Missing atmospheric noble gases in a large, tropical lake: the case of Lake Kivu, East-Africa

Fabian Bärenbold[1]*, Martin Schmid[1], Matthias S. Brennwald[2] and Rolf Kipfer[2,3]

[1] *Eawag, Swiss Federal Institute of Aquatic Science and Technology, Surface Waters - Research and Management, Kastanienbaum, Switzerland*
[2] *Eawag, Swiss Federal Institute of Aquatic Science and Technology, Water Resources and Drinking Water, Dübendorf, Switzerland*
[3] *ETH Zurich, Inst. of Biogeochemistry and Pollution Dynamics & Inst. of Geochemistry and Petrology, Zürich, Switzerland*

**Corresponding author, e-mail: fabian.baerenbold@eawag.ch*

Abstract

Lake Kivu is a 485 m deep tropical rift lake in East-Africa and well-known for its very high concentrations of dissolved carbon dioxide and methane in the stratified deep waters. In view of future large-scale methane extraction for power production, there is a need for predicting the evolution of gas concentrations and lake stability using numerical modelling. However, knowledge about the geochemical origin and transport processes affecting dissolved gases in the lake is still partially missing. Due to their inert nature, the analysis of dissolved noble gases can help to shed light on such questions. To learn more about transport processes in Lake Kivu, we extended a well-established sampling method for dissolved noble gases to work in the lake's high gas pressure waters. The results of our analysis show a distinct non-atmospheric isotopic signal in the deep waters (below 250 m) with $^{3}He/^{4}He$ and $^{40}Ar/^{36}Ar$ ratios ~250% and ~20% higher than air saturated water (ASW). Moreover, the gas concentration profiles reveal a striking lack of atmospheric noble gases in the deep waters with respect to ASW. While Ne is depleted by ~45%, the more soluble ^{36}Ar and Kr even decrease by ~70%. In contrast, ^{4}He concentrations increase

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with depth by a factor of up to ~600. We attribute this excess He and the increases in $^{3}He/^{4}He$ and $^{40}Ar/^{36}Ar$ to the inflow of magmatic gases into Lake Kivu, along with a significant contribution of radiogenic ^{4}He. To explain the depletion of atmospheric noble gases, we present and discuss three different scenarios, namely continuous outgassing, the inflow of depleted groundwater and a large past outgassing event. Due to the best agreement with our observations, we conclude that the inflow of depleted groundwater is likely responsible for the observed atmospheric noble gas depletions.

Keywords: noble gases; Lake Kivu; depletion; groundwater; volcanic region

1 Introduction

Meromictic Lake Kivu is part of the East African rift system and is located on the border between Rwanda and the Democratic Republic of the Congo. It has a surface area of 2386 km^2 and a maximum depth of 485 m. The rather small catchment area of around 5100 km^2 (excluding lake area) includes part of the Virunga volcano chain to the North of the lake. In this northernmost part of the catchment, there is no surface runoff (Figure 1), but the rainfall feeds several subaquatic groundwater sources, which provide around 45 % of the total inflow into the lake (1). Due to high salinity and carbon dioxide (CO_2) content, some of these sources stratify close to the lake bottom, while two large, less dense sources remain at ~180 and ~250 m (2,3). Consequently, steep physical and chemical gradients can be observed at these depths due to the dilution of upwelling deep water rich in nutrients, gases and salts (4). This situation leads to a strong density stratification, which suppresses turbulent mixing and therefore attenuates the upward transport of gases and nutrients (2). In fact, the stratification effectively prevents annual mixing below a depth of around 50 – 65 m and thus enables the accumulation of CO_2 and biologically produced methane (CH_4) (5,6) over hundreds of years in the vertically stratified and horizontally mixed deep waters.

On one hand, the high CH_4 concentrations of up to 20 mmol/L (2) represent a valuable resource, which is commercially exploited for electricity production by a 26 MW power plant since December 2015. On the other hand, the high total dissolved gas pressure (TDGP) in Lake Kivu is also a looming danger with a

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possible gas eruption endangering the life of around 2 million people around the lake. Indeed, the analysis of sediment cores in Lake Kivu indicates that mixing events have taken place in the past (7) and that the most recent (partial) mixing event may have happened about 1000 years ago (8).

In view of future large-scale gas extraction and changing lake temperatures (9), it is important to predict the lake's response to such changes. A one-dimensional model has been used in the past to understand gas and nutrient dynamics (2) and to predict the effect of gas extraction on stratification stability, nutrients and gas concentrations (10). Since the development of this model, detailed investigations allowed better constraining the nutrient and methane cycles in the lake (4,6). Furthermore, some of the subaquatic groundwater sources were located in the lake by Ross et al., (3). Nevertheless, there still persists a gap of knowledge regarding transport processes within Lake Kivu as well as the origin and gas content of the groundwater inflows.

The chemically and biologically inert noble gases can provide valuable insight into gas and water dynamics of water bodies (see review by Kipfer et al., (11)). In particular, noble gas profiles could help

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67 constraining turbulent mixing in Lake Kivu or reveal potential outgassing processes (11,12). In addition,
68 noble gas isotopic ratios can give hints about the origin of inflowing magmatic gases or fluids (13).

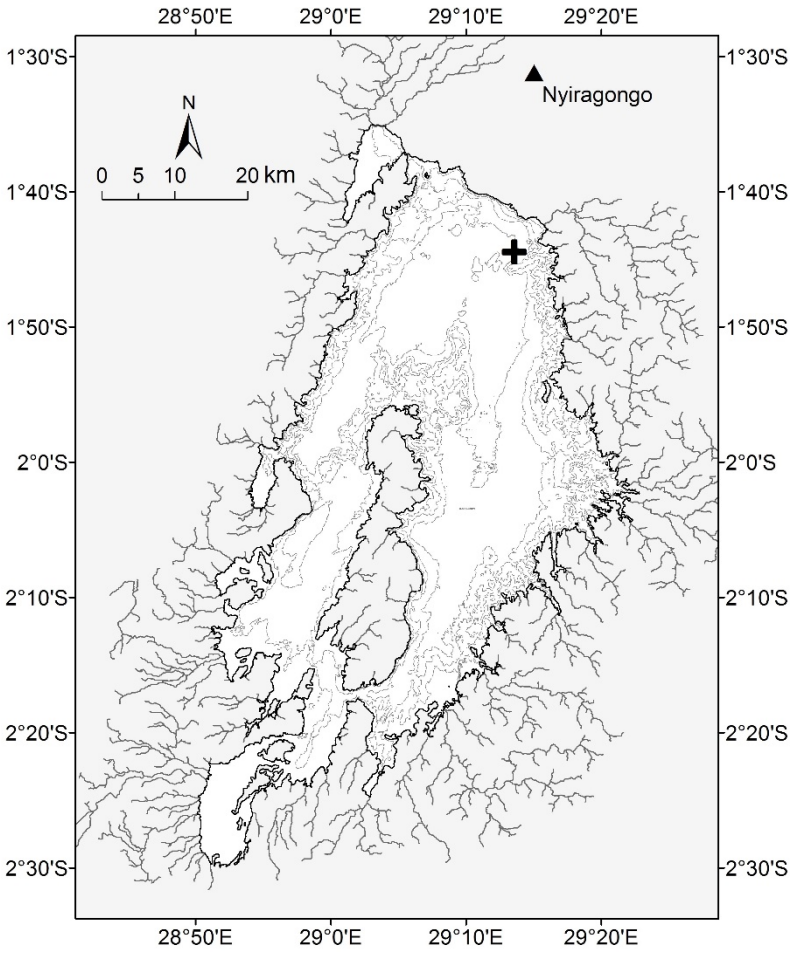

Figure 1: Lake Kivu bathymetry with contour lines every 100 m and surface tributaries. The cross indicates the sampling site (1.74087°S/29.22602°E) with a depth of 413 m. The triangle represents the active Nyiragongo volcano. Note the absence of surface run-offs in the northernmost region due to infiltration into the porous volcanic rock.

69

70 In this work, we present an extensive dataset of noble gas concentrations from two field campaigns which
71 took place at the northern shore of the Rwandan part of Lake Kivu. We start by describing the specially
72 designed sampling equipment for the high gas pressure conditions in Lake Kivu. Thereafter, we present
73 and discuss the recorded noble gas concentrations and isotope ratios in detail. In particular, we evaluate
74 three different scenarios to explain the observed depletion of atmospheric noble gases in the deep waters.

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2 Materials and Methods

2.1 Sampling site and time

Water sampling was performed on the research platform of the LKMP (Lake Kivu Monitoring Programme) 5 km off-shore in the northern part of the lake (Figure 1), From there, a maximum sampling depth of around 410 m could be reached. An additional sample was taken from a boat 7 km further off-shore at a depth of 440 m. We took 6 samples in January 2017 between 0 and 200 m and 11 samples in March 2018 between 100 and 440 m.

Horizontal mixing dominates vertical mixing in Lake Kivu due to negligible vertical turbulent diffusion (2) and a very slow upwelling (< 1 m/year, (4)) and thus, the lake can be assumed to be horizontally mixed below 65 m. The high horizontal homogeneity is documented by well-matching vertical conductivity and temperature profiles in different parts of the lake (3). Therefore, we can group together the samples from different locations and years and merge them into one depth profile.

2.2. Description of sampling method and analysis

Dissolved gas sampling is challenging in water bodies where TDGP exceeds atmospheric pressure (in Lake Kivu TDGP > 15 bar in the stratified deep waters). When the oversaturated water is lifted to the surface, the lack of hydrostatic pressure typically leads to severe loss of dissolved gases. To overcome this degassing of samples, we modified an existing in-situ sampling technique. As a starting point, we used the standard noble gas sampling technique described in (14): copper tubes are flushed and filled with ~45 g of sampling water, sealed gas-tight using the clamps of a metal rack and later degassed and analyzed in the laboratory using mass spectrometry. In lakes without excessive gas content, the water is usually sampled using a standard Niskin sampling bottle, retrieved and filled into the copper tube at atmospheric pressure. The absence of atmospheric contamination is ensured by continuous flushing of the copper tube prior to closing it.

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This sampling method was first extended to outgassing lakes by Winckler et al. (15). They developed a special in-situ sealing mechanism (see Figure 2 in (15)), using tapered metal plugs, which are pressed on the copper tube ends by the force of large springs. To keep the copper tube open, the springs are compressed by tripping levers which are attached to the triggering mechanism of a standard Niskin bottle by a thin steel cable. In the field, the whole setup is lowered to the required depth and a falling weight is used to release the springs and therefore close the copper tube. Back at the surface, the sample is permanently sealed using the metal clamps. We applied this method in January 2017, but observed gas loss in the samples below 200 m, and thus concluded that the springs were not strong enough to prevent gas loss above a certain TDGP.

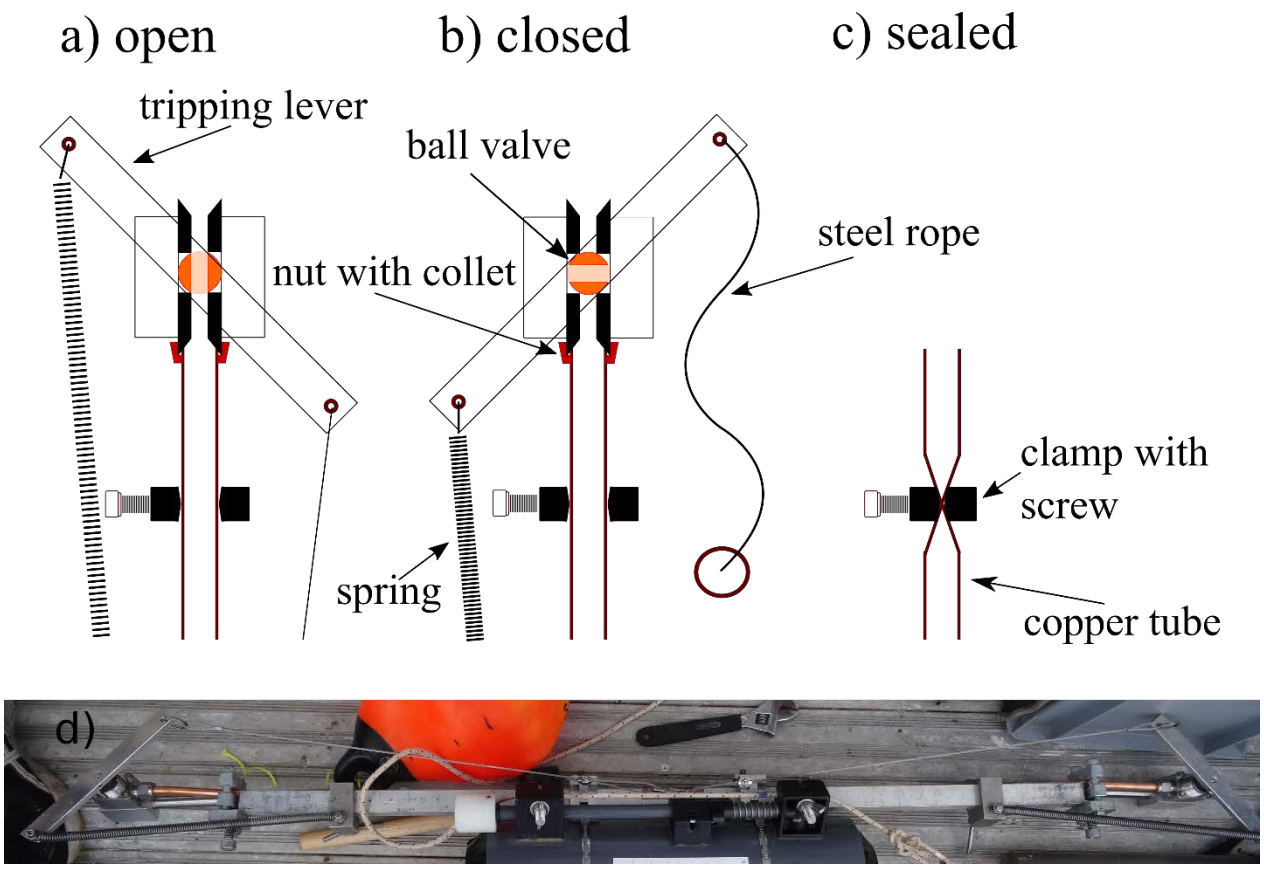

Figure 2: Schematic view and photo of the novel in-situ sealing mechanism using spring-loaded ball valves (Swagelok, pressure-proof to 172 bar). a) the tensioned steel rope keeps the ball valve open; b) the steel rope is detached (by a falling weight) and the spring closes the ball valve; c) the sample is permanently sealed using a metal clamp; d) photo of deployed sampling mechanism including a Niskin bottle (to use its trigger mechanism) and a buoy to keep the device upright in the water.

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Therefore, we developed a new in-situ sealing-mechanism using pressure-proof Swagelok ball valves (gastight up to 172 bar according to the manufacturer) instead of plugs (Figure 2). The valves are attached on each side of the copper tube using vacuum seals and preloaded using metal springs (Figure 2a). At the required sampling depth, the ball valves are triggered by a falling weight which closes the ball valves by detaching the steel ropes (Figure 2b). Once retrieved, the samples are sealed permanently using the clamps of the metal rack (Figure 2c). Finally, the samples are analyzed for noble gases ^{4}He, ^{20}Ne, ^{40}Ar, ^{86}Kr and ^{136}Xe as well as isotope ratios ^{3}He/^{4}He, ^{20}Ne/^{22}Ne and ^{40}Ar/^{36}Ar at the Noble Gas Laboratory at ETH Zurich, Switzerland (14). Note that in the following sections, we usually give the total elemental concentrations (computed from the isotopes) if not mentioned otherwise. The analytical uncertainty (1σ) for gas concentrations and ^{3}He/^{4}He was determined to be between 0.5 and 1%, whereas for ^{20}Ne/^{22}Ne and ^{40}Ar/^{36}Ar it was found to be around 0.2% (14). For this work, we chose to specify the uncertainty at the 3σ level (i.e. a 99.7% probability that the true value lies within the error margins). However, due to the special gas composition in Lake Kivu samples with high amounts of CH_4 and CO_2, these uncertainties are estimated slightly higher at 5% (instead of 3%) for gas concentrations as well as ^{3}He/^{4}He, and 1 % (instead of 0.6%) for ^{20}Ne/^{22}Ne and ^{40}Ar/^{36}Ar.

3 Results

3.1 Noble gas concentrations

The elemental noble gases Ne, Kr and Xe, as well as the isotope ^{36}Ar are called atmospheric noble gases in the following because these elements/isotopes are predominantly of atmospheric origin in the environment (11). The observed concentrations of these gases are presented in Tables 1 and 2, and Figure 3 shows the depth profiles of Ne, ^{36}Ar and Kr, normalized to the concentration of air saturated water (ASW) at 25 °C and salinity of 0‰ (ASW calculated according to Weiss (16), Weiss (17) and Weiss and Kyser (18)).

In the top 100 m, the concentrations of Ne, ^{36}Ar and Kr are approximately constant and close to ASW at 25 °C and 0 ‰ S (~5 % lower). Below, the concentrations consistently decrease with depth. This decrease

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is probably linked to the inflows of subaquatic groundwater sources which were previously postulated and observed by (2) and (3), as summarized in Table 3. Between ~100 and 200 m, a gradual decrease is observed, in line with a diffuse groundwater source between 135 and 180 m (3). The largest concentration gradient is observed at ~250 m where a strong, fresh groundwater point source enters the lake and dilutes the upwelling deep water, which is rich in nutrients and dissolved gases (2,4). Below ~265 m, we observe a depletion of ~45% of Ne and even ~70% of the more soluble ^{36}Ar and Kr with respect to ASW. Note that although the salinity in Lake Kivu is rather high, this only results in a change in noble gas solubility (i.e. the Henry coefficient) of around 3 – 4% and therefore, cannot explain the observed noble gas depletions of ~45 and ~70% respectively.

Table 1: Measured noble gas concentrations (in ccSTP/g) and isotope ratios. Air saturated water (ASW) concentrations are calculated according to (16,17,18) assuming a temperature of 25 °C and a salinity of 0‰. Note that we cannot explain the Xe concentrations and that they are not further discussed in this work.

Depth [m]	^{3}He/^{4}He	He	^{20}Ne/^{22}Ne	Ne	^{40}Ar/^{36}Ar	Ar	Kr	Xe
40	3.23E-06	7.19E-08	9.78	1.47E-07	296.1	2.34E-04	5.10E-08	6.89E-09
78	3.06E-06	1.90E-06	9.78	1.47E-07	297.4	2.40E-04	5.24E-08	7.07E-09
86	3.11E-06	2.61E-06	9.78	1.47E-07	298.3			
98	2.99E-06	3.92E-06	9.80	1.43E-07	298.8	2.36E-04	5.08E-08	7.29E-09
137	3.05E-06	6.20E-06	9.78					
167	3.31E-06	7.05E-06	9.78	1.36E-07	302.8	2.19E-04	4.71E-08	7.78E-09
196	3.13E-06	8.60E-06	9.79	1.34E-07	303.9	2.03E-04	4.34E-08	7.53E-09
213	3.29E-06	1.04E-05	9.78	1.28E-07	307.4	1.96E-04	4.19E-08	8.87E-09
254	3.68E-06	1.13E-05	9.78	1.20E-07	313.9	1.81E-04	3.92E-08	7.81E-09
273	4.41E-06	1.91E-05	9.79	1.03E-07	327.6	1.22E-04	2.29E-08	5.12E-09
294	4.16E-06	1.97E-05	9.80	9.69E-08	330.5	1.11E-04	2.13E-08	5.59E-09
337	4.33E-06	2.14E-05	9.81	9.47E-08	344.0	1.11E-04	2.29E-08	7.64E-09
348	4.72E-06	2.48E-05	9.80	9.18E-08	348.7			
368	4.79E-06	2.35E-05	9.77	8.92E-08	347.4	1.18E-04	2.18E-08	8.61E-09
390	4.57E-06		9.78	8.90E-08	352.9			
408	5.03E-06	2.38E-05	9.83	8.78E-08	350.6	9.41E-05	1.62E-08	8.05E-09
440	4.80E-06		9.81	8.43E-08	363.6			
Uncertainty	5 %	5 %	1 %	5 %	1 %	5 %	5 %	5 %
ASW	1.36E-06	3.83E-08	9.78	1.55E-07	295.5	2.46E-04	5.37E-08	7.41E-09

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Table 2: Noble gas concentrations (in ccSTP/g) and isotope ratios calculated from Table 1 (CO_2 and CH_4 data from M. Halbwachs and J.-C. Tochon in (2))

Depth [m]	^{3}He	R/R_{air}	^{36}Ar	$^{40}Ar^*$	$^{3}He/^{40}Ar^*$	$^{4}He/^{40}Ar^*$	$CO_2/^{3}He$ [x10^9]	$CH_4/^{3}He$ [x10^9]
40	2.32E-13	2.38	7.91E-07					
78	5.83E-12	2.25	8.05E-07					
86	8.11E-12	2.29						
98	1.17E-11	2.20	7.91E-07					
137	1.89E-11	2.24						
167	2.33E-11	2.43	7.23E-07					
196	2.69E-11	2.30	6.69E-07					
213	3.43E-11	2.42	6.39E-07					
254	4.15E-11	2.70	5.75E-07	1.06E-05	3.92E-06	1.07		
273	8.44E-11	3.24	3.71E-07	1.19E-05	7.08E-06	1.60	18.0	4.0
294	8.20E-11	3.06	3.35E-07	1.17E-05	6.99E-06	1.68	19.1	4.2
337	9.27E-11	3.18	3.22E-07	1.56E-05	5.93E-06	1.37	21.4	4.5
348	1.17E-10	3.47					17.2	3.6
368	1.12E-10	3.52	3.40E-07	1.77E-05	6.37E-06	1.33	17.9	3.7
390		3.36						
408	1.20E-10	3.69	2.69E-07	1.48E-05	8.09E-06	1.61	17.6	3.5
440		3.53						

Conversely, the Xe profile (not plotted in Figure 3) is devoid of any significant vertical structure, but exhibits a large variability. This is surprising as we are not aware of any process which would influence Xe fundamentally differently from Ne, ^{36}Ar and Kr in Lake Kivu. We thoroughly checked the data, but we found that samples from different lakes measured in the same measurement batch did not show any unusual behavior of Xe. In addition, the Lake Kivu Xe measurements are consistent over two different sampling campaigns and measurement batches in two different years. As we don't find any reason to discard the data, but cannot offer any explanation for this peculiar behavior of Xe in Lake Kivu we report the data in Table 1, but we do not further discuss it.

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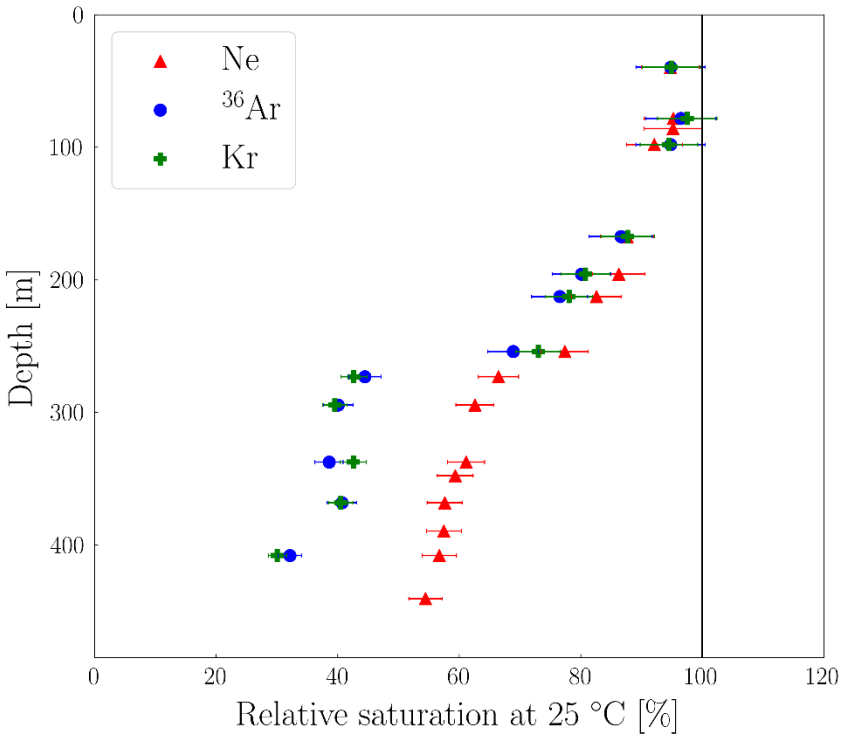

Figure 3: Depth profiles of noble gas concentrations Ne, ^{36}Ar and Kr measured in January 2017 and March 2018. Concentrations are normalized to the respective concentration of air saturated water at 25 °C and 0‰ S. ASW would be 3 to 4% smaller if S = 6‰ was used instead (maximum value in Lake Kivu, see Figure 4). ^{36}Ar is calculated from ^{40}Ar concentration and ^{40}Ar/^{36}Ar ratio measurements.

Table 3: Depths, discharges, temperature and salinity of groundwater sources according to (2) and (3), who used a 1D lake model to estimate the sources and their properties. The groundwater sources 1 and 2 are called "fresh", while the warmer, saltier sources 3-6 are called "hydrothermal" in this work. For the latter, the noble gas saturation depends on which scenario is chosen to explain the atmospheric noble gas depletion patterns (see discussion section).

No.	Depth [m]	Discharge [m^3/s]	Temp. [°C]	Salinity [g/L]	Atm. noble gas conc.
1	135 - 180	22	22.7 – 23.2	2.1 – 2.5	Close to ASW
2	250 - 255	15	23.3	2.7 – 3.1	Close to ASW
Total fresh		37			
3	315	1	25.2	3.4	Depleted?
4	365	1.5	24.5	5.5	Depleted?
5	425	0.8	25.3	5.8	Depleted?
6	465	1.25	26.0	6.0	Depleted?
Total hydrothermal		4.55			

In contrast to the atmospheric noble gases, He concentrations show a strong increase with depth by a factor of up to ~600 compared to ASW in Lake Kivu (Table 1 and Figure 4). Such high He concentrations

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176 are commonly observed in lakes in volcanic environments and, according to Kipfer et al., (11) can be
177 ascribed to input of gases originating from the earth's mantle and/or radiogenic production within the
178 crust. Figure 4 also shows that the He concentrations correlate very well with salinity.

179 Depleted noble gas concentrations have already been observed in crater lakes Nyos and Monoun in
180 Cameroon, but with much higher variability (19). These lakes are much smaller than Lake Kivu but both
181 also have a history of gas eruptions (21,22) and are also located close to a volcanically active region. The
182 ^{20}Ne, ^{36}Ar and ^{84}Kr concentrations measured in these lakes are similar to our results in Lake Kivu (60 –
183 70% depletion in Nyos and 70 – 80% depletion in Monoun). However, unfortunately Nagao et al. (19) did
184 not further discuss this unusual depletion of atmospheric noble gases.

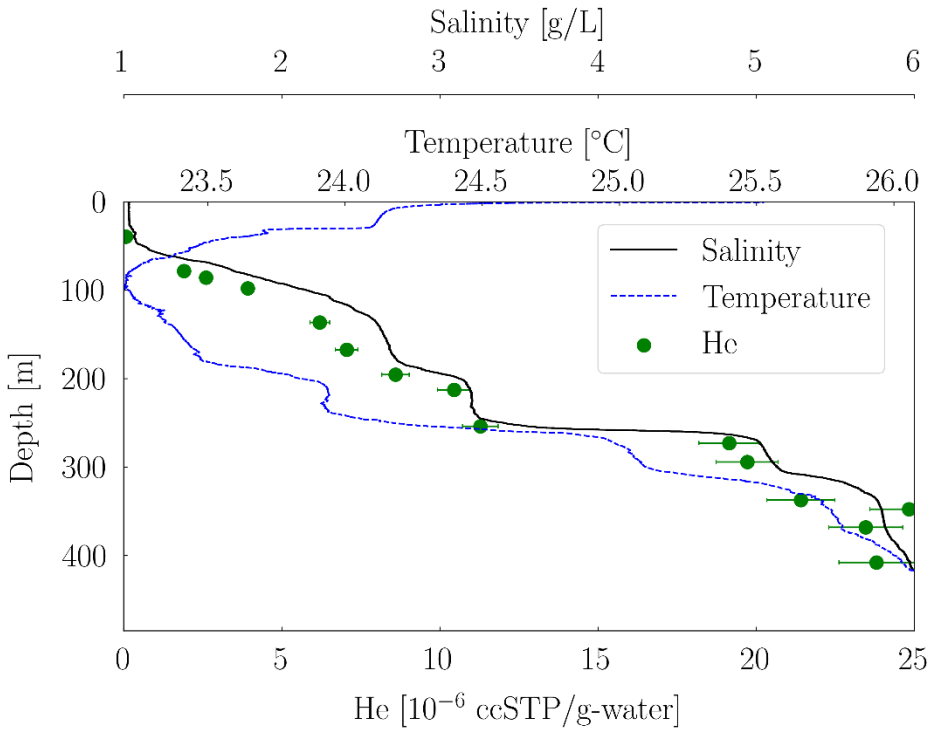

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Figure 4: The depth profile of Helium is shown along with salinity and temperature. ASW for He at 25 °C and 0‰ S is 0.038 x 10^{-6} ccSTP/g. Conductivity and temperature were recorded using a conductivity-temperature-depth profiler (CTD) from Sea & Sun in 2017 and 2018 (F. Bärenbold, unpubl.). Salinity is derived from conductivity using ionic composition according to (20). In Lake Kivu, salinity is mainly responsible for the density stratification.

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3.2 Noble gas ratios

The noble gas ratios $^{3}He/^{4}He$ and $^{40}Ar/^{36}Ar$ increase by around 60 and 20 % respectively from the lake surface to the bottom layer (Figures 5a and c; Table 1). At the surface, the $^{40}Ar/^{36}Ar$ ratio is close to air saturated water (ASW) and starts to slightly increase below 100 m. Between 200 and 300 m, the increase is more marked, but not as steep as the salinity and He gradients in Figure 4. In contrast to $^{40}Ar/^{36}Ar$, the $^{3}He/^{4}He$ ratio is still around 2.5 times above ASW at the lake surface, but exhibits a similar decrease below ~200 m. A very different behavior can be seen for the $^{20}Ne/^{22}Ne$ ratio (Figure 5b) which remains perfectly constant from 0 to 440 m. The maximum $^{40}Ar/^{36}Ar$ ratio of ~ 365 found in the Lake Kivu deep waters is roughly similar to the maximum value of 350 observed for fumaroles of the nearby Nyiragongo volcano, whereas it is around half for $^{3}He/^{4}He$ (~5 x 10^{-6} in Lake Kivu, ~11 x 10^{-6} in the fumaroles)(13).

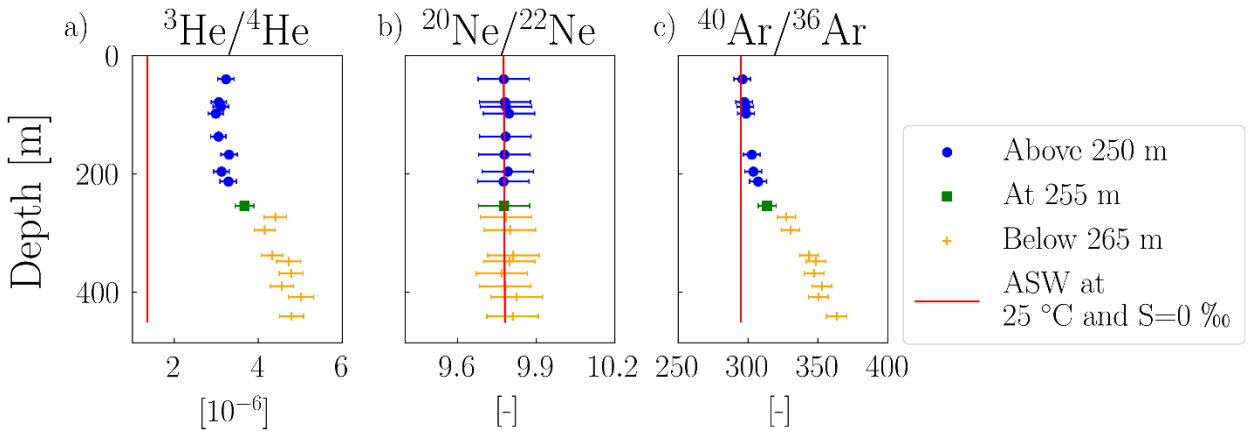

Figure 5: Depth profiles of measured isotopic ratios $^{3}He/^{4}He$, $^{20}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$. The ratios in air saturated water (ASW) are shown for comparison.

4 Discussion

4.1 Why are the atmospheric noble gases depleted?

As noble gases are inert, only physical gas processes can be responsible for any deviation of the measured concentrations from ASW at the respective temperature and salinity. In Lake Kivu (but also in Lakes Nyos

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and Monoun), the depletion could be caused by 1) continuous outgassing either due to bubbles released from the sediment or from a point source, 2) the inflow of hydrothermal water which is itself depleted with respect to ASW or 3) a relic from a past, large outgassing event. In the following, we will evaluate the consistency of each of the three scenarios with regard to our observations.

4.1.1 Scenario 1: Continuous deep water outgassing

Scenario 1 implies stripping of noble gases out of the deep water by gas bubbles containing mostly CH_4 and CO_2. Such bubbles could either originate from point sources (e.g. bubble seeps at the bottom, see for example (12)) or from homogeneous ebullition at the sediment interface (23). However, Lake Kivu is very deep and although its total dissolved gas pressure (TDGP) is very high, it is still significantly below hydrostatic pressure (a maximum of around 50% is reached at 320 m, F. Baerenbold unpubl.). Therefore, bubbles tend to redissolve at any depth. If the bubbles were produced by point sources, they would have to travel all the way up to the mixed zone (above 50 m). Otherwise, we would observe an accumulation of noble gases at some depths due to redissolution of bubbles. The existence of such accumulations is not supported by our data, which show a monotonous decrease with depth.

The bubble dissolution model used in (24) predicts that bubbles would need to have a diameter larger than around 20 mm in order to reach the mixed layer from the deepest point of Lake Kivu. This diameter is much larger than bubble sizes observed for deep seeps (25,26). It therefore seems unlikely that gas bubbles generated in the deep water can reach the lake surface. Conversely, if the gas bubbles were created homogeneously at the lake-sediment interface, they would not necessarily need to reach the surface to generate a net upwards transport of noble gases. In fact, bubbles could simply be generated at the sediment interface, migrate upwards a certain distance and redissolve. Due to the fact that there is a continuous lake-sediment interface at all depths, the result of such homogenous outgassing would be a depletion of noble gases in the deep waters.

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Although there are no observations of major continuous outgassing in Lake Kivu, there is some indication of a free gas phase in the sediment (Figure 6 in (8)) and even a possible gas emanating structure (Figure 4a in (27)). Potentially, larger noble gas stripping gas bubbles could originate from such free gas phases or gas emanating structures.

In addition to a depletion of atmospheric noble gas concentrations, continuous outgassing should also alter noble gas isotope ratios in the deep water by means of isotope fractionation at the bubble interface. The reason for this is the difference in molecular diffusion between the isotopes. This process is explained in detail in (28), and we can use Equation (1) in (28) to check whether our measured $^{20}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$ ratios agree with a Rayleigh fractionation pattern. For this purpose, we use the Ne and Ar diffusion coefficients found by (29) and our Ne and ^{36}Ar concentrations at the deepest sampling depth. The results of this calculation indicate a $^{40}Ar/^{36}Ar$ ratio of ~315 for an Ar depletion of ~70% for the deepest sample of this work. This means that only around 30 % of the observed increase of $^{40}Ar/^{36}Ar$ (up to ~365, Figure 5c) compared to ASW can be explained by bubble stripping. Furthermore, a $^{20}Ne/^{22}Ne$ ratio of around 9.72 is predicted for the deepest sample if bubble stripping were responsible for the Ne depletion of ~45% in Lake Kivu. However, we observe a constant $^{20}Ne/^{22}Ne$ ratio of ~9.78 through all depths in Lake Kivu (Figure 5b). Based on the uncertainty of 1% attributed to the $^{20}Ne/^{22}Ne$ ratio, a systematic depletion of $^{20}Ne/^{22}Ne$ down to 9.72 cannot be excluded, but seems very unlikely. And, even if outgassing was responsible for the observed atmospheric noble gas depletion, we need a second process to explain the observed enrichment of ^{40}Ar compared to ^{36}Ar.

4.1.2 Scenario 2: Inflow of noble gas depleted groundwater

In scenario 2, the atmospheric noble gas concentrations of inflowing deep hydrothermal groundwater (Table 3) are assumed to be significantly below ASW. One mechanism which can lead to inflow of noble gas depleted water is described in (15) for the Red Sea and in (30) for the Michigan basin. Adapted for Lake Kivu, the mechanism works as follows: i) groundwater is heated up in the volcanically active subsoil thus leading to a free gas/steam phase, ii) the noble gases preferentially partition into the gas/steam phase

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and iii) gas and water phases are separated, and only the water phase, now depleted in noble gases, reaches the lake. In Lake Kivu, the water temperature close to supposed hydrothermal groundwater inflows exceeds that of the lake water by a few degrees (Table 1 in (3)), which suggests that indeed the groundwater had been heated up before entering the lake. Other possible causes for noble gas depletion in groundwater are sketched in (30), including gas exchange between groundwater and an initially noble gas free oil phase. As heavier noble gases are more soluble in oil, this would explain why ^{36}Ar and Kr are more depleted in Lake Kivu compared to Ne. Incidentally, oil prospection is indeed going on in the Lake Kivu region (31).

4.1.3 Large past outgassing event

Scenario 3 assumes at least one large outgassing event to have happened in the past, which is supported by observations in sediment cores (8,32,33). During such an event, not only large parts of the main gases CO_2 and CH_4 would leave the lake, but also most of the atmospheric noble gases would be stripped. Subsequently, groundwater inflow and exchange with the atmosphere would slowly increase the noble gas concentrations until they reach values close to ASW again after hundreds of years. Note that in this scenario, in contrast to scenario 2, the hydrothermal groundwater sources are assumed to have noble gas concentrations close to ASW.

We can do a plausibility check for this scenario by comparing the residence time of the deep water (i.e. below ~265 m) to the time elapsed since the last supposed lake overturn. If one of these times is much larger than the other, we can exclude scenario 3 because of either too slow or too fast flushing of the water since the last overturn. However, both times are comparable and estimated to around 1000 years (see (2) for residence time and (8) for time elapsed since lake overturn). Based on this, we can expect the deep water to be completely replaced by hydrothermal groundwater within 1000 years. This means that there was enough inflow of noble gas saturated groundwater to bring the deep lake water close to saturation again. The reason why our observations differ from saturation could be explained by the absence of

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mixing processes in this assessment. Mixing may retain an unknown fraction of the depleted lake water in the deep layers, thus keeping this scenario within the realms of possibility.

Yet, due to their high density (as suggested by (3)), the deep groundwater sources 4 - 6 (Table 3) should stratify at the lake bottom. And since in scenario 3 (and also 1), we assume that these sources are close to saturation in atmospheric noble gases, we would expect increasing atmospheric noble gas concentrations with depth towards the lake bottom for these scenarios. This seems to be in contradiction to our data, as we recorded constant or rather monotonously decreasing atmospheric noble gas concentrations with depth below 265 m (Figure 3). Therefore, our data does not support the concept of the deep waters being refilled with atmospheric noble gases from the deep groundwater sources as suggested in scenarios 1 and 3.

4.1.4 Most realistic scenario

Scenario 1, the large-scale continuous outgassing is not very likely to happen in Lake Kivu due to i) the tendency of bubbles to redissolve at any depth and ii) the constant $^{20}Ne/^{22}Ne$ ratio, which suggests that isotope fractionation is not taking place. Similarly, we can reject scenario 3 by the lack of increasing noble gas concentrations towards the lake bottom. Therefore, we retain scenario 2, the inflow of atmospheric noble gas depleted groundwater, as the most promising scenario for the observed depletions in the lake. Furthermore, the almost perfect correlation between Ne, ^{36}Ar and Kr (Figure 6b and c) supports the view that this one mechanism can explain the depletion of all the atmospheric noble gas species.

As explained, in scenario 2 a fraction of the atmospheric noble gases is lost to a gas/steam phase in the subsoil. In principle, we would expect that a larger fraction of Ne is lost compared to the more soluble ^{36}Ar and Kr, which would lead to a larger depletion of Ne in the lake. However, we actually observe a larger depletion for ^{36}Ar and Kr and less depletion for Ne. Possible explanations for this observation include the contact of the hydrothermal groundwater sources with a (noble gas free) oil phase rather than steam (30) or the presence of large amounts of excess air (11).

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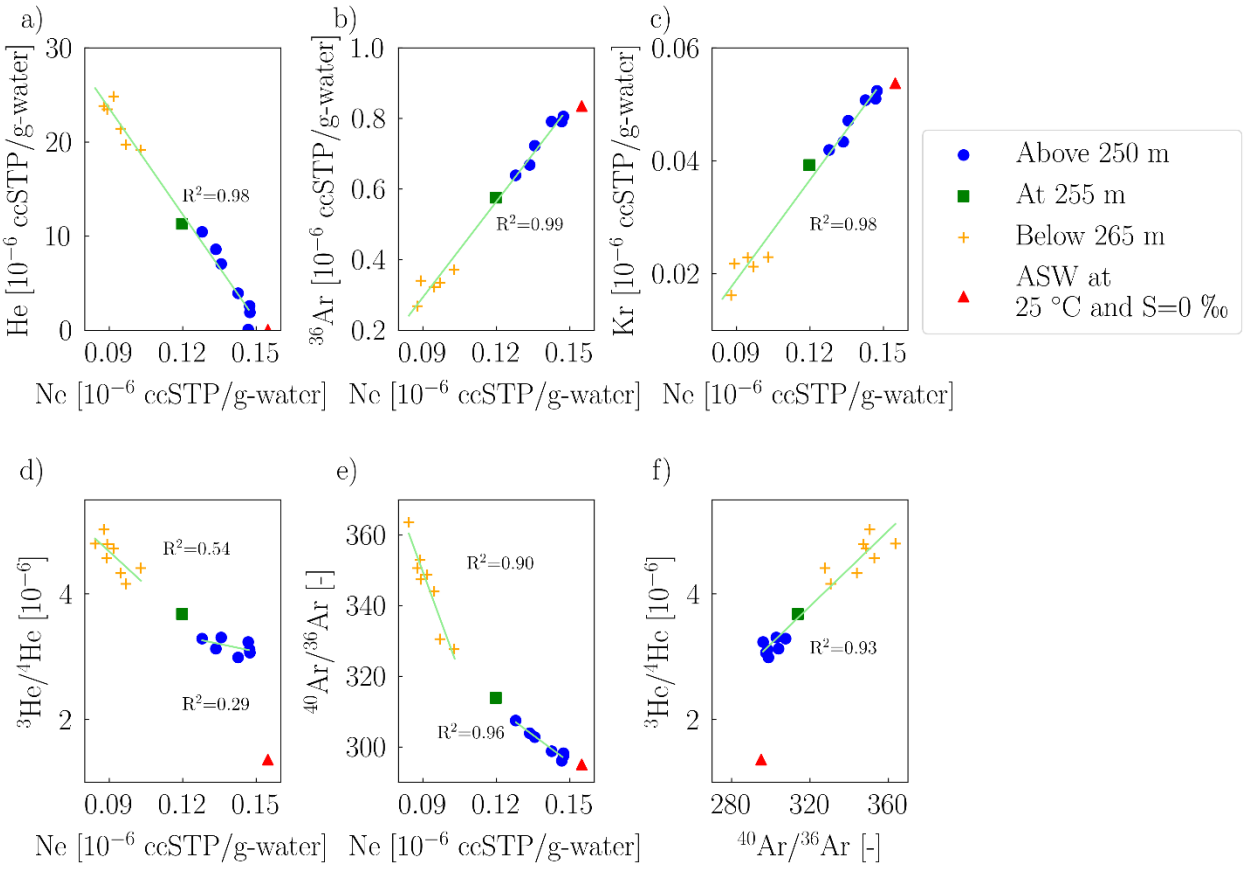

Fig. 6. a) – c) Noble gas concentrations are plotted against Ne, along with a linear fit. We have $R^2 > 0.98$ for the correlation between He, ^{36}Ar, Kr and Ne. d)-e) The relationship between noble gas ratios $^3He/^4He$ and $^{40}Ar/^{36}Ar$ against Ne is explained using two linear fits with different slopes. f) $^3He/^4He$ is plotted against $^{40}Ar/^{36}Ar$. The red triangle shows air saturated water at T = 25 °C and S = 0‰.

4.2 Inflow of magmatic ^3He, ^{40}Ar and CO_2

The increasing $^3He/^4He$ and $^{40}Ar/^{36}Ar$ ratios with depth (Figure 5a and c) confirm the presence of magmatic gases and/or fluids in Lake Kivu, as suggested by (13). These results are similar to reported observations from Lakes Nyos and Monoun (19). Furthermore, the monotonous increase with depth of these isotope ratios indicate that the main source has to be located close to the lake bottom (i.e. below the maximum sampling depth of 440 m). For scenario 2 of section 4.1., this suggests that ascending magmatic gases mix with groundwater in the subsoil, subsequently enter the lake and stratify at the lake bottom. The linear relationship between Ne, $^3He/^4He$ and $^{40}Ar/^{36}Ar$ on Figures 6d) and e) below 265 m confirms this link between atmospheric noble gas depletion and magmatic gases. However, the slope of this relationship

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changes above 250 m. There, the inflow of a different kind of groundwater is supposed at ~250 – 255 m and 135 – 180 m ((2,3) and Table 3). The hypothesis of inflow of groundwater admixed with magmatic gases is also in line with the explanation of Nagao et al. (19) for enriched $^{3}He/^{4}He$ and $^{40}Ar/^{36}Ar$ ratios in volcanic lakes Nyos and Monoun in Cameroon. The comparatively higher $^{3}He/^{4}He$ and $^{40}Ar/^{36}Ar$ values found in these lakes (up to ~8 x 10^{-6} and ~550 respectively, compared to ~5 x 10^{-6} and ~365 in Lake Kivu) can be readily explained by a higher fraction of magmatic gases in the respective mixture.

We can further use our isotope data to compute the $^{3}He/^{40}Ar^{*}$ ratio, where $^{40}Ar^{*}$ is the excess, non-atmospheric ^{40}Ar, computed as $^{40}Ar^{*} = {}^{36}Ar\,[(^{40}Ar/^{36}Ar)_{measured} - (^{40}Ar/^{36}Ar)_{air}]$. The $^{3}He/^{40}Ar^{*}$ values in the deep water of Lake Kivu of 0.6 - 0.8 x 10^{-5} (Table 2) are somewhat smaller than maximum values found for the Nyiragongo crater fumaroles of around 1.1 x 10^{-5} (calculated from the data in (13)). In addition, we can use the CO_2 measurements of M. Halbwachs and J.-C. Tochon (published in (2)) together with our ^{3}He measurements to derive the $CO_2/^{3}He$ ratio (Table 2). We find values of 17 – 21 x 10^{9} in the Lake Kivu deep waters which agree very well with the Nyiragongo crater gas values of ~20 x 10^{9} found by Tedesco et al. (13). The $CO_2/^{3}He$ ratios therefore confirm that the CO_2 in Lake Kivu is mostly of volcanic origin.

4.3 Input of radiogenic ^{4}He and its link with atmospheric noble gas depletion

Figures 4 and 6a show that the He concentrations correlate very well with salinity and Ne concentrations (and thus the concentrations of the other atmospheric noble gases ^{36}Ar and Kr). These correlations strongly suggest that the He excess in Lake Kivu is governed by the same mechanism as these quantities, i.e. by the hydrothermal groundwater inflows. However, the admixture of magmatic gases (previous section) and the dilution by fresh water sources (Table 3) alone are not sufficient to explain the observed He concentration and $^{3}He/^{4}He$ ratio profiles. Specifically, the He concentration in the (supposedly) ASW saturated fresh groundwater sources is >2 orders of magnitude lower than in the deep water and therefore, there is simply not enough ^{4}He to generate the observed $^{3}He/^{4}He$ profile. To show this, we use the total hydrothermal and fresh discharges given in Table 3. In this situation, ~4.55 m^3/s of deep water with 2.4 x

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10^{-6} ccSTP/g He and a $^{3}He/^{4}He$ ratio of 5.03 x 10^{-6} (Table 1) are diluted by ~37 m^3/s with He = 3.8 x 10^{-8} ccSTP/g and $^{3}He/^{4}He$ = 1.36 x 10^{-6} (i.e. ASW, see Table 1). The resulting $^{3}He/^{4}He$ ratio at ~100 m depth is only ~1% lower than at 410 m due to the large difference in total He concentration between the two components. However, in our data we observe a change of the $^{3}He/^{4}He$ ratio from ~5 x 10^{-6} to ~3 x 10^{-6}, i.e. a decrease of 40%. To explain this large difference, we suggest the contribution of radiogenic ^{4}He (with $^{3}He/^{4}He=10^{-8}$), produced in the rocks (11). We calculate that we need ~50 times more ^{4}He from radiogenic production than from the ASW saturated groundwater sources to obtain the observed change with depth of He concentration and $^{3}He/^{4}He$ ratio in Lake Kivu.

Moreover, the measured $^{3}He/^{4}He$ ratios in the deep waters of Lake Kivu are only around half of that in its supposed source, i.e. the magmatic gases of the Nyiragongo volcano. The mixture of these magmatic gases with ASW saturated groundwater cannot produce water with high He and $^{3}He/^{4}He$ values at the same time. If the mixture involves enough groundwater to lower the $^{3}He/^{4}He$ ratio to around 50% of its original value, the corresponding decrease in He concentration would be 98 %. Once again, the contribution of both radiogenic and magmatic He is required to explain the observed He concentrations and $^{3}He/^{4}He$ ratios.

Overall, we suggest that the observed He concentration and $^{3}He/^{4}He$ ratio profiles can be explained by a combination of hydrothermal He inflow with ~50% He derived from magmatic gases and ~50% of radiogenic ^{4}He (the effect of ASW saturation is negligible) and fresh groundwater inflow with ~98% He from radiogenic ^{4}He and ~2% from ASW saturation.

5 Conclusion

We successfully analyzed noble gas concentrations in highly gas-rich Lake Kivu. The in-situ noble gas sampling showed a remarkable depletion of atmospheric noble gases Ne, ^{36}Ar and Kr by about 45 to 70% compared to ASW. In addition, magmatic noble gas isotopes ^{40}Ar and ^{3}He, as well as radiogenic ^{4}He are enriched in the deep waters. The $^{3}He/CO_2$ ratio observed in the deep water is very similar to values found

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for the Nyiragongo crater gas, supporting the idea that the CO_2 in Lake Kivu is indeed mostly of magmatic origin.

We presented three possible mechanisms which could lead to the observed noble gas depletion. Scenario 1, the continuous stripping of noble gases in the lake by bubbles, is not supported by our $^{20}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$ profiles. There is no fractionation in the $^{20}Ne/^{22}Ne$ profile, which indicates that kinetic fractionation during bubble formation did not occur. Scenario 3 consists of an initially atmospheric noble gas free lake (after an overturn) and the gases are resupplied by hydrothermal sources. This scenario is largely compatible with reported residence time and groundwater discharges. However, the salinity profile suggests that the groundwater sources stratify at the lake bottom and thus we should observe the largest concentrations of atmospheric noble gases close to the bottom. In contrast, our observations show the lowest concentrations at the largest depths.

Scenario 2, the inflow of noble gas depleted groundwater, is best supported by our data. The arguments in favor include positive temperature spikes (as observed by (3)) at supposed locations of groundwater inflows and a very good correlation between atmospheric noble gases and He, indicating that the depletion of atmospheric gases and the enrichment of He have a common origin. We also observe that Ne is less depleted than the more soluble ^{36}Ar and Kr. To explain this, a considerable amount of excess air needed to be trapped during original infiltration of the water, which later formed the hydrothermal sources (11).

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