Geochemical monitoring of volcanic lakes. A generalized box model for active crater lakes

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ABSTRACT

In the past, variations in the chemical contents (SO_4^{2-}, Cl^-, cations) of crater lake water have not systematically demonstrated any relationships with eruptive activity. Intensive parameters (i.e., concentrations, temperature, pH, salinity) should be converted into extensive parameters (i.e., fluxes, changes with time of mass and solutes), taking into account all the internal and external chemical–physical factors that affect the crater lake system. This study presents a generalized box model approach that can be useful for geochemical monitoring of active crater lakes, as highly dynamic natural systems. The mass budget of a lake is based on observations of physical variations over a certain period of time: lake volume (level, surface area), lake water temperature, meteorological precipitation, air humidity, wind velocity, input of spring water, and overflow of the lake. This first approach leads to quantification of the input and output fluxes that contribute to the actual crater lake volume. Estimating the input flux of the "volcanic" fluid (Q_f - kg/s) — an unmeasurable subsurface parameter — and tracing its variations with time is the major focus during crater lake monitoring. Through expanding the mass budget into an isotope and chemical budget of the lake, the box model helps to qualitatively characterize the fluids involved. The (calculated) Cl^- content and δD ratio of the rising "volcanic" fluid defines its origin. With reference to continuous monitoring of crater lakes, the present study provides tips that allow better calculation of Q_f in the future. At present, this study offers the most comprehensive and up-to-date literature review on active crater lakes.

1. Introduction

The crater lakes that top active volcanoes are windows into the deeper parts of the volcano hydrothermal systems. More than 80 post-Holocene volcanoes worldwide have a lake in their craters [Simkin et al. 1981, Delmelle and Bernard 2000a]. A permanent crater lake should meet a combination of physical constraints: (i) the bottom of the lake should be protected against water seepage by physical sealing; (ii) the meteorological precipitation should be abundant (snowfall and its melt water, rainfall); (iii) the input of "volcanic" fluid should be sustained; and (iv) the heat input from the active volcano should be limited, to avoid drying out of the lake by evaporation [Brown et al. 1989, Pasternack and Varekamp 1997]. The necessary coincidence of these physical factors stresses the vulnerability of the accumulated water masses inside active volcanic craters.

In historical times, only 8% of volcanic eruptions have occurred beneath water bodies (crater lakes or shallow seawater), although these eruptions have produced about 20% of the total fatalities [Mastin and Witter 2000]. Phreatic or phreatomagmatic explosions through crater lakes can eventually expulse water from the crater basin and generate base surges, lahars, tsunamis or seiches [Sheridan and Wohletz 1983, Mastin and Witter 2000]. Coincidences between eruptive and seismic activities at volcanoes with crater lake systems have been described in previous studies [Hurst and McGinty 1999, Christenson 2000, Martínez et al. 2000, Obha et al. 2008]. Recent modeling of eruptions from beneath active crater lakes has stated that the eruption style depends on the lake depth, the eruption pressure, and the mass ratio of lake water to superheated vapor [Morrissey et al. 2010]. Even during non-eruptive periods or quiescent degassing, crater lakes can pose indirect volcanic risks. The acidic crater lake brines can seep into the volcanic edifice, dissolve the wall rock, and decrease the volcano flank stability [Rowe and Brantley 1993, Pasternack and Varekamp 1994, Rowe et al. 1995, Sanford et al. 1995, Delmelle and Bernard 2000b, Kempter and Rowe 2000, Taran et al. 2008, Varekamp et al. 2001, Varekamp 2008, Varekamp et al. 2009]. These processes can lead to lahars, or flank failure and sector collapses [López and Williams 1993, Kerle and van Wijck de Vries 2001, Reid 2004, Procter et al. 2010], which can trigger major eruptions [Voight et al. 1983]. The distribution of acidic brines into the hydrological network and plume emission into the

atmosphere can affect vegetation and agricultural activity, leading to human health problems [Sriwana et al. 1998, Delmelle and Bernard 2000b, Heikens et al. 2005, Löhr et al. 2005, van Rotterdam-Los et al. 2008]. In dormant volcanic systems, the CO_2-rich lake bottom waters can lead to catastrophic turnovers (Nyos-type events), followed by the dispersion of a toxic CO_2 cloud in the area around the lake [Kling et al. 1987, JVGR 1989, Evans et al. 1994, Kusakabe et al. 2000a, Chiodini et al. 2010].

The presence of a water body (a hydrothermal system or crater lake) along up-rising patterns of volcanic gases causes water vapor and acidic gas species (CO_2, SO_2-H_2S, HCl, HF) to dissolve, which establishes particular P-T-pH-redox conditions inside the volcano hydrothermal system. In active crater lakes, the acidic species are abundant, for creation of a pH lower than 3.8 to lose CO_2 to the atmosphere as a gas phase. The chemical–physical parameters of crater lakes can reflect and preserve signals related to eventual changes in volcanic activity. This "memory" of crater lakes provides an extra tool, as compared to open-conduit degassing volcanoes, where the recording of variations of gas discharge rates related to deep fluid inputs is directly lost to the atmosphere, often without being detected. When using crater lake chemistry and dynamics as monitoring tools, the challenge is to decipher the degassing history of the volcano over a period of observation.

Over the four decades of crater lake research, some crater lakes that manifest eruptive activity have been extensively studied (Ruapehu, New Zealand; Poás, Costa Rica; Lake Yugama, Japan, Copahue, Argentina-Chile; Santa Ana, El Salvador; Rincón de la Vieja, Costa Rica; Raoul, Kermadec Islands; Voui, Vanuatu) [Giggenbach 1974, Brown et al. 1989, Oppenheimer and Stevenson 1989, Takano and Watanuki 1990, Hurst et al. 1991, Rowe et al. 1992a, Rowe et al. 1992b, Christenson and Wood 1993, Christenson 1994, Ohba et al. 1994, Rowe 1994, Takano et al. 1994, Rowe et al. 1995, Christenson 2000, Ohba et al. 2000, Varekamp et al. 2001, Bernard and Mazot 2004, Tassi et al. 2005, Christenson et al. 2007, Ohba et al. 2008, Bani et al. 2009, Christenson et al. 2010a, Ohsawa et al. 2010]. The time series of datasets and the interpretations for these events can be considered the first examples of discontinuous volcanic monitoring using crater lake chemistry and dynamics. In the present study, we propose the box model approach for active crater lake systems, to better understand how physical and chemical changes in a crater lake can be related to possible variations in volcanic activity. We give tips on how to improve each parameter that contributes to the box model, to better constrain the relationships between a deep fluid input and its effects on crater lake chemical–physical properties. Moreover, this report presents the most complete bibliographical compilation on active crater lakes at present, as a helpful guide for future studies.

2. Active crater lakes

Volcanic lakes are classified into various groups according to their state of activity, based on their physical and chemical characteristics, such as low-activity to peak-activity lakes and no-activity lakes [Pasternack and Varekamp 1997], and CO_2-dominated, quiescent and "active" crater lakes [Varekamp et al. 2000]. Active crater lakes are generally gas dominated, and the solute compounds in crater lake water are thought to depend on the fluid dynamics in the magmatic–hydrothermal systems. Variations in the absolute concentrations of chemical compounds in crater lake waters are only partly indicative of variations in the degassing regime. In some cases, the cation (Al^{3+}, $Fe^{2/3+}$, Ca^{2+}, Na^+, K^+, Mg^{2+}, Mn^{2+}), SiO_2, and SO_4^{2-} and Cl^- contents in lake waters act as precursors of eruptive activities [Ohba et al. 2008]. However, many nonvolcanic processes (e.g. dilution, evaporation, water mass loss, secondary mineral precipitation) affect the absolute solute contents, which prevents a systematic interpretation of the temporal patterns of compositional parameters. Increases in the Mg^{2+}/Cl^- ratio of crater lake water have been interpreted as eruption precursors at Ruapehu volcano since the 1970's [Giggenbach 1974, Christenson 2000, Christenson 2010a], and in Lake Yugama in the 1980-1990's [Ohba et al. 2008]. In volcano hydrothermal systems, Cl^- is generally considered a conserved species [Pasternack and Varekamp 1994], while Mg^{2+} results from water–rock interactions that involve an unaltered rock (~fresh magma). Therefore, Mg^{2+}/Cl^- increases in lake water are believed to indicate the intrusion of a new magma batch at shallow depth [Giggenbach 1974]. However, for hyperacidic lakes (pH $\leq$0; e.g. Poás), Cl^- can escape at the lake surface as a gas phase, while Mg^{2+} remains unaffected, making the Mg^{2+}/Cl^- indicator often useless for the monitoring of set-ups [Rowe et al. 1992a]. Thiosulfate concentrations in acidic lake water have been correlated to pre-eruption activities of subaqueous fumaroles [Takano 1987, Takano and Watanuki 1990]. Thus, thiosulfates can sometimes be used as volcanic precursors, but these species can be detected in only a few lakes, depending on the temperature regime and SO_2/H_2S ratio of the entering volcanic fluid [Takano 1987]. The use of these geochemical parameters can help to provide a better understanding of the volcanic activity beneath crater lakes, although they are not systematically applicable for each crater lake. As volcano monitoring aims to quantify variations with time of parameters sensitive to changes in the volcanic status, it is recommended to convert the intensive parameters (solute concentrations and their ratios, pH and temperature) into extensive parameters (mass fluxes of water or chemical compounds).

3. The box-model approach

In highly dynamic systems like active crater lakes, the main concept is the residence time of the lake water, which can be defined as [Varekamp 2003, Taran and Rouwet 2008]:

$$R = V/F \qquad (1)$$

where R is the residence time (s) at a certain time of observation, V is the lake volume (or mass) at a certain time of observation (kg), and F is the difference between the input and output water fluxes at a certain time of observation (kg/s). This definition of the residence time assumes steady-state for water (total input = total output, constant lake water volume), which is almost never the case for highly dynamic active crater lakes [Varekamp 2003]. On the other hand, the volume of a crater lake arises from the difference between the input and output fluxes of the water mass added to the lake water volume at the previous time of observation (Figure 1). If the observation or sampling frequency is higher than the residence time of the lake water, the input and output fluxes can be assumed to be constant for the observation period, and the water mass budget of the lake can be expressed in a differential form:

$$V_L = \qquad\qquad\qquad (2)$$
$$V_{L0} + Q_f \Delta t + Q_m \Delta t + Q_{sp} \Delta t - Q_e \Delta t - Q_s \Delta t - Q_o \Delta t$$

where V_L is the resulting crater lake volume (kg), V_{L0} is the crater lake volume at the previous time of observation (kg), Q_f is the input flux of "volcanic" fluid from beneath the lake (kg/s), Q_m is the input flux of meteorological water (kg/s), Q_{sp} is the input flux of water from springs located outside the lake (kg/s), Q_e is the evaporative flux of water from the lake surface (kg/s), Q_s is the seepage flux of water out of the lake system (kg/s), Q_o is the overflow flux of water out of the lake basin (kg/s), Δt is the period (s) between two times of observation of the crater lake ($\approx$ sampling frequency). In Equation (2), all of the fluxes are positive. The "volcanic" fluid can be defined as a fumarolic condensate that enters the lake bottom either as a vapor from the underlying volcano hydrothermal system, or directly, as an often highly saline and acidic liquid brine. To apply the mass balance to an active crater lake, it is thus strictly necessary that the observation period is shorter than the residence time of the crater lake water. If not, possible indicators of the changes in the activity of the volcano hydrothermal system will be "flushed out" of the lake before being detected. For example, at Lake Yugama (Kusatsu-Shirane volcano, Japan), R is less than one year, so a monthly sampling frequency is adequate to detect possible variations in activity [Ohba et al. 1994, 2000, 2008]; while the El Chichón crater lake has a very low R of ~2 months, and thus requires a sampling frequency of at least monthly [Taran and Rouwet 2008].
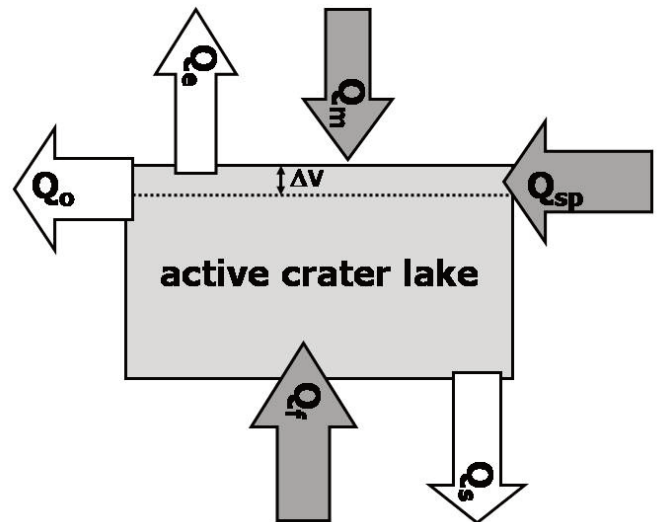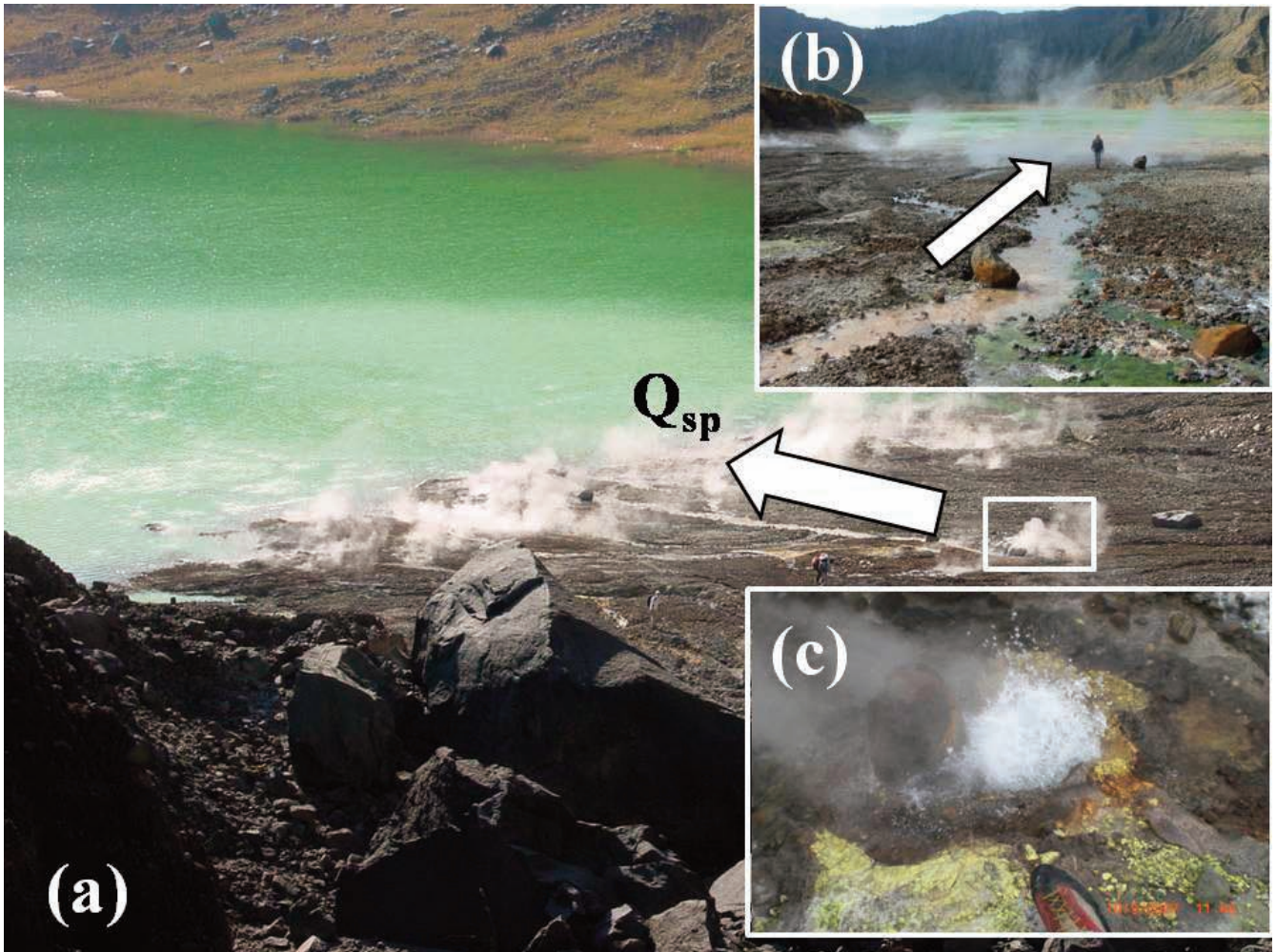

Figure 1. Box model for active crater lakes, observed for a period of time t_0 to t.

3.1. Lake depth, surface area and volume

The first unknown parameter in Equation (2) is the variation in the lake volume (V_L - V_{L0}). In general, the lake volume is deduced empirically and independently for each crater lake [Hurst et al. 1991, Ohba et al. 1994, Martínez et al. 2000, Rouwet et al. 2004, Tassi et al. 2009]. The lake surface area can be obtained by global-positioning system (GPS) measurements in the field [Rouwet et al. 2008], topographic maps, satellite images [Zlotnicki et al. 2008], or photographic methods [Rouwet et al. 2004, Rouwet 2011]. The lake depth can be obtained by direct measurements or by echo-sounding surveys along horizontal profiles from a raft [Takano et al. 2004, Christenson et al. 2010b]. On actively degassing lakes, bottom profiles from echo-sounding can be disturbed by the rising bubbles [Caudron and Bernard 2010]. The lake volume can be highly variable due to the presence of sulfur pools at the lake bottom [Oppenheimer and Stevenson 1989, Hurst et al. 1991, Christenson and Wood 1993, Takano et al. 1994], secondary mineral precipitation [Christenson et al. 2010a] and changes in the sedimentary regime [Rouwet 2011], phreatic eruptions breaching the lake bottom sediments [Bani et al. 2009, Rouwet et al. 2010], or dome intrusion that results in uplift of the lake bottom [Bernard et al. 2010]. To improve the accuracy and frequency of depth measurements, floating buoys with pressure gauges have been recently installed on lakes, to register variations in hydrostatic pressure (Y. Taran and A. Bernard, person. comm.).

3.2. Input flux of volcanic fluid

The input flux of volcanic fluids (Q_f), i.e. the only real "volcanic" factor that affects the crater lake mass balance, is an unknown parameter. However, quantifying Q_f and its variations with time will provide insights into possible variations in volcanic activity, which is within the scope of volcano monitoring programs. Solving Equation (2) for this "volcanic" parameter (Q_f) is possible when the physical "non-

Figure 2. Discharge of a thermal spring (Qsp) towards an active crater lake (El Chichón, Chiapas, Mexico). (a) The white arrow indicates the discharge of thermal spring water towards the lake. The people indicate the scale (photograph: D. Rouwet). (b) A detail of the stream flow (photograph: Y. Taran), and (c) Geyser-like thermal spring, with a shoe to indicate scale (photograph: D. Rouwet). The white box indicates the location of the geyser-like thermal spring, enlarged in (c).

volcanic" factors Q_m, Q_{sp}, Q_e, and Q_s are fully understood and quantified.

3.3. Input flux of meteorological water

The input flux of meteorological water (Q_m) to a crater lake system depends on the precipitation rate, which commonly refers to a certain period (e.g. daily), and on the surface of the catchment area for meteorological precipitation. To measure the precipitation rate, a rain gauge should be installed as near as possible to the lake. For lakes in tropical or temperate areas, the meteorological precipitation is a real-time parameter, whereas for lakes in cold areas (high altitudes and/or latitudes), meteorological precipitation is often snow, which will be released into the lake with a time delay, after the snow melts in spring and summer. The catchment area of meteorological precipitation is the crater surface area, and considered in this way, it is the total amount of meteorological water that finally contributes to the crater lake water volume by direct entrance, superficial run off or after infiltration. In reality, part of the meteorological water is dissipated by permeation through the volcanic edifice, and by evaporation from the ground of the emerged catchment area before contributing to the lake water volume. Such losses strongly depend on the subsurface structure and hydrogeology of the summit system, which is generally a poorly constrained factor. To deduce the "effective catchment area" for meteorological precipitation [Ohba et al. 1994], it is best to observe the direct effects of short-term major rain events on the (sudden) lake volume increase. Nevertheless, it is not always possible to observe such events. For this reason, taking the crater area as the catchment area for meteorological precipitation is often the best alternative, although this can cause overestimation of the Q_m value.

3.4. Input flux of spring water

Thermal or cold springs can significantly affect the mass balance of a crater lake [Ohba et al. 1994, Delmelle et al. 1998, Stimac et al. 2004, Rouwet et al. 2008]. For example, a geyser-like spring is a major fluid source for the El Chichón lake (Chiapas, Mexico) [Taran et al. 1998, Rouwet et al. 2004, Rouwet et al. 2008, Taran and Rouwet 2008] (Figure 2). The input flux of springs (Q_{sp}) located outside the catchment area

Figure 3. Evaporation (Q_e) from Poás crater lake, Costa Rica (December 2009; photograph: D. Rouwet). The lake temperature was ~45 ˚C, while the ambient temperature was ~10 ˚C.

of a lake can be directly measured in the field, by means of a flow-meter device.

3.5. Evaporative output flux

The most prominent feature that proves that a crater lake acts as a calorimeter and window into the volcano hydrothermal system beneath the lake is the evaporative heat and mass loss from the lake surface (Figures 3, 4). The evaporative output (Q_e) strongly depends on the difference between the temperatures of the lake surface and the ambient air above the lake, and the air humidity at the lake water temperature. The Brown et al. [1989] equation, which was applied for the first time at Poás Laguna Caliente (Costa Rica), is the most widely accepted method to calculate the evaporative heat loss (H_L - W/m²) at the lake surface from the latent heat of vaporization of water (L - MJ/kg):

$$H_L = LE(q_w - q_a)u \qquad (3)$$

where E is the average particle flux, which is dependent on temperature and wind speed; u is the friction velocity (m/s), which is dependent on wind speed; q_w is the saturation vapor concentration of water in air at the lake temperature

(kg/m³); and q_a is the vapor concentration in air at the ambient temperature (kg/m³). Generally, a low wind speed of 2 m/s is accepted to calculate the evaporative mass losses, considering that a crater lake surface is often screened from the dominant strong winds at high elevations of volcano summits by the crater rim [Brown et al. 1989, Taran and Rouwet 2008] (Figure 3). Oppenheimer [1997] suggested that the bulk temperature measured a few centimeters beneath the lake surface is tenths to a few degrees higher than the real surface water temperatures (skin effect). Often, the measured temperature thus erroneously results in overestimations of calculated evaporative fluxes. However, as broadly discussed in the literature, the wind speed immediately above the lake surface probably dwarfs the ΔT and humidity effects [Brown et al. 1989, Adams et al. 1990, Hurst et al. 1991, Ohba et al. 1994]. Hurst et al. [1991] stated that «the calculation of evaporative losses is not straightforward with experimentally based formulae in apparent conflict». With the present instrumental means, it is impossible to measure the water (vapor) lost from a crater lake surface by evaporation. To date, no direct and consistent measurements of wind speed above crater lakes have been produced. It is strongly recommended to install permanent

Figure 4. Evaporation (Q_e) from Paulina Lake, Newberry Caldera, Oregon, USA (August 2010; photograph: D. Rouwet). The lake temperature was ~18 ˚C, while the ambient temperature was ~5 ˚C.

meteorological stations to measure wind speed and direction, air humidity and temperature, and atmospheric pressure near the lake shore, coupled with a fixed temperature probe in the lake, to enhance the confidence of the Q_e parameter in Equation (3).

3.6. Seepage output flux

The seepage loss (Q_s) through the crater lake floor is an important subsurface process. A reliable estimation of the seepage flux can be carried out through solving the mass balance for Q_s during quiescent periods of short duration, assuming a zero Q_f [Rouwet et al. 2004]. Although it is often considered as constant afterwards, Q_s is probably highly variable with time, and depends on: (i) the hydrostatic loading of the lake water mass [Terada et al. 2010]; (ii) the lake bottom surface area [Taran and Rouwet 2008]; (iii) the physical sealing of the lake bottom by clays [Rouwet 2011], secondary minerals or molten sulfur pools [Oppenheimer and Stevenson 1989, Hurst et al. 1991, Christenson and Wood 1993, Takano et al. 1994]; and (iv) the opening and sealing of fractures. During periods of peak activity, upward steam pressures probably inhibit direct seepage at the lake bottom, or force the lake water to infiltrate through alternative routes. Moreover, phreatic eruptions can breach the lake bottom sediments or sulfur pools, strongly modifying the morphology and permeability of the lake bottom, and inevitably affecting the lake seepage. Understanding the local tectonics inside and around craters can help to locate possible seepage routes. Structural mapping using CO_2 flux surveys on and around crater lakes can give qualitative insights into the fluid migration regimes [Mazot and Taran 2009, Mazot et al. 2011]. Geophysical surveys (self potential, resistivity, magnetometry, microgravimetry) can increase the knowledge of the seepage regime of crater fluids [Fournier et al. 2004, Rymer et al. 2009, Fournier et al. 2010, Jutzeler et al. 2011]. These indirect approaches, however, do not help to quantify the seepage output flux. The results of hydrological and geophysical findings can be subjected to hydrogeochemical modeling to verify if the deduced fluid circulations are physically possible [Christenson et al. 2010a]. By trial-and-error, this can allow a semi-quantitative estimation of the permeability that controls the seepage.

3.7. Overflow output flux

Some lakes can reach the crater rim and overflow towards the volcano flank (e.g. Lake Nyos, Cameroon;

Ruapehu, New Zealand; Boiling Lake, Dominica) [Tuttle et al. 1987, Christenson 2000, Schaefer et al. 2008, Fournier et al. 2009, Christenson et al. 2010a]. In some cases, this overflow can have disastrous effects, leading to destructive lahars descending from volcano flanks (Chiginagak, Alaska; Ruapehu, New Zealand) [Schaefer et al. 2008, Procter et al. 2010]. Such overflows (Q_o) can also be induced intentionally by human engineering, as drainage tunnels, to control the lake water volume, to avoid overflows leading to lahars or dissolved gas accumulation in the bottom waters of "Nyos-type" lakes (e.g. Kelud, Indonesia; Lago Albano, Italy) [Bernard and Mazot 2004, Carapezza et al. 2008]. As is the case for the input flux of spring waters, the overflow output flux of lake water can be generally measured directly in the field. Most crater lakes, however, do not show overflow ($Q_o = 0$ kg/s).

4. Isotope and chemical budget analysis

So far, the lake water chemistry has not been necessary to calculate the input and output fluxes that affect the mass budget, which is based only on the physical variations of the crater lake (lake level, surface area, volume, temperature, atmospheric parameters, meteorological precipitation). However, when lake water sampling is possible, the box-model approach can be expanded to the isotope and chemical budget of the crater lake. This has the great advantage that sources can be better characterized, physical processes can be detailed, and fluxes of chemical compounds can be calculated. Considering that active crater lakes do not have a chemocline, due to lake convection [Christenson and Wood 1993, Christenson 1994], a water sample from the surface is generally representative of the vertical water column. Sampling and analytical procedures should remain identical during a period of monitoring, to avoid data inconsistencies. When crater walls are nearly vertical, a rappel descent is necessary (e.g. Irazú, Costa Rica), or specific sampling devices have to be lowered into the lake from the crater rim (Rincón de la Vieja, Costa Rica and Aso, Japan) [Tassi et al. 2005, Miyabuchi and Terada 2009]. At erupting volcanoes, sampling can become extremely dangerous.

4.1. Isotope budget

As all of the terms in Equation (2) represent water masses, by multiplying each term with the corresponding values of the water isotopic composition (δD or $\delta^{18}O$), the isotope budget of a crater lake is given by (Figure 5):

$$V_L \, \delta D_L = V_{L0} \, \delta D_{L0} + Q_f \, \delta D_f \Delta t + Q_m \, \delta D_m \Delta t + Q_{sp} \, \delta D_{sp} \Delta t - Q_e \, \delta D_e \Delta t - Q_s \, \delta D_s \Delta t - Q_o \, \delta D_o \Delta t \qquad (4)$$

where δD is the water isotopic composition, where the L, L0, f, m, sp, e, s, and o subscripts refer to the lake water, the lake water at the previous time of observation, the volcanic
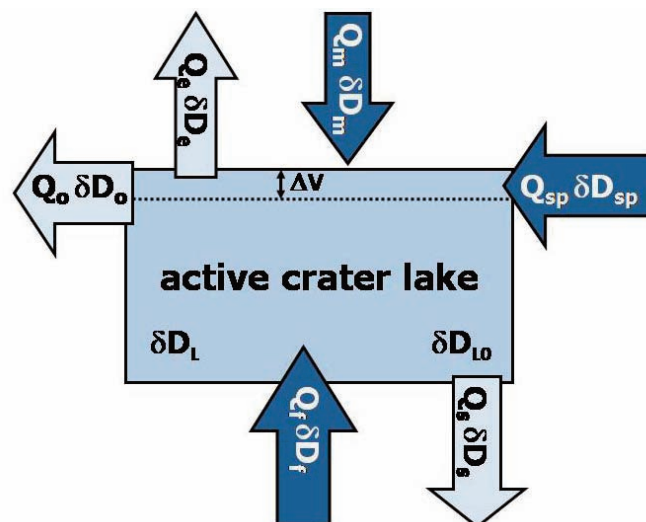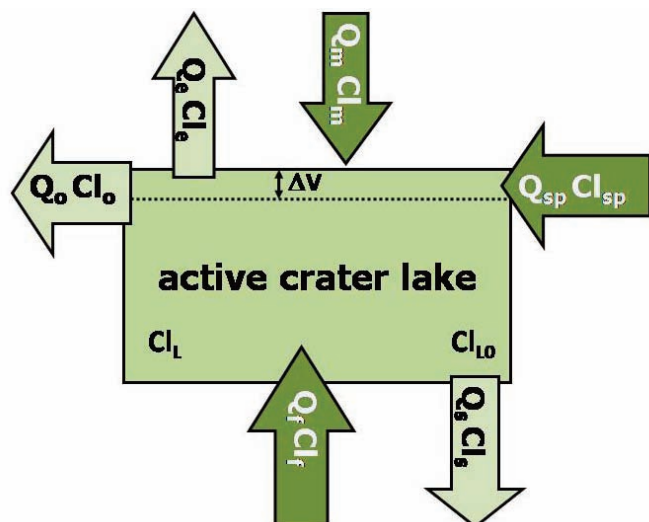

Figure 5. Box model for the isotope budget, observed for a period of time t_0 to t.

fluid entering from beneath the lake, the meteorological water, the spring water discharging into the lake, the vapor coming off the lake surface, the seeping lake water, and the overflowing lake water, respectively. δD is conveniently used because: (i) the $\delta^{18}O$ is sensitive to O-exchange between oxidized S-species and the water in variable thermal regimes [Kusakabe et al. 2000b], which is a common situation for active crater lakes; and (ii) the $\delta^{18}O$ shows a positive isotope shift due to water–rock interaction processes, which are abundant in volcano hydrothermal systems [Craig 1963, Giggenbach and Stewart 1982]. The isotope balance approach goes beyond a pure mass balance of crater lakes, as the isotopic composition of the contributing fluids provides qualitative insight into the chemical and physical processes that control isotopic fractionation. Moreover, with the δD budget, we consider only the water, without considering the chemical compounds entering through the gas phase.

The only fluids that are impossible to sample are the entering volcanic fluid (f) and the steam coming off the lake by evaporation (e). Therefore, solving Equation (4) for δD_f or δD_e is most adequate, although one of the two parameters has to be deduced or calculated separately. If the rising volcanic fluid is assumed to be pure magmatic (andesitic) water, the δD_f is expected to range from $-30‰$ to $-10‰$ [Taran et al. 1989, Giggenbach 1992]. However, this assumption is not straightforward, as the condensing volcanic fluid does not necessarily directly originate from the magma, but can be influenced by boiling and steam separation processes, lake recycling, or mixing processes. The isotopic composition of local meteorological water can be determined for rain water samples (δD_m). The δD_{sp} is directly obtained from the analysis of the spring water sample. The δD_{sp} of each specific period of observation is often preferred to a long-term average δD_{sp}. The isotopic composition of steam that originates from heated water bodies has been discussed in the literature [Giggenbach 1978, Giggenbach

Figure 6. Box model for the chlorine budget, observed for a period of time t_0 to t.

and Stewart 1982]. The δD_e of the vapor released at the lake surface is subject to kinetic or equilibrium fractionation, and strongly depends on: (i) the differences between the temperature of the top layer of the lake water and the ambient temperature above the lake [Ohba et al. 2000, Taran and Rouwet 2008]; (ii) the humidity of the boundary layer (the air layer immediately above the lake surface) [Varekamp and Kreulen 2000, and references herein]; (iii) the pH; and (iv) the salinity of the lake water [Horita et al. 1993a, 1993b]. The kinetics and equilibrium isotopic fractionation for δD_e under a large variety of clearly controllable conditions is quantified in experimental set-ups [Horita and Wesolowski 1994, Cappa et al. 2003]. Nevertheless, the natural system, i.e. the evaporating crater lake, is far from an experimentally stable situation, which forces assumptions to be adopted regarding the calculated δD_e introduced in Equation (4). Different equations to calculate δD_e can be applied, although the exact isotopic composition of the evaporative steam from a crater lake at the moment of observation will hardly ever coincide with the calculated δD_e. The δD_s and δD_o values introduced in Equation (4) are simply taken to be the average of δD_L for the period of observation (($\delta D_L + \delta D_{L0}$)/2). Among the parameters in Equation (4), δD_e is the one with the largest uncertainty. A challenge for the future is to find an adequate technique to sample the evaporative steam.

4.2. Chemical budget

As already emphasized by the mass balance approach, increased release of volcanic fluids related to changes in volcanic activity are masked by nonvolcanic fluid contributions. The only certainty is that the main anionic species (Cl^-, SO_4^{2-}, F^-) and acidity originate from a magmatic-related fluid entering the lake, i.e. volcanic fluid and/or thermal springs. Dilution by meteorological and/or spring water, salinity increase by evaporation, and element loss through seepage or lake overflow are inevitable.

Following the above statements, it is not safe to suggest that an increase in the anionic content of crater lake waters is only due to the enhanced input of the volcanic fluid. Chloride is considered be chemically conserved in acidic hydrothermal environments, while sulfur species are subject to precipitation as secondary minerals (anhydrite, alunite, native sulfur). For this reason, past studies have basically used Cl^- as the guiding species in chemical balances [Ohba et al. 1994, Rouwet et al. 2004, Rouwet et al. 2008, Taran and Rouwet 2008]. Based on Equation (2), we can now multiply each term with the corresponding Cl^- content (Figure 6):

$$V_L\,Cl_L = V_{L0}\,Cl_{L0} + Q_f Cl_f \Delta t + Q_m Cl_m \Delta t + Q_{sp} Cl_{sp} \Delta t -$$
$$- Q_e\,Cl_e\,\Delta t - Q_s\,Cl_s\,\Delta t - Q_o\,Cl_o\,\Delta t \qquad (5)$$

where Cl is the Cl^- content, and the L, L0, f, m, sp, e, s, and o subscripts are those used in Equation (4). Equations (2), (4) and (5) can be solved mathematically for the desired unknown parameter. For El Chichón crater lake, Q_{sp} was calculated [Rouwet et al. 2004, 2008], while Cl_f was estimated for Yugama Lake following a similar approach [Ohba et al. 2000]. It is clear that the expression "Q Cl Δt" represents a Cl^- mass, and Equation (5) respects the relative proportions of Cl^- given by the various Q Δt.

The entering volcanic fluid cannot be sampled; therefore, the most common procedure is to calculate Cl_f using Equation (5), when the other parameters are known. Unless acidic rain is formed due to the absorption of plume gases into the clouds, the entrance of Cl^- from meteorological water can be neglected ($Cl_m = 0$ mg/l). Spring waters can be sampled and Cl_{sp} should thus be known. A significant HCl loss by evaporation occurs from the surface of hot hyper-acidic lakes (e.g. Poás, Costa Rica; Aso, Japan). In this case, Cl_e is the unknown term because the Cl_2-rich vapour is still impossible to sample. A promising tool is to determine the chemical species in evaporation plumes at active crater lakes by direct plume measurements [Christenson et al. 2010a, Christenson et al. 2010b, Shinohara et al. 2010]. For lower temperature, lower acidity lakes, Cl_2 is not lost from the lake surface ($Cl_e = 0$ mg/l). For the Cl^- lost by seepage, it is most correct to use the average Cl^- content of the lake water for the period of observation ($Cl_s = (Cl_L + Cl_{L0})/2$). If overflow occurs, the same is true for Cl_o ($Cl_o = (Cl_L + Cl_{L0})/2$).

At El Chichón, no volcanic Cl^- is thought to enter the lake system, and the geyser-like springs were found to be the only Cl^- source for the crater lake during the period 1995-2007 [Rouwet et al. 2004, Rouwet et al. 2008, Taran and Rouwet 2008]. Following similar approaches, Ohba et al. [1994, 2000] calculated a Cl_f even higher than the Cl^- contents in high-temperature volcanic gases, which suggested that volcanic fluids entering beneath crater lakes are Cl^--enriched due to multi-step steam separation processes, and probably to lake water recirculation. By

multiplying Cl_f by Q_f, Cl^- fluxes can be calculated. In our opinion, monitoring Cl^- fluxes of the volcanic fluid is the most direct way to detect changes in volcanic input.

5. Conclusions

Based on a literature review, this study offers a generalized box-model approach that can be applied in continuous or discontinuous geochemical monitoring of active crater lakes. Intensive geochemical parameters (solute concentrations, pH) do not systematically relate to variations in eruptive activities at volcanoes with crater lakes. On the contrary, the box model allows the calculation of extensive parameters (mass fluxes), providing a better representation of the chemical–physical variations with time. By quantification of the nonvolcanic factors that affect the physical–chemical state of an active crater lake, the box model allows calculation of the volcanic input flux (Q_f), which cannot be measured directly. A challenge for the future is to better constrain these nonvolcanic factors, in order to better define Q_f. As well as giving insights into the changes in volcanic activity (Q_f), an understanding of the seepage (Q_s) and overflow (Q_o) regime of crater lake systems can be useful in volcanic surveillance of indirect risks related to crater lakes (impact of contaminants on the environment, flank failure, lahars).

The error of discontinuous monitoring methods is impossible to quantify, as it largely depends on: (i) the error in the single contributing parameters; (ii) the residence time of the lake water specific for each lake; (iii) the related sampling/observation frequency, which depends on access to the crater lake (~safety limits during eruptive cycles, logistics); and (iv) the averaging of the values for observation periods longer than the residence time of the lake. Evolution towards continuous monitoring (visual-thermal cameras, and meteorological stations with data transmission systems, P-T-pH-conductivity probes) will increase the frequency, quality and safety of the data gathering. The quantitative and qualitative characterization of temporal variations in the volcanic and nonvolcanic parameters of the box model offers a means to better constrain the physical and chemical processes that occur in crater lakes with volcano hydrothermal systems. Beyond the concept of continuous *versus* discontinuous monitoring, this box model is applicable for low-cost (mass budget), over medium-cost (chemical and isotope budget) to high-cost (continuous) monitoring set-ups. If volcano monitoring is a too ambitious goal for some crater lakes, within the limits of the available means, the box model proposed here will definitely help to develop basic conceptual models of crater lakes with volcano hydrothermal systems.

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