Geochemical and biochemical evidence of lake overturn and fish-kill at Lake Averno, Italy.

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Abstract

Lake Averno is situated in the homonymous crater in the northwestern sector of the Campi Flegrei active volcanic system in Campania region, Italy. In February 2005 a fish kill event was observed in the lake, prompting a geochemical survey to ascertain the possible cause. In February 2005 a geochemical survey revealed that the lake water was unstratified chemically and isotopically, presumable, as a result of lake overturn. This fish-kill phenomenon was recorded at least two other times in the past. In contrast to the February 2005 results, data collected in October 2005, shows the Lake Averno to be stratified, with an oxic epilimnion (surface to 6 m) and an anoxic hypolimnion (6 m to lake bottom at about 33 m).

Chemical and isotopic composition of Lake Averno waters suggests an origin by mixing of shallow waters with a Na-Cl hydrothermal component coupled with an active evaporation process. The isotopic composition of Dissolved Inorganic Carbon, as well as the composition of the non-reactive dissolved gas species again supports the occurrence of this mixing process.

Decreasing levels of SO_4 and increasing levels of H_2S and CH_4 contents in lake water with depth, strongly suggests anaerobic bacterial processes are occurring through decomposition of organic matter under anoxic conditions in the sediment and in the water column. Sulfate reduction and methanogenesis processes coexist and play a pivotal role in the anaerobic environment of the Lake Averno. The sulfate reducing bacterial activity has been estimated in the range of 14-22 $\mu mol \cdot m^{-2} \cdot day^{-1}$.

Total gas pressure of dissolved gases ranges between 800 and 1400 mbar, well below the hydrostatic pressure throughout the water column, excluding the possibility, at least at the survey time, of a limnic eruption.

Vertical changes in the density of lake waters indicate that overturn may be triggered by cooling of epilimnetic waters below 7°C. This is a possible phenomenon in winter periods if atmospheric temperatures remain frosty for enough time, as occurred in February 2005.

The bulk of these results strongly support the hypothesis that fish kill was caused by a series of events that began with the cooling of the epilimnetic waters with breaking of the thermal stratification, followed by lake overturn and the rise of toxic levels of H_2S from the reduced waters near the lake bottom.

Keywords: Lake Averno, dissolved gases, stable isotopes, fish kill event, Sulfate Reduction Bacterial.

1. Introduction

In February 2005 an event of fish kill occurred at Lake Averno sited in the Campi Flegrei caldera (Fig. 1). This phenomenon was recorded at least other two times in the past; February 2003 and January 2002 (personal communication ASL NA2 Servizio Veterinario). The happenings of previous events of fish kill are probable, but no secure data are available. The media attributed the cause to the volcanic activity of the area, being the Lake Averno considered to be the entrance of the underworld since Greek and Roman times. As the lake is located inside the active volcanic district of Campi Flegrei the repeated occurrence of this phenomenon and the supposed volcanic cause alerted the citizens and the local authority. After the February 2005 event, a series of geochemical investigations on the lake were conducted in order to understand the origin of the fluids and the processes occurring in the lake and to provide insight on the triggering factor of these repeated events. This paper reports the results of these investigations.

2. Geological and hydrogeological settings

The Campi Flegrei District (CFD) area is located within the Campanian Plain, which is bordered by the Southern Apennines. This mountain chain results from deformation of the African continental margin and is composed of a variety of Mesozoic and Palaeogenic palaeogeographic domains (D'Argenio et al., 1973). The Campi Flegrei caldera, the main feature of the CFD, includes a continental and a submerged part. It is a resurgent nested structure formed during two major caldera collapses related to the eruptions of the Campanian Ignimbrite (CI, 39 ky BP; Fedele et al., 2004 and references therein) and the Neapolitan Yellow Tuff (NYT, 15 ky BP; Deino et al., 2004 and references therein), respectively (Orsi et al., 1996).

Volcanological, geophysical and geochemical evidences (De Vita et al., 1998; De Vita et al., 1999; Dellino et al., 2001; Zimanowski et al., 2003) support the hypothesis that remnant(s) of the magma source feeding the large eruptive events of CI and NYT are involved in more recent volcanic episodes (e.g. Agnano-Monte Spina eruption, 4ky BP) and still supply heat and deep fluid release in the CFD, contributing to surface fluids emissions. The last eruption was in 1538, after about 3.0 ky of quiescence, and formed the Mt. Nuovo cone (Di Vito et al., 1987), sited few hundred meters SE of the Lake Averno. At present fumarole emissions and diffuse degassing from soils at Solfatara of Pozzuoli (Chiodini et al., 2001), and the presence of submarine fumaroles and thermal waters represent the more evident manifestations of persisting magmatic activity.

Lake Averno sits in a homonymous crater generated during two eruptions (3.7 - 4.5 ky BP, Orsi et al., 2004). The lake is in the northwestern sector of the Campi Flegrei caldera, at the intersection of NE-SW and NW-SE fault systems (Orsi et al., 2004). The lake (0.55 km^2) occupies most of the bottom of the volcanic crater with steep slopes, up to 110 m high. A gap in the crater rim is present in the southern sector.

Two main aquifers are present in the area, one is composed of relatively low to moderately permeable pyroclastic products, cinerite and alluvial deposits (scoriae, pumice, lapilli) and the other is composed of less permeable tuffaceous rocks.

Although the alternation of these rocks could indicate subterranean circulation in several overlapping aquifers, this phenomenon was only found on a local scale, because less permeable layers are discontinuous and reconstruction of the piezometric morphology revealed the existence of a single main aquifer with flow toward the coast. From the hydrogeological point of view, the Averno Lake represents the outcropping of the water table, also fed by a direct meteoric water supply and drained toward sea by a canal almost 1 km long with averaged flow of about 40 l/s (Improta et al., 2004).

3. Field and analytical methods

Lake waters were surveyed on February 11th 2005, along a vertical profile in the center of the lake, three days after that an event of fish kill occurred.

Another survey has been carried out eight months later on October 27th 2005. In both surveys samples were collected along a vertical profile, both profiles reached the bottom of the lake to a deep of about 33 m.

The temperature, Eh and pH were measured by means of a multiparameter probe (Hydrolab multiprobe) equipped with a data logger for data storage. The nominal precisions are as follows: depth ±0.05 m; Eh ± 20mV; temperature ±0.01 C; pH ±0.05 pH-units.

Prior to the current study on 5th October 1999, a water profile study with pH, T and dissolved oxygen saturation percentage was conducted using a CDT Hydrolab multiparameter probe.

A small diameter (3 mm) polyethylene tube was used for water sampling, fixed close to the probe sensors and lowered to the chosen depth. Water was pumped to the surface by means of a manual vacuum pump not exceeding 0.2 bar of pressure difference in order to avoid gas separation in the pipe. Samples were collected after displacement of a water volume at least twice the inner volume of the pipe. Two sample aliquots, filtered (0.45 μm) and filtered-acidified (with HCl 1:1) were collected in polyethylene bottles for analysis of anions, hydrogen and oxygen isotopic composition and cations respectively. Alkalinity was measured just after sampling by acidimetric titration (HCl 0.05N).

The dissolved gas composition (CO_2, N_2, O_2, Ar, CH_4, He, H_2S) was determined in the samples collected during the two post event surveys. The analyses were performed following a modified method based on Chiodini (1996). Samples were collected in pre-evacuated 200 ml glass vials equipped with a Teflon stopcock fixed with a rubber O-ring. The water is forced to flow through a tube until no air bubbles were present by means of three way valve coupled with a syringe. The tube was then connected to the vial, avoiding trapped air during the operation, and the valve was opened until a volume of water, V_{liq} (about 65-80% of the total vial volume, V_{tot}) has been obtained. The gas phase separated in the headspace of the vial, of volume $V_{gas} = V_{tot}-V_{liq}$, was analyzed by a gas-chromatograph equipped with TCD detectors through a unique injection on two columns (Molecular Sieve 5Å capillary 30m x 0.53mm x 50µm and Hysep Q packed 90' x ¼') using He as carrier gas on both columns. The partial pressure of each gas species (CO_2, N_2, O_2, Ar, CH_4, H_2S) was determined referring to standards at different pressures. Helium partial pressure in the head space of the vials was determined, on a second injection, by a leak detector (detection limit 0.00015 mbar). Based on the partial pressure (p_i), the numbers of moles $n_{i,g}$ of each gas species contained in $V_{gas}+V_{inj}$ (where V_{inj} is the measured volume of the gas injection line) are calculated through the ideal gas law. After computing the partial pressures in the headspace of the vials ($p_{i,g}=(p_i*(V_{gas}+V_{inj}))/V_{gas}$), the number of moles of each gas species $n_{i,l}$ remaining in the liquid are calculated by means of the Henry's law (constants from Wilhelm et al., 1977), assuming that the gas phase separated in the headspace of the vial is in equilibrium with the liquid at laboratory temperature. The sum $n_{i,g} + n_{i,l}$ gives the total moles of each gas species in the water sample. The effect of salinity on gas solubility, i.e. *salting-out* effect, was not considered in the computation, as salinities of the examined solutions are relatively low.

Major ions (Na, K, Mg, Ca, NH_4, Cl, NO_3 and SO_4) were determined by ion chromatography in water samples. For the determination of $\delta^{13}C$ of Total Dissolved Inorganic Carbon (TDIC), carbon species were precipitated in the field as $SrCO_3$ by adding $SrCl_2$ and NaOH in solid state. Carbonate precipitates were filtered and washed with CO_2-free distilled water under nitrogen atmosphere. Carbon, oxygen and hydrogen isotope analyses were performed at the Geochemistry Laboratory of INGV-Osservatorio Vesuviano using a Finnigan Delta plusXP continuous flow mass spectrometer coupled with GasbenchII device (analytical errors are: $\delta D \pm 1‰$, $\delta^{18}O \pm 0.08‰$ and $\delta^{13}C \pm 0.06‰$). Analytical results are reported in Table 1.

4. Physical and chemical characteristics of Lake Averno

During the two surveys conducted in 2005, a marked difference between the two vertical profiles is observed. The vertical profiles of T, pH, Eh and pO_2 in the 27th October 2005 campaign, appear to be very similar to the profile carried out on October 5th 1999 (Figs. 2a-d), indicating that Lake Averno, at these times, is made up of two distinct water masses. The oxic epilimnion ranges from the surface to a depth of about 6 m, and the anoxic hypolimnion extends from 6 m to lake bottom at about 33 m. This interface is marked by strong variations in the chemico-physical parameters as shown in the vertical profiles reported in Figs. 2 a-d together with data relative to 11th February 2005 campaign, carried out after the fish kill event occurred. Considering the profile obtained on October 2005, oxygen partial pressure exhibits a maximum value of 134 mbar in the oxic epilimnion water body and rapidly decreases to 0.5 mbar at a depth of 9 meters. Temperature changes from 20°C at 6m to 12.4°C at 9 m; pH changes from 8.83 at 6 m to 7.56 at 9 m; Eh decreases from +177 mV at 6 m to -113 mV at 9 m. Also HCO_3 and SO_4 show different distributions along the water column (Fig. 3a, b). The epilimnion has HCO_3 of 360-380 ppm, SO_4 of 177 ppm, Ca of 35 ppm (Fig. 3c) and NH_4 below the detection limit (<0.05 ppm, Fig. 3d). In hypolimnetic waters the concentration of HCO_3 is about 415 ppm to a depth of 30 m deep and increases to 725 ppm at lake bottom. The concentration of Ca is about 50 ppm to a depth of 30 m and increases to 74 ppm at maximum depth, NH_4 shows an averaged value of about 7 ppm in the water column to a depth of 30 m and 36 ppm at lake bottom.

A marked difference can be seen when comparing the profile of February 2005 to the stratified profiles seen in October of 1999 and 2005 (Figs. 2 and 3).

The survey of 11th February does not show the presence of two distinct water bodies, but instead shows a mixed homogeneous water column. In particular the oxygen partial pressure in the entire water column is constant and lower than 1 mbar, also temperature and pH remain constant in the entire water column.

5. Dissolved gases

During the two post-event surveys conducted in the 2005, 20 samples were analyzed for dissolved gases chemical composition (Table 1).

The vertical distributions in terms of molar concentrations of CO_2, CH_4, N_2, Ar, O_2, H_2S and He are plotted in Figs. 4a, b for both surveys. N_2 is the main gas species in the entire water column except for the bottom layer where CO_2 and CH_4 show higher values. Also in terms of partial pressures, N_2 is the dominant constituent at any depth (800-1000 mbar), apart from the bottom layer where CH_4 shows a pressure of about 1000 mbar in October 2005 (Fig.5).

Despite what would be expected if the lake waters were fed by direct supply of volcanic gases, pCO_2 values in all profiles result are very low (Fig. 6). In the February 2005, profile pCO_2 values vary from 6.3 to 8.2 mbar in the entire water column except for bottom waters where a value of 15 mbar was recorded. October 2005 data show, pCO_2 values varying from 1.5 – 3.8 mbar in the epilimnion and pCO_2 values from 9 to 12 mbar in the water column from 9 to 30 m deep, with the exception of 29 mbar measured at a depth of 18 m. A maximum pCO_2 value of 42 mbar characterized the bottom layer. Figure 6 also shows the agreement between the pCO_2 values computed directly from the result of the analysis of dissolved gases and those computed on the basis of chemical composition, pH and temperature of the waters assuming equilibrium conditions among dissolved carbonate species (by means of the PHREEQC code; Parkhurst and Appelo, 1999). The good agreement between the two independently evaluated pCO_2 confirms the reliability of the method used for the sampling and analysis of dissolved gases and the assumption of equilibria conditions among dissolved carbonate species.

Lowering of pCO_2 (October 2005 profile) in epilimnetic waters with respect to the hypolimnion is likely due to photosynthetic utilization and/or re-equilibration of dissolved gases with the atmosphere. In fact the epilimnetic waters exhibit pCO_2 values very close to the atmospheric one (about 0.35 mbar, Fig. 6).

H_2S was measured only for samples collected during the October 2005 survey. In these samples H_2S is below the detection limit (pH_2S >0.01 mbar) in the entire water column except at a depth of 18m (2.7 mbar) and for the deepest three data points (27, 30 and 33 m) where H_2S reaches a maximum partial pressure of 4.5 mbar.

N_2 and Ar molar contents are compared in the Figure 7, whit reference compositions for air saturated water (ASW) (i.e. the expected composition of meteoric waters in equilibrium with air at temperatures of 0 – 15°C and pressures of 1 bar, representative of the possible conditions of the recharge waters). Most of the samples fit the theoretical meteoric waters composition. Only the sample collected at lake bottom, when the lake appears stratified (October 2005 profile), is significantly depleted in the atmospheric components. It furthermore must be noted that this bottom sample is characterized by a higher salinity with respect to the surface samples.

Total gas pressure ranges between 800 and 1400 mbar, and is well below the hydrostatic pressure throughout the whole water column (Fig. 8), probably as a consequence of the recent episode of water overturn that is expected to have triggered the removal of accumulated gases. In this condition, gas exsolution cannot take place, excluding the possibility, at least at this time, of a gas-driven waters overturn (limnic eruption). This occurrence also implies that the higher saline water stratified at the lake bottom has a different origin and may represent an input of degassed thermal waters.

In Figure 9 relative molar compositions of non-reactive dissolved gas species (N_2, Ar, He) are considered in order to investigate the origin of dissolved gases in the lake waters. Figure 9 also shows dissolved gas composition of groundwaters and thermal waters of Campi Flegrei area for comparison (Caliro, 2004). Inspection of the figure reveals that the lake waters deviate slightly from a pure meteoric composition (Air Saturated Waters, ASW) toward a composition similar to that of hydrothermal gases discharged in the Campi Flegrei (Solfatara fumaroles; Caliro et al., 2007). This behavior is similar to that shown by the Campi Flegrei waters, where an input of hydrothermal fluids has been recognized (Aiuppa et al., 2006). However, Total Dissolved Inorganic Carbon (TDIC), CH_4 and N_2 relative molar concentration reported in the ternary diagram of Figure 10 show a marked trend between an ASW mixed with a hydrothermal component, and a CH_4-rich composition. This evidence suggests that further processes must occur in the lake changing the composition of these reactive dissolved gases. In particular, the increase of CH_4, with depth may suggest the occurrence of bacterial processes under anoxic conditions in sediments and in the water column (see section 8), followed by upward diffusion in overlying water layers. However, carbon isotopic composition of TDIC is not consistent with a pure organic origin (see section 6.2).

6. Chemical and isotopic composition of waters.

Relative concentrations of dissolved SO_4, Cl and HCO_3 in lake waters are compared with the compositions of local groundwaters (Valentino et al., 1999; Valentino and Stanzione, 2003, 2004; Caliro 2004; Aiuppa et al., 2006), showing the existence of three main water types in the area (Fig. 11):

i) Chloride-rich groundwaters, having chloride as the prevalent anion species and sodium as the main dissolved cation, suggesting the existence of a Na-Cl brine component recharging the shallow aquifer (Aiuppa et al., 2006), with a composition similar to that of thermal brines encountered at depth in drillings within the geothermal reservoir (Guglielminetti, 1986);

ii) HCO_3-rich groundwaters: most of them are characterized by a low salinity and low temperatures (TDS ~ 0.5 g l^{-1}; T< 20°C) and have Ca as the main dissolved cation. These waters can be considered representative of the meteoric recharge (Aiuppa et al., 2006);

iii) Sulfate-rich groundwaters characterized by low pH values (1.6-2.4), high discharge temperature (47-95 °C) and intermediate TDS (2.5-5 g l^{-1}). These waters are located in the Solfatara crater area and show a chemical composition typical of volcano-hosted active epithermal systems (steam-heated groundwaters).

The chemical composition of the Averno waters appears similar to that of the groundwaters present in the area and in particular suggests an origin by mixing of HCO_3-shallow waters and a Na-Cl thermal component (Fig. 11). The decrease in SO_4 content with depth (Fig. 3b), in particular for the higher saline waters sampled at the lake bottom, again suggests the occurrence of bacterial processes under anoxic conditions (sulfate reduction) in sediments and in water column (see section 8). A near saturation condition of the lake waters with respect to Fluorite (SI 0.08 ± 0.25, Table 1) may account for their relatively high F contents.

6.1 Water isotopic composition

The isotopic composition of the surveyed lake waters varies in a narrow range for both oxygen ($\delta^{18}O$ -0.5 to -1.5‰ vs. V-SMOW) and hydrogen (δD -5 to -13‰ vs. V-SMOW), showing an isotopic "shift" from local meteoric water of about 5‰ and 25‰ for oxygen and hydrogen respectively (Figs. 12 and 13). In the February 2005 profile the oxygen isotopic composition results are homogeneous with values ranging from -1.16 to -1.22‰ (within the analytical error) again supporting lake water overturn and mixing at this time. In contrast, waters collected during the October 2005 profile show a distinct shift at a depth of 6 meters; an almost uniform oxygen isotopic composition with average value of -0.55‰ for the epilimnetic waters (surface to 6 m), an average value of -1.34‰ for the hypolimnion waters (6 to 33 m deep) (Fig. 12). A similar behavior is shown by the hydrogen isotope data.

The more positive isotopic composition of lake waters with respect to local meteoric water suggests the occurrence of the evaporation process. In particular, the slightly more positive and homogenous isotopic composition of epilimnetic waters (October 2005 profile) compared to the deeper waters supports the occurrence of evaporation along with considerable water circulation in the epilimnion during the period between the two surveys.

The stable isotope evolution of lake waters as a function of evaporation and mass fluxes has been studied in detail (e.g. Gat, 1981, 1996; Gonfiantini, 1986), with the main principles established by Craig and Gordon (1965). Most crater lakes also have strong inputs of local meteoric waters, and the isotopic enrichments from hydrothermal additions and evaporation are usually expressed as shifts (δD and $\delta^{18}O$) from local meteoric water. Isotopic characteristics of crater lakes and geothermal pools show “flat slopes” of the isotopic evolution lines, and in general can be explained as the result of the enhanced kinetic fractionation at higher temperatures (Giggenbach and Stewart, 1982; Rowe, 1994; Varekamp and Kreulen, 2000). The $\delta D/\delta^{18}O$ "slope" due to evaporation is a function of the lake water temperature and atmospheric humidity; it is about 5 for lakes at ambient temperature, and may decrease to 1 for warm lake waters (Matsubaya and Sakai, 1978; Rowe, 1994).

Considering that, Lake Averno was known since the Roman age, its total volume ($6.0*10^6$ m^3) did not change with time, being drained by a pipe toward the sea (40 l/s) and fed by groundwater and direct meteoric supply, the almost homogenous isotopic composition due to "periodically" water overturn, it is reasonable to assume that the lake has reached a steady state condition from isotopic point of view.

On the base of these assumptions and following the approach described by Gonfiantini (1986) for constant volume and well mixed lakes, the steady value of water isotopic composition as a function of the fraction of inflowing water lost by evaporation (x) is given by:

$$\delta_S = \frac{\delta_I(1-h+\Delta\varepsilon)+x(h\,\delta_a+\Delta\varepsilon+\varepsilon/\alpha)}{(1-x)(1-h+\Delta\varepsilon)+x/\alpha} \qquad (1$$

Where δ_I is the isotopic composition of the infiltration water, h the relative humidity of the air, $\Delta\varepsilon=(1-h)\times 14.2$, δ_a is the isotopic composition of water vapor of the air (-12‰ for oxygen and -86‰ for hydrogen, Gonfiantini, 1986), α the equilibrium fractionation factor at given temperature and $\varepsilon = \alpha - 1$.

The steady state water compositions at different fractions of evaporation, computed starting from local meteoric water composition ($\delta^{18}O$ -6.4‰, δD -34‰, Baldi et al., 1975; Bolognesi et al., 1986) and considering the local averaged air temperature of 16.4°C and the averaged relative humidity of 65%, are reported in Figure 13 together with the isotopic composition of the lake waters. Lake waters lie along this theoretical evaporation trend, characterized by $\delta D/\delta^{18}O$ slope of about 5, supporting the occurrence of the evaporation process and indicating a fraction of evaporation of inflowing water of about 20%.

Although the evaporation process starting from pure meteoric water may explain the observed isotopic composition, this is not supported by chemical data that suggest a mixing between shallow water and a NaCl component (Fig. 11).

Figure 14 shows Cl concentration vs. the oxygen isotopic composition of Lake Averno waters together with the composition of groundwaters in the Campi Flegrei area (Valentino et al., 1999; Caliro, 2004). The mixing trend between local groundwaters and the NaCl hydrothermal component, as well as the theoretical evaporation line of lake waters is shown. The intersection of these two lines (point A in Fig. 14) may indicates the composition of the mixed water feeding the lake characterized by a slightly more positive oxygen isotopic composition and higher Cl content with respect to local recharge. Waters collected at the lake bottom (AV33 and AV31) during the two surveys exhibit a high Cl content and slightly negative $\delta^{18}O$ with respect to the uppermost lake waters, suggesting a possible input at the lake bottom of a variable mixed hydrothermal component with lake water. Although the data are not sufficient to constrain the composition of this component it is reasonable to assume that it may have a composition like point B or varying along the line labeled "input at lake bottom" in Figure 14.

6.2 Carbon isotopic composition

The isotopic composition (expressed in δ notation) of TDIC relative to surveyed waters ranges from -5.3 to -6.3‰ vs. PDB, except for the epilimnetic waters (October 2005) that show more positive values of about -2.9‰. These isotopic values are consistent neither with a pure organic origin ($\delta^{13}C$ -25‰; Faure, 1986) nor with a pure volcanic/hydrothermal source (Solfatara fumaroles, $\delta^{13}C$ -1.4 ±0.4‰; Caliro et al., 2007).

The analytical values are compared with those of groundwaters of the Campi Flegrei (Caliro, 2004) in Figure 15. The carbon isotopic composition of the Campi Flegrei groundwaters is compatible with a mixing process between a shallow component with an organic carbon signature and a deep hydrothermal component (Caliro, 2004). The lake waters are also compatible with such a mixing process and in particular the more positive values shown by the epilimnetic waters (October 2005 profile) are probably due to light carbon CO_2 consumption by photosynthesis and/or to carbon isotopic re-equilibration process of water with the atmosphere. In fact, these waters experienced a CO_2 loss approaching to the atmospheric CO_2 partial pressure (Fig. 6). In order to evaluate qualitatively the effect of the CO_2 loss on the isotopic composition of TDIC, the fractionation factors $\alpha_{CO2\text{-}sol}$ of CO_2 with respect to the carbon in the solution have been computed, for the lake waters, assuming isotopic equilibrium at the temperature of the solution between CO_2, H_2CO_3, HCO_3 and CO_3 species by means of the following equation (Caliro et al., 2005):

$$\alpha_{CO2\text{-}sol} = (\alpha_{CO2\text{-}H2CO3}\,[H_2CO_3] + \alpha_{CO2\text{-}HCO3}\,[HCO_3] + \alpha_{CO2\text{-}CO3}\,[CO_3]) \,/\, [TDIC] \qquad (2)$$

isotopic fractionation factors between carbon species couples, are taken from Deines et al. (1974). The resulting fractionation factor $1000\ln\alpha_{CO2\text{-}sol}$ is about -8.0‰ for epilimnetic waters (0 to 6 m) that means a $\delta^{13}C$ of about -11.0‰ for the degassed CO_2. The occurrence of both processes: CO_2 consumption by photosynthesis and carbon isotopic re-equilibration process of water with the atmosphere (CO_2 degassing), can explain the more positive isotopic composition of the remaining dissolved carbon with respect to the hypolimnetic waters.

7. Water density in the Lake Averno

The chemical, physical, and isotopic homogeneity of Averno Lake waters on February 11th 2005 (Figs. 2, 3 and 12), strongly suggests that the lake experienced an overturn event prior to the survey. The possibility of this phenomenon is shown below, based on water densities.

The density of an aqueous solution, ρ_s (g/cm^3), at a given temperature, is linked to the density of pure water, ρ_w, (Keenan et al., 1969) by means of the following relationship (Aguilera et al, 2000):

$$\rho_s = \frac{(1000 + \Sigma C_i)}{(1000/\rho_w + \Sigma C_i V_i / MW_i)} \qquad (3$$

where V_i is the conventional partial molal volume of the i^{th} solute in cm^3/mol, C_i is its concentration in g/kg and MW_i is its molecular weight. Conventional standard partial molal volumes for the ionic solutes (Na, K, Mg, Ca, HCO_3, SO_4 and Cl) are given by Shock and Helgeson (1988) and for dissolved CO_2 by Shock et al. (1989).

Lowering of Ca contents in the epilimnion waters (see section 4) may be due to precipitation of calcite being these waters oversaturated with respect to calcite (Fig. 16). The presence of precipitated calcite particles in epilimnetic waters contributes to a density increase in these waters. This effect can be taken into account using the following equation (Aguilera et al., 2000):

$$\rho_s = \frac{(1000 + \Sigma C_i + \Delta m_{Ca} MW_{cal})}{(1000/\rho_w + \Sigma C_i V_i / MW + \Delta m_{Ca} V_{cal}\ )} \qquad (4$$

where it is assumed that all Ca lost in epilimnetic waters remains there as calcite. This is only true at steady state when the settling rate of calcite particles equals the diffusion rate of Ca across the metalimnion. Because the settling rate is probably larger than the diffusion rate, the calculated densities are probably maximum values.

The results for the samples collected during the October 2005 survey when the lake was stratified, are shown in Fig. 17 where density is reported versus temperature at various depths. Due to different temperatures and salinities of the water layers, the epilimnion waters are less dense than the hypolimnion waters. The densities of epilimnetic waters may increase upon cooling, moving along the density-temperature line in Figure 17, approaching those of the hypolimnetic waters at about 7°C. Attainment of this condition may trigger water overturn in the lake. This occurrence has been investigated, hypothesizing that the more superficial water layer (0-6m) reaches thermal equilibrium with the atmosphere. The calculated density of the surface layer taking into account the monthly averaged air temperatures recorded in the area, is shown in Figure 18. Because the temperatures and the densities of waters between 12 and 30 m deep appear stable in the different profiles, we assume that no significant changes occurred at depth over time. The density of the shallow layer may become higher than the density of the hypolimnetic waters, perturbing the lake zonation, when the temperature drops below 7°C. This phenomenon may occur when the atmospheric temperature remains below this value for along enough time period, as occurred in February 2005. The events of January 2002 and February 2003 may also be attributed to the same process because, in these periods, the averaged atmospheric temperature was frosty for a long time (Fig. 18).

Another way to trigger overturn is to provide heat to hypolimnetic waters, e. g. through a sudden input of hot waters at the lake bottom, but there is no evidence for such an event.

8. Organotrophic and chemosynthetic bacterial processes

Lake Averno has been affected for a long time by intermittent organic enrichment from sewages discharges (Improta et al., 2004) and the organic matter accumulated in the bottom sediments, may be considered the main cause of oxygen depletion in the water column. As oxygen becomes depleted and redox conditions change, other electron acceptors are utilized by different types of anaerobic bacteria. In lakes where the hypolimnion is anoxic for much of the stratified period, the majority of hypolimnetic metabolism occurs via anaerobic pathways (Sorokin, 1970; Houser et al., 2003). The microbial decomposition of organic matter consumes electron acceptors, produces CO_2, H_2S and CH_4, and regenerates dissolved nutrients (e.g., soluble reactive phosphorus and NH_4) at rates that are determined, in part, by the rate of organic matter mineralization. Hydrogen sulfide (H_2S), the end product of Bacterial Sulfate Reduction (SBR), is known to be highly toxic to eukaryotic organisms because it inhibits cytochrome c oxidase, the last step of the respiratory chain. It is, also, known to be able to cause fish dead in micromolar range (Bagarinao, 1992).

The vertical profiles of O_2, Eh, H_2S, CO_2 and CH_4 relative to the 27th October 2005 campaign, show an evident vertical zonation, indicating microbial processes were occurring either in the water column and/or in the sediments of Lake Averno (Figs. 2c,d and 4).

It is possible to distinguish three zones: the upper aerobic zone, down to a depth of 6 m; a second zone characterized by a rapid increase of H_2S, CO_2 and contemporaneous sharp decrease of O_2 concentration and a third anaerobic zone characterized, in near bottom water, by high concentrations either of H_2S, CO_2 and CH_4. An increase CH_4 with depth is evident, indicating decomposition of organic matter under anoxic conditions in sediments. An increase of CO_2 content with depth is also evident, but it can not be linked to an organic production, at least as main source. In fact, if the increase of CO_2 (and TDIC) with depth were associated to bacterial production a strong variation in carbon isotope composition toward very negative values should be expected (about $\delta^{13}C$ -25‰ for organic CO_2, Faure, 1986). Contrary, TDIC isotopic composition of the hypolimnetic waters remains almost constant in the water column ($\delta^{13}C$ -6.1±0.2 ‰; TDIC 7.2 ±0.2 mM) until the depth of the 33 m. Furthermore the bottom sample, which is characterized by the higher TDIC content (14.5 mM), shows a more positive isotopic value ($\delta^{13}C$ -5.4‰), excluding a significant addition of organic carbon and again suggesting a hydrothermal input in the lake bottom water.

In the upper zone there is a clear O_2 maximum between -3 and -9 m resulting from the intensive photosynthesis of phytoplankton stratified at the thermo-cline and the presence of light and nutrients, in particular ammonium ion, transported to this zone from the deep layers (Fig. 3d) (Sorokin, 1970). Moreover the concurrent depletion of methane and oxygen between -9 and -6 m is the effect of aerobic methane oxidation. In the second zone, at -18 m, there is a H_2S maximum (420 μmol/l), probably produced by an intense rate of BSR. This microbial process is fed by the supply of fresh organic matter from the upper zone where intensive biosynthesis by bacteria, both the photosynthetic anoxygenic purple bacteria and the chemosynthetic colorless sulfur bacteria can occur (Sorokin, 1970; Ivanov et al., 2001). In fact, a layer of water of characteristic pink color was observed during the 13th October 1999 campaign owing to the presence of these bacteria.

Moreover a drop of methane concentration from 247 μM at -18 m depth to 103 μM a -15 m is observed. The high negative correlation (Spearman Rank = -0.80; n=12; $p<0.05$) between methane and sulfate concentrations could support the hypothesis of anaerobic oxidation of methane with concurrent sulfate reduction (Ivanov et al., 1989; Treude et al., 2005).

Below -18 m there is a third hydro chemical zone characterized by the highest concentrations of H_2S, CO_2 and CH_4 at the bottom. The shape of CH_4, CO_2 and H_2S profiles as well as the steps in the redox variation suggest both the existence of a biological/chemical mechanism hiding the slow diffusion of these substances from the bottom to the above water layers and a density separation of deepest waters due to higher salt content.

The importance of BSR in lakes depends on the rate of organic input and the availability of sulfate. The threshold sulfate concentration below which no BSR rate occurs have been found between 8 and 40 μM (Holmer and Storkholm, 2001). In the lake Averno the sulfate content attains a very high concentration (>1.8mM) and it remains almost constant along the water column, though shows a slight decrease at the thermocline, and a sharp decrease at the bottom where it is reasonably to hypothesize an intensive BSR activity (Fig. 3b).

If it assumed that the bottom waters are in steady state, the consumption of sulfate due to the BSR activity must be balanced by diffusion from the upper layers. Fick's first law of diffusion was used to determine the rate of water sulfate diffusion and consequently the BSR rate (Sinke et al., 1992). In order to estimate the diffusion gradient it is used a simple linear equation which resulted in a sulfate concentration gradient of 21 $\mu mol\ l^{-1}\ cm^{-4}$. Since the molecular diffusion coefficient of SO_4^{2-} corrected for in situ temperature (9°C) was of $7 \times 10^{-6}\ cm^{-2}s^{-1}$, (Li and Gregory, 1974) sulfate reduction rate of 14 $\mu mol\ m^{-2}\ day^{-1}$ has been obtained.

On the other hand if the Fick's first law of diffusion is applied to H_2S gradient (Purdy et al., 2001), considering its molecular diffusion coefficient of 11 x 10^{-5} $cm^{-2}s^{-1}$ (Tamimi et al., 1994), BSR rate accounts for 22 μmol m^{-2} day^{-1}, that is close to the rate resulting by SO_4 gradient.

During the February 2005 campaign the vertical profiles show a breaking of the vertical stratification: methane is present up to the surface, oxygen is absent along the whole water column, and a redox discontinuity remains only in the bottom waters. Unfortunately sulfide data were not recorded at this time but the presence of sulfide up to the surface can be inferred from the white colour of water of lake Averno observed during the fish kill. This phenomenon of white waters is known as caused by the sudden arrival of high content of H_2S (10-20 mg/l) in the water mass oxygen saturated with the transformation of sulfide in molecular sulfur (S_0) and drop in pH (<7.5) (Sorokin, 1970; Castel et. al., 1996) according to the balance equation $H_2S + \frac{1}{2} O_2 \rightarrow S^o + H_2O$.

The bulk of these results strongly support the hypothesis that the fish kill was caused by the breaking of the thermal stratification, and resulting rise of toxic levels of H_2S.

Conclusion

The chemical and isotopic composition of Averno waters suggests an origin by mixing of shallow waters and a Na-Cl-rich hydrothermal component, showing similar composition to that of the groundwaters present in the area. The isotopic composition of Total Dissolved Inorganic Carbon also indicates a mixing process between a shallow organic source and a hydrothermal component. An active evaporation process is inferred by isotopic composition of lake waters, indicating a fraction of evaporation of inflowing water of about 20%. Non-reactive dissolved gas species (Ar, N_2, He) also support a hydrothermal input in the lake waters, in particular the dissolved gas appears to be controlled by addition in the atmospheric equilibrated waters (infiltrating waters) of fluids with a composition similar to that emitted at Solfatara fumarolic field.

Because SO_4 is strongly affected by microbial activity the lowering of SO_4 content, and the increase of CH_4 content shown by lake water with depth, in particular for the waters sampled at lake bottom, suggest the occurrence of bacterial processes under anoxic conditions in sediments and in the water column.

In fact, the vertical profiles of the 27th October 2005 campaign show an evident vertical zonation of the microbial processes occurring either in the water column and/or in the sediments. Three zones can be distinguished: the upper aerobic zone, down to a depth of 6 m; a second zone characterized by a rapid increase of H_2S, CO_2 and contemporaneous sharp decrease of O_2 concentration and a third anaerobic zone characterized, in near bottom water, by high concentrations of H_2S, CO_2 and CH_4. Decomposition of organic matter under anoxic condition in bottom sediments has resulted in increased levels of CH_4 with depth. Although, bacterial process may also produce CO_2, the increase of TDIC with depth shown by the lake waters can not be linked, at least as the main source, to such a process. In fact, TDIC carbon isotopic composition of the bottom sample, characterized by the higher TDIC content (14.5 mM), show a more positive isotopic value ($\delta^{13}C$ -5.4‰) with respect to the hypolimnetic waters ($\delta^{13}C$ -6.1±0.2 ‰; TDIC 7.2 ±0.2 mM), excluding a significant addition of isotopically light organic carbon and again suggesting a hydrothermal input in the lake bottom water.

Sulfate reduction and methanogenetic processes coexist and play a pivotal role in the anaerobic environment of Lake Averno. The BSR activity has been estimated through the application of Fick's first law to the sulfate and sulfide concentrations gradient and accounts for about 14 and 22 $\mu mol\ m^{-2} day^{-1}$ respectively.

Based on the vertical distribution of physico-chemical and isotopic parameters of lake waters surveyed on 11th February 2005, after the fish kill event occurred, the lake appears unstratified, showing an almost homogeneous composition in the entire water column, indicating lake waters had overturned. The uprising of reduced and sulfide-bearing waters can be considered the responsible agents of fish kill, due to the H_2S toxicity and to consumption of dissolved oxygen. A strong proof in favor of this theory is the phenomenon of white waters during the fish kill: "white water" is known to be caused by the sudden arrival of high content of H_2S in the oxygen zone with the transformation of sulfide in molecular sulfur (S_0) and drop in pH (<7.5). A different picture arises from data collected on 27th October 2005 eight months later when the Lake Averno appears stratified showing an oxic epilimnion, ranging from the surface to a depth of about 6 m, and an anoxic hypolimnion extending from this depth to the lake bottom.

Vertical changes in the density of lake waters indicate that overturn may be triggered by cooling of shallow waters below 7°C. This is a possible phenomenon in winter periods if atmospheric temperatures remain cool for enough time, as occurred in February 2005. The events of January 2002 and February 2003 may also be attributed to the same process.

The bulk of these results strongly support the hypothesis that the fish kill has been caused by the breaking of the thermal stratification, followed by the rise of toxic levels of H_2S from lake bottom to surface waters.

However, CH_4-producing bacteria in lake sediments may generate a CH_4 excess in deep lake waters if the producing rate is higher than the diffusion rate in the uppermost water layers. The accumulation of CH_4 in deep water, also due to its low solubility may increase total gas pressure and trigger gas-driven overturn perturbing lake stratification. Unfortunately, no data is available to calculate the CH_4 production rate. At the time of last survey total gas pressure (0.9 to 1.4 bar) in lake waters was always below the hydrostatic pressure excluding, at least at this time, the possibility of a limnic eruption.

Further investigations in order to establish the bacterial CH_4 producing rate and monitoring of relevant chemical and physical parameters and dissolved gas composition of Lake Averno waters should be carried out on a regular basis to better define the triggering mechanism of recorded events.

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References

Aguilera, E., Chiodini, G., Cioni, R., Guidi, M., Marini, L. and Raco, B., 2000. Water chemistry of Lake Quilotoa (Ecuador) and assessment of natural hazards. J. Volcanol. Geotherm. Res., 97(1-4): 271-285.

Aiuppa, A., Avino, R., Brusca, L., Caliro, S., Chiodini, G., D'Alessandro, W., Favara, R., Federico, C., Ginevra, W., Inguaggiato, S., Longo, M., Pecoraino, G. and Valenza, M., 2006. Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: Insights from island of Ischia and Phlegrean Fields (Campanian Volcanic Province, Italy). Chem. Geol., 229(4): 313-330.

Bagarinao T., 1992. Sulfide as an environmental factor and toxicant: tolerance and adaptations in aquatic organisms. Aquatic Toxicology 24: 21-62.

Baldi, P., Ferrara, G. C. and Panichi, C. (1975) Geothermal research in western Campania (southern Italy): chemical and isotopic studies of thermal fluids in the Campi Flegrei. Proc. 2nd U.N. Symp. on Development and Use of Geothermal Resources, San Francisco, 687- 697.

Bolognesi, L., Noto, P. and Nuti, S. (1986) Studio chimico ed isotopico della solfatara di Pozzuoli: ipotesi sull'origine e sulle temperature profonde dei fluidi. Rend. Soc. It. Mineral. Petrol. 41(2), 281-295.

Caliro, S., 2004. Volcanic and non volcanic degassing in Campania region (southern Italy). Ph. D. Thesis Thesis, Univerisità degli Studi di Napoli "Federico II", Naples, 177 pp.

Caliro, S., Chiodini, G., Avino, R., Cardellini, C. and Frondini, F., 2005. Volcanic degassing at Somma-Vesuvio (Italy) inferred by chemical and isotopic signatures of ground water. Appl. Geochem., 20(6): 1060-1076.

Caliro, S., Chiodini, G., Moretti, R., Avino, R., Granieri, D., Russo, M. and Fiebig, J., 2007. The origin of the fumaroles of La Solfatara (Campi Flegrei, South Italy). Geochimica et Cosmochimica Acta, 71(12): 3040.

Castel, J., Caumette, P. and Herbert, R., 1996. Eutrophication gradients in coastal lagoons as exemplified by the Bassin d'Archachon and the Etang du Prevost. Hydrobiologia, 329: ix-xxviii

Chiodini, G., 1996. Gases dissolved in groundwaters: analytical methods and examples of applications in central Italy. In: L. Marini and G. Ottonello (Editors), Rome Seminar on Environmental Geochemistry. Pacini Editore, Castelnuovo d Porto, Rome (Italy), pp. 135-148.

Chiodini, G., Frondini, F., Cardellini, C., Granieri, D., Marini, L. and Ventura, G., 2001. CO_2 degassing and energy release at Solfatara Volcano, Campi Flegrei, Italy. J. Geophys. Res., 106(8): 16,213-16,221.

Craig, H. and Gordon, L.I., 1965. Deuterium and oxygen 18 variations in the ocean and the marine atmosphere. Stable isotopes oceanographic studies and paleotemperatures, Spoleto Conferences in Nuclear Geology. CNR, Lab. Geologia Nucleare, Pisa, Italy, pp. 1-130.

D'Argenio, B., Pescatore, T.S. and Scandone, P., 1973. Schema geologico dell'Appennino Meridionale. Acc. Naz. Lincei, Quad. 183: 49-72.

Deines, P., Langmuir, D. and Harmon, R.S., 1974. Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. Geochim. Cosmochim. Acta, 38: 1147-1164.

Deino, A.L., Orsi, G., De Vita, S. and Piochi, M., 2004. The age of the Neapolitan Yellow Tuff caldera-forming eruption (Campi Flegrei Caldera, Italy) assessed by ^{40}Ar/ ^{39}Ar dating method. Journal of Volcanology and Geothermal Research, 133(1-4): 157-170.

De Vita, S., Di Vito, M.A., Isaia, R., Orsi, G., Civetta, L., Marotta, E., Pappalardo, L., Piochi, M., D'Antonio, M., Di Cesare, T., Fisher, R.V., Deino, A., Southon, J. and Ort, M., 1998. The Agnano-Monte Spina eruption; the largest explosive event of the last 5 ka in the densely populated, restless Campi Flegrei caldera. Officine grafiche napoletane Francesco Giannini & Figli s.p.a., Naples, Italy (ITA).

De Vita, S., Orsi, G., Civetta, L., Carandente, A., D'Antonio, M., Deino, A., Di Cesare, T., Di Vito, M.A., Fisher, R.V., Isaia, R., Marotta, E., Necco, A., Ort, M.H., Pappalardo, L., Piochi, M. and Southon, J., 1999. The Agnano-Monte Spina eruption (4100 years BP) in the restless Campi Flegrei Caldera (Italy). J. Volcanol. Geotherm. Res., 91(2-4): 269-301.

Dellino, P., Isaia, R., La Volpe, L. and Orsi, G., 2001. Statistical analysis of textural data from complex pyroclastic sequences; implications for fragmentation processes of the Agnano-Monte Spina Tephra (4.1 ka), Phlegraean Fields, southern Italy. Bull. Volcanol., 63(7): 443-461.

Di Vito, M.A., Lirer, L., Mastrolorenzo, G. and Rolandi, G., 1987. The Monte Nuovo eruption (Campi Flegrei, Italy). Bull. Volcanol., 49: 608-615.

Faure, G., 1986. Inorganic geochemistry. Macmillan Pub. Com, 627. pp.

Fedele, F., Giaccio, B., Isaia, R., Orsi, G., Carroll, M., and Scaillet, B., 2004. Potential climatic impact of the Campanian ignimbrite eruption (ca. 40,000 yr BP) and the middle to upper Palaeolithic change in Europe. International Geological Congress, Abstracts = Congres Geologique International, Resumes, 32, Part 2: 1358.

Gat, J.R., 1981. Lakes., In: Stable Isotope Hydrology. Deuterium and Oxygen-18 in the Water Cycle. Technical reports Series, 210. IAEA Vienna, 203-222 pp.

Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrological cycle. Annu. Rev. Earth Planet. Sci., 24: 225-262.

Giggenbach, W.F. and Stewart, M.K., 1982. Processes controlling the isotopic composition of steam and water discharges from steam vents and steam-heated pools in geothermal areas. Geothermics, 11: 71–80.

Gonfiantini, R., 1986. Environmental isotopes in lake studies, In: Fritz, P., Fontes, J.Ch. (Eds.), Handbook of Environmental Isotope Geochemistry. Vol. 2, The Terrestrial Environment, B. Elsevier, Amsterdam, 113-168 pp.

Guglielminetti, M., 1986. Mofete geothermal fields. Geothermics, 15: 781-790.

Holmer, M. and Storkholm, P., 2001. Sulphate reduction and sulphur cycling in lake sediments: a review. Freshwater Biology, 46: 431-451.

Houser, J.N., Bade, D.L., Cole, J.D. and Pace, M.L., 2003. The dual influences of dissolved organic carbon hypolimnetic metabolism: organic substrate and photosyntetic reduction. Biogeochemistry, 64: 247-269.

Improta, C., Andini S., Ferrara L., 2004. Chemical and ecotoxicological characterization of Averno Lake. Bull. Environ. Contam. Toxicol. 72: 472-481.

Ivanov, M. V., Lein, A. Yu., Reeburgh, M. S. and Skyring, G. W., 1989. Interaction of sulphur and carbon cycles in marine sediments. In: Brimblecombe, P. and Lein, A. Yu. (Eds). Evolution of the Global Biogeochemical Sulphur Cycle. Wiley, Chichester, pp. 125-79.

Ivanov, M.V., Rusanov, I.I., Pimenov, N.V., Bairamov, I.t., Yusupov, S.K., Savvichev, A.S., Lein, Y.A. and Sapozhnikov, V.V., 2001. Microbial Processes of the Carbon and Sulfur Cycles in Lake Mogil'noe. Microbiology, 70(5): 675-686.

Li, Y-H and Gregory, S., 1974. Diffusion of ions in sea water and in deep sea sediments. Geochim. Cosmochim. Acta 39:703-714

Keenan, J.H., Keyes, P.G. and Hill, P.G., 1969. Steam Tables: Thermodynamic Troperties of Water Including Vapor, Liquid, and Solid Phases. John Wiley, New York, 162 pp.

Matsubaya, O. and Sakai, H., 1978. D/H and $^{18}O/^{16}O$ fractionation factors in evaporation of water at 60 and 80°C. Geochem. J., 12: 121-126.

Orsi, G., de Vita, S. and Di Vito, M., 1996. The restless, resurgent Campi Flegrei nested caldera (Italy): constraints on evolution and configuration. J. Volcanol. Geotherm. Res., 74: 179-214.

Orsi, G., Di Vito, M.A. and Isaia, R., 2004. Volcanic hazard assessment at the restless Campi Flegrei caldera. Bull. Volcanol., 66: 514-530.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 310 p.

Purdy, K.J., Hawes I., Bryant, Fallik A.E., and Nedwell D.B., 2001. Estimates of sulphate reduction rates in Lake Vanda, Antarctica support the proposed recent history of the lake. Antarctic Science, 13: 393-399.

Rowe Jr, G.L., 1994. Oxygen, hydrogen and sulfur isotope systematics of the crater lake system of Poas volcano, Costa Rica. Geochem. J., 28: 263-287.

Shock, E.L. and Helgeson, H.C., 1988. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C. Geochim. Cosmochim. Acta, 52: 2009-2036.

Shock, E.L., Helgeson, H.C. and Sverjensky, D.A., 1989. Calculations of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: standard partila molal properties of inorganic neutral species. Geochim. Cosmochim. Acta, 53: 2157-2183.

Sinke, A.J.C., Cornelese, A.A., Cappenberg, T.E., and Zehnder, A.J.B., 1992. Seasonal-variation in sulphate reduction and methanogenesis in peaty sediment of eutrophic Lake Loosdrecht, The Netherlands. Biogeochemistry, 16: 43-61

Sorokin, Y.I., 1970. Interrelations between sulphur and carbon turnover in leromintic lakes. Arch.

Hydrobiol., 66: 391-446.

Tamimi, A., Rinker E.B., Sandall O.C., 1994. Diffusion Coefficients for Hydrogen Sulfide, Carbon Dioxide, and Nitrous Oxide in Water over the Temperature Range 293-368 K. J. Chem. Eng. Data , 39: 330-332.

Treude T., Niggemann J., Kallmeyer J., Wintersteller P., Schubert, C. J., Boetius A., Jørgensen1 B.B., 2005. Anaerobic oxidation of methane and sulfate reductionalong the Chilean continental margin. Geochim. Cosmochim. Acta, 69 (11): 2767–2779.

Valentino, G.M., Cortecci, G., Franco, E. and Stanzione, D., 1999. Chemical and isotopic compositions of minerals and waters from the Campi Flegrei volcanic system, Naples, Italy. J. Volcanol. Geotherm. Res., 91(2-4): 329-344.

Valentino, G.M. and Stanzione, D., 2003. Source processes of the thermal waters from the Phlegraean Fields (Naples, Italy) by means of the study of selected minor and trace elements distribution. Chem. Geol., 194(4): 245-274.

Valentino, G.M. and Stanzione, D., 2004. Geochemical monitoring of the thermal waters of the Phlegraean Fields. J. Volcanol. Geotherm. Res., 133(1-4): 261-289.

Varekamp, J.C. and Kreulen, R., 2000. The stable isotope geochemistry of volcanic lakes, with examples from Indonesia. J. Volcanol. Geotherm. Res., 97(1-4): 309-327.

Wilhelm, E., Battino, R. and Wilcock, R.J., 1977. Low-pressure solubility of gases in liquid water. Chem. Rev., 77(2): 219-262.

Zimanowski, B., Wohletz, K., Dellino, P. and Buettner, R., 2003. The volcanic ash problem. J. Volcanol. Geotherm. Res., 122(1-2): 1-5.

Sample	Date	T °C	pH	Eh (mV)	E.Cond.	Depth	HCO$_3$	F	Cl	SO$_4$	Li	Na	NH$_4$	K	Mg	Ca	δD	δ^{18}O	si_Calc	si_Fluorit
AV1	11/02/05	9.50	7.54	125	2666	1	401	6.1	550	186	0.31	517	7.6	53.8	13.5	25.6	-10.31	-1.16	-0.31	0.15
AV3	11/02/05	9.33	7.61	91	2694	3	402	6.6	561	166	0.36	520	4.3	55.2	13.4	25.8	-10.18	-1.19	-0.23	0.23
AV6	11/02/05	9.32	7.63	76	2712	6	404	7.1	576	179	0.38	517	4.0	57.1	15.0	25.4	-10.07	-1.18	-0.22	0.28
AV9	11/02/05	9.32	7.65	64	2730	9	403	3.4	565	177	0.34	522	5.8	54.4	13.2	25.2	-9.96	-1.21	-0.20	-0.36
AV15	11/02/05	9.31	7.68	48	2747	15	403	4.1	562	184	0.46	522	5.0	56.3	14.2	25.8	-9.42	-1.19	-0.17	-0.20
AV20	11/02/05	9.31	7.68	44	2758	20	404	2.4	566	165	0.33	523	4.2	57.0	13.8	25.5	-13.26	-1.17	-0.16	-0.65
AV25	11/02/05	9.31	7.70	45	2766	25	405	5.5	558	170	0.31	526	6.0	59.0	14.0	25.7	-12.24	-1.19	-0.14	0.07
AV31	11/02/05	9.73	7.16	-97	2942	31	472	4.9	592	175	0.36	551	12.0	64.2	16.0	35.8	-10.30	-1.22	-0.47	0.09

Sample	Date	CO$_2$m/l	pCO2	pCO2(eq)	Ar m/l	pAr	O$_2$ m/l	pO$_2$	N$_2$ m/l	pN$_2$	CH$_4$ m/l	pCH$_4$	H$_2$S m/l	pH$_2$S	He m/l	pHe	P$_{TOT}$	δ^{13}CTDIC	TDIC mol/l
AV1	11/02/05	4.24E-04	7.8	8.7	1.93E-05	10.23	1.66E-06	1.0	7.54E-04	885	1.36E-04	69.3	n.a.	n.a.	9.83E-09	0.0245	973	-5.32	7.03E-03
AV3	11/02/05	4.52E-04	8.3	7.3	2.22E-05	11.69	2.80E-06	1.6	8.60E-04	1005	2.02E-04	102.6	n.a.	n.a.	8.51E-09	0.0212	1130	n.a.	6.98E-03
AV6	11/02/05	3.47E-04	6.4	7.0	1.73E-05	9.10	1.35E-06	0.8	6.28E-04	733	1.59E-04	80.6	n.a.	n.a.	1.18E-08	0.0295	830	-5.85	7.00E-03
AV9	11/02/05	4.27E-04	7.8	6.6	2.01E-05	10.58	1.47E-06	0.8	7.48E-04	874	2.10E-04	106.5	n.a.	n.a.	7.41E-09	0.0184	1000	n.a.	6.95E-03
AV15	11/02/05	4.40E-04	8.1	6.3	1.98E-05	10.42	1.70E-06	1.0	7.20E-04	841	2.01E-04	102.2	n.a.	n.a.	7.93E-09	0.0197	962	-5.30	6.94E-03
AV20	11/02/05	4.48E-04	8.2	6.2	1.96E-05	10.33	1.31E-06	0.8	7.70E-04	899	2.19E-04	111.1	n.a.	n.a.	8.95E-09	0.0223	1030	n.a.	6.95E-03
AV25	11/02/05	3.78E-04	6.9	6.0	1.88E-05	9.93	1.17E-06	0.7	7.20E-04	841	2.02E-04	102.7	n.a.	n.a.	9.25E-09	0.0230	961	-6.07	6.95E-03
AV31	11/02/05	8.47E-04	15.8	24.3	1.87E-05	9.97	5.87E-07	0.3	7.33E-04	864	8.62E-04	442.7	n.a.	n.a.	1.49E-08	0.0371	1333	n.a.	9.05E-03

Sample	Date	T °C	pH	Eh (mV)	E.Cond.	Depth	HCO$_3$	F	Cl	SO$_4$	Li	Na	NH$_4$	K	Mg	Ca	δD	δ^{18}O	si_Calc	si_Fluorit
AV1	27/10/05	20.72	8.82	178	2742	1	368	3.8	555	178	0.51	541	n.d.	56.7	18.2	34.1	-5.29	-0.52	1.13	-0.36
AV3	27/10/05	20.55	8.84	177	2715	3	362	5.4	542	179	0.56	551	n.d.	54.7	20.5	35.1	-11.11	-0.51	1.15	-0.03
AV6	27/10/05	19.99	8.83	177	2733	6	380	4.4	555	177	0.42	553	n.d.	62.1	20.3	37.9	-8.89	-0.62	1.19	-0.17
AV9	27/10/05	12.4	7.56	-113	2782	9	416	5.1	526	166	0.39	513	7.9	53.0	17.2	45.6	-14.20	-1.39	0.03	0.20
AV12	27/10/05	9.53	7.57	-105	2784	12	401	4.6	541	164	0.32	514	5.7	54.0	17.8	47.1	-12.69	-1.34	-0.01	0.16
AV15	27/10/05	9.12	7.59	-102	2755	15	400	5.0	525	164	0.34	536	5.9	53.1	19.8	51.0	-13.12	-1.39	0.03	0.28
AV18	27/10/05	9.07	7.53	-127	2687	18	430	4.5	546	171	0.54	564	11.6	54.9	19.0	51.8	-13.09	-1.25	0.01	0.18
AV21	27/10/05	9.07	7.54	-132	2519	21	402	3.3	537	164	0.34	526	7.0	53.7	20.6	48.6	-12.35	-1.35	-0.03	-0.11
AV24	27/10/05	9.06	7.55	-136	2559	24	427	4.9	535	162	0.36	537	7.7	56.7	18.9	49.2	-10.86	-1.29	0.01	0.24
AV27	27/10/05	9.06	7.56	-142	2616	27	422	4.4	550	163	0.41	533	6.3	54.8	19.0	50.7	-12.02	-1.37	0.02	0.15
AV30	27/10/05	9.05	7.57	-149	2855	30	418	4.8	539	165	0.35	537	5.2	54.5	19.4	49.3	-13.06	-1.40	0.02	0.22
AV33	27/10/05	9.42	7.05	-241	3706	33	725	4.1	618	99	0.49	566	36.7	68.6	22.7	74.3	-12.45	-1.50	-0.09	0.24

Sample	Date	CO$_2$m/l	pCO2	pCO2(eq)	Ar m/l	pAr	O$_2$ m/l	pO$_2$	N$_2$ m/l	pN$_2$	CH$_4$ m/l	pCH$_4$	H$_2$S m/l	pH$_2$S	He m/l	pHe	P$_{TOT}$	δ^{13}CTDIC	TDIC mol/l
AV1	27/10/05	6.71E-05	1.8	0.42	1.86E-05	12.35	1.85E-04	135.0	7.05E-04	1015	4.54E-07	0.3	n.d.	n.d.	5.81E-09	0.0149	1165	-2.91	5.66E-03
AV3	27/10/05	1.45E-04	3.8	0.39	2.08E-05	13.77	6.58E-06	4.8	7.89E-04	1133	5.62E-07	0.4	n.d.	n.d.	4.99E-09	0.0128	1156	-2.98	5.54E-03
AV6	27/10/05	5.84E-05	1.5	0.41	1.49E-05	9.77	9.43E-05	67.8	5.58E-04	795	3.57E-07	0.2	n.d.	n.d.	6.19E-09	0.0159	874	-2.72	5.84E-03
AV9	27/10/05	4.40E-04	8.9	8.8	1.79E-05	10.08	8.39E-07	0.5	6.54E-04	813	9.42E-05	51.7	n.d.	n.d.	5.42E-09	0.0136	884	-6.35	7.24E-03
AV12	27/10/05	4.57E-04	8.4	8.0	1.84E-05	9.72	1.49E-06	0.9	6.89E-04	809	1.01E-04	51.7	n.d.	n.d.	4.05E-09	0.0101	880	-6.36	7.00E-03
AV15	27/10/05	4.48E-04	8.2	7.6	2.01E-05	10.52	1.00E-06	0.6	7.57E-04	881	1.03E-04	52.2	n.d.	n.d.	4.62E-09	0.0115	952	-6.06	6.97E-03
AV18	27/10/05	1.61E-03	29.3	9.3	1.91E-05	10.01	n.d.	n.d.	7.16E-04	833	2.25E-04	113.8	4.20E-04	2.68	6.28E-09	0.0156	988	-5.83	7.55E-03
AV21	27/10/05	5.01E-04	9.1	8.5	1.74E-05	9.12	3.62E-07	0.2	6.50E-04	756	2.48E-04	125.1	n.d.	n.d.	5.59E-09	0.0139	900	-6.17	7.05E-03
AV24	27/10/05	5.13E-04	9.3	8.9	1.99E-05	10.40	n.d.	n.d.	7.02E-04	816	2.59E-04	131.0	n.d.	n.d.	4.55E-09	0.0113	967	-5.98	7.48E-03
AV27	27/10/05	6.79E-04	12.3	8.6	1.87E-05	9.77	n.d.	n.d.	6.84E-04	795	2.77E-04	140.0	1.73E-05	0.11	3.41E-09	0.0085	957	-6.36	7.39E-03
AV30	27/10/05	5.53E-04	10.0	8.3	1.81E-05	9.50	n.d.	n.d.	6.80E-04	790	2.71E-04	136.8	2.60E-06	0.02	5.20E-09	0.0129	947	-5.92	7.29E-03
AV33	27/10/05	2.29E-03	42.2	47.4	1.00E-05	5.29	n.d.	n.d.	3.05E-04	358	2.01E-03	1026	7.08E-04	4.56	3.17E-09	0.0079	1436	-5.42	1.45E-02

Table 1 Chemical-physical parameters and analytical results of the sampled water during the two surveys of February and October 2005. Chemical concentrations of ions are in mg/kg, partial pressures of dissolved gases are in mill bar, isotopic composition are in delta notation per mill vs. V-SMOW for hydrogen and oxygen and vs. PDB for carbon. Saturation indexes of calcite and fluorite and pCO$_{2(eq)}$ have been computed by means of PHREQC code (Parkhurst and Appelo, 1999)

Figure captions

Fig. 1. Sketch map of the Campi Flegrei caldera. Major structural features and the location of Lake Averno are indicated.

Fig. 2. Vertical profiles of (a) temperature, (b) pH, (c) Eh in mV, (d) O_2 partial pressure, in Lake Averno waters relative to different surveys. In spite to the almost homogeneous composition in the entire water column relative to the February 11th 2005 survey, during the October 27th 2005 survey the Lake appears stratified showing an oxic epilimnion, ranging from the surface to a depth of about 6 m, and an anoxic hypolimnion extending to the lake bottom

Fig. 3. Vertical profiles of concentration expressed in mg/kg of: (a) HCO_3 , (b) SO_4, (c) Ca, (d) NH_4, in Lake Averno waters relative to the February 11th 2005 and the October 27th 2005 surveys.

Fig. 4 Vertical profiles of molar concentrations of N_2, O_2, Ar, CO_2, CH_4, H_2S and He in Lake Averno waters, relative to surveys carried out on (a) February 11th 2005 and on (b) October 27th 2005.

Fig. 5. Vertical profiles of CH_4 partial pressure relative to February and October 2005 surveys. In both profiles, higher pressures are reached at Lake bottom.

Fig. 6. Vertical profiles of CO_2 partial pressure relative to February and October 2005 surveys. White symbols refer to pCO_2 values of measured dissolved gases, while black symbols refer to pCO_2 values computed on the basis of chemical composition, pH and temperature of the waters assuming equilibrium conditions among dissolved carbonate species.

Fig. 7. N_2 vs. Ar molar contents of the dissolved gas of Lake Averno waters. The expected composition of meteoric waters in equilibrium with air at temperatures of 0 – 15°C and pressures of 1 bar is reported as reference. Only the bottom sample of October 2005 survey is significantly depleted in atmospheric components.

Fig. 8. Vertical profiles of total gas pressure relative to February and October 2005 surveys. Pressures are always below the hydrostatic pressure at these times.

Fig. 9. Ternary diagram of non reactive gas species Ar, N_2, He (relative concentrations in mol/l). in the diagram dissolved gas composition of groundwaters and thermal waters of Campi Flegrei area (Caliro, 2004) are reported for comparative purposes. The position of samples in the diagram suggests a hydrothermal input in lake waters.

Fig. 10. Ternary diagram of TDIC, CH_4 and N_2 relative molar concentration. In the diagram composition of the hydrothermal component (Caliro et al., 2007) and the composition of ASW are also reported.

Fig. 11. Triangular SO_4-HCO_3-Cl diagram for Lake Averno waters (values are in mg/kg). composition of groundwaters and thermal waters of Campi Flegrei area are reported for comparative purposes.

Fig. 12. Vertical profiles of δ^{18}O of Lake waters relative to February and October 2005 surveys. The homogeneous compositions of the water column in the February samples, suggest water overturn at this time.

Fig. 13. δD vs. δ^{18}O plot of Averno waters relative to February and October 2005 surveys. In the diagram the computed evaporation evolution showing a slope of about 5 (see text) is also reported together with the local meteoric water line.

Fig. 14. δ^{18}O vs. Cl content of Lake waters. Composition of groundwaters and thermal waters of Campi Flegrei area are reported for comparison together with the mixing between meteoric water and hydrothermal component, the evaporation evolution of the lake waters and the possible composition of the hydrothermal input inferred by the bottom water layer composition.

Fig. 15. Diagram of Total Dissolved Inorganic Carbon (TDIC) and its carbon isotopic composition (δ^{13}C ‰) of the sampled lake waters. Groundwaters of the Campi Flegrei and the mixing process between a shallow component with organic signature and a deep hydrothermal component (Caliro, 2004) are also reported for comparison. Lake waters are also compatible with the same mixing process.

Fig. 16. Calcite Saturation Index along the vertical profiles relative to February and October 2005 surveys.

Fig. 17. Density vs. Temperature diagram for the samples collected on October 2005 survey. The line representing the density variation of epilimnetic waters with temperature is also reported. The density of epilimnion may approach that of hypolimnion for temperature lower than 7°C, triggering water overturn.

Fig. 18. Chronogram of density variation of the epilimnion computed considering the monthly averaged temperature of the area. Densities of 12-30 m deep layers, of the bottom layer and the occurrences of fish kill events are also reported.

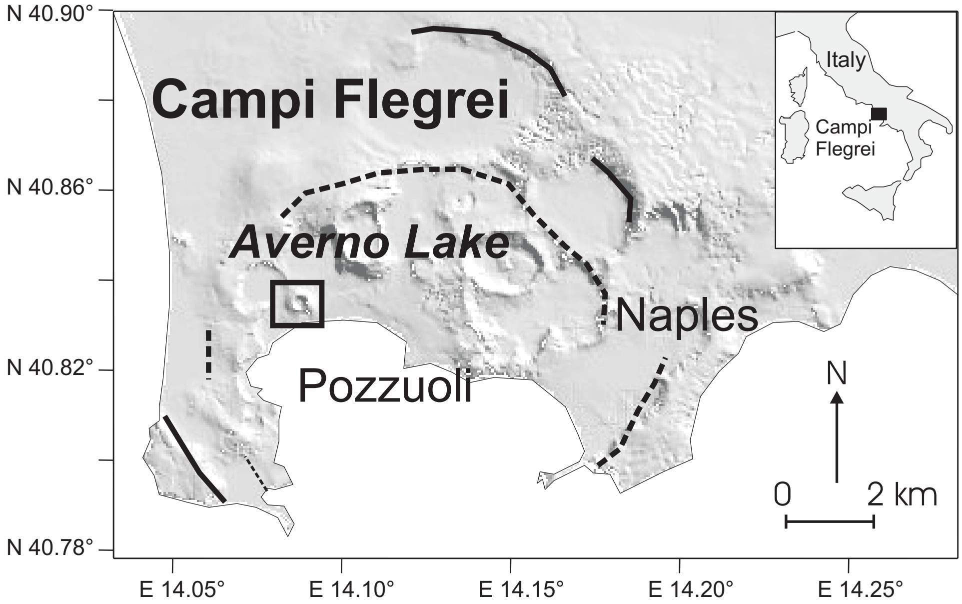
N 40.90°
N 40.86°
N 40.82°
N 40.78°
E 14.05°
E 14.10°
E 14.15°
E 14.20°
E 14.25°
Campi Flegrei
Averno Lake
Naples
Pozzuoli
N
0
2 km
Italy
Campi Flegrei

Fig 1

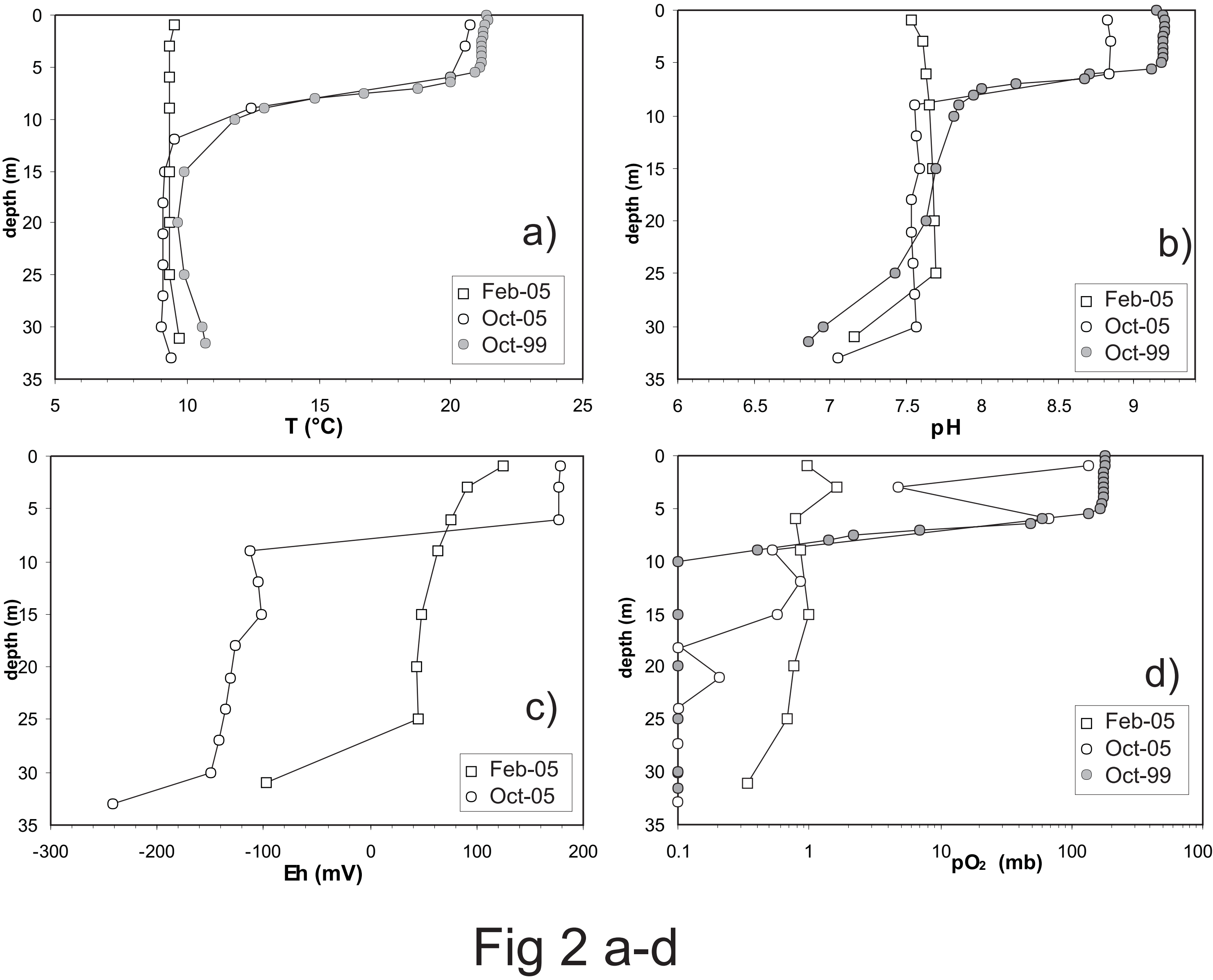
a)
depth (m)
T (°C)
Feb-05
Oct-05
Oct-99
b)
depth (m)
pH
Feb-05
Oct-05
Oct-99
c)
depth (m)
Eh (mV)
Feb-05
Oct-05
d)
depth (m)
pO2 (mb)
Feb-05
Oct-05
Oct-99

Fig 2 a-d

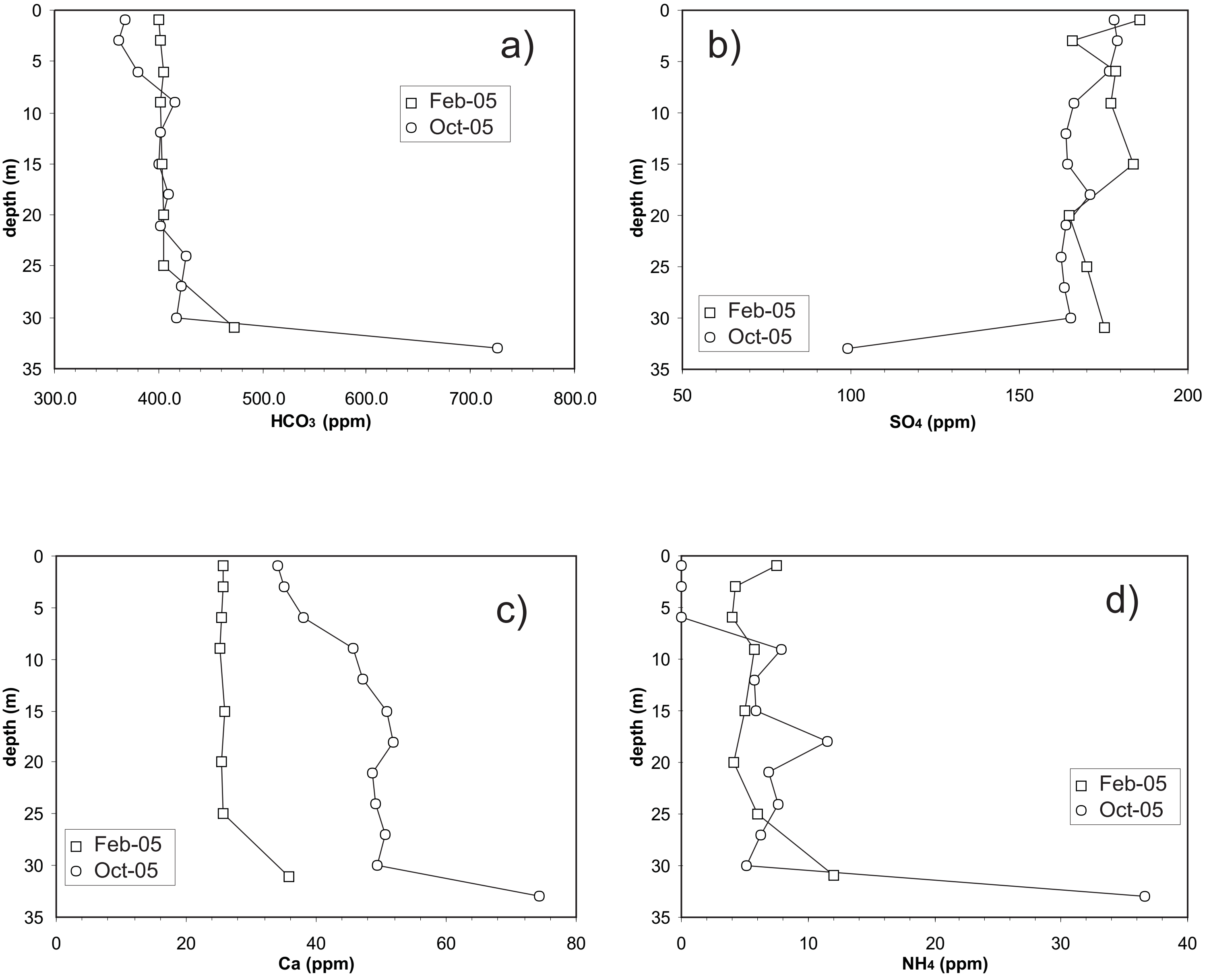
a)
Feb-05
Oct-05
depth (m)
0
5
10
15
20
25
30
35
300.0
400.0
500.0
600.0
700.0
800.0
HCO3 (ppm)
b)
Feb-05
Oct-05
depth (m)
50
100
150
200
SO4 (ppm)
c)
Feb-05
Oct-05
depth (m)
0
20
40
60
80
Ca (ppm)
d)
Feb-05
Oct-05
depth (m)
0
10
20
30
40
NH4 (ppm)

Fig 3a-d

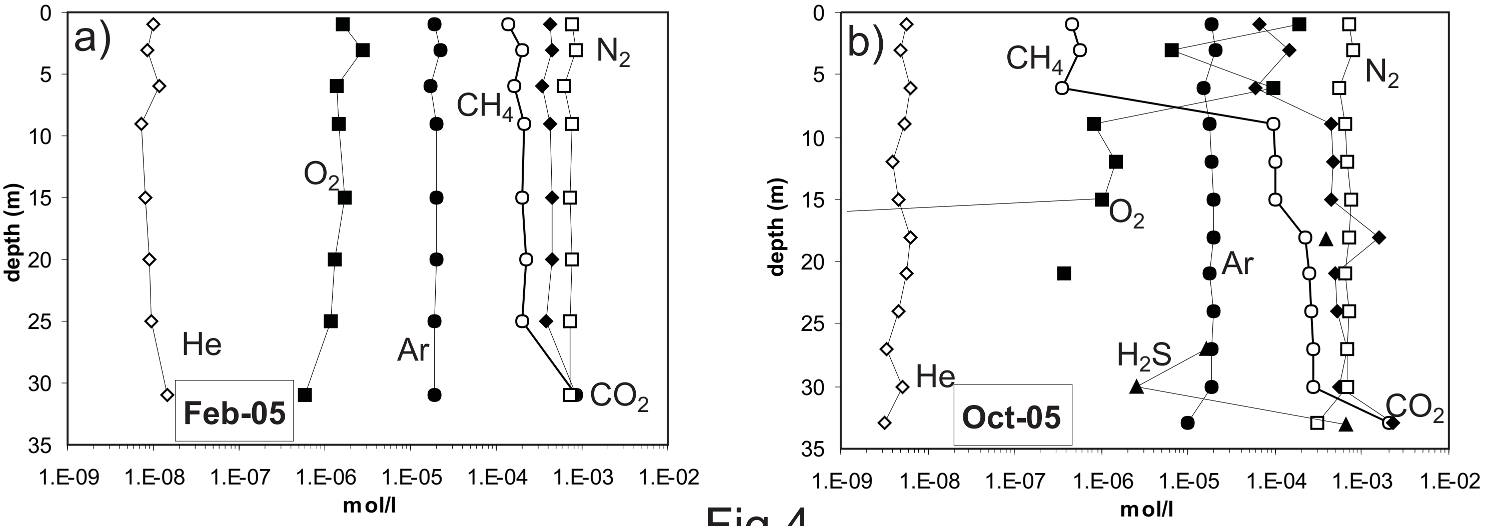

Fig 4

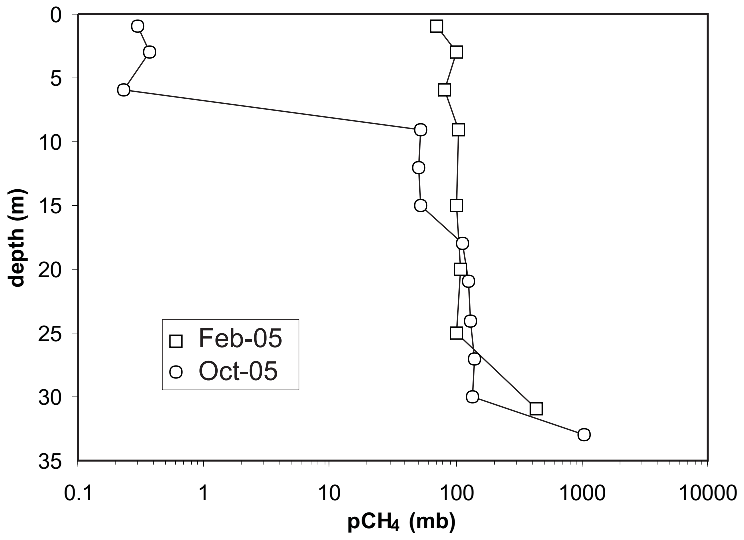

Fig 5

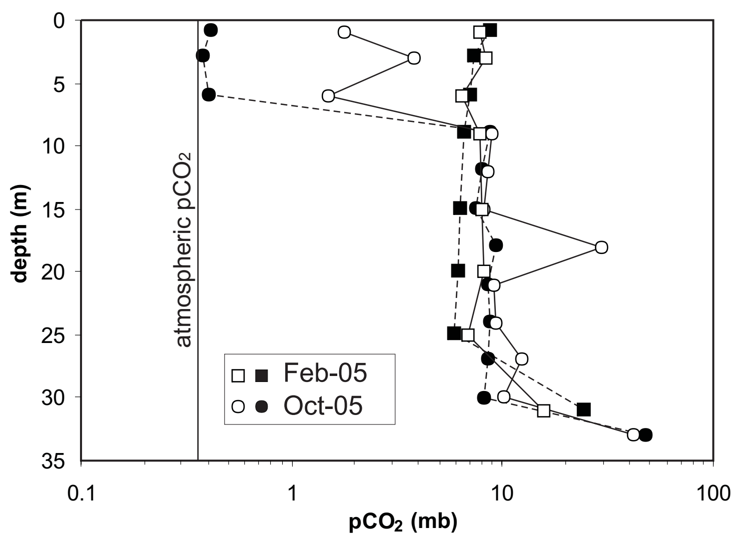

Fig 6

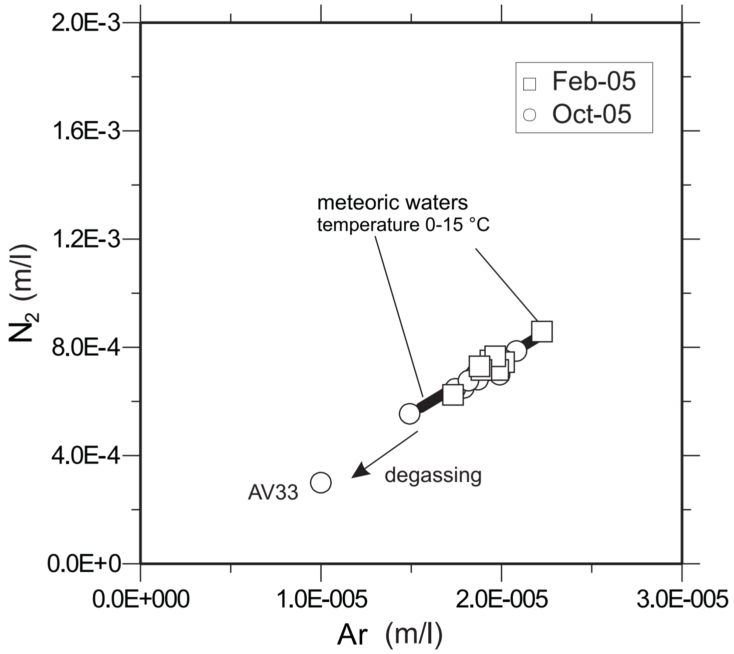

Fig 7

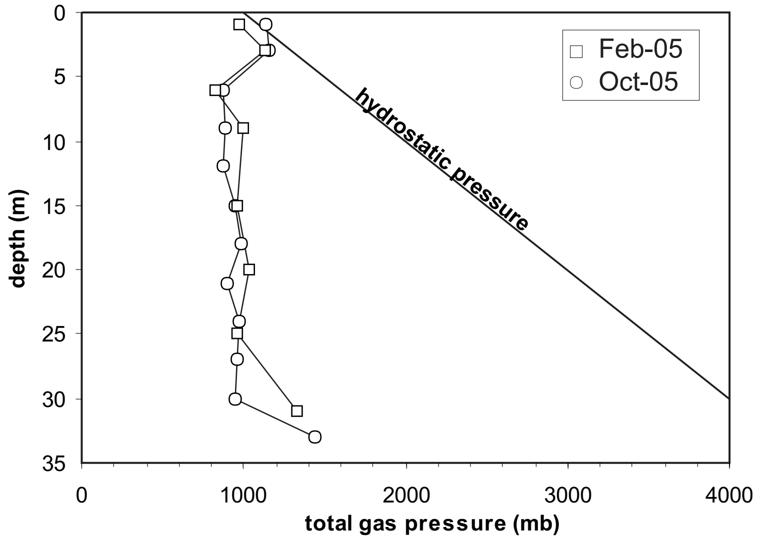

Fig 8

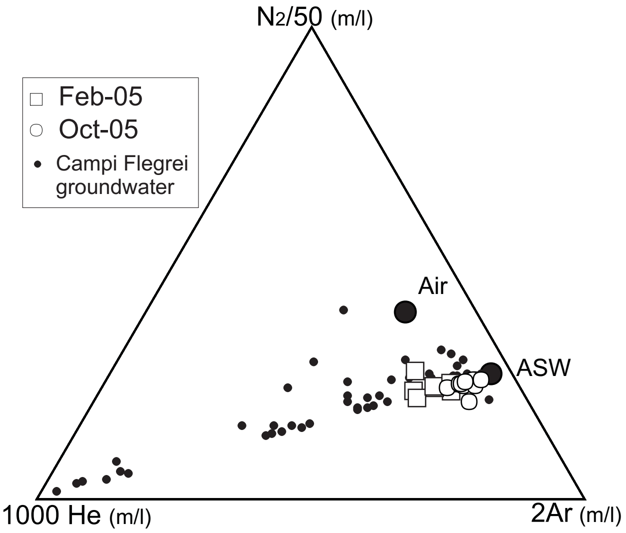

Fig 9

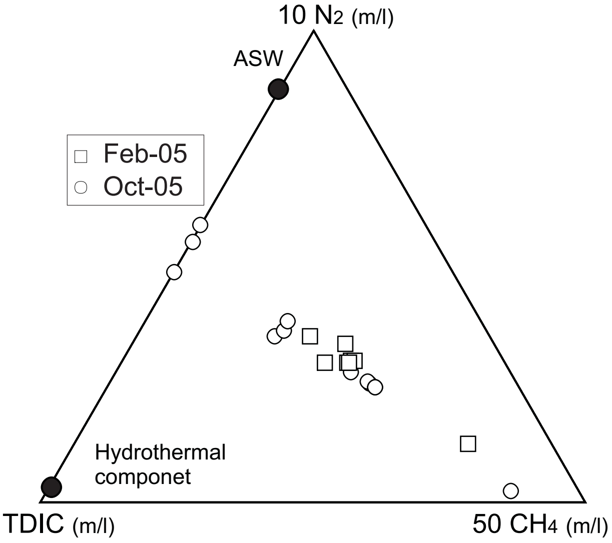

Fig10

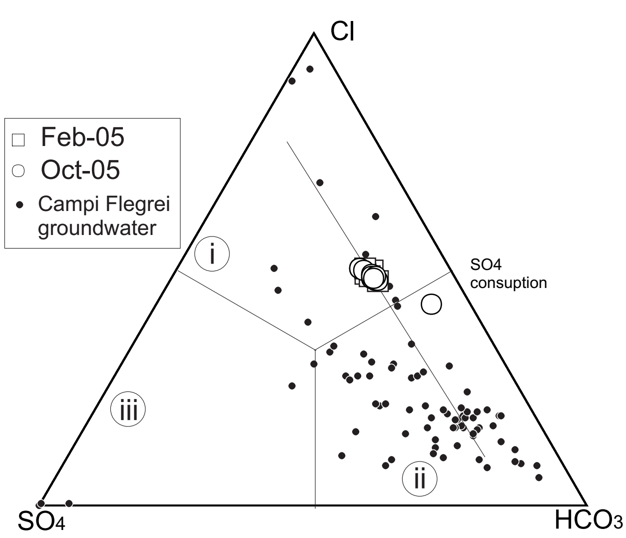

Fig11

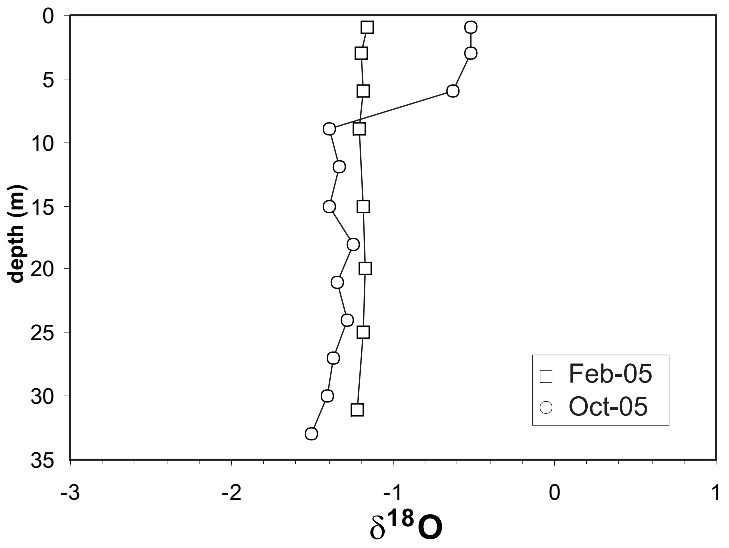

Fig12

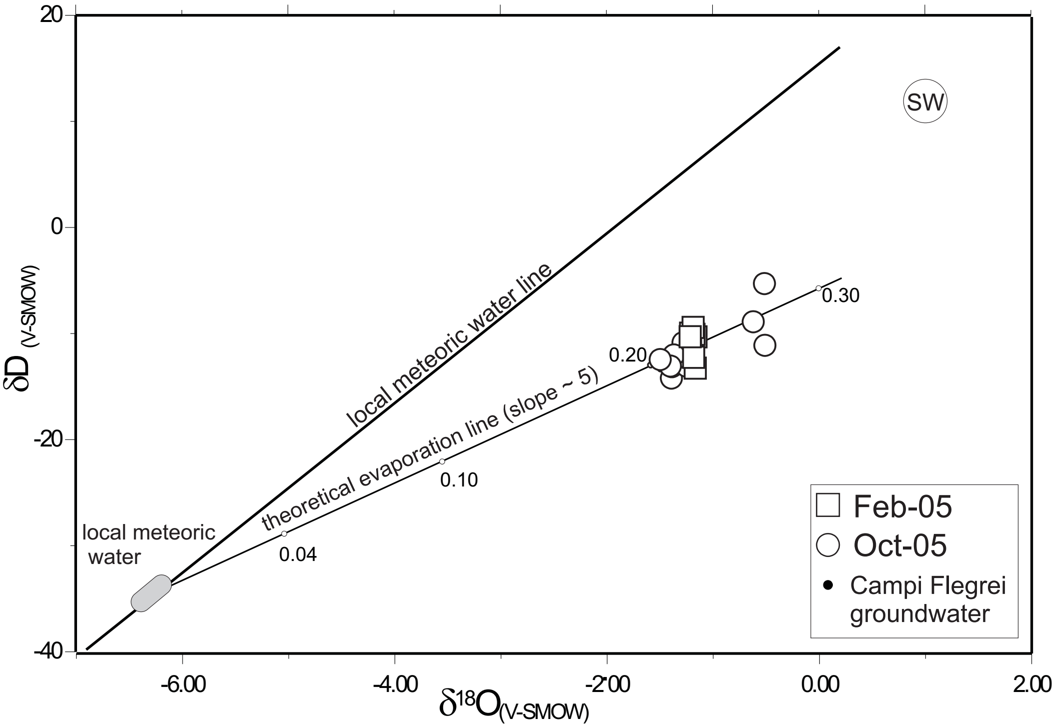
20
0
-20
-40
δD (V-SMOW)
-6.00
-4.00
-2.00
0.00
2.00
δ18O(V-SMOW)
SW
local meteoric water line
theoretical evaporation line (slope ~ 5)
local meteoric water
0.04
0.10
0.20
0.30
Feb-05
Oct-05
Campi Flegrei groundwater

Fig13

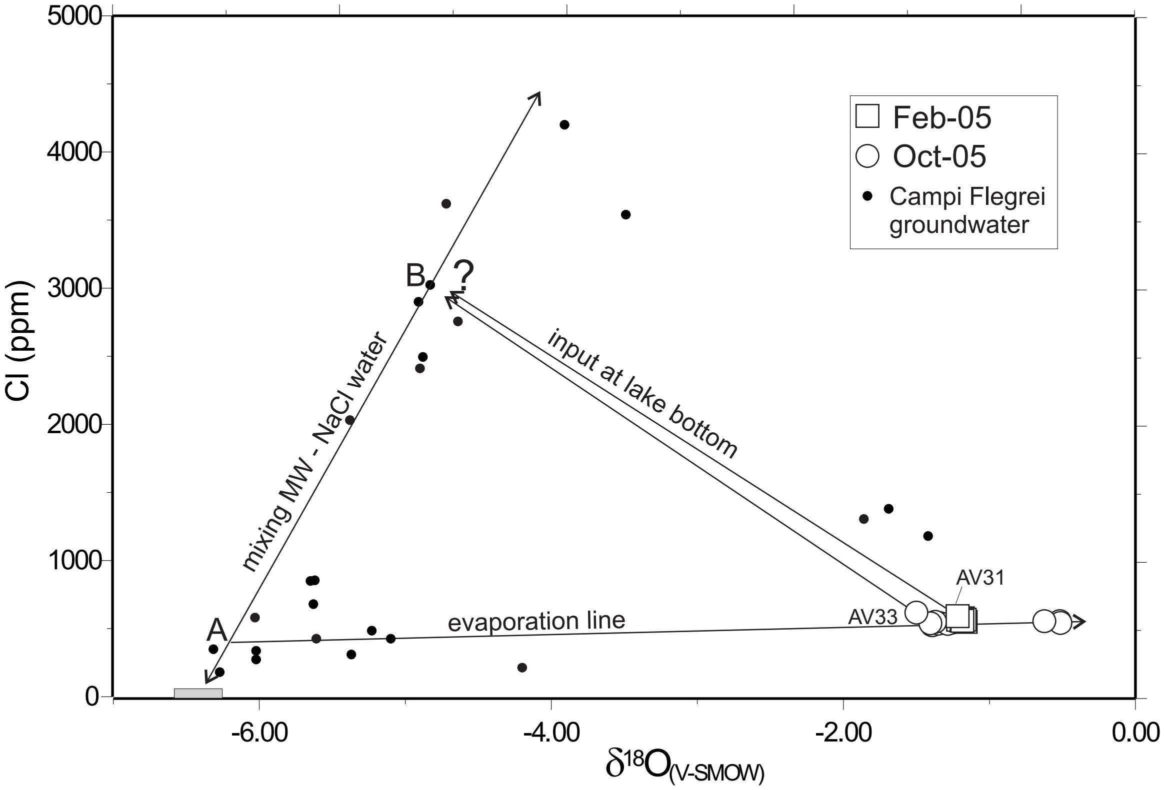
5000
4000
3000
2000
1000
0
Cl (ppm)
-6.00
-4.00
-2.00
0.00
δ18O(V-SMOW)
Feb-05
Oct-05
Campi Flegrei groundwater
A
B
?
mixing MW - NaCl water
input at lake bottom
evaporation line
AV31
AV33

Fig14

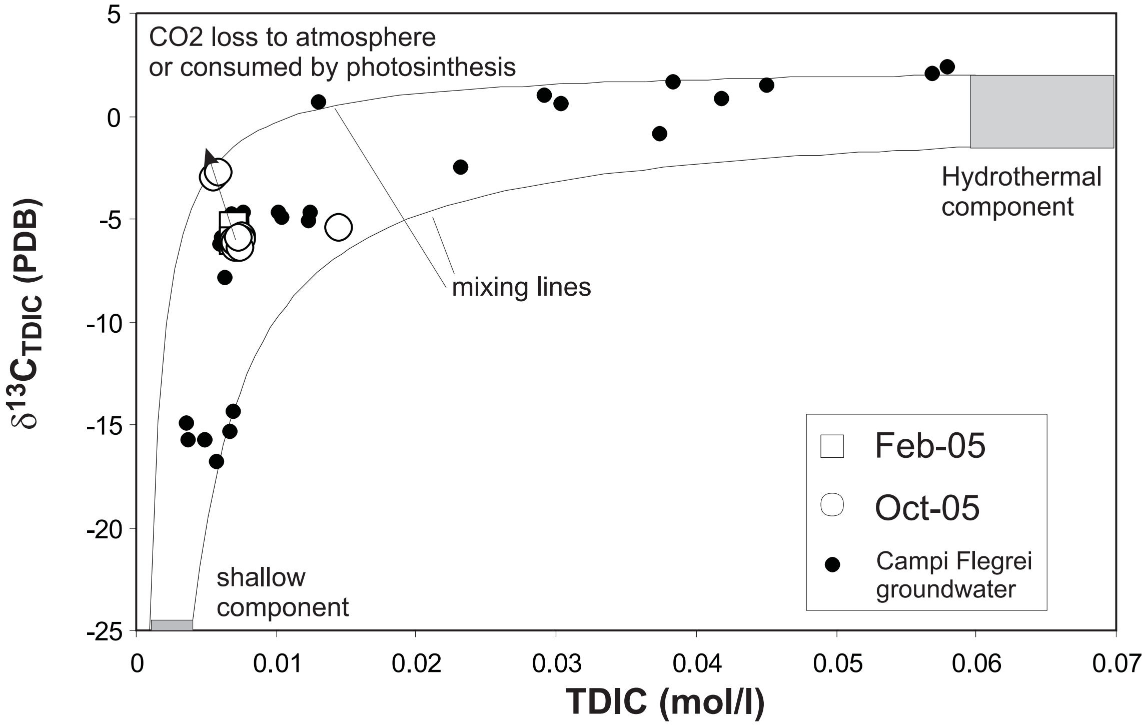
CO2 loss to atmosphere
or consumed by photosinthesis
Hydrothermal
component
mixing lines
shallow
component
Feb-05
Oct-05
Campi Flegrei
groundwater
$\delta^{13}C_{TDIC}$ (PDB)
TDIC (mol/l)
5
0
-5
-10
-15
-20
-25
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07

Fig15

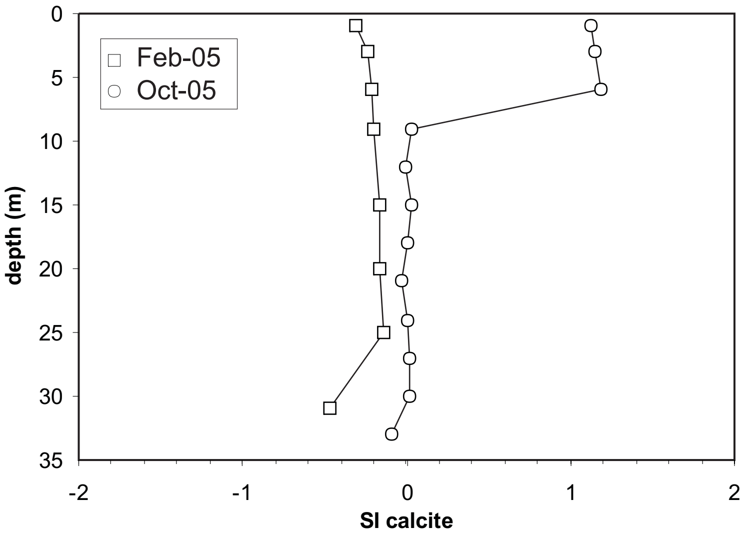
Feb-05
Oct-05
depth (m)
SI calcite
0
5
10
15
20
25
30
35
-2
-1
0
1
2

Fig16

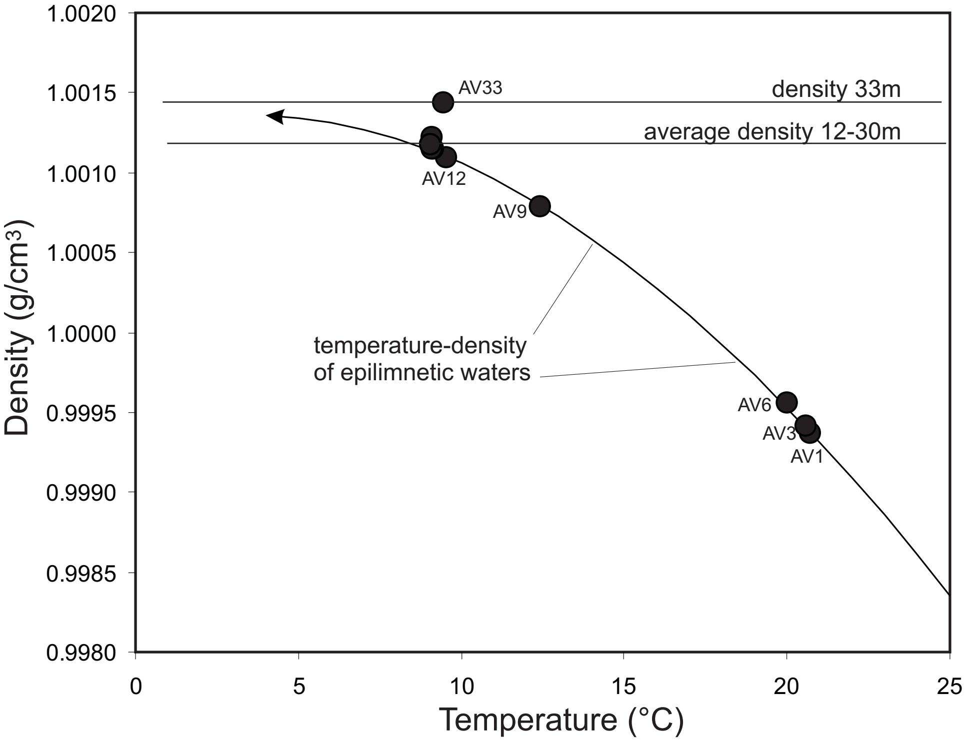
1.0020
1.0015
1.0010
1.0005
1.0000
0.9995
0.9990
0.9985
0.9980
Density (g/cm³)
AV33
density 33m
average density 12-30m
AV12
AV9
temperature-density
of epilimnetic waters
AV6
AV3
AV1
0
5
10
15
20
25
Temperature (°C)

Fig17

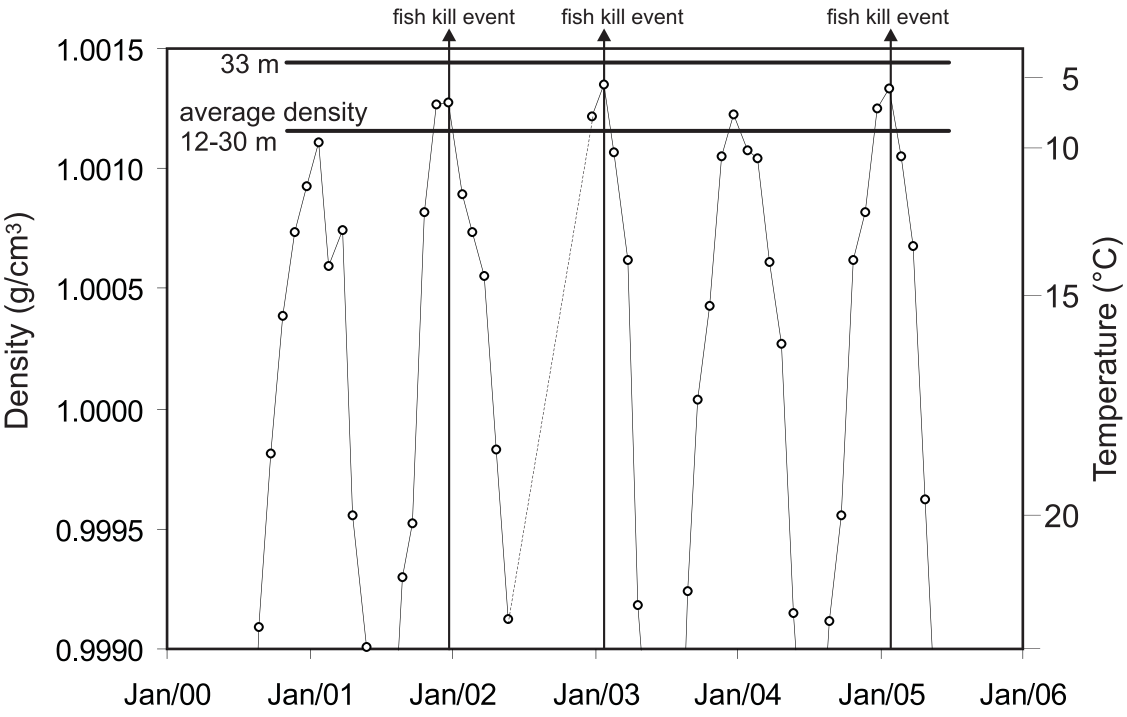
fish kill event
fish kill event
fish kill event
1.0015
1.0010
1.0005
1.0000
0.9995
0.9990
Density (g/cm³)
33 m
average density
12-30 m
5
10
15
20
Temperature (°C)
Jan/00
Jan/01
Jan/02
Jan/03
Jan/04
Jan/05
Jan/06

Fig18