



## Hydrogeochemical surveillance at El Chichón volcano crater lake, Chiapas, Mexico



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### ABSTRACT

El Chichón volcano has an eruptive record of at least 12 major eruptions in the Holocene, the latest one in March–April 1982 causing the worst volcanic disaster in the history of Mexico. After about 6 centuries of quiescence, this eruption destroyed a large dome and opened a 1 km wide crater. A lake, formed within the crater shortly after the eruption, has been an important source of information about the evolution of the post-eruptive processes. The fluctuations of the crater lake water physicochemical parameters, observed since 1983, have allowed in identifying hydrothermal waters and H<sub>2</sub>S-rich gases, influenced by tectonic and meteorological effects, as the main contributors to its composition. Here we propose some methods to help in assessing the state of the volcano derived from the relative contribution of these factors as an easy to implement volcanic surveillance method in potentially active volcanoes with crater lakes, or other volcano-influenced water sources.

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### 1. Introduction

The management of volcanic hazard should include systematic monitoring and interpretation of diverse parameters providing information about the internal condition and processes within a volcanic system. Pre- and syn-eruptive hydrogeochemical changes have been observed at several volcanoes (Hirabayashi et al., 1982; Takahashi et al., 1988; De la Cruz-Reyna et al., 1989; Martini et al., 1991; Gíslason et al., 1992; Shevenell and Goff, 1995; Tilling and Jones, 1996; Fischer et al., 1997; Quattrocchi et al., 2000; Varekamp et al., 2001; Federico et al., 2004; Armienta et al., 2008; Capasso et al., 2014). Nowadays, hydrogeochemical monitoring represents an important tool (Marrero et al., 2005; Rouwet et al., 2009; Capasso et al., 2014; Ingebritsen et al., 2014), that jointly with other seismic, geodetic and gravimetric monitoring data supply valuable information to reduce the degree of non-uniqueness of the interpretations. Such information furnishes a more accurate evaluation of the more likely volcanic activity scenarios, making it possible to issue adequate and on-time warnings of changes in a volcano condition. Of particular interest are volcanoes maintaining crater lakes, as in some cases waters of such lakes have shown precursory chemical changes reflecting volcanic unrest. The Yugama crater lake located in the summit of Mt Kusatsu-Shirane volcano showed chemical changes 1 year in advance to its 1976 eruption (Ossaka et al., 1980), and after the explosive

eruptions occurred in 1982 and 1983 (Ohba et al., 2008). Additionally, sulfate concentrations increased and polythionate decreased before its 1982 eruption (Takano and Watanuki, 1990). Similarly, polythionate concentrations decreased before a phreatic eruption at Poás volcano, and increased before the development of magmatic activity (Rowe et al., 1992). At Ruapehu volcano Mg/Cl ratio in the lake water increased during and after eruptive periods (Giggenbach, 1983). At Popocatepetl volcano, sulfate and Mg/Cl increased prior to the onset of its current eruptive period (Armienta et al., 2000). Recently, at Dominica, Lesser Antilles, chemistry of geothermal systems was included as a tool for volcano monitoring (Joseph et al., 2011)

The eruption of El Chichón volcano in 1982 was one of the worst disasters occurring in México in the past century, causing nearly 2000 fatalities (De la Cruz-Reyna and Martin del Pozzo, 2009). Less than 1 month after the eruption, three small lakes formed in the crater, that later coalesced into a single, larger one that remains to the present, with significant fluctuations in shape and dimensions. The chemical characterization of the lake water was first reported by Casadevall et al. (1984) and diverse studies of the lake chemistry have been carried out afterwards (Armienta and De la Cruz-Reyna, 1995; Taran et al., 1998; Armienta et al., 2000; Tassi et al., 2003; Rouwet et al., 2004, 2008, 2009; Taran et al., 2008; Morton-Bermea et al., 2010; Cuoco et al., 2013).

We have monitored the chemical composition of El Chichón volcano crater lake for about 25 years. First sampling campaigns following the lake formation were irregular, and often after long time intervals at one lake shore location only; however the sampling frequency increased

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afterwards and other 5 sampling points were included since 2003. The information that may be extracted from any evolving processes indeed depends on the sampling frequency. The Nyquist–Shannon sampling theorem states that it is only possible to observe processes evolving over times twice the sampling period (Nyquist, 2002), condition that may become awkward in an irregular sampling. From the balance between estimated lake volumen, precipitation and spring waters input, Taran and Rouwet (2008), and Rouwet et al. (2014) concluded that El Chichón lake has an estimated residence time of 2 months, thus requiring a monthly sampling to detect hydrogeochemical changes related to that process. However, longer sampling periods should provide information on seasonal and non-seasonal longer duration cycles.

In the present work the lake water chemistry evolution is discussed aiming to develop an improved methodology for volcanic activity level assessment at El Chichón, understood as a measure of the changes in the level of interaction between magmatic gases and the lake water. Specific observations of chemical species concentrations and data processing methods are proposed as part of a monitoring protocol to assess the level of volcanic activity, and associated hazards. The proposed methodology is focused on straightforward procedures, useful even in a framework of limited technological conditions, providing basic factors for hazard assessment and an increased capability to issuing early warnings to civil protection authorities.

## 2. El Chichón Volcano. Geological setting and eruptive history

El Chichón is an active trachyandesitic volcano located in the Chiapanecan Volcanic Arc, so isolated within a sedimentary mountain range that was not even recognized as a volcano until 1928 (Müllerried, 1933). It is located at 17.36° N, 93.23° W, in a tropical forest zone having an average precipitation around 4000 mm/yr (as a mean of the National Meteorological Service stations located in towns around the volcano). The volcano stands over a basement of middle Cretaceous to middle Miocene marine limestones, claystones and sandstones (Damon and Montesinos, 1978; Canul and Rocha, 1981; Canul et al., 1983; Duffield et al., 1984; García-Palomo et al., 2004; Macías et al., 2008; Garduño-Monroy et al., 2014).

There are three main models explaining the El Chichón origins: The subduction process of the Cocos plate under the North American plate, complicated by the awkward geometry of the plate boundary fault system and a close interaction with the Caribbean plate (Damon and Montesinos, 1978; Luhr et al., 1984; Mora et al., 2007; Manea and Manea, 2008; Mazot et al., 2011); the subduction of a different south-west dipping slab from the Gulf of Mexico resulting from the collision of Yucatán block with Mexico (Kim et al., 2011); a rift magmatism related to the melting and dehydration of that slab (Arce et al., 2014).

At least 12 major eruptions have occurred at El Chichón in the Holocene, and more precisely in the past 8000 years, with repose intervals lasting between 100 to 600 years (Tilling et al., 1984; Espíndola et al., 2000; Macías et al., 2003, 2008; De la Cruz-Reyna and Martin Del Pozzo, 2009; Layer et al., 2009; Tilling, 2009; Mendoza-Rosas and De la Cruz-Reyna, 2010). In March–April 1982, El Chichón volcano suddenly reawakened with a weeklong series of eruptive outbursts reaching VEI 5, producing the worst volcanic disaster in the recorded history of Mexico, killing nearly 2000 people, and causing severe economic loss (Yokoyama et al., 1992; De la Cruz-Reyna and Martin Del Pozzo, 2009; Tilling, 2009; De la Cruz-Reyna and Tilling, 2014). This eruption, occurred after about 550 years of quiescence (Macías et al., 2003), destroying a dome about 1.5 km diameter in its base and 300 m height, and forming a 1 km wide, 200 m deep crater. The final, most explosive phases devastated an area about 10 km around the volcano, and caused heavy ashfalls on locations several hundred kilometers from the summit (Varekamp et al., 1984). A few weeks later, on April 25, three lakes were observed in the crater that later merged into a bigger lake, first observed in November, 1982 (Casadevall et al., 1984).

The analysis of the El Chichón eruptive history has allowed to estimate the probabilities of future eruptions (Mendoza-Rosas and De la Cruz-Reyna, 2010), and several scenarios are possible: a long quiescence period; an effusive dome-emplacment phase that may turn explosive due to magma water interactions, or an open vent major explosive eruption such as those occurred 900, 2000 and 2400 yr BP (Macías, 2007). What kind of precursors may we expect for each possible scenario? Whatever those precursors are, they would make sense only when compared to a background activity and its evolution. Here we intend to outline such evolving background, and propose a viable methodology to continue the acquisition and processing of data. Such methods must account for the difficult logistic and sampling conditions at El Chichón crater lake, and the limited funds that may realistically become available in a permanent hydrogeochemical surveillance program.

## 3. The crater lake

After its coalescence, the early shallow lake (1–3.3 m deep) covered an area of about  $1.4 \times 10^5$  m<sup>2</sup> on the central crater floor (Casadevall et al., 1984). However, its shape and dimensions have changed along the years (Rouwet, 2011). The chemistry of El Chichón crater lake water has also fluctuated since the first sampling in 1983 reported in Casadevall et al. (1984). Lower acidity was measured in 1986 (pH of 2.5) with respect to 1983 (pH 0.56) (Armienta et al., 2000). Afterwards, pH values have been varying around 2.5. Proportion and concentrations of main ions have shown strong changes along the years. The crater-lake was acid, calcium chloride type in 1983. Afterwards, predominance of main anions has fluctuated between chloride and sulfate, and among magnesium, sodium, and calcium for main cations (Armienta and De la Cruz-Reyna, 1995; Armienta et al., 2000, 2008). Armienta et al. (2000) concluded that the magmatic contribution to the crater lake water had a decreasing trend between 1983 and 2000. Hydrogeochemical changes have been attributed to diverse processes such as variations of the hydrothermal water supply and the volcanic gas input, as well as precipitation–dissolution and oxidation–reduction reactions within the lake water (Armienta et al., 2008). Tassi et al. (2003) related the behavior of the magmatic–hydrothermal system of El Chichón to the interaction between a deep magmatic source and a shallow cold aquifer, combined with changes in the permeability of the system. Rouwet et al. (2009) and Peiffer and Taran (2013) attribute the non-homogeneous permeability to changes in the crater lake size covering more pumiceous sands. Taran et al. (1998, 2008) and Rouwet et al. (2008, 2009) related changes in the crater-lake chemistry to the activity and influence of near-neutral geyser-like springs (Soap Pool) into the lake water.

## 4. Sampling and analytical methods

Sites sampled from January 2003 to April, 2014 were located along the eastern shore of the lake, as illustrated in Fig. 1. Temperature and pH have been measured in the field with a Hanna pH-meter calibrated in situ with buffer solutions at the same temperature of the water before each reading. Location M6 has been sampled since 1983. Some partial analytical results have been reported elsewhere (Armienta and De la Cruz-Reyna, 1995; Taran et al., 1998; Armienta et al., 2000, 2008). The changing dimensions of the lake makes impossible to sample exactly the same points in every field campaign. Moreover, in some occasions, the increased size of the lake prevented reaching some of the sampling points.

Chemical analyses of main ions have been performed at the Laboratorio de Química Analítica, Instituto de Geofísica, UNAM, following Standard methods (APHA, 1995, 2005). Sodium and potassium were measured by atomic emission spectroscopy adding LiNO<sub>3</sub> to control ionization. Concentrations of calcium and magnesium were determined by complexometric titration with EDTA. Sulfates were measured by turbidimetry. Chloride and fluoride concentrations were determined by

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