Geochemistry of the Albano and Nemi crater lakes in the volcanic district of Alban Hills (Rome, Italy)

M. L. Carapezza^{1*}, M. Lelli² and L. Tarchini³

¹INGV-Sezione Roma 1, Via di Vigna Murata, 605 – 00143 Roma, ²CNR, Istituto di Geoscienze e Georisorse, Via Moruzzi, 1 – 56100 Pisa, ³Università Roma Tre, Dipartimento di Scienze Geologiche, Largo S. Leonardo Murialdo, 1 – 00146 Roma.

Abstract

Lake Albano, located 20 km to the SE of Rome, is hosted within the most recent crater of the quiescent Alban Hills volcanic complex that produced hydromagmatic eruptions in Holocene times. Stratigraphic, archaeological and historical evidence indicates that the lake level underwent important variations in the Bronze Age. Before the IV century B.C. several lahars were generated by water overflows from the lake and in the IV century B.C. Romans excavated a drainage tunnel. The lake is located above a buried carbonate horst that contains a pressurized medium-enthalpy geothermal reservoir from which fluids escape to the surface to produce many important gas manifestations of mostly CO₂. Previous studies recognized the presence of gas emissions also from the crater bottom. In 1997 the possibility of a Nyos-type event triggered by a lake rollover was considered very low, because the CO₂ water concentration at depth was found to be far from saturation. However, considering the high population density nearby, the Italian Civil Protection Department recommended that periodical monitoring be carried out. To this scope we initiated in 2001 a systematic geochemical study of the lake. Thirteen vertical profiles have been repeatedly carried out in 2001-2006, especially in the deepest part of the lake (167m in 2005), measuring T, pH, dissolved O₂ and electrical conductivity. Water samples were collected from various depths and chemically and isotopically analysed. Two similar profiles have been measured also in the nearby

^{*}Corresponding author. Tel.: +39-06-51860370

Fax: +39-06-51860565; E-mail: carapezza@ingv.it

Nemi crater lake. Results indicate that in the 4.5 years of monitoring the pressure of gas dissolved in the Lake Albano deep waters remained much lower than the hydrostatic pressure. A CO_2 soil survey carried out on the borders of the two lakes, indicates the presence of some zones of anomalous degassing of likely magmatic origin. A water overturn or a heavy mixing of deep and shallow waters likely occurred in winter 2003-2004, when cold rainfall cooled the surface water below 8.5 °C. Such overturns cause only a limited gas exsolution from the lake when the deep water is brought to a few meters depth but can explain the observed decrease with time of dissolved CO_2 at depth and related water pH increase. A gas hazard could occur in the case of a sudden injection through the lake bottom of a huge quantity of CO_2 -rich fluids, which might be caused by earthquake induced fracturing of the rock pile beneath the lake. A limnic gas eruption might also occur should CO_2 concentration build up within the lake for a long time.

Keywords: Albano and Nemi crater lakes, geochemical monitoring, water overturn and gas hazard, CO₂ diffuse degassing.

1. Introduction

Alban Hills are a quiescent volcanic complex, on whose north-western slope the city of Rome is located (Fig. 1). The complex is affected by a strong degassing of deep fluids of likely magmatic origin (mostly CO_2 and H_2S , with a ³He/⁴He ratio up to 1.90 R/Ra similar to that of the fluid inclusions in olivine and clinopyroxene phenocrysts of the volcanic rocks; Carapezza and Tarchini, 2007). Seismic swarms of low-medium magnitude (M_{max} =4.5) episodically occur and the central part of the volcanic edifice centred on Lake Albano has experienced a 30 cm uplift in the period 1951-1997 (Amato et al., 1995; Chiarabba et al., 1997; Anzidei et al., 1998; Riguzzi et al., 2002). The discovery of Holocene primary volcanic deposits and of syn-eruptive lahars indicates the persistence until very recent time of eruptive hydro-magmatic activity at the Albano crater lake (Funiciello et al., 2002 and 2003). Evidence has been provided that some inter-eruptive lahar and fluvial deposits of the Ciampino plain (Fig. 1) have been generated by water overflows from Lake

Albano (Funiciello et al., 2002 and 2003). Of particular interest is the description reported by several ancient historians (from Plutarcus to Titus Livius, see Funiciello et al., 2002) of a sudden lake overflow occurring in the IV century B.C., an event that induced the Romans to excavate a drainage tunnel that has since kept the lake level 70 m below the lowest crater rim. During these historic events a lake rollover may have occurred, perhaps triggered by a sudden injection to the lake bottom of hot CO₂-rich fluids. The presence in the Alban Hills and on the bottom of Lake Albano of several zones of strong CO₂ degassing, together with the observed relation between earthquakes and the increase of gas output and of the temperature of springs and wells (Chiodini and Frondini 2001; Funiciello et al., 2002) results from the existence at depth of a pressurized geothermal aquifer, rich in CO₂ and with a temperature of 100-110 °C (Carapezza et al., 2005). Seismic shaking could produce a strong injection of fluids into the lake bottom that in turn could cause a overturn of the lake and dangerous release of a CO₂ cloud, as recently occurred at lakes Nyos and Monoun in Cameroon (Sigurdsson et al., 1987; Barberi et al., 1989; Rice, 2000). Earlier work (1997 survey by Cioni et al., 2003) showed that Lake Albano did contain slightly elevated concentrations of CO₂, but these were likely too low to constitute a great hazard. However, it is important that the geochemistry of the Lake Albano be periodically investigated, in order to check for evidence of deep gas input or the existence of conditions for a gas accumulation in its deep water. In this paper we describe the results of several geochemical surveys carried out on Lake Albano from 2001 to 2006. For the sake of completeness, some geochemical investigations were carried out also on the nearby Nemi crater lake (Fig. 1).

2. The Lake Albano

The lake is hosted within coalescent craters formed by hydromagmatic eruptions, arranged on an ellipse with 3.5 km and 2.2 km axes (Fig. 2). The direction of the major axis is NW-SE, corresponding to that of a buried structural high of the carbonate basement, whose bordering faults are the main pathways for the deep gas escape (Carapezza et al., 2003). The lake maximum depth

was 167 m in 2006 (Anzidei et al., 2006), the greatest of the Italian crater lakes. The study of the cored lake sediments (Guilizzoni and Oldfield, 1996; Oldfield, 1996) has shown strong variations in the carbonate precipitation, likely related to variations in the output of CO_2 at depth, and evidence has been provided for the existence of CO_2 emissions on the lake bottom (Caputo et al., 1986). The occurrence in the past of strong variations of the lake level is supported by archaeological evidence indicating a migration of the Bronze age settlements, from sites that were on the lake shore in Medium Bronze (3.5 Ka) when the lake level was probably similar to the present one, to sites located at higher elevations in the Final Bronze (3.2 – 3.0 Ka) (Chiarucci, 1987).

The geochemistry of the lake has been studied by Martini et al. (1994), Pedreschi (1995) and Cioni et al. (2003). The latter is the most complete study and describes the results of investigations carried out in December 1997. Temperature (T), dissolved oxygen (O₂), pH and electrical conductivity (EC) were measured along a vertical profile down to a depth of 130 m using a multiparametric probe (Idronaut, Ocean Seven 401). The lake water was sampled at several depths and analysed for major components and dissolved gases.

2.1. Physico-chemical characteristics of the lake water

In order to follow the temporal evolution of the physico-chemical conditions of the lake water, 13 new profiles have been carried out from July 2001 to January 2006, using the same probe, sampling and analytical techniques of Cioni et al. (2003). In July 2001, three vertical profiles were measured along the lake major axis; in June 2003, three vertical profiles were measured oriented transversally to the previous ones (Fig. 2), one of which was located near a zone on the eastern border of the lake, where an anomalous CO₂ flux had been measured, as will be shown later. In May 2004 two profiles were measured in the deepest part of the lake, one of which was measured again in November 2004, January, May, July and October 2005 and in January 2006. In the 2001 and 2003 surveys, the water was sampled at 10 m depth intervals, whereas in the remaining 2004-2006 surveys water samples were collected only at the surface and at the highest depth. In the following sections we discuss only

the profiles in the deepest part of the lake. Profiles in the shallower areas indicate that there is horizontal homogeneity in the lake water in all investigated zones and periods.

Except for seasonal changes in the upper part of the water column, the vertical profiles of T and dissolved O₂ (Fig. 3A and 3C) remained substantially unchanged in the 4.5-year observation period and are similar to those observed by Cioni et al. (2003) in 1997. These profiles confirm that Lake Albano is constituted by: (i) an oxygen-rich epilimnion above the thermocline at 30m depth, (ii) a zone of reduced oxygen down to 60-70m that is probably the depth of seasonal mixing, and (iii) an anoxic hypolimnion down to the lake bottom. The epilimnion temperature changes with the season and the specific climatic conditions at the moment of the survey. It was 9-14 °C during winter and 25-27 °C in summer. Temperature decreases rapidly with depth, but remains nearly constant at about 9 °C in the hypolimnion. In late winter the epilimnion temperature may approach that of the hypolimnion and the lake stability is reduced. Deeper mixing of the water column may occur and the rise of nutrient-rich hypolimnetic water to the surface can produce algal blooms as the one observed in February 2004 at -10 m and -20 m. Such eutrophication represents a potential biological hazard as algal biomass is mainly composed of cyanobacteria producing hepatic toxins and neurotoxins (Elwood and Albertano, 2005). The intense biological activity in the epilimnion and at the transition with the thermocline may also explain, together with winter water mixing, the dissolved O₂ variations observed at those depths (Fig. 3C). The pH value, that is 8.0-8.8 in the surface level, decreases to values of 6.63-6.98 in the hypolimnion. In the period from May 2005 to the last survey of January 2006 a thermal inversion was observed at 32-100m depth (see the encircled area in Fig. 3A) with the temperature that becomes lower than the apparently constant 9 °C of the deepest water body. This indicates a water mixing occurred during a cold winter, which is confirmed also by the pH values below 80m that tend to increase with time (Fig. 3B). This pH increase at depth reflects also the decrease of the dissolved CO_2 (see section 2.3 and Fig. 7).

2.2. Lake water chemistry

The variations of major components are shown in Fig. 4. The concentrations of K, Na, Mg and Cl are the same at all depths, and in all surveys, in the limit of the analytical uncertainties. [SO₄] decreases with depth, probably due to sulphate reduction by bacterial activity in the anoxic hypolimnion. The increase with depth of [Ca] and [HCO₃] (see Fig. 4A and 4B) can be explained by calcite precipitation in the shallow waters followed by dissolution in the hypolimnion. Fig. 5 actually shows that Lake Albano shallow waters, above about 50m depth, are oversaturated with calcite, dolomite and possibly also magnesite and become carbonate undersaturated at depth. It is also clear that in 2005-2006 the deep water was less undersaturated in carbonate than in 1997. In the June 2003 survey a sudden increase of [Ca] and [HCO₃] with a decrease of [SO₄] was observed between 87 and 89m depth (Fig. 4). The decrease, with respect to the previous surveys, of the concentration-depth gradient for these constituents at 50-87m depth interval, suggests a possible influence of the Ca and bicarbonate-poor shallow water at that depth interval. It is also evident a [Ca] and [HCO₃] decrease since October 2005 in the deepest part of the lake, in agreement with the decrease of dissolved [CO₂] (see section 2.3 and Fig. 7 and) and the pH increase (Fig. 3B).

2.3. Dissolved gas in the lake water

Concentrations of dissolved gases in the lake water are reported in Fig. 6A. Nitrogen is the dominant component in the shallow water, followed by O_2 (which is zero below 60m depth), CO_2 , Ar and CH_4 . The concentration of N_2 and Ar remains constant at any depth, whereas [CO_2] and [CH_4] increase with depth and CO_2 becomes the major component at depth below 70-80m (Fig. 6A). The CH_4 increase with depth reflects at least partly an origin by decomposition of the organic matter in the anoxic sediments of the lake bottom. In terms of partial pressure (Fig. 6B), N_2 is the dominant constituent at any depth, with a value close to 0.8 bar that remains constant from the surface to the lake bottom, whereas the P_{CH4} becomes higher than the P_{CO2} at depth below 60m. A variation in the dissolved gas content in the deepest part of the lake was observed since November 2004, with a significant decrease in CO_2 and nearly costant [N_2] and [CH_4] values (Fig. 7). This could indicate that an appreciable exchange between deep and shallow waters occurred in 2003-

2004 winter. This is supported also by the algal bloom observed in February 2004 (Elwood and Albertano, 2005).

The comparison of the concentrations of CH₄, CO₂ and N₂ with the gases of the hydrothermal systems and those of liquid and gaseous hydrocarbon fields, indicates that a combination of two processes is needed to explain the concentration of the gas dissolved in the Lake Albano water: a decomposition of organic matter that increases the CH₄/CO₂ ratio (Cioni et al., 2003) and an injection from depth of a CO₂-rich gas. The presence of a deep component in the dissolved gas is indicated also by ³He/⁴He isotopic ratio of the dissolved helium, which has a R/Ra ratio of 1.30 (where Ra is the atmospheric isotopic ratio). This value falls in the ³He/⁴He range of the gas emissions of Alban Hills (0.94-1.90; Carapezza and Tarchini, 2007), whereas R/Ra values of 1.17-1.70 have been found in the fluid inclusions of the volcanic olivine phenocrysts (Martelli et al., 2004). These He isotopic ratios are low if compared with island arc and MORB volcanoes; however they are characteristic of the Roman Comagmatic Province and have been explained with a deep involvement of continental crust in the genesis of the magmas (Peccerillo and Panza, 1999). The δ^{13} C of the total dissolved carbon is 3.8-3.9 ‰ vs PDB in the hypolimnion and remained almost constant with time.

The oxygen isotopic composition of the lake waters shows a good correlation with depth and the δ^{18} O increases with time in the deep samples, likely reflecting the influence of mixing with superficial waters (Fig. 8A). The $\delta D - \delta^{18}$ O variations (Fig. 8B) are compatible with a simple evaporation process of local meteoric waters.

3. The Lake Nemi

The lake occupies the southern part of a complex crater structure elongated NNE-SSW (Fig. 1) and produced by violent phreatomagmatic eruptions that occurred in the third phase of Alban Hills volcanic activity (De Rita and Narcisi, 1983). The lake has a maximum surface of 1.6 km², a

perimeter of 4.5 km, an average depth of 16 m and a maximum depth of 32 m. A 1650 m long tunnel was excavated in the pre-Roman time at 320 m a.s.l. This tunnel was active regularly until 1928. From October 1928 to July 1932, the lake level was lowered to -21.6 m with respect to the inlet to recover two Roman ships. Only in 1944 the original level was restored and since then, due to strong exploitation of the water of the lake and of the peripheral aquifer, the tunnel worked sporadically after exceptional rainfalls.

Two vertical profiles (Nemi 1 and 2) were carried out in May 2004 with the same probe previously described, to a depth of 28 m (bottom at 30 m). The T, pH and dissolved O_2 values are shown in Fig. 9A and the profile location is indicated in Fig. 10. The dissolved O_2 shows a small increase between 5 and 10 m depth, then it decreases progressively and deep waters, below -25 m, are anoxic. Temperature was 19.9 °C at the surface and from -20m to the bottom it remained constant at 8°C; pH was 8.83 at the surface and 7.37 at the bottom, and the values are similar to those reported by Martini et al. (1994). As in Lake Albano a slight increase of [HCO₃] and [Ca] and a decrease of [SO₄] with depth are observed (Fig. 9B).

4. CO₂ soil flux from Albano and Nemi crater rims

The only known gas manifestation near the two crater lakes is the so-called Acqua Acetosa spring on the eastern border of Lake Albano (AA in Fig. 1). This was once a water spring that is presently dry and emits a strong flux of CO₂ (61.6 kg·m⁻²day⁻¹); its He isotopic composition (R/Ra=1.28; Carapezza and Tarchini, 2007) indicates the presence of a fluid component of deep origin. In order to evaluate the diffuse CO₂ degassing, a CO₂ flux survey was carried out on the shores -usually very narrow- of Lakes Albano and Nemi with 376 measurement points (Fig. 10) by the accumulation chamber method (see Chiodini et al., 1998 and Carapezza and Granieri, 2004 for method description). The main statistical parameters of the CO₂ soil flux are reported in Table 1. On a normal probability plot with logarithmic scale (Fig. 11) it is possible to distinguish the background from the anomalous values (Sinclair, 1974). Background threshold was identified at a flexus with a log value of 3.45 (corresponding to a CO₂ soil flux lower thanf 32 $g \cdot m^{-2} day^{-1}$). The CO₂ fluxes lower than the threshold are likely produced by the "respiration" of the vegetated soils that characterize the surveyed area (De Jong and Schappert, 1972). At Albano, the background population represents the 29.5 % of the measures, whereas at Nemi nearly 2/3 of the measured fluxes (62.7%) are within the background. For fluxes within background therefore there is no evidence of any endogenous degassing. At Lake Nemi two anomalous populations were found representing 28.4 and 9% of the measurements respectively (Table 1). A weak anomalous flux, with values around or slightly higher than 100 $g \cdot m^{-2} da y^{-1}$, was found on the southern and northern borders of Lake Nemi. In the latter zone the anomalies are aligned NNE-SSW along the main axis of the volcanic structure (Fig. 10). On Lake Albano shores four anomalous populations were recognized (Table 1), but Population B has rather low flux values (33 to 66 $g \cdot m^{-2} day^{-1}$) that could still reflect a biological CO₂ component. Populations C and D have increasingly higher values (Table 1) that certainly reflect CO₂ endogenous degassing. Finally, an advective CO₂ flux is likely associated to the highest values (4 points with a mean flux of 2416 g·m⁻²day⁻¹). The more pronounced flux anomaly is found on the eastern shore of Lake Albano, near and to the SE of Acqua Acetosa gas emission (Fig. 10). It extends for about 700m and CO₂ soil flux has an average value of 227 $g \cdot m^{-2} day^{-1}$, with a maximum of 3000 $g \cdot m^{-2} day^{-1}$. Because of the steep morphology and the dense vegetation, it was impossible to perform flux measurements on a regular extended grid. This prevented to obtain a CO₂ flux map of the narrow investigated area, that is limited to one side by the lake and to the other by the steep inner crater wall. However, the main anomalies seem to be elongated on a NE-SW direction whose prolongation toward SW encounters the zone of gas emission of the deepest part of the lake (see inferred faults in Fig. 10). These CO₂ soil fluxes, although much lower than those of the main degassing structures of Alban Hills (e.g. Cava dei Selci, CS in Fig. 1, releases 95.7 tons/day from a surface of 12,000 m² and single points have fluxes over 50,000 g·m⁻²day⁻¹; Carapezza et al., 2003), are much higher than those produced by biological activity and indicate that a significant output of deep gas occurs particularly on the eastern border of Lake Albano crater.

5. Conclusions

The data collected in the new 2001-2006 surveys and those of Cioni et al. (2003) indicate that the water chemistry of the crater lakes of Albano and Nemi derives from the circulation of meteoric water within permeable volcanic layers of the Alban Hills complex. The concentration of dissolved gases and their isotopic composition suggest that some CO₂ is injected from depth into the Lake Albano bottom. The total dissolved gas pressure is, however, at nearly any depth much lower than the hydrostatic pressure (Fig. 12) and only a limited gas exsolution is to be expected if, for any reason, a relevant volume of deep water is brought to the surface. Fig. 12 shows that the December 1997 deep water would have exolved gas at depth of only 4 m, and that saturation depth decreased in the following years (from -2m in 2003 to zero after 2004) because of the reduction of dissolved [CO₂]. The water density variation due to temperature, to the chemical composition and to the presence of calcite microcrystals in the upper part of the lake (Cioni et al., 2003) indicate that a lake overturn could occur, should the surface temperature drop below 8.5 °C, a phenomenon that is certainly possible in case of heavy rainfall in harsh winters. Should such an overturn occur rather frequently, no relevant quantities of CO₂ could accumulate in the deepest part of the lake. A phenomenon of this kind occurred at the end of 2003-2004 winter and produced the geochemical variations observed in the deepest part of the lake, i.e. the decrease of dissolved CO₂ and pH increase (Figs. 3B and 6A) and an algal bloom in the epilimnion. On the other hand, the high CO₂ diffuse soil emission (Carapezza and Tarchini, 2007), the high P_{CO2} values in the waters and the high CO₂ and Rn concentration in the ground (Chiodini and Frondini, 2001; Pizzino et al., 2002; Beaubien et al., 2003) indicate that Alban Hills is one of the areas in Central Italy with the highest release of endogenous gas. The most abundant deep gas is CO₂ that can have a magmatic or mantle origin or be generated at least partly by metamorphic decarbonation (Carapezza and Tarchini,

2007). The carbonate horst beneath Lake Albano is confined below an impervious cap and represents a permeable structure that entraps the fluids rising from depth, giving rise to a pressurized medium-enthalpy geothermal reservoir. From this reservoir the fluids escape towards the surface along the main faults and fractures of the carbonate horsts. The entity of upward degassing is obviously controlled by the rock permeability and increases if local earthquakes produce an appreciable rock fracturing. Therefore, although geochemistry indicates that at present the conditions do not exist for the exsolution of great quantities of CO₂ from the Lake Albano, also in case of a sudden overturn of its waters, an hazard could occur in case of energetic seismic swarms with hypocenters beneath the lake that could induce a significant increase of the influx of gas and hot water from the lake bottom. As there is evidence of CO₂ emission from below the lake bottom, gas hazard could rise also if the CO₂ concentration in the deep lake water builds up to create dangerous conditions for a limnic eruption. This likely requires a long time without lake overturns that reduce the deep [CO₂] as shown in this paper. In any case, considering that the area is very densely populated and that in spring and summer times the lake shores are full of tourists, it is convenient that geochemical monitoring of the lake be continued, possibly with some permanent stations recording the main physico-chemical parameters at depth.

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Figure captions

Fig. 1. Digital elevation model of the Alban Hills volcanic district with the location of the crater lakes Albano and Nemi. a) Ciampino plain Holocene syn- and inter-eruptive lahar deposits; b) structural highs (+) and lows (-) of the carbonate basement revealed by gravity anomalies; c) main strike-slip faults; d) main normal faults; e) gas manifestation sites (CS= Cava dei Selci, AA= Acqua Acetosa).

Fig. 2. Bathymetric map of Lake Albano with location of the geochemical vertical profiles carried out in 2001-2006. The sites of the gas emissions on the bottom and on the eastern border of the lake are also indicated.

Fig. 3. Vertical profiles measured in the deepest part of Lake Albano (48 and A03 in Fig.2) in 2001-2006. A: variation with depth of temperature; B: variation with depth of pH; C: variation with depth of the dissolved O_2 . The 1997 profiles are from Cioni et al. (2003).

Fig. 4. Variation with depth of the concentration of cations (A), HCO₃ (B) and anions (C) in the Lake Albano waters from July 2001 to January 2006. The 1997 profiles are from Cioni et al. (2003).

Fig. 8. Saturation index of carbonate minerals in Lake Albano water calculated following the procedures of Cioni et al. (2003).

Fig. 6. Variation with depth of the content (molalities A) and partial pressure (B) of dissolved gases (CO₂, N₂, CH₄, O₂ and Ar) in the Lake Albano waters. In the June 2003 profile the sum of O₂ and Ar is reported but direct measurements of dissolved O₂ (Fig. 3C) indicate that the O₂ content is zero below 70m depth.

Fig. 7. Concentration (molalities) of dissolved CO_2 , N_2 and CH_4 in the deepest water sample collected in the 1997-January 2006 surveys (depth range=152-160m). The 1997 data are from Cioni et al. (2003).

Fig. 8. A: Variation with depth of the oxygen isotopic composition in the water samples of Lake Albano collected in June 2003-January 2006 surveys (analytical error: ± 0.1). B: Isotopic composition of oxygen vs deuterium in the waters of Lake Albano and Nemi. The isotopic changes induced by evaporation are indicated. The isotopic composition of the local meteoric waters is from Longinelli and Selmo (2003).

Fig. 9. A: variation with depth of T, pH and dissolved O_2 measured in May 2004 in the Lake of Nemi. B: variation with depth of the concentration of the anions and cations in mg/l (except for HCO₃ in meq/l) in the Lake Nemi waters. See Fig. 10 for the location of water sampling points.

Fig. 10. Diffuse CO_2 soil degassing from the shores of the crater lakes Albano and Nemi. The diameter of the circles expresses the CO_2 soil flux values (see scale). Black dots: measurement points and flux lower than 32 g·m⁻²day⁻¹ (background); black square: sampling sites of Nemi waters.

Fig. 11. Normal probability plot (log scale) of the soil flux measurements (376 sampling points) on the shores of Albano and Nemi crater lakes; see Fig. 10 for point location.

Fig. 12. Variation with depth of the total pressure of the gases dissolved in the Lake Albano water in the period December 1997-January 2006, compared to the hydrostatic pressure. Open symbols on the upper part of the hydrostatic pressure line indicate the depth at which gas would have exsolved should the deepest water have been brought to the surface. The 1997 profile is from Cioni et al. (2003).

Figures



Figure 1



Prospection site:☆Jul.'01; ●Jun.'03; ■ from May'04 to Jan.'06 (A02 only on May'04) ■ Gas manifestation from the bottom and the border of the lake (AA= Acqua Acetosa)

Figure 2











Figure 5





Figure 6



Figure 7



Figure 8





Figure 9







Figure 11



Figure 12