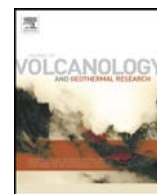




Contents lists available at ScienceDirect

Journal of Volcanology and Geothermal Research

journal homepage: www.elsevier.com/locate/jvolgeores

Water and dissolved gas geochemistry at Coatepeque, Ilopango and Chanmico volcanic lakes (El Salvador, Central America)

J. Cabassi^{a,b,*}, F. Capecchiacci^{a,b}, F. Magi^{a,c}, O. Vaselli^{a,b}, F. Tassi^{a,b}, F. Montalvo^d, I. Esquivel^d, F. Grassa^e, A. Caprai^f^a Dipartimento di Scienze della Terra, University of Florence, Via G. La Pira 4, 50121 Florence, Italy^b CNR – Istituto di Geoscienze e Georisorse, Via G. La Pira 4, 50121 Florence, Italy^c Dipartimento di Scienze della Terra, University of Pisa, Via Santa Maria 53, 56126 Pisa, Italy^d Ministerio de Medio Ambiente y Recursos Naturales, Kilómetro 5½ Carretera a Santa Tecla, calle y colonia Las Mercedes, San Salvador, El Salvador^e Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy^f CNR – Istituto di Geoscienze e Georisorse, Via G. Moruzzi 1, 56124 Pisa, Italy

ARTICLE INFO

Article history:

Received 16 January 2019

Received in revised form 17 April 2019

Accepted 18 April 2019

Available online 22 April 2019

Keywords:

Volcanic lakes

El Salvador

Water geochemistry

Dissolved gas geochemistry

Stable isotopes

Unusual chemical compositions

ABSTRACT

Coatepeque (on the E slope of Santa Ana Volcano), Ilopango (inside Ilopango Caldera) and Chanmico (associated with San Salvador Volcano) are volcanic lakes in El Salvador, showing a thermocline at a relatively shallow depth (from 30 to 40 m, from 20 to 40 m and from 5 to 15 m depth, respectively) and anoxic conditions below 33, 24 and 4 m depth, respectively. The Na⁺–Cl[–] composition of the Coatepeque and Ilopango lakes, displaying TDS values up to 1226 and 1216 mg/L, respectively, is likely due to hydrothermal fluids that feed these two lakes, as also confirmed by Cl[–]/Br[–] molar ratios \leq 650, high As, B, Li and Si contents and Cl[–]/SO₄^{2–} ratio $>$ 1. The Mg²⁺–HCO₃[–] water composition of Lake Chanmico, whose TDS values were between 566 and 856 mg/L, suggests water–rock interaction processes with mafic/ultramafic rocks variably affected by serpentinization processes, which produced high Mg²⁺, Si and B concentrations. Waters at depth were characterized by the presence of CO₂ from an extra-lacustrine source, as suggested by $\delta^{13}\text{C-CO}_2$ values significantly less negative than those typically related to biogenic processes, albeit this gas was found in smaller quantities when compared to those recorded in other meromictic lakes hosted in quiescent volcanic systems (e.g. Lake Kivu in DRC, Monticchio, Albano and Averno lakes in Italy, Hule and Rio Cuarto lakes in Costa Rica, Lake Pavin in France). The occurrence of CH₄, whose concentrations in Lake Chanmico were up to two orders of magnitude higher than those recorded in Coatepeque and Ilopango lakes, suggests bacterial methanogenesis.

© 2019 Published by Elsevier B.V.

1. Introduction

Volcanic lakes are peculiar natural systems, although they represent a relatively common feature of active and quiescent volcanoes and mostly associated with subduction-related environments, particularly in sub- to tropical areas. They show a large variability in terms of size as they are hosted within maar as well as giant calderas (Rouwet and Tassi, 2014; Varekamp, 2015). The existence and persistence of a volcanic lake are governed by the balance between water inputs (e.g. precipitation, inflows) and outputs (e.g. evaporation, seepage, outlets). Volcanic lakes can be divided into: i) *high-activity and medium-activity lakes*, where significant amounts of heat and acidic hydrothermal- to magmatic-dominated fluids are released and ii) *low activity lakes*, i.e. acidic sulfate lakes with TDS $<$ 10 g/L or CO₂-dominated lakes,

characterized by deep fluid inputs at relatively low rate (Pasternack and Varekamp, 1997; Rouwet et al., 2014; Varekamp, 2015). The latter, namely *bio-activity lakes* (Cabassi et al., 2014), characterized by relatively low temperature and salinity, neutral to slightly acidic pH and permanent thermal and chemical stratification (Rouwet et al., 2014), are particularly prone to the development of CO₂(CH₄)-rich gas reservoirs at depth, significantly mediated by bacterial activity (e.g. Caliro et al., 2008; Tassi et al., 2009; Cabassi et al., 2013; Tassi and Rouwet, 2014; Tassi et al., 2018a, 2018b). Gas accumulation can eventually trigger limnic eruptions, a typical feature of Nyos-type lakes (e.g. Tassi and Rouwet, 2014; Costa and Chiodini, 2015; Kling et al., 2015; Kusakabe, 2015).

The chemistry of waters from volcanic lakes exhibits large variations, i.e. from meteoric-like to hyper-saline and acidic, strictly depending on: i) rate of input from the underlying volcanic-hydrothermal system; ii) input of meteoric water; iii) activity of microbial populations along the water column; iv) interactions with different types of rocks (Varekamp, 2015; Paternoster et al., 2016). Anion concentrations in

* Corresponding author at: Department of Earth Sciences, University of Florence, Via G. La Pira, 4, 50121 Florence, Italy.

E-mail address: jacopo.cabassi@gmail.com (J. Cabassi).

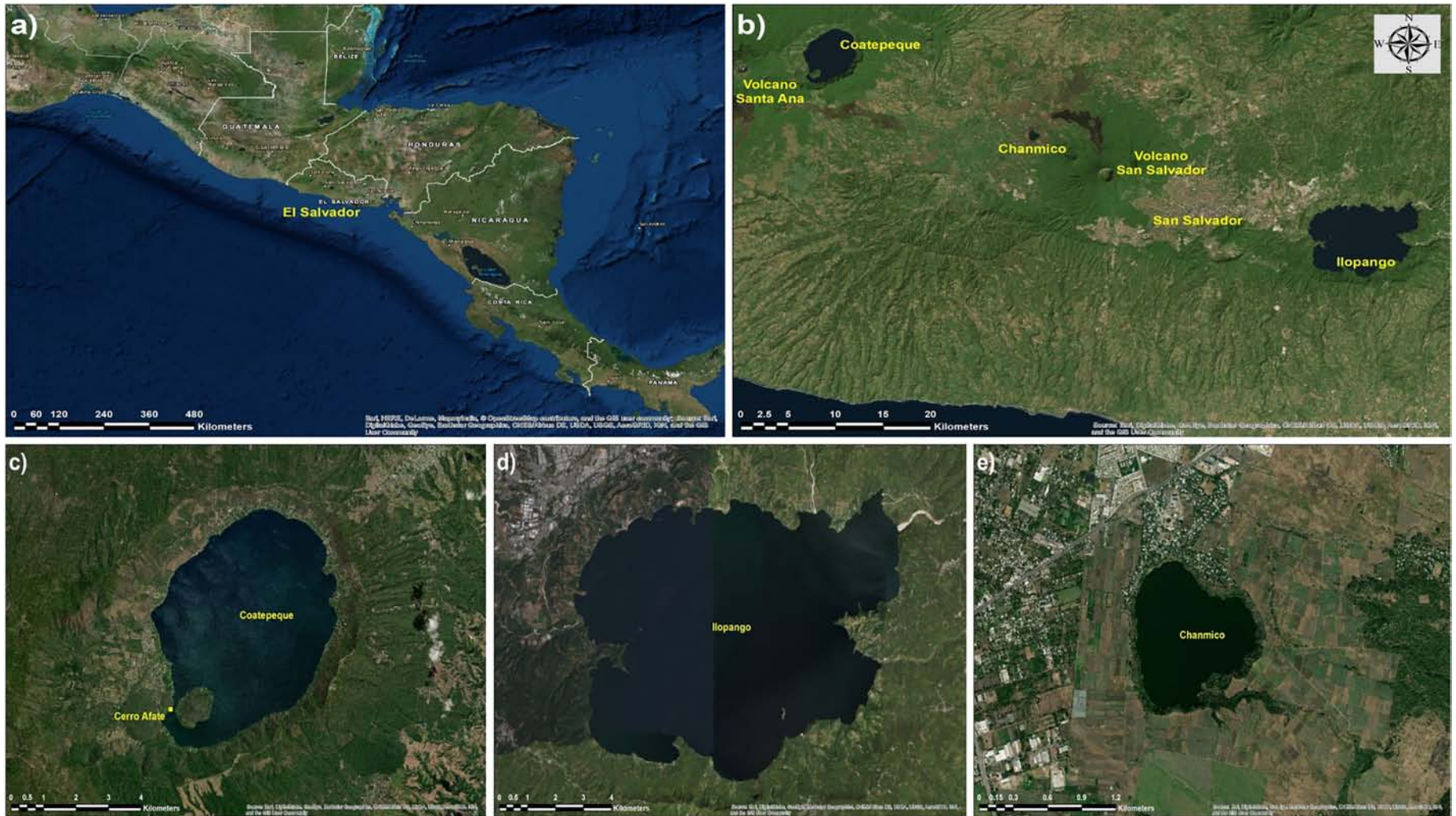


Fig. 1. a–e – Location of El Salvador (a) and the volcanic lakes of Coatepeque, Ilopango and Chanmico within the Central-American state (b). Aerial views of Coatepeque (c), Ilopango (d) and Chanmico (e) lakes.

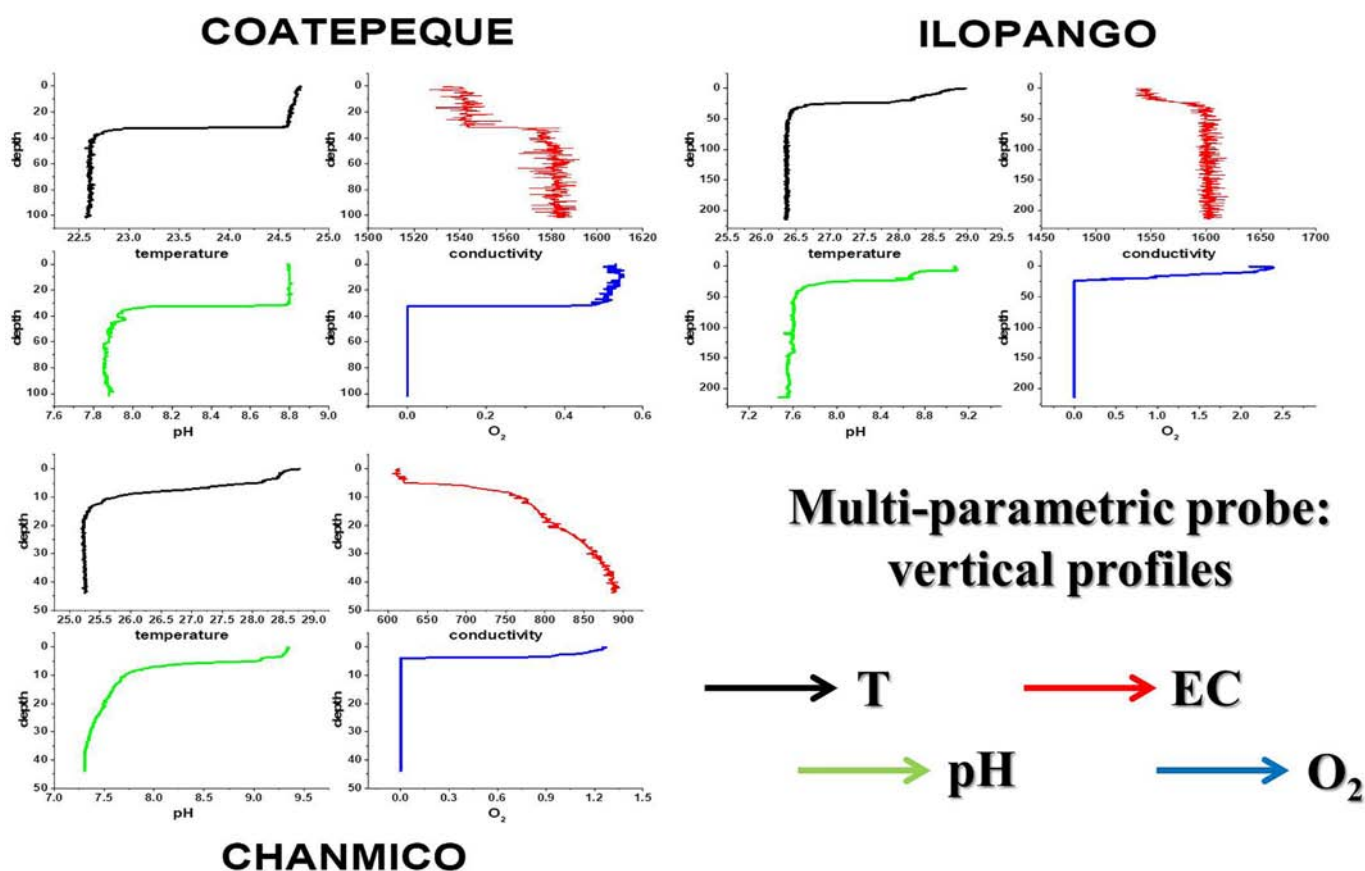


Fig. 2. Vertical profile of temperature ($^{\circ}\text{C}$), conductivity (EC, in mS/cm), pH, dissolved O_2 (in $\mu\text{mol/L}$) for the volcanic lakes of Coatepeque, Ilopango and Chanmico.

volcanic lakes are usually considered as related to dissolution of volcanic-hydrothermal gases (Christenson and Tassi, 2015), though the feeding fluids in quiescent volcanoes mostly consist of CO_2 with minor amounts of Cl^- and S -bearing acidic gases (Pasternack and Varekamp, 1997). In contrast, the composition of cations is mostly due to water-rock interaction processes in either groundwater or hydrothermal system below the lakes (Sriwana et al., 2000; Varekamp, 2015). Gases dissolved within the lakes are related to different sources: (i) deep fluid inputs, (ii) air-water exchange through the lake surface, and (iii) metabolic processes of microbial communities (Christenson and Tassi, 2015). Consequently, water and dissolved gas chemistry of volcanic lakes is of paramount importance to obtain insights into the origin and evolution of the fluids entering the lacustrine system (e.g. Rowe et al., 1992; Christenson, 2000; Anzidei et al., 2008).

El Salvador (Central America; Fig. 1a) is a land of volcanoes, being located within the volcanic belt known as Central American Volcanic Front (CAVF) that extends from Guatemala to Costa Rica and is related to the subduction of the Cocos Plate beneath the Caribbean Plate (Corti et al., 2005; Agostini et al., 2006 and references therein). In El Salvador, many lakes are associated with volcanic systems, considered as quiescent or showing moderate hydrothermal activity (Alegria, Apastepeque, Aramuaca, Cuscachapa, Coatepeque, Ilopango, Verde lakes; Rouwet, 2013), or characterized by strong fumarolic emissions (Lake Santa Ana; Bernard et al., 2004; Hernández et al., 2007; Scolamacchia et al., 2010; Colvin et al., 2013; Laiolo et al., 2017). This work focuses on Lake Coatepeque (close to Santa Ana Volcano) and Lake Ilopango (inside the Ilopango Caldera) (Fig. 1b), which are of particular interest for the volcanological community, since they show evidences of fluid inputs from the underlying magmatic-hydrothermal systems (e.g. Mann et al., 2004; Richer et al., 2004; Salazar et al., 2004; FORGAES and SNET, 2006; Aleman Alberto and Guerrero Nolasco, 2007; Lopez et al., 2004, 2009, 2012; Rodriguez et al., 2014; Saxby

**Multi-parametric probe:
vertical profiles**

et al., 2016; Martínez-Hackert et al., 2017; Ambury, 2017). Laguna de Chanmico (associated with the San Salvador Volcano; Fig. 1b) is also investigated, since, to the best of our knowledge, no detailed geochemical information is presently available for this lake, and it is not included in the VOLADA database (Rouwet, 2013; Rouwet et al., 2014). Physico-chemical, chemical and isotopic features along the water column from the lake surface to the maximum depth were investigated to understand (i) the processes controlling the chemistry of waters and dissolved gases and (ii) the possible role of microbial activity.

2. Volcanological and limnological outlines

Lake Coatepeque (Fig. 1c) is a large crater lake located to the east of the Coatepeque Caldera, being part of the Santa Ana–Izalco–Coatepeque volcanic complex (Lopez et al., 2012). It formed 50–70 ka as a result of a volcanic collapse (Pullinger, 1998). Post-caldera eruptions produced basaltic cinder cones and lava flows near the western margin of the caldera and rhyodacitic lava domes along a NE-SW-oriented fracture. Examples of this activity are the wooded island of Isla de Cabra (or Cerro Grande) and the dome of Cerro Pacho (7–10 ka), the latter characterized by gas and thermal emissions (Pullinger, 1998; FORGAES and SNET, 2006; Rodriguez et al., 2014). The lake has an area of 25.3 km^2 and a maximum depth of 115 m (SNET, 2000) and is hosted within an elliptical-shaped crater with main axes of $\sim 6.9 \text{ km}$ (NE-SW) and $\sim 4.9 \text{ km}$ (NW-SE), respectively. The surface waters of the lake have changed color 5 times in the last twenty years (1998, 2006, 2012, 2016, and 2017). These episodes were interpreted as due to a flowering of cyanophyte micro-algae that constitute part of the lake's phytoplankton (MARN, 2017).

Lake Ilopango (Fig. 1d) is hosted within the Ilopango Caldera, whose last collapse occurred approximately 1.6 ka (Lopez et al., 2012). In the past 57 ka, at least four large silicic explosive eruptions took place in

Table 1

Temperature, pH, main and minor (in mg/L) and trace (in µg/L) species and water and TDIC isotopes along the vertical profiles of the Coatepeque, Ilopango and Chanmico lakes. n.d.: not detected. n.a.: not analyzed.

	Depth (m)	Temperature (°C)	pH	HCO ₃ ⁻ (mg/L)	F ⁻ (mg/L)	Cl ⁻ (mg/L)	Br ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	NH ₄ ⁺ (mg/L)	TDS (mg/L)	As (µg/L)	B (µg/L)
Coatepeque	0	24.7	8.79	323	0.67	294	0.80	0.09	224	25	89	223	40	n.d.	1219	104	970
	5	24.7	8.8	333	0.62	258	0.91	0.02	178	21	83	213	39	0.08	1127	98	1170
	10	24.7	8.8	325	0.83	267	0.80	0.04	174	21	83	213	38	n.d.	1123	98	1240
	15	24.6	8.8	342	0.62	267	0.87	0.09	174	22	84	214	39	0.10	1144	94	1680
	20	24.6	8.8	345	0.75	277	0.88	0.08	186	23	86	224	41	0.10	1184	92	1970
	25	24.6	8.8	343	0.69	267	0.93	0.02	195	20	84	232	38	n.d.	1181	92	2200
	30	24.6	8.79	342	0.70	239	1.0	0.04	207	21	85	218	38	n.d.	1152	94	2680
	40	22.7	7.92	326	0.69	271	0.93	0.06	197	23	85	217	40	0.10	1160	88	2850
	60	22.6	7.87	358	0.69	286	0.96	0.11	208	26	86	220	40	0.14	1225	93	1960
	80	22.6	7.85	329	0.74	286	0.98	0.05	208	24	87	223	44	0.10	1203	90	2110
	100	22.6	7.88	336	0.68	285	1.0	0.04	204	24	85	211	37	0.18	1184	93	2410
110	22.6	7.88	357	0.65	279	0.92	0.14	200	25	87	210	38	0.10	1198	94	2390	
Ilopango	0	29	9.07	342	0.37	375	1.2	0.08	54	49	15	317	30	0.03	1183	644	7870
	5	28.7	9.08	340	0.60	367	0.96	0.12	57	50	15	319	32	0.16	1182	631	7620
	10	28.5	8.73	331	0.71	368	1.2	0.45	59	50	15	313	32	0.02	1170	641	8240
	15	28.3	8.68	354	0.46	347	1.1	0.56	59	51	15	321	31	0.16	1181	648	8960
	20	28.1	8.69	347	0.40	374	1.3	0.04	56	49	15	319	31	0.50	1193	629	9620
	25	27	7.97	344	0.51	351	1.1	0.09	58	50	15	317	31	0.31	1168	629	8400
	30	26.6	7.8	349	0.48	347	1.0	0.66	59	49	15	319	34	0.06	1173	633	8100
	40	26.4	7.66	354	0.44	347	0.82	n.d.	70	51	15	325	32	0.40	1195	639	8300
	70	26.4	7.61	345	0.56	364	1.1	n.d.	76	51	15	330	33	0.41	1216	633	8480
	100	26.4	7.6	366	0.56	351	1.2	n.d.	76	50	14	319	31	0.26	1208	632	8920
	140	26.4	7.61	340	0.68	325	1.2	0.47	68	47	13	305	29	0.62	1130	634	8400
180	26.4	7.56	339	0.62	346	1.2	0.24	64	50	15	317	32	0.13	1165	626	8630	
220	26.4	7.5	330	0.70	337	1.2	n.d.	69	49	14	315	31	0.17	1147	631	8350	
Chanmico	0	28.8	9.34	310	0.33	11	0.01	0.02	107	19	64	42	12	0.47	566	7.4	100
	5	28.1	9.02	314	0.36	11	0.02	0.04	111	21	65	42	11	0.25	576	6.1	210
	10	25.8	7.71	410	0.50	13	0.01	9.5	116	35	74	47	12	4.9	721	6.1	200
	15	25.3	7.59	417	0.33	12	0.02	13	109	38	75	46	12	5.0	728	8.0	190
	20	25.2	7.5	426	0.45	13	0.02	0.55	122	40	76	48	12	5.9	745	7.1	190
	25	25.2	7.42	461	0.47	14	0.02	0.04	125	44	78	48	13	8.0	792	9.3	170
	30	25.2	7.36	481	0.58	15	0.02	0.36	110	44	76	46	14	9.0	797	9.8	170
	35	25.2	7.32	500	0.40	15	0.02	0.50	114	48	80	49	15	10	832	9.7	170
	40	25.2	7.3	504	0.33	14	0.02	0.77	104	47	79	48	13	11	822	10	160
	45	25.2	7.3	520	0.82	17	0.02	0.08	119	47	80	48	13	11	856	12	140
47	25.2	7.3	522	0.38	15	0.01	0.25	112	47	80	48	13	11	848	13	140	
Cerro Afate	/	>60	7.5	336	0.82	528	2.0	0.65	149	67	38	392	45	1560	1243	7740	

Table 1 (continued)

	Ba (µg/L)	Cd (µg/L)	Co (µg/L)	Cu (µg/L)	Fe (µg/L)	Li (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Sb (µg/L)	Si (mg/L)	Sr (µg/L)	Zn (µg/L)	δD-H ₂ O ‰ V-SMOW	δ ¹⁸ O-H ₂ O ‰ V-SMOW	δ ¹³ C-TDIC ‰ V-PDB	
Coatepeque	8.8	n.d.	1.4	7.6	0.26	554	4.8	0.76	14	31	0.80	111	3.3	4.7	1.4	0.8	
	8.3	n.d.	1.7	7.4	0.67	540	4.9	0.52	16	35	1.0	110	1.0	3.7	1.5	0.6	
	8.5	n.d.	1.7	7.5	1.2	564	4.8	1.2	16	41	1.2	110	1.5	4.5	1.5	0.9	
	7.4	0.80	n.d.	2.3	1.9	531	n.d.	n.d.	14	26	0.85	102	n.d.	3.8	1.4	-0.8	
	7.7	0.89	n.d.	2.2	1.8	521	n.d.	n.d.	16	36	0.84	101	0.13	4.4	1.5	0.3	
	7.5	0.95	0.23	1.8	0.68	509	n.d.	0.04	18	42	0.84	101	0.69	2.7	1.5	0.9	
	7.6	0.89	0.29	1.8	0.68	514	n.d.	0.32	22	41	0.90	101	0.23	2.6	1.4	0.6	
	7.4	0.82	n.d.	1.6	1.1	546	n.d.	n.d.	0.36	10	0.84	107	n.d.	4.6	1.5	1.5	
	11	0.72	n.d.	1.5	1.0	558	n.d.	n.d.	2.2	16	1.6	136	5.3	3.4	1.5	-0.9	
	8.2	0.83	n.d.	2.7	1.3	537	n.d.	n.d.	4.6	15	0.97	114	0.99	3.0	1.5	-0.9	
	14	0.83	n.d.	4.0	3.7	559	n.d.	n.d.	4.1	23	1.5	136	6.6	2.9	1.4	-1.3	
	12	0.79	n.d.	3.3	1.0	544	n.d.	n.d.	7.0	26	1.6	137	4.2	1.4	1.4	-1.3	
	Ilopango	84	0.62	1.6	8.3	0.87	665	4.8	0.52	18	27	7.2	271	0.69	-2.1	1.1	-1.9
		81	0.28	1.7	7.9	n.d.	651	4.8	0.47	20	34	7.1	260	6.6	-2.5	1.1	3.6
82		0.61	2.1	7.7	n.d.	639	4.7	1.0	25	39	7.1	262	5.3	-2.2	1.1	3.0	
82		0.58	2.7	7.5	1.5	665	4.8	2.3	25	47	7.2	264	4.2	-2.5	1.2	2.9	
80		0.79	2.9	7.5	0.57	629	4.7	1.8	27	50	6.9	261	2.4	-2.9	1.2	2.5	
81		0.29	1.0	7.4	n.d.	667	4.7	0.44	3.6	10	7.4	275	5.0	-2.6	1.1	2.1	
84		0.23	1.1	7.2	0.18	676	13	0.30	5.1	14	8.8	277	7.7	-2.4	1.1	-0.3	
81		0.32	1.1	7.3	1.6	692	11	0.14	5.6	17	9.5	278	5.6	-2.4	1.1	0.2	
76		0.24	1.2	7.2	0.29	691	4.8	0.23	8.2	18	9.6	275	8.8	-2.5	1.1	0.1	
75		0.20	1.1	7.4	n.d.	688	4.8	0.87	11	22	9.6	274	8.1	-3.1	1.1	-0.2	
76		0.07	1.2	7.6	3.4	680	4.8	0.43	10	27	9.5	276	6.4	-3.1	1.3	-0.4	
78		0.33	1.3	7.7	n.d.	654	4.7	0.50	10	32	7.8	270	5.3	-2.6	1.4	0.9	
78		0.30	1.3	7.8	n.d.	664	4.7	0.36	13	31	7.9	270	4.0	-2.9	1.3	2.5	
Chanmico		n.d.	0.32	n.d.	1.6	5.8	8.5	n.d.	n.d.	6.6	21	21	59	0.23	-7.2	0.5	0.5
	n.d.	0.35	n.d.	1.6	0.61	6.1	14	n.d.	6.9	28	20	57	4.4	-10.6	0.3	-0.8	
	2.0	0.37	n.d.	1.1	7.4	6.5	323	n.d.	13	29	23	98	n.d.	-15.1	-0.6	-4.3	
	3.8	0.36	n.d.	1.0	6.6	6.1	303	n.d.	11	33	24	111	n.d.	-17.6	-1.0	-4.6	
	5.0	0.35	n.d.	1.1	4.5	5.4	299	n.d.	14	35	23	115	n.d.	-17.1	-1.1	-3.8	
	7.3	0.38	n.d.	1.1	2.0	5.7	305	n.d.	15	33	23	126	n.d.	-17.1	-1.2	-2.2	
	9.0	0.42	n.d.	1.0	1.0	4.8	312	n.d.	15	38	24	131	n.d.	-18.4	-1.4	-4.2	
	10	0.34	n.d.	0.96	0.87	4.6	316	n.d.	15	41	23	134	n.d.	-19.3	-1.4	-5.3	
	12	0.42	0.06	0.93	1.7	4.5	328	n.d.	15	34	24	141	n.d.	-19.6	-1.4	-6.1	
	11	0.37	0.18	1.0	0.97	4.8	323	n.d.	17	44	24	141	n.d.	-20.4	-1.5	-5.5	
	11	0.54	n.d.	1.0	2.5	4.3	321	n.d.	17	46	24	141	n.d.	-19.9	-1.5	-6.4	
	Cerro Afate	105	n.a.	<1	<1	66	1800	22	n.d.	n.a.	109	n.a.	n.a.	<1	-51.0	-6.6	n.a.

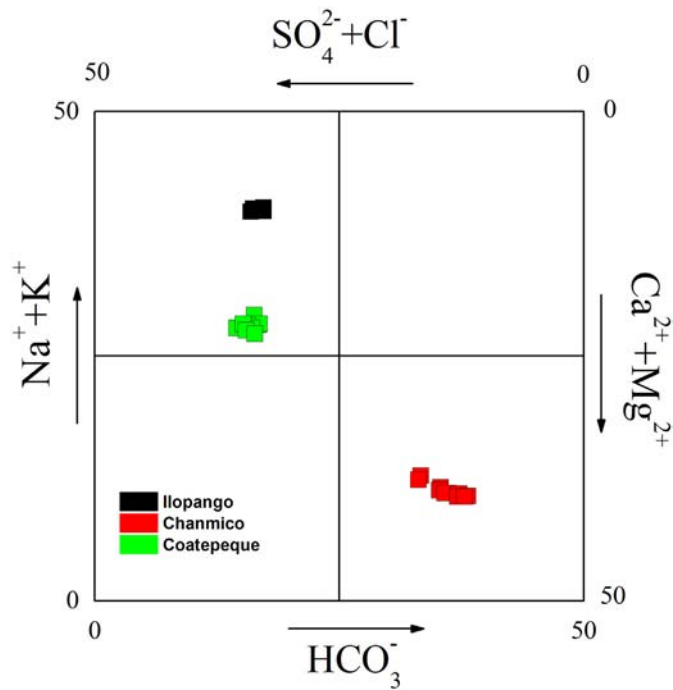


Fig. 3. Classification diagram of Langelier and Ludwig (1942).

the caldera, the last of which (6th century CE) partly devastated the local Mayan civilization (Mann et al., 2004 and references therein) and was probably also responsible for the extreme short-term climate cooling occurred 535–536 CE (Dull et al., 2010). The recent volcanic activity within the lake (1879 and 1880) formed the dome of Islas Quemadas (Richer et al., 2004). Saxby et al. (2016) suggested that magma is presently stored at about 6 km below the caldera. Lake Ilopango has estimated area and volume of 70.6 km² and 9.97 km³, respectively, a perimeter of 52.5 km and steep sides sloping to a maximum depth of ~240 m (SNET, 2000; Lopez et al., 2004; Esquivel, 2016). The Chaguite River to the west and the Desagüe River to the east are the main tributary and emissary, respectively (Lopez et al., 2004).

Lake Chanmico (Fig. 1e) occupies the crater bottom of a monogenetic volcano on the northwest side of the San Salvador Volcano, which generated phreatomagmatic events in recent times (400 BCE–250 CE) (Sofield, 1998; Ferrés et al., 2011), as testified by the presence of surge, fall, and debris-flow deposits. The lake has an almost circular shape (0.78 km²) and a diameter of ~1 km.

3. Materials and methods

3.1. Water and dissolved gas sampling

Water and dissolved gas samples were collected in November 2016 along a vertical profile from the lake surface to the maximum depth, at regular depth intervals of 5 m. A small diameter (6 mm) Rilsan© tube, lowered at the sampling depth and connected to a 100 mL syringe equipped with a three-way teflon valve, was used to pump up the water (single hose method; Tassi and Rouwet, 2014). One water sample from the Cerro Afate (16 P 222396 1531972) mineral spring located near Lake Coatepeque (Fig. 1c) was also collected. Two non-filtered and two filtered (0.45 μm) and acidified (with ultrapure HCl and HNO₃, respectively) water samples were collected in polyethylene bottles for the analysis of anions, water isotopes (δD-H₂O and δ¹⁸O-H₂O) and cations and trace species, respectively, after the displacement of a water volume at least twice the inner volume of the tube.

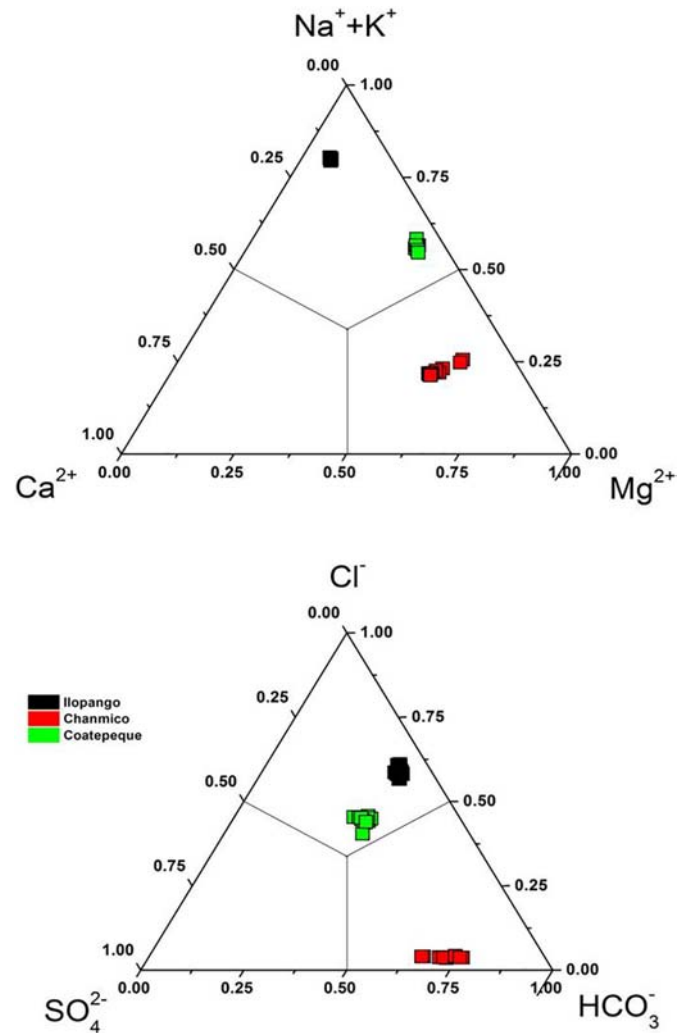


Fig. 4. Cation (up) and anion (down) triangular diagrams.

The isotope analyses of total dissolved inorganic carbon (δ¹³C-TDIC) were carried out on samples collected in 12 mL glass bottles with the addition of a few mL of anhydrous H₃PO₄ to prevent any fractionation process of carbon isotopes due to the presence of bacterial activity. Dissolved gases were collected using pre-evacuated 250 mL glass vials equipped with a Teflon stopcock. Once the vial was connected to the Rilsan© tube through the three-way valve, the stopcock was opened to allow water entering up to about three fourths of the vial inner volume (Tassi et al., 2008, 2009).

3.2. Field measurements

Lake water temperature, dissolved O₂, electrical conductivity (EC, temperature compensated) and pH were measured using a multi-parametric probe (Idromarambiente SCRL IP-188A) equipped with a data logger for data storage. The probe (data acquisition frequency of 5 s) was very slowly lowered from the surface to the maximum lake depth to obtain a measurement interval each 15 cm. The nominal precisions were, as follows: depth ±0.05 m; temperature ±0.03 °C; O₂ ± 1.56 μmol/L; EC ±0.01 mS/cm and pH ±0.1.

3.3. Chemical and isotopic analysis

3.3.1. Lake waters

Alkalinity was measured by acidimetric titration (AC) with 0.01 N HCl using a Metrohm 794 automatic titration unit. The analytical error

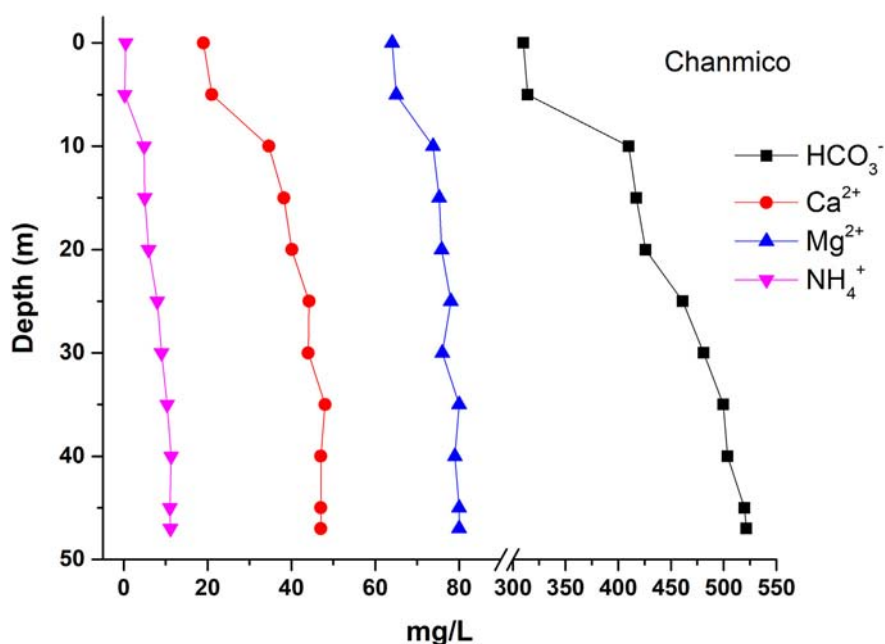


Fig. 5. Vertical distribution of HCO_3^- , Ca^{2+} , Mg^{2+} and NH_4^+ (in mg/L) for the Lake Chanmico.

for AC analysis was $\leq 5\%$. The main anions (Cl^- , SO_4^{2-} , NO_3^- , Br^- , and F^-) and cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and NH_4^+) were analyzed by ion chromatography (IC) using Metrohm 761 and Metrohm 861 chromatographs, respectively. Trace elements (As, B, Ba, Cd, Co, Cu, Fe_{tot} , Li, Mn, Ni, Pb, Sb, Si, Sr and Zn) were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Perkin Elmer Optima

Table 2
Concentrations of dissolved gases (in $\mu\text{mol/L}$) and carbon isotopes in CO_2 along the vertical profiles of the Coatepeque, Ilopango and Chanmico lakes. n.d.: not detected.

	$\mu\text{mol/L}$	Depth (m)	CO_2	N_2	Ar	CH_4	H_2	He	Gas Total	$\delta^{13}\text{C-CO}_2$
Coatepeque		5	1.2	491	11.7	n.d.	n.d.	0.011	504	n.d.
		10	1.1	511	12.2	n.d.	n.d.	0.003	524	-9.0
		15	1.3	505	11.9	n.d.	n.d.	0.002	518	n.d.
		20	1.5	495	11.8	n.d.	n.d.	0.003	508	n.d.
		25	5.9	506	11.9	n.d.	n.d.	0.002	524	n.d.
		30	51	505	11.6	n.d.	n.d.	0.005	568	-6.0
		40	58	501	11.5	0.21	n.d.	0.006	571	n.d.
		60	115	498	11.7	2.3	0.2	0.012	627	-8.2
		80	107	508	11.3	5.4	0.8	0.015	633	n.d.
		100	308	505	11.2	8.5	1.3	0.014	834	-8.8
		110	411	515	11	12	1.5	0.021	951	-8.3
Ilopango		5	1.1	455	11.9	n.d.	n.d.	0.003	468	n.d.
		10	1.2	463	12.2	n.d.	n.d.	0.003	476	n.d.
		15	1.2	469	12.3	n.d.	n.d.	0.002	483	n.d.
		20	2.8	471	12.2	n.d.	n.d.	0.004	486	n.d.
		25	3.9	477	12.1	0.05	n.d.	0.003	493	n.d.
		30	8.1	468	11.9	0.11	0.1	0.004	488	-7.7
		40	12	466	12	0.09	0.3	0.003	490	n.d.
		70	13	451	11.8	0.13	0.2	0.005	476	-8.7
		100	16	482	11.5	3.6	0.5	0.004	514	-8.2
		140	23	481	11.6	4.4	0.9	0.006	521	-9.1
		180	41	485	11.4	4.6	0.8	0.005	543	-6.5
	220	52	493	11.3	5.9	1.1	0.007	563	-8.2	
Chanmico		5	2.1	492	12.3	3.9	0.2	0.002	511	n.d.
		10	3.6	495	12.2	16	0.5	0.002	527	-9.9
		15	4.5	475	12.4	118	0.6	0.003	611	n.d.
		20	5.6	483	12.1	215	1.1	0.002	717	-11.7
		25	24	490	12.2	231	1.6	0.003	759	-11.9
		30	55	485	12.1	233	2.2	0.004	787	-11.6
		35	181	491	12	344	2.1	0.005	1030	-11.6
		40	213	489	11.8	455	2.5	0.004	1171	-12.4
		45	239	485	11.7	467	2.6	0.006	1205	-11.1
		47	208	483	11.6	481	2.9	0.008	1187	-11.5

8000. The analytical error for IC and ICP-OES analysis were $< 5\%$ and $< 10\%$, respectively.

The $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios of water (expressed as $\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$ ‰ vs. V-SMOW) were determined by isotope ratio mass spectrometry (IRMS). Oxygen isotopes measurements were carried out by using a Gas Bench peripheral coupled with a Thermo Delta V mass spectrometer. A TC-EA peripheral interfaced by means of a ConFloIV with Thermo Delta XP mass spectrometer was used for hydrogen isotopes. The analytical error for IRMS was $\pm 0.1\%$ for $\delta^{18}\text{O}$ and better than $\pm 1\%$ for δD .

The $^{13}\text{C}/^{12}\text{C}$ of Total Dissolved Inorganic Carbon (TDIC), expressed as $\delta^{13}\text{C-TDIC}$ ‰ vs. V-PDB, were analyzed at INGV-Palermo laboratories with a CF-IRMS technique, following the procedure described by Salata et al. (2000). $\delta^{13}\text{C-TDIC}$ measurements were carried out by using a Finnigan Delta Plus XP equipped with a Thermo TRACE CG. A detailed description of the analytical system can be found in Grassa et al. (2010). The analytical precision was better than 0.1‰.

3.3.2. Dissolved gases

The chemical composition of the inorganic dissolved gases in the headspace of the sampling flasks (CO_2 , N_2 , Ar, H_2 and He) was determined by gas chromatography (GC) using a Shimadzu 15A equipped with a 5 m long stainless steel column packed with Porapak 80/100 mesh and a Thermal Conductivity Detector (TCD), whereas CH_4 was analyzed using a Shimadzu 14A equipped with a 10 m long stainless steel column packed with Chromosorb PAW 80/100 mesh coated with 23% SP 1700 and a Flame Ionization Detector (FID) (Vaselli et al., 2006). The analytical error for GC analysis was $\leq 5\%$. The number of moles of each gas species in the liquid ($n_{i,l}$) was calculated on the basis of those in the flask headspace ($n_{i,g}$) by means of the Henry's law constants and assuming that in the sampling flasks the separated gas phase was in equilibrium with the liquid (Wilhelm et al., 1977). The total moles of each gas species in the water sample was given by the sum of $n_{i,l}$ and $n_{i,g}$.

The isotopic composition of dissolved CO_2 ($\delta^{13}\text{C-CO}_2$ expressed as ‰ vs. V-PDB) was determined by analyzing the $^{13}\text{C}/^{12}\text{C}$ values of CO_2 in the sampling flask headspace ($\delta^{13}\text{C-CO}_{2\text{meas}}$) using a Finnigan Delta S mass spectrometer, after a two-step extraction and purification procedures of the gas mixtures by using liquid N_2 and a solid-liquid mixture of liquid N_2 and trichloroethylene (Evans et al., 1998; Vaselli et al., 2006).

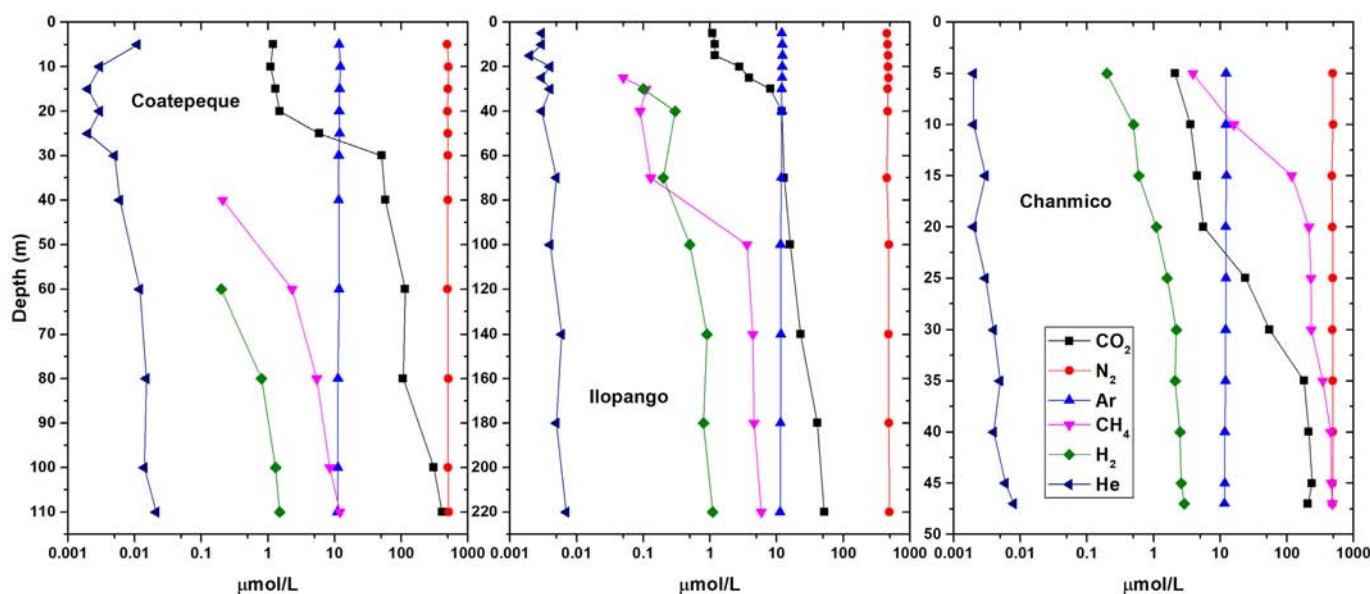


Fig. 6. Concentrations (in $\mu\text{mol/L}$) of CO_2 , N_2 , Ar , CH_4 , H_2 and He along the vertical profiles for the Coatepeque, Ilopango and Chanmico lakes.

Internal (Carrara and San Vincenzo marbles) and international (NBS18 and NBS19) standards were used to estimate accuracy. The analytical error and the reproducibility were $\pm 0.05\%$ and $\pm 0.1\%$, respectively. The $\delta^{13}\text{C}$ values of dissolved CO_2 were then calculated from the measured $\delta^{13}\text{C}-\text{CO}_{2\text{meas}}$ on the basis of the enrichment factor (ϵ_1) for gas-water isotope equilibrium proposed by Zhang et al. (1995), as follows:

$$\epsilon_1 = \delta^{13}\text{C}-\text{CO}_2 - \delta^{13}\text{C}-\text{CO}_{2\text{meas}} = (0.0049 \times T) - 1.31 \quad (1)$$

where temperature (T) is expressed in $^\circ\text{C}$.

4. Results

4.1. Vertical profiles of water temperature, EC, pH and dissolved O_2

Temperature, EC, pH, and dissolved O_2 concentrations along the vertical profiles of the five lakes are shown in Fig. 2. The Coatepeque,

Ilopango and Chanmico volcanic lakes showed a thermocline at 30–40 m, 20–40 m and 5–15 m depth, respectively, separating the relatively warm shallow waters, where temperature ranged from 29 (Ilopango and Chanmico) to 25 $^\circ\text{C}$ (Coatepeque), and the hypolimnetic waters, showing 26, 25 and 23 $^\circ\text{C}$, respectively. At the thermoclines, slight conductivity increases (from 1540 to 1580, from 1550 to 1600 and from 625 to 800 $\mu\text{S/cm}$, respectively) and pH decreases (from 8.8 to 7.9, from 8.6 to 7.6 and from 9 to 7.5, respectively) were recorded. In the hypolimnion, the vertical profiles of temperature, EC and pH did not show substantial variations, excepting Lake Chanmico that showed a EC increase (up to 895 $\mu\text{S/cm}$) and a gradual pH decrease (down to 7.3). Anaerobic waters were below 33, 24 and 4 m depth, at Coatepeque, Ilopango and Chanmico respectively, whilst above these depths dissolved O_2 was up to 0.55, 2.39 and 1.27 mg/L, respectively.

4.2. Chemical and isotopic composition of the lake waters

Chemical composition (main and trace solutes, in mg/L), total dissolved solids (TDS, in mg/L) and $\delta\text{D}-\text{H}_2\text{O}$, $\delta^{18}\text{O}-\text{H}_2\text{O}$ ($\%$ V-SMOW) and $\delta^{13}\text{C}-\text{TDIC}$ ($\%$ V-PDB) values of three lakes are listed in Table 1.

The Coatepeque and Ilopango waters were $\text{Na}^+-\text{Cl}^- (\text{SO}_4^{2-})$ and $\text{Na}^+-\text{Cl}^- (\text{HCO}_3^-)$ (Na^+ up to 232 and 330 mg/L, Cl^- up to 294 and 375 mg/L, SO_4^{2-} up to 224 and 76 mg/L, HCO_3^- up to 358 and 366 mg/L, respectively), with TDS values up to 1226 and 1216 mg/L, respectively, whereas those from Lake Chanmico showed a $\text{Mg}^{2+}-\text{HCO}_3^-$ composition and TDS values between 566 and 856 mg/L (Figs. 3–4). Cerro Afate mineral spring near Lake Coatepeque was Na^+-Cl^- , with a TDS value of 1560 mg/L (Table 1). At Chanmico, HCO_3^- , Ca^{2+} , Mg^{2+} and NH_4^+ concentrations increased with depth (up to 522, 48, 80 and 11 mg/L, respectively; Fig. 5). Conversely, no substantial chemical variations were measured along the water columns of Coatepeque and Ilopango (Table 1). F^- , Br^- , NO_3^- and K^+ abundances were up to 0.83, 1.3, 13 and 44 mg/L, respectively.

All the three lakes showed relatively high contents of B (up to 9.6 mg/L at Ilopango), Si (up to 24 mg/L at Chanmico) and Sr (up to 278 $\mu\text{g/L}$ at Ilopango). Coatepeque and Ilopango were also characterized by relatively high concentrations of As (up to 104 and 648 $\mu\text{g/L}$, respectively) and Li (up to 564 and 692 $\mu\text{g/L}$, respectively), whilst those of Ba and Mn were up to 84 (Ilopango) and 328 (Chanmico) $\mu\text{g/L}$, respectively. The highest concentrations of Pb and Sb (27 and 50 $\mu\text{g/L}$, respectively) were measured at 20 m depth in the Lake Ilopango, whereas

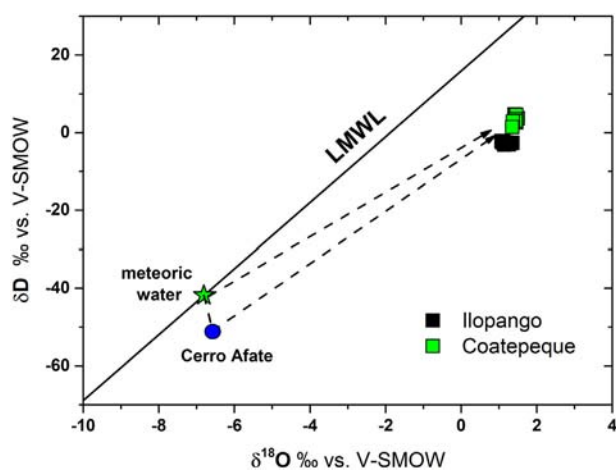


Fig. 7. δD vs. $\delta^{18}\text{O}$ (in $\%$ vs. V-SMOW) binary diagram of the Coatepeque (green) and Ilopango (black) lake waters. Green star: the isotopic composition of the local meteoric water (from IAEA/WMO, 2018, Coatepeque site); blue circle: isotopic composition of Cerro Afate hot spring; black line: the local meteoric water line (from IAEA/WMO, 2018, Coatepeque site). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

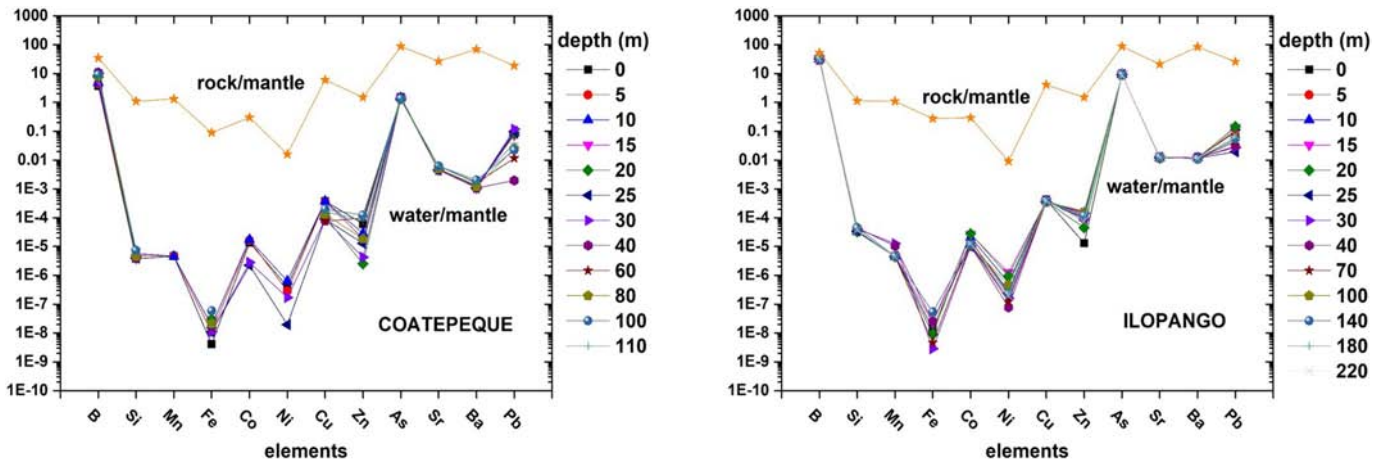


Fig. 8. Normalized concentrations of B, Si, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Ba and Pb to the Earth primitive mantle (Palme and O'Neill, 2014) along the vertical profile of Coatepeque and Ilopango lakes compared with those measured in the Balsamo basaltic lava rock samples (Agostini et al., 2006; Tonarini et al., 2007) or, for Zn and As, with those measured in basement andesites (Rapprich and Hradecký, 2005).

those of other trace elements (Cd, Co, Cu, Fe, Ni and Zn) were <10 µg/L. Cerro Afate mineral spring showed high contents of As, B and Li (1243, 7740 and 1800 µg/L, respectively; Table 1).

The δD-H₂O values of Coatepeque, Ilopango and Chanmico lakes varied from 1.4 to 4.7‰, from -3.1 to -2.2‰ and from -20.4 to -7.2‰ vs. V-SMOW, respectively, whilst those of δ¹⁸O-H₂O ranged from 1.4 to 1.5‰, from 1.1 to 1.4‰ and from -1.5 to 0.5‰ vs. V-SMOW, respectively. The δD-H₂O and δ¹⁸O-H₂O values of Cerro Afate mineral spring were -51 and -6.6‰ vs. V-SMOW, respectively. The δ¹³C-TDIC values of Coatepeque, Ilopango and Chanmico lakes ranged from -1.3 to 1.5‰, from -1.9 to 3.6‰ and from -6.4 to 0.5‰ vs. V-PDB, respectively.

4.3. Chemical and isotopic composition of dissolved gases

The chemical (in µmol/L) and isotopic (δ¹³C-CO₂) composition of the dissolved gases (CO₂, N₂, Ar, CH₄, H₂ and He) and the total gas concentration (in µmol/L) are reported in Table 2.

Nitrogen was the most abundant dissolved gas in the three lakes (ranging from 451 to 515 µmol/L) and did not vary significantly with depth. On the contrary, CO₂ concentrations were increasing with

depth, reaching the highest values at the lake bottoms (411, 52 and 239 µmol/L at Coatepeque, Ilopango and Chanmico, respectively; Fig. 6). Deeper waters also showed increasing contents of H₂ (up to 2.9 µmol/L at Lake Chanmico) and CH₄. Argon and He contents (up to 12.4 µmol/L) were almost constant along the vertical profile, excepting He at Lake Coatepeque that increased up to 0.021 µmol/L. The total gas concentration at Coatepeque, Ilopango and Chanmico lakes was up to 951, 563 and 1205 µmol/L, respectively.

The δ¹³C-CO₂ values at Coatepeque, Ilopango and Chanmico ranged from -9.0 to -6.0‰, from -9.1 to -6.5‰ and from -12.4 to -9.9‰ vs. V-PDB, respectively, although no carbon isotope analyses were carried out on samples with very low dissolved CO₂.

5. Discussion

5.1. Processes controlling lakes water chemistry

5.1.1. Lake Coatepeque and Lake Ilopango

Coatepeque and Ilopango lakes were characterized by a Na⁺-Cl⁻ composition, unlikely related to input of seawater, given that the two

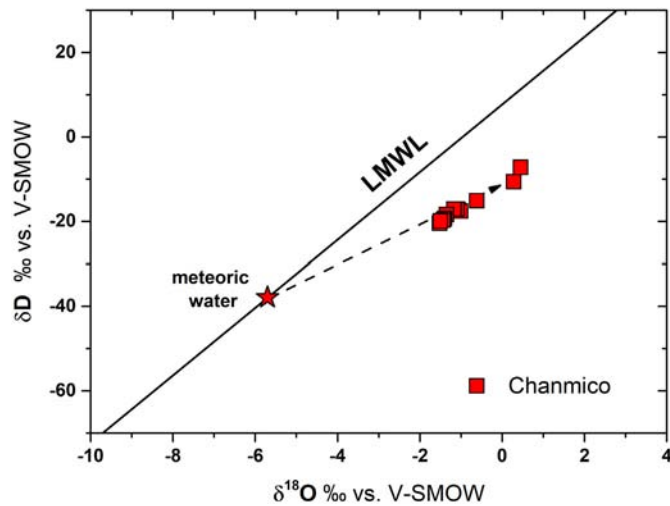


Fig. 9. δD vs. δ¹⁸O (in ‰ vs. V-SMOW) binary diagram of the Chanmico (red) lake waters. Red star: isotopic composition of the local meteoric water (from IAEA/WMO, 2018, San Andres site); black line: local meteoric water line (from IAEA/WMO, 2018, San Andres site). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

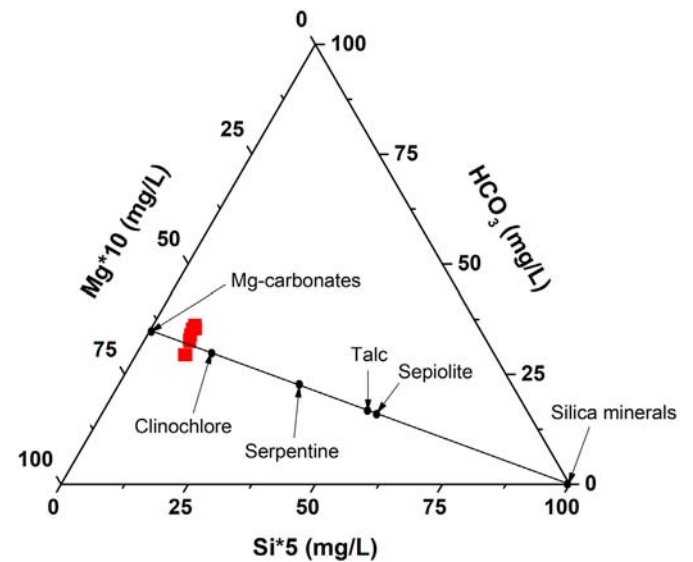


Fig. 10. Si*5-Mg*10-HCO₃ triangular diagrams for the Chanmico lake waters. Black circles: expected compositions of the aqueous phase controlled by CO₂-driven dissolution of Mg-bearing solid phases (Fantoni et al., 2002).

Table 3
Saturation indexes with depth of selected minerals for Lake Chanmico.

	Depth (m)	si_Aragonite	si_Brucite	si_Calcite	si_Chrysotile	si_Diopside	si_Enstatite	si_Forsterite	si_Huntite	si_Magnesite	si_Quartz	si_Sepiolite	si_Talc
Chanmico	0	0.1664	-2.8564	0.3118	2.7201	-1.2426	-1.0604	-4.129	0.6996	0.645	0.8178	4.0262	6.3353
	5	0.2016	-2.8981	0.347	2.6299	-1.2651	-1.0965	-4.2115	0.7026	0.6358	0.8252	3.9404	6.2614
	10	0.4457	-3.0633	0.5912	2.3918	-1.2165	-1.1722	-4.4679	1.1172	0.6979	0.9208	3.9736	6.2192
	15	0.4853	-3.0912	0.6308	2.3636	-1.1918	-1.181	-4.5079	1.1569	0.6991	0.9412	4.0109	6.2328
	20	0.5048	-3.1091	0.6503	2.2958	-1.2237	-1.2076	-4.5532	1.1725	0.698	0.9327	3.8939	6.1484
	25	0.5411	-3.1706	0.6866	2.1124	-1.316	-1.2686	-4.6756	1.2288	0.7047	0.9332	3.6508	5.9659
	30	0.5226	-3.2558	0.6681	1.8989	-1.4366	-1.3327	-4.825	1.1319	0.6785	0.9543	3.4366	5.7946
	35	0.4266	-3.5377	0.5721	1.0252	-2.0115	-1.6287	-5.4028	0.6969	0.5656	0.9403	2.2247	4.8928
	40	0.3929	-3.6039	0.5384	0.8477	-2.1273	-1.6843	-5.5246	0.5759	0.5364	0.9508	2.0233	4.7365
	45	0.3836	-3.6408	0.5291	0.7372	-2.2045	-1.7211	-5.5983	0.5495	0.5307	0.951	1.8764	4.6262
	47	0.4167	-3.5762	0.5622	0.9409	-2.0668	-1.6516	-5.4642	0.6859	0.5652	0.9558	2.1642	4.8396

lakes are located at about 50 and 30 km, respectively, from the Pacific coast. The most reliable explanation for this peculiar chemistry implies the input of deep-seated fluids. In fact, these waters showed features typical of hydrothermal fluids, as follows: i) relatively high TDS values; ii) Cl^-/Br^- molar ratios in the range of geothermal brines (≤ 650) (Fontes and Matray, 1993; Davis et al., 2001; Risacher et al., 2011); iii) high As, B and Li concentrations (Table 1) (e.g. Brondi et al., 1973; Aggarwal et al., 2000 and references therein; Webster and Nordstrom, 2003; Aiuppa et al., 2006; Göb et al., 2013; Cinti et al., 2015, 2017); iv) relatively high Si content; v) $\text{Cl}^-/\text{SO}_4^{2-}$ ratio > 1 . Anomalously high As and B concentrations, i.e. higher than the drinking water standard for As (0.01 mg/L; US EPA, 2001) and guideline for B (0.5 mg/L; WHO, 2003), were already reported by other studies carried out at Lake Ilopango (Ransom, 2002; Lopez et al., 2009, 2012). Accordingly, based on gravimetric and seismic data and diffuse CO_2 flux and radon concentrations, Lopez et al. (2004, 2012) and Saxby et al. (2016) suggested the occurrence of a hydrothermal system at a depth of few km beneath the southern part of Lake Ilopango. Input of hydrothermal fluids into Lake Ilopango is also supported by the occasional observation of floating sulfur nodules at the lake surface during occasional roll-over episodes (Lopez et al., 2004; Varekamp, 2015) and the occurrence of hot water springs near the Island of Cerro Los Patos (Lopez et al., 2009).

The $\delta\text{D}-\text{H}_2\text{O}$ vs. $\delta^{18}\text{O}-\text{H}_2\text{O}$ diagram (Fig. 7), a useful tool to investigate potential water sources feeding the lakes (Varekamp and Kreulen, 2000 and references therein), also reporting the local meteoric water line (from IAEA/WMO, 2018, Coatepeque site), shows that Coatepeque and Ilopango waters are enriched in ^2H and ^{18}O with respect to the mean

local meteoric water (from IAEA/WMO, 2018, Coatepeque site). For both lakes, this may depend on evaporation processes of (i) the lake-feeding meteoric water, (ii) a mature hydrothermal component deriving from prolonged water-rock interactions, like the Cerro Afate hot spring entering Lake Coatepeque or (iii) both the two processes (Fig. 7). According to these hypotheses, in order to verify whether the observed chemistry was due to a mixture between meteoric and more saline (hydrothermal) waters, a chemical two-component (meteoric and hydrothermal) mixing model was developed by using the geochemical code PHREEQC 3.3.7.11094 (Inl.dat database; Parkhurst and Appelo, 1999). The simulation included the Cerro Afate spring, assumed as the hydrothermal endmember, and a generic low-salinity water, assumed as the meteoric endmember since, to the best of our knowledge, no chemical data of local rainwater are available. Focusing on the main anion (Cl^-), which can be considered a useful geochemical tracer, the result of the simulation shows that the water composition of Lake Coatepeque can be reproduced by mixing the meteoric and hydrothermal end-members by ~45%–55%, respectively. Such a high hydrothermal fluid contribution for Coatepeque is also supported by literature, reporting the presence of gas emissions nearby Cerro Pacho, as well as a number of hot springs discharging at the lake shores (Salazar et al., 2004; FORGAES and SNET, 2006; Lopez et al., 2012; Rodriguez et al., 2014). When considering the same meteoric and hydrothermal end-members of Lake Coatepeque, the Cl^- simulation indicates that a ~30%–70% mixing may reproduce the water composition of Lake Ilopango. The relatively high SO_4^{2-} concentrations (Table 1) of Lake Coatepeque can possibly be ascribed to dissolution of H_2S (e.g. Lopez et al., 2012; Tassi et al., 2018a) from the volcanic-hydrothermal system of the nearby Santa Ana volcano. The relatively high concentrations of HCO_3^- in both Coatepeque and Ilopango lakes are likely controlled by

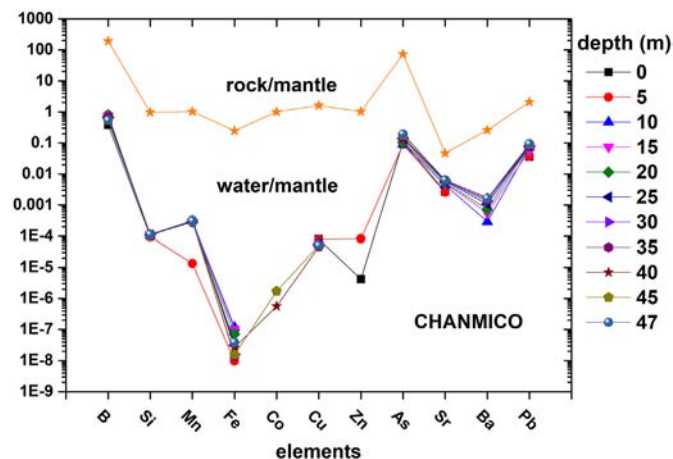


Fig. 11. Normalized concentrations of B, Si, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Ba and Pb to the Earth primitive mantle (Palme and O'Neill, 2014) along the vertical profile of Lake Chanmico normalized to those of Earth's mantle (Palme and O'Neill, 2014) and compared with those measured in a serpentinized peridotite (Schwarzenbach et al., 2014) belonging to the Santa Elena Ophiolite (Costa Rica). B and As were normalized to serpentinitic rock composition from Boström and Valdes (1969), Bonatti et al. (1984) and Martin et al. (2016).

Table 4

CO_2 and CH_4 concentrations (in mmol/L) at the bottom of Coatepeque, Ilopango and Chanmico lakes compared to those measured at Lake Kivu (Tassi et al., 2009), Costa Rican and Italian volcanic lakes (Cabassi et al., 2013, 2014) and Lake Pavin (Zimmer et al., 2015). n.a.: not analyzed.

Lakes (bottom)	Depth (m)	CO_2 (mmol/L)	CH_4 (mmol/L)	
Coatepeque	110	0.4	0.012	El Salvador volcanic lakes this work
Ilopango	220	0.052	0.0059	
Chanmico	47	0.21	0.48	
Kivu (DRC)	470	137	17	Tassi et al., 2009
Monticchio Grande	35	4.9	0.39	Italy volcanic lakes Cabassi et al., 2013
Monticchio Piccolo	38	14	5	
Averno	33	5.2	1.1	
Albano	167	1.9	0.4	
Hule	21	1.1	0.23	Costa Rica volcanic lakes Cabassi et al., 2014
Rio Cuarto	67	1.8	2.8	
Pavin (France)	90	9.6	n.a.	Zimmer et al., 2015

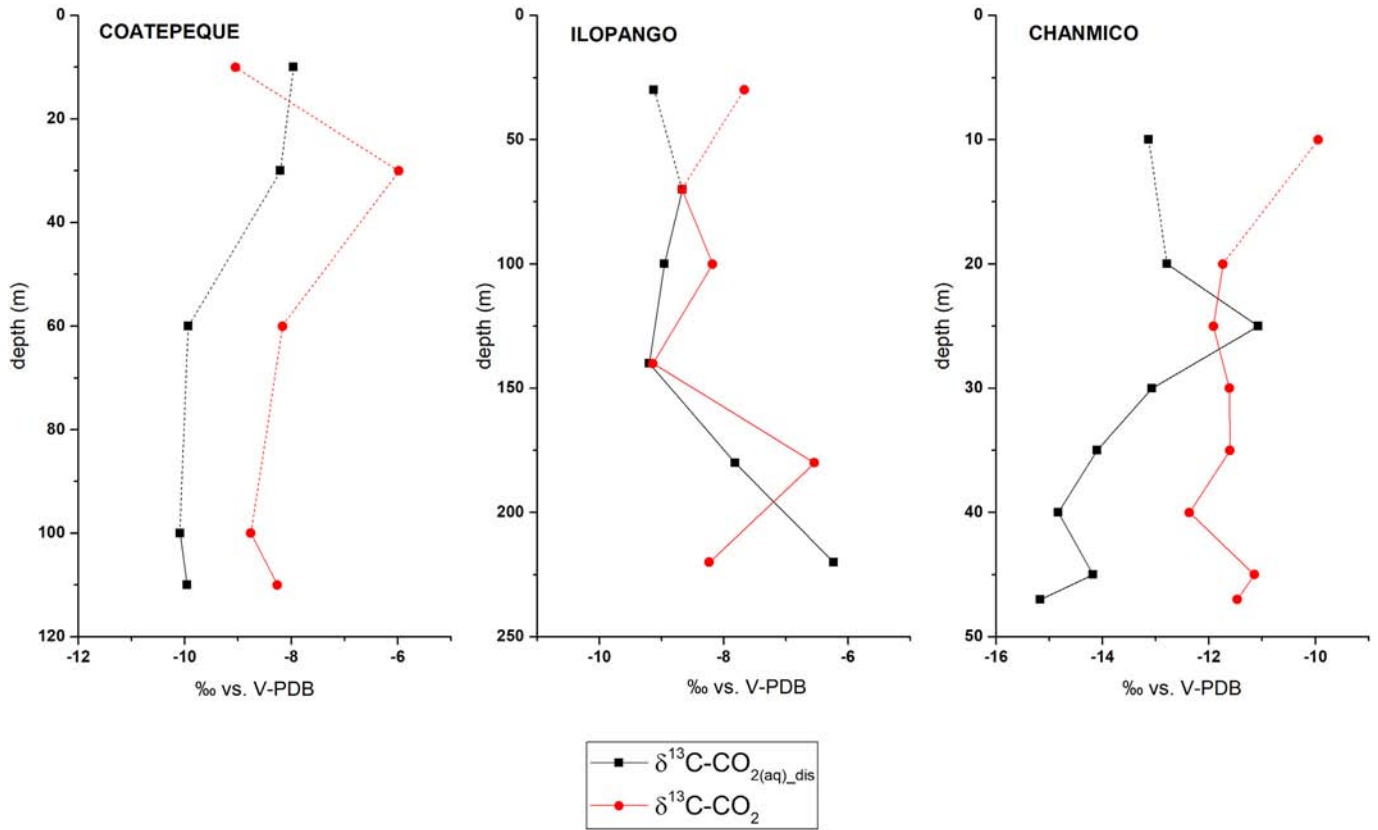


Fig. 12. Vertical profile of the theoretical $\delta^{13}\text{C-CO}_2(aq)_{dis}$ vs. measured $\delta^{13}\text{C-CO}_2$ values of the three lakes.

CO_2 dissolution, as follows:



By assuming that the basement below Coatepeque and Ilopango lakes is mainly consisting of Miocene to Pliocene volcanic rocks (Balsamo Formation, Lexa et al., 2011), the concentrations of B, Si, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Ba and Pb (ordered according to their atomic weight) along the vertical profile of the two lakes were normalized to those of primitive mantle (Palme and O'Neill, 2014) and compared with those measured in the Balsamo basaltic lava samples ("ES 43" and "ES 7" for Coatepeque and Ilopango, respectively; Agostini et al., 2006; Tonarini et al., 2007), equally normalized to the primitive mantle composition. Zinc and As concentrations in the lakes were normalized to those measured in the andesitic basement ("inferior andesites"; Rapprich and Hradecký, 2005) since no data were available for the Balsamo lavas. The spider diagrams of Fig. 8 show that most elements (especially Fe and Ni) were preferentially retained in the host rock or precipitated from the aqueous solution due to the neutral-to-alkaline pH, whereas B and As, being more mobile, are enriched in the liquid phase, testifying once again an input of hydrothermal fluids inside the lake basins.

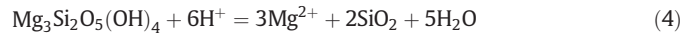
5.1.2. Lake Chanmico

As shown in the $\delta\text{D-H}_2\text{O}$ vs. $\delta^{18}\text{O-H}_2\text{O}$ diagram (Fig. 9), in which the local meteoric water line and the mean local meteoric water composition (from IAEA/WMO, 2018, San Andres site) are also reported, the δD and $\delta^{18}\text{O}$ positive shifts of Lake Chanmico waters seem to be caused by evaporation processes. Isotope fractionation only affects surface waters, whilst deep waters are preserved to be exposed to air during lake stratification. The propagation along a well-defined line of the

evaporating waters was modeled by Lefkowitz et al. (2017), to which attention is drawn here.

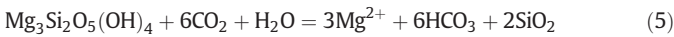
It is worth noting that $\text{Mg}^{2+}-\text{HCO}_3^-$ chemistry, such as that of Lake Chanmico, is generally produced by water-rock interaction with mafic or ultramafic rocks, e.g. resulting by the hydrolysis of Mg-bearing silicates (e.g. Barnes et al., 1967; Dotsika et al., 2009). For example, Mg-rich waters from two Ethiopian lakes (Hayq and Ardibo) are reported to be originated by leaching processes of strongly altered basalts (Ayenew, 2005 and references therein). Unfortunately, no information about the composition of the rock formations below Lake Chanmico is available, although it is reasonable to assume that the lake substrate consists of basaltic to andesitic rocks associated with the eruptive episodes of the San Salvador volcanic complex (e.g. Ferrés et al., 2013). Nevertheless, $\text{Mg}^{2+}-\text{HCO}_3^-$ waters are also commonly found associated with rocks variably affected by metamorphic processes such as serpentinization (Bruni et al., 2002 and references therein). Mafic-ultramafic igneous ophiolitic complexes (mostly of Cretaceous and pre-Cretaceous age) are known to form part of the basement of Central America, from Guatemala to Panama (e.g. Walther et al., 2000; Alvarado et al., 2007 and references therein).

Serpentine dissolution can be described (Barnes et al., 1967; Marques et al., 2008), as follows:



This process might explain the relatively high Mg^{2+} and Si concentrations measured in the Chanmico waters, both increasing towards the lake bottom, and those of B, which tends to be enriched in serpentinic rocks (e.g. Su and Suarez, 2004; Boschetti et al., 2013; Pabst et al., 2015 and references therein). In the Si- HCO_3^- -Mg triangular diagram, where the expected compositions of the aqueous phases produced by dissolution of Mg-bearing solid phases are also reported (modified after Fantoni et al., 2002; Fig. 10), Lake Chanmico shows

$\text{HCO}_3^-/\text{Mg}^{2+}$ molar ratios close to 2, i.e. the theoretical value expected for Mg-bearing solid phase, and plots to the left of the serpentine composition. This is apparently confirming the occurrence of serpentine dissolution, in analogy to what reported in other studies (Fantoni et al., 2002; Margiotta et al., 2012; Langone et al., 2013). Such a process can be associated with the precipitation of minerals richer in SiO_2 with respect to serpentine. Saturation indexes (calculated through PHREEQC 3.3.7.11094 software using the *llnl.dat* database; Parkhurst and Appelo, 1999) demonstrate that Lakes Chanmico is oversaturated with respect to sepiolite and talc, undersaturated in typical minerals pertaining to ultramafic rocks (e.g. enstatite and forsterite) and slightly saturated in calcite and quartz (Table 3). The HCO_3^- increase with depth, coupled with that of dissolved CO_2 (Figs. 5–6 and Tables 1–2), may be controlled by the following reaction involving serpentine (e.g. Kojima et al., 1997):



The primitive mantle-normalized (Palme and O'Neill, 2014) concentrations of B, Si, Mn, Fe, Co, Cu, Zn, As, Sr, Ba and Pb along the vertical profile of Lake Chanmico and of a serpentinized peridotite ("SE10_02"; Schwarzenbach et al., 2014) belonging to the Santa Elena Ophiolite (Costa Rica), i.e. the nearest and one of the largest areas of Central America with mafic and ultramafic lithologies, are reported in the spider-diagram of Fig. 11. For B and As rock content, we used as reference serpentinitic rock composition from Boström and Valdes (1969), Bonatti et al. (1984) and Martin et al. (2016). The figure shows that B, As, Sr, Ba and Pb are more easily mobilized by water-rock interaction processes with respect to Fe, Co and Zn, which are basically retained in the host rock or precipitate once in solution. The increase with depth of Sr, Ba and Pb (Table 1) is possibly related to the dissolution of calcite (with $\text{Sr} > \text{Ba}$ and Pb), which is commonly associated with serpentinized rocks (e.g. Apollaro et al., 2011), as also suggested by the increase of Ca^{2+} .

Eventually, the increase of ammonium along the vertical profile is likely related to microbial activity occurring in the hypolimnion and within the bottom sediments (Molongoski and Klug, 1980; Buresh and Patrick, 1981; Rysgaard et al., 1994).

5.2. Processes governing the chemical and isotopic composition of dissolved gases

Atmospheric gases, i.e. N_2 , O_2 and Ar, enter the lakes through their surface (Weiss, 1970), a process that is controlled by atmospheric pressure and water and air temperature, and/or as input of sub-lacustrine meteoric-recharged air-saturated springs. Accordingly, Ar showed no significant variations with depth, behaving inertly and being only affected by advection and diffusion processes. A similar behavior was observed for N_2 . The N_2/Ar ratios in the Coatepeque, Ilopango and Chanmico lakes are in the range of ASW (air saturated water), confirming that no addition of N_2 from an extra-atmospheric source occurred. Oxidative processes, mainly consisting of biological oxidation of organic matter throughout the lakes water body, were likely responsible of the depletion of O_2 that produced the anaerobic hypolimnion observed in all the study lakes.

The He/Ar ratio in Lake Coatepeque is up to 0.0019, i.e. one order of magnitude higher than that of ASW, suggesting an extra-atmospheric He source(s), possibly related to the adjacent Santa Ana volcanic system, although this hypothesis should be confirmed by $^3\text{He}/^4\text{He}$ values, which were not available for the present study. On the contrary, the He/Ar ratios of Ilopango and Chanmico lakes are in the range of ASW. The increasing concentrations of H_2 with depth measured in all the study lakes were likely related to mineralization processes of organic matter under anaerobic conditions at the water-sediment interface and activity of microbial populations that

used this gas as electron donor (Mah et al., 1977; Zehnder, 1978; Thauer and Badziong, 1980).

The Coatepeque, Ilopango and Chanmico deep waters are characterized by significant concentrations of dissolved CO_2 and CH_4 , which is a common feature of lakes hosted in quiescent volcanic systems (e.g. Cabassi et al., 2013, 2014; Tassi and Rouwet, 2014). The highest CO_2 concentrations at the maximum lake depths (Table 2) are consistent with the addition of an extra-lacustrine CO_2 source from the lake bottom, according to: i) lake water chemistry (see previous section) and ii) $\delta^{13}\text{C}-\text{CO}_2$ values (Table 2), which are significantly less negative than those typically produced by biogenic processes ($\delta^{13}\text{C}-\text{CO}_2 \leq -20\%$ vs. V-PDB; Faure, 1986; O'Leary, 1988; Hoefs, 2009) and consistent with the isotopic value measured at Cerro Pacho, close to Lake Coatepeque ($\delta^{13}\text{C}-\text{CO}_2 = -10.7\%$). The concentration of CO_2 at the bottom of the three Salvadorian lakes is however lower than that observed in other volcanic lakes hosting gas reservoirs at depth (e.g. Lake Kivu, Tassi et al., 2009; Italian lakes, Cabassi et al., 2013; Costa Rican lakes, Cabassi et al., 2014; Lake Pavin, Zimmer et al., 2015; Table 4), although this gas significantly increased with depth in all the study lakes (Table 2).

In order to elucidate the processes controlling the $\delta^{13}\text{C}-\text{CO}_2$ values of the lakes waters, the isotope mass balance and the measured $\delta^{13}\text{C}-\text{TDIC}$ values were used to compute the $\delta^{13}\text{C}$ values of $\text{CO}_{2(\text{aq})}$ resulting from $\text{CO}_{2(\text{g})}$ dissolution ($\delta^{13}\text{C}-\text{CO}_{2(\text{aq})_dis}$), as explained in detail in Venturi et al. (2017), as follows:

$$\delta^{13}\text{C}-\text{CO}_{2(\text{aq})_dis} = \delta^{13}\text{C}-\text{TDIC} - \varepsilon_2 \times (\text{HCO}_3^-)/(\text{TDIC}) \quad (6)$$

where HCO_3^- and TDIC are in mmol/L and the enrichment factor ε_2 quantifies the isotopic fractionation caused by the reaction between dissolved CO_2 and HCO_3^- (Mook et al., 1974), as follows:

$$\varepsilon_2 = \delta^{13}\text{C}-\text{HCO}_3^- - \delta^{13}\text{C}-\text{CO}_2 = 9866/T(\text{K}) - 24.12 \quad (7)$$

The theoretical $\delta^{13}\text{C}-\text{CO}_{2(\text{aq})_dis}$ values of the three lakes are compared with the measured $\delta^{13}\text{C}-\text{CO}_2$ values in Fig. 12. The discordancy between measured and calculated values, suggesting that no isotopic equilibrium between CO_2 and the dissolved carbonate species is achieved, is particularly large for waters from Lake Chanmico, likely due to (bio)chemical processes affecting the chemical equilibrium of reaction (6), as already documented for other volcanic lakes (e.g. Tassi et al., 2009; Cabassi et al., 2013, 2014). Such an isotopic disequilibrium is also confirmed by the comparison of measured vs. theoretical pH values, the latter being calculated assuming the equilibrium at the following reaction:



and using the Henderson–Hasselbalch equation (Po and Senozan, 2001 and references therein):

$$\text{pH} = \text{pKa} + \log [\text{HCO}_3^-]/[\text{CO}_2] \quad (9)$$

The results show that the difference between theoretical and measured pH values for Lake Chanmico is up to 1.9, which is likely determined by biogeochemical reactions controlling the carbon cycle within Lake Chanmico involving both CO_2 and CH_4 . These concentrations are higher than those of CO_2 towards the lake bottom. In fact, such a relatively high CH_4 content, being one and two orders of magnitude higher than that at Coatepeque and Ilopango, respectively, and in the range of that measured in Monticchio Grande, Albano and Hule volcanic lakes (Table 4), suggests the occurrence of bacterial methanogenesis, although this hypothesis should be confirmed by $\delta^{13}\text{C}-\text{CH}_4$ and $\delta\text{D}-\text{CH}_4$ (e.g. Schoell, 1980; Schoell et al., 1988), which are not available for this study. A biogenic source at Lake Chanmico is also consistent with the $\delta^{13}\text{C}-\text{TDIC}$ values (Table 1), being significantly

more negative than those of the other two lakes. However, substantial amounts of CH₄ could also be produced through catalyzed abiotic methanation at low temperatures, a process known to be occurring on serpentinized ultramafic rocks (Etiopie et al., 2011, 2013) that likely caused the peculiar water chemistry of the lake.

6. Conclusions

This study presented an exhaustive chemical and isotopic dataset of Coatepeque, Ilopango and Chanmico volcanic lakes (El Salvador), which showed peculiar chemical compositions, i.e. Na⁺–Cl[–] and Mg²⁺–HCO₃[–], respectively.

The chemical composition of Coatepeque and Ilopango lakes resembled those of fluids related to geothermal and/or volcanic systems (e.g. relatively high TDS values, Cl[–]/Br[–] molar ratios ≤ 650, high As, B, Li and Si concentrations and Cl[–]/SO₄^{2–} ratio > 1), whereas the Mg²⁺–HCO₃[–] waters of Lake Chanmico are likely originated through interaction processes with mafic/ultramafic rocks affected by serpentinization, which allowed to explain the high Mg²⁺, Si and B concentrations. To the best of our knowledge, such chemical compositions are rather unique for volcanic lakes hosted in quiescent volcanic systems. The δD–H₂O vs. δ¹⁸O–H₂O values indicate that the lakes waters are affected by evaporation processes. The relatively stable stratification of the lake waters favors the development of anoxic hypolimnion, characterized by the presence of CO₂, even if in smaller quantities with respect to other meromictic volcanic lakes (e.g. Lake Kivu in DRC, Monticchio, Albano and Averno lakes in Italy, Hule and Rio Cuarto lakes in Costa Rica, Lake Pavin in France), and CH₄, whose concentrations in Lake Chanmico are up to two orders of magnitude higher than those of Coatepeque and Ilopango lakes, suggesting bacterial methanogenesis. However, the δ¹³C–CO₂ values of the lakes are consistent with the addition of an extra-lacustrine CO₂ source from the bottom.

However, further investigations regarding i) the isotopic signature of helium and methane (δ¹³C–CH₄ and δD–CH₄ values) and ii) the presence and distribution along the water column of the microbial populations would help to shed light on the overall biogeochemical processes acting inside the water bodies of the three lakes from El Salvador.

Acknowledgements

This work was financially supported by the laboratories of Fluid Geochemistry and Stable Isotopes of the Department of Earth Sciences of the University of Florence and CNR-IGG and the Cooperation Project between Italy and El Salvador “Sa.Pe.Vo.” (Resp. AC). We greatly appreciated the suggestions and precise corrections of the reviewers, whom we thank very much.

References

- Aggarwal, J.K., Palmer, M.R., Bullen, T.D., Arnosson, S., Ragnarsdottir, K.V., 2000. The boron isotope systematic of Icelandic geothermal waters: 1. Meteoric water charged systems. *Geochim. Cosmochim. Acta* 64, 579–585.
- Agostini, S., Corti, G., Doglioni, C., Carminati, E., Innocenti, F., Tonarini, S., Manetti, P., Di Vincenzo, G., Montanari, D., 2006. Tectonic and magmatic evolution of the active volcanic front in El Salvador: insight into the Berlin and Ahuachapan geothermal areas. *Geothermics* 35, 368–408.
- Aiuppa, A., Avino, R., Brusca, L., Caliro, S., Chiodini, G., D'Alessandro, W., Favara, R., Federico, C., Ginevra, W., Inguaggiato, S., Longo, M., Pecoraino, G., Valenza, M., 2006. Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: insights from Island of Ischia and Phlegrean Fields (Campanian Volcanic Province, Italy). *Chem. Geol.* 229, 313–330.
- Aleman Alberto, E.M., Guerrero Nolasco, E.N., 2007. Evaluación de la calidad del agua en el Lago de Coatepeque en el periodo de Junio-Agosto de 2006.
- Alvarado, G.E., Dengo, C., Martens, U., Bundschuh, J., Aguilar, T., Bonis, S.B., 2007. Stratigraphy and geologic history. In: Bundschuh, J., Alvarado, G.E. (Eds.), *Central America: Geology, Resources and Hazards*. vol. 1. Taylor & Francis, London, pp. 345–394.
- Ambury, L., 2017. Correlating the vertical water column temperature to water color change event of Caldera Lake Coatepeque, El Salvador. US Hydro 2017 Conference, Galveston, TX.
- Anzidei, M., Carapezza, M.L., Esposito, A., Giordano, G., Tarchini, L., Lelli, M., 2008. The Albano Maar lake high resolution bathymetry and dissolved CO₂ budget (Colli Albani District, Italy): constrains to hazard evolution. *J. Volcanol. Geotherm. Res.* 171, 258–268.
- Apollaro, C., Marini, L., Critelli, T., Barca, D., Bloise, A., De Rosa, R., Liberi, F., Miriello, D., 2011. Investigation of rock-to-water release and fate of major, minor, and trace elements in the metabasalt–serpentinite shallow aquifer of Mt. Reventino (CZ, Italy) by reaction path modelling. *Appl. Geochem.* 26 (9–10), 1722–1740.
- Ayeneu, T., 2005. Major ions composition of the groundwater and surface water systems and their geological and geochemical controls in the Ethiopian volcanic terrain. *SINET Ethiop. J. Sci.* 28 (2), 171–188.
- Barnes, I., LaMarche Jr., V.C., Himmelberg, G.R., 1967. Geochemical evidence of present-day serpentinization. *Science* 56, 830–832.
- Bernard, A., Escobar, C.D., Mazot, A., Gutiérrez, R.E., 2004. The acid crater lake of Santa Ana volcano, El Salvador. *Geol. Soc. Am. Spec. Pap.* 375, 121–133.
- Bonatti, E., Lawrence, J.R., Morandi, N., 1984. Serpentinization of oceanic peridotites: temperature dependence of mineralogy and boron content. *Earth Planet. Sci. Lett.* 70, 88–94.
- Boschetti, T., Etiopie, G., Pennisi, M., Romain, M., Toscani, L., 2013. Boron, lithium and methane isotope composition of hyperalkaline waters (Northern Apennines, Italy): terrestrial serpentinization or mixing with brine? *Appl. Geochem.* 32, 17–25.
- Boström, K., Valdes, S., 1969. Arsenic in ocean floors. *Lithos* 2 (4), 351–360.
- Brondi, M., Dall'Aglio, M., Vitroni, F., 1973. Lithium as pathfinder element in the large scale hydrothermal exploration for hydrothermal systems. *Geothermics* 2, 142–153.
- Bruni, J., Canepa, M., Chiodini, G., Cioni, R., Cipolli, F., Longinelli, A., Marini, L., Ottonello, G., Vetuschi Zuccolini, M., 2002. Irreversible water–rock mass transfer accompanying the generation of the neutral Mg–HCO₃ and high-pH, Ca–OH spring waters of the Génova province Italy. *Appl. Geochem.* 17, 455–474.
- Buresh, R.J., Patrick, W.H., 1981. Nitrate reduction to ammonium and organic nitrogen in an estuarine sediment. *Soil Biol. Biochem.* 13, 279–283.
- Cabassi, J., Tassi, F., Vaselli, O., Fiebig, J., Nocentini, M., Capecchiacci, F., Rouwet, D., Biccocchi, G., 2013. Biogeochemical processes involving dissolved CO₂ and CH₄ at Albano, Averno, Monticchio meromictic volcanic lakes (Central-Southern Italy). *Bull. Volcanol.* 75, 683.
- Cabassi, J., Tassi, F., Mapelli, F., Borin, S., Calabrese, S., Rouwet, D., Chiodini, G., Marasco, R., Chouala, B., Avino, R., Vaselli, O., Pecoraino, G., Capecchiacci, F., Biccocchi, G., Caliro, S., Ramirez, C., Mora-Amador, R., 2014. Geosphere-biosphere interactions in bio-activity volcanic lakes: evidences from Hule and Rio Cuarto (Costa Rica). *PLoS One* 9 (7), e102456.
- Caliro, S., Chiodini, G., Izzo, G., Minopoli, C., Signorini, A., Avino, R., Granieri, D., 2008. Geochemical and biochemical evidence of lake turnover and fish kill at Lake Averno, Italy. *J. Volcanol. Geotherm. Res.* 178, 305–316.
- Christenson, B., 2000. Geochemistry of fluids associated with the 1995/96 eruption of Mt. Ruapehu, New Zealand: signatures and processes in the magmatic-hydrothermal system. *J. Volcanol. Geotherm. Res.* 97, 1–30.
- Christenson, B., Tassi, F., 2015. In: Rouwet, D., Christenson, B., Tassi, F., Vandemeulebrouck, J. (Eds.), *Gases in volcanic lake environments*. “Volcanic Lakes, Advances in Volcanology”. Springer-Heidelberg, pp. 125–153 https://doi.org/10.1007/978-3-642-36833-2_2.
- Cinti, D., Poncia, P.P., Brusca, L., Tassi, F., Quattrocchi, F., Vaselli, O., 2015. Spatial distribution of arsenic, uranium and vanadium in the volcanic-sedimentary aquifers of the Vicano-Cimino Volcanic District (Central Italy). *J. Geochem. Explor.* 152, 123–133.
- Cinti, D., Tassi, F., Procesi, M., Brusca, L., Cabassi, J., Capecchiacci, F., Delgado Huertas, A., Gallii, G., Grassa, F., Vaselli, O., Voltattorni, N., 2017. Geochemistry of hydrothermal fluids from the eastern sector of the Sabatini Volcanic District (central Italy). *Appl. Geochem.* 84, 187–201.
- Colvin, A., Rose, W.I., Varekamp, J.C., Palma, J.L., Escobar, D., Gutiérrez, E., Montalvo, F., Maclean, A., 2013. Crater lake evolution at Santa Ana volcano following the 2005 eruption. In: Rose, W.I., Palma, J.L., Delgado Granados, H., Varley, N. (Eds.), *Understanding Open Vent Volcanism and Related Hazards*. *Geol Soc America Special Paper* 498(2), pp. 23–44 [https://doi.org/10.1130/2013.2498\(00\)](https://doi.org/10.1130/2013.2498(00)).
- Corti, G., Carminati, E., Mazzarini, F., Oziel Garcia, M., 2005. Active strike-slip faulting in El Salvador, Central America. *Geology* 33 (12), 989–992. <https://doi.org/10.1130/G21992.1>.
- Costa, A., Chiodini, G., 2015. Modelling air dispersion of CO₂ from limnic eruptions. In: Rouwet, D., Christenson, B., Tassi, F., Vandemeulebrouck, J. (Eds.), *Volcanic Lakes, Advances in Volcanology*. Springer-Heidelberg, pp. 451–465 https://doi.org/10.1007/978-3-642-36833-2_2.
- Davis, S.N., Cecil, L.D., Zreda, M., Moyses, S., 2001. Chlorine-36, bromide, and the origin of spring water. *Chem. Geol.* 179, 3–16.
- Dotsika, E., Poutoukis, D., Tzavidopoulos, I., Maniatis, Y., Ignatiadou, D., Raco, B., 2009. A natron source at Pikrolimni Lake in Greece? Geochemical evidence. *J. Geochem. Explor.* 103, 133–143.
- Dull, R., Southon, J.R., Kutterolf, S., Freundt, A., Wahl, D., Sheets, P., 2010. Did the TBJ Ilopango eruption cause the AD 536 event? *American Geophysical Union, Fall Meeting 2010*, Abstract #V13C-2370.
- Esquivel, I., 2016. Levantamiento batimétrico y medición de parámetros físico-químicos en el Lago de Ilopango, El Salvador. Bachelor thesis. Universidad de El Salvador.
- Etiopie, G., Schoell, M., Hogsörmez, H., 2011. Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): understanding gas exhalation from low temperature serpentinization and implications for Mars. *Earth Planet. Sci. Lett.* 310 (1–2), 96–104.
- Etiopie, G., Ehlmann, B.L., Schoell, M., 2013. Low temperature production and exhalation of methane from serpentinized rocks on Earth: a potential analog for methane production on Mars. *Icarus* 224 (2), 276–285.
- Evans, W.C., White, L.D., Rapp, J.B., 1998. Geochemistry of some gases in hydrothermal fluids from the southern Juan de Fuca ridge. *J. Geophys. Res.* 15, 305–313.

- Fantoni, D., Brozzo, G., Canepa, M., Cipolli, F., Marini, L., Ottonello, G., Vetuschi Zuccolini, M., 2002. Natural hexavalent chromium in groundwaters interacting with ophiolitic rocks. *Environ. Geol.* 42, 871–882.
- Faure, G., 1986. *Inorganic Geochemistry*. Macmillan Pub Com, p. 627.
- Ferrés, D., Delgado Granados, H., Hernández, W., Pullinger, C., Chávez, H., Castillo Taracena, C.R., Cañas-Dinarte, C., 2011. Three thousand years of flank and central vent eruptions of the San Salvador volcanic complex (El Salvador) and their effects on El Cambio archeological site: a review based on tephrostratigraphy. *Bull. Volcanol.* 73, 833. <https://doi.org/10.1007/s00445-011-0465-0>.
- Ferrés, D., Delgado Granados, H., Gutiérrez, R.E., Farraz, I.A., Hernández, E.W., Pullinger, C.R., Escobar, C.D., 2013. Explosive volcanic history and hazard zonation maps of Boquerón Volcano (San Salvador volcanic complex, El Salvador). In: Rose, W.I., Palma, J.L., Delgado Granados, H., Varley, N. (Eds.), *Understanding Open-vent Volcanism and Related Hazards: Geological Society of America Special Paper*. vol. 498, pp. 201–230. [https://doi.org/10.1130/2013.2498\(12\)](https://doi.org/10.1130/2013.2498(12)).
- Fontes, J.C., Matray, J.M., 1993. *Geochemistry and origin of formation brines from the Paris Basin, France*. *Chem. Geol.* 109, 177–200.
- FORGAES & SNET, 2006. *Investigaciones hidrogeológicas, hidrologías e hidroquímicas en el Lago Coatepeque*. Unión Europea (Resumen ejecutivo).
- Göb, S., Loges, A., Nolde, N., Bau, M., Jacob, D.E., Markl, G., 2013. Major and trace element compositions (including REE) of mineral, thermal, mine and surface waters in SW Germany and implications for water–rock interaction. *Appl. Geochem.* 33, 127–152.
- Grassa, F., Capasso, G., Oliveri, Y., Sollami, A., Carreira, P., Carvalho, M.R., Marques, J.M., Nunes, J.C., 2010. Nitrogen isotopes determination in natural gas: analytical method and first results on magmatic, hydrothermal and soil gas samples. *Isot. Environ. Health Stud.* 46 (2), 141–155.
- Hernández, P.A., Pérez, N.M., Varekamp, J.C., Henriquez, B., Hernández, A., Barrancos, J., Padron, E., Calvo, D., Melian, G., 2007. Crater lake temperature changes of the 2005 eruption of Santa Ana Volcano, El Salvador, Central America. *Pure Appl. Geophys.* 164, 2507–2522.
- Hoefs, J., 2009. *Stable Isotope Geochemistry*. 6th edn. Springer, Berlin, p. 288.
- IAEA/WMO, 2018. *Global Network of Isotopes in Precipitation*. The GNIP Database Accessible at: <https://nucleus.iaea.org/wiser>.
- Kling, G.W., Evans, W.C., Tanyileke, G.Z., 2015. The comparative limnology of Lakes Nyos and Monoun, Cameroon. In: Rouwet, D., Christenson, B., Tassi, F., Vandemeulebrouck, J. (Eds.), *Volcanic Lakes, Advances in Volcanology*. Springer-Heidelberg, pp. 401–425. https://doi.org/10.1007/978-3-642-36833-2_2.
- Kojima, T., Nagamine, A., Ueno, N., Uemiyama, S., 1997. Absorption and fixation of carbon dioxide by rock weathering. *Energy Convers. Manag.* 38, S461–S466.
- Kusakabe M (2015) Evolution of CO₂ content in Lakes Nyos and Monoun, and sub-lacustrine CO₂-recharge system at Lake Nyos as Envisaged from CO₂/³He ratios and noble gas signatures. “Volcanic Lakes, Advances in Volcanology.” Ed: D. Rouwet, B. Christenson, F. Tassi, J. Vandemeulebrouck. DOI https://doi.org/10.1007/978-3-642-36833-2_2, Springer-Heidelberg, 427–450.
- Laiolo, M., Coppola, D., Barahona, F., Benítez, J.E., Cigolini, C., Escobar, D., Funes, R., Gutierrez, E., Henriquez, B., Hernandez, A., Montalvo, F., Olmos, R., Ripepe, M., Finizola, A., 2017. Evidences of volcanic unrest on high-temperature fumaroles by satellite thermal monitoring: the case of Santa Ana volcano, El Salvador. *J. Volcanol. Geotherm. Res.* 340, 170–179.
- Langelier, W., Ludwig, H., 1942. Graphical methods for indicating the mineral character of natural waters. *J. Am. Water Assoc.* 34, 335–352.
- Langone, A., Baneschi, I., Boschi, C., Dini, A., Guidi, M., Cavallo, A., 2013. Serpentinite-water interaction and chromium(VI) release in spring waters: examples from Tuscan ophiolites. *Ophiolite* 38 (1), 41–57. <https://doi.org/10.4454/ofiolite.v38i1.415>.
- Lefkowitz, J.N., Varekamp, J.C., Reynolds, R.W., Thomas, E., 2017. A tale of two lakes: the Newberry Volcano twin crater lakes, Oregon, USA. *Geol. Soc. Lond., Spec. Publ.* 437 (1), 253–288.
- Lexa, J., Šebesta, J., Chavez, J., Hernandez, W., Pécskay, Z., 2011. Geology and volcanic evolution in the southern part of the San Salvador Metropolitan Area. *J. Geosci.* 56, 105–140.
- Lopez, D.L., Ransom, L., Pérez, N.M., Hernández, P.A., Monterrosa, J., 2004. Dynamics of diffuse degassing at Ilopango Caldera, El Salvador. In: Rose, W.I., Bommer, J.J., Lopez, D.L., Carr, M.J., Major, J.J. (Eds.), *Natural Hazards in El Salvador*. Boulder, Colorado. Geological Society of America Special Paper 375, pp. 191–202.
- Lopez, D.L., Ransom, L., Monterrosa, J., Soriano, T., Barahona, F., Olmos, R., Bundschuh, J., 2009. Volcanic arsenic and boron pollution of Ilopango Lake, El Salvador. In: *Natural Arsenic in Groundwaters of Latin America*. Arsenic in the Environment, 1. Taylor & Francis (CRC Press), London, United Kingdom, pp. 129–143.
- Lopez, D.L., Bundschuh, J., Birkle, P., Armienta, M.A., Cumbal, L., Sracek, O., Cornejo, L., Ormachea, M., 2012. Arsenic in volcanic geothermal fluids of Latin America. *Sci. Total Environ.* 429, 57–75.
- Mah, R.A., Ward, D.M., Baresi, L., Glass, T.L., 1977. Biogenesis of methane. *Annu. Rev. Microbiol.* 31, 309–341.
- Mann, C.P., Stix, J., Vallance, J.W., Richer, M., 2004. Subaqueous intracaldera volcanism, Ilopango Caldera, El Salvador, Central America. In: Rose, W.I., Bommer, J.J., Lopez, D.L., Carr, M.J., Major, J.J. (Eds.), *Natural Hazards in El Salvador*. Geological Society of America, Boulder, Colorado, pp. 159–174 Special Paper 375.
- Margiotta, S., Mongelli, G., Summa, V., Paternoster, M., Fiore, S., 2012. Trace element distribution and Cr(VI) speciation in Ca-HCO₃ and Mg-HCO₃ spring waters from the northern sector of the Pollino massif, southern Italy. *J. Geochem. Explor.* 115, 1–12.
- MARN, 2017. *Informe técnico sobre cambio de color en las aguas del Lago de Coatepeque*. Technical report. Ministerio de Medio Ambiente y Recursos Naturales de El Salvador.
- Marques, J.M., Carreira, P.M., Carvalho, M.R., Matias, M.J., Goff, F.E., Basto, M.J., Graça, R.C., Aires-Barros, L., Rocha, L., 2008. Origins of high pH mineral waters from ultramafic rocks, Central Portugal. *Appl. Geochem.* 23, 3278–3289.
- Martin, C., Flores, K.E., Harlow, G.E., 2016. Boron isotopic discrimination for subduction-related serpentinites. *Geology* 44 (11), 899–902.
- Martínez-Hackert, B., Bajo Sanchez, J.V., Figueroa, C., 2017. Active volcanoes under water and inland: using hydrography on Coatepeque Caldera Lake, El Salvador. US Hydro 2017 Conference, Galveston, TX.
- Molongoski, J.J., Klug, M.J., 1980. Anaerobic metabolism of particulate organic matter in the sediments of a hypereutrophic lake. *Freshw. Biol.* 10, 507–518.
- Mook, W.G., Bommerson, J.C., Staverman, W.H., 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planet. Sci. Lett.* 22, 169–176.
- O’Leary, M.H., 1988. Carbon isotopes in photosynthesis. *BioScience* 38, 328–336.
- Pabst, S., Zack, T., Savov, I., et al., 2015. Evidence for boron incorporation into the serpentine crystal structure. *Am. Mineral.* 96 (7), 1112–1119. <https://doi.org/10.2138/am.2011.3709>.
- Palme, H., O’Neill, H., 2014. *Cosmochemical estimates of mantle composition*. Treatise on Geochemistry, 2nd edition Elsevier.
- Parkhurst, D.L., Appelo, C.A.J., 1999. *User’s Guide to PHREEQC, Version 2: A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations*. U.S. Geol. Surv.: Earth Sci. Information Center, Open-File Reports Section (Distributor).
- Paternoster, G.B., Varekamp, J.C., 1997. Volcanic lake systematic I. Physical constraints. *Bull. Volcanol.* 58, 528–538.
- Paternoster, M., Mongelli, G., Caracausi, A., Favara, R., 2016. Depth influence on the distribution of chemical elements and saturation index of mineral phases in twins maar lakes: the case of the Monticchio lakes (southern Italy). *J. Geochem. Explor.* 163, 10–18.
- Po, H.N., Senozan, N.M., 2001. The Henderson-Hasselbalch equation: its history and limitations. *J. Chem. Educ.* 78 (11), 1499.
- Pullinger, C., 1998. *Evolution of the Santa Ana Volcanic Complex, El Salvador*. Michigan Technological University (M. Sc. in Geology).
- Ransom, L., 2002. *Volcanic Diffuse Soil Degassing and Lake Chemistry of the Ilopango Caldera System, El Salvador, Central America*. MSc Thesis. Ohio University, Athens (OH).
- Rapprich, V., Hradecký, P., 2005. The Cintopeque Range of central El Salvador: geology, magma origin, and volcanism. *Bull. Geosci.* 80, 277–286.
- Richer, M., Mann, C.P., Stix, J., 2004. Mafic magma injection triggers eruption at Ilopango Caldera, El Salvador, Central America. In: Rose, W.I., Bommer, J.J., Lopez, D.L., Carr, M.J., Major, J.J. (Eds.), *Natural Hazards in El Salvador*. Boulder, Colorado, Geological Society of America Special Paper vol. 375, pp. 175–189.
- Risacher, F., Fritz, B., Hauser, A., 2011. Origin of components in Chilean thermal waters. *J. S. Am. Earth Sci.* 31, 153–170.
- Rodríguez, R., Olmos, R., Payes, J., 2014. Medición de gas Radón (Rn²²²) en aguas termales del Cerro Pacho, Caldera Coatepeque, El Salvador. *Rev. Geol. Am. Central* 50, 71–82.
- Rouwet, D., 2013. VOLADA - a collaborative data base on Volcanic Lakes. <https://vlab.org/resources/2437>.
- Rouwet, D., Tassi, F., 2014. An overview of the structure, hazards, and methods of investigation of Nyos-type lakes from the geochemical perspective. *J. Limnol.* 73 (1). <https://doi.org/10.4081/jlimnol.2014.836>.
- Rouwet, D., Tassi, F., Mora-Amador, R., Sandri, L., Chiarini, V., 2014. Past, present and future of volcanic lake monitoring. *J. Volcanol. Geotherm. Res.* 272, 78–97.
- Rowe, G.L., Ohsawa, S., Takano, B., Brantley, S.L., Fernandez, J.F., Barquero, J., 1992. Using crater lake chemistry to predict volcanic activity at Poás volcano, Costa Rica. *Bull. Volcanol.* 54, 494–503.
- Rysgaard, S., Risgaard-Petersen, N., Sloth, N.P., Jensen, K., Nielsen, L.P., 1994. Oxygen regulation of nitrification and denitrification in sediments. *Limnol. Oceanogr.* 39, 1643–1652.
- Salata, G.G., Roelke, L.A., Cifuentes, L.A., 2000. A rapid and precise method for measuring stable carbon isotope ratios of dissolved inorganic carbon. *Mar. Chem.* 69, 153–161.
- Salazar, J.M.L., Hernández, P.A., Pérez, N.M., Olmos, R., Barahona, F., Cartagena, R., Soriano, T., López, D.L., Sumino, H., Notsu, K., 2004. Spatial and temporal variations of diffuse CO₂ degassing at Santa Ana-Izalco-Coatepeque volcanic complex, El Salvador, Central America. In: Rose, W.I., Bommer, J.J., Lopez, D.L., Carr, M.J., Major, J.J. (Eds.), *Natural Hazards in El Salvador*. Boulder, Colorado, Geological Society of America Special Paper vol. 375, pp. 129–149.
- Saxby, J., Gottsmann, J., Cashman, K., Gutiérrez, E., 2016. Magma storage in a strike-slip caldera. *Nat. Commun.* 7, 12295. <https://doi.org/10.1038/ncomms12295>.
- Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta* 44, 646–661.
- Schoell, M., Tietze, K., Schoberth, S., 1988. Origin of the methane in Lake Kivu (east-central Africa). *Chem. Geol.* 71, 257–265.
- Schwarzenbach, E.M., Gazel, E., Caddick, M.J., 2014. Hydrothermal processes in partially serpentinized peridotites from Costa Rica: evidence from native copper and complex sulfide assemblages. *Contrib. Mineral. Petrol.* 168, 1079. <https://doi.org/10.1007/s00410-014-1079-2>.
- Scolamacchia, T., Pullinger, C., Caballero, L., Montalvo, F., Beramendi Orosco, L.E., González Hernández, C., 2010. The 2005 eruption of Llamatepec (Santa Ana) volcano, El Salvador. *J. Volcanol. Geotherm. Res.* 189, 291–318.
- SNET, 2000. *Cuerpos de Agua Continentales de El Salvador*. Report. Servicio Nacional de Estudios Territoriales, El Salvador.
- Sofield, D.J., 1998. *History and Hazards of San Salvador Volcano, El Salvador*. Thesis of Master of Science in Geology. Michigan Technological University.
- Sriwana, T., van Bergen, M.J., Varekamp, J.C., Sumarti, S., Takano, B., Van Os, B.J.H., Leng, M.J., 2000. Geochemistry of the acid Kawah Putih Lake, Patuha volcano, West Java, Indonesia. *J. Volcanol. Geotherm. Res.* 97, 77–104.
- Su, C., Suarez, D., 2004. Boron release from weathering illites, serpentine, shales, and illitic/palygorskitic soils. *Soil Sci. Soc. Am. J.* 68 (1), 96–105.

- Tassi, F., Rouwet, D., 2014. An overview of the structure, hazards, and methods of investigation of Nyos-type lakes from the geochemical perspective. *J. Limnol.* 73 (1), 39–54.
- Tassi, F., Vaselli, O., Luchetti, G., Montegrossi, G., Minissale, A. (2008) Metodo per la determinazione dei gas disciolti in acque naturali. *Int Rep CNR-IGG, Florence*, n° 10450, pp. 11. (In Italian).
- Tassi, F., Vaselli, O., Tedesco, D., Montegrossi, G., Darrah, T., Cuoco, E., Mapendano, M., Poreda, R., Delgado Huertas, A., 2009. Water and gas chemistry at Lake Kivu (DRC): geochemical evidence of vertical and horizontal heterogeneities in a multi-basin structure. *Geochim. Geophys. Geosyst.* 10 (2). <https://doi.org/10.1029/2008GC002191>.
- Tassi, F., Fazi, S., Rossetti, S., Pratesi, P., Ceccotti, M., Cabassi, J., et al., 2018a. The biogeochemical vertical structure renders a meromictic volcanic lake a trap for geogenic CO₂ (Lake Averno, Italy). *PLoS One* 13 (3), e0193914. <https://doi.org/10.1371/journal.pone.0193914>.
- Tassi, F., Cabassi, J., Andrade, C., Callieri, C., Silva, C., Viveiros, F., Corno, G., Vaselli, O., Selmo, E., Gallorini, A., Ricci, A., Giannini, L., Cruz, J.V., 2018b. Mechanisms regulating CO₂ and CH₄ dynamics in the Azorean volcanic lakes (São Miguel Island, Portugal). *J. Limnol.* <https://doi.org/10.4081/jlimnol.2018.1821>.
- Thauer, R.K., Badziong, W., 1980. Respiration with sulfate as electron acceptor. In: Knowles, C.J. (Ed.), *Diversity of Bacterial Respiratory Systems*. CRC, Boca Raton, pp. 65–85.
- Tonarini, S., Agostini, S., Doglioni, C., Innocenti, F., Manetti, P., 2007. Evidence for serpentinite fluid in convergent margin systems: the example of El Salvador (Central America) arc lavas. *Geochim. Geophys. Geosyst.* 8, Q09014. <https://doi.org/10.1029/2006GC001508>.
- US EPA, 2001. *National Primary Drinking Water Standards*. United States Environmental Protection Agency (EPA 816-F-01-007).
- Varekamp, J.C., 2015. The chemical composition and evolution of volcanic lakes. In: Rouwet, D., Christenson, B., Tassi, F., Vandemeulebrouck, J. (Eds.), *Volcanic Lakes, Advances in Volcanology*. Springer-Heidelberg, pp. 93–123 https://doi.org/10.1007/978-3-642-36833-2_2.
- Varekamp, J.C., Kreulen, R., 2000. The stable isotope geochemistry of volcanic lakes, with examples from Indonesia. *J. Volcanol. Geotherm. Res.* 97, 309–327.
- Vaselli, O., Tassi, F., Montegrossi, G., Capaccioni, B., Giannini, L., 2006. Sampling and analysis of fumarolic gases. *Acta Vulcanol.* 1–2, 65–76.
- Venturi, S., Tassi, F., Bicchieri, G., Cabassi, J., Capocchiacci, F., Capasso, G., Vaselli, O., Ricci, A., Grassa, F., 2017. Fractionation processes affecting the stable carbon isotope signature of thermal waters from hydrothermal/volcanic systems: the examples of Campi Flegrei and Vulcano Island (southern Italy). *J. Volcanol. Geotherm. Res.* 345, 46–57.
- Walther, C.H.E., Flueh, E.R., Ranero, C.R., von Huene, R., Strauch, W., 2000. Crustal structure across the Pacific margin of Nicaragua: evidence for ophiolitic basement and a shallow mantle siver. *Geophys. J. Int.* 141 (3), 759–777.
- Webster, J.G., Nordstrom, D.K., 2003. Geothermal Arsenic. The source, transport and fate of arsenic in geothermal systems. In: Welch, A.H., Stollenwerk, K.G. (Eds.), *Arsenic in Groundwater: Geochemistry and Occurrence*. Kluwer Academic Publishers, pp. 101–126.
- Weiss, R., 1970. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.* 17, 721–735.
- WHO, 2003. *Boron in drinking-water. Background Document for Development of WHO Guidelines for Drinking-water Quality*. World Health Organization, Geneva, Switzerland.
- Wilhelm, E., Battino, R., Wilcock, R.J., 1977. Low-pressure solubility of gases in liquid water. *Chem. Rev.* 77 (2), 219–262.
- Zehnder, A.J.B., 1978. Ecology of methane formation. In: Michell R (ed) *Water Pollution Microbiology*. Wiley, New York, pp. 349–376.
- Zhang, J., Quay, P.D., Wilbur, D.O., 1995. Carbon isotope fractionation during gas–water exchange and dissolution of CO₂. *Geochim. Cosmochim. Acta* 59, 107–114.
- Zimmer, M., Tassi, F., Vaselli, O., Kujawa, C., Cabassi, J., Erzinger, J., 2015. The gas membrane sensor (GMS) method: a new analytical approach for real-time gas concentration measurements in volcanic lakes. *Geol. Soc. Lond., Spec. Publ.* 437 (1), 223–232.