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ISOTOPE CHARACTERISTICS OF THE WATER AND SEDIMENT IN VOLCANIC LAKE SAINT ANA, EAST-CARPATHIANS, ROMANIA

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Abstract: The paper gives the results of an isotope investigation carried out on the waters of the crater-lake, Lake Saint Ana (Sf. Ana), of the Ciomadul Mountain, which is located in the Harghita Mountains of the East Carpathians in Romania. The main purpose of this study was to ivestigate the isotope signature of the lake water. The collected water samples were examined for stable carbon, oxygen and hydrogen isotopes, and for noble gas concentrations, and, in addition, for radiocarbon and tritium. Sediment samples were collected for tritium measurement. The measured stable oxygen and hydrogen shows that the lake was subject to mixing before the sampling and there is ~50 % evaporation loss. The stable carbon analysis shows that there is an abundant volume of volcanic degassed CO_2 surplus which can be derived from the mantle. The ^{14}C activity of the lake's dissolved inorganic carbon is significantly less than the ^{14}C content of recent atmospheric carbon. This reservoir effect is supposed to be caused by the volcanic degassed CO_2 with no ^{14}C content. Depletion of radiocarbon in the order of 85–92.5 pMC could indicate a reservoir age of 950–1650 years. The tritium values of the lake water confirm the mixing theory of the lake and the tritium content of the sediment pore water shows that the lake discharges into the Ciomadul Mountain. The helium isotope ratios indicate a minor helium flux of mantle origin.

Keywords: Lake Saint Ana, Carpathians, Hydrology, Isotopes, Volcanic activity, Reservoir effect

1. INTRODUCTION

In the past couple of decades, many geochemical and geophysical investigations have been published on the areas of the East and South Carpathians (Pécskay et al., 1995; Vaselli et al., 2002; Karátson 1996). Many studies suggest the continued presence of a local hot magma chamber in the area beneath the Ciomadul volcano. It represents the main area of the present work, Lake Saint Ana. The seismic waves of the southern edge of the Harghita Mountains (Popa et al., 2005), the intense thermal anomaly of the Carpathian Region (Demetrescu & Andreescu, 1994) and the high $^{3}He/^{4}He$ irregularity in the natural gases, thermal waters and mineral waters (Vaselli et al., 2002) can prove the suggestion. One goal of this study is to estimate the recent volcanic activity of the Ciomadul volcano through the presence of the mantle gases in the lake water. It is probable that the volcanic activity in the area will increase, particularly that of the Ciomadul volcano, in the future (Harangi & Szakács 2005).

Our further aim was to provide basic hydrological information of Lake Saint Ana due to studying stable and radioactive isotopes in the lake water. The lake is the only existing volcanic lake in the Eastern Carpathians. Numerous

palaeoclimatological studies in this area have been performed recently (Magyari et al., 2009; Magyari et al., 2014; Karátson et al., 2013; Feurdean et al., 2012; Buczkó et al., 2013; Magyari et al., 2012). Stable isotopes (^{2}H and ^{18}O) in water act as natural tracers in understanding the mixing procedures within Lake Saint Ana. Radioisotope analysis is also commonly used in the investigation of lake water and sediment (Stiller et al., 1975; Carmi et al., 1984). Tritium has been used to understand the lake's dynamics and the discharge process going within the lake is another objective of this work. Recent studies have investigated the isotopic compositions of lakes in different climatic regions (Aeschbach-Hertig et al., 1999; Dettman et al., 2005; Bianchini et al., 2013; Halder et al., 2013).

The Ciomadul Mountain (46° 7'32.11"N, 25°53'14.61"E) has recent post-volcanic phenomena which exist in the area in the form of carbon dioxide degassing (Frunzeti and Baciu 2011). ^{14}C as a natural radioisotope of carbon can be a tool in establishing the mean residence time of carbon in the lake. Lake sediments have been used for estimating the accurate dating. On the other hand, an apparent radiocarbon age could be caused by the so-called reservoir effect, which occurs when there is another source of carbon other than the atmosphere. Estimation of the reservoir effect is the final object in this paper.

2. STUDY AREA

The Ciomadul volcano represents the last stage of volcanic activity within the volcanic belt of the Carpathian–Pannonian Region (Pécskay et al., 1995). The correct age has, so far, been questioned: previous research has shown that the activity was during 1–0.22 Ma (Moriya et al., 1996) and the last eruption is dated at 10,700 ± 180 yr BP (Juvigne et al., 1994) or earlier, >36,770 and 42,650 cal yr BP, which is the age of the Tuşnad pyroclastic flow (Moriya et al., 1995). According to recent research, the last eruption was at about 27,500 ± 260 yr BP (29,500 cal BC) or 39,000 (41,300 cal BC) based on the dating of two charcoal samples near Tuşnad and Bixad (Harangi et al., 2010) which could indicate two different volcanic events. The bedrock of the volcano is a flysch formation, consisting of sandstones and conglomerate, which is covered by lava domes and pyroclastic deposits of dacite magma, with a type of a calc-alkaline character (Seghedi et al., 1987; Szakács & Seghedi, 1987). The surface manifestations of post-volcanic phenomena are present in the area in the form of mofettas, fumaroles, solfataras and mineral springs.

Lake Saint Ana (946 m a.s.1., in Romania) formed in a crater. It is the youngest crater of the Ciomadul volcano and it is a unique volcanic feature in Eastern Europe (Fig. 1). The Ciomadul is a single volcano with two craters: the older is Mohos which is a peat bog, and the younger Saint Ana. The Mountain is part of the Neogene-Quaternary volcanic range of the East Carpathians (Mason et al., 1998). The lake has a surface area of 22 ha, a maximum depth of ~7 m and sediment of ~12 m thick (Magyari et al., 2009).

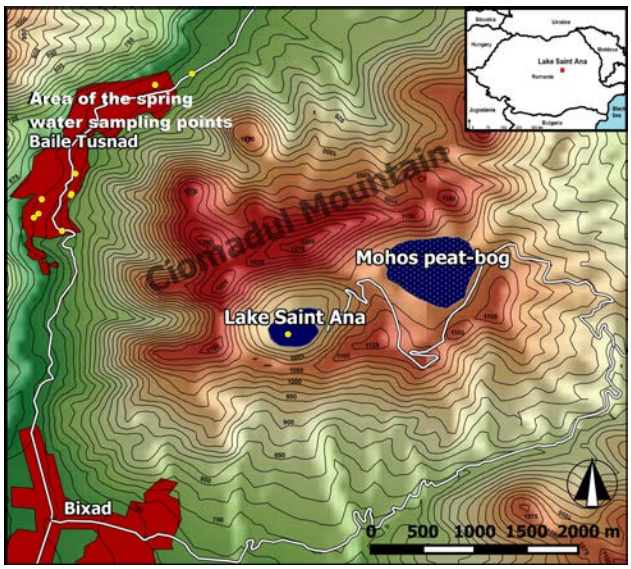

Figure 1. The location of the studied area

The water body of Saint Ana is very clear and the biogenic activity is relative low. Every winter the water of the lake is covered with ice of more than a half metre thick. The lake has no inflow or outflow water stream on the surface. The source of the water is derived from precipitation and the run-off water from the nearby slopes. Researchers assume the possibility of discharge, because the sum of the precipitation (800–1000 mm per year) (Karátson et al., 2013) and the run-off inflow is much larger than the estimated evaporation rate (500 mm/year). The mixing of the lake water column occurs twice a year, typically in spring and autumn and showing an oligotrophic pattern (Magyari et al., 2006).

3. METHODS

Water sampling from Lake Saint Ana was undertaken in February 2012, when the lake had been covered with ice, as horizontal sampling is much easier at this time. Samples of lake water were taken near the middle of the lake at the deepest point at depth intervals of 1 m from the surface to the bottom. Four sediment samples from bottom of the lake were taken for tritium analysis of the porous water at 1 m depth intervals to a depth of 4 m in

February 2012. In April 2014, spring-water samples were taken near the Ciomadul in the Băile Tușnad area to find out the interconnection between lake water and springs.

Isotopic analyses were carried out with an automated GASBENCH II sample preparation device attached to a Thermo Finnigan Delta Plus XP mass spectrometer (Vodila et al., 2011). Hydrogen and oxygen isotopes of the water, and the carbon isotopes of the dissolved inorganic carbon, were measured; they are expressed as δ^2H, $\delta^{18}O$, and $\delta^{13}C$ values relative to V-PDB for $\delta^{13}C$ and V-SMOW for δ^2H and $\delta^{18}O$, following the equation: $\delta = (R_{sample}/R_{standard}-1)*1000$, where R is the $^2H/H$, $^{18}O/^{16}O$ or $^{13}C/^{12}C$ ratio in the sample or in the international standard. The precision of the measurements is better than ± 0.2 ‰ for $\delta^{18}O$ and ±3‰ for δ^2H then ±0.1‰ for $\delta^{13}C$.

The ^{14}C measurement from the dissolved inorganic carbon (DIC) from the water samples were measured using an accelerator mass spectrometer designed for carbon isotopes (EnvironMICADAS AMS). Water samples (300 - 500 ml) were collected from the lake and dissolved CO_2 was extracted by the addition of 85% H_3PO_4 into the samples in vacum line. (Molnár et al., 2013a). The obtained pure CO_2 gas was converted to graphite by the sealed tube graphitization method (Rinyu et al., 2013). The ^{14}C measurements from the graphite targets were taken with a MICADAS type AMS (Molnár et al., 2013b). The overall measurement uncertainty for each sample was below 5%, including normalization, background subtraction, and counting statistics. The results were corrected for decay of the standard and for isotope fractionation using the ^{13}C measurement.

The noble gas and tritium measurements were carried out with a VG5400 noble gas mass spectrometer (Fisons Instruments). The noble gas samples dissolved in the lake water were stored in copper tubes sealed by stainless-steel pinch-off clamps. The water samples were passed through an automatic gas extraction and purification system before the mass spectrometric measurement of the noble gas concentrations as well as the $^3He/^4He$ isotope ratios (Papp et al., 2012). The results of the isotope ratios are given relative to the air in the form of R/R_A, where R_A is the ratio for the atmospheric standard, and R is the measured helium isotopic composition of the sample. The tritium concentration in water was determined using the ^3He ingrowth method. The measurement technique has a detection limit of 0.012 TU, and the precision is 2.4% between 1 and 20 TU (Palcsu et al., 2010).

4. RESULTS AND DISCUSSION

4.1. The stable oxygen and hydrogen isotope composition of lake water

The dynamics of the lake are not fully understood, but with isotopic investigations we can obtain more information, such as source and origin of the lake water and subterranean outflow beneath lake. The oxygen and hydrogen isotopic composition of the meteoric water in the hydrological cycle undergoes a fractionation process, hence each geographic location shows a specific precipitation composition depending on the latitude, altitude, distance from the sea and the elevation, and has a seasonal variability as well (Clark & Fritz, 1997).

The measured oxygen values of the lake are between -2.2 ‰ and -1.7 ‰ (Fig. 2). The sample just below the ice has the most negative $\delta^{18}O$ value (-2.2 ‰). We can assume that, the whole water body was mixed, and that the precipitation fell on the upper layer of the lake before the water froze. Additionally, the freezing of ice on the top of the water can dilute the top water layers in heavy isotopes. The vapour pressure and freezing point is lower for HDO than H2O so the heavier molecules showing a small preference to enter ice, in this case the concentration of D in the solid phase is higher than in the liquid. (Hoefs 1978).

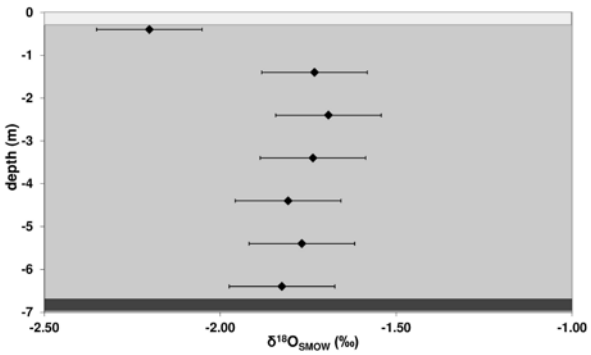

Figure 2. The measured oxygen values of Lake Saint Ana water as a function of depth

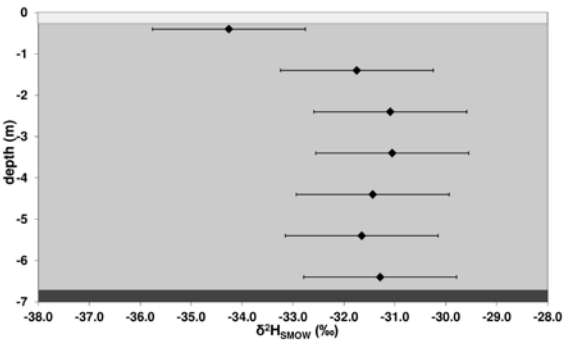

Figure 3. The measured hydrogen isotopes of Lake Saint Ana water as a function of depth

The hydrogen isotopic composition of the lake is between -31.1 ‰ and -34.3 ‰ (Fig. 3) and the hydrogen isotopes are directly proportional to the oxygen isotope values, therefore mixing and freezing of the upper layer occurred as well.

$\delta^{18}O$ and $\delta^{2}H$ in precipitation show a distinct empirical relationship, described by the Global Meteoric Water Line (GMWL, $\delta^2H=8*\delta^{18}O+10$), as the majority of δ^2H and $\delta^{18}O$ in precipitation are falling close to this line (Craig 1961). The local values may be different from this line, but the linear relationship does not change. There is no measured stable isotope composition for the precipitation near the lake; therefore, this was calculated using the Debrecen precipitation data adjusted for the distance from the oceans and the altitude. The formula can be found in the work of Clark & Fritz (1997). Using this method, the estimated values were calculated as -75 ‰ for hydrogen and -10.5 ‰ for oxygen. These estimated stable isotope values in the study area are very similar to that of local spring waters (Table 1). The average δ^2H and $\delta^{18}O$ are -77.3 and 11.2 respectively. These values somewhat more negative than that of precipitation. It can be explained that recharging water has more negative stable isotope composition than average precipitation does, since winter precipitation with negative values contributes to recharge more significantly then summer precipitation. All water samples of the lake have very positive delta values (Fig. 2 and 3) lying below the GMWL. Assuming these waters had enriched in heavy isotopes due to evaporation, a line was plotted from the measured oxygen and hydrogen isotope ratios in Lake Saint Ana and to the estimated precipitation values. The equation of the line is obtained to be $\delta^2H =4.98*\delta^{18}O-22.71$ (see Fig. 4). A strong evaporation effect was established using the lake water regression line. The lake has a boundary layer with saturated water vapour pressure at the observed temperature above the lake surface and equilibrium fractionation occurs between the water body and the boundary layer and kinetic fractionation between the boundary layer and the atmosphere (Barbieri et al., 2013; Craig & Gordon 1965). Kinetic fractionation is larger for ^{18}O than for ^{2}H, therefore the lake's evaporation line is more depressed than that of GMWL. As suggested by Gonfiantini (1986), the slope of this evaporation line could help in estimating the ambient humidity, which is an important environmental parameter in determining the evaporation effect. Therefore, the humidity results in a line with a slope of about 5 on a $\delta^{18}O$ vs. δ^2H plot which means that the ambient humidity is about ~60 %. The evaporation effect is calculated by Gonfiantini's estimations which examine the evaporation in lakes through the oxygen and the deuterium values (Gonfiantini 1986). The water lost by evaporation can be estimated based on the remainder isotope fraction of lake water relative to the started statement of the lake water (precipitation) and the humidity can be calculated through the slope of the GMWL (Gonfiantini 1986). It shows that the enrichment in 18O is from -10.5 ‰ to -1.8 ‰ for ~50 % evaporative loss and in 2H it is from -75 ‰ to -31.8 ‰ for ~50 % evaporative loss. Consequently, the lake has about ~50 % evaporation loss. The measured oxygen isotope compositions of the spring waters are between -9.6 ‰ and -13.3 ‰, and the hydrogen isotope compositions are -88.5 ‰ and -70.1‰, which reflect the estimated precipitation values (Table 1). No clear evidence can be seen with respect to the lake water discharge in the springs.

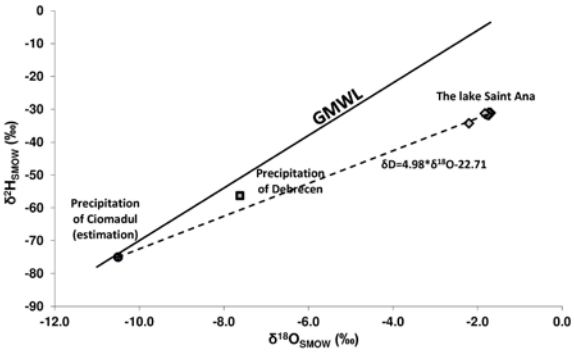

Figure 4. Delta plot for Lake Saint Ana showing the extent to which the lake water has been modified by evaporation compared to precipitation. The following signals are used: estimated precipitation of Ciomadul ●; precipitation of Debrecen ■; delta values of lake water ◊; GMWL: thick line; evaporation line of the lake: dotted line

Table 1. The measured stable hydrogen and oxygen isotope ratios of the spring-water samples

Name	**$\delta^{18}O$**	**$\delta^{2}H$**
Veresvíz spring 1	-10.7	-74.1
Veresvíz spring 2	-9.6	-70.1
Tiszás spring	-10.3	-71.2
Ilona spring	-11.1	-77.5
Apor spring	-11.0	-77.0
Mikes spring	-11.5	-78.0
Főkút spring	-13.3	-88.5
Rudi spring	-11.6	-77.1
Komlósároki spring	-11.1	-78.3
Ifjúsági spring	-11.4	-81.3

4.2. The stable carbon isotope composition of DICs

The origin of CO_2 in Lake Saint Ana can be deduced from the $\delta^{13}C$ of the DIC. The main source of

carbon in the lake is controlled by several biogeochemical processes, photosynthesis and exchanges with the atmospheric CO_2 (Bareši´ca et al., 2011), degassed CO_2 released by the volcanic activity.

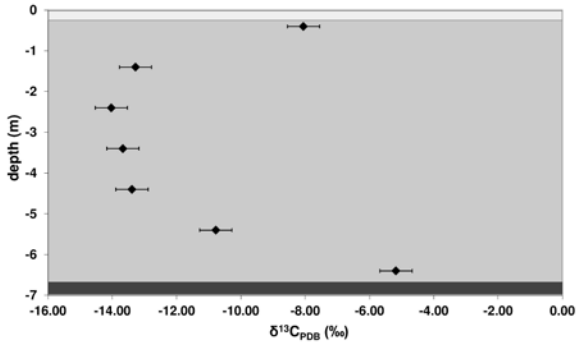

Figure 5. The measured stable carbon isotopes in water of Lake Saint Ana as a function of depth.

The depth profiles of the $\delta^{13}C$ in Fig. 5 range from -5.18 ‰ to -14.03 ‰. The profile shows some trends; therefore, at the top of the lake it is -8.04 ‰ and it depleted with depth. The top layer is mixed with atmospheric CO_2, which is -8 to -9 ‰ (Ribas-Carbo et al., 2002) and it reduces (~-13.5 ‰) due to the microbiological processes beneath the lake. After a depth of 5 m, the carbon isotope composition becomes heavier again, reaching a value of -5.18 ‰ at the deepest point of the lake. The diffused emission of the volcanic activity can catch up with the carbon isotopic composition due to mixing with the volcano-originated CO_2. According to the literature, this CO_2 can be derived from the mantle, because the mantle-derived CO_2 $\delta^{13}C$ values are between -4 and -7 ‰ (Vaselli et al., 2002). The enriched value of DIC in the bottom of lake indicates volcanic degassing as well as the increase by depth and it represents an important source of carbon in the lake water.

4.3. The ^{14}C in DIC

The ^{14}C radioisotope is a commonly used for dating of groundwater. It has a half-life of 5730 years which makes it useful for chronological research. Water dating uses dissolved inorganic/organic carbon in the water samples. The lake water samples show a relative low amount of DIC; less than 1.3 mg_{carbon}/l_{water} to a depth of 4 m, increasing to 5–7 mg_{carbon}/l_{water} at the bottom of the lake. This surplus DIC could be caused by the volcanic degassed CO_2.

The ^{14}C contents of the water samples are in the range from 92.5 pMC to 85 pMC see Fig. 6. Radicarbon activity changes spatially within the lake due to the difference in relative contribution from various carbon sources. As the present ^{14}C activity of the atmospheric CO_2 is 104 pMC (Molnár et al., 2010), the dilution of the radiocarbon might be caused by a fossil carbon source or older organic matter decomposition. The ^{14}C activity of the lake's DIC is significantly less than the ^{14}C content of the atmosphere. This reservoir effect might be caused by the volcanic degassed CO_2 with no ^{14}C content. This phenomenon is important in the radiocarbon dating of the lake bulk sediment when aquatic organic matter is dated. The observed depletion of radiocarbon in the order of 92.5–85 pMC could indicate a shift in the conventional ^{14}C ages of up to about 950–1650 years. So the ages are apparently increasing. These age shifts could be important for the paleo-ecological chronology of Lake Saint Ana (see: Magyari et al., 2006; Magyari et al., 2009; Hubay et al., 2014).

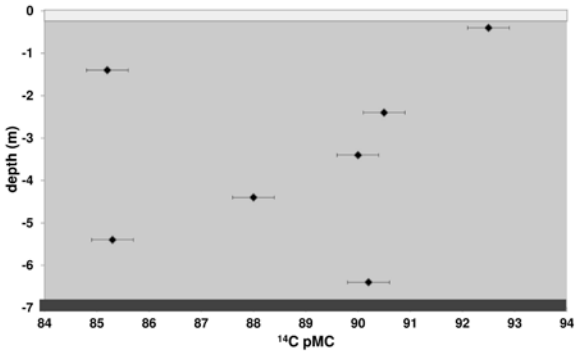

Figure 6. The ^{14}C content of the water samples of Lake Saint Ana as a function of depth

4.4. The tritium values of the lake water and lake-sediment deposits

Tritium (^3H) is a commonly used short-lived radioisotope of hydrogen with a half-life of 12.32 years (Lucas & Unterweger, 2000) and is used to identify modern recharge. Tritium is naturally produced in the atmosphere when cosmic rays react with atmospheric nuclei. During the nuclear weapon tests between 1951 and 1980, a large amount of ^3H was released into the stratosphere and in precipitation the greatest volume of all was in 1963. ^3H enters the groundwater-system by precipitation infiltration in the form of $^3H^1HO$. The tritium concentration in precipitation all over the world is about 2-20 TU. This value is an average of 10.4±0.3 TU in Debrecen, Hungary, which is located at a distance of 350 km from Ciomadul, and an average of 11.66 TU in Râmnicu Vâlcea, Romania, at a distance of 170 km from the sampling area (Varlam et al., 2013). In the case of Lake Saint Ana, whose water source is simply precipitation, tritium has been

directly added. The tritium values can answer the question of infiltration and the mixing procedures.

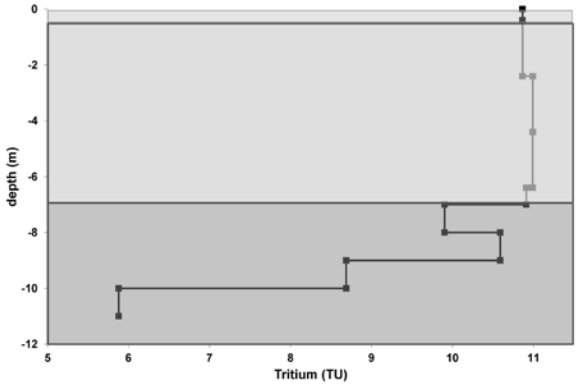

Figure 7. The tritium values of the lake water and lake-sediment deposit of Lake Saint Ana as a function of depth (SD=0.3)

The depth profile of the tritium values shows an average ~10.9 TU everywhere independent of the depth (Fig. 7). This means that the whole lake was subject to mixing before the sampling. These values are lower than the tritium content of the precipitation because it is added to an extant water mass within the tritium already decays. The tritium content of the lake is close to the present tritium concentration of the precipitation.

The tritium content of the lake sediment was measured to obtain basic hydrological information on the lake processes. The appearance of the tritium in lake sediment helps in identifying the infiltration process of the lake. The measured values decrease from 9.9 TU to 5.8 TU according to depth, and there is a raised value 10.6 TU at a depth of 2 m, which might be attributed to the nuclear bomb. These values confirm our assumption that the lake has a recharge into the Ciomadul Mountain.

4.5. The measured noble gas isotope ratios and concentrations

Helium isotope ratios dissolved in the water contribute to understanding whether the gas flux of mantle origin occurs through the lake sediment. The helium isotopic ratios measured in six water samples are reported in figure 8. The R/R_a value of the samples characterizes the origin of the gases. Samples with about 6.1–6.7 R/R_a have a typical mantle origin (Dunai & Baur 1995). The R/R_a ratio of 0.002–0.01 indicates a crustal derivation. The measured samples are in the range of 0.97–1.07 and this value increases with depth see figure 8. Helium ratio is highest at the bottom and decrease from the bottom to the surface due to mixing. The depth of the lake is very less 7 m so chances of escape or mixing is prominent, that causes lesser helium ratio. Previous studies in the Harghita Mountains showed that 50% of the gas samples were of mantle origin, and the remainder of mantle-derived magma, which, at depth, is still cooling and degassing (Vaselli et al., 2002).

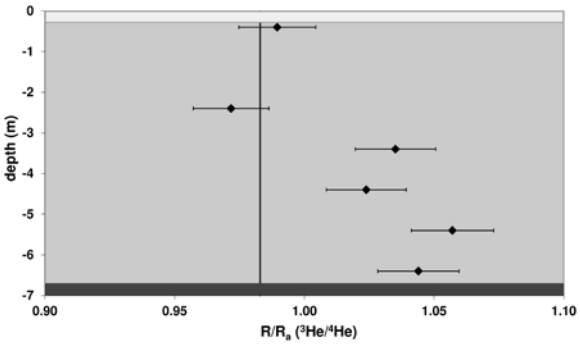

Figure 8. The measured helium isotopic ratio of the water samples of Lake Saint Ana as a function of depth

The concentrations of noble gas were measured in all water samples from each metre of depth. The measured helium concentration is between (4.16 and 4.45)·10^{-8} cm^3STP/g see Fig. 9. In the top layer of the lake the helium concentration is 4.22·10^{-8} cm^3STP/g and in the middle of the lake the helium concentration reaches 4.45·10^{-8} cm3STP/g, mostly due to the presence of air excess. In the bottom layer, this value is about 4.16–4.20·10^{-8} cm3STP/g as a result of mixing with diffuse gases which might originate from the deposits on the lake-bed.

In estimating the origin of the gas flux through the lake sediment, the $CO_2/^3He$ ratio may be an indicator. If the $CO_2/^3He$ ratio is between 10^9 and 10^{10}, the origin of the CO_2 is almost entirely the mantle. Above 10^{10} the CO_2 is predominantly of crustal origin (Sherwood-Lollar et al., 1997). In the previous section, we could see that there might be some excess inorganic carbon dissolved in the water. If this excess is supposed to be free of radiocarbon and in the form of CO_2, we can calculate its concentration. Assuming $6mg_{carbon}/litre_{water}$, an average DIC concentration in the bottom layer, and 88 pMC for radiocarbon, 0.47 ccSTP/litre is obtained for the excess CO_2 (note that the radiocarbon content in the atmospheric CO_2 is 104pMC). On the other hand, a slight excess of ^3He can be seen in the helium isotope ratio. The R/R_a ratios are between 1.04 and 1.07 in the deepest layers. The helium isotope ratio of water in solubility equilibrium with the ambient atmosphere is 0.983, hence the excess ^3He concentration in the bottom layer is 4.5·10^{-12} ccSTP/litre (the total

helium concentration is $4.18 \cdot 10^{-5}$ ccSTP/litre). What contributes to the increase of the $^3He/^4He$ isotope ratio? First, the radioactive decay of tritium; and second gas flux through the lake sediment. Since the lake had been subjected to mixing and the dissolved gases had re-equilibrated with the atmosphere about four months before the sampling, the tritium decay could produce $5 \cdot 10^{-13}$ ccSTP/litre of ^3He. Subtracting the tritiogenic ^3He contribution from the overall ^3He excess, we can achieve $4.5 \cdot 10^{-12}$ ccSTP/litre. The ratio of the excess CO_2 and the excess ^3He is then $1.2 \cdot 10^{11}$. This value is obviously within the crustal range of $CO_2/^3He$ ($>10^{10}$) indicating either that the CO_2 cannot be purely of mantle origin, or that the ^3He of mantle origin is lost during the over mixing of the lake in autumn and spring, while the CO_2 remains dissolved in the water in hydro-carbonate form.

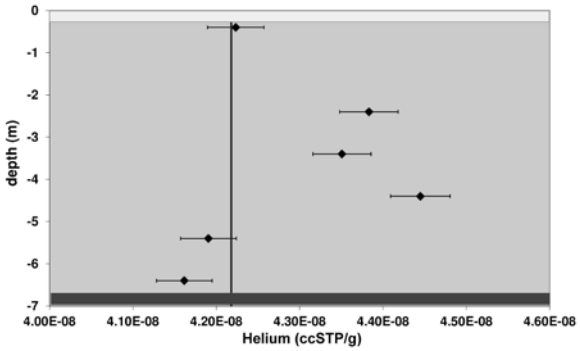

Figure 9. The measured helium concentration of Lake Saint Ana as a function of depth

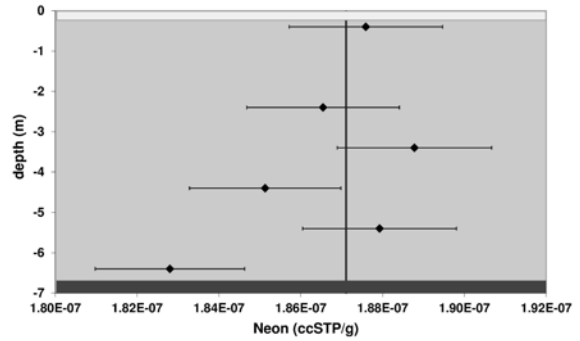

Figure 10. The measured neon concentration of Lake Saint Ana as a function of depth

Having looked at the other noble gases, other processes can be revealed. The noble gases dissolve in the water during contact with the atmosphere when the temperature and the pressure are determined and they do not change over time because they neither participate in biological nor in geochemical processes (Varsányi et al., 2011). The concentrations of noble gases (such as neon, argon, krypton and xenon) in the water samples were also determined.

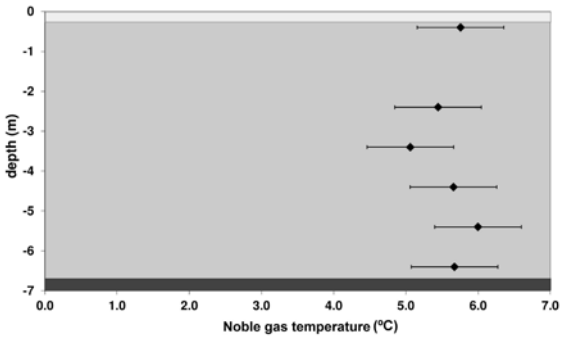

Figure 11. Noble gas recharge temperature of Lake Saint Ana as a function of depth

The concentration of neon is almost constant (Fig. 10), as well as the heavier noble gases (not shown here). Its values are in the range $(1.83–1.89) \cdot 10^{-7}$ cm^3STP/g. In addition to the air pressure, the solubility of noble gas has a temperature dependence called noble gas temperature which allows us to determine the temperature of solubility. Recharge temperatures were calculated using noble gas concentrations. According to the noble gas solubility temperatures, the lake-waters equilibrated at about 5–6°C see figure 11. Such constant values can be caused by the mixing of the lake water which occurs twice a year and this 5–6°C temperature is an average recharge temperature.

5. CONCLUSION

The isotopic analyses display that there is a mixing procedure in the Lake Saint Ana. Additionally, significant recharge occurs in the Ciomadul Mountain through the lake sediment, as indicated by recent tritium amounts found in the pore water at several-metre depths. Another purpose of this study to estimate the recent volcanic activity of the Ciomadul through the presence of mantle gases and the isotope results show some similarity with mantle origin for helium and CO_2. The ratio of the excess CO_2 and the excess ^3He was found to be $1.2 \cdot 10^{11}$, which is within the crustal range of $CO_2/^3He$ ($>10^{10}$) indicating that these gases cannot be purely of mantle origin. They can be either older organic material in the sediment with some radiocarbon content or the weathering of carbonate minerals with no radiocarbon. Due to an old carbon source, the DIC in the water (during wintertime) has a reservoir effect which could indicate a 950–1650 year shift in radiocarbon dating.

This study is an advanced investigation of Lake Saint Ana, and the results will strongly contribute to further sediment, geological and paleo-climate research.

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