High Temperature Noble Gas Thermometry in Lake Kivu

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Abstract

Due to their biological and chemical inertness, noble gases in natural waters are widely used to trace natural waters and to determine ambient temperature conditions during the last intensive contact with the atmosphere (equilibration). Thus far, only common environmental conditions have been considered, and hence investigated temperatures have almost never exceeded 35 °C, but environmental scenarios that generate higher surface-water temperatures (such as volcanism) exist nonetheless. We make use of newly determined solubility data at higher temperatures to analyze data of unexpectedly low noble gas concentrations in the deep water of Lake Kivu by applying various approaches of noble gas thermometry. Noble gas concentration ratios and least squares fitting of individual concentrations indicate that the data agrees best with the assumption that deep water originates from groundwater formed at temperatures of about 65 °C. Thus, no form of degassing is required to explain the observed noble gas depletion: the deep water currently contained in Lake Kivu has most probably never experienced a large scale degassing event. This conclusion is important as limnic eruptions were feared to threaten the lives of the local population.

Keywords: Lake Kivu; Noble gas thermometry; Groundwater formation; Soil temperature; Volcanism; Ebullition.

1 Introduction

Dissolved gases in natural waters are inherited from the atmosphere by equilibrium dissolution and are therefore sensitive to the various conditions of air-water gas exchange. Due to their chemical and biological inertness and their extremely homogeneous composition in the Earth's atmosphere, the noble gases in particular present themselves as ideal geochemical tracers. Measurements of their concentrations have been widely used to reconstruct ambient temperatures during the last intensive contact with the atmosphere (equilibration) (Aeschbach-Hertig & Solomon, 2013; Mazor, 1972; Benson, 1973). This approach, called *noble gas thermometry*, can track groundwater recharge temperatures (Stute et al., 1995; Beyerle et al., 1998; Weyhenmeyer et al., 2000), analyze temperature variations in the past (Stute & Schlosser, 1993; Seltzer et al., 2021) and reconstruct deep ocean recharge temperatures (Loose et al., 2016). Noble gas thermometry has usually focused on equilibration temperatures below 35°C (Aeschbach-Hertig et al., 1999). However, environmental scenarios that generate much higher surface-water temperatures exist (volcanic activity etc.).

Lake Kivu, located at the foot of the Nyiragongo volcano, could be such an example of higher temperatures. It contains vast amounts of dissolved carbon dioxide and methane (Tietze et al., 1980; Bärenbold, Schmid, et al., 2020; Boehrer et al., 2019). Most of the CO_2 is of geogenic origin and is brought into the lake by the sub-lacustrine springs and hydrothermal systems (Deuser et al., 1973; Schoell et al., 1988) and by few surface rivers from the Nyamulagira volcanic field (Balagizi et al., 2015). The CH_4 is mainly produced from bacterial reduction of magmatic CO_2 and to a lesser extent from the fermentation of organic material in the sediments. The methane deposit is of great economic value and is being exploited for the production of energy (Boehrer et al., 2019; Schmid et al., 2019; Bärenbold, Boehrer, et al., 2020). The resulting immense gas pressures have been feared to trigger a limnic eruption, as it happened at Lake Nyos and Lake Monoun in Cameroon in 1986 and 1984, respectively, and therefore pose a threat to over 2 million local inhabitants of the region (Kusakabe, 2017; Sigurdsson et al., 1987; Kling et al., 1994; Lorke et al., 2004; Boehrer et al., 2021). The recent Nyiragongo volcano eruptions of January 2002 and May 2021 reminded of the precarious situation: magma coming into contact with the deep waters of Lake Kivu could result in local heating and the formation of bubbles which - in the worst case - could trigger a large scale ebullition. In addition, strong earthquakes and large landslides have been listed among external factors that could give rise to a limnic eruption of Lake Kivu, as the lake is located in the floor of a young seismically active rift (Balagizi et al., 2018). The Lake Kivu basin is abound with important tectonic features such as faults, fractures and fissures related to volcanic eruptions and to the rift opening (Balagizi et al., 2016; Pouclet et al., 2016).

Recent measurements (Bärenbold, Schmid, et al., 2020) have found unusually low concentrations of Ne, Ar and Kr in the deep water of Lake Kivu when compared to air-saturated water. At first sight, this could be interpreted as the residual feature of stripped noble gases after a limnic eruption caused by large amounts of escaping methane and carbon dioxide. A closer look revealed that degassing alone could not explain the stronger depletion of heavy noble gases compared to lighter ones ($\sim 70\%$ for Ar and Kr compared to $\sim 45\%$ for Ne). Bärenbold et al. (2020) hence concluded that the groundwater which feeds the lake from below was most probably already depleted of noble gases when it entered the lake.

We explore the possibility of higher equilibration temperatures being responsible for the noble gas depletion in Lake Kivu's deep water, as groundwater entering below 260 m is enriched in cations and alkalinity and thus deemed to originate from hydrothermal sources

(Ross et al., 2015). We therefore use the extended solubilities of Schwenk et al. (2022) to make a larger domain of temperatures accessible to noble gas thermometry. We estimate equilibration temperatures from (1) the saturation concentrations of each noble gas, (2) ratios of dissolved noble gases and (3) also apply a least squares fitting using the PANGA software (Jung & Aeschbach, 2018) that allows for excess air formation and an optimized fit to conclude on the origin of the noble gas deficit.

2 Noble Gases in Natural Waters

The partial pressure an atmospheric gas i exerts on a water surface can be related to its water-side concentration in the most common form of Henry's law:

$$p_i = K_{H,i} C_{W,i}, \tag{1}$$

where p_i is the partial pressure of a gas i in the atmosphere, $C_{W,i}$ is the concentration of that gas in water and $K_{H,i}$ is its *Henry coefficient* (Aeschbach-Hertig et al., 1999). Rewriting Equation 1 in the form:

$$C_{W,i} = L_i \cdot p_i, \tag{2}$$

allows us to define the *solubility* $L := 1/K_H$, which describes how much gas is dissolved in the water phase at a certain partial pressure. If the water-side concentration is given in $\mathrm{cm^3STPg^{-1}}$, then the solubility has the units $\mathrm{cm^3STPg^{-1}atm^{-1}}$. If equilibration is assumed to take place at 100% saturation vapor pressure, one can rewrite Equation 2 and explicitly indicate dependencies on temperature T and altitude z to give:

$$C_{W,i}(T,z) = L_i(T) \cdot (p_{\mathrm{atm}}(z) - e_s(T)) \cdot x_i, \tag{3}$$

where $p_{\mathrm{atm}}(z) = p_0 \cdot \exp(-z/H)$ is the total atmospheric pressure at altitude z without regard to weather variability (and $H = 8700\,\mathrm{m}$ is the scale height assuming a mean temperature of the relevant air column of 25 °C), $e_s(T)$ is the saturation vapor pressure at temperature T and x_i is the atmospheric mixing ratio of the gas i. This concentration is also called the *equilibrium concentration* $C_i^{\mathrm{eq}}(T, p(z))$. When using this formulation it is clear that the concentration goes to zero at the boiling point, where $e_s(T) = p_{\mathrm{atm}}(z)$. The saturation vapor pressure required in Equation 3 was calculated using the IAPWS formulation (IAPWS,

1992). Using any form of the Magnus equation would deliver large errors for temperatures above 60 °C (Huang, 2018).

Very few assumptions must be made when using the equilibrium concentration for equilibration temperature reconstruction: calculations of water-side concentrations under various conditions such as different altitudes or no full saturation can be easily applied according to Equation 3. This work utilizes recently published solubilites (Schwenk et al., 2022) that are valid from 0 to 80 °C and are used to depict the equilibrium concentrations of Ne, Ar, Kr and Xe for an altitude of 1460 m (Lake Kivu's surface) in Figure 1.

In groundwater, the concentrations of dissolved noble gases are usually found to be in excess due to the entrapment of air bubbles under higher hydrostatic pressure during formation (Aeschbach–Hertig et al., 2000). The unfractionated air (UA) model describes the complete dissolution of entrapped air bubbles by adding an excess air component A, given in $\mathrm{cm^3STPg^{-1}}$, multiplied with the atmospheric abundance x_i, to the equilibration concentration C_i^{eq}:

$$C_i(T, p(z), A) = C_i^{eq}(T, p(z)) + Ax_i. \tag{4}$$

This model is the most simple, since it has only three free parameters (two if pressure is assumed) and is therefore the one we applied. More complex models can be found in Aeschbach-Hertig & Solomon (2013).

Natural waters often contain contributions to certain noble gas isotopes that are produced in the subsurface (mainly the Earth's crust) by radioactive decay of parent isotopes (radiogenic), by nuclear reactions (nucleogenic) or as products of nuclear fission (fissiogenic). The most prominent and ubiquitous radiogenic noble gas isotope is ^{4}He, which is abundantly produced in the decay chains of U and Th present in rocks and minerals. The minor He isotope ^{3}He often has a nucleogenic contribution, but is also prominently contained in fluids of magmatic (or Earth mantle) origin. Another important radiogenic isotope is ^{40}Ar (from the decay of ^{40}K), which is produced in the crust and also contained in magmatic sources, but usually negligible in shallow groundwaters because of the high atmospheric abundance of Ar. For Ne, the nucleogenic contribution to the rare isotope ^{21}Ne can be relevant in very old groundwaters. Similarly, fissiogenic components of certain Kr and especially Xe isotopes exist, but are usually insignificant in shallow groundwaters.

The presence of non-atmospheric noble gas components can be identified through isotope ratios that deviate from those in the atmosphere, and when reconstructing equilibration temperatures it is crucial to correct for these contributions, which are not described by the above discussed models (Aeschbach-Hertig & Solomon, 2013). This is possible for Ne and the heavier noble gases by resorting to isotopes of purely atmospheric origin, such as the minor Ar isotope ^{36}Ar. No such isotope exists for He, therefore He is usually not considered in noble gas thermometry.

Natural waters can become depleted in noble gases through gas stripping upon bubble formation. This process depletes lighter elements more than heavier elements due to their higher diffusivity (Bourg & Sposito, 2008; Brennwald et al., 2005; Aeschbach-Hertig et al., 2008).

2.1 Noble Gas Thermometry

In noble gas thermometry one assumes the conditions of groundwater formation (simple, full equilibration according to Equation 3 or more complex models such as the UA model from Equation 4) and infers the temperatures from measurements of noble gas concentrations. In this work we consider three approaches: noble gas saturation temperatures, noble gas concentration ratio temperatures, and inverse modelling of more complex cases using the PANGA software (Jung & Aeschbach, 2018).

The approach of noble gas saturation temperatures assumes simple, full equilibration during groundwater formation. Temperatures T_i^{sat} are thus calculated by numerically inverting the equilibrium concentration C_i^{eq} (Equation 3). Uncertainties are determined through the min/max evaluation of temperatures at the upper and lower error bounds of concentration measurements. Figures 1 a) - d) show the equilibrium concentrations evaluated using the recently determined solubilities by Schwenk et al. (2022) from 0 to 80 °C and an altitude of $z = 1460$ m for Ne (a), Ar (b), Kr (c) and Xe (d). We find that the progression is strictly monotonic in all cases, thus allowing for an unambiguous selection of T_i^{sat}.

Benson (1973) argued that noble gas concentration ratios can provide a better equilibration temperature indicator than individual gas concentrations, since effects of pressure, humidity and salinity approximately cancel out (Benson, 1973). The noble gas ratio temperatures $T^{\mathrm{NGR}}(i/j)$ can be obtained from measured concentrations $C_{W,i}$ and $C_{W,j}$ of gases

i and j by numerically inverting:

$$\frac{C_{W,i}}{C_{W,j}} = \frac{x_i}{x_j}\frac{L_i(T)}{L_j(T)}. \tag{5}$$

Unlike the saturation temperatures, ratio temperatures do not depend on altitude. The graphical displays (Figure 1 e) and f)) are thus globally valid. The uncertainties are determined by evaluating the temperatures at the respective upper/lower and lower/upper error bounds of concentration measurements. Figure 1 e) shows the Ar to Ne and Figure 1 f) the Kr to Ne concentration ratios evaluated using solubilities from 0 to 80 °C (Schwenk et al., 2022). Here we also detect a strictly monotonic progression, which makes the noble gas ratio temperature selection unambiguous.

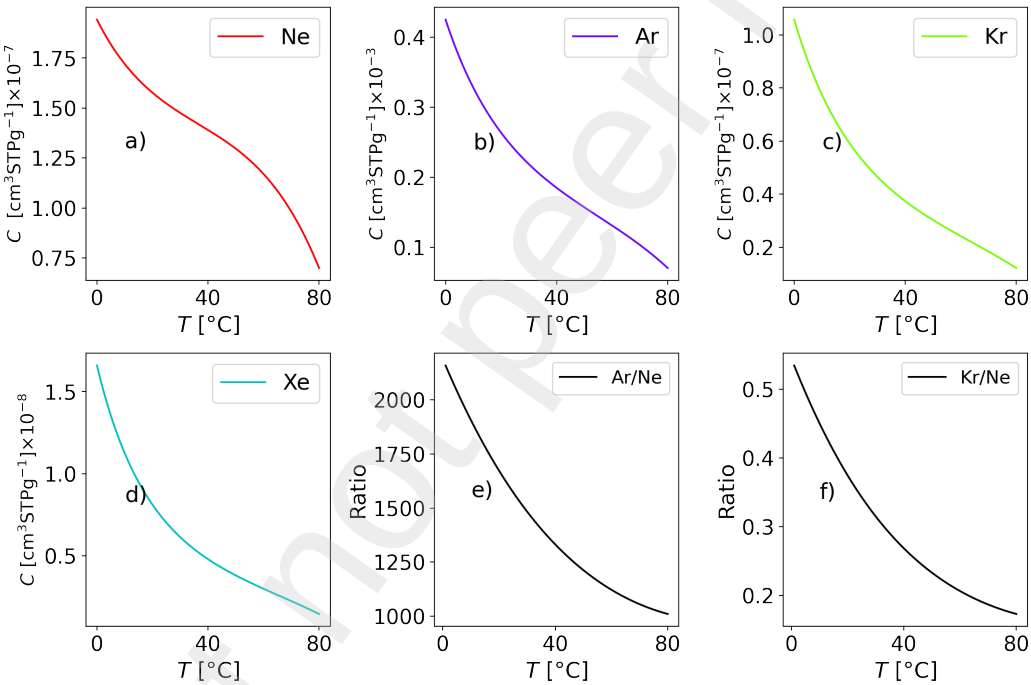

Figure 1. a) - d): Equation 3 evaluated using the newly determined solubilities (Schwenk et al., 2022) from 0 to 80 °C at an altitude of $z = 1460$ m for Ne (a), Ar (b), Kr (c) and Xe (d). The concentration ratios are also evaluated from 0 to 80 °C for Ar to Ne (e) and Kr to Ne (f).

The PANGA software calculates the UA-model temperatures T^{UA} using the best estimates of the different groundwater model parameters through typical methods of inverse modeling and simultaneous fitting of multiple noble gas concentrations (Jung & Aeschbach, 2018). In this work the UA model was applied using the Ne, Ar and Kr concentrations with the altitude set to $z = 1460$ m. Concentration measurements C_i^{meas} and

the UA-model temperatures were used to calculate the relative excesses/deficits given by $\Delta_i = C_i^{\mathrm{meas}}/C_i^{\mathrm{eq}}(T^{\mathrm{UA}}) - 1$. PANGA delivers uncertainties for the excess air parameter A and the temperature T^{UA} (Jung & Aeschbach, 2018).

3 Lake Kivu

Lake Kivu is a large lake (485 m max depth and 238 km^2 surface area) located at an altitude of 1460 m in the tectonic and volcanic rift valley of East Africa (Bärenbold, Schmid, et al., 2020; Ross et al., 2015). Within the same rift, the lakes Tanganyika and Malawi are located to the south and Lake Edward and Lake Albert are located to the north. High volcanoes, e.g. Nyiragongo, block the way to the north, and hence the discharge from Lake Kivu flows to the south as the Rusizi River into Lake Tanganyika (Figure 2). Surface inflow happens from small rivers around Lake Kivu, surface run-off and direct precipitation onto the water surface. The location in the tropics at 2 °C south results in two rainy seasons. The lake is meromictic, i.e. the water of the lake is only recirculated to a limited depth during the cool and windy season, leaving the waters below about 80 m depth permanently stratified. The layers below 80 m are entirely deprived of oxygen.

Groundwater inflow to the lake is known and has mainly been documented from the north, where active volcanoes dominate the geology (Schmid et al., 2002). The soil in this area originates from acid metamorphic and volcanic parent materials, and is characterized by the presence of thin to large fractures varying from shallow to deep, in addition to fissures acting as high-rate water infiltrating sites. The high water permeability of this soil is responsible for the fact that no surface rivers drain the Nyiragongo volcanic field, whereas only two rivers are found to the extreme south part of Nyamulagira volcano, both discharging into Kabuno bay (Balagizi et al., 2015). In this area, three main groundwater recharge zones are identified based on stable isotopes from precipitation, rivers and springs: the lower altitude recharge zone ranging from altitudes of $\sim$ 1800 to 2150 m asl, an intermediate zone ranging from $\sim$ 2180 to 2500 m, and the third zone located at higher altitudes ranging from $\sim$ 2620 to 3220 m (Balagizi et al., 2022). In the lake, two depth horizons are known for the inflow of groundwater into the deep waters: warm subaquatic groundwater discharge (SGD) (of higher density due to elevated salinity and high content of carbon dioxide and methane) entering between maximum depth and 450 m and a strong input at around 260 m depth of cool and fresh SGD (Ross et al., 2015). This results in a temperature profile that increases from 23 °C in the upper layer to 26 °C in the lower layer (see Figure 3), while

electrical conductivity rises from roughly 2 mS/cm to 5 mS/cm. The surplus of groundwater causes a slow vertical upwelling of water masses. Waters in the deepest layers are enriched in cations and alkalinity and therefore all deemed to originate from hydrothermal sources, while the upper layers consist of a mixture of volcanic and fresher groundwater (Ross et al., 2015; Bärenbold et al., 2022). The increased temperature of the deep SGDs is hypothesized to originate from a deep magma reservoir existing below Lake Kivu.

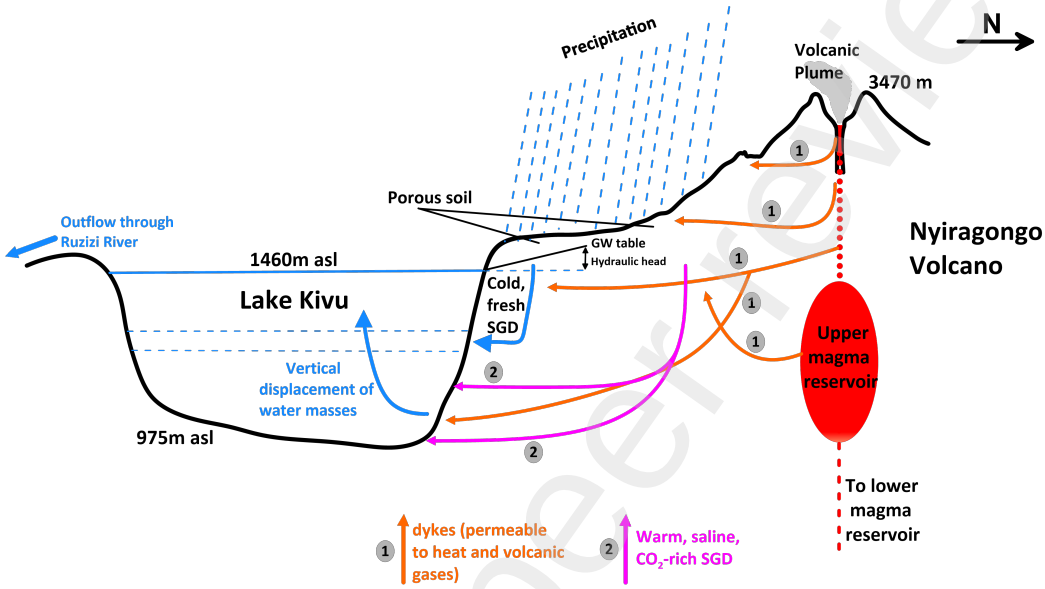

Figure 2. Sketch (not to scale) of the location and the hydrological situation of Lake Kivu within the East African Rift Valley. From the Nyiragongo magma reservoir, heat and volcanic gases could be injected through permeable fractures (proposed by Ross et al., 2015 and Balagizi et al., 2016) and could possibly heat groundwater before it is completely sealed off from the atmosphere, thus allowing for an equilibration at high temperatures. Some of these fractures extend beneath Lake Kivu (Villeneuve, 1980; Wauthier et al., 2012; Balagizi et al., 2018).

3.1 Noble Gases in Lake Kivu

Bärenbold et al. (2020) provide a comprehensive dataset of noble gas concentrations and isotopic ratios in Lake Kivu. Their findings, depicted in Figures 3 e) to f), defy expectations: noble gases (Ne, Ar, Kr) are strongly depleted in the deep waters of Lake Kivu with respect to air saturated water (ASW) at the conditions of the lake surface (1460 m, 25 °C). Ne is depleted by $\sim$ 45% and the more soluble heavy noble gases Ar (^{36}Ar) and kypton by $\sim$ 70%. Xe measurements show peculiar variabilities and were therefore discarded by the authors. He concentrations and the ^{40}Ar/^{36}Ar ratio increase with depth and thus deliver strong evidence for the existence of magmatic sources. The ^{20}Ne/^{22}Ne ratio is constant

at the atmoshperic value (Bärenbold, Schmid, et al., 2020). These results are extremely curious since groundwater almost always shows excess air components that lead to higher concentrations contrary to the observations in Lake Kivu.

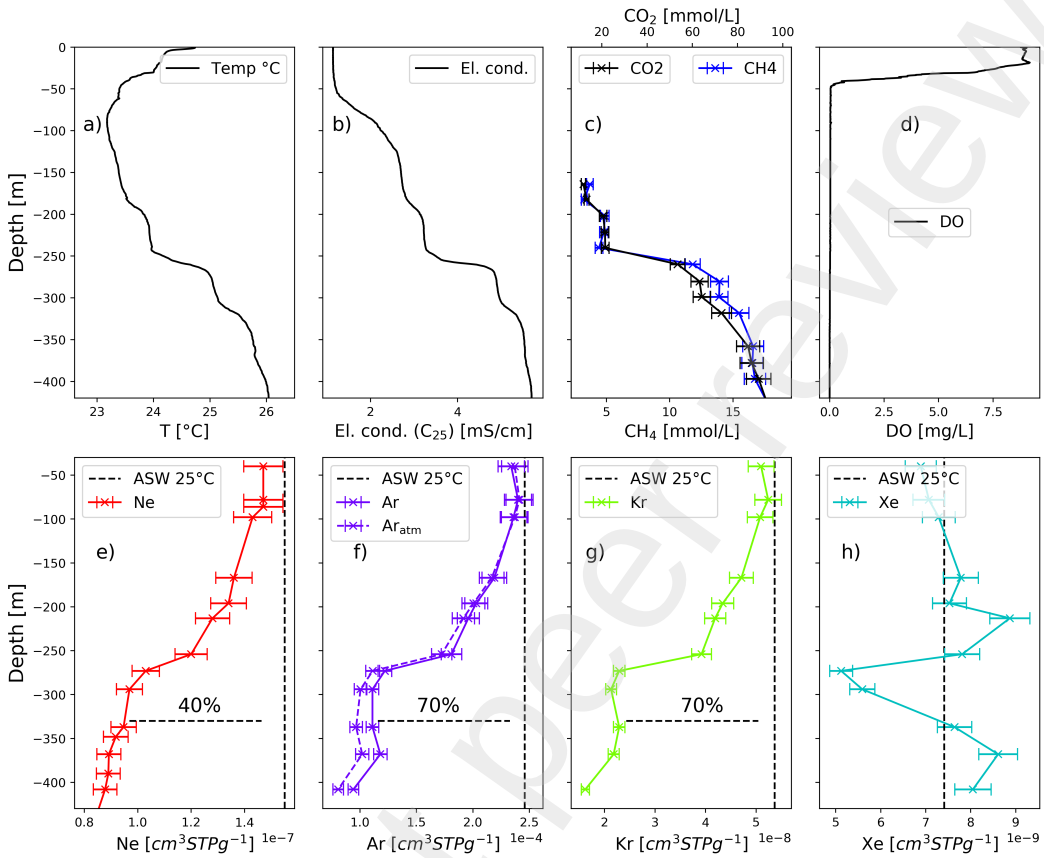

Figure 3. Vertical profiles in Lake Kivu: a) Temperature, b) electrical conductivity normalized to 25 °C, c) dissolved CH_4 and CO_2 and d) dissolved oxygen (Boehrer et al., 2019). The increasing salinity and CO_2 allow for stability of the stratification even though the temperature increases with depth. e) - h) show the noble gas concentrations (Bärenbold, Schmid, et al., 2020), whereby in f) the total Ar and the corrected atmospheric Ar (dashed lines, see Equation 6) are shown. Black dashed lines in e) - h) show concentrations obtained through equilibration at 25 °C and Lake Kivu's altitude, called air saturated water (ASW).

Bärenbold et al. (2020) ruled out two possible explanations of the noble gas deficits in the deep water: continuous outgassing by bubble-stripping should lead to kinetic fractionation of the $^{20}Ne/^{22}Ne$ ratio and also should affect Ne more strongly than Ar and Kr; a large scale limnic eruption in the past was deemed implausible since after a general gas depletion the lowest layers of the lake, which are replenished by the subaquatic groundwater inflows, should be the first to return to saturation, in contrast to observations. The authors conclude that the most realistic scenario is hydrothermal groundwater being heated in the

volcanic subsoil and partitioning with a gas or steam phase, thereby losing noble gases and entering the deep water already depleted. One issue with this scenario however, as stated by the authors, is that one would expect a larger depletion in Ne than in Ar and Kr due to the lower solubility of lighter noble gases. Instead of contact with steam they therefore suggest that hydrothermal groundwater either exchanges noble gases with an oil phase or that large amounts of excess air occured during groundwater formation, which could have enriched Ne in the initial groundwater. We instead propose and investigate whether the depletion can be explained by higher temperatures during groundwater formation.

He has significant sources and hence was not included in further considerations; nor did we use Xe, as it showed such inconsistencies that Bärenbold et al. (2020) discarded it. Since ^{40}Ar can have magmatic sources and the ^{40}Ar/^{36}Ar ratio in the deep water is up to 20% higher than the atmospheric value we calculated the atmospheric Ar using ^{36}Ar:

$$C\left(\mathrm{Ar_{atm}}\right) = C\left(^{36}\mathrm{Ar}\right)/0.003336. \tag{6}$$

C($\mathrm{Ar_{meas}}$)-C($\mathrm{Ar_{atm}}$) equals the magmatic ^{40}Ar and it correlates to the measured ^{3}He concentration with a linear correlation coefficient of $R^2 = 0.96$, showing that this is a good correction.

4 Results

The noble gas saturation temperatures T_i^{sat} are presented in Figure 4 a) for Ne (red), Ar (purple), atmospheric Ar (purple dashed line) and Kr (green) under the assumption of an equilibration altitude of $z = 1460\,\mathrm{m}$ (Lake Kivu's surface altitude). The measured in-situ temperature is also shown (black). In the upper 100 m, the noble gas saturation temperatures correspond to the measured in situ-temperature. This is expected, since the upper layers mix annually and thus equilibrate with the atmosphere. Below 260 m, the depth at which measured noble gas concentrations decrease dramatically, temperatures of 60 to 65 °C (Kr, Ar) and 70 to 75 °C (Ne, $\mathrm{Ar_{atm}}$) are found.

The noble gas ratio temperatures are depicted in Figure 4 b). In the upper layers all noble gas ratio temperatures lie at $\sim 25\,°\mathrm{C}$ and below $\sim 260\,\mathrm{m}$ they all show a sharp increase to higher temperatures. The Ar to Ne temperature that corrects for contributions of magmatic Ar (dashed purple line) delivers higher temperatures than the other ratio temperatures throughout the lower layers.

In the T^{UA} evaluation the excess air variable A is included in the optimization procedure. The temperatures T^{UA}, excess air parameters A and the relative excesses/deficits Δ_i are depicted in Figure 4 b) - d). PANGA delivers temperatures of $\sim 25\,^{\circ}\mathrm{C}$ for the upper layers, $\sim (65 \pm 2)\,^{\circ}\mathrm{C}$ for the lower layers below 260 m, and $\sim (75 \pm 2)\,^{\circ}\mathrm{C}$ for the deepest measurement. The excess air parameter A fluctuates around a small negative value not far from zero within the error bounds. A negative value for A indicates undersaturation but is not physical because it corresponds to simply removing a certain amount of atmospheric air from the water, for which no known process exists. However, negative values of A could be due to either degassing or equilibration at a lower atmospheric pressure, i.e., a higher altitude.

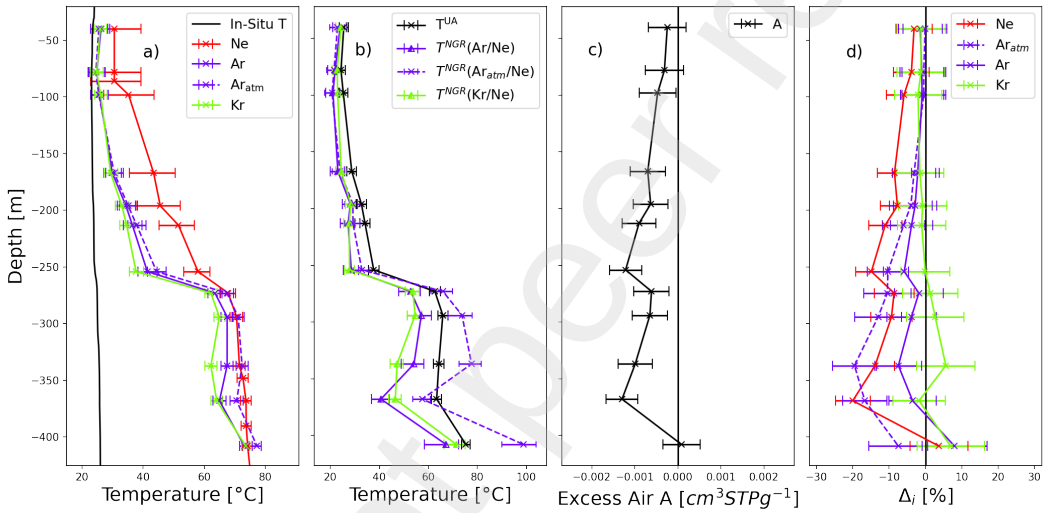

Figure 4. Results: a) The measured in-situ temperature (black) and the noble gas saturation temperatures T_i^{sat} obtained for Ne (red), Ar (purple), atmospheric Ar (purple dashed) and Kr (green) under the assumption of an equilibration altitude of z = 1460 m (lake level). b) -d) Optimization results from PANGA and temperatures derived from Kr/Ne and $\mathrm{Ar_{atm}}$/Ne ratios for Lake Kivu, assuming equilibration at lake level and unfractionated excess air (UA-model): b) noble gas temperatures against depth. c) unfractionated excess air parameter (deficit for negative value) d) relative excess/deficit Δ_i against depth.

By setting the equilibration altitude to $\sim$2200 m, an altitude that not only provides a sufficient hydraulic head for the water to enter the lake, but is also easily reached by the intermediate groundwater recharge zone around the Nyiragongo volcano that ranges from $\sim$ 2180 to 2500 m, one obtains values for A that instead fluctuate around zero and the resulting temperatures remain close to unchanged. When applying this altitude the values for Δ_i also shift closer to zero in the deeper layers. It is thus possible to explain the observed noble gas

concentrations through the single mechanism of a high temperature equilibration at a high altitude.

Xe measurements were discarded by the authors of Bärenbold et al. (2020) since they showed a puzzling structure. Using the UA-model temperatures, the theoretically expected concentration of Xe was calculated and the difference to the actual Xe concentration interpreted as a theoretical "excess Xe" (Figure 5). Excess Xe is positive over the entire water column, indicating the presence of a possible source. In addition, we find a correlation of excess Xe with magmatically attributed ^{3}He and excess ^{40}Ar ($R^2 \sim 0.92$).

Noticeable concentrations of fissiogenic xenon have so far however only been found in waters that are many millions of years old, owing to the very small subsurface production rates of Xe isotopes (Lippmann et al., 2003). The travel time of the groundwater that discharges into the deep parts of Lake Kivu is unknown but is constrained by the fact that the current hydrogeologic situation in the Virunga volcanic Province at the northern shore of Lake Kivu only evolved in the late Pleistocene and the Holocene. The activity of the volcanoes Nyiragongo and Nyamulagira began 14 - 10 kyr ago, which led to the closure of the lake's outflow to the north and consequently a strong lake level rise and the start of subaquatic volcanism (Ross et al., 2014). The possibility of finding a strong xenon component of magmatic or fissiogenic origin in the lake or the surrounding groundwater could therefore constitute an exciting finding.

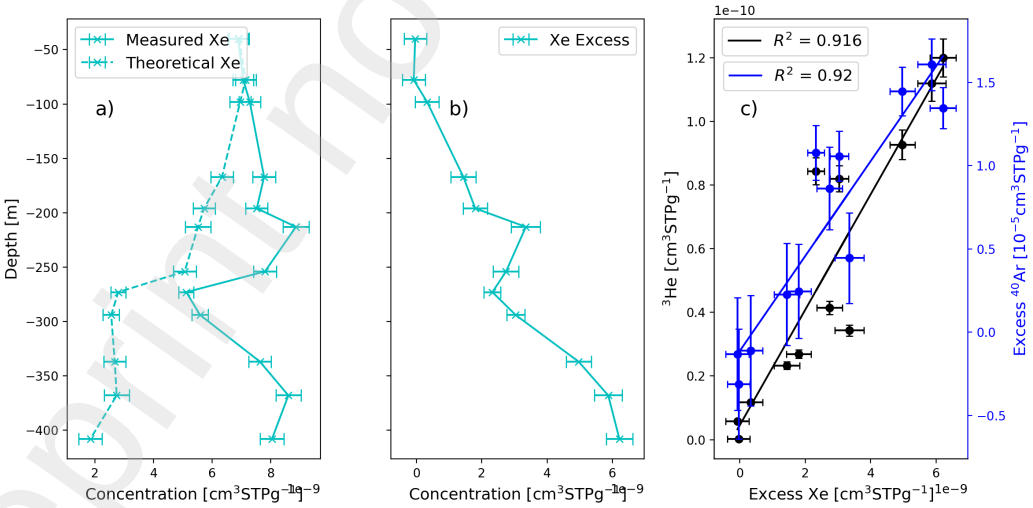

Figure 5. Excess Xe: a) Measured Xe concentrations in Lake Kivu (solid line) and theoretically expected Xe (dashed line). b) Theoretical excess Xe profile. c) Correlation of measured ^{3}He (black) and calculated excess ^{40}Ar (blue) to the theoretical excess Xe.

5 Conclusions

This is the first study to implement noble gas thermometry at high temperatures and the first to apply it to lakes. We used the new solubility functions from Schwenk et al. (2022) to analyze measurements made by Bärenbold et al. (2020) in Lake Kivu where the deep water is dominated by groundwater inflow. The results indicate that the observed noble gas deficits can entirely be explained through groundwater formation at high temperatures. For the upper layers, i.e., as far as seasonal recirculation operates, our approach delivered the expected temperatures of 25 °C. We discovered that for an equilibration altitude of some hundred meters above Lake Kivu's surface level, groundwater formation temperatures for the deep layers below 260 m of (65 ± 2) °C and for the deepest measurement a temperature of (75 ± 2) °C can entirely explain the observed noble gas concentrations in Lake Kivu.

Our findings are in contrast to earlier investigations (Mazor, 1972), which had found that hydrothermal waters had been equilibrated at atmospheric temperatures and pressures and heated only later, at larger depth. We do not challenge this general understanding of hydrothermal water formation. However, noble gas concentrations indicate equilibration at higher temperatures in the Lake Kivu area and this could also be the case in other volcanic locations. The inferred case of air equilibration under hydrothermal conditions followed by cooling in the subsurface requires an extension of the usual range of NGT determination.

Most importantly for the local population, however, the missing noble gases in Lake Kivu can be explained by equilibration at higher temperatures and hence are not indicative of catastrophic ebullition events. Lowering the gas pressure in Lake Kivu's deep water would however still contribute to safety and must be continued with the necessary caution.

6 Outlook

Our approach of noble gas thermometry can be applied to other cases where groundwater formation could take place at higher temperatures. In addition, a search for high groundwater temperatures close to the surface in areas around the Nyiragongo volcano may be stimulated by our results. In addition, more measurements of noble gases in Lake Kivu, especially of Xe, if possible of multiple isotopes, would better constrain fits and factors such as gases of volcanic origin. One could also make use of the high-temperature solubility functions from Schwenk et al. (2022) to create a high-temperature subsurface equilibration model that might even better explain the noble gas signatures.

Acknowledgments

CS did the numerical calculations and was the primary author. SN updated the PANGA software for our purposes. CMB provided geological expertise. WA contributed his expertise on noble gas thermometry. BB developed the idea of the study and provided expertise. All authors contributed to the writing and all authors participated in the whole process of this study.

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