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ORIGINAL ARTICLE

Hydrogeochemical processes controlling water and dissolved gas chemistry at the Accesa sinkhole (southern Tuscany, central Italy)

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ABSTRACT

The 38.5 m deep Lake Accesa is a sinkhole located in southern Tuscany (Italy) that shows a peculiar water composition, being characterized by relatively high total dissolved solids (TDS) values (2 g L^{-1}) and a Ca(Mg)-SO_4 geochemical facies. The presence of significant amounts of extra-atmospheric gases (CO_2 and CH_4), which increase their concentrations with depth, is also recognized. These chemical features, mimicking those commonly shown by volcanic lakes fed by hydrothermal-magmatic reservoirs, are consistent with those of mineral springs emerging in the study area whose chemistry is produced by the interaction of meteoric-derived waters with Mesozoic carbonates and Triassic evaporites. Although the lake has a pronounced thermocline, water chemistry does not show significant changes along the vertical profile. Lake water balance calculations demonstrate that Lake Accesa has >90% of its water supply from sublacustrine springs whose subterranean pathways are controlled by the local structural assessment that likely determined the sinking event, the resulting funnel-shape being then filled by the Accesa waters. Such a huge water inflow from the lake bottom (~$9\cdot10^6$ m^3 yr^{-1}) feeds the lake effluent (Bruna River) and promotes the formation of water currents, which are able to prevent the establishment of a vertical density gradient. Consequently, a continuous mixing along the whole vertical water column is established. Changes of the drainage system by the deep-originated waters in the nearby former mining district have strongly affected the outflow rates of the local mineral springs; thus, future intervention associated with the ongoing remediation activities should carefully be evaluated to preserve the peculiar chemical features of Lake Accesa.

Key words: Central Italy, lake chemistry, Lake Accesa, sinkholes, lake water balance, structural geology setting.

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INTRODUCTION

Karst sinkholes are a common feature in the Tyrrhenian side of central-southern Italy (Santo *et al.,* 2011, and references therein). The occurrence of ground collapses, basically produced by internal erosion and deformation processes caused by subsurface karstification (Williams, 2003; Sauro, 2003; Waltham *et al.,* 2005), is likely favored by seismic activity (Del Prete *et al.,* 2010) and circulation of CO_2(H_2S)-rich fluids (Duchi *et al.,* 1986; Billi *et al.,* 2007; Frondini *et al.,* 2008). An enhanced hydrothermal activity in this area was interpreted as related to a heat flow anomaly (Gianelli *et al.,* 1997; Batini *et al.,* 2003; Bellani *et al.,* 2004) and extensional structures coeval with the emplacement of granitoids at depth in the Late Miocene, exposed or drilled during mining exploitation (Serri *et al.,* 1993; Dini *et al.,* 2005; Benvenuti *et al.,* 1994). Hydrothermal fluid patterns are currently controlled by Early Pliocene-Present high angle normal to strike-slip faults giving rise to local tectonic depressions (Bertini *et al.,* 1991; Carmignani *et al.,* 1994; Jolivet *et al.,* 1998; Rossetti *et al.,* 2011; Brogi *et al.,* 2005; Liotta *et al.,* 2010).

Lake Accesa (42°59' N; 10°53' E; 157 m asl) is a water-filled sinkhole located 5 km from the town of Massa Marittima (southern Tuscany, central Italy) and 12 km west of the Tyrrhenian Sea coast, located at the southern border of *Colline Metallifere* mining district, which is marked by ore-deposits and widespread hydrothermal mineralization (Serri *et al.,* 1991) (Fig. 1a). Exploitation activity of metal deposits since pre-Roman Age (~2500 yrs BP) is here testified by the presence of a necropolis and an Etruscan settlement (Lobell, 2002). In the past century, mineral exploitation mainly focused on the Cu-Pb-Zn-Ag deposit of Fenice Capanne (Mascaro *et al.,* 2001), and the pyrite deposits of Niccioleta and Gavorrano (Fig. 1b). In historic times, water from Lake Accesa was used to wash minerals from the Island of Elba and other regional and local mines (Rizzotto, 1981). The existence of the lake, which has an effluent (Bruna River) and no tributaries, seems to depend on the occurrence of mineral springs mainly discharging from the lake bottom, *e.g.* Paradiso spring, and partly by subaerial contribution, Inferno spring (Magny *et al.*, 2007; Negri, 2008; Vannière *et al.,* 2008).

In this work, the chemical and isotopic compositions of water and dissolved gases of Lake Accesa are presented and discussed. The main goal is to investigate the role played by i) the external fluid source(s) and ii) biogeochemical processes, such as water-rock interactions and microbial activity, for determining the lake chemistry along the vertical profile.

GEOSTRUCTURAL OUTLINES OF THE STUDY AREA

Southern Tuscany is characterized by a thinned continental crust and lithosphere (Nicolich, 1989) that has favored the presence of a high heat flow, the most relevant expressions being represented by the Larderello-Travale and Mt. Amiata geothermal fields (Batini *et al.*, 2003 and references therein) and a large number of gas(CO_2-H_2S)-rich thermo-mineral springs (Minissale, 2004; Minissale *et al.*, 1997, and references therein). This tectonic setting results from the convergence and collision (Cretaceous-Early Miocene) between the Adria Plate and the Sardinia-Corsica Massif with the consequent stacking of the tectonic units and their subsequent compression (to the East) and extension (to the West) from the Early-Middle Miocene to Present (Elter *et al.*, 1975; Carmignani *et al.*, 1995, 2001, and references therein) and late-Apenninic magmatism (Tanelli, 1983; Lattanzi *et al.,* 1994; Costagliola *et al.,* 2008). Historically-exploited base metal-sulfur ore deposits and S-bearing mineralizations that form the mining district of *Colline Metallifere*, are hosted within sedimentary and Palaezoic (phyllites) and Triassic (dolostone and gypsum/anhydrite) rocks that are covered by Ligurian Units produced by an extensional detachment occurring in Middle-Late Miocene (Arisi Rota and Vighi, 1971; Tanelli, 1983).

In the study area large outcrops of Mesozoic limestone deposits occur and are able to host large volume of meteoric waters that interact with deep-originated CO_2-H_2S-rich fluids favoring the formation of sinkholes and dolines (Nisio *et al.*, 2007; Caramanna *et al.*, 2008; Liotta *et al.*, 2010). The funnel-shaped Lake Accesa, originated by karstic collapse, is located at the intersec-

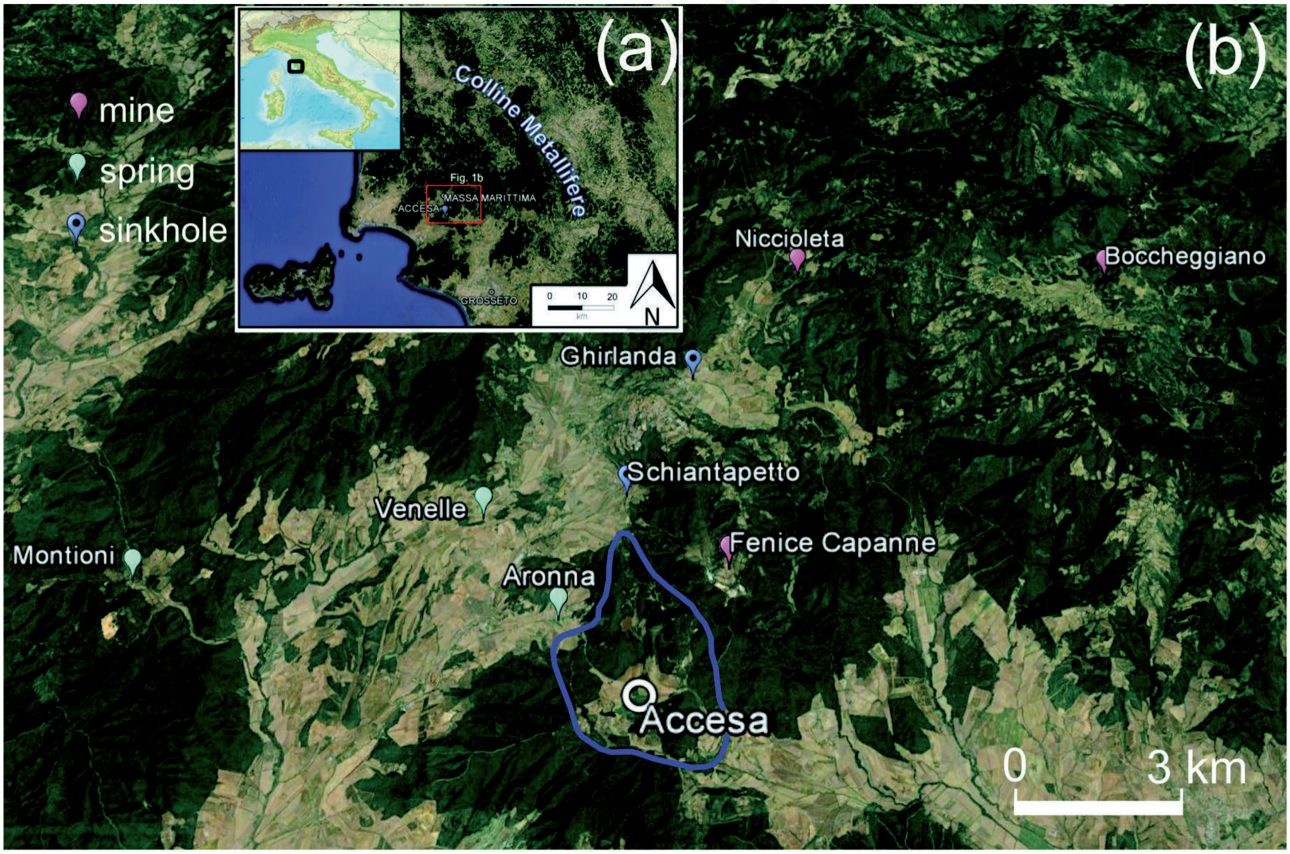

Fig. 1. Geographic map of the (a) southern Tuscany with the location of the Colline Metallifere mining district, and (b) the study area with the location of i) Lake Accesa and its catchment area, ii) Aronna Venelle and Montioni springs, iii) Ghirlanda and Schiantapetto sinkholes, iv) Niccioleta, Boccheggiano and Fenice Capanne mines (image Landsat ©2014 Google).

tion of two NW- and NE-trending faults (Merciai, 1933; Magny *et al.*, 2007; Negri *et al.*, 2008; Vanniere *et al.*, 2008) (Fig. 2), which allow the uprising of subaqueous springs feeding the lake (Negri, 2008). It is worthwhile to mention that the NW-trending fault system is also controlling spring waters (Aronna and Venelle; Bencini *et al.*, 1977; Celati *et al.*, 1990; Fig. 1b), located in correspondence of small karstic depressions north of Lake Accesa, and other sub-circular depressions (Ghirlanda and Schiantapetto, Caramanna *et al.*, 2008) occurring nearby (Fig. 1b).

SAMPLING AND ANALYTICAL METHODS

Field measurements and water and dissolved gas sampling

In May 2012, water depth (m), temperature (°C), pH, dissolved O_2 (µmol/L), and electrical conductivity (EC in S cm^{-1}), corrected at room ambient temperature: 20 °C, were measured along the lake vertical profile using a Hydrolab multiparameter probe (Idroprobe) equipped with a data logger for data storage. The nominal precisions are: depth, ±0.05 m; temperature, ±0.03 °C; pH, ±0.1; O_2, ±2 µmol/L; EC, ±5 S cm^{-1}.

On the same date, water and dissolved gas sampling was carried out from the lake surface to the bottom at intervals of 5 m at a site corresponding to the deepest point of the lake (42°59'16" N, 10°53'44" E). The sampling equipment consisted of a set of 10 m long Rilsan® tubes (ϕ=6 mm) connected by steel connectors. Once the Rilsan® tube was lowered to the chosen depth, water was pumped up to the surface by means of a 150 mL glass syringe equipped with a three-way valve and transferred into plastic bottles after the displacement of a water volume double than the inner volume of the Rilsan tube (Tassi *et al.,* 2009). One water sample from the Aronna (43°00'18" N, 10°52'36" E) mineral spring located near the lake (Fig. 1) was also collected.

Filtered aliquots of water were transferred in 125 mL polyethylene bottles for the analysis of anions, cations (acidified with HCl 30% wt) and trace species (acidified with ultrapure HNO_3 65% wt). An aliquot (8 mL) of water was collected in plastic tubes filled with 2 mL of a Cd-NH_4 solution for the determination of the reduced sulfur

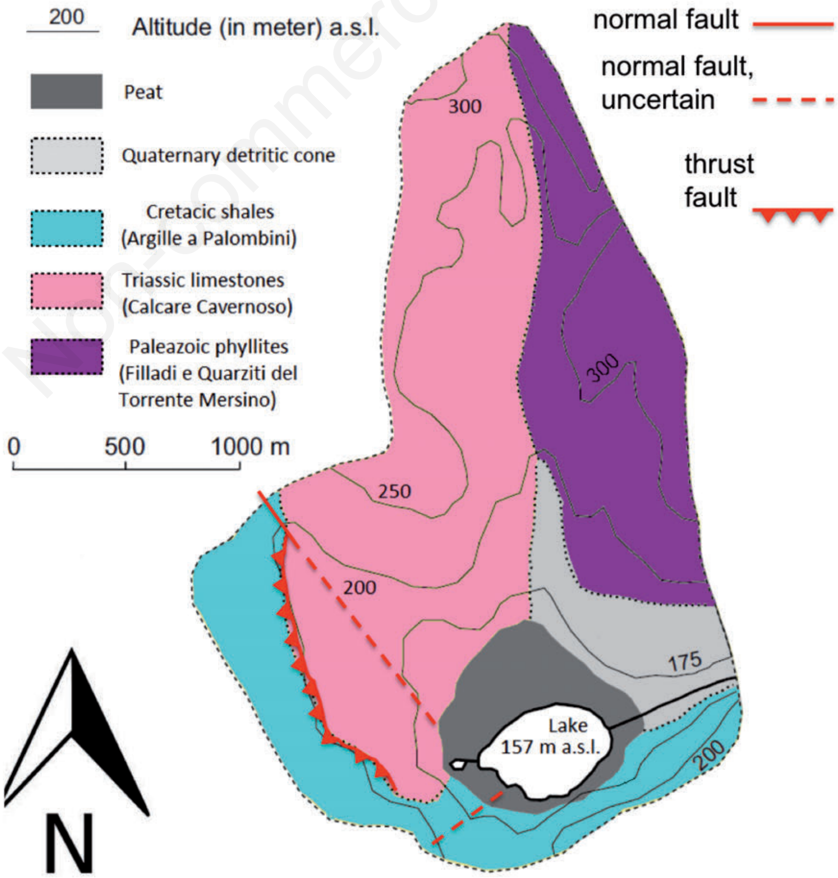

Fig. 2. Schematic geostructural map of Lake Accesa catchment area (modified after Magny *et al*., 2007).

species (H_2S, HS^- and S^{2-}, expressed as ΣS^{2-}) according to Montegrossi *et al.* (2006). Water samples collected in 500 mL polyethylene bottles with the addition of $HgCl_2$ were used for the analysis of δ^2H, $\delta^{18}O$, $\delta^{34}S$-SO_4 and $\delta^{13}C$ of total dissolved inorganic carbon (TDIC). Dissolved gases were sampled using pre-evacuated 250 mL glass vials equipped with a Teflon stopcock that were connected to the Rilsan tube and filled with water up to about three fourths of their inner volume (Chiodini, 1996; Tassi *et al.,* 2008). Flow rate measurements of the Bruna River emissary were carried out at La Pesta site, about 600 m downstream of Lake Accesa, using a mechanical current-meter method. Stream section and velocity were measured using a steel tape and a current meter, respectively.

Chemical and isotopic analysis of waters

Total alkalinity (HCO_3^- in Tab. 1) was analyzed via acidimetric titration with 0.01 N HCl using a Metrohm 794 automatic titration unit. Major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+) and anions (Cl^-, SO_4^{2-}, NO_3^-, Br^- and F^-) were analyzed by ion chromatography (Metrohm 861 and 761 IC, respectively). Reduced sulfur species (ΣS^{2-}) were analyzed as SO_4^{2-} by ion chromatography (Metrohm 761 IC), as described in Montegrossi *et al.* (2006). Selected minor and trace elements (Al^{3+}, As, B, Fe_{tot}, Li^+, Mn^{2+}, Rb^+, Sr^{2+} and Zn^{2+}) were analyzed at the CSA Laboratory (Rimini, Italy) by ICP-MS on the samples acidified with 1% ultra-pure HNO_3. Analytical errors for chemical analysis of major, minor and trace compounds were <5%. Water isotopes (expressed as $\delta^{18}O$ and δ^2H ‰ *vs* V-SMOW) in water samples were analyzed using a Finnigan Delta Plus XL mass spectrometer according to standard protocols. Oxygen isotopes were analyzed using the CO_2–H_2O equilibration method proposed by Epstein and Mayeda (1953). Hydrogen isotopes were analyzed on H_2 produced after the reaction of 10 mL of water with metallic zinc at 500 °C (Coleman *et al.,* 1982). Analytical errors for $\delta^{18}O$ and δ^2H analysis were ±0.1% and ±1%, respectively. The ^3H content (TU, tritium unit; 1 TU=119 Bq m^{-3}) in one selected sample (Lake Accesa, 15 m depth) was determined at the Geoisotopical Unit of Public Health, Department of Chemistry (Koper, Slovenia) using Liquid Scintillation Counting (LSC) technique. For the analysis, 500 mL of sample were transferred to a pyrex container with carborundum (SiC), adding 250 mg of $Na_2S_2O_3$ and 500 mg of Na_2CO_3. Blank and samples were prepared by mean of a distillation apparatus. The analytical error was 1 Bq m^{-3} on 100 Bq m^{-3} (1%). The $^{13}C/^{12}C$ ratios of total dissolved inorganic carbon (TDIC; expressed as $\delta^{13}C$-TDIC ‰ *vs* V-PDB) were determined on CO_2 produced by reaction of 3 mL of water with 2 mL of anhydrous phosphoric acid in vacuum (Salata *et al.,* 2000) using a Finnigan Delta Plus XL mass spectrometer. The recovered CO_2 was analyzed using a Finningan Delta S

Tab. 1. Temperature, pH and chemical composition of water samples collected from the vertical profile of Lake Accesa at depth intervals of 5 m. Chemical data for the Aronna spring are also reported. Concentrations are in mg L^{-1}.

Sample	Depth	pH	T	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	SO_4^{2-}	NO_3^-	Cl^-	F^-	Br^-	HS^-	Al^{3+}	As	B	Fe^{3+}	Li^+	Mn^{2+}	Rb^{+1}	Sr^{2+}	Zn^{2+}	TDS
Lake Accesa	0	7.90	20.6	470	104	13	2.9	0.17	270	1290	2.6	36	1.2	0.075	137	0.004	0.014	1.52	<0.005	0.049	0.009	0.024	7.1	0.005	2336
“	5	7.86	20.4	460	105	12	3.2	0.17	270	1270	2.9	37	1.0	0.077	136	0.003	0.014	1.58	0.007	0.052	0.009	0.024	7.2	0.006	2306
“	10	7.70	20.1	450	103	13	2.9	0.23	280	1250	3.4	43	2.5	0.074	137	0.002	0.011	1.61	0.005	0.051	0.009	0.024	7	0.012	2294
“	15	7.94	11.0	460	102	14	3.2	0.06	280	1250	2.1	36	1.2	0.072	161	0.006	0.010	1.52	0.007	0.048	0.010	0.024	7	0.011	2319
“	20	8.00	9.3	450	101	12	3.0	0.14	270	1260	2.3	37	1.3	0.078	138	0.003	0.010	1.52	0.007	0.048	0.011	0.024	6.9	0.013	2283
“	25	8.09	8.9	450	102	13	3.8	0.09	270	1260	2.6	38	1.8	0.071	130	0.003	0.010	1.52	0.006	0.048	0.020	0.024	6.8	0.011	2279
“	30	8.02	8.6	460	102	13	2.6	0.11	270	1280	2.0	35	1.3	0.074	157	0.002	0.010	1.56	<0.005	0.049	0.019	0.024	6.9	0.015	2332
“	35	8.00	8.5	440	102	13	4.6	0.18	280	1290	3.1	37	1.3	0.073	109	0.002	0.010	1.52	<0.005	0.048	0.023	0.024	6.9	0.016	2288
“	38.4	8.01	8.4	450	101	12	3.9	0.22	270	1290	2.2	37	1.4	0.076	112	0.002	0.010	1.53	<0.005	0.048	0.025	0.023	6.8	0.014	2288
Aronna		7.03	22.7	470	113	11	4.2	0.60	280	1230	2.7	32	1.5	0.067	109	0.002	0.048	1.85	<0.005	0.051	<0.001	0.035	n.a.	0.019	2256

TDS, total dissolved solids.

mass spectrometer after two-step extraction and purification procedures of the gas mixtures by using liquid N_2 and a solid–liquid mixture of liquid N_2 and trichloroethylene (Evans *et al.,* 1998; Vaselli *et al.,* 2006). Internal (Carrara and San Vincenzo marbles) and International (NBS18 and NBS19) standards were used for estimating the external precision. The analytical error and the reproducibility were ±0.05% and ±0.1%, respectively.

The analysis of $^{34}S/^{32}S$ ratios of SO_4^{2-} ($\delta^{34}S$-SO_4 expressed as ‰ *vs* V-CDT) was carried out at Iso-Analytical laboratory in UK. Prior to the analysis an appropriate amount of sample was used to precipitate barium sulfate by the addition of a 10% (w/v) barium chloride solution. The resulting precipitate was collected via centrifugation and dried. Using an automatic sampler, reference or sample material plus vanadium pentoxide catalyst were dropped into a furnace held at 1080 °C and then combusted at ~1700° C in the presence of oxygen. Combusted gases were then swept in a helium stream over combustion catalysts (tungstic oxide/zirconium oxide) and through a reduction stage of high purity copper wires to produce SO_2, N_2, CO_2, and water. Water was removed using a Nafion™ membrane. Sulfur dioxide was resolved from N_2 and CO_2 on a packed GC column at 45 °C. The resultant SO_2 peak entered the ion source of the IRMS (Isotope-Ratio Mass Spectrometer) where it was ionized and accelerated. Gas species of different mass were separated in a magnetic field and measured on a Faraday cup universal collector array. Analysis was based on monitoring of m/z 48, 49 and 50 of SO^+ produced from SO_2 in the ion source. The reference material used for analysis was IA-R061 (Iso-Analytical working standard barium sulfate, $\delta^{34}S = +20.33$‰ *vs* V-CDT). IA-R025 (Iso-Analytical working standard barium sulfate, $\delta^{34}S = +8.53$‰ *vs* V-CDT), IA-R026 (Iso-Analytical working standard silver sulfide, $\delta^{34}S = +3.96$‰ *vs* V-CDT) and IA-R061 were used for calibration and correction of the ^{18}O contribution to the SO+ ion beam. Working standards were traceable to NBS-127 (barium sulfate, $\delta^{34}S = +20.3$‰ *vs* V-CDT), IAEA-SO-5 (barium sulfate, $\delta^{34}S = +0.5$‰ *vs* V-CDT) and IAEA-S-1 (silver sulfide, $\delta^{34}S = -0.3$ ‰ *vs* V-CDT).

Chemical and isotopic analysis of dissolved gases

The composition of the inorganic gas compounds (CO_2, N_2, Ne, O_2 and Ar) stored in the headspace of the sampling flasks was determined using a Shimadzu 15A gas chromatograph (GC) equipped with a 5 m long stainless steel column packed with Porapak 80/100 mesh and a Thermal Conductivity Detector (TCD), whereas CH_4 was analyzed using a Shimadzu 14A GC equipped with a 10 m long stainless steel column packed with Chromosorb PAW 80/100 mesh coated with 23% SP 1700 and a Flame Ionization Detector (FID) (Vaselli *et al.,* 2006; Tassi *et al.,* 2008). The analytical error for GC analysis was ≤5%.

The $^{13}C/^{12}C$ ratios of CO_2 in the headspace of the sampling flasks ($\delta^{13}C$-CO_2 expressed as ‰ *vs* V-PDB) were analyzed using the same instrument and purification procedure used for the determination of the $\delta^{13}C$-TDIC values. The $^{13}C/^{12}C$ ratios of dissolved CO_2 ($\delta^{13}C$-CO_{2aq}) were recalculated on the basis of $\delta^{13}C$-CO_2 values, considering the isotopic fractionation caused by gas release from water occurred during the sampling procedure was quantified by using the ε_1 fractionation factor for the gas-water equilibrium (Zhang *et al.,* 1995), as follows:

$$\varepsilon_1 = \delta^{13}C\text{-}CO_{2aq} - \delta^{13}C\text{-}CO_2 = (0.0049 \cdot T) -1.31 \quad \text{(eq. 1)}$$

where temperature (T) is expressed in °C.

The analysis of $\delta^{13}C$ in CH_4 ($\delta^{13}C$-CH_4 expressed as ‰ *vs* V-PDB) was carried out by mass spectrometry (Varian MAT 250) according to the procedure described by Schoell (1980). The analytical error was ± 0.15‰.

RESULTS

Lake morphology

Up to 500 bathymetric data, measured with a GPSMAP® 526s (Garmin, Olathe, KS, USA) ecosounder, were used to reconstruct the lake morphology (Fig. 3). The lake has a sub-circular shape, a diameter of ~400 m, a maximum depth of 38.5 m, a surface area of 16×10^4 m^2 and a volume of 2.39×10^6 m^3. The catchment area (Fig. 2), delimited by small hills culminating at 350 m asl, covers 5 km^2. In this area, the outcropping geological formations include: Paleazoic phyllites, Triassic limestones, Cretacic shales and Quaternary debris. The Lake Accesa lies on peat deposits (Fig. 2). In 1912, the lake level was artificially lowered to extend arable lands. This intervention significantly diminished the submerged littoral platform that currently account for a 5-20 m wide carbonate bench. Below this zone, the lake profile shows a steep slope, followed by a gentle slope that reaches the sub-horizontal bottom of the lake (Fig. 3).

Vertical profiles of temperature, EC, pH and dissolved O_2

Temperature, EC, pH, and dissolved O_2 concentrations measured along the vertical profiles of Lake Accesa are shown in Fig. 4 a-d. The lake had a thermocline at 10-15 m depth, where temperature decreased from 20 to 9 °C and then remained relatively constant down to the bottom (Fig. 4a). EC values did not significantly change with depth, showing a slight increase from 1.93 to 1.98 mS cm^{-1} (Fig. 4b). In the very first 3 m, the pH values abruptly decreased from 7.9 to 7.7, then progressively increased, reaching 8.1 at 25 m depth, whereas they slight decreased to 8.0 toward the bottom (Fig. 4c). Dissolved O_2 concentrations strongly increased, from 250 to 380 μmol L^{-1}, at ~10 m depth, in correspondence of the thermocline. Thus, the O_2 increasing trend is to be interpreted as related to an increase of O_2 solubility at decreasing temperatures. Below this depth O_2 concentrations decreased reaching the minimum vales of 215 µmol L^{-1} at the lake bottom (Fig. 4d).

Chemical and isotopic ($\delta^{18}O$, $\delta^{2}H$, 3H, $\delta^{13}C$-TDIC and $\delta^{34}S$-SO_4) composition of lake water

The lake is characterized by a relatively high total dissolved solids (TDS) (up to 2336 mg L^{-1} at the bottom) and a Ca-SO_4 composition (Ca and SO_4 concentrations were up to 470 and 1290 mg L^{-1}, respectively) (Tab. 1). Mg^{2+}, ΣS^{2-} and HCO_3^- concentrations were relatively high (up to 105, 161 and 280 mg L^{-1}), whereas minor concentrations of Cl^- (<43 mg L^{-1}), Na^+ (<14 mg L^{-1}), K^+ (<4.6 mg L^{-1}), Sr^{2+} (up to 7.2 mg L^{-1}), NO_3^- (<3.4 mg L^{-1}), B (up to 1.6 mg L^{-1}), F^- (up to 2.5 mg L^{-1}) and NH_4^+ (<0.23 mg L^{-1}) were measured. Concentrations of other trace elements (Al^{3+}, As, Br^-, Fe_{tot}, Li^+, Mn^{2+}, Rb^+, and Zn^{2+}) were <0.1 mg L^{-1} (Tab. 1). In agreement with the relatively constant EC values along the vertical profile (Fig. 4b), all the analyzed ion species did not show any significant variation (Tab. 1).

The $\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O values (Tab. 2) varied in a narrow range, from -5.94 to -5.72‰ *vs* V-SMOW and from -42.4 to -37.8‰ *vs* V-SMOW, respectively. The $\delta^{13}C$-TDIC values ranged from -2.5 to 0.33 ‰ *vs* V-PDB. No clear trends with depth were shown by these isotopic parameters. The ^{3}H value was 3 TU (Tritium Unit). The $\delta^{34}S$ values, measured in water samples collected from the lake surface and at the depths of 15 and 35 m, slightly increased with depth, from 13.70 to 14.12‰ *vs* V-CDT.

Chemical and isotopic (δ13C-CO2aq) composition of dissolved gases

The chemical composition of dissolved gases (Tab. 3) was largely dominated by atmospheric-related compounds, *i.e.*, N_2 (from 569 to 589 mol L^{-1}) and O_2 (from 216 to 329 mol L^{-1}), with minor amounts of noble gases (Ar and Ne up to 15 and 0.008 mol L^{-1}, respectively). Extra-atmospheric gas species mainly consisted of CO_2, whose concentrations were from 2.1 to 81 mol L^{-1}) significantly increased with depth, and relatively low CH_4 concentrations (up to 21 mol L^{-1}) in the deepest water layers (≥35 m depth). $\delta^{13}C$-CO_{2aq} values (measured in dissolved gas samples collected from depth ≥20 m) ranged

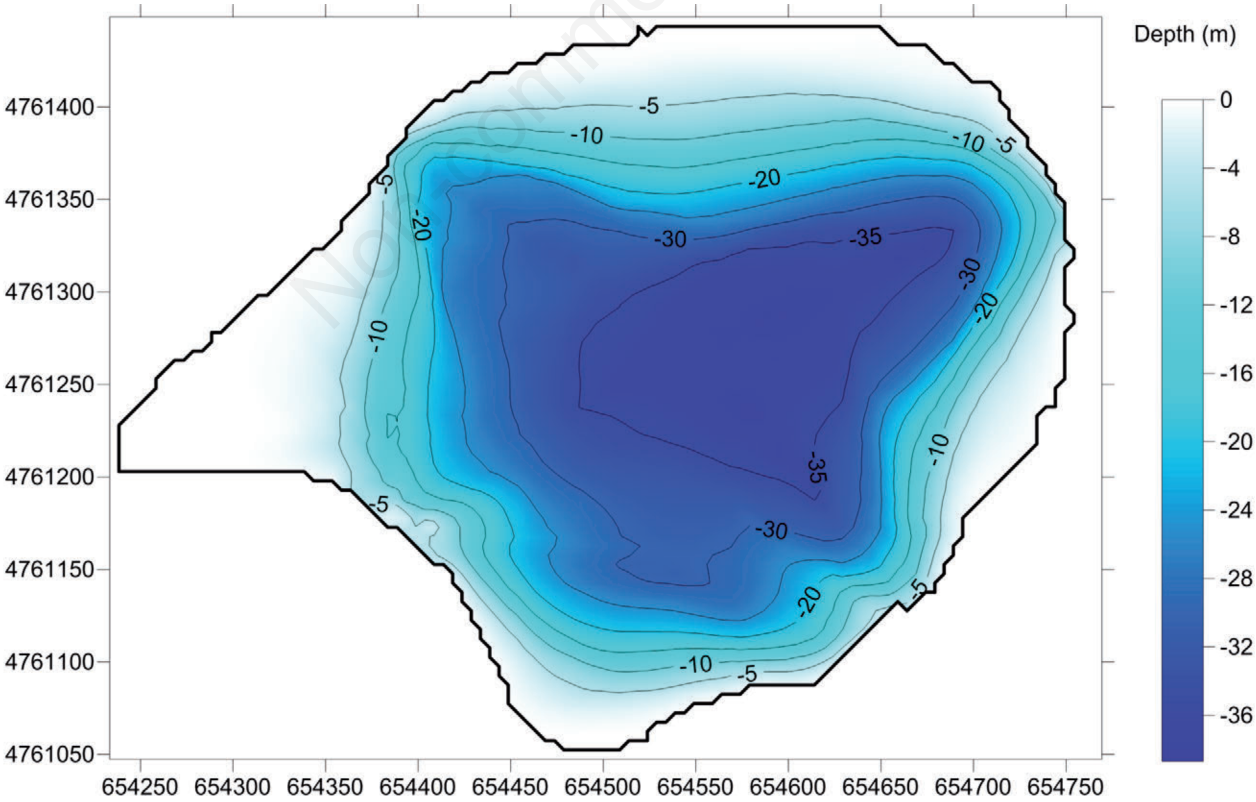

Fig. 3. Bathymetric map of Lake Accesa.

from -11.79 to -9.24‰ *vs* V-PDB, whereas the δ^{13}C-CH$_4$ values were -68.5 and -71.3‰ *vs* V-PDB at the depths of 35 and 38.4 m, respectively.

DISCUSSION

Processes controlling the lake water chemistry

The most striking chemical feature of Lake Accesa water is its high salinity (TDS values >2000 mg L^{-1}), significantly higher than that of sinkhole lakes (Nisio *et al.,* 2007; Caramanna *et al.,* 2008; Tassi *et al.,* 2012), and other types of lakes in Italy (Ambrosetti *et al.,* 1992; Guilizzoni and Lami, 1992; Marchetto *et al.,* 1995; Salmaso and Mosello, 2010), including those hosted in volcanic systems (Mosello *et al.,* 2004; Ellwood *et al.,* 2009; Cabassi *et al.,* 2013), which are typically mainly fed by meteoric water. Few exceptions are the Vescovo lakes in the Pontina Plain (Central Italy) that have a Na$^+$-Cl$^-$ composition and TDS values >2000 mg L^{-1} (Tuccimei *et al.,* 2005), and some small sinkhole lake in the S. Vittorino Plain (Rieti province, Central Italy) that show chemical features resembling those of Lake Accesa (Nisio *et al.,* 2007; Caramanna *et al.,* 2008). In both cases, the water chemical composition was interpreted as related to inputs of hydrothermal fluids.

The Ca-SO$_4$ composition of Lake Accesa water closely resembles those shown by thermal springs of Central Italy, which are fed by hydrothermal reservoirs recharged by meteoric water interacting with carbonate-evaporite embedding formations (Bencini *et al.,* 1977; Minissale and Duchi, 1988; Celati *et al.,* 1990, Capaccioni *et al.*, 2001; Boschetti *et al.,* 2005), including the Aronna spring (Tab. 1) and other mineral water discharges, *e.g.* Venelle and Montioni, located nearby the study area (Minissale, 2004) (Fig. 1b). This suggests that all the mineral springs of the study area are related to the same hydrological circuit that also feeds the springs discharging from the lake bottom. Accordingly, modifications of the hydrologic cycle caused by the opening of galleries draining Niccioleta and Boccheggiano mine waters have caused a significant change of the outflow rate of these mineral springs (Tesser, 2012). Considering that: i) spring waters have a salinity up to two orders of magnitude higher than that of rainwater and show significant CO$_2$ contents (Tab. 3); and ii) the lake have a marked thermocline, the lack of significant variations in water chemistry along the lake vertical profile (Tab. 1) is quite peculiar. Water density indeed increases with both increasing salinity and dissolved CO$_2$ (Imboden and Wüest, 1995), and is inversely correlated to water temperature (Wüest *et al.,* 1996). According to the classification proposed by Hutchinson (1957), inflow at depth of saline water in lakes is able to cause ectogenic meromixis, crenogenically meromictic lakes owe their permanent stratification to inflow of surface water runoff, whereas thermobaric stratification can occur when solar radiation produces a vertical gradient of lake water temperature. Water vertical convection at Lake Accesa is possibly related on the input rates from the different water sources, *i.e.* sublacustrine springs and rainwater, that can be evaluated on the basis of a simple hydrological balance of lake water. According to the observations reported in literature (Magny *et al.,* 2007; Negri*,* 2008) and those carried out for the present study, the volume of Lake Accesa (V) can reasonably be as-

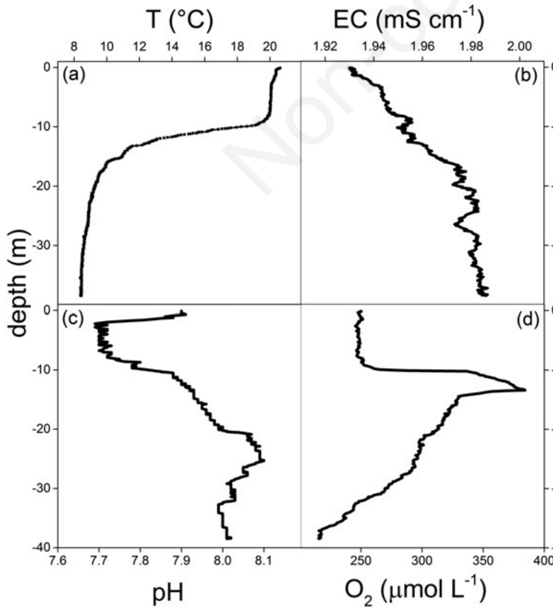

Fig. 4. Vertical profiles of a) temperature (T; °C); b) electrical conductivity (EC; mS cm^{-1}); c) pH; d) dissolved oxygen (O$_2$; mol L^{-1}) of Lake Accesa.

Tab. 2. Isotopic composition (δ^{18}O, δ^{2}H, ^{3}H, δ^{13}C-TDIC and δ^{34}S) of water samples collected from the vertical profile of Lake Accesa at depth intervals of 5 m. δ^{34}S values for the Aronna spring are also reported.

Sample	Depth	δ^{18}O	δ^{2}H	^{3}H	δ^{13}C-TDIC	δ^{34}S
Lake Accesa	0	-5.76	-40.2	nd	-1.10	13.70
"	5	-5.72	-39.1	nd	0.33	nd
"	10	-5.82	-37.8	nd	-2.50	nd
"	15	-5.79	-40.1	3	-0.80	13.97
"	20	-5.8	-42.4	nd	-1.99	nd
"	25	-5.94	-40.2	nd	-2.14	nd
"	30	-5.79	-38.7	nd	-2.25	nd
"	35	-5.75	-38.1	nd	-2.47	14.12
"	38.4	-5.79	-38.0	nd	-0.86	nd
Aronna		nd	nd	nd	nd	14.12

nd, not detected.

sumed constant in the last decades. At a first approximation, under a steady-state condition, the water mass budget (MB) of the lake is equal to 0 and can be expressed in a differential form, as follows:

$$MB = 0 = Q_r + Q_{sp} - Q_e - Q_s - Q_{et} - Q_o \qquad \text{(eq. 2)}$$

where Q_r is the amount of rainwater in the catchment area, Q_{sp} is the water input from the sublacustrine springs, Q_e is the evaporative loss of water from the lake surface, Q_{et} of rainwater loss from the soil of the catchment area due to evapotranspiration, Q_s is the seepage water loss from the lake, Q_o is the overflow flux through the Bruna River.

According to our measurements, the discharge rate of the Bruna River (Q_o) is $9.5 \cdot 10^6$ m^3 yr^{-1}. Assuming that the mean rainfall rate in this areas is 745 mm yr^{-1} (Vannière *et al*., 2008), and considering that the catchment area of the lake is $5 \cdot 10^6$ m^2, Q_r is equal to $3.7 \cdot 10^6$ m^3 yr^{-1}, although this value is to be considered overestimated since a significant percentage of rainwater infiltrates through soil and does not reach the lake. Q_e, calculated using the annual mean temperature (13°C; Vannière *et al*., 2008) and the approach suggested by Dragoni and Valigi (1994), is $2.5 \cdot 10^5$ m^3 yr^{-1}, whereas Q_{et}, calculated using the Thornthwaite equation (Thornthwaite, 1948), is $2.9 \cdot 10^6$ m^3 yr^{-1}. The Q_s value is likely to be considered negligible with respect to the other input and output factors, since the bottom of the lake is almost impermeable being covered by a thick silt layer (Negri, 2008). Therefore, solving eq. (2) sublacustrine spring discharges into Lake Accesa (Q_{sp}) is calculated at $8.95 \cdot 10^6$ m^3 yr^{-1}, a value that is higher with respect to most thermal springs in Tuscany and comparable with those of the Aronna and Venelle springs (Celati *et al.,* 1990). As expected, Q_{sp} basically constitutes the main water source for the lake, since it is more than one order of magnitude higher than the net amount of rainwater input into the lake (Q_r - Q_{et}). Moreover, our data indicate that the theoretical renewal time of Lake Accesa water, *i.e.*, the ratio between the volume of the lake and the volume of its outflow, is <3 months, which suggests a relatively high hydrological vivacity that contributes to counteract the establishment of a chemical stratification (Ambrosetti *et al.,* 2003).

As shown in the δ^2H *vs* δ^{18}O diagram (Fig. 5), Lake Accesa, as well as the Aronna spring (Minissale and Vaselli, 2011), is characterized by a δ^{18}O positive shift with respect to the Local Meteoric Water Line (LMWL)

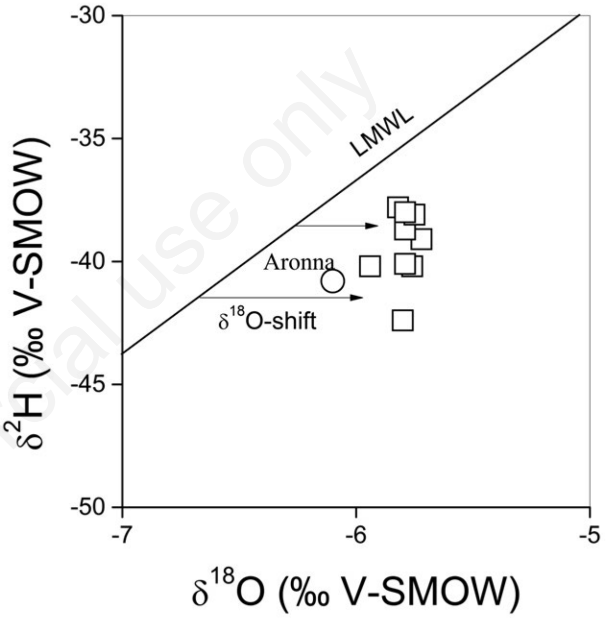

Fig. 5. δ^2H *vs* δ^{18}O binary diagram for Lake Accesa (open square) and Aronna (open circle) waters. The Local Meteoric Water Line (LMWL) proposed by Longinelli and Selmo (2003) for Central Italy is also reported.

Tab. 3. Chemical and isotopic (δ^{13}C-CO$_2$ and δ^{13}C-CH$_4$) compositions of dissolved gases collected from the vertical profile of Lake Accesa at depth intervals of 5 m. Concentrations of dissolved gases are in mol L^{-1}. Dissolved gas composition for the Aronna spring is also reported.

Sample	Depth	CO_2	N_2	CH_4	Ar	O_2	Ne	$\delta^{13}C\text{-}CO_{2aq}$	$\delta^{13}C\text{-}CH_4$	TOT
Lake Accesa	0	2.1	589	nd	15	250	0.008	nd	nd	856
"	5	9.3	578	nd	15	249	0.008	nd	nd	851
"	10	12	569	nd	14	275	0.008	nd	nd	870
"	15	15	581	nd	14	329	0.008	nd	nd	939
"	20	39	578	nd	15	313	0.008	-11.8	nd	945
"	25	45	582	nd	14	296	0.007	-9.24	nd	937
"	30	49	577	nd	14	270	0.007	-11.1	nd	910
"	35	58	572	13	14	238	0.007	-11.6	-68.5	895
"	38.4	81	570	21	14	216	0.007	-11.7	-71.3	902
Aronna		615	455	0.54	10	61	0.007	-12.2	nd	1142

nd, not detected.

proposed by Longinelli and Selmo (2003) for Central Italy, indicating the occurrence of a significant interaction with rocks. Furthermore, the water isotopic data confirm that the origin of lake water and the Aronna spring are intimately related, and indicate that meteoric water feeding the deep hydrothermal system permeate into the soil at an altitude of ~200-400 m. The nearby *Colline Metallifere* (Fig. 1) likely represents the main recharge area, as also supported by the ^{3}H concentration (3 TU), suggesting that Lake Accesa is a mix of submodern (*i.e.*, prior to 1950s) and modern water. Rainwater permeating at depth interacts with the Mesozoic carbonate sequence and anhydrite-rich Triassic layers. Dissolution of $CaMg(CO_3)_2$ and $Ca(Mg)SO_4$ produces the relatively high TDS values characterizing Lake Accesa. The Ca-SO_4 composition is produced by subsequent calcite and dolomite precipitation that controls the HCO_3^- concentrations, whereas SO_4-bearing minerals (gypsum and anhydrites) are under-saturated (Tab. 4). The difference between the δ^{13}C-TDIC values of the lake (Tab. 2) and the δ^{13}C values of carbonate minerals in this region (from +1.5 to +3.5‰ *vs* V-PDB; Cortecci and Lupi, 1994) is produced during the dissolution process that at 25°C causes an isotopic fractionation of 2.4‰ (Bottinga, 1968). Similarly, the variations of the δ^{13}C-TDIC values measured along the lake vertical profile are possibly related to secondary calcite and dolomite precipitation. The δ^{34}S-SO_4 values (Tab. 2) are slightly less positive than those of the Triassic anhydrites ranging from +15‰ to +20‰ *vs* V-CDT (Cortecci *et al.,* 1981; Dinelli *et al.,* 1999), confirming that water-rock interactions involving this evaporitic formation is the dominant source of SO_4^{2-} for Lake Accesa. However, considering that isotopic fractionation caused by dissolution of solid sulfates in water is negligible (Tuttle *et al.,* 2009), minor sulfur contribution from ^{32}S-rich sulfide deposits (Cortecci *et al.,* 1983) cannot be excluded. This hypothesis is also supported by the anomalously high ΣS^{2-} concentrations measured both in the lake and Aronna waters (Tab. 1), even higher than most of the SO_4^{2-}–rich springs in Italy (Montegrossi *et al.,* 2006). This chemical feature is likely related to leakage of S-bearing polymetallic minerals from the nearby mining area of Fenice Capanne. Production of reduced S-bearing chemical species from microbial activity is indeed expected to be negligible, since the lake lacks of anaerobic layers (Tab. 3) where SO_4^{2-} reduction can occur.

Tab. 4. Saturation indices for calcite, dolomite, anhydrite and gypsum calculated for Lake Accesa water at depth intervals of 5 m using the PHREEQC v2.18 software package (Parkhurst and Appelo, 1999).

Sample	Depth	SI Dolomite	SI Calcite	SI Anhydrite	SI Gypsum
Lake Accesa	0	2.03	1.21	-0.52	-0.17
"	5	1.96	1.16	-0.53	-0.18
"	10	1.64	1.01	-0.54	-0.19
"	15	1.73	1.12	-0.61	-0.16
"	20	1.75	1.14	-0.62	-0.15
"	25	1.88	1.21	-0.63	-0.15
"	30	1.75	1.15	-0.62	-0.14
"	35	1.71	1.12	-0.63	-0.14
"	38.4	1.70	1.12	-0.63	-0.14

SI, saturation indices.

Dissolution of carbonates and sulfates is the main source for the relatively high concentrations of Sr^{2+} (up to 7.2 mg/L), typically substituting Ca^{2+} in crystal lattice of these minerals. The relatively low concentrations of Na^+ and Cl^-, which are the typical main constituents of geothermal fluids, suggest that contribution of deep geothermal fluids from the Larderello-Travale geothermal systems that are located only 30 kilometers N-W of Lake Accesa, are unlike.

Origin of dissolved gases

As already mentioned, lake water chemistry does not show significant changes along the vertical profile. On the contrary, the composition of dissolved gases, which is largely dominated by atmospheric gases maintaining the same concentrations at different depths (Tab. 3), is marked by increasing dissolved CO_2 concentrations and, at >30 m depth, by the presence of significant amounts of CH_4. Carbon dioxide and CH_4 are commonly produced in lakes by microbial activity.

Production of CO_2 from decomposition of organic matter through microbial activity can occur at both anaerobic and aerobic conditions (Rudd *et al.,* 1974; Rich, 1975; Hanson and Hanson, 1996; Lopes *et al.,* 2011). These processes are counteracted by CO_2 consumption that in the epilimnion proceeds through oxygenic photosynthesis mainly carried out by microalgae and cyanobacteria (Nelson and Ben-Shem, 2004), whereas at anaerobic conditions is mainly related to the activity of methanogens, a group of microorganisms phylogenetically affiliated to the kingdom *Euarchaeota* of the domain *Archaea* (Woese *et al*., 1990). Considering i) the availability of free O_2 along the whole vertical profile, excluding the occurrence anaerobic processes; and ii) the relatively high concentrations of dissolved CO_2 measured in Aronna spring whose chemistry is evidently similar to that of the sublacustrine discharges, CO_2 in Lake Accesa likely has an external origin. Moreover, the □δ^{13}C-CO_{2aq} values of the lake are similar to those characterizing most CO_2-rich springs of central Italy (Minissale *et al.,* 2002, and references therein). Therefore, the origin of CO_2 may be related to mixing of deep hydrothermal fluids, having□δ^{13}C-CO_2 values that range from -2 to +3‰ *vs* V-PDB, with isotopically light CO_2 (<-20‰ *vs* V-PDB) likely deriving from a shallow biogenic source (Deines *et al.,* 1974; Rose and Davisson, 1996) and/or from isotopic carbon fractionation caused by limestone precipitation affecting deep uprising fluids (Minissale, 2004). It is worth noting that the differences between δ^{13}C-TDIC and δ^{13}C-CO_{2aq} values (Tabs. 2 and 3, respectively) are consistent with the values (9-10‰) theoretically predicted for isotopic fractionation occurring during the transformation of dissolved CO_2 into HCO_3^- (Mook *et al.,* 1974).

The extremely negative carbon isotopic signature of CH_4 (Tab. 3) clearly indicates that this gas originates from methanogenic activity (Schoell, 1980; Whiticar, 1999), a process that in the hypolimnion of lakes typically proceeds through CO_2 reduction (Belyaev *et al.,* 1975; Winfrey *et al.,* 1977; Schoell *et al.,* 1988). Therefore, CH_4 is produced within the bottom sediments and is released to the lake through diffusion and/or carried by the sublacustrine springs. Once in the lake, CH_4 is readily oxidized, as also testified by the decrease of O_2 concentrations (Tab. 3), indicating the occurrence of O_2-consuming reactions.

CONCLUSIONS

Lake Accesa is hosted in a basin produced by karst collapse(s) whose origin is likely related to sub-surface circulation of Ca-SO_4 fluids produced by interaction of meteoric water with rocks of Mesozoic carbonate and Triassic evaporite formations. These fluids represent the main water source for the lake, whereas direct contribution of rainwater accounts for less than 10% of the total water inflow. This hydrological cycle (Fig. 6) depends on the local structural assessment consisting of NNW and ENE-oriented fault systems. As a result, the total outflow of mineral water from the study area is one of the highest of Tuscany (Celati *et al.,* 1990) and in general of the Tyrrhenian side of central-southern Italy (Minissale, 2004). The occurrence of relatively high saline sublacustrine springs that discharge into CO_2-rich Lake Accesa and a pronounced thermocline (Fig. 4a) could determine favorable conditions for a density gradient able to produce a chemical stratification. Italian lakes having morphological features similar to those of Lake Accesa, *i.e.*, Averno and Monticchio Lakes (Cabassi *et al.,* 2013), are meromictic.

Notwithstanding these evidences, at Lake Accesa no significant variations of water chemistry with depth were recognized. A possible explanation is that the huge amount of mineral water recharging the lake from depth and then discharged through the Bruna River, which determines a relatively short renewal time for lake water (<3 months), is able to promote convective mixing of the water column. A continuous vertical circulation allows oxygenated shallow waters to reach the deep lake waters, preventing decomposition of organic material and dissolution of its end product that could contribute to enhance a vertical density gradient (Boehrer and Schultze, 2008). However, the vertical water mixing cannot prevent the instauration of a thermocline during the warm season, when solar radiation is able to rapidly increase the temperature of the shallow water layer thus seasonally maintaining a temperature vertical gradient.

The peculiar chemistry of Lake Accesa is the result of a complex combination of geostructural assessment, hydrological patterns and geochemical processes. Past experiences (Tesser, 2012) have shown that changes of the water drainage system in the nearby mining district have a strong influence on the deep-originated water supply for the lake,

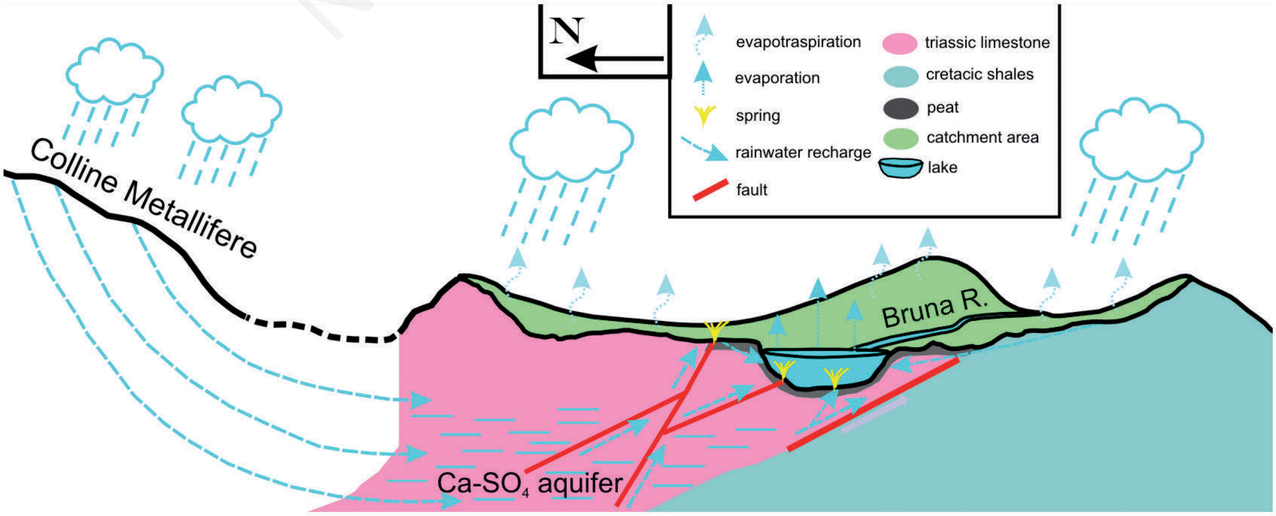

Fig. 6. Schematic model for the hydrological cycle of Lake Accesa.

thus possible future intervention should be carefully evaluated to preserve this unique natural environment.

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