pH and EC (Fig. 2a–d) indicate that Lake Quilotoa is made up of two distinct water masses. The oxic epilimnion ranges from the surface to a depth of about 14 m, and the anoxic hypolimnion extends from 17 m to lake bottom.

Concentrations of Li, Na, K, Mg, Cl, $SO_4$, B and $SiO_2$ do not vary with depth, outside the analytical uncertainties, whereas profiles of Ca, Mn, $HCO_3$ and F show significant variations (Fig. 2e–h). The epilimnion has Ca contents of 400–440 mg/kg, Mn concentrations close to 3.4 mg/kg, $HCO_3$ contents of 1170–1250 mg/kg and F contents of 0.11–0.12 mg/kg. In hypolimnetic waters, the concentrations of all these species are higher than in the epilimnion. Calcium, $HCO_3$ and F are at all hypolimnetic depths close to 610, 1660 and 0.20 mg/kg, respectively, whereas Mn fluctuates in the range 4.3–5.0 mg/kg.

In spite of these vertical changes in chemistry, all lake waters have an ion composition of Na > Mg > Ca > K and Cl > $SO_4$ > $HCO_3$.

## 5. Processes governing the chemistry of Lake Quilotoa and other Crater lakes

In addition to Lake Quilotoa, other Crater lakes compared here (Table 2) include El Chichón (Casadevall et al., 1984), Kawah Ijen (Delmelle and Bernard, 1994), Monoun (Sigurdsson et al., 1987), Monticchio Piccolo (Chiodini et al., 1997), Nyos (Giggenbach, 1990), Poás (Brantley et al., 1987; Rowe et al.,1992), Ruapehu (Christenson and Wood, 1993), Segara Anak (unpublished data), Soufriere of St. Vincent (Sigurdsson, 1977), Yugama and Yakeyama (Takano and Watanuki, 1990).

### 5.1. Cl, $SO_4$ and $HCO_3$

Following Giggenbach (1988), the water chemistry of Lake Quilotoa and other Crater lakes is initially investigated in terms of relative Cl, $SO_4$ and $HCO_3$ contents (Fig. 3). Fig. 3 also shows the Cl/$SO_4$ ratios of volcanic gas discharges (Giggenbach, 1996 and references therein), obtained by summing all $H_2S$ and $SO_2$ as $SO_4$. Most volcanic gases have Cl/$SO_4$ ratios <0.45, but the fumarole discharges of Klyuchevskoy volcano (KL) have Cl/$SO_4$ ratio as high as 5.7. Crater lakes with acidic waters and negligible $HCO_3$ span the same range of Cl/$SO_4$ ratios, with Yakeyama (YA) close to the $SO_4$ vertex and El Chichón (CH) and one sample of the Soufriere of St. Vincent (SV, collected during the climax of the

Table 1

Physical and chemical characteristics of Lake Quilotoa waters in November 1993. Fe concentration is below detection limit (2 mg/kg) in all the samples. Alk = Alkalinity. Concentrations of $HCO_3$ and $CO_2$, $P_{CO_2}$ values and saturation indices were calculated by means of an updated version of WATEQ (Truesdell and Jones, 1974); $HCO_3$ identifies carbonate alkalinity, which includes $HCO_3^-$, $CO_3^{2-}$, $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, etc.

| Depth (m) | Li (mg/kg) | Na (mg/kg) | K (mg/kg) | Mg (mg/kg) | Ca (mg/kg) | Alk as $HCO_3$ (mg/kg) | $SO_4$ (mg/kg) | Cl (mg/kg) | $SiO_2$ (mg/kg) | Mn (mg/kg) | F (mg/kg) | B (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 3.8 | 2420 | 191 | 758 | 401 | 1355 | 2520 | 4190 | 118 | 3.40 | 0.112 | 159 |
| 4 | 3.7 | 2410 | 198 | 769 | 411 | 1360 | 2500 | 4200 | 116 | 3.33 | 0.112 | 159 |
| 8 | 3.8 | 2420 | 193 | 756 | 416 | 1370 | 2560 | 4180 | 117 | 3.30 | 0.122 | 159 |
| 12 | 3.7 | 2410 | 195 | 758 | 444 | 1440 | 2550 | 4160 | 117 | 3.42 | 0.122 | 159 |
| 14 | 3.7 | 2425 | 194 | 761 | 446 | 1460 | 2560 | 4165 | 116 | 3.47 | 0.142 | 158 |
| 16 | 3.7 | 2430 | 192 | 761 | 553 | 1790 | 2550 | 4120 | 115 | 3.94 | 0.183 | 158 |
| 20 | 3.7 | 2440 | 193 | 758 | 606 | 1950 | 2560 | 4100 | 115 | 4.95 | 0.213 | 156 |
| 25 | 3.7 | 2400 | 197 | 758 | 614 | 1900 | 2450 | 4110 | 115 | 4.34 | 0.213 | 155 |
| 50 | 3.8 | 2400 | 192 | 753 | 611 | 1910 | 2470 | 4120 | 115 | 4.51 | 0.213 | 157 |
| 200 | 3.7 | 2400 | 192 | 768 | 614 | 1910 | 2480 | 4120 | 115 | 4.27 | 0.213 | 156 |

| Depth (m) | T (°C) | EC (μS/cm) | pH | $O_2$ (% sat) | $HCO_3$ (mg/kg) | $CO_2$ (mg/kg) | $P_{CO_2}$ (mbar) | $SI_{cal}$ | $SI_p$ | $SI_{dol}$ | $SI_{gyp}$ | $SI_{flu}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 13.9 | 12,900 | 7.54 | 93.6 | 1170 | 50 | 24 | 1.00 | 0.69 | 2.46 | −0.33 | −2.53 |
| 4 | 13.8 | 12,800 | 7.54 | 92.0 | 1170 | 46 | 22 | 1.05 | 0.72 | 2.56 | −0.32 | −2.52 |
| 8 | 13.5 | 12,800 | 7.55 | 92.2 | 1180 | 46 | 22 | 1.07 | 0.73 | 2.57 | −0.31 | −2.43 |
| 12 | 13.3 | 12,700 | 7.12 | 71.7 | 1250 | 134 | 64 | 0.69 | 0.34 | 1.78 | −0.28 | −2.40 |
| 14 | 13.3 | 12,700 | 7.03 | 66.9 | 1280 | 167 | 80 | 0.61 | 0.26 | 1.62 | −0.28 | −2.27 |
| 16 | 13.5 | 12,800 | 6.40 | 10.3 | 1565 | 877 | 420 | 0.16 | −0.23 | 0.63 | −0.20 | −1.96 |
| 20 | 13.6 | 12,900 | 6.34 | 0.1 | 1700 | 1060 | 511 | 0.17 | −0.16 | 0.62 | −0.16 | −1.80 |
| 25 | 13.6 | 12,900 | 6.35 | 0.0 | 1660 | 1000 | 481 | 0.18 | −0.21 | 0.63 | −0.17 | −1.79 |
| 50 | 13.6 | 12,900 | 6.35 | 0.0 | 1660 | 1000 | 481 | 0.18 | −0.20 | 0.63 | −0.17 | −1.79 |
| 200 | 13.6 | 13,000 | 6.35 | 0.0 | 1650 | 1000 | 481 | 0.18 | −0.22 | 0.63 | −0.17 | −1.79 |

Table 2
Chemical composition of waters from Crater lakes (n.a. = not analyzed; n.d. = not detectable)

| Lake | Code | Date | Depth (m) | T (°C) | pH | Na (mg/kg) | K (mg/kg) | Mg (mg/kg) | Ca (mg/kg) | Al (mg/kg) | Fe (mg/kg) | HCO$_3$ (mg/kg) | SO$_4$ (mg/kg) | Cl (mg/kg) | SiO$_2$ (mg/kg) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| El Chichon | CH | 01/83 | 0 | 56.0 | 0.56 | 607 | 232 | 424 | 2110 | 745 | 914 | n.d. | 3550 | 24 000 | 257 | Casadevall et al. (1984) |
| Kawah Ijen | KI | 09/90 | 0 | 37.0 | 0.18 | 585 | 1700 | 688 | 1100 | 5490 | 1860 | n.d. | 59 300 | 22 100 | 145 | Delmelle and Bernard (1994) |
| Monoun | MO | 02/85 | 90 | 22.0 | 6.00 | 26 | 5.5 | 29 | 42 | n.a. | 290 | 1000 | < 1 | 3.4 | 50 | Sigurdsson et al. (1987) |
| Monticchio Piccolo | PI | 08/93 | 33 | 9.4 | 6.27 | 45 | 28 | 15 | 44 | n.a. | 171 | 702 | 1.1 | 20 | n.a. | Chiodini et al. (1997) |
| Nyos | NY | 04/09/86 | 201 | 23.0 | 5.70 | 19 | 7.0 | 57 | 46 | 0.2 | 71 | 725 | 0.11 | 0.8 | 56 | Giggenbach (1990) |
| Poas | PO | 24/01/85 | 0 | 44.0 | 0.14 | 770 | 300 | 790 | 1200 | 3000 | 1400 | n.d. | 49 500 | 25 400 | 107 | Brantley et al. (1987); Rowe et al. (1992) |
| Ruapehu | RU | 12/90 | 0 | 24.0 | 0.72 | 358 | 151 | 322 | 927 | 1440 | 443 | n.d. | 21 400 | 6990 | 135 | Christenson and Wood (1993) |
| Segara Anak | SA | 02/96 | 0 | 21.0 | 7.10 | 414 | 25 | 133 | 283 | 0.03 | n.a. | 454 | 1050 | 408 | 97 | Unpublished data |
| Soufriere St Vincent | SV | 22/01/72 | 0 | 61.0 | 5.75 | 221 | 26 | 125 | 86 | n.a. | 19 | 8.5 | 130 | 783 | 143 | Sigurdsson (1977) |
| Soufriere St Vincent | SV | 17/07/72 | 0 | 37.0 | 7.45 | 275 | 29 | 154 | 85 | n.a. | 0.6 | 226 | 125 | 938 | 126 | Sigurdsson (1977) |
| Yakeyama | YA | 12/06/86 | 0 | 29.6 | 2.20 | 2.0 | 1.8 | 1.2 | 2.2 | 9.9 | 4.9 | n.d. | 378 | 1.0 | 103 | Takano and Watanuki (1990) |
| Yugama | YU | 06/10/77 | 0 | 17.7 | 1.00 | 16 | 12 | 10 | 110 | 116 | 100 | n.d. | 2550 | 2820 | 232 | Takano and Watanuki (1990) |
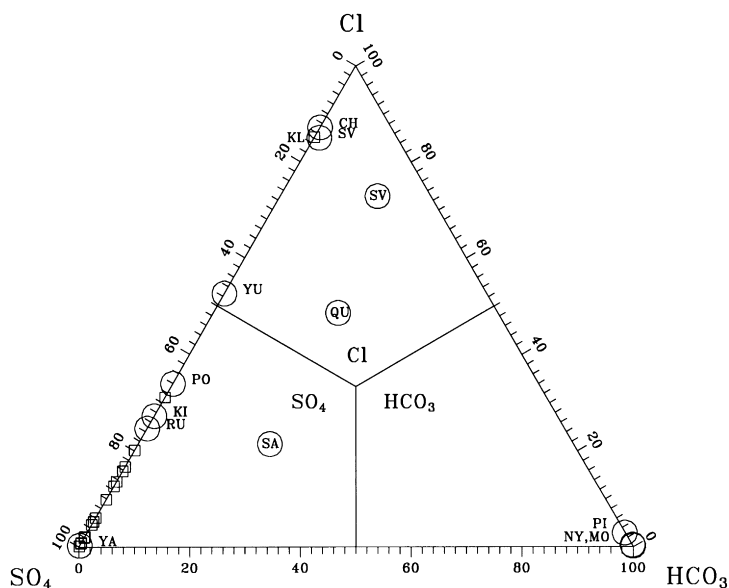
Fig. 3. Plot of relative $HCO_3$, $SO_4$, and Cl contents on weight (mg/kg) basis (from Giggenbach, 1988) of Lake Quilotoa and other Crater lakes (circles). Samples codes are given in Table 2. $Cl/SO_4$ ratios of volcanic gas discharges (Giggenbach, 1996 and references therein) are also shown (squares) for reference.

1971–1972 eruption) overlapping volcanic gas KL. Relative Cl, $SO_4$ and $HCO_3$ contents of these Crater lakes are evidently dominated by inflow and absorption of volcanic gases rich in both HCl and S-gases, although magmatic $H_2S_{(g)}$ and $SO_{2(g)}$ are involved in various reactions in the aqueous phase, such as disproportionation of $SO_2$ (Giggenbach, 1987):

$$4H_2O + 4SO_2 = 3H_2SO_4 + H_2S \qquad (1)$$
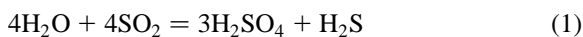
reduction to elemental S (Mizutani and Sugiura, 1966) and production of polythionates (Takano and Watanuki, 1990).

Lakes Nyos (NY), Monoun (MO) and Monticchio Piccolo (MP) plot instead close to the $HCO_3$ vertex. The waters of these lakes receive input of mantle and/ or metamorphic $CO_2$ from below and organic $CO_2$ from decomposition of plants and animals, as suggested by Mortimer's experiments (Wetzel, 1983). Conversion of $CO_2$ to $HCO_3$ through rock titration (weathering of silicates) controls most chemical characteristics of these lakes. Quilotoa (QU), Segara Anak (SA) and the sample of the Soufriere of St. Vincent (SV) collected after the end of the 1971– 1972 eruption occupy an intermediate position indicating the past absorption of magmatic gases in lake waters. Nevertheless, the initial acidity of these aqueous solutions, which is due to the presence of strong acids (e.g. $H_2SO_4$, HCl, HF), has been totally neutralized through water-rock interaction. Instead, input of $CO_2$ and its conversion to $HCO_3$ through rock titration is probably taking place at present, at least at Lake Quilotoa. Upon cessation of input of Cl– S-bearing magmatic gases, water composition of any Crater lake is expected to shift from acid–$SO_4$–Cl type to neutral-$HCO_3$ type, with a rate that largely depends upon the mass and energy balance of the lake and the chemistry of the gas entering the system (Pasternak and Varekamp, 1997).

Lake Quilotoa waters have comparatively high Cl/ $SO_4$ ratios, although they are lower than those of El Chichon and St. Vincent Crater lakes. This suggests possibly the removal of S or addition of Cl or both. Addition of Cl can be related to inflow of neutral Na– Cl geothermal waters or brines. Sulfur removal can take place as: (1) precipitation of $SO_4$-minerals (mainly gypsum, alunite and jarosite) and elemental S; and (2) bacterial reduction of $SO_4^{2-}$ to $S^{2-}$ and precipitation of sulfide minerals. Precipitation of gypsum was recognized at Ruapehu and Poas (Rowe et al., 1992). Natroalunite was observed to precipitate
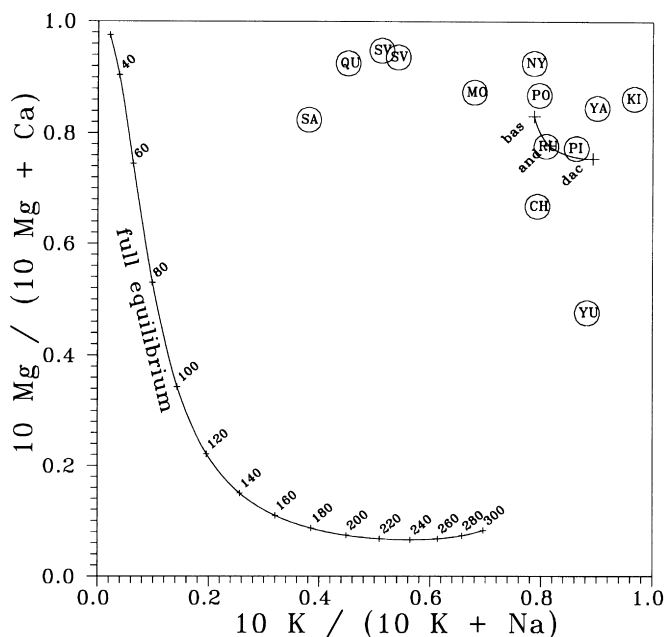
Fig. 4. Plot of 10 K/(10 K + Na) ratio vs 10 Mg/(10 Mg + Ca) ratio on weight (mg/kg) basis of Lake Quilotoa and other Crater lakes. Samples codes are given in Table 2. The full equilibrium lines refers to aqueous solutions which have attained equilibrium with the thermodynamically stable mineral assemblage with the composition of an average crustal rock (adapted from Giggenbach, 1988, considering the Na/K geothermometer of Fournier, 1979).

from Crater lake waters at Yugama and Ruapehu. In particular Giggenbach (1974) reported the following stoichiometry for natroalunite in a suspended sample $Na_{0.56}K_{0.44}Al_3(SO_4)_2(OH)_6$.

Elemental S was recognized as suspended material and/or surface scum at Kawah Ijen, Yugama, Ruapehu and El Chichon and a liquid S level was suggested to be present below the bottom of lakes Poas (Bennett and Raccichini, 1978), Ruapehu and Yugama. Reduction of $SO_4$ can be accomplished by a number of heterotrophic, anaerobic bacteria, such as *Desulfovibrio* and *Desulfotomaculum* (Wetzel, 1983), whose possible role in Crater lakes deserves further investigation.

## 5.2. Sodium, K, Mg and Ca

In the square plot of Fig. 4 (Giggenbach, 1988) relative Na, K, Mg and Ca contents of lake waters are compared with those of both: (1) geothermal waters in full equilibrium, at varying temperatures, with a thermodynamically stable mineral assemblage with the composition of an average crustal rock; and

(2) typical basalts, andesites and dacites. Apart from Lake Yugama that has an unusually low Mg/Ca ratio, most Crater lakes of both acid–$SO_4$–Cl type and neutral-$HCO_3$ type have Mg/Ca and K/Na ratios similar to those of volcanic rocks and/or magmas with which they get in contact. This suggests that cationic constituents of most Crater lakes derive dominantly from dissolution of local volcanic rocks or magmas, as already recognized elsewhere (e.g. Christenson and Wood, 1993). However Lakes Quilotoa, Segara Anak and Soufriere of St. Vincent have comparatively low K/Na ratios, that might be due to precipitation of alunite.

## 5.3. Silica

Aqueous $SiO_2$ concentrations of Lake Quilotoa are, at 114–118 mg/kg, slightly higher than saturation values with respect to the most soluble $SiO_2$ mineral, amorphous silica, at the temperature of lake waters (Fig. 5). This condition is closely approximated in other Crater lakes, such as Ruapehu and Yugama, although the silica minerals observed in suspended
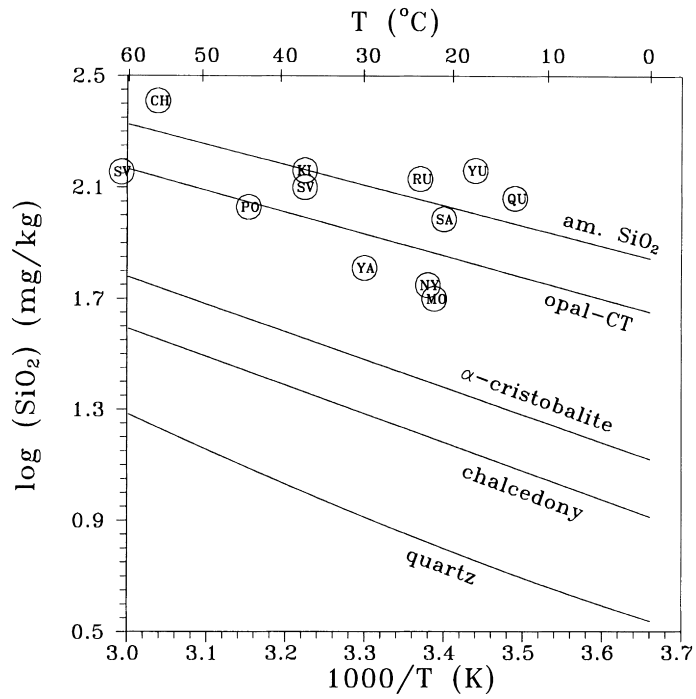
Fig. 5. Plot of log $SiO_2$ vs $1/T$ (K) of Lake Quilotoa and other Crater lakes. Samples codes are given in Table 2. Also shown are the solubility curves of quartz, chalcedony, α-cristobalite, opal-CT and amorphous silica (Fournier, 1991).
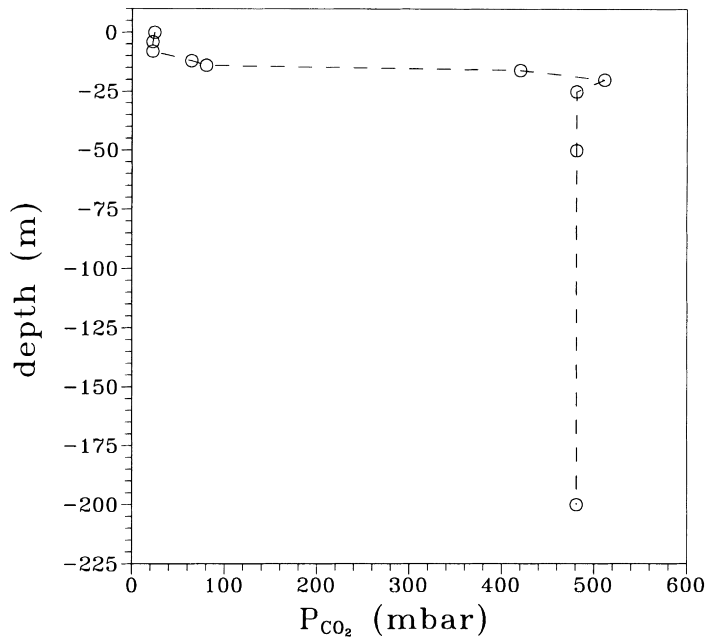


Fig. 6. Lake Quilotoa: vertical profile of $CO_2$ partial pressure in November 1993 at station 4.
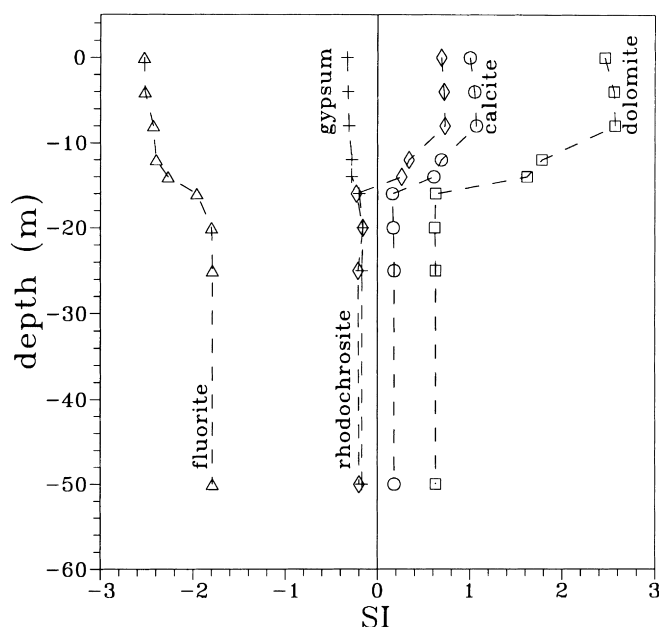
Fig. 7. Lake Quilotoa: vertical profiles of the saturation index with respect to calcite, dolomite, rhodochrosite, gypsum and fluorite.

materials in these two sites are opal CT and quartz + cristobalite, respectively. In the Crater Lake of Kawah Ijen volcano, instead, amorphous silica together with α-cristobalite compose most of the suspended solids.

Silica contents of all the Crater lakes are much higher than expected if they were controlled by diatom algae assimilation. In that case $SiO_2$ contents should be in the mg/kg range.

### 5.4. Carbon dioxide

Partial pressures of $CO_2$ were calculated using an updated version of WATEQ (Truesdell and Jones, 1974). $P_{CO_2}$ values range from 20 to 80 mbar in the epilimnion and are close to 480 mbar below 20 m (Fig. 6). Lowering of $CO_2$ in epilimnetic waters with respect to the hypolimnion is likely due to loss to the atmosphere and photosynthetic utilization. Dilution is ruled out because the chemical concentrations of several solutes remain constant at any depth.

Due to the lack of data on gas chemistry, the $N_2$ partial pressure in lake waters ($P_{N_2}$) at any depth is assumed to be fixed by equilibrium with the atmosphere (in analogy with observations elsewhere, e.g. Chiodini et al., 1997) at 530 mbar. Total gas pres-

sures, $P_{tg}$, are close to 1010 mbar at any depth below 20 m, even without considering the possible presence of $CH_4$. Since $P_{tg}$ values below 20 m are higher than local $P_{atm}$ (670 mbar), some gas exsolution might occur if deep waters were suddenly brought to the surface.

## 6. State of saturation of Lake Quilotoa waters with respect to relevant mineral phases

The available analytical data allows one to evaluate the state of saturation with respect to some relevant minerals, i.e. carbonates, sulfates and fluorides, whereas aluminum-silicates cannot be taken into account. In spite of these limitations, speciation calculations (that were performed by means of an updated version of WATEQ, Truesdell and Jones, 1974; Fig. 7) indicate that the epilimnion is oversaturated (SI's > 0.5) with respect to dolomite, calcite and rhodochrosite, slightly undersaturated with respect to gypsum (SI close to −0.33) and strongly undersaturated with respect to fluorite (SI ≤ −2.4). Hypolimnetic waters are close to saturation with respect to calcite, dolomite, rhodochrosite and gypsum, and are
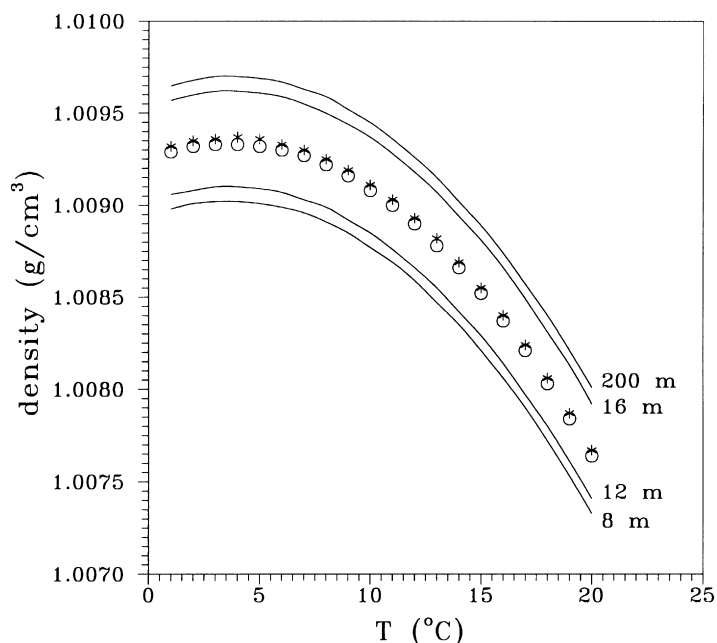
Fig. 8. Lake Quilotoa: expected changes in density with temperature for samples collected at 8, 12, 16 and 200 m depth. Lines refer to calculations carried out considering the effect of dissolved substances only. Circles and asterisks indicate expected densities at 8 and 12 m, respectively, which have been computed considering the contribution of dissolved substances and suspended particles.

strongly undersaturated with respect to fluorite, although Ca contents are larger than in shallow waters.

The decrease in $CO_2$ concentration in epilimnetic waters apparently brings about precipitation of either: calcite and rhodochrosite; a Mn-poor, calcite-rhodochrosite solid solution; or calcite and Mn-oxyhydroxides, as suggested by the lower Ca, Mn and $HCO_3$ concentrations. In $O_2$-rich waters the initial, metastable intermediate of Mn oxidation is hausmannite ($Mn_3O_4$), the thermodynamically stable form is birnessite ($MnO_2$) but the most common products are either the Mn(III) oxyhydroxide ($\gamma$-MnOOH) or a disordered vernadite ($\delta$-$MnO_2$) (Davison, 1993). The kinetics of Mn(II) oxidation is likely controlled by bacteria, as generally observed in natural waters (Davison, 1993). Presence of a substrate is also important to Mn precipitation and particles of calcite could play this role. The Fe concentration in Lake Quilotoa waters is below the instrumental detection limit, so it is not possible to investigate its behavior. However, dissolved Fe(II) is probably oxidized to Fe-

oxyhydroxide in the upper part of the hypolimnion, as commonly observed in lakes with anoxic hypolimnion (Davison, 1993). In that case, particles of Fe-oxyhydroxide do not provide a substrate for Mn precipitation, as the latter takes place in the epilimnion.

Although epilimnetic waters are strongly oversaturated with respect to dolomite, this solid phase does not seem to precipitate, as suggested by the flat vertical profile of Mg. This is probably due to kinetic constraints. The decrease in F could be due to its absorption on precipitating carbonate minerals or to inglobation of F in other solid phases, e.g. apatite. However, because of the lack of data on dissolved $PO_4$, this observation cannot be substantiated.

The fate of suspended particles in epilimnetic waters is largely affected by lake currents and biological processes, and settling velocities are usually much smaller than those calculated by Stokes's law (Schwarzenbach et al., 1993). Therefore, particles of calcite precipitated as a result of $CO_2$ loss, can remain in suspension in epilimnetic waters for long periods of time, perhaps several months or more.

## 7. Density distribution in Lake Quilotoa

Carbon dioxide concentrations vary from 46 to 167 mg/l in the epilimnion while they remain close to 1000 mg/l in hypolimnetic waters. These changes in $CO_2$ concentration are more pronounced than vertical variations in temperature and other solutes (see above) and, consequently, they have a strong influence on the density profile of Lake Quilotoa.

The density of an aqueous solution, $\rho_s$ (g/cm$^3$), at a given temperature, is related to the density of pure water, $\rho_w$, at the same temperature (Keenan et al., 1969) by means of the following relationship (Giggenbach, 1990, modified):

$$\rho_s = \frac{(1000 + \sum C_i)}{(1000/\rho_w + \sum C_i V_i / MW_i)} \qquad (2)$$

where $V_i$ is the conventional partial molal volume of the $i$th solute in cm$^3$/mol, $C_i$ is its concentration in g/kg and $MW_i$ is its molecular weight. Conventional standard partial molal volumes are given by Shock and Helgeson (1988) for the ionic solutes introduced in Eq. (2) (Na, K, Mg, Ca, $HCO_3$, $SO_4$ and Cl) and by Shock et al. (1989) for dissolved $CO_2$ ($V_{CO_2}$ is equal to 32.8 cm$^3$/mol at 25°C and 1 bar).

The presence of suspended solid particles, mainly precipitated calcite, in epilimnetic waters contributes to enhance their densities. This effect can be taken into account modifying Eq. (2) as follows:

$$\rho_s^* = \frac{(1000 + \sum C_i + \Delta m_{Ca} MW_{cal})}{(1000/\rho_W + \sum C_i V_i / MW_i + \Delta m_{Ca} V_{cal})} \qquad (3)$$

This equation assumes that all Ca lost in epilimnetic waters remains there as calcite. This is only true at steady state and if the settling rate of calcite particles equals the diffusion rate of Ca across the metalimnion. Because the settling rate is probably larger, the calculated densities are probably maximum values. Only the results for the samples collected at 8, 12, 16 and 200 m are shown in Fig. 8 as these depths cover the epi-, meta-, and hypolimnion. At the time of the survey (November 1993) the lake was stratified, but the epilimnion was not much lighter than the hypolimnion. The densities of epilimnetic waters may approach those of hypolimnetic water through cooling of about 4°C, and lake stratification may be perturbed. Another way to trigger circulation is to provide heat to hypolimnetic waters. This can occur either through an influx of hot waters from a hydrothermal system, probably existing at depth, or through a conspicuous increase in the heat flux. The latter would imply uprising and stationing of a magma body at shallow crustal levels, while the former could be triggered by tectonic activity. As reported by historical chronicles, major earthquakes brought about the overturning of lake waters both in 1740 and 1797 (Minard Hall, written communication).

## 8. Conceptual geochemical model of Lake Quilotoa

The constancy of Li, Na, K, Mg, Cl, $SO_4$, B and $SiO_2$ concentrations from lake surface to lake bottom suggests that physical, chemical and biological processes had not enough time, after the last overturn, to modify the vertical distribution of these constituents in lake waters. In most lakes, Na, K, Mg and Cl are comparatively conservative and experiment only minor fluctuations in space and time from biotic utilization or biotically mediated environmental changes (Wetzel, 1983). In general, $SO_4$ contents are remarkably affected by microbial metabolism (Wetzel, 1983), but $SO_4$ concentrations in Lake Quilotoa waters are so high ($\sim$2500 mg/kg) that a relatively long time is required to significantly decrease $SO_4^{2-}$ contents in deep lake waters through reduction to $S^{2-}$.

Therefore, the interval of time between the last overturn and November 1993 might be relatively long, but it cannot be established on the basis of one survey only. In addition, the lake may not be close to steady state.

## 9. Assessment of natural hazards

In November 1993 $P_{CO_2}$ values in lake waters were close to 480 mbar at all depths below 20 m. Assuming a constant $P_{N_2}$ of 530 mbar, total gas pressure might be close to 1010 mbar at any depth below 20 m. Since this value is greater than local atmospheric pressure, some gas exsolution might occur if deep waters were suddenly brought to the surface, but the risk of a large limnic eruption is nil at present. However, the input of significant amounts of metamorphic and/or magmatic $CO_2$, in consequence of a reactivation of the volcanic system is not nil, based on the past history of Quilotoa volcano.

Another possible evolution of Crater lake chemistry might be due to input of magmatic fluids from below. As an initial step, it is useful to refer to the end point of bicarbonate titration driven by injection of an 'average arc volcanic gas' with a molar $H_2O:CO_2:SO_2$ ratio close to 93:5:2 (e.g. Pasternak and Varekamp, 1997), neglecting rock–water interaction. In this simplified framework, the $H_2SO_4$ produced through reaction (1) would produce 27 mmol $CO_2$/kg water by complete titration of $HCO_3$ ion and the magmatic $CO_2$ directly added to lake waters would be 52 mmol/kg. Adding these inputs to the $CO_2$ already present (23 mmol/kg) and multiplying by Henry's Law constant at 13.5°C ($K_{H,CO_2} = 20.95$ bar kg/mol; Wilhelm et al., 1977) we obtain a $P_{CO_2}$ of 2.2 bar. This is a minimum value, as heating of lake waters is not taken into account. Considering that 977 mmol of magmatic steam are involved in the process and mix with 1 kg of lake water at 13.5°C, the final temperature of lake water would be close to 25°C, assuming all latent heat is transferred to the lake and enthalpy conservation (the final lake temperature also depends on the temperature of the magmatic gases). The $P_{CO_2}$ of lake water at 25°C would be close to 3.1 bar, as the $K_{H,CO_2}$ is 29.46 bar kg/mol.

At 25°C, hypolimnetic waters are much lighter than epilimnetic waters (Fig. 8) and circulation can take place. Actually circulation might occur even earlier, when deep waters reach temperatures close to 16°C. Thermally induced convective movements in the hypolimnion could allow gas separation thus preventing accumulation of gases ($CO_2$). In this scenario the risk of a limnic eruption would be very low. On the other hand, a large inflow of relatively cool $CO_2$-rich gases, or possibly a long interval between overturns, could lead to a gas buildup in hypolimnetic waters.

Therefore, it is wiser to obtain more data from periodical geochemical surveys of Lake Quilotoa, in order to determine the actual seasonal behavior of this lake and to measure the $CO_2$ flux from the volcano, than project these simple calculations over long spans of time.

## Acknowledgements

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