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Volcanic lakes of the Azores archipelago (Portugal): Geological setting and geochemical characterization

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Abstract

A representative set of 30 lakes from the Azores archipelago (Portugal) has been studied to obtain data on their volcanic setting and water geochemistry. The majority of the studied lakes are located inside volcanic craters and subsidence calderas, while the remaining lakes are located in topographic depressions not associated with volcanic centres, in depressions of tectonic origin and inside lava caves. In general, the Azorean volcanic lakes are small, with surface areas between 8.94×10^{-4} km^2 and 4.35 km^2 and volumes between 2.4×10^3 and 4.78×10^7 m^3; median = 3.99×10^4 m^3, presenting maximum depths between 0.8 and 33 m. Mostly of the Na–Cl to Na–HCO_3 type, the lake waters are generally low temperature (11.9–24.6 °C), very dilute (TDS range between 11.0 and 356.2 mg/L; median = 36.8 mg/L) and a clear exception is Furna do Enxofre lake (Graciosa island) that shows a Mg trend. Two types of lake waters can be recognized: 1) one is characterized by Na/Cl ratio close to the seawater value and have evolved, and evolve by marine contribution; and 2) Na–HCO_3 type waters that, in addition to sea-salt input, have been influenced by other processes (e.g., water–rock interaction, hydrothermal seepage into the lake bottom) evident from higher total CO_2 content (365.1 mg/L) and SiO_2 content (74.9 mg/L), as well demonstrated by in the Furna do Enxofre lake. Nevertheless, volcanic contribution cannot be excluded for some lakes as Furna do Enxofre.

Vertical profiles made at the deepest lakes of São Miguel reveal that major-ion content varies little with depth, largely independent of the occurrence of thermally driven density stratification in summer for some lakes. However, dissolved CO_2 increases with depth and is kept in the hypolimnion in summer, whereas the HCO_3^- content is stable, suggesting that CO_2 release exceeds acidity neutralization by water–rock interaction. During winter, without stratification, the dissolved CO_2 increase is less sharp for the majority of the lakes, with the exception of Furnas and Furna do Enxofre lakes. The CO_2 enrichment observed for certain lakes (e.g., Furna do Enxofre and Furnas) implies a volcanic input. Moreover, as these lakes themselves are located near hydrothermal surface manifestations, they therefore offer good targets of volcano monitoring in the Azores.
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Keywords: crater lakes; Azores; fluid geochemistry; hydrogeochemical profiles; carbon dioxide

1. Introduction

Despite the small area of the earth's land surface occupied by lakes (~2% of the total, 2.5×10^6 km^2), lakes have always received much attention as they are often useful for several purposes, from drinking water sources to recreational uses (Wetzel, 1983). Due to their geological setting and hydrogeochemical characteristics, volcanic lakes comprise a distinct group, and approximately 16% of the 714 active volcanoes of Holocene age or younger have lakes (Rowe et al., 1992a; Simkin and

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Siebert, 1994; Delmelle and Bernard, 2000). Nevertheless, we assumed that the number of volcanic lakes worldwide may be higher, both due to the lakes emplaced in older volcanoes and to the ephemeral character of many of these lakes. Eruptive events have taken place in 55 volcanic lakes, and since 1500 AD there have been more than 32,000 casualties associated with the more hazardous volcanic eruptions in lakes, mainly victims of hydrovolcanic eruptions and lahars (Delmelle and Bernard, 2000). The sudden emission of large volumes of CO_2 from lakes, like in lakes Monoun and Nyos (Cameroon), is another hazardous process related to volcanic lakes (Sigurdsson et al., 1987; Sigurdsson, 1988; Sigvaldasson, 1989; Kusakabe et al., 1989; Giggenbach, 1990; Rice, 2000). An assessment of the hazards associated with eruptions through lakes was published recently by Mastin and Witter (2000).

Classification systems of volcanic lakes have been published, based on physical and geochemical characteristics (Pasternak and Varekamp, 1997; Delmelle and Bernard, 2000; Varekamp et al., 2000; Marini et al., 2003). Considering the relative proportion of meteoric water and volcanic contributions, volcanic lakes present a large range in geochemical characteristics (Delmelle and Bernard, 2000; Varekamp et al., 2000): (1) lakes with pH around neutrality and low TDS ($TDS < 100$ mg/kg); (2) acid lakes, presenting a pH between 2 and 6 and TDS lower than 2000 mg/kg; and (3) hyperacid lakes, with pH lower than 1, and classified as brines due to their TDS values ($TDS > 100{,}000$ mg/kg). The volcanic contribution has many forms, from hydrothermal seepage to gaseous input to lakes, and Ronde et al. (2002) have recently published a paper elaborating these processes.

Several studies have involved volcanic monitoring using geochemical data collected in volcanic lakes worldwide (Rowe et al., 1992a,b; Christenson, 2000; Martinez et al., 2000; Kusakabe et al., 2000; Varekamp et al., 2001), recognizing the influence of dormancy and eruptive processes over lake characteristics, as shown for example by Fazlullin et al. (2000).

The Azores archipelago is located in the North-Atlantic Ocean, between 37°N and 40°N latitude and 25°W and 31°W longitude, about 1500 km from mainland Portugal. Composed of nine volcanic islands, Azores has an area of 2333 km^2 and 246,030 inhabitants, mainly living in São Miguel (54.1%) and Terceira (23.3%). In the archipelago, lakes have been essentially used for recreational purposes; only two natural lakes are used as sources of potable water. Studies about hydrogeochemistry of the Azores lakes are rare in the literature, and few references about research linking water chemistry and volcanism can be found (Martini et al., 1994; Cruz et al., 2002; Cruz et al., 2003a,b).

The 88 surface lakes in the Azores occupy a total surface area of 9.5 km^2 (0.4% of the entire archipelago area); they only recently have received increased attention due to eutrophication problems (see, for example, Porteiro, 2000; DROTRH-INAG, 2001; UNL, 1991). Two other lakes occur inside lava caves in Graciosa and Terceira islands. The volume of water contained in Azores lakes is equal to 9.0×10^7 m^3, 93% of which corresponds to São Miguel lakes, 5% to Flores lakes and the remaining to lakes in Terceira, Pico and Corvo. Sete Cidades lake (São Miguel island) holds 4.78×10^7 m^3 and is the most voluminous lake (DROTRH-INAG, 2001).

In this paper, we present the major-ion composition of 30 lakes distributed as follows: São Miguel (17 lakes), Terceira (4 lakes), Pico (5 lakes), Graciosa (1 lake), Corvo (1 lake), and Flores (2 lakes), to characterize the geochemical processes that control water composition (Fig. 1). For a small number of samples, their trace-element compositions are also discussed. For the deepest lakes from São Miguel island (Sete Cidades, Fogo, Furnas, Congro, Santiago) vertical hydrogeochemical profiles are also shown to characterize variations with depth according to conditions of thermally controlled density stratification (summer) and mixing through the water column (winter). Emphasis will be given to variations in dissolved CO_2 and total CO_2 contents with depth, to determine CO_2 enrichment from volcanic input.

Lake-water composition is strongly affected by biological processes and, despite not being the focus of the present paper, these processes should be taken in consideration. For example, photosynthesis implies the uptake of CO_2, phosphate and nitrogen, which in turn are converted to organic matter, contributing toward pH increase, in a process that is light-dependent (Stumm and Morgan, 1981; Berner and Berner, 1987). Moreover, the breakdown of the dead organic matter, deposited in the bottom of the lake, involves the release of dissolved CO_2. Therefore, the balance between the consumption and the release of CO_2 has to be addressed, regarding the overall objective of the paper, which is the volcanic influence on lake geochemistry.

In addition to CO_2, other species that are related with processes as water–rock interaction or hydrothermal waters seepage in lakes, are also influenced by biological activity, such as SiO_2, Fe and Ca^{2+} (Wetzel, 1983). A good example is the SiO_2 content in lake waters, which is affected by the uptake from diatoms and as an example it was established that this type of algae are rather important in the Furnas lake planktonic algae community (Gonçalves, 1997).

2. Geological and geomorphological setting

2.1. Geology of the Azores archipelago

The Azores islands are spread along a NW–SE-trending strip, 600-km long, in a complex geodynamic setting. The archipelago is located near the triple junction of the North American, Eurasian and African plates, with the Mid-Atlantic Rigde (MAR) dividing Flores and Corvo islands, to the West, from the remaining islands located to the East. Terceira, Pico Faial, São Jorge and Graciosa, constitutes the Central Group, while São Miguel and Santa Maria islands belong to the Eastern Group of islands. Despite the largely volcanic origin of the islands, at Santa Maria,

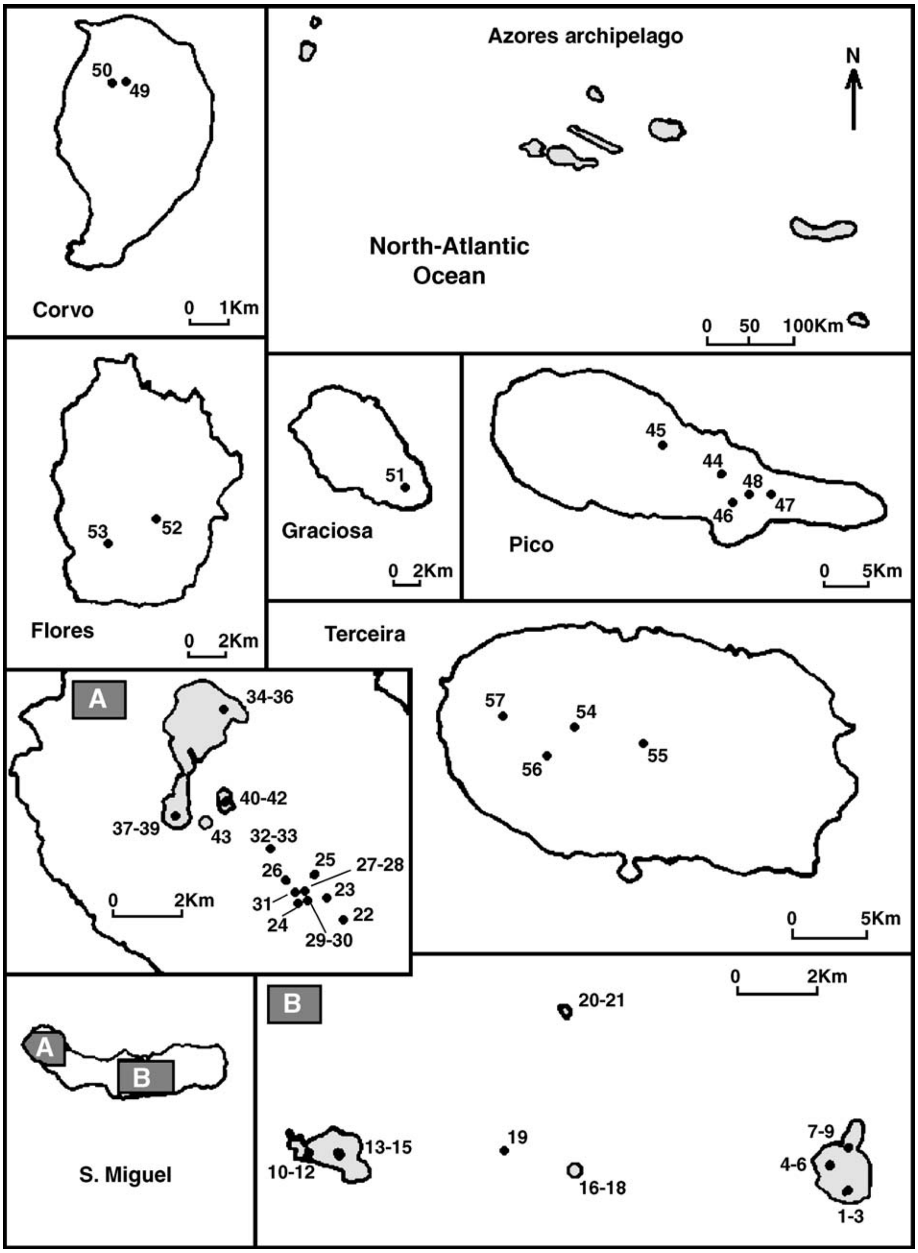

Fig. 1. Setting of the Azores archipelago in the North Atlantic ocean. The locations of the volcanic lakes studied in the present paper are also shown compare with numbers in Tables 1 and 2.

where the oldest volcanic outcrops have been dated from 8.12×10^6 yr (Abdel-Monen et al., 1975), a major sedimentary unit, made of marine and terrestrial sediments, is interbedded in the volcanic succession. Pico is the younger island, with the oldest subaerial lava flows being dated from about 3×10^5 yr (Chovelon, 1982). Volcanic rocks mainly belong to the alkaline basalt series, contrasting with the tholeitic trend from the MAR, but some transitional basalts occur on a few islands.

The volcanic geology of the archipelago exhibits various eruptive styles. The volcanic construction of Santa Maria, São Jorge and Pico islands, as well as larger areas of other islands (e.g., Faial and São Miguel), is related with Hawaiian to Strombolian eruptions. Therefore, subaerial pahoehoe and aa basaltic lava flows are interbedded with pyroclastic deposits, and several scoria and spatter cones are scattered along tectonic lineaments. The western sector of Pico island corresponds to a basaltic central volcano 2354 m a.s.l., built by a succession of summit eruptions of fluid basaltic lava flows and minor volumes of tephra (França et al., 2006-this issue; Nunes, 1999). The geology of São Miguel is dominated by three active composite volcanoes (Sete Cidades, Fogo, Furnas), associated with highly explosive eruptions of magmas of trachytic nature, which explain the large Quaternary calderas that occupy the summit of these volcanoes (Booth et al., 1978; Moore, 1990; Guest et al., 1999; Forjaz, 1984). The recent activity of these volcanoes is mainly explosive in character, with Plinian, subplinian, and phreatomagmatic activity, producing a high volume of pumice fall deposits, pyroclastic flows, surges, lahars and domes and trachytic lava flows.

Table 1
Location and physical description of the studied lakes (Ref. according to Table 2 and Fig. 1)

Ref.	Name	Island	Altitude (m)	Area (km^2)	Max. depth (m)	Volume (10^3 m^3)	Volc. setting
1–9	Furnas	Smg	281	1.90	12.0	9212.5^c	Cald
10–15	Fogo	Smg	575	1.48	30.0	18040.8^c	Cald
16–18	Congro	Smg	420	4×10^{-2}	16.0	280.8^c	EC–maar s.l.
19	Areeiro	Smg	630	1×10^{-2}	2.7		EC–SC
20;21	São Brás	Smg	610	6×10^{-2}	2.3		EC–maar s.l.
22	Peixe	Smg	615		1.5	2.4^c	d
23	Carvão	Smg	678	1×10^{-2}	2.0	10.6^c	d
24	Caldeirão Grande	Smg	720	1×10^{-2}	2.5	11.5^c	EC–SC
25	Pau Pique	Smg	700		4.5		EC–SC
26	Éguas N	Smg	825	1×10^{-2}	0.8	3.9^c	EC–SC
27;28	Empadadas N	Smg	740	2×10^{-2}	5.3	37.0^c	EC–SC
29;30	Empadadas S	Smg	742		3.0	4.9^c	EC–SC
31	Rasa1	Smg	765	4×10^{-2}	0.8	12.2^c	d
32;33	Canário	Smg	745	2×10^{-2}	3.0	18.8^c	EC–maar s.l.
34–39	Sete Cidades	Smg	259	4.35	33.0	47760.5^c	Cald
40–42	Santiago	Smg	355	0.24	29.0		EC–maar s.l.
43	Rasa2	Smg	544	4×10^{-2}	4.0	754.1^c	EC–maar s.l.
44	Caiado	Pico	805	5.38×10^{-2}	3.6	90.3^c	d
45	Capitão	Pico	785	3.35×10^{-2}	3.5	42.8^c	DT
46	Paul	Pico	785	1.56×10^{-2}	7.5^a	290.0^a	DT
47	Peixinho	Pico	865	1.56×10^{-2}	7.9	48.3^c	d
48	Rosada	Pico	898	1.25×10^{-2}	5.2	27.3^c	EC–SC
49;50	Caldeirão (E+W)	Corvo	405	0.31	1.4	156.4^c	Cald
51	Enxofre	Gra	~83	8.74×10^{-3b}	22.5^b		in LC
52	Lomba	Flores	645	2.10×10^{-2d}	17.0^d	297.0^c	EC–maar s.l.
53	Rasa	Flores	528	0.10d	16.0^d	1356.5^c	EC–maar s.l.
54	Negro	Ter	542	6.25×10^{-3}	1.87^e	3.0^e	d
55	A. Carvão	Ter	509	8.94×10^{-4f}	15.0^f		in LC
56	Falca	Ter	500		3.0	6.6^c	EC–SC
57	Negra St. B.	Ter	836		4.0	12.0	Cald

Location: Smg — São Miguel island; Pico — Pico island; Corvo — Corvo island; Grac — Graciosa island; Flores — Flores island; Ter — Terceira island. Volcanological settings: Cald — subsidence caldera; EC — maar s.l.–hydrovolcanic crater; EC–SC — scoria cone crater; d — depression not associated to volcanic centres; DT — tectonic depression (e.g., sag pond); in LC — inside lava cave. Data sources: a — HP (1986); b — Ogawa (1989); c — Porteiro (2000); d — Azevedo (1998); e — Dias (1986); f — SEE/OGVA (unpublished results). Other data is from the present work and from Constância et al. (1997).

The geology of Terceira depicts two active composite volcanoes with calderas, that dominate the central-north area of the island (Pico Alto volcano) and the westernmost area (Santa Bárbara volcano), linked by a NW–SE-trending fissural zone, which shows several scoria cones, and the 1761 AD eruption vent (Nunes, 2000). Materials erupted from the fissural zone also covers the SW area of Terceira, over the composite volcanoes of Guilherme Moniz, in the central–south sector of the island, and Cinco Picos, both structures with calderas. This latter volcano corresponds to the older composite volcano of Terceira island, and outcrops are distributed mainly to the East.

The geology of Faial is dominated by an active composite volcano with a summit caldera, located in the central–east sector of the island, and the recent explosive activity produces thick pumice fall deposits, lahars and pyroclastic flows (Chovelon, 1982; Coutinho, 2000). The geology of its western sector is characterized mostly by eruption of basaltic lava flows and pyroclastic materials from scoria cones, which are spread along eruptive fissures. The SE area of Graciosa island also hosts an active composite volcano with a summit caldera, contrasting with the NW platform, which is built from eruptions forming scoria cones and is where the most recent volcanic activity occurred.

The volcanic formations on Flores island can be grouped as follows: the Upper complex, represented by subaerial lava flows and pyroclastic deposits, overlying the Basal complex, older than 500,000 yr BP and corresponding to products erupted from submarine volcanic episodes (Azevedo, 1998). The younger volcanic eruptions were to hydrovolcanic nature and have been dated from about 3000 yr (Mourisseau, 1987). The geology of the remaining island from the Western Group of Azores (Corvo), is dominated by a composite volcano with a summit caldera, while the southernmost area corresponds to a small lava delta (França et al., 2002).

Since settlement in the 15th century, 26 eruptions have taken place in the Azores (Weston, 1964; França et al., 2003), the most recent event being a submarine eruption, about 10 km NW of Terceira island, that took place between 1998 and 2000 (Forjaz et al., 2001; Gaspar et al., 2001). Of the original 26 historical eruptions, two events involved some interaction with lake waters, both events on São Miguel island (1563 AD and 1630 AD). The 1563 AD plinian eruption occurred inside Fogo volcano caldera, with a first phase undoubtedly presenting a hydrovolcanic character, which can be drawn from the historical records and geological field evidences (Wallenstein, 1999). The explosive activity started on 28 June and lasted until 3 July of 1563 AD, and the volcanic sequence resulting from the eruption shows deposits with a magmatic character interbedded with ash levels that represents episodes of water–magma interaction.

The 1630 AD activity corresponds to a subplinian/phreatomagmatic eruption, which occurred in the southern sector of the Furnas volcano caldera complex, destroying two lakes in the surrounding area as shown by the historical records. The initial phase of the eruption was magmatic in character, later succeeded by phreatomagmatic activity that

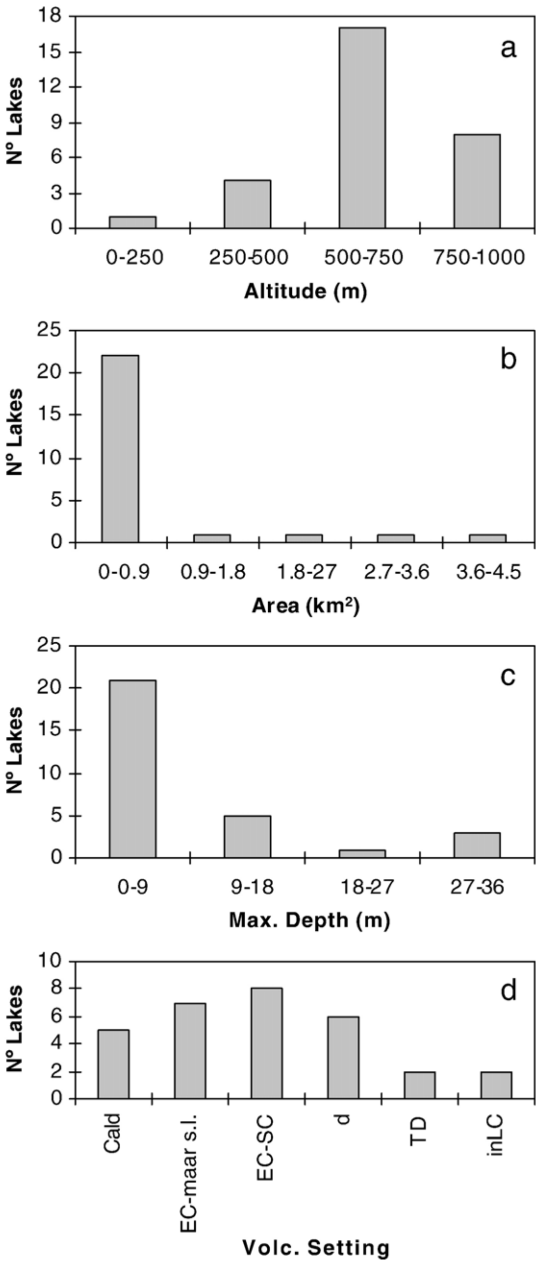

Fig. 2. Histograms for some descriptive features for studied lakes; a — altitude; b — surface area; c — maximum depth; d — volcanological settings (data from Table 1).

Table 2
Chemical data for the studied lake waters

Ref	Name	Island	pH	T (°C)	EC (μS/cm)	TDSc (mg/L)	HCO_3 (mg/L)	Cl (mg/L)	SO_4 (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Dissolved CO_2 (mg/L)	Total CO_2 (mg/L)	SiO_2 (mg/L)	Charge balance (%)
1	Furnas (south)—S	Smg	8.34	21.5	140	62.0	46.4	15.6	4.8	18.5	11.4	2.2	2.8	1.5	34.9	11.6	4.3
2	Furnas (south)—M	Smg	8.28	21.2	140	61.6	48.2	16.3	4.8	17.8	11.5	2.2	2.7	1.9	36.7	11.6	1.1
3	Furnas (south)—B	Smg	7.28	20.3	143	63.6	50.0	16.3	4.8	18.5	12.2	2.3	2.7	12.2	48.3	13.7	2.1
4	Furnas (deepest)—S	Smg	7.63	21.2	139	61.1	48.2	16.3	5.2	18.7	10.1	2.2	2.5	3.4	38.2	11.3	0.8
5	Furnas (deepest)—M	Smg	7.53	21.0	140	60.8	47.6	16.3	4.8	18.4	10.2	2.3	2.5	4.5	38.8	9.8	1.2
6	Furnas (deepest)—B	Smg	6.56	19.2	152	64.8	53.7	16.3	5.0	17.8	11.6	2.5	3.4	23.4	62.1	13.1	0.1
7	Furnas (north)—S	Smg	7.12	21.1	139	61.6	47.6	16.3	4.7	17.6	10.2	2.3	3.1	5.4	39.7	13.5	1.2
8	Furnas (north)—M	Smg	6.99	20.1	140	63.8	48.8	16.0	4.8	18.0	12.1	2.3	3.2	12.9	48.1	12.8	3.7
9	Furnas (north)—B	Smg	6.51	18.9	152	61.0	50.6	16.0	5.5	17.9	10.5	2.1	3.0	27.8	64.3	14.3	−1.1
10	Fogo (south)—S	Smg	7.26	18.1	49	27.3	6.1	11.7	4.1	8.2	1.9	0.7	0.6	1.3	5.7	2.4	−2.4
11	Fogo (south)—M	Smg	6.95	17.7	47	26.2	6.7	12.1	3.9	7.4	1.7	0.8	0.4	1.6	6.4	2.4	−9.0
12	Fogo (south)—B	Smg	5.93	13.2	47	25.4	6.1	11.7	4.1	5.7	1.8	0.9	0.6	10.5	14.9	2.8	−12.8
13	Fogo (north)—S	Smg	6.42	18.1	47	26.3	6.1	12.4	4.0	6.5	1.8	0.8	0.5	1.4	5.8	2.5	−12.0
14	Fogo (north)—M	Smg	6.67	18.1	47	24.1	6.1	12.1	3.8	5.4	1.7	0.8	0.4	1.4	5.8	4.3	−18.2
15	Fogo (north)—B	Smg	6.83	17.9	48	24.9	6.1	12.4	3.6	5.9	1.7	0.8	0.4	1.6	6.0	6.8	−16.0
16	Congro—S	Smg	9.42	22.9	122	51.4	29.3	16.0	5.0	12.0	8.9	2.2	2.1			1.1	−0.2
17	Congro—M	Smg	7.06	16.0	107	51.2	26.8	15.3	5.7	11.2	9.4	2.2	2.2	9.5	28.9	1.2	1.6
18	Congro—B	Smg	6.56	14.4	117	55.0	37.8	15.3	4.8	11.6	12.6	2.1	2.5	16.4	43.7	13.9	−1.0
19	Areeiro—S	Smg	6.65	24.0	45	25.0	2.4	12.8	3.5	5.4	0.9	1.0	0.5	1.4	3.2	0.4	−13.3
20	São Brás—S	Smg	5.48	23.6	62	23.8	2.4	11.4	3.3	5.4	1.2	1.0	0.5	1.7	3.5	0.4	−7.3
21	São Brás—B	Smg	5.70	22.3	43	24.9	2.4	12.1	3.7	5.4	1.3	1.0	0.5	2.6	4.4	1.0	−9.7
22	Peixe—S	Smg	7.45	18.7	187	48.0	21.4	17.0	3.2	8.7	3.1	2.6	3.6	6.4	21.8	1.0	−2.6
23	Carvão—S	Smg	7.69	15.7	105	35.9	14.6	13.9	2.9	8.3	1.7	1.7	2.0	4.4	15.0	6.7	−3.4
24	Caldeirão Grande—S	Smg	6.83	15.7	98	35.6	9.2	14.6	3.8	9.0	1.5	1.4	1.6	1.0	7.6	4.6	−0.8
25	Pau Pique—S	Smg	7.56	16.6	51	29.1	2.4	13.5	3.9	6.4	1.0	1.3	0.6	1.2	3.0	0.6	−6.9
26	Éguas—S	Smg	6.88	16.3	66	36.8	2.4	17.0	4.4	8.3	2.3	1.4	0.9	2.4	4.2	0.3	−2.7
27	Empadadas (north)—S	Smg	7.62	19.1	43	27.5	3.7	13.5	1.4	6.1	1.0	1.1	0.8	1.6	4.2	3.3	−5.2
28	Empadadas (north)—B	Smg	6.24	16.7	47	29.8	5.5	12.4	2.0	6.7	1.0	1.3	0.9	7.6	11.6	1.3	−1.9
29	Empadadas (south)—S	Smg	7.40	18.1	63	36.7	6.7	14.9	2.9	8.3	1.1	1.5	1.3	2.2	7.0	0.9	−1.5
30	Empadadas (south)—B	Smg	7.00	18.0	62	33.8	7.3	14.9	3.5	8.0	1.1	1.6	1.3	2.3	7.6	3.4	−4.0
31	Rasa1—S	Smg	7.34	17.8	50	27.5	2.4	12.8	3.9	7.1	0.9	1.1	0.6	11.3	13.1	0.7	−3.5
32	Canário—S	Smg	6.31	19.2	45	27.2	2.4	13.1	2.6	6.5	0.8	1.1	0.6	2.0	3.8	0.8	−4.6
33	Canário—B	Smg	6.40	19.1	46	26.8	2.4	13.1	3.6	7.0	0.8	1.0	0.5	1.5	3.3		−6.3
34	Sete Cidades (north)—S	Smg	7.69	20.6	110	45.1	23.2	17.0	3.7	14.3	3.3	1.6	1.2	2.7	19.4	0.3	−3.7

Table 2 (*continued*)

Ref	Name	Island	pH	*T* (°C)	EC (μS/cm)	TDSc (mg/L)	HCO$_3$ (mg/L)	Cl (mg/L)	SO$_4$ (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Dissolved CO$_2$ (mg/L)	Total CO$_2$ (mg/L)	SiO$_2$ (mg/L)	Charge balance (%)
35	Sete Cidades (north)—M	Smg	7.14	19.1	99	43.5	22.6	16.5	3.6	14.1	3.0	1.4	1.2	3.8	20.1	0.3	−4.2
36	Sete Cidades (north)—B	Smg	6.66	15.0	99	42.9	22.6	16.1	3.4	14.8	3.2	1.4	0.8	7.8	24.1	0.5	−2.3
37	Sete Cidades (south)—S	Smg	9.21	21.1	125	52.0	32.9	17.2	3.7	20.6	2.9	1.1	1.9			1.9	−0.5
38	Sete Cidades (south)—M	Smg	7.47	16.5	122	50.5	33.6	16.5	3.3	20.6	2.6	1.2	1.6	5.7	29.9	2.0	0.0
39	Sete Cidades (south)—B	Smg	6.59	14.5	127	49.5	34.8	15.4	2.7	20.3	2.6	1.2	1.9	14.0	39.1	0.3	1.2
40	Santiago—S	Smg	9.01	19.7	123	46.2	32.3	14.7	3.3	20.3	2.5	1.0	1.1			0.4	0.3
41	Santiago—M	Smg	7.70	14.5	121	48.7	34.8	14.7	3.5	22.0	2.6	1.1	1.2	4.6	29.7	3.3	1.7
42	Santiago—B	Smg	6.59	13.4	121	48.0	34.2	17.0	3.7	20.2	2.5	1.0	1.3	8.7	33.3	1.5	−1.2
43	Rasa2—S	Smg	6.12			25.8	1.2	12.4	2.4	7.5	1.0	0.8	0.5	1.8	2.7	2.3	2.7
44	Caiado—S	Pico	6.62	17.7	26	17.3	1.8	10.1	1.4	2.7	0.2	0.6	0.4	7.5	8.8	0.9	−27.7
45	Capitão—S	Pico	6.02	16.0	31	22.9	4.9	9.6	1.7	4.5	0.4	1.1	0.8	4.2	7.7	2.0	−6.6
46	Paul—S	Pico	5.79	17.0	28	11.0	2.1	5.2	1.1	2.7	0.3	0.4	0.4	21.2	22.7	1.5	−6.8
47	Peixinho—S	Pico	6.98	17.7	33	20.3	5.5	9.4	2.4	4.0	0.7	0.8	1.0	9.4	13.4	5.6	−13.2
48	Rosada—S	Pico	6.17	17.5	27	17.2	2.4	8.2	1.4	3.5	0.5	0.7	0.6	0.8	2.6	0.3	−10.3
49	Caldeirão E—S	Corvo	6.83	23.0	82	45.2	3.1	25.2	4.4	12.4	0.3	1.5	0.2			<0.05	−11.5
50	Caldeirão W—S	Corvo	7.06	24.6	79	39.2	2.8	21.3	4.7	10.5	0.2	1.4	0.2			<0.05	−11.7
51	Enxofre—S	Gra	6.07	16.1	623	356.2	258.0	71.4	37.6	47.3	19.0	37.7	29.5	179.0	365.1	74.9	−0.6
52	Lomba—S	Flores	6.40	12.5	40	31.7	7.6	12.8	1.1	7.2	0.5	1.1	1.4				−2.2
53	Rasa—S	Flores	5.60	12.5	73	36.1	13.2	16.0	1.6	9.6	0.5	1.7	1.4				−4.5
54	Negro—S	Ter	5.88	20.0	76	45.6	3.1	22.0	4.6	11.6	1.5	1.7	1.2	7.0	9.2	0.6	−1.7
55	A. Carvão—S	Ter	7.80	11.9	146	51.3	42.7	18.5	1.3	27.1	2.9	0.2	0.7	2.6	33.4	73.6	2.2
56	Falca—S	Ter	5.39	20.0	75	36.9	3.7	18.1	6.1	8.0	0.8	1.4	1.1	4.7	7.3	4.7	−12.6
57	Negra St. B.—S	Ter	4.91	19.7	74	36.6	3.1	19.2	3.3	8.3	0.5	1.5	0.8	3.3	5.5		−10.4
		Max	9.42	24.6	623.0	356.2	258.0	71.4	37.6	47.3	19.0	37.7	29.5	179.0	365.1	74.9	4.3
		Min	4.91	11.9	26.0	11.0	1.2	5.2	1.1	2.7	0.2	0.2	0.2	0.8	2.6	0.3	−27.7
		Median	6.83	18.1	77.5	36.8	7.3	15.3	3.7	8.7	1.7	1.3	1.1	4.0	13.2	2.3	−2.6
		Average	6.91	18.3	96.2	44.9	22.6	15.7	4.2	11.9	3.8	2.0	1.8	9.5	26.3	6.9	−4.5

Name refers to lake and to water column position (S — surface; M — middle; B — bottom). TDSc corresponds to calculated TDS. Data from samples #52 and #53 are from Azevedo (1998).

Location: Smg — São Miguel island; Pico — Pico island; Corvo — Corvo island; Gra — Garciosa island; Flores — Flores island; Ter — Terceira island.

produced pyroclastic surges that killed about 80 people (Cole et al., 1995). The explosive activity lasted about 3 days and was characterized by a succession of phreatomagmatic and magmatic phases, followed by the extrusion of a trachytic lava dome during the subsequent two months.

Numerous thermal springs as well as fumarolic fields and steaming grounds are spread along the archipelago (in all the islands but Santa Maria and Corvo), and these are the surface manifestation of hydrothermal systems at depth (Ferreira and Oskársson, 1999; Cruz et al., 1999; Cruz and França, 2001, 2003; Cruz, 2003).

2.2. Volcanic lakes setting

The locations of the volcanic lakes characterized in the present paper are shown in Fig. 1. Table 1 depicts the lakes names and the location, as well as the altitude, area, maximum depth, reservoir volume and the volcanological setting.

Lakes are located between 83 and 898 m a.s.l. (average = 613 m; median = 637.5 m; Fig. 2a) and present a large range in surface area values (8.94×10^{-4}–4.35 km^2; average = 0.35 km^2). However, the median value of the lake-surface area (0.02 km^2) shows clearly that the majority of the lakes have a very small area (Fig. 2b). The

Table 3
Trace elements composition for selected lake water

Ref	Name	Island	Fe (μg/L)	Al (μg/L)	As (μg/L)
1	Furnas (south)—S	Smg			
2	Furnas (south)—M	Smg	47	32	0.66
3	Furnas (south)—B	Smg			
4	Furnas (deepest)—S	Smg	39	24	0.66
5	Furnas (deepest)—M	Smg			
6	Furnas (deepest)—B	Smg	241	71	1.78
7	Furnas (north)—S	Smg			
8	Furnas (north)—M	Smg			
9	Furnas (north)—B	Smg	74	27	0.66
10	Fogo (south)—S	Smg	44	59	0.28
11	Fogo (south)—M	Smg	16	62	0.26
12	Fogo (south)—B	Smg	17	33	0.26
13	Fogo (north)—S	Smg	69	75	0.32
14	Fogo (north)—M	Smg			
15	Fogo (north)—B	Smg	69	138	0.24
16	Congro—S	Smg	12	53	0.16
17	Congro—M	Smg	19	17	0.14
18	Congro—B	Smg			
19	Areeiro—S	Smg		37	0.05
20	São Brás—S	Smg		30	0.21
21	São Brás—B	Smg			
22	Peixe—S	Smg	239	82	0.27
23	Carvão—S	Smg	136	19	0.09
24	Caldeirão Grande—S	Smg	185	45	0.09
25	Pau Pique—S	Smg	36	70	0.11
26	Éguas—S	Smg	26	69	0.07
27	Empadadas (north)—S	Smg	89	201	0.25
28	Empadadas (north)—B	Smg			
29	Empadadas (south)—S	Smg	37	28	
30	Empadadas (south)—B	Smg			
31	Rasa1—S	Smg	11	14	0.08
32	Canário—S	Smg	27	49	0.13
33	Canário—B	Smg			
34	Sete Cidades (north)—S	Smg		16	0.35
35	Sete Cidade (snorth)—M	Smg		14	0.32
36	Sete Cidades (north)—B	Smg		14	0.31
37	Sete Cidades (south)—S	Smg		23	0.90
38	Sete Cidades (south)—M	Smg		9	0.96
39	Sete Cidades (south)—B	Smg	11	8	0.56
40	Santiago—S	Smg	29	68	0.80
41	Santiago—M	Smg	6	15	0.93
42	Santiago—B	Smg	72	25	1.08
43	Rasa2—S	Smg	282	159	0.60
44	Caiado—S	Pico			
45	Capitão—S	Pico			
46	Paul—S	Pico			
47	Peixinho—S	Pico			
48	Rosada—S	Pico			
49	Caldeirão E—S	Corvo			
50	Caldeirão W—S	Corvo			
51	Enxofre—S	Gra	590	17	0.22
52	Lomba—S	Flores			
53	Rasa—S	Flores			
54	Negro—S	Ter			
55	A. Carvão—S	Ter			
56	Falca—S	Ter			
57	Negra St. B.—S	Ter			

Name refers to lake and water column position (S — surface; M — middle; B — bottom).

Location: Smg — São Miguel island; Pico — Pico island; Corvo — Corvo island; Gra — Garciosa island; Flores — Flores island; Ter — Terceira island.

maximum depth ranges between 0.8 and 33.0 m, with an average value of 8.7 m. Greatest depths are found for the larger lakes occupying the summit calderas of the Quaternary active composite volcanoes of São Miguel island (Sete Cidades, Fogo and Furnas), as well as in smaller lakes related with explosive craters resulting from hydrovolcanic eruptions (Congro and Santiago). The median value (4.0 m) shows that the majority of the lakes have small maximum depths (Fig. 2c). Because of the small surface area and maximum depth observed for the majority of the lakes, reservoir volumes are correspondingly smaller, ranging between 2.4×10^3 and 4.78×10^7 m^3 (average $=3.27\times10^6$ m^3; median $=3.99\times10^4$ m^3). The larger volumes correspond to Sete Cidades, Fogo and Furnas lakes (São Miguel) that occupy the summit subsidence calderas of composite volcanoes.

In Fig. 2d, the volcanological settings of the studied lakes are shown, demonstrating that half of the lakes are located inside explosive craters, namely in scoria cones (26.7%) or in hydrovolcanic craters (23.3%), while 16.7% of the lakes are located in the bottom of subsidence calderas. Therefore, 66.7% of the lakes are related with craters or calderas, which is common for volcanic lakes worldwide; lakes contained by lava flow-dams and lahar deposit-dams are less common (Delmelle and Bernard, 2000; Varekamp et al., 2000).

Less common types of lakes include: (1) lakes located in topographic depressions not directly associated with volcanic landforms (20.0%); (2) lakes in depressions of tectonic origin (e.g., sag ponds; 6.7%); and (3) lakes occupying lava caves (6.7%).

3. Results

3.1. Methodology

Water samples were collected at 30 lakes, with the majority of the samples collected immediately below the lake surface. For the deepest lakes on São Miguel island (Furnas, Fogo, Congro, Sete Cidades, Santiago, São Brás, Empadadas North and South), samples were collected at the surface, at the middle of the water column and at the lake bottom, and were labelled, respectively, as “S”, “M” and ”B.” Several vertical profiles were determined during the summer and winter periods, collecting samples every meter of the water column, using a sampling bottle.

During sample collection, the pH, temperature, and water conductivity also were measured, and alkalinity and dissolved CO_2 were determined on site by titration. In the field, samples were filtered through 0.2 μm Millipore membranes (cellulose acetate) and kept in doubled capped HDPE bottles. Samples for determination of cations were acidified with suprapur concentrated nitric acid. Anions were determined by ionic chromatography and major cations by atomic-absorption spectrometry. Si, Fe, Al and As were analysed by ICP-MS in the Activation Laboratories (Canada). Si determination for Caldeirão lake (Corvo) was made by the silicomolybdic method using a spectrophotometer. Charge-balance errors are shown in Table 2, and the average value is equal to − 4.5%.

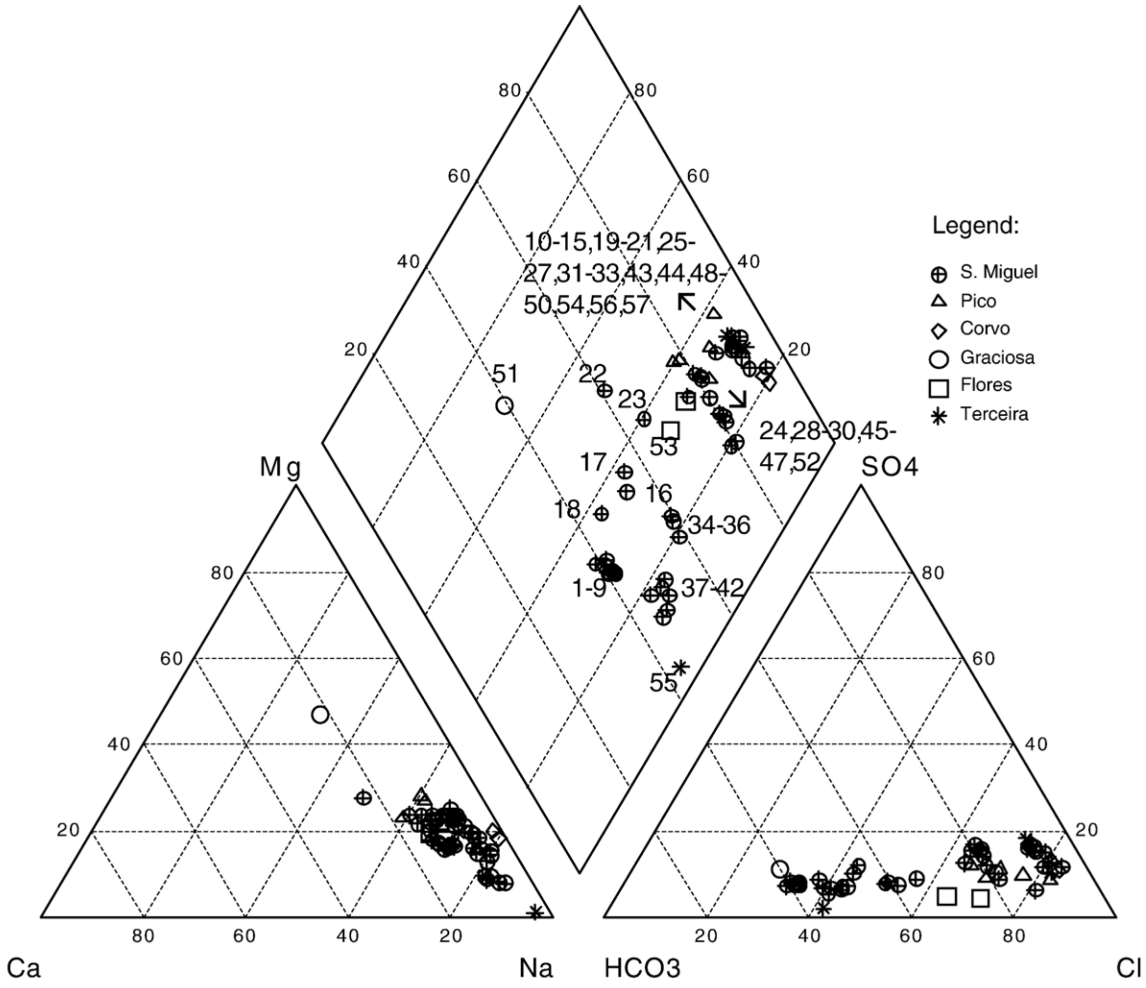

Fig. 3. Piper plot showing major-ion chemistry for the lake waters analysed (data from Table 2).

3.2. Analytical data

The chemical composition and main variables (pH, temperature, electrical conductivity, calculated TDS) are given in Table 2, and some trace-element data for São Miguel and Graciosa lakes are shown in Table 3. Water samples mainly belong to the Na–Cl to Na–HCO_3 types, with the exception of the Furna do Enxofre lake (#51), which exhibits a Mg signature (Fig. 3). The dissolved constituents reveal a relative distribution, which shows a decreasing order for cations $Na^+ > Mg^{2+} > K^+ > Ca^{2+}$ and for anions $Cl^- > HCO_3^- > SO_4^{2-}$.

The water samples present a large range of pH values (4.91–9.42; average = 6.91; median = 6.83); the highest values are observed for surface samples from on the southern area of Sete Cidades lake (so-called Lagoa Verde; #37), Congro lake (#16) and Santiago lake (#40). Values decrease with depth in these lakes, and the surface pH data are related to the developing eutrophication process. The majority of the water samples are low temperature, ranging between 11.9 and 24.6 °C, with an average value of 18.3 °C and a median value of 18.1 °C.

Electrical conductivity of the water samples ranges from 26 to 623 μS/cm. The highest value is observed at

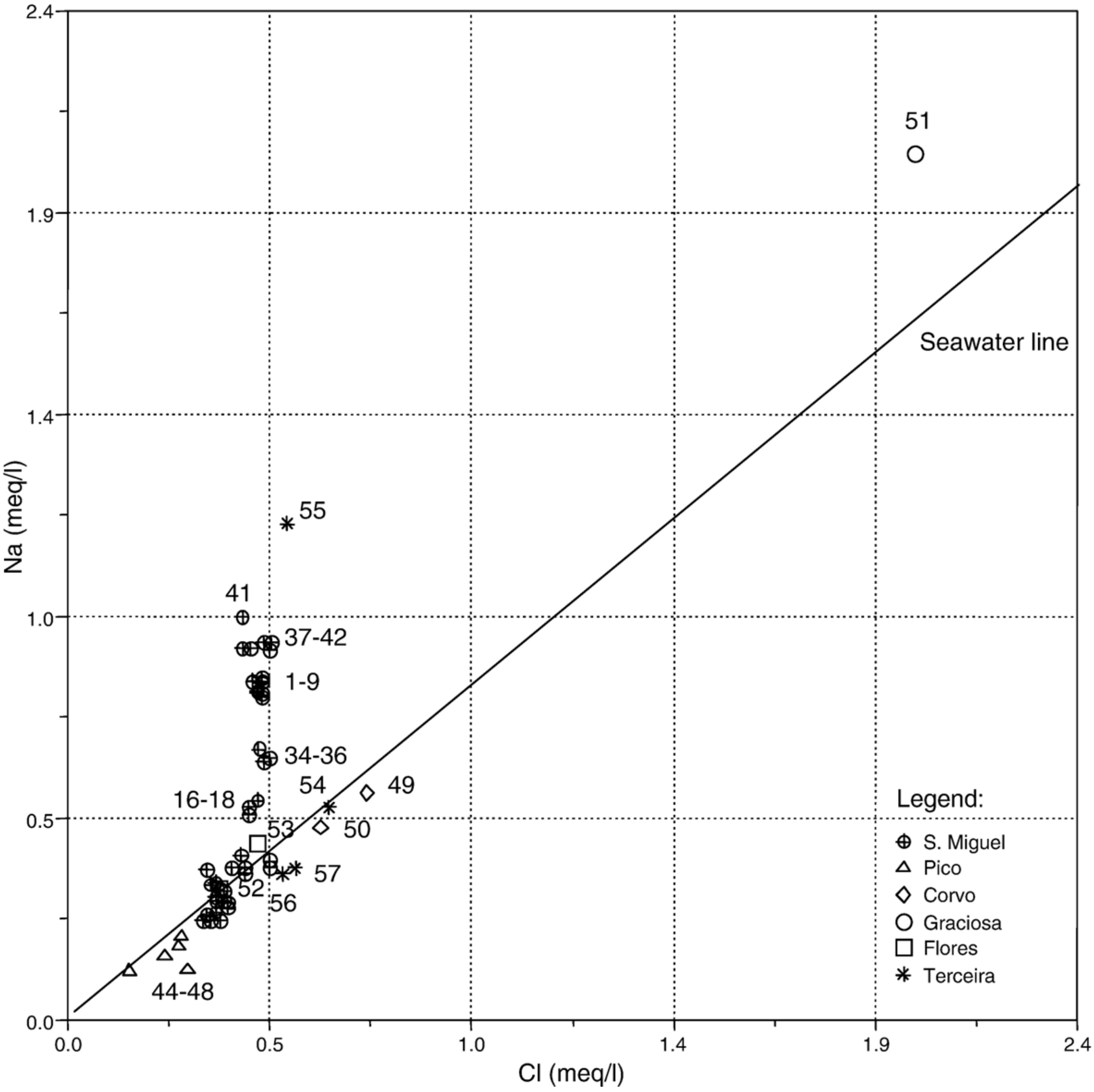

Fig. 4. Relationship between Cl^- (in meq/L) and Na^+ (in meq/L), showing that numerous samples fall far beyond the seawater line.

Furnas do Enxofre lake (#51; Graciosa island); excluding this result, the conductivity range is narrow (26–187 μS/cm), which is consistent with a median value of 77.4 μS/cm. Calculated TDS data also show that samples can be classified as fresh water, representing low mineralization (11.0–356.2 mg/L; median = 36.8 mg/L), with the highest value observed at Furna do Enxofre (#51) and the lowest values for lakes on Pico island.

Water samples are characterized by low total CO_2 contents, which range between 2.6 to 365.1 mg/L (median = 13.2 mg/L). As for calculated TDS, the maximum total CO_2 content is again observed at Furna do Enxofre lake (#51), and results for the other samples range between 2.6 and 64.3 mg/L (median = 13.1 mg/L). Variations with depth of total CO_2, dissolved CO_2 and HCO_3^- are discussed below.

4. Discussion

4.1. General hydrogeochemistry

The influence of the marine contribution explains the numerous samples close to the seawater line in the Cl^- vs. Na^+ plot (Fig. 4), as it is the case for lakes from São Miguel (#10–15, 19–33, 43), as well as lakes from Corvo (#49, 50), Pico (#44, 45, 46, 47, 48), Flores (#52,

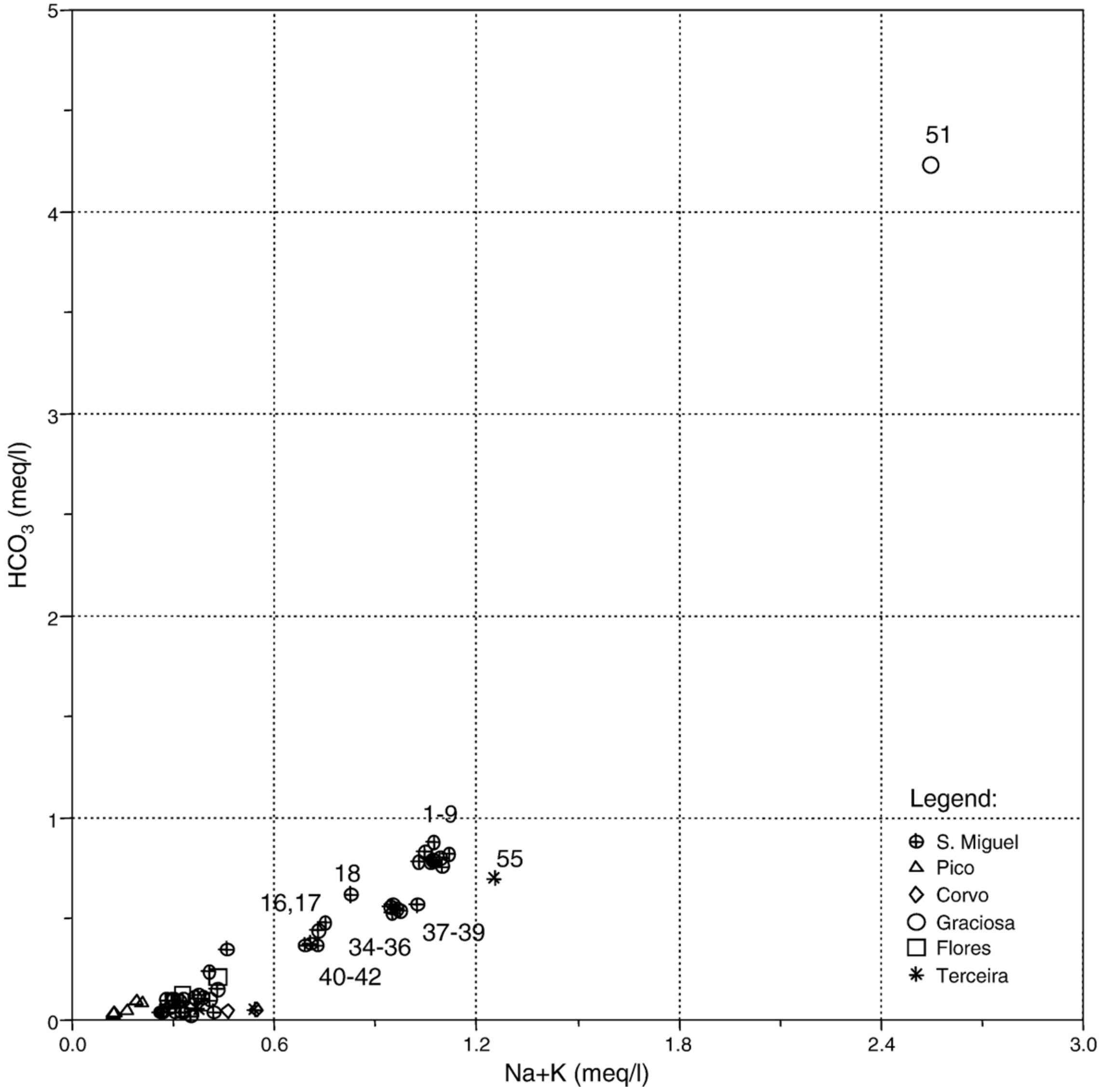

Fig. 5. Alkali metals (in meq/L) vs. HCO_3^- (in meq/L) content plot.

53) and Terceira (#54, 56, 57). This trend suggests that those lakes are strongly influenced by sea-salt spray. The other samples define a trend related with sodium enrichment independent of chloride concentration, suggesting other geochemical processes besides marine input (#1, 2, 3, 4, 5, 6, 7, 8, 9, 16, 17, 18, 37, 38, 39, 40, 41, 42, 51, 55) to explain the overall mineralization increase.

The plot of the alkali metals vs. HCO_3^- also reveals two trends (Fig. 5): (1) lake waters that plot close to the origin of the graphic, with low bicarbonate content, suggesting an increase of alkali metals unrelated with HCO_3^-; and (2) a group of lake waters which shows a close positive relation between $Na^+ + K^+$ and HCO_3^-. The first trend is associated with the same group of samples that evolve mainly by sea-salt addition, while the second trend suggests some degree of water–rock interaction (#1, 2, 3, 4, 5, 6, 7, 8, 9, 16, 17, 18, 34, 35, 36, 37, 38, 39, 40, 41, 42, 51, 55). This HCO_3^- enrichment controls water mineralization for these samples, as well for samples #22, 23, and 53, as suggested by the close relation between TDSc and HCO_3^-. This latter evolutionary trend can be also associated with a volcanic contribution.

The majority of the lake waters have low-SiO_2 concentrations, between < 0.05 and 74.9 (median = 2.3 mg/L), and the maximum values are observed for lakes occupying lava caves (#51, 55). The SiO_2 vs. $Na^+ + K^+$ plot

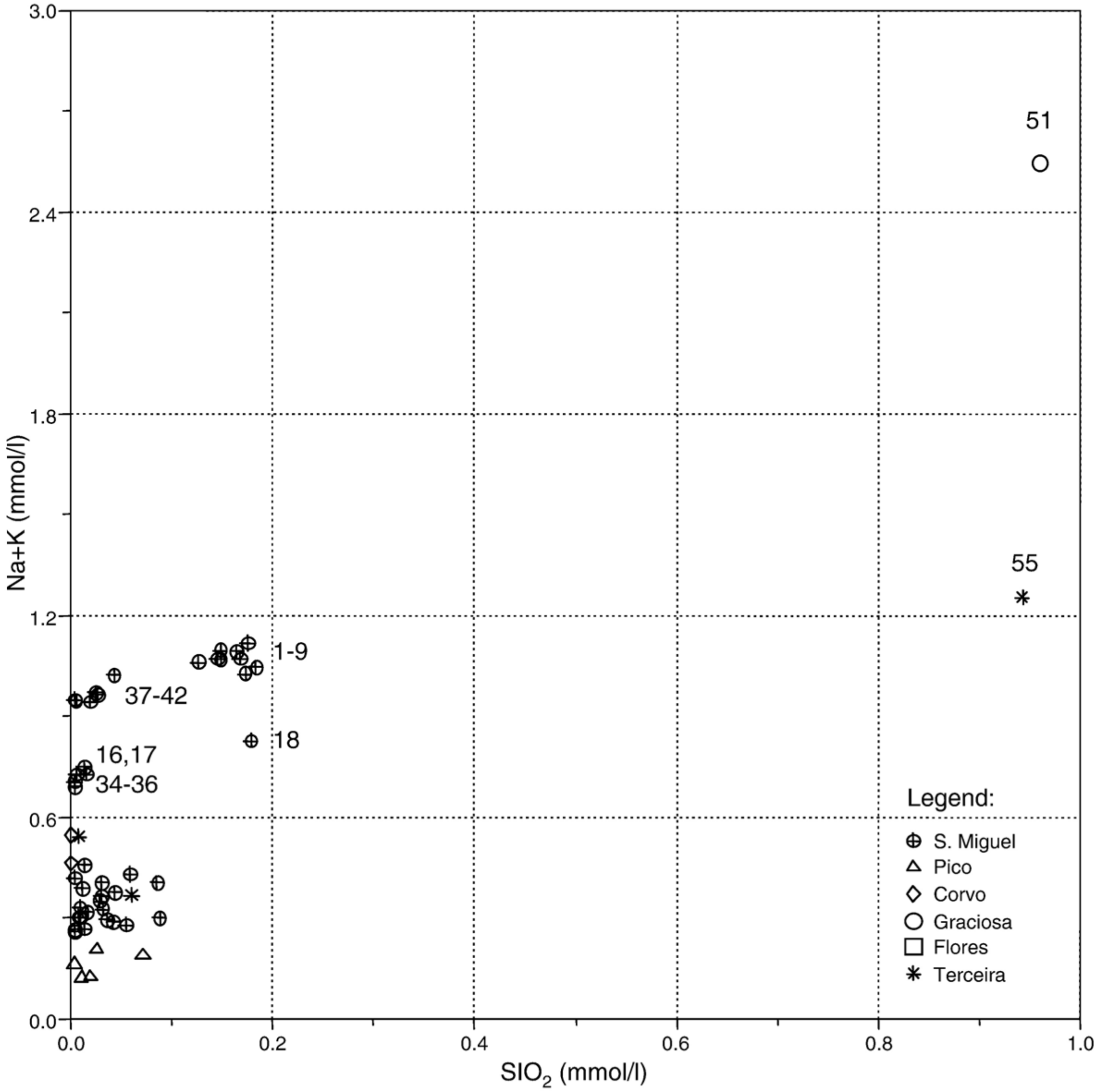

Fig. 6. Relationship between SiO_2 (in mmol/L) and $Na^+ + K^+$ (in mmol/L).

reveals a relationship between these species for samples with the higher SiO_2 content, suggesting the influence of the hydrolysis of silicate minerals (Fig. 6). Nevertheless, SiO_2 content can be also derived from hydrothermal waters seepage in the bottom of the lakes, and this input is not clearly discriminated on the previous plot. Nonetheless, the majority of the samples define a trend of $Na^+ + K^+$ increase independently of the SiO_2 content (Fig. 6), and the lack of a linear relation can reflect the effect of biological uptake by diatoms.

Volcanic contributions, such as seepage of hydrothermal waters or volatiles input in the lake bottom, are better revealed by the HCO_3^- vs. As in Fig. 7, where Furna do Enxofre lake (#51) clearly plots to the far right, a CO_2-dominated volatile source is suggested. Other lakes with higher HCO_3^- contents define a trend with As enrichment. We suggest that this latter trend is related to hydrothermal water seepage into the bottom of the lake, which is compatible with the high As contents determined in geothermal waters from São Miguel island (Carvalho, 1999). It should be noted that, inside Furna do Enxofre lava cave, there is a fumarolic field, with a boiling pool and steaming ground where CO_2 is the main component in the emissions (respectively, about 99% and 94%; Ferreira et al., 1993).

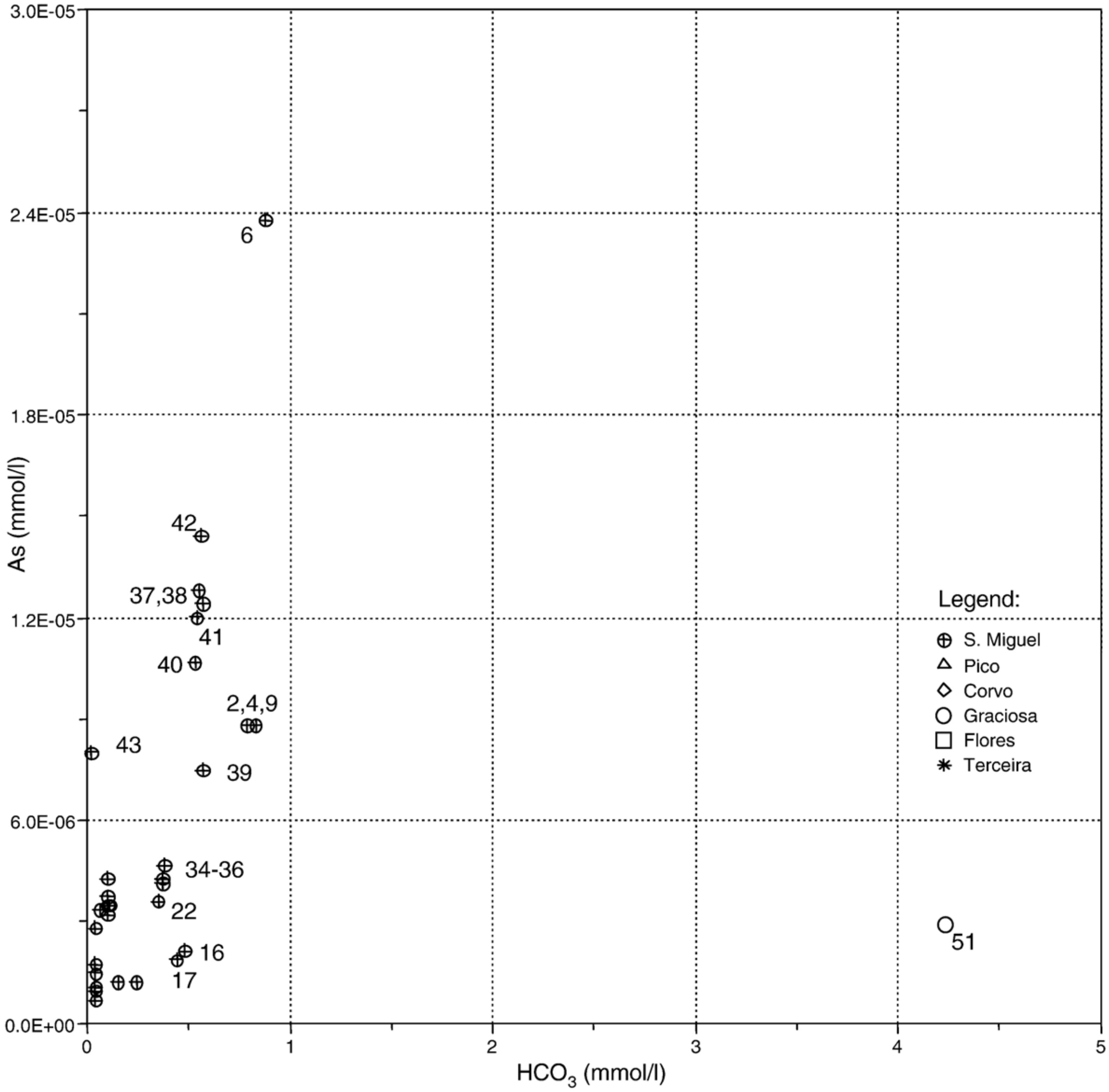

Fig. 7. Relationship between HCO_3^- (in mmol/L) and As (in mmol/L).

4.2. Saturation state

Saturation indexes for some mineral species were investigated using hydrogeochemical software HIDSPEC (Carvalho and Almeida, 1989), at the measured lake temperature. The majority of the studied lake waters are undersaturated in amorphous silica (Fig. 8), and only samples #51 and 55 are oversaturated. The saturated state in relation to SiO_2 mineral phases observed in a few lakes reflect the SiO_2 enrichment in lake waters and, as discussed previously, can be considered as the result of hydrothermal waters discharge in the bottom of the lakes and water–rock interaction. Nevertheless, SiO_2 content also can be affected by biological uptake.

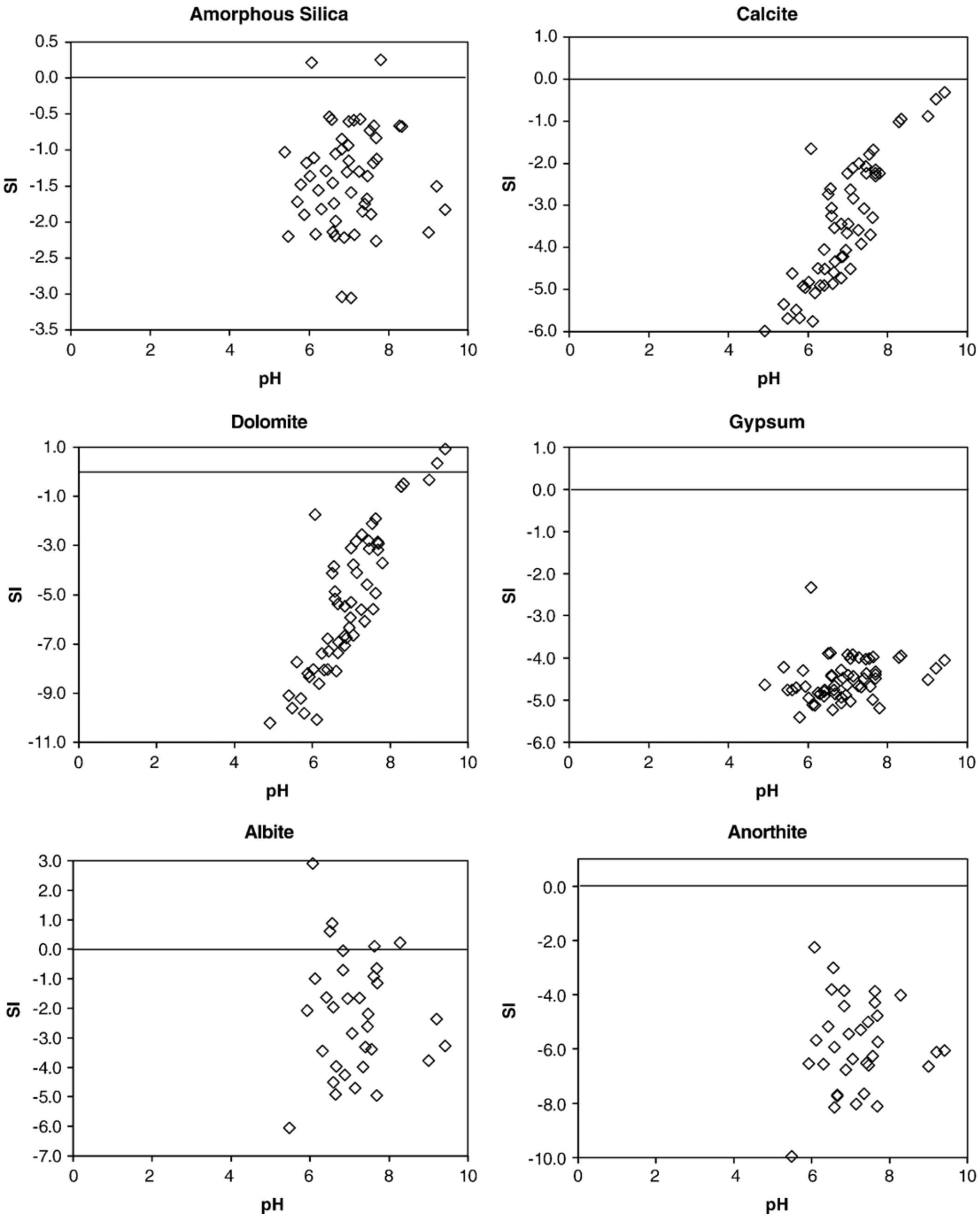

Fig. 8. Plot of the saturation state for amorphous silica, secondary and plagioclase minerals.

Table 4
Results from the PCA analysis: vectors, eigenvalues and cumulative variance (large vector in bold)

No.	Eigenvalue	Cumulative variance (%)
1	**9.32973**	**71.77**
2	**1.41294**	**82.64**
3	**1.12126**	**91.26**
4	0.44374	94.67
5	0.34966	97.36
6	0.20236	98.92
7	0.07252	99.48
8	0.03828	99.77
9	0.01565	99.89
10	0.01071	99.98
11	0.00189	99.99
12	0.00118	100.00

Considering saturation state in relation to carbonate minerals (calcite and dolomite) all samples are undersaturated with these minerals, reflecting the low alkali–earth metals content, with the exception of samples #16 and 37 (dolomite; Fig. 8). All the samples are also undersaturated with respect to gypsum (Fig. 8). The saturation states with respect to the various phases reveal that only a very limited number of studied lakes precipitation of minerals can affect species concentration in water.

The saturation indexes in relation to plagioclase end-member phases also reveal that the majority of lake waters are undersaturated in albite and anorthite (Fig. 8). Only samples #2, 4, 6, 9, 51 are oversaturated in relation to albite, corresponding mainly to samples from Furnas lake, which are influenced by hydrothermal waters seepage and by rock leaching. Regarding anorthite, the undersaturation is expected, as at surface PCO_2, the crystallization of kaolinite and calcite, will not allow anorthite saturation. Nevertheless, as discussed above, calcite saturation was even not reached in studied lakes.

4.3. *Multivariate analysis*

With the objective of assessing the various volcanic lake samples and to identify the operative geochemical processes, we applied a set of multivariate analysis techniques, namely cluster and principal-component analysis (PCA). An example of the contribution of these statistical methods to crater lake studies can be drawn from the work by Varekamp et al. (2000). The statistical software used was ANDAD 6.00, from the Geo-Systems Center (IST; CVRM, 2000).

From a raw matrix of *N* rows of observations by *P* columns of variables, PCA defines eigenvectors revealing the underlying structure of a dataset (Davis, 1986). Cluster analysis defines groups of more or less homogeneous lake waters, and the resulting dendogram corresponds to the graphic display of the groups. For this study, *Q*-mode and *R*-mode cluster analysis was applied in an attempt to classify the respective observations and variables.

4.3.1. *Principal-component analysis (PCA)*

PCA was applied to a dataset of 47 lake water analyses and 13 variables from the original Table 2, with the exception of samples #16, 33, 37, 40, 43, 49, 50, 52, 53, 57 (because these analyses are not complete; see Table 2); the eigenvalues and the percentage of the variance explained are shown in Table 4.

Plotting the scores of variables and samples according to the principal-component axis identifies some geochemical processes that influence lake-water chemistry (Fig. 9). In fact, pH, temperature, conductivity and the species HCO_3^-, SiO_2, Na^+ and K^+ demonstrate negative scores along axis 2, contrasting with Mg^{2+}, SO_4^{2-}, Ca^{2+}, Cl^- and total and dissolved CO_2 that are characterized by positive scores along the same axis. Therefore, we suggest that negative scores along axis 2 represent water–rock interaction and hydrothermal water seepage, while positive scores over axis 2 will represent mainly CO_2-dominated volatile input, thereby explaining the cases where dissolved CO_2 content controls total CO_2 in lake waters. SO_4^{2-} could be explained by oxidation of reduced sulphur species, but the association with Cl^- suggests a marine contribution. The position of the sample #51 (Furna do Enxofre lake) along axis 2 confirm this interpretation and is in agreement with our previous discussion (see also Fig. 7).

Compared with the position of variables, the majority of the samples plot on the opposite side along axis 1,

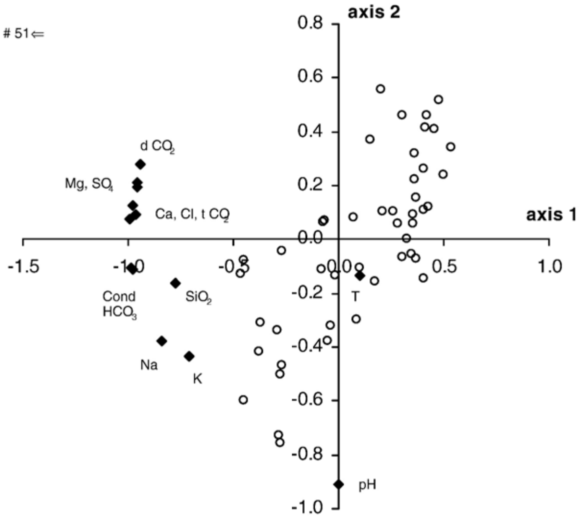

Fig. 9. Results of principal-component analysis (PCA): axis 1 vs. axis 2 plot for variables ($n=13$) and observations ($n=47$). See text for discussion.

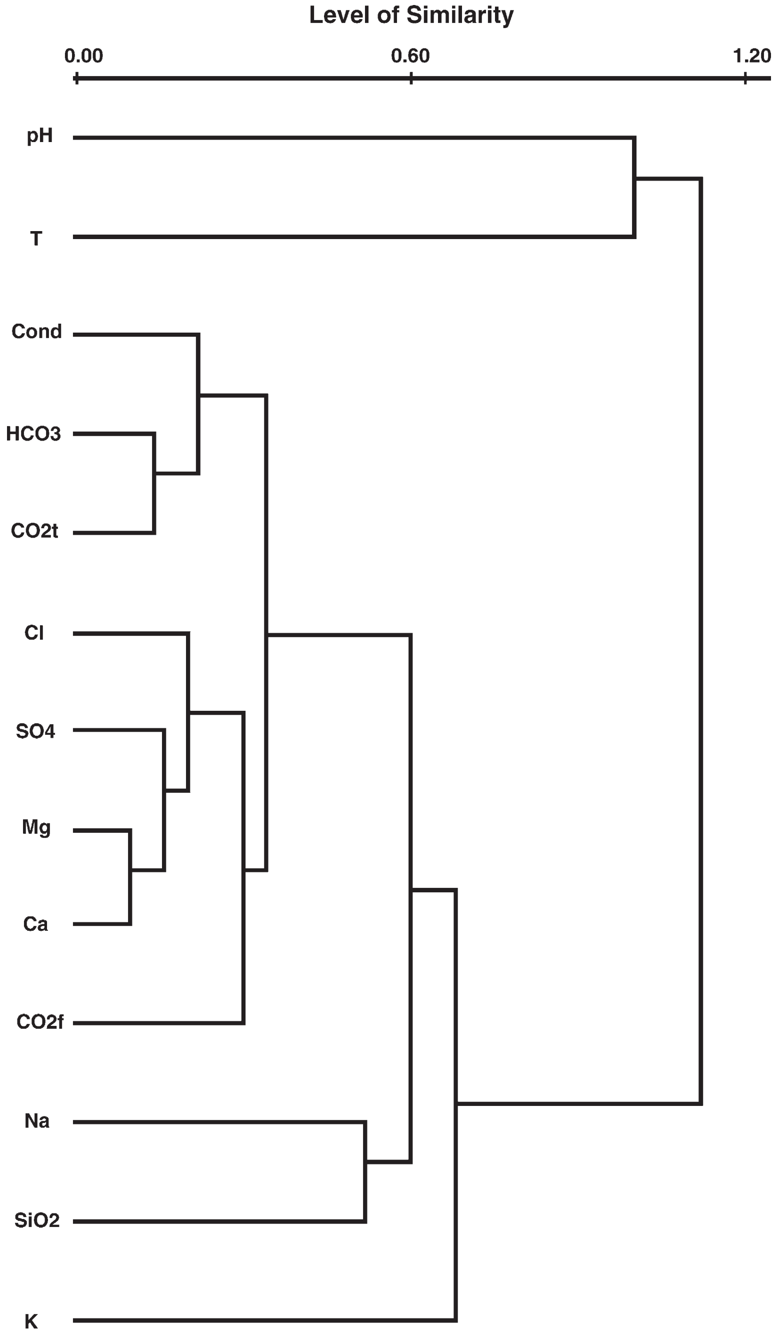

Fig. 10. Dendogram of *R*-mode analysis. See text for discussion.

corresponding to positive scores, which results from the low mineralization, as water conductivity presents a negative score along axis 1.

4.3.2. Cluster analysis

Results from the *R*-mode analysis reveal several groups (Fig. 10). One of the groups shown by the dendogram reflects the relation between conductivity–HCO_3^-–total CO_2, revealing the control of water mineralization exerted by the carbonate species, as this group presents a close relation also with dissolved CO_2.

Dissolved CO_2 is also associated with a group involving Cl^-–SO_4^{2-}–Mg^{2+}–Ca^{2+}. The association between the pair Cl^-–SO_4^{2-} suggests the marine contribution to the composition of the majority of studied lake waters. The explanation for the association

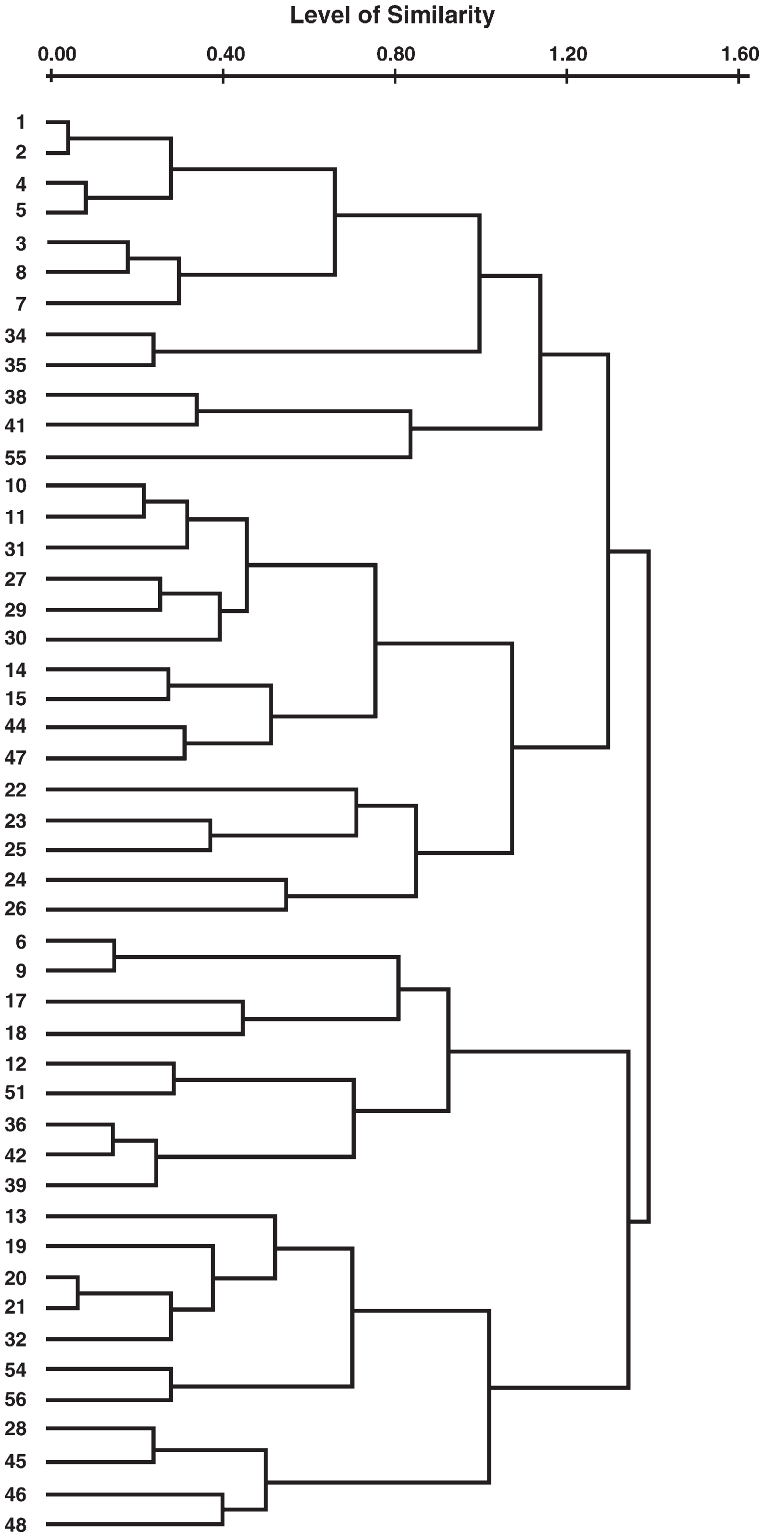

Fig. 11. Dendogram of *Q*-mode analysis. See text for discussion.

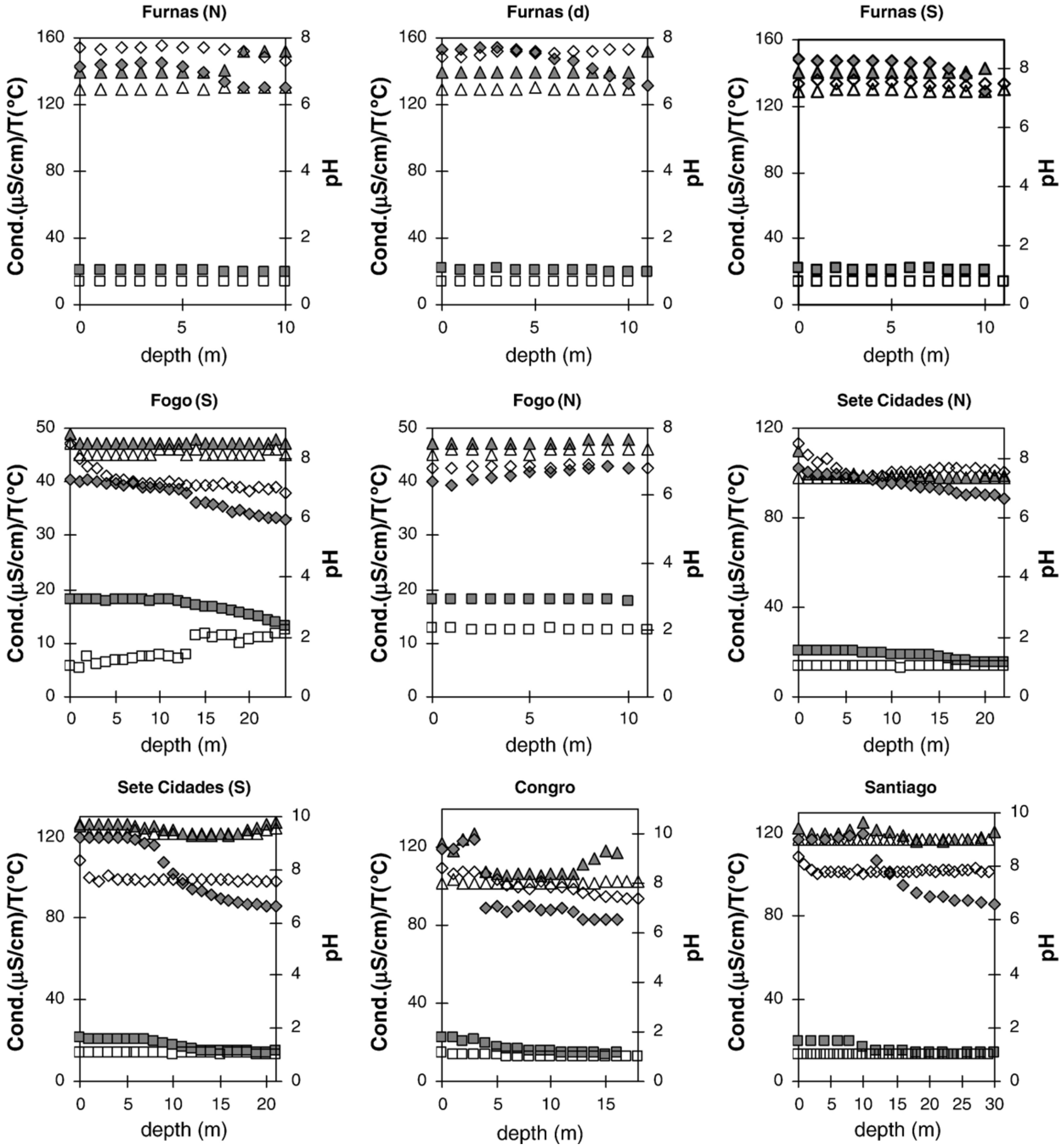

Fig. 12. Variation of pH (◇), temperature (□; in °C) and lake water electrical conductivity (Δ; in μS/cm) with depth for selected lakes in São Miguel; filled symbols — summer; open symbols — winter.

with dissolved CO_2 also suggests that, in these lakes CO_2, will be essentially derived from organic matter decomposition, which is compatible with the eutrophication process underway in numerous lakes from the Azores archipelago. The pair Na^+–SiO_2 has a closer association, suggesting the water–rock contribution to lake chemistry. Nevertheless, hydrothermal water seepage into the lakes is not excluded.

The dendogram of the Q-mode cluster analysis reveals several groups of lake waters, that are referred according to numbers in Table 2 (Fig. 11). Group 1 consists of samples #1, 2, 3, 4, 5, 7, 8, 34, 35, 41, 55 and is mainly made of samples of larger lakes in collapse calderas. This group shows a weaker relation to a second group made of 15 samples (#10, 11, 14, 15, 22, 24, 23, 25, 26, 27, 29, 30, 31, 44, 47), corresponding to Fogo lake (in a subsidence caldera), and to a set of smaller lakes, mainly located in explosive craters. All samples have a common character determined by low mineralization and the sea-salt input to the water composition.

Group 3 (#6, 9, 12, 17, 18, 36, 39, 42, 51) represents a set of lake waters that were mainly collected at the bottom of the deeper lakes, and also to Furna do Enxofre lake (#51). Therefore, this group reflects mainly total CO_2 enrichment, which may have different magnitudes (next section) and, besides the expected contribution from organic matter decomposition, could result from a volcanic source, as previously proposed for Furna do Enxofre lake (#51).

The group 4 of lake waters corresponds to samples #13, 19, 20, 21, 28, 32, 45, 46, 48, 54, 56, presenting a weak relation with the previous group. Group 4 is represented mainly by small lakes, whose waters have evolved mainly from marine contribution.

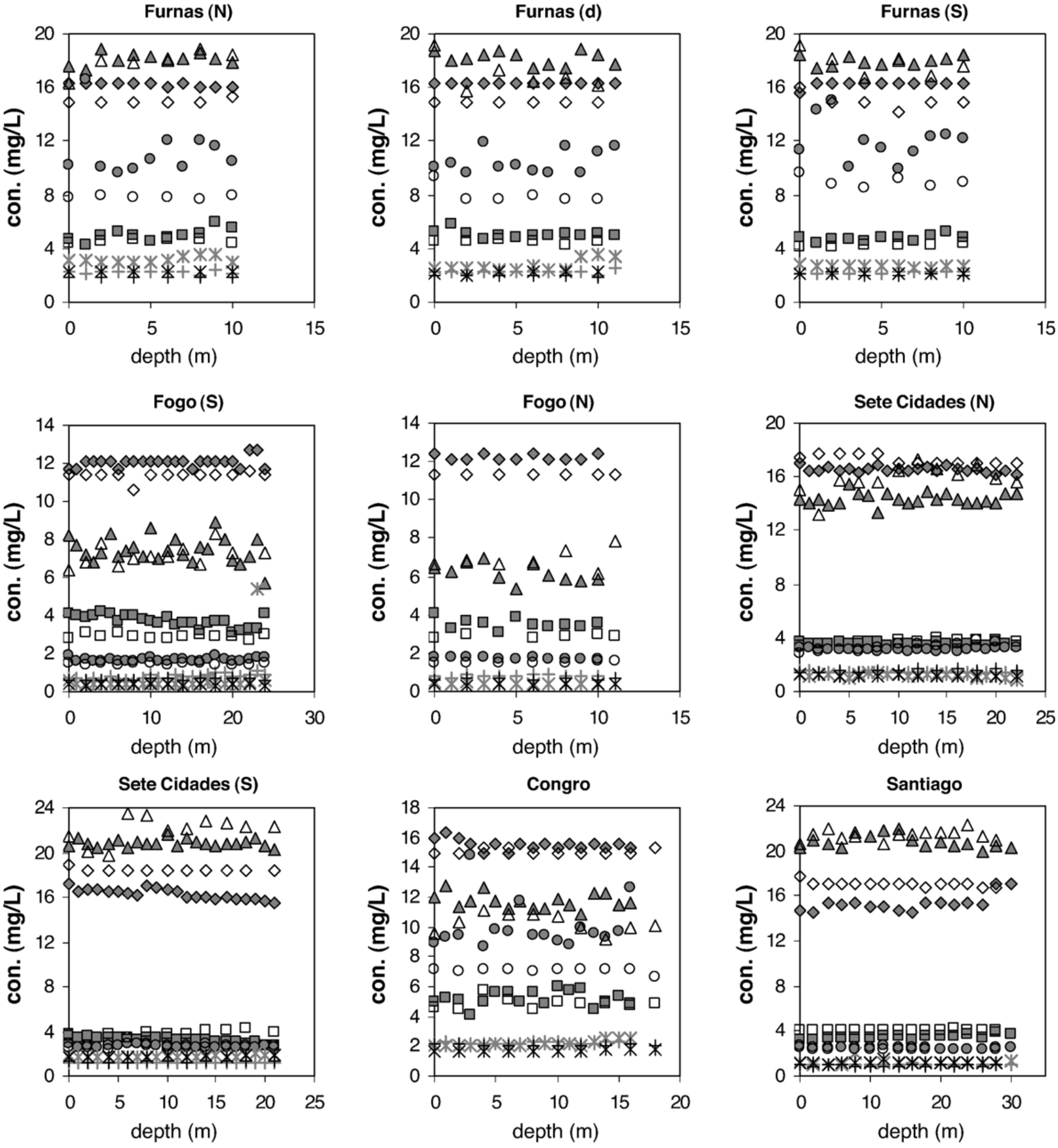

Fig. 13. Major-ion variation with depth for selected lakes in São Miguel; Cl^-(◇); SO_4^{2-} (□); Na^+ (Δ); K^+ (O); Mg^{2+} (+); Ca^{2+}(✱); filled/gray symbols — summer; open/black symbols — winter.

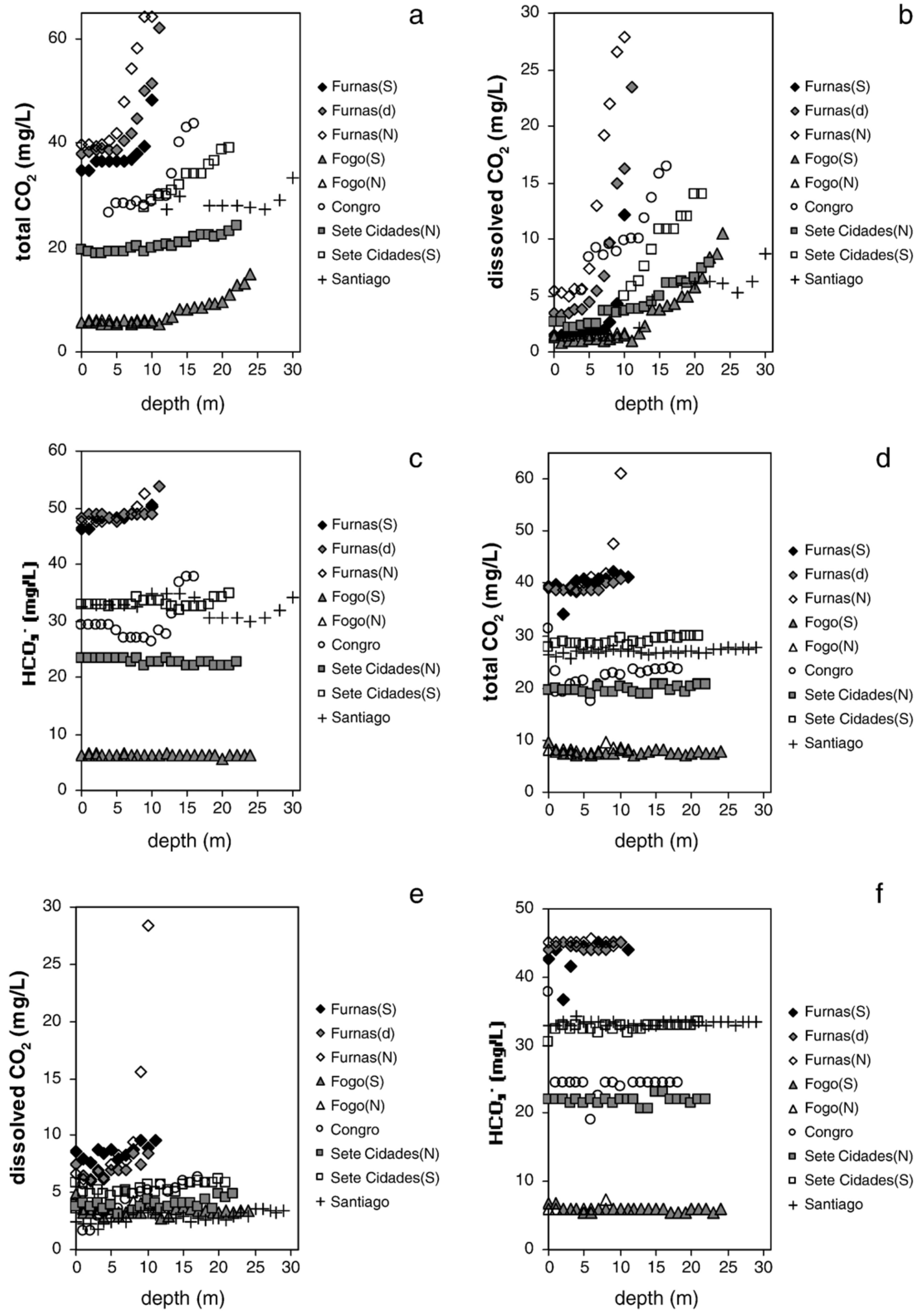

Fig. 14. Variation of total CO_2, dissolved CO_2, and HCO_3^- with depth for selected lakes in São Miguel. a, b, c — summer; d, e, f — winter.

4.4. Geochemical profiles

For selected volcanic lakes from São Miguel island, vertical profiles were measured in the summer period (early September) and in winter (January). Three profiles were made at Furnas lake, respectively, near the north margin (10 m deep), in the deepest zone (11 m deep), and at the southern margin (11 m deep), where surface hydrothermal activity occurs with discharge of thermal waters and fumaroles. Two vertical profiles were also constructed at Fogo and Sete Cidades lakes (south and north), respectively, 10 and 24 m deep, and 21 and 22 m deep. For each of the Congro and Santiago lakes, only a single profile was made because of the low-surface area of these lakes, respectively, 16 and 30 m deep.

The pH, temperature and conductivity profiles are shown in Fig. 12. Water conductivity is rather constant with depth except for the bottom levels at Furnas and Congro. The water pH exhibits a slight decrease with depth, and for depths greater than 15 m, lake waters are always acid. Significant is the thermally driven density stratification observed in summer periods at Fogo southern profile, as well as at Sete Cidades, Congro and Santiago lakes, and the difference of temperature between epilimnion and hypolimnion reaches a maximum of 6.3 °C (Congro lake) and 8.5 °C (Santiago lake). In winter, only the vertical profile made at Fogo (south) revealed water stratification, with lower temperatures near the surface (Fig. 12). Major ion and SiO_2 profiles reveal no major variations with depth in either summer or winter (Fig. 13).

In Fig. 14, total CO_2, dissolved CO_2 and HCO_3^- content are plotted as a function of lake depth. A comparison of the various plots shows that the total CO_2 increase is related to increase in dissolved CO_2 content, as HCO_3^- is relatively stable except for a slight enrichment observed at Furnas lake (>20 mg/L), Congro, Sete Cidades (south) and Santiago lake. This fact suggests that, for the majority of the lakes, CO_2 production exceeds the mechanisms of neutralising fluid acidity and converting dissolved CO_2 to HCO_3^- by water–rock interaction. This latter observation is compatible with the conductivity increases in Furnas and Congro lakes, which can be explained partly by a water–rock input, with the observable HCO_3^- enrichment a result of neutralising fluid acidity.

The CO_2 enrichment with depth in these lakes can be explained by CO_2 derived from organic matter decomposition as well as by discharge of hydrothermal waters and volcanic gases, which from the published data has a CO_2-dominated composition (Ferreira, 1994; Ferreira and Oskársson, 1999). However, because the lakes are not set in active volcanoes, where surface hydrothermal activity is observable (as thermal and mineral waters discharges and fumarolic fields), sometimes near the lake margins or in the vicinity of important tectonic lineaments, this explanation cannot preclude a volcanic input.

From a comparison of summer and winter conditions, it is possible to see that, for the winter profiles, the difference between total and dissolved CO_2 content in lake surface and bottom samples is smaller, and only for the Furnas profile (made closer to the north margin) does the CO_2 enrichment have the same magnitude as observed in the summer period. This can be explained by the fact that the lack of thermal stratification in winter enables greater water mixing along the water column, while in summer CO_2 is trapped in the hypolimnion.

5. Conclusions

Even though 88 surface lakes that are located in the Azores archipelago (Portugal), their waters only recently received attention because of their eutrophication. Therefore, studies about hydrogeochemistry of the Azores lakes and their volcanic setting are uncommon in the international literature. In this paper, we present new data for a representative group of 30 lakes to remedy this deficiency.

The majority of the studied waters are associated with lakes in craters or subsidence calderas, corresponding to fresh and very diluted waters mainly of the Na–Cl and Na–HCO_3 types. In general, these lakes are small and shallow, as the maximum depth of the lakes studied was 33 m.

Using their major-ion composition, it is possible to distinguish two major groups of lake waters, based on the processes that influenced hydrogeochemical evolution: (1) those that evolve mainly by marine contribution, due to atmospheric sea salt transport, with a relative Na–Cl composition close to seawater; and (2) those which, despite the marine contribution, were influenced by other superimposed processes as water–rock interaction and hydrothermal waters seepage. This latter process explains the relative Na^+ enrichment compared to seawater, as well as the higher SiO_2 content observed in these lakes. However, a contribution by a CO_2-dominated volatile source cannot be excluded for certain lakes, as for example Furna do Enxofre.

Total CO_2 varies in the range between 2.6 and 365.1 mg/L, with a median value equal to 13.2 mg/L. Therefore, the majority of the samples present a low-CO_2 content, compatible with an origin related with organic matter decomposition. However, certain lakes (e.g., Furna do Enxofre and Furnas lakes) have higher CO_2 contents, implying a greater volcanic contribution. The features of these lakes more closely resemble hydrothermal surface manifestations, with thermal waters and fumarole discharges.

Vertical profiles made for São Miguel lakes revealed the influence of thermal stratification, as CO_2 content corresponds to a large extent to effects of temperature-driven circulation. An illustrative example is Furnas lake, where in the summer dissolved CO_2 is retained in the hypolimnion, while in winter—without stratification but with a mixing regime—enrichment in dissolved CO_2 content in the lake bottom is less sharp. In this lake, dissolved CO_2 enrichment is not balanced by processes that neutralise fluid acidity and produce HCO_3^-, for example, silicate-mineral dissolution is essentially constant along the water column. Our results emphasize the opportunity to include lake-water geochemistry as another diagnostic tool for the geochemical surveillance studies that are presently in development for volcanoes in the Azores archipelago.

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