Water chemistry of Lake Albano (Italy)

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Abstract

Lake Albano was stratified at the time of our survey, in December 1997, in agreement with previous observations [Martini et al., Geochem. J. 28 (1994) 173–184; Cioni et al., Report for the Civil Protection Department (1995); Pedreschi, Accad. Lucch. Sci. Lett. Arti (1995) 39]. In the absence of phenomena induced by seismic activity, either local or regional, lake stratification may be perturbed by cooling of shallow waters below $\sim 8.5°C$. Circulation is expected to homogenize lake waters and eventually to trigger gas exsolution when total gas pressure exceeds hydrostatic pressure. In December 1997, total gas pressure in lake water was very close to atmospheric pressure (0.9–1.3 bar) at all depths, possibly due to the occurrence of a recent episode of circulation and presumed gas exsolution. The state of saturation of Lake Albano waters and the similarity of the relative concentrations of Na, K, Mg, and Ca in lake waters, local groundwaters, and local volcanic rocks indicate that Na, K, Mg, and Ca concentrations in Lake Albano waters are mainly governed by incongruent dissolution of local volcanic rocks, coupled with minor calcite precipitation at shallow depths.
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1. Introduction

In active volcanoes, the interaction between water masses contained in crater lakes and rising magmas may bring about high-energy hydrovolcanic eruptions, such as base surges (e.g., Taal volcano, Philippines) and debris flows (e.g., Kelut volcano, Indonesia). These events have killed many people in the last 500 years (e.g., Delmelle and Bernard, 2000; Rodolfo, 2000).

In non-active volcanoes, deep waters of crater lakes may accumulate gases rich in CO_2 and other carbon components, mainly CH_4. If these gas-rich deep waters are shifted towards the surface by an external cause (e.g., earthquakes, landslides, cold rains, strong winds) catastrophic gas exsolution occurs. Events of this kind, known as limnic eruptions (Sabroux et al., 1987), occurred in the 1980s from the Cameroonian Lakes Nyos and Monoun, causing ~ 1800 casualties (Sigurdsson et al., 1987; Giggenbach, 1990 and references therein).

In Italy, gas accumulation takes place in the deep waters of Lake Piccolo of Monticchio, Vulture volcano (Chiodini et al., 1997, 2000a). In principle, gas accumulation could also occur in

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Lake Albano, which, with a surface area of ~ 5.70 km^2, is the major lake of the Alban Hills volcano. Lake Albano is located in a roughly elliptical depression with a 3.5-km-long NW-trending major axis and a 2.2-km-long minor axis. It is a relatively deep (maximum depth of ~ 175 m), funnel-shaped volcanic lake and its walls are very steep, except on the northwestern side. Water level cannot rise above 293 m a.s.l., due to the presence of an artificial drain excavated by the Romans in the 4th century B.C. Its construction was probably decided as in 390 B.C. "water flooded out of the lake, ... not because of rainfall or of any other natural reason", as reported by Titus Livius in *Ab Urbe Condita Libri CXLII*. This decision was evidently taken since the lake is located at ~ 20 km SE of Rome.

The Alban Hills region is characterized by high CO_2 fluxes and sudden episodes of gas release, and is frequently affected by seismic activity (see below). In principle, the high gas fluxes as well as lake morphology and bathymetry could favor gas accumulation in the deep waters of Lake Albano, whereas seismic activity could trigger gas discharge.

The waters of Lake Albano were studied by Martini et al. (1994), who reported a comparatively high CO_2 concentration, 222 mg/kg, in deep lake waters and unusual cation concentrations in both surface waters and deep waters, with K > Na on a weight basis. To investigate this rather atypical water chemistry and to gather data on other dissolved gases, we carried out a survey of lake waters in December 1997. The purpose of this paper is to present and discuss available geochemical data and to assess the risk of gas accumulation in the deep waters of Lake Albano.

2. Geology, hydrogeology, and seismicity

The most prominent features of the Alban Hills volcano (Fig. 1) are the Tuscolano-Artemisio and the Faete (or Campi di Annibale) edifices (De Rita et al., 1995). The activity of the Tuscolano-Artemisio edifice occurred from 600 to 300 ka, consisted of the eruption of several ignimbrites and subordinate lava flows, and ended with the collapse of the Tuscolano-Artemisio caldera. Inside this collapsed area, the Faete edifice was built from 300 to 200 ka. It was characterized by prevailing strombolian eruptions and by large extrusions during its late period. Again, the activity of the Faete edifice terminated with a summit caldera collapse. The most recent volcanic activity occurred from 200 ka to 20 ka and consisted of violent hydromagmatic eruptions from several craters in the western and subordinate northern sectors of the Alban Hills volcano. All these craters are tuff rings and erupted wet and dry surges and lahars. In particular, the Albano volcano-tectonic structure is made up of at least five coalescent craters, located along NW–SE regional fractures.

The products of the Alban Hills volcano are low in SiO_2, 42–50 wt%, very rich in K_2O, 5.5–10%, relatively high in CaO, 9–12%, and comparatively low in MgO, 3.5–7% (Trigila et al., 1995). Most rock types can be classified as K-foidites, phonotephrites, and tephrites based on the total alkali–silica diagram (Le Bas et al., 1986). The mineralogy of these volcanic products consists of phenocrysts of clinopyroxene and leucite in a groundmass of the same phases, plus magnetite and less common nepheline–kalsilite, melilite, olivine, phlogopite, calcite and sanidine.

According to Boni et al. (1995), three hydrogeologic units are present in the Alban Hills region. The volcanic products host a multilayered aquifer flowing outwards, i.e., towards the periphery of the volcano. In particular, the Lake Albano basin is fed by a westward-flowing perched aquifer extending to the interior of the Tuscolano-Artemisio caldera. Volcanic rocks are separated from the underlying basal complex by clays and marls of Plio–Pleistocene age. These are expected to act as an aquiclude, at least where they are sufficiently thick and continuous. The heterogeneous Meso–Cenozoic basal complex hosts several aquifers, mainly in fractured limestones and dolomites, separated by impervious clay layers.

Most of the information on local seismicity was provided by the study of the seismic swarm of April 1989–March 1990 (Amato et al., 1994; Amato and Chiarabba, 1995). Out of the over 3000 earthquakes detected, 1156 events were lo-
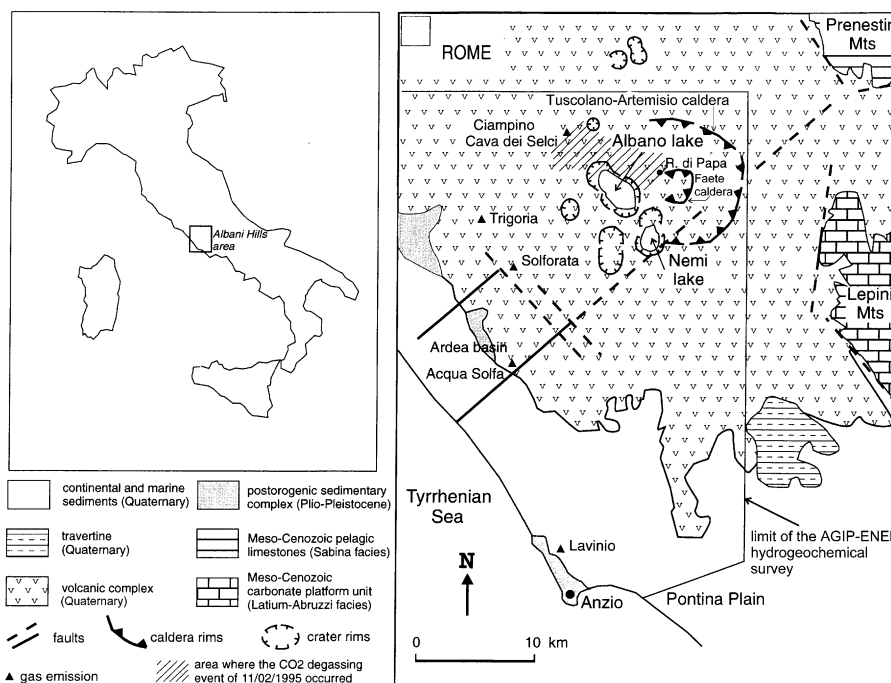
Fig. 1. Simplified geological map of the Alban Hills volcano.

cated. They have M_{max} of 4.2–4.5 and are mostly found within the area where recent hydromagmatic activity took place, whereas the eastern sector of the Tuscolano-Artemisio caldera was found to be aseismic (Fig. 2). Hypocenters are grouped in two clusters. The first cluster, north of Lake Albano, is located at depths of 3–5 km, whereas the second cluster, between lakes Nemi and Albano, is found at depths of 4–6 km. Based on the frequency content of recorded waveform, the 1989–90 sequence was probably dominated by tectonic-like events. However, seismicity was probably triggered by increased pore pressure.

3. Carbon dioxide degassing from the Alban Hills region

This matter was recently investigated by Chiodini and Frondini (2001). In several zones of the Alban Hills region, such as Lavinio, Acqua Solfa-Ardea, Solforata, Trigoria, and Cava dei Selci-Ciampino (Fig. 1), large amounts of CO_2-rich gases of deep provenance are discharged from

soil. The CO_2 output from two of these areas, Cava dei Selci and Solforata, amounts to 6.1×10^8 mol/yr. This high gas output poses a risk for the life of human beings and animals, which should be taken seriously. The last lethal accidents occurred in October 1999 and in March 2000 when 30 cows and five sheep, respectively, died at Cava dei Selci.

Groundwaters rich in CO_2 are present in several localities, especially in the northern and western sectors of the Alban Hills region. They usually cluster in areas of positive gravity anomalies, which reflect the presence of structural highs of the carbonate basal complex, covered by impervious clays and marls. These structures act as buried traps for the CO_2 of deep provenance, as testified by the Torre Alfina geothermal field (Barelli et al., 1978; Chiodini, 1998). Based on the CO_2 distribution in groundwaters and the water flux discharging from the volcanic aquifer, Chiodini and Frondini (2001) computed a total output of deep CO_2 from the Alban Hills (surface area 1516 km^2) of 4.2×10^9 mol/yr. According to Chiodini and Frondini (2001), this figure, which
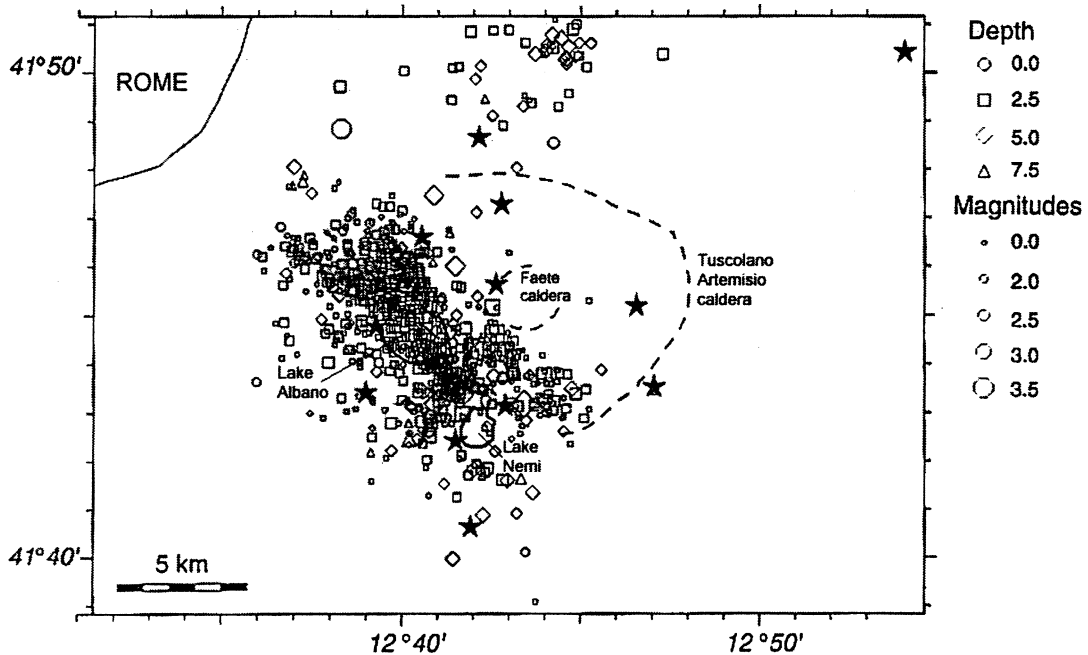
Fig. 2. Epicentral distribution of the events recorded during the 1989–1990 seismic swarm in the Alban Hills volcano. Stars indicate local seismic stations (after Amato et al., 1994).

includes the CO_2 directly released from Cava dei Selci and Solforata, underestimates the real CO_2 output for two reasons: (1) not all the gases of deep provenance accumulate in groundwaters and (2) the contribution of direct gas discharges from soil is underestimated. The corresponding CO_2 flux, 2.8×10^6 mol/km²/yr, is within the range of the flux calculated for the carbonate aquifers of central Italy, 9.0×10^3–9.3×10^6 mol/km²/yr (Chiodini et al., 2000b), and is ca. three times greater than the baseline value from areas of high heat flow (Kerrick et al., 1995).

A sudden release of CO_2-rich gases from the soil and shallow water wells occurred on November 2, 1995 in the ~10-km-long area between Ciampino and Rocca di Papa (Chiodini and Frondini, 2001, and references therein). This densely inhabited area is very close to Lake Albano (Fig. 1), but it seems that the November 2, 1995 event did not affect lake waters, as suggested by the vertical profiles of temperature, dissolved O_2, pH, p_{CO2}, and electrical conductivity (EC) measured 2 days after the gas release episode (Cioni et al., 1995). The area impacted by this

event partly coincides with the zone affected by the April 1989–March 1990 seismic swarm (Fig. 2), although available data are insufficient to establish the possible relationship between the seismic phenomena and the degassing event. Similar gas emissions took place in this same area in the past, as documented by historic chronicles (Funiciello et al., 1992; Voltaggio and Barbieri, 1995).

4. Field and laboratory work

In December 1997, lake waters were surveyed for temperature, dissolved O_2, pH and EC along a vertical profile. Then water samples were collected at 10, 30, 50, 70, 90, 110, and 130 m depth for chemical analysis of the main components, some trace elements, and dissolved gases.

Physico-chemical parameters were measured twice along the vertical profile, downward and upward, by means of OCEAN SEVEN 401 manufactured by Idronaut, Italy. This instrument is made up of a multi-sensor probe connected to a portable computer. The probe holds the sensors

for the determination of pressure (depth) and physico-chemical parameters. A microprocessor, built into the probe, carries out the electronic scanning of the parameters every 29 ms, transforms the analog signals into digital signals and transmits them to the computer through a mono-conductor cable. The nominal precisions are as follows: pressure ~ 5 mbar, i.e., 0.05 m in depth; temperature $\sim 0.02°C$; $O_2 \sim 6.3$ μmol/l; pH ~ 0.05 pH units; EC ~ 20 mS/cm.

For water sampling, a polyethylene pipe was lowered to the chosen depth maintaining its submerged end very close to the temperature-O_2-pH-EC sensors. Water was pumped to the surface by means of a manual vacuum pump. Samples were collected after displacement of a water volume at least twice the inner volume of the pipe. Raw, filtered (0.45 μm) and filtered–acidified (with HCl 1:1) samples were collected and stored in polyethylene bottles. Total alkalinity was measured immediately by acidimetric titration. Total H_2S was also determined in the field by means of the methylene blue colorimetric method.

Lake waters were also collected in evacuated bottles equipped with a three-way valve, to determine the concentrations of dissolved gases. Each bottle was connected to the surface end of the polyethylene pipe. A reservoir and a manual vacuum pump were fitted downstream of the bottle. First the pipe was flushed with lake water, accumulating it in the reservoir; then lake water was allowed to enter the sampling bottle and fill about four-fifths of it. Since no gas bubbles were observed in the pipe upstream of the bottle, samples can be considered to be fully representative of lake waters.

In the IGG-CNR laboratory, water samples were analyzed as follows: (1) Li, Na, K, Mg, Ca, Fe, Mn by AAS and/or AES; (2) Cl, SO_4, NO_3 by ion chromatography; (3) B, SiO_2 by visible spectrophotometry.

In addition, the partial pressures of CO_2, CH_4, N_2, O_2, and Ar were determined, at the Osservatorio Vesuviano-INGV laboratory, by gas chromatography (GC) in the headspace gas of the bottles equipped with a three-way valve. Each bottle was weighed before and after sampling to determine the amount of water sampled. The head

space gas volume, at known pressure and temperature conditions (pressure is measured by means of a high-precision manometer at the GC inlet), was obtained by difference between the volume of the bottle and the volume of sampled water. The molal concentrations of CO_2, CH_4, N_2, O_2, and Ar in water were obtained through simple mass balance calculations, assuming equilibrium partitioning between the headspace gas and the aqueous solution (gas solubilities from Wilhelm et al., 1977). See Cioni et al. (1998) and Chiodini (1998) for further details.

Analytical results are reported in Table 1. Concentrations of B (< 0.1 mg/kg), NO_3 (< 0.1 mg/kg), and Li (≤ 0.01 mg/kg) are not reported.

5. Vertical distribution of physical and chemical parameters in Lake Albano

The vertical profile of dissolved O_2 indicates that Lake Albano is made up of: (1) the oxic epilimnion, from the surface to a depth of ~ 25 m, (2) a rather thick thermocline (also known as the metalimnetic zone); and (3) the anoxic hypolimnion extending from ~ 55 m depth to lake bottom (Fig. 3a). The epilimnion has rather constant temperature ($\sim 14°C$) and pH (~ 8.5), whereas in the hypolimnion temperature and pH decrease with increasing depth from 9.6 to 8.9°C and from 7.2 to 6.6 pH units, respectively (Fig. 3b,c).

These temperatures of deep lake waters compare with the 9°C measured at 140–160 m by Martini et al. (1994) and with the temperatures recorded in the hypolimnion on November 4, 1995 (Cioni et al., 1995), 2 days after the gas release episode (see above). According to Pedreschi (1995) shallow waters exhibit marked temperature oscillations, whereas bottom waters have temperatures ranging between 7.0 and 8.5°C, suggesting an appreciable thermal stratification. Although these data are somewhat lower than other measurements, the conclusions of Pedreschi (1995) are certainly right.

Concentrations of Na, K, Mg, and Cl remain constant, within analytical uncertainties, at any depth, SO_4 concentration decreases with depth,

Table 1
Chemical data of Lake Albano waters in December 1997

Depth	Temperature	EC	pH	Ca	Mg	Na	Na*	K	Alkalinity	SO_4	Cl	SiO_2	Charge balance	TDS	CH_4	CO_2	N_2	Ar	O_2	H_2S
m	°C	mS/cm		mg/l	mg/l	mg/l	mg/l	mg/l	mg HCO_3/l	mg/l	mg/l	mg/l	%	mg/l	μmol/l	μmol/l	μmol/l	μmol/l	μmol/l	μmol/l
−10	14.1	363	8.49	22.4	16.5	31.7	21.4	48.1	268	7.2	18.5	0.5	+0.1	448	0.51	144	667	16.9	268	0
−30	10.8	352	7.71	26.7	16.5	31.5	21.2	47.5	282	7.1	18.5	1.0	−0.2	475	4.84	335	762	19.5	230	0
−50	9.8	352	7.37	30.1	16.7	31.5	21.2	48.1	296	6.9	18.5	1.5	−0.4	491	4.08	373	768	19.3	94	0
−70	9.2	375	6.86	38.5	16.8	32.0	21.7	48.8	320	5.8	18.5	4.0	+0.4	564	180	1230	774	19.5	0	18
−90	9.0	386	6.64	41.4	16.7	31.5	21.3	48.2	334	4.8	18.3	5.4	−0.4	624	397	2120	782	19.7	0	35
−110	8.9	386	6.59	42.0	16.8	31.0	20.9	47.7	339	4.4	18.2	5.6	−0.9	647	499	2570	726	18.6	0	35
−130	9.0	382	6.58	42.3	16.7	31.6	21.5	48.1	345	3.8	18.0	6.2	−1.2	706	741	3660	726	18.5	0	26

Temperature, EC, pH, and O_2 were obtained by the multi-sensor probe. Na* indicates the difference between analytical Na and Na contributed by meteoric recharge.

whereas concentrations of Ca, HCO_3, and SiO_2 increase with depth (Fig. 3d–f). Iron and Mn concentrations also increase with depth (Table 1). All lake waters have $HCO_3 > Cl > SO_4$ (in equivalent units), whereas cation composition (in equivalent units) changes from $Na > Mg > K > Ca$ near the surface to $Ca > Mg = Na > K$ at deep levels. Changes in SO_4 content are likely due to bacteria-mediated sulfate reduction in the anoxic hypolimnion, whereas other chemical changes are discussed below.

6. Gas chemistry

The vertical distributions of molal concentrations and partial pressures of CO_2, CH_4, N_2, O_2, and Ar are plotted in Fig. 4a,b. In terms of molal concentrations, N_2 is the dominant constituent in shallow lake waters whereas CO_2 prevails below 70 m depth. Oxygen is the second major component at the shallow depths (< 20 m), whereas it is virtually 'absent' in deep lake waters (70–130 m depth), where log m_{O2} is -69.1 to -70.7 based on the HS^-/SO_4^{2-} redox couple, or -33.2 to -39.2 based on $Fe(OH)_{3(s)}/Fe^{2+}$ equilibrium, as indicated by speciation calculations carried out by means of the EQ3NR software code (Wolery, 1992). Carbon dioxide and CH_4 increase with depth by one and three orders of magnitude, respectively. Nitrogen and Ar experience, instead, negligible changes with depth and the p_{N2}/p_{Ar} ratio is very close to the atmospheric value, 84, at all depths.

In terms of partial pressures, N_2 is the dominant constituent at any depth, whereas the second major component is O_2 in shallow waters and CH_4 in deep waters. These gases are the main contributors to total gas pressures due to their low solubilities in water. In contrast, the contribution of CO_2 to total gas pressures is subordinate even though it is the major constituent in deep lake waters on a concentration basis. Total gas pressure, obtained by summing the partial pressures of each gas component, ranges between 0.9 and 1.3 bar and is always lower than hydrostatic pressures at any depth above 130 m (Fig. 4c). Therefore, gas exsolution cannot take place
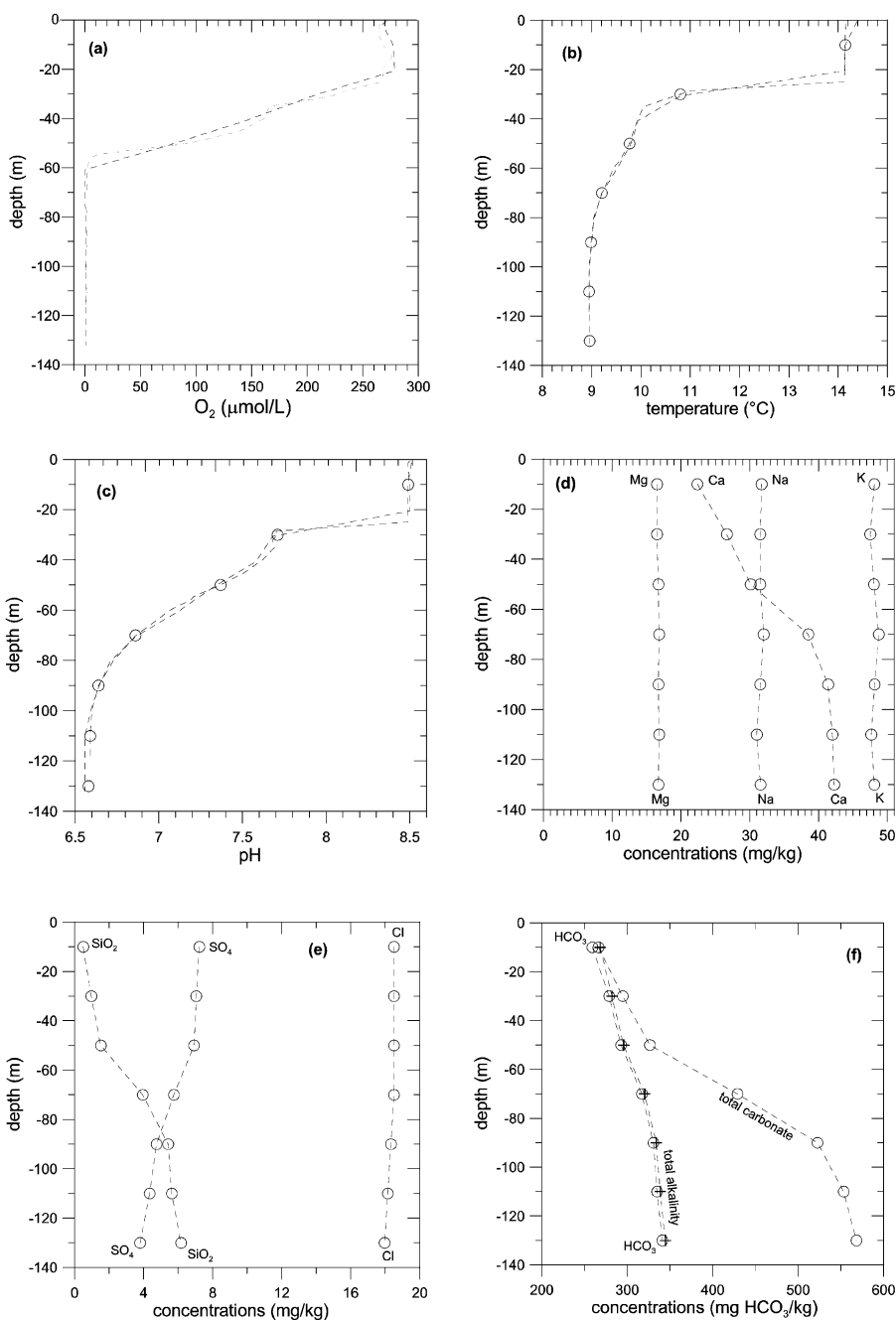
Fig. 3. Vertical profiles of (a) dissolved O_2, (b) temperature, (c) pH, (d) Na, K, Mg, and Ca, (e) SO_4, Cl, and SiO_2, (f) total alkalinity, HCO_3, and total carbonate in Lake Albano waters in December 1997.

from Lake Albano waters, at least above 130 m. The only information available below this depth is related to the sample collected by Martini et al. (1994) at 160 m depth, whose measured CO_2 concentration is 5.05 mmol/kg, corresponding to a p_{CO2} of 0.098 bar. Interestingly, these values lie along the prolongation of the CO_2 profiles in Fig. 4a,b. Estimated p_{CH4} and p_{N2} at 160 m depth,
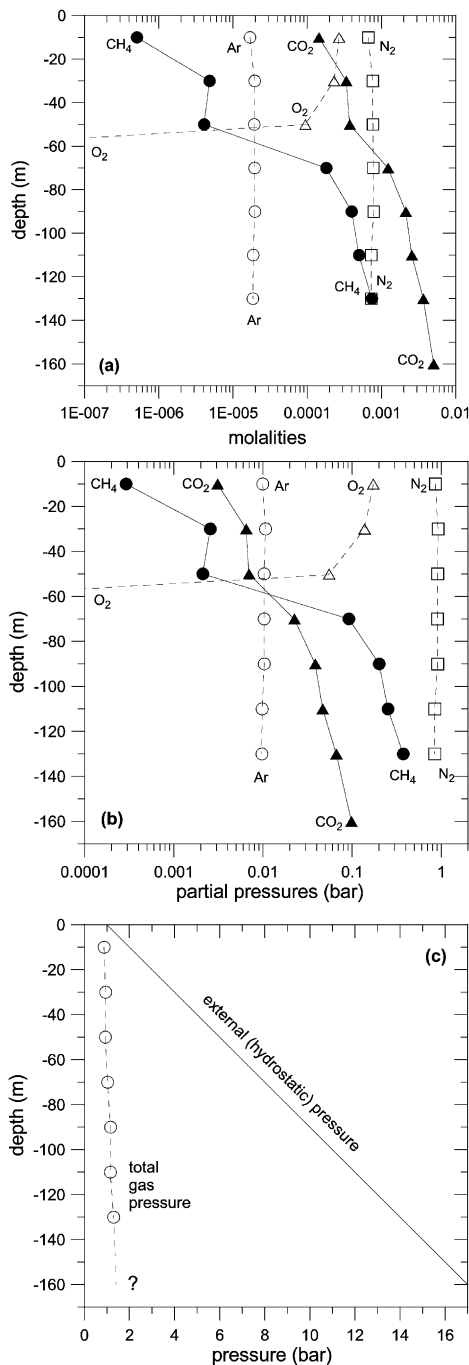
Fig. 4. Vertical profiles of (a) molal concentrations of CO_2, CH_4, N_2, O_2, and Ar, (b) partial pressures of the same gas constituents and (c) total gas pressure in Lake Albano waters in December 1997. The concentration and partial pressure of CO_2 at 160 m depth are from Martini et al. (1994). Total gas pressure at 160 m depth was estimated as explained in the text.
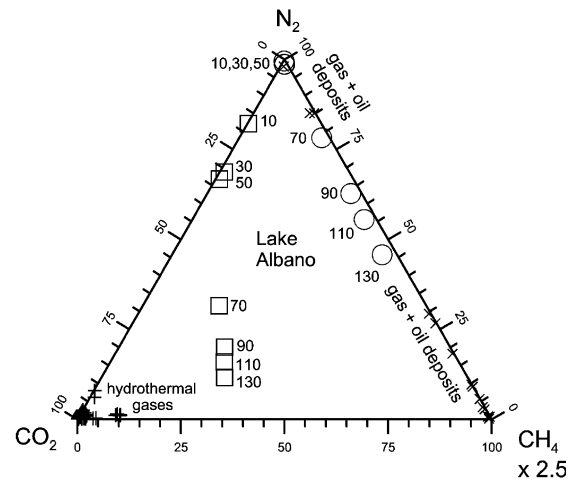

Fig. 5. Relative partial pressures (circles labelled by depth) and relative molal concentrations (squares labelled by depth) of CH_4, CO_2, and N_2 in Lake Albano waters. Relative partial pressures of CH_4, CO_2, and N_2 in natural gases from gas and oil deposits (×, from Sokolov, 1974) and hydrothermal gases (+, from Chiodini and Marini, 1998) are shown for reference.

obtained by extrapolation of the corresponding profiles, are 0.5 and 0.85 bar, respectively, and total gas pressure is 1.4 bar (Fig. 4c). Consequently, gas exsolution seems unlikely at 160 m depth as well. Incidentally, the concentrations of dissolved CO_2 (see above) and HCO_3, 262 mg/kg, reported by Martini et al. (1994) constrain the pH at 6.32, in agreement with our data, but in contrast with the pH value reported by Martini et al. (1994), 5.55.

The incremental increases in CO_2 and CH_4 with depth indicate that they are largely produced through decomposition of organic matter under anoxic conditions in sediments, followed by upward diffusion in overlying waters. The organic origin of C gases of Lake Albano is corroborated by Fig. 5, where both relative partial pressures and relative molal concentrations of CH_4, CO_2, and N_2 in Lake Albano waters are compared with relative partial pressures of the same constituents in gases from gas and oil deposits (from Sokolov, 1974) and in hydrothermal gases (from Chiodini and Marini, 1998). In terms of partial pressures, Lake Albano is similar to the N_2-CH_4-rich gases from gas and oil deposits and to-

tally different from the CO_2-rich hydrothermal gases. Assuming that a gas phase enters the lake from below and that gas species are completely dissolved and are not involved in aqueous speciation reactions, molal concentrations of lake waters are expected to represent the composition of the source gas instead of partial pressures. Since relative molalities of CH_4, CO_2, and N_2 in Lake Albano waters are intermediate between those of hydrothermal gases and of gases from gas and oil deposits, neither of these two sources alone explains the composition of Lake Albano gases. In other words, admitting input in the lake of hydrothermal CO_2-rich gases from below, decomposition of organic matter has to be invoked to explain the shift towards high CH_4/CO_2 molal ratios, with respect to the hypothetical hydrothermal source.

In anaerobic sediments organic matter is converted to CH_4 and CO_2 in two steps (Wetzel, 1983). In the first step, proteins, carbohydrates, and fats are converted mainly into fatty acids by acid-forming bacteria, which are facultatively and obligately anaerobic. In the second step, the organic acids (e.g., acetic acid) are converted to CH_4 and CO_2 by CH_4-producing bacteria, which are strictly anaerobic. Generally, CH_4 is mainly produced via the intermediate acetic acid in lake sediments (Phelps and Zeikus, 1984; Kuivila et al., 1989):

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (1)$$

whereas the remainder of CH_4 is produced through CO_2 reduction, by enzymatic addition of hydrogen derived from the organic acids:

$$CO_2 + 8H \rightarrow CH_4 + 2H_2O \qquad (2)$$
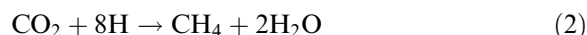
This second reaction is the primary pathway for CH_4 formation in marine sediments (Crill and Martens, 1986; Hoehler et al., 1994).

In Lake Albano sediments, CH_4 production could be sustained not only by settling organic matter but also by external CO_2 coming from below (see above), chiefly along the main tectonic structures present in the lake area. If the flux of external CO_2 is higher than the amount of CO_2 consumed by CH_4-producing bacteria in lake sediments, excess CO_2 could even accumulate in

sediments and deep lake waters. This possibility can neither be confirmed nor rejected on the basis of available data.

Assuming that the concentrations of SO_4^{2-}, NO_3^-, and NO_2^- in interstitial waters are very low relative to the total concentration of inorganic C carbon species, which is a reasonable hypothesis on the basis of the concentrations of these constituents in lake waters, it seems likely that these alternative electron acceptors do not inhibit methanogenesis. Besides some sulfate-reducing bacteria and the methanogens can coexist. The CH_4 and CO_2 released from the sediments diffuse upward into the overlying hypolimnetic waters of Lake Albano. Consequently, CH_4 is oxidized to CO_2, mostly in the metalimnetic water by CH_4-oxidizing bacteria, which are strict aerobes although they tolerate microaerobic conditions.

Since the diffusion coefficients of CH_4 and CO_2 differ only by 2–4% between 5 and 15°C (Jähne et al., 1987), the ratio between the fluxes of these two gases is approximately equal to the ratio between their concentration gradients, in accordance with Fick's first law. Hence the CO_2 flux through the hypolimnion is ∼4.3 times greater than the CH_4 flux (40.5 μmol/l/m versus 9.35 μmol/l/m, respectively).

7. Density distribution

At a given temperature, the density of an aqueous solution, ρ_s (g/cm³), is related to the density of pure water, ρ_w, by the following equation (Giggenbach, 1990, modified):

$$\rho_s = \frac{1000 + \sum C_i}{\dfrac{1000}{\rho_w} + \dfrac{\sum C_i \cdot V_i}{MW_i}} \qquad (3)$$

where V_i is the conventional partial molal volume of the i-th solute in cm³/mol, C_i is its concentration in g/kg and MW_i is its molecular weight. Conventional partial molal volumes are given by Shock and Helgeson (1988) for the ionic solutes introduced in Eq. 3 (Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, SO_4^{2-}, and Cl^-), by Shock et al. (1989)
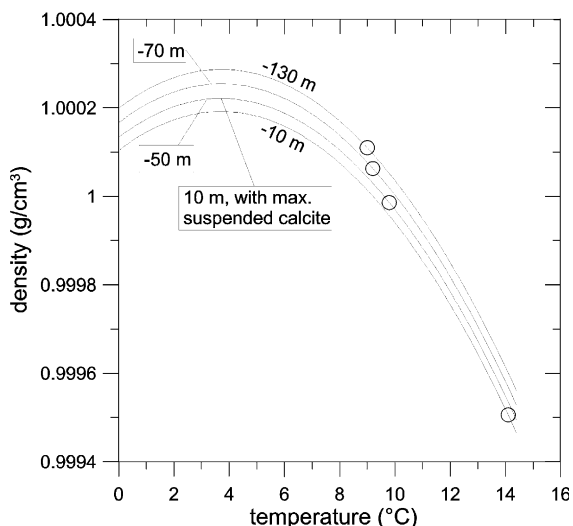
Fig. 6. Density–temperature plot for Lake Albano waters. Curves outline expected density changes with temperature at different depths assuming constant chemical composition. Circles refer to densities and temperatures in December 1997.

for dissolved inorganic neutral species (CO_2, N_2, O_2, and SiO_2), and by Shock and Helgeson (1990) for CH_4.

Computed densities of the aqueous solutions sampled at 10, 50, 70, and 130 m at different temperatures are shown in Fig. 6. The corresponding curves of other samples plot in between and are not reported since they would clutter the diagram unnecessarily. Circles refer to densities and temperatures in December 1997 when we surveyed the lake. At that time, Lake Albano was stratified. However, densities of epilimnetic waters may increase and get close to those of hypolimnetic waters when cooled to temperatures of ∼7°C or lower.

The temperature decrease needed to overturn lake waters might be even smaller considering that suspended solid particles, such as calcite in shallow epilimnetic waters (only the sample collected at 10 m depth is oversaturated with calcite, see below), turbidity introduced by runoff, and dry dust deposition might increase the density of epilimnetic waters. In particular, the effect of suspended calcite particles can be evaluated by means of the following equation (Aguilera et al., 2000):

$$\rho_s = \frac{1000 + \sum C_i + n_{CaCO_3} \cdot MW_{CaCO_3}}{\dfrac{1000}{\rho_w} + \dfrac{\sum C_i \cdot V_i}{MW_i} + n_{CaCO_3} \cdot V_{CaCO_3}} \qquad (4)$$

where n_{CaCO3}, MW_{CaCO3}, and V_{CaCO3} represent the moles of precipitated calcite, its molecular weight and its molar volume, respectively. n_{CaCO3} is taken equal to the difference between the Ca concentration in the hypolimnion and that in the epilimnetic water. Eq. 4 assumes that all Ca lost from a given volume of epilimnetic water remains there as suspended calcite. This assumption is fulfilled if the settling rate of calcite particles is equal to the diffusion rate of Ca across the metalimnion. If the settling rate is greater than the Ca diffusion rate, computed densities represent maximum values. The density-temperature curve computed through Eq. 4 for the 10 m sample is superimposed onto that obtained through Eq. 3 for the 50 m water. Therefore, the density of shallow water approaches that of deep waters through cooling at temperatures of ∼8.5°C. The occurrence of this event, which is possible during cold winter periods, could trigger circulation of lake waters and degassing.

8. Processes governing the chemistry of Lake Albano waters

8.1. Na, K, Mg and Ca

Relative concentrations of dissolved Na, K, Mg, and Ca in lake waters are compared with the compositions of local groundwaters and of local K-rich rocks in the triangular plots of Fig. 7. Groundwater data are available in the GEOCH data bank (Principe et al., 1994) and refer to 293 shallow wells and 63 springs surveyed in 1981 by AGIP-ENEL for assessing the geothermal potential of the Alban Hills region. Data of volcanic rocks, mostly K-foidites, phonotephrites, and tephrites, are taken from Trigila et al. (1995).

The triangular plot Ca–Mg–K (Fig. 7a) shows a good correspondence between deep lake waters and rock compositions, whereas shallow lake waters are slightly depleted in Ca, due to calcite precipitation (see below). In this plot ground-

waters interacting with volcanic rocks have relative cation concentrations similar to those of volcanic rocks whereas groundwaters hosted in the clayey–marly complex have lower relative K contents.

The triangular plot Ca–Na–K (Fig. 7b) shows that both lake waters and groundwaters of the volcanic cover are significantly enriched in Na with respect to local rocks, possibly because a large fraction of dissolved Na is contributed by rains. To investigate this possibility, the amount of Na present in the meteoric recharge was subtracted from the analytical concentration of Na, C_{Na}, for both lake waters and groundwaters, by means of the following equation:

$$C_{Na}^{*} = C_{Na} - \frac{C_{Na,SW}}{C_{Cl,SW}} \cdot C_{Cl} \qquad (5)$$

where $C_{Na,SW}$ and $C_{Cl,SW}$ are the average seawater concentrations of sodium and chloride, respectively (Berner and Berner, 1996). In the absence of chemical data on local precipitations, use of Eq. 5 appears reasonable since rainwaters of marine origin occurring in near-coastal regions, like the area of Lake Albano which is located at ~ 22 km distance from the sea, have Na/Cl ratios very close to the seawater value (Appelo and Postma, 1996; Berner and Berner, 1996).

Because of this correction lake waters and groundwaters in volcanic rocks are shifted towards the field of rock compositions and partly overlap it in the triangular plot Ca–Na–K of Fig. 7c. However, they still appear to be somewhat enriched in Na relative to local rocks, possibly due to (a) insufficient correction for the Na contributed by the meteoric recharge, (b) preferential leaching of Na with respect to other cations during water–rock interaction, or (c) preferential in-
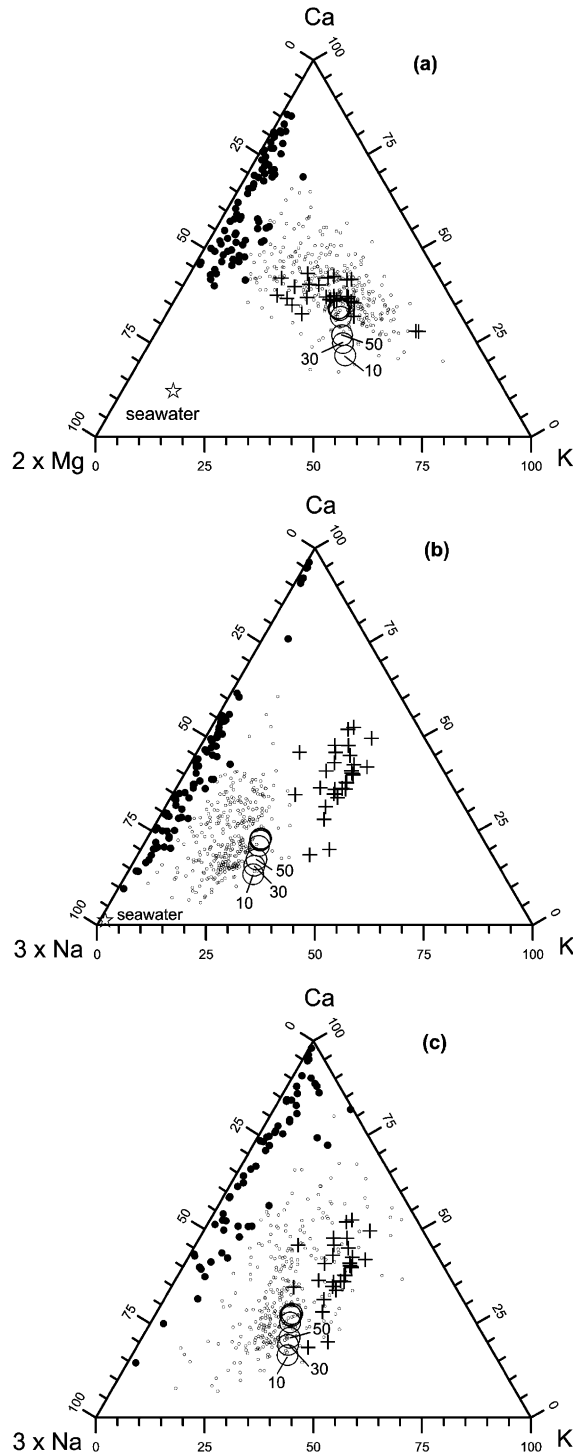

Fig. 7. Relative concentrations of (a) Ca, Mg, and K and (b,c) Ca, Na, and K in Lake Albano waters (large open circles labelled by depth), groundwaters interacting with volcanic rocks (small open circles), groundwaters hosted in the clayey–marly complex (closed circles) and volcanic rocks of the Alban Hills region (crosses). In panel c meteoric contribution has been subtracted from the analytical concentration of Na as described in the text.
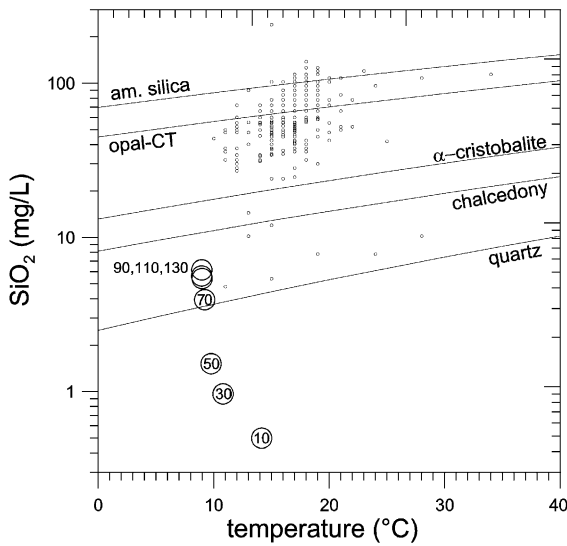
Fig. 8. Plot of SiO_2 vs. temperature in Lake Albano waters (large circles labelled by depth) and local groundwaters (small circles). The solubility curves of quartz, chalcedony, α-cristobalite, opal-CT, and amorphous silica (Fournier, 1991) are also shown.

corporation of Ca, Mg, and K, with respect to Na, into product solid phases. Although the area is densely inhabited, anthropogenic pollution seems a less unlikely explanation, since this enrichment in Na characterizes most groundwaters hosted in the volcanic complex.

Summing up, in spite of possible uncertainties, Ca, Mg, and K concentrations of lake waters and groundwaters of the volcanic cover appear to be mostly derived by rock dissolution, whereas Na is contributed by both meteoric recharge ($\sim$1/3) and water–rock interaction ($\sim$2/3).

8.2. Silica

Fig. 8 shows that dissolved SiO_2 concentrations of local groundwaters in volcanic rocks range between $\sim$30 and $\sim$100 mg/l and are intermediate between amorphous SiO_2 and α-cristobalite solubilities. Lake Albano waters have much lower concentrations, 4–6 mg/l in the hypolimnion, and < 0.5–1.5 mg/l at shallower depths.

It seems likely that dissolved SiO_2 concentrations are mainly governed by water–rock interaction processes in groundwaters and by diatom

algal assimilation in shallow lake waters. Dissolution of both inorganic silica minerals and opaline silica secreted by diatoms, upon death and sinking, could explain the increase in aqueous SiO_2 with depth.

9. State of saturation of Lake Albano waters

The saturation state of Lake Albano waters with respect to relevant solid phases has been investigated by means of the EQ3NR software code (Wolery, 1992). Calculations were carried out for the analytical values, referring to the COM thermodynamic database. This is the most complete database and includes 972 aqueous species, 944 minerals, and 88 gases, whose thermodynamic data are chiefly derived from SUPCRT92 (Johnson et al., 1992). Since leucite ($KAlSi_2O_6$), the main rock-forming mineral of the Alban Hills rocks and other volcanics of central-southern Italy, is not present in the database, we estimated its Gibbs free energy of formation from the elements, $\Delta G°_f$, at 298.15 K and 1 bar. This was done through the empirical correlation between $\Delta G°_f$ and the number of O atoms in the formula, N_O, based on the existing data of kalsilite

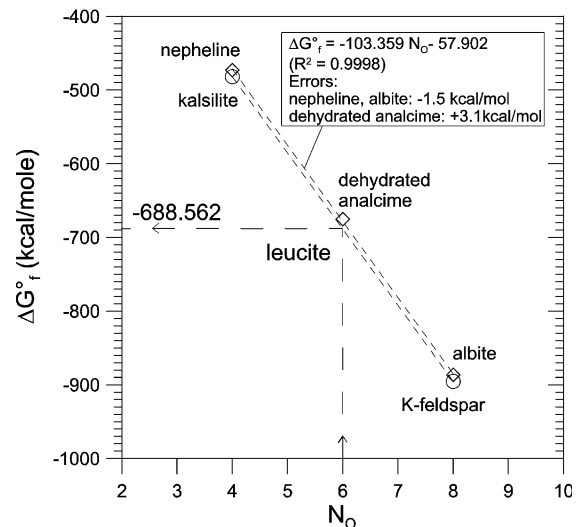Fig. 9. Plot of Gibbs free energy of formation from the elements, $\Delta G°_f$, at 298.15 K and 1 bar vs. the number of O atoms in the formula, N_O, for K- and Na-Al-silicates.
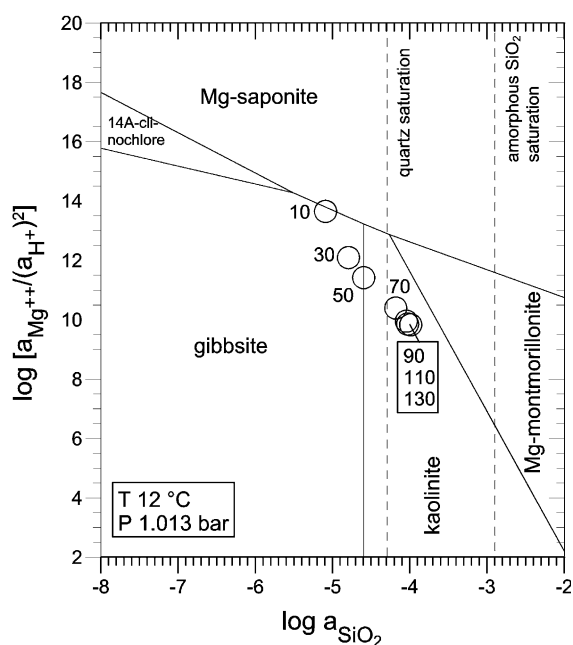
Fig. 10. Activity plots of log $[a_{Mg^{2+}}/(a_{H^+})^2]$ vs. log a_{SiO2} for Al-Si minerals at 12°C and 1.013 bar. Circles labelled by depth identify Lake Albano waters.

(KAlSiO$_4$) and K-feldspar (KAlSi$_3$O$_8$), obtaining a value of −688.562 kcal/mol (Fig. 9). The uncertainty of this value can be estimated referring to the sodic counterparts nepheline (NaAlSiO$_4$), dehydrated analcime (NaAlSi$_2$O$_6$), and albite (NaAlSi$_3$O$_8$). The differences between the reported $\Delta G°_f$ (Helgeson et al., 1978) and the predicted values is −1.5 kcal/mol for nepheline and albite and +3.1 kcal/mol for dehydrated analcime (Fig. 9). These are relatively small compared to the $\Delta G°_f$ values, but are of the same order of magnitude of the Gibbs free energy of hydrolysis reactions, $\Delta G°_r$. The $\Delta G°_r$ of leucite, which refers to the following reaction:

$$\text{leucite} + 4H^+ = K^+ + Al^{3+} + 2SiO_{2(aq)} + 2H_2O \tag{6}$$
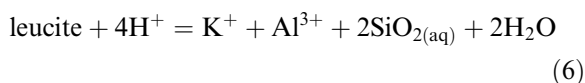
is, in fact, −7.247 kcal/mol and the corresponding log K value is 5.31. Assuming that the minimum uncertainty on the $\Delta G°_r$ of leucite is 1.5 kcal/mol, the minimum error on log K is 1.10. Varying the log K value of leucite by this amount did not

significantly change the conclusions of the speciation/saturation calculations (see below).

Another problem is the computation of the state of saturation of lake waters with respect to aluminum silicates, since analytical data are not available for Al. As common practice (e.g., Reed and Spycher, 1984), this problem was circumvented assuming saturation with respect to a suitable Al mineral. Based on activity plots prepared assuming Al conservation (e.g., Fig. 10), kaolinite and gibbsite were chosen as Al buffers for hypolimnetic and epilimnetic waters, respectively.

Since precipitation of Fe-oxyhydroxide usually occurs in lakes with anoxic hypolimnion, especially in its upper parts (Davison, 1993), f_{O2} was assumed to be constrained by the equilibrium between Fe^{2+} and ferrihydrite in the hypolimnetic waters of Lake Albano. Redox conditions were assumed to be fixed by measured O_2 concentration in the metalimnion and in the epilimnion.

Results of speciation calculations (Fig. 11) indicate that lake waters are undersaturated, at all depths, with respect to the primary phases of volcanic rocks, i.e., leucite, clinopyroxene (diopside), nepheline, and kalsilite, as well as to several clay minerals, such as saponites, beidellites, montmorillonites, and illite. Therefore these primary phases can dissolve and these secondary clay minerals cannot precipitate. Due to the high K concentrations, lake waters are close to saturation or oversaturated with muscovite, but the production of this phase is unlikely due to the slow rate of precipitation/dissolution reactions (Knauss and Wolery, 1989; Nagy, 1995).

Shallow lake waters (≤ 50 m depth) are oversaturated with respect to dolomite, but the precipitation of this mineral is also unlikely due to kinetic reasons (Plummer et al., 1978; Hardie, 1987). Calcite precipitation, due to the decrease in CO_2 concentration and/or biological utilization, is expected at very shallow depth and it is favored by the relatively high rate of precipitation/dissolution reactions (Chou et al., 1989; Plummer et al., 1978). Since particles of calcite can persist in suspension for long periods of time, they might perturb density distribution and lake stability (see above). Deep waters are undersaturated with respect to all carbonate minerals.

10. Conclusions

Lake Albano waters are undersaturated with respect to the primary minerals of local volcanic rocks and to most secondary minerals typically produced during water–rock interaction, including clays and carbonates. Only muscovite at any depth, ferrihydrite in the hypolimnion, and both dolomite and calcite in the epilimnion could precipitate from lake waters. However, the formation of authigenic muscovite and dolomite is likely hindered by kinetic reasons, leaving calcite and ferrihydrite as the only two solid product minerals in shallow and deep waters, respectively. Based on this evidence and taking into account that the relative concentrations of the main cations in lake waters are close to those in local groundwaters and in local volcanic rocks, it can be concluded that Na, K, Mg, and Ca concentrations in lake waters are chiefly controlled by incongruent rock dissolution, apart from minor calcite precipitation at shallow depths.

Based on the vertical distribution of dissolved O_2, temperature, and pH Lake Albano was stratified at the time of our survey, in December 1997, in agreement with previous observations (Martini et al., 1994; Cioni et al., 1995; Pedreschi, 1995). Vertical changes in the density of lake waters indicate that overturn may be induced by cooling of shallow waters below ∼8.5°C, which is a possible phenomenon in cold winter periods. Lake stratification may also be perturbed by local seismic activity, which is rather frequent and intense in the Lake Albano area (Amato et al., 1994; Amato and Chiarabba, 1995). In addition, past occurrence of regional earthquakes is suggested by historical chronicles. Overturn is expect to trigger exsolution of accumulated gases, if any.

The flat vertical profiles of Cl, Na, K, Mg, N_2, and Ar suggest that physical, chemical, and biological processes have not had enough time to change the vertical distribution of these chemical
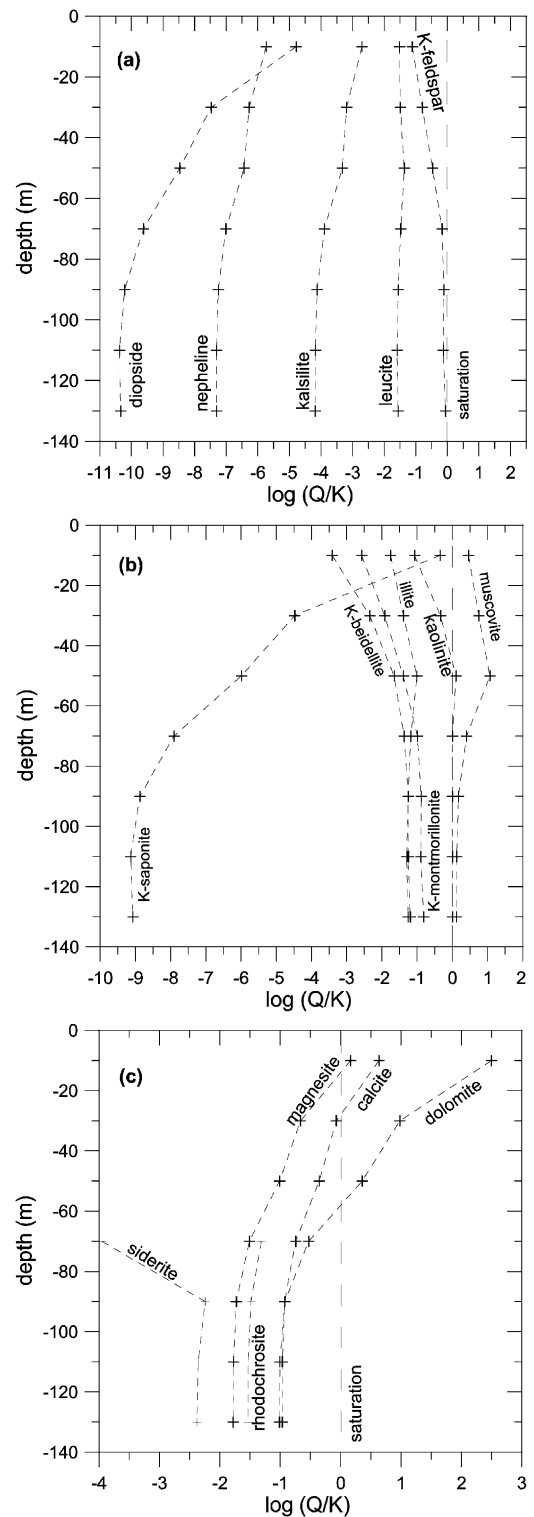

Fig. 11. Vertical profiles of the saturation index with respect to (a) rock-forming minerals of volcanic rocks of the Alban Hills region, (b) phyllosilicates minerals, and (c) carbonate minerals.

components in lake waters since the last overturn. However, since these chemical constituents have comparatively conservative behavior in most lakes and generally show only minor variations in space and time due to biological processes (Wetzel, 1983), the length of time required to perturb their vertical profiles might be comparatively long. Therefore, the absence of vertical changes of Cl, Na, K, Mg, N_2, and Ar is not particularly informative.

On the other hand, SO_4 is strongly affected by microbial activity (Wetzel, 1983), and Ca and SiO_2 are remarkably influenced by precipitation of calcite (induced by CO_2 loss or biota activity or both) and opaline silica secreted by diatoms. A relatively short time is probably sufficient to perturb the vertical profiles of these components, but the rates of the processes governing SO_4, Ca, and SiO_2 cannot be established based on the results of a single survey.

Lake Albano waters are also characterized by a remarkable increase with depth in CO_2 and CH_4 concentrations, of one and three orders of magnitude, respectively. Assuming that Lake Albano behaves as a closed system with respect to C species, the distribution of CO_2 and CH_4 in lake waters would be governed by the balance between (1) the photosynthetic production, in the trophogenic epilimnion, of organic matter, which settles into the anoxic hypolimnion upon death of the organisms, and (2) the decomposition of organic matter and the consequent generation of CO_2 and CH_4 occurring under the anoxic conditions of lake sediments, as commonly observed in lakes (Wetzel, 1983, pp. 213–216). Gases would then diffuse upwards from the sediments to the overlying lake waters. However, in this region of high CO_2 flux (Chiodini and Frondini, 2001), production of CO_2 and CH_4 in the sediments of Lake Albano could be sustained not only by settling organic matter but also by input of external CO_2 from below, essentially along the main tectonic structures underlying the lake area. Moreover, if the flux of CO_2-rich deep gases is higher than the amount of CO_2 consumed by CH_4-producing bacteria in lake sediments, excess CO_2 could even accumulate in deep lake waters.

In spite of the presence of these different sources of CO_2 and CH_4, total gas pressure in lake waters was very close to atmospheric pressure (range 0.9–1.3 bar) at all depths, from the surface to 130 m depth, in December 1997. Although this virtual lack of gas accumulation with respect to the atmospheric pressure at any depth might be fortuitous, it might be explained by the occurrence of a recent episode of water circulation and gas exsolution. Monitoring of relevant chemical and physical parameters of Lake Albano waters should be carried out on a regular basis to investigate this subject further.

Acknowledgements

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