

## Noble gases in Lakes Nyos and Monoun, Cameroon

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(Received August 4, 2009; Accepted June 4, 2010)

He, Ne and Ar isotopic ratios and concentrations of noble gases in different depths of Lakes Nyos and Monoun in Cameroon, West Africa, were investigated. Samples were collected in November 1999, January 2001 and December 2001. Improved sampling method applied in 2001 enabled us to detect detailed isotopic distribution in the lakes. Concentrations of Ne and Xe in the lake waters were low by factors of ~10 and ~3, respectively, compared with those of air saturated water (ASW), whereas in CO<sub>2</sub> gas they were depleted by 2 orders of magnitude compared with those in air. In contrast, He was strongly enriched in lake water by more than three orders of magnitude compared to ASW. <sup>3</sup>He/<sup>4</sup>He ratios of 8 × 10<sup>-6</sup> (Lake Nyos) and 5 × 10<sup>-6</sup> (Lake Monoun) indicated recharge of magmatic gases of mantle origin to the lakes, though the ratios were lowered by the addition of radiogenic <sup>4</sup>He from crustal rocks. A small contribution (<2%) of MORB-like Ne was detected in both lake waters. A simple mixing between two end members, i.e., atmosphere and gases from a deep-seated reservoir, can explain the noble gas signatures. Depth profile of He concentration in Lake Nyos showed a clear layered structure with a maximum at 190 m, 20 m above the lake bottom. Below this depth, <sup>3</sup>He/<sup>4</sup>He ratio decreased slightly, suggesting that the fluid from the deep-seated reservoir is supplied to the lake mainly at *ca.* 190 m. C/<sup>3</sup>He ratios were 1.5 × 10<sup>10</sup> and 0.6 × 10<sup>10</sup> in deep and shallow layers of Lake Nyos, respectively. The C/<sup>3</sup>He ratio was 1.7 × 10<sup>10</sup> at Lake Monoun. A gas recharge model to explain the observed layered structure in Lake Nyos is presented.

Keywords: noble gases, depth profile of noble gases, Lake Nyos, Lake Monoun, Cameroon volcanic line

### INTRODUCTION

Lakes Nyos and Monoun in Cameroon, West Africa, are volcanic crater lakes situated along the 1600 km long Cameroon Volcanic Line (CVL) which trends from the Atlantic Ocean into mainland Africa. The CVL consists of three sections: oceanic, continental, and their boundary in the middle (e.g., Halliday *et al.*, 1990; Barfod *et al.*, 1999; Aka *et al.*, 2001, 2004a, 2004b). Lake Nyos is a maar, which has surface area of 1.58 km<sup>2</sup> and a maximum water depth of about 210 m with a flat bottom. The lake's geological and petrological background can be found in, e.g., Fitton and Dunlop (1985), Kling *et al.* (1987), Kusakabe *et al.* (1989). The last eruption age has been suggested as about 400 years by radiocarbon method (Lockwood and Rubin, 1989), while much older K–Ar ages (>100,000 yrs) have been reported (Freeth and Lockwood, 1988). Recently an eruption age of ~4000 yrs has been proposed using the U–Th–Ra disequilibria by Aka *et al.* (2008).

Lake Monoun is located *ca.* 100 km south of Lake Nyos and 10 km north of the town Foubot at an altitude of 1080 m in the western highlands of Cameroon. At least 34 volcanic cones are recognized in the Foubot volcanic area of ~300 km<sup>2</sup>. The eastern part of the lake is only about 350 m in diameter, and its maximum depth is approximately 100 m (Sigurdsson *et al.*, 1987).

Gas disasters occurred in August 15, 1984 at Lake Monoun and in August 21, 1986 at Lake Nyos, with the total number of victims of 37 (Monoun) and 1746 (Nyos) associated with the death of numerous cattle (e.g., Sigurdsson *et al.*, 1987; Kling *et al.*, 1987; Sigvaldason, 1989). After the gas disasters, geochemical studies have been carried out to clarify the cause(s) of the gas burst, where the lakes' depth profiles of temperature, electric conductivity, pH, ionic and gas concentrations, isotopic compositions of C, H and O etc. were reported (e.g., Sigurdsson *et al.*, 1987; Kling *et al.*, 1987; Evans *et al.*, 1993; Kusakabe *et al.*, 1989, 2000, 2008). It has been found that the CO<sub>2</sub> derived from an underlying magmatic source accumulates in the bottom layers of the lakes as revealed by gradual increase of CO<sub>2</sub> in the lakes. Carbon isotopic ratios of the dissolved CO<sub>2</sub> gases and isotopic ratios of the associated helium were δ<sup>13</sup>C ≈ -3.5‰ and

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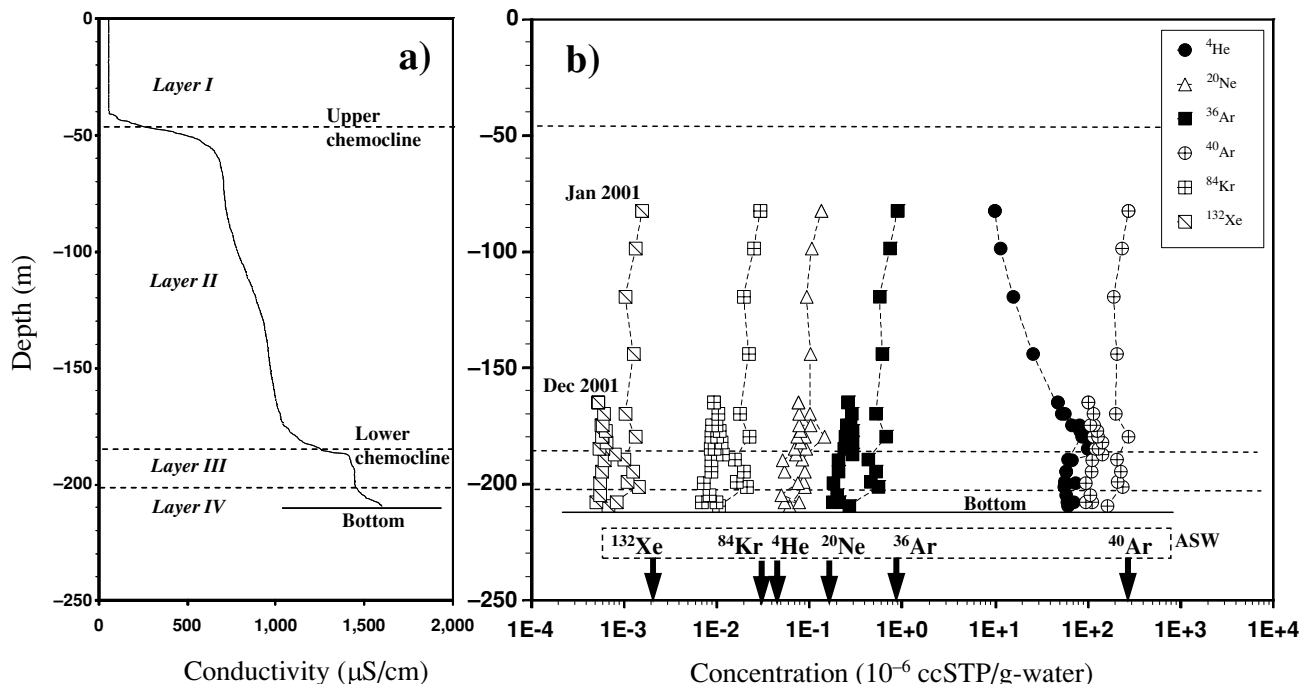


Fig. 1. a) Chemical structure of Lake Nyos as expressed by electric conductivity of water at 25°C. Two chemoclines and four stratified layers are defined (see Kusakabe *et al.*, 2008). b) Depth profiles of  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  concentrations in water ( $10^{-6}$  ccSTP/g-water) measured at Lake Nyos in January 2001 and December 2001. Noble gas concentrations in air saturated water (ASW) at 30°C (Table 2: Kipfer *et al.*, 2002) are also shown by arrows for comparison.

$-7\%$  and  $^3\text{He}/^4\text{He} \approx (7.7\text{--}8.0) \times 10^{-6}$  and  $5.0 \times 10^{-6}$  for Lakes Nyos and Monoun, respectively (Kling *et al.*, 1987; Kusakabe *et al.*, 1989; Sano *et al.*, 1987). Sano *et al.* (1990) reported precise depth profiles of  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  and He concentrations for Lake Nyos for the first time. Based on the He data, they estimated He and C fluxes of  $(2.4 \pm 0.4) \times 10^5$  and  $(7.2 \pm 3.8) \times 10^{15}$  atoms/cm<sup>2</sup> sec, respectively, and C/ $^3\text{He}$  ratio of  $(3.0 \pm 1.5) \times 10^{10}$  for Lake Nyos. Although the area is volcanically quiescent, magmatic volatiles are continuously released as exemplified by many soda springs in the nearby areas (e.g., Kusakabe and Sano, 1992). The magmatic CO<sub>2</sub> gas is continuously recharged at a rate of  $\sim 120$  mega-mole/yr and  $\sim 8$  mega-mole/yr into bottom waters of Lakes Nyos and Monoun, respectively, (Kling *et al.*, 2005; Kusakabe *et al.*, 2008). The lakes show characteristic stratified structures separated by clear chemoclines. Based on the electric conductivity profiles, stratified waters at Lakes Nyos and Monoun were grouped as layers I, II and III, separated by upper and lower chemoclines (Kusakabe *et al.*, 2008). Layer IV was also defined as a layer characterized by a sharp increase in electric conductivity near the bottom (see Fig. 1a).

A HIMU-like Pb isotopic signature with enrichment in radiogenic  $^{206}\text{Pb}$  characterizes upper mantle beneath the CVL at the continent-ocean boundary, while it be-

comes less radiogenic toward both ends of the line. On the contrary, Nd isotopes show an opposite regional change (e.g., Halliday *et al.*, 1988, 1990; Barfod *et al.*, 1999). Barfod *et al.* (1999) studied He, Ne and Ar in ultramafic xenoliths, basaltic lavas and CO<sub>2</sub>-rich gases from the CVL, and reported that He was slightly more enriched in radiogenic  $^4\text{He}$  ( $^3\text{He}/^4\text{He} = (7\text{--}9.4) \times 10^{-6}$ ) than MORB-type He ( $^3\text{He}/^4\text{He} = (11\text{--}12) \times 10^{-6}$ ), while Ne isotopic composition was MORB-like with maximum values of  $^{20}\text{Ne}/^{22}\text{Ne} = 11.87$  and  $^{21}\text{Ne}/^{22}\text{Ne} = 0.0508$ . The accompanied Ar had  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of  $>1650$ . They concluded that mantle beneath the CVL is indistinguishable from HIMU mantle with respect to  $^3\text{He}/^4\text{He}$  ratios, but MORB-like Ne is still preserved. Based on the analysis of  $^3\text{He}/^4\text{He}$  ratios in mafic phases in basalts and ultramafic xenoliths from 10 volcanic centers on the CVL, Aka *et al.* (2004b) reported symmetrical distribution of the  $^3\text{He}/^4\text{He}$  ratios along CVL. MORB-like  $^3\text{He}/^4\text{He}$  ratios were observed at both ends of CVL, i.e.,  $11.6 \times 10^{-6}$  for Annobon Island in the Atlantic Ocean (oceanic sector) and  $11.0 \times 10^{-6}$  for Ngaoundere in the northeastern part of CVL (continental sector). Interestingly, the lowest  $^3\text{He}/^4\text{He}$  ratios of  $4.3 \times 10^{-6}$  which indicated an enhanced radiogenic signature were observed for the samples from Bioko, Etinde and Mount Cameroon situated at the continent-ocean boundary of CVL. This is consistent with

the geographical distribution of  $^{206,208}\text{Pb}/^{204}\text{Pb}$  reported for CVL by Halliday *et al.* (1988, 1990).

We collected gas and water samples from various depths in Lakes Nyos and Monoun in November 1999, January 2001 and December 2001. Isotopic compositions of He, Ne and Ar as well as concentrations of all noble gases were measured to evaluate the magmatic source beneath the lakes. We found that the concentrations of Ne, Ar, Kr and Xe (except He) in  $\text{CO}_2$  gas exsolved from the lake water are more than 2 orders of magnitude lower than those in atmosphere. Accordingly, minimization of atmospheric contamination during sampling was essential to obtain representative noble gas compositions in the lake water. We present here detailed noble gas isotopic compositions of the lakes for the first time because no noble gas data except He have been reported yet for the lakes.

## EXPERIMENTAL METHODS

### *Sampling methods*

We employed four different sampling methods to collect gases dissolved in lake water during the fieldwork at Lakes Nyos and Monoun from 1999 to 2001. Because of very low concentrations of noble gases in  $\text{CO}_2$  gas exsolved from lake waters, it was essential to avoid atmospheric contamination during sampling. Atmospheric contamination of noble gases for the different methods will be evaluated later.

(1) “Al-bag method”: In 1999 a laminated aluminum-plastic bag with a capacity of 10 L (hereafter called as Al-bag) was connected to a Niskin water sampler. Air inside the bag was pumped out using a syringe before connecting it to the Niskin sampler. Exsolved  $\text{CO}_2$ -rich gases from the water inside the Niskin sampler were transferred to the Al-bag through a hole of the sampler after retrieval. The gas inside the Al-bag was then transferred to a sampling gas bottle (50–100 cc) attached with vacuum-tight stopcocks at both ends. Samples were collected from 9 and 7 different depths at Lake Nyos (0–200 m in depth) and Lake Monoun (25–95 m in depth), respectively (Appendix 1).

(2) “Stainless steel cylinder”: In 1999 the US team used an evacuated stainless steel bottle attached with metal valves which were operated from the surface of the lake by sending a sliding messenger (Evans *et al.*, 1993). The bottle was sent to a desired depth and filled with  $\text{CO}_2$ -rich lake water. In the laboratory gas dissolved in the water was separated using a vacuum line for analysis. Part of the gas from each bottle was sealed in a He-impermeable borosilicate glass ampoule with breakable seal, and supplied to us for noble gas analysis.

(3) “Flute de Pan”: As will be described later, gases collected by the Al-bag method were found heavily con-

taminated by atmospheric noble gas. So we collected samples from Lake Nyos in January 2001 using the “Flute de Pan” which had been deployed by the French scientific team. The Flute de Pan consisted of 11 plastic hoses, each having a different intake depth (83–210 m). Bubbling  $\text{CO}_2$ -rich gas spouting out of the hose were introduced in a basin filled with surface water of the lake, and then the bubbles were collected in a sampling glass bottle using a funnel. Although contamination of air dissolved in the water was still suspected to some extent especially for heavy noble gases, this sampling method was found promising since we could greatly reduce air contamination compared with the Al-bag method.

(4) “Plastic hose method”: This is essentially the same as the Flute de Pan method. In December 2001, we deployed a single plastic hose (12 mm I.D.) to a desired depth of the lake. The sampling depth was measured with a calibrated wire that was attached to the hose. After water inside the hose was pumped up, exsolved  $\text{CO}_2$  gas was allowed to pass through a sampling glass bottle, which was directly connected to the plastic hose to avoid air contamination. We waited for long enough to ensure that the water and gas coming out of the hose represented water from a target depth. With this method we were able to avoid air contamination almost completely judging from  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of the samples as discussed later.

The sampling in January 2001 by the “Flute de Pan” was performed just before the initiation of the Nyos and Monoun Degassing Project (NMDP) at Lake Nyos. In December 2001, about 10 months after degassing started, we measured the depth profiles of noble gases as precisely as possible around the lower chemocline at ~180 m deep. We collected 17 samples from 13 different depths from close to bottom (208 m) to 165 m.

### *Analytical methods*

An aliquot of each gas sample in glass bottle was sealed in a glass ampoule (~5 cc) with breakable seal. Absolute amount of  $\text{CO}_2$  gas (ccSTP) inside the ampoule was calculated based on its volume, pressure and temperature of the gas. The pressure and the temperature were measured at the time of sealing; the gas pressure was measured by a Hg-manometer. The volume was obtained by measuring weight of water filled in the empty ampoule after noble gas measurement.

For noble gas analysis, several ampoules were attached to a noble gas purification line connected on-line to a modified-VG5400 (MS-III) noble gas mass spectrometer at the Geochemical Research Center, University of Tokyo. Noble gases introduced into the purification line were purified by two Ti–Zr getters heated to about 800°C and separated into three fractions, i.e., He, Ne and Ar–Kr–Xe. The Ar–Kr–Xe mixture was separated from He and Ne by adsorbing them on a charcoal trap cooled at liquid

Table 1. Isotopic ratios of He, Ne and Ar in waters and gases collected from Lakes Nyos and Monoun, Cameroon

Sample name	Depth (m)	$^4\text{He}/^{20}\text{Ne}$	$^3\text{He}/^4\text{He}$ ( $10^{-6}$ )	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$	$^{38}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}/^{36}\text{Ar}$
Lake Nyos							
January 2001 (Flute de Pan method)							
NY01Jan-210	-209.8	994	7.93 ± 0.12	10.016 ± 0.026	0.02991 ± 0.00035	0.18823 ± 0.00063	604.46 ± 1.26
NY01Jan-210	-209.8		7.78 ± 0.05	10.115 ± 0.018	0.03019 ± 0.00023	0.18861 ± 0.00061	598.79 ± 0.89
NY01Jan-202	-201.6	624	7.93 ± 0.13	9.817 ± 0.024	0.02939 ± 0.00027	0.18824 ± 0.00048	433.51 ± 1.05
NY01Jan-199	-199.2	648	7.96 ± 0.14	9.821 ± 0.019	0.02949 ± 0.00020	0.18821 ± 0.00070	454.99 ± 0.95
NY01Jan-195	-195.0	655	7.91 ± 0.12	9.827 ± 0.021	0.02944 ± 0.00028	0.18800 ± 0.00060	438.52 ± 1.13
NY01Jan-190	-189.9	735	7.98 ± 0.14	9.812 ± 0.019	0.02963 ± 0.00021	0.18841 ± 0.00044	479.17 ± 1.03
NY01Jan-180	-180.0	598	8.00 ± 0.12	9.801 ± 0.019	0.02934 ± 0.00014	0.18819 ± 0.00044	407.39 ± 0.84
NY01Jan-170	-170.0	515	8.04 ± 0.12	9.773 ± 0.017	0.02926 ± 0.00016	0.18854 ± 0.00051	381.63 ± 0.74
NY01Jan-144	-144.4	253	7.92 ± 0.15	9.772 ± 0.017	0.02906 ± 0.00016	0.18796 ± 0.00064	338.30 ± 0.83
NY01Jan-120	-119.7	166	8.08 ± 0.13	9.760 ± 0.023	0.02897 ± 0.00020	0.18874 ± 0.00050	327.84 ± 0.67
NY01Jan-99	-98.8	108	8.10 ± 0.39	9.785 ± 0.022	0.02915 ± 0.00021	0.18842 ± 0.00044	317.12 ± 0.67
NY01Jan-83	-82.9	74.3	7.93 ± 0.14	9.749 ± 0.016	0.02886 ± 0.00014	0.18842 ± 0.00040	309.84 ± 0.64
December 2001 (Plastic hose method)							
NY01Dec-208	-208.0	1107	7.89 ± 0.07	9.91 ± 0.015	0.03002 ± 0.00040	0.18809 ± 0.00091	539.16 ± 0.94
NY01Dec-208	-208.0	913	7.89 ± 0.11	9.90 ± 0.019	0.02983 ± 0.00047	0.18780 ± 0.00083	531.13 ± 0.69
NY01Dec-205	-205.0	1172	7.77 ± 0.08	9.86 ± 0.021	0.03010 ± 0.00043	0.18784 ± 0.00064	536.29 ± 0.66
NY01Dec-200	-200.0	982	7.91 ± 0.11	9.91 ± 0.011	0.03017 ± 0.00026	0.18799 ± 0.00057	528.97 ± 1.02
NY01Dec-195	-195.0	1082	7.89 ± 0.08	9.93 ± 0.014	0.03020 ± 0.00032	0.18748 ± 0.00059	526.97 ± 0.54
NY01Dec-190	-190.0	1317	7.77 ± 0.06	9.85 ± 0.015	0.03029 ± 0.00027	0.18825 ± 0.00052	541.42 ± 0.87
NY01Dec-188	-187.5	1588	7.94 ± 0.08	9.87 ± 0.013	0.02992 ± 0.00036	0.18815 ± 0.00080	497.43 ± 0.68
NY01Dec-185	-185.0	1311	7.97 ± 0.10	9.86 ± 0.012	0.03003 ± 0.00050	0.18807 ± 0.00056	507.62 ± 0.52
NY01Dec-185	-185.0	1439	8.03 ± 0.07	9.89 ± 0.013	0.03010 ± 0.00026	0.18797 ± 0.00050	511.11 ± 1.35
NY01Dec-183	-182.5	1327	7.92 ± 0.06	9.89 ± 0.014	0.03003 ± 0.00031	0.18824 ± 0.00087	490.09 ± 0.58
NY01Dec-180	-180.0	1185	7.85 ± 0.10	9.82 ± 0.018	0.02986 ± 0.00021	0.18782 ± 0.00077	466.25 ± 0.80
NY01Dec-180	-180.0	1236	8.12 ± 0.07	9.88 ± 0.007	0.02981 ± 0.00015	0.18763 ± 0.00027	466.12 ± 0.65
NY01Dec-178	-177.5	1038	7.89 ± 0.07	9.85 ± 0.012	0.02973 ± 0.00015	0.18835 ± 0.00058	434.95 ± 0.39
NY01Dec-175	-175.0	870	8.08 ± 0.07	9.86 ± 0.014	0.02963 ± 0.00025	0.18781 ± 0.00046	419.13 ± 0.51
NY01Dec-175	-175.0	794	7.95 ± 0.10	9.86 ± 0.008	0.02974 ± 0.00021	0.18771 ± 0.00056	419.20 ± 0.44
NY01Dec-170	-170.0	737	8.18 ± 0.08	9.86 ± 0.010	0.02944 ± 0.00015	0.18770 ± 0.00034	401.34 ± 0.71
NY01Dec-165	-165.0	631	8.13 ± 0.09	9.85 ± 0.008	0.02954 ± 0.00012	0.18805 ± 0.00032	387.68 ± 0.46

Sample name	Depth (m)	$^4\text{He}/^{20}\text{Ne}$	$^3\text{He}/^4\text{He}$ ( $10^{-6}$ )	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$	$^{38}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}/^{36}\text{Ar}$
Lake Monoun							
December 2001 (Plastic hose method)							
MN01Dec-95	-95	1076	4.99 ± 0.06	9.865 ± 0.020	0.02963 ± 0.00029	0.1879 ± 0.0004	468.94 ± 0.63
MN01Dec-85	-85	1333	5.06 ± 0.07	9.849 ± 0.027	0.02982 ± 0.00034	0.1881 ± 0.0003	479.39 ± 0.50
MN01Dec-70	-70	1137	5.04 ± 0.07	9.851 ± 0.015	0.02999 ± 0.00021	0.1881 ± 0.0006	473.38 ± 0.65
MN01Dec-65	-65	1222	4.99 ± 0.07	9.877 ± 0.011	0.02959 ± 0.00026	0.1880 ± 0.0005	471.88 ± 0.88
MN01Dec-60	-60	1367	5.12 ± 0.07	9.881 ± 0.020	0.02986 ± 0.00040	0.1880 ± 0.0004	473.91 ± 0.80
MN01Dec-55	-55	1146	5.03 ± 0.07	9.874 ± 0.006	0.02992 ± 0.00030	0.1877 ± 0.0004	462.49 ± 0.62
MN01Dec-45	-45	107	5.14 ± 0.07	9.812 ± 0.006	0.02906 ± 0.00007	0.1876 ± 0.0005	316.59 ± 0.44
MN01Dec-35	-35	369	5.13 ± 0.07	9.876 ± 0.005	0.02933 ± 0.00008	0.1874 ± 0.0004	343.17 ± 0.34
Air (Ozima and Podosek, 2002)		0.32	1.40	9.80	0.0290	0.1880	296.0

nitrogen temperature. Ne was separated from He by adsorbing Ne onto a cryogenically cooled sintered stainless steel trap at a temperature of 15 K. He, Ne and Ar isotopic ratios and absolute abundances of all noble gases ( $^4\text{He}$ ,  $^20\text{Ne}$ ,  $^36\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$ ) were measured with the noble gas mass spectrometer. Sensitivities and mass discrimination correction factors of the mass spectrometer were determined by measuring known amounts of atmospheric gas with the same procedures applied to samples. The mass discrimination factor for  $^3\text{He}/^4\text{He}$  was determined by measuring a laboratory He standard gas with  $^3\text{He}/^4\text{He} = 1.71 \times 10^{-4}$ , which was prepared by mixing known amounts of pure  $^3\text{He}$  and  $^4\text{He}$ . Uncertainty for the ratio is estimated as  $\approx 1\%$  based on experimental errors in estimation of absolute amount of each helium gas sealed in an ampoule. Accuracy of the  $^3\text{He}/^4\text{He}$  ratio of our laboratory He standard gas was confirmed by analyzing  $^3\text{He}/^4\text{He}$  ratio of HESJ (He Standard of Japan:  $^3\text{He}/^4\text{He} = (28.88 \pm 0.14) \times 10^{-6}$ , Matsuda *et al.*, 2002), i.e., measured  $^3\text{He}/^4\text{He}$  ratio of HESJ using our laboratory standard ( $^3\text{He}/^4\text{He} = 1.71 \times 10^{-4}$ ) agreed with those using atmospheric He ( $^3\text{He}/^4\text{He} = 1.4 \times 10^{-6}$ ) as standard (see table 1 in Matsuda *et al.*, 2002). Mass resolution of the mass spectrometer was about 600 ( $M/\Delta M$ ), which was high enough to separate a  $^3\text{He}$  peak from HD and  $\text{H}_3$  peaks. Correction for doubly charged  $^{40}\text{Ar}$  and  $\text{CO}_2$  ions, which may affect  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  measurement, was performed by measuring  $^{40}\text{Ar}^+$  and  $\text{CO}_2^+$  before and after Ne analysis and by experimentally determined  $^{40}\text{Ar}^{++}/^{40}\text{Ar}^+$  and  $\text{CO}_2^{++}/\text{CO}_2^+$  ratios under same condition for Ne analysis. The contributions of  $^{40}\text{Ar}^{2+}$  and  $\text{CO}_2^{2+}$  to  $^{20}\text{Ne}^+$  and  $^{22}\text{Ne}^+$  were found as low as  $<0.4\%$  and  $<0.01\%$ , respectively, throughout the measurement.

The D/H analysis of water samples was carried out using hydrogen prepared from water by the use of a classic uranium reduction method, with a stable isotope ratio mass spectrometer (Micromass SIRA-10). The  $^{18}\text{O}/^{16}\text{O}$  analysis was carried out using an automated  $\text{CO}_2\text{-H}_2\text{O}$  equilibration technique, with a stable isotope ratio mass spectrometer (Micromass PRISM). The isotopic ratios were expressed in the conventional  $\delta$ -notation with the VSMOW as the standard. The  $^{13}\text{C}/^{12}\text{C}$  analysis of  $\text{CO}_2$  gas was made for an aliquot after the noble gas analysis had been done, using a stable isotope ratio mass spectrometer (Micromass PRISM).  $\delta^{13}\text{C}$  values were expressed relative to the VPDB standard.

## RESULTS

Isotopic ratios of He, Ne and Ar of the samples from Lakes Nyos and Monoun are listed in Table 1 which includes data for samples collected using the Flute de Pan and plastic hose methods only. Those from the Al-bag and SS-cylinder methods were given in Appendix 1. Er-

Table 2. Concentrations of noble gases in CO<sub>2</sub> gas and in water, and elemental abundance ratios normalized to <sup>36</sup>Ar for the samples from Lakes Nyos and Monoun, Cameroon

Sample name	<sup>4</sup> He	<sup>20</sup> Ne	<sup>36</sup> Ar	<sup>40</sup> Ar	<sup>84</sup> Kr	<sup>132</sup> Xe	<sup>4</sup> He/ <sup>36</sup> Ar	<sup>20</sup> Ne/ <sup>36</sup> Ar	<sup>84</sup> Kr/ <sup>36</sup> Ar	<sup>132</sup> Xe/ <sup>36</sup> Ar	<sup>4</sup> He/ <sup>40</sup> Ar
Concentration in CO <sub>2</sub> gas (ppm)											
Lake Nyos											
January 2001 (Flute de Pan method)											
NY01Jan-210	7.76	0.00780	0.0344	20.8	0.00136	0.000088	225	0.227	0.0394	0.0025	0.373
NY01Jan-210											
NY01Jan-202	7.30	0.0117	0.0721	31.2	0.00276	0.000190	101	0.162	0.0383	0.0026	0.234
NY01Jan-199	7.34	0.0113	0.0601	27.4	0.00217	0.000143	122	0.189	0.0360	0.0024	0.268
NY01Jan-195	7.63	0.0117	0.0679	29.7	0.00255	0.000164	112	0.172	0.0376	0.0024	0.257
NY01Jan-190	8.29	0.0113	0.0582	27.8	0.00215	0.000137	142	0.194	0.0369	0.0024	0.298
NY01Jan-180	21.8	0.0365	0.168	68.4	0.00565	0.000337	130	0.217	0.0337	0.0020	0.319
NY01Jan-170	15.2	0.0296	0.154	58.7	0.00526	0.000307	99.1	0.192	0.0342	0.0020	0.260
NY01Jan-144	8.54	0.0338	0.201	67.9	0.00733	0.000425	42.5	0.168	0.0365	0.0021	0.126
NY01Jan-120	6.02	0.0362	0.222	72.7	0.00752	0.000401	27.2	0.163	0.0339	0.0018	0.083
NY01Jan-99	5.83	0.0539	0.379	120	0.01286	0.000685	15.4	0.142	0.0339	0.0018	0.049
NY01Jan-83	6.13	0.0825	0.5442	169	0.01805	0.000968	11.3	0.152	0.0332	0.0018	0.036
December 2001 (Plastic hose method)											
NY01Dec-208	7.72	0.0070	0.0268	14.5	0.00130	0.000109	288	0.260	0.0483	0.0040	0.534
NY01Dec-208	9.09	0.0100	0.0232	12.3	0.00090	0.000065	392	0.429	0.0387	0.0028	0.737
NY01Dec-205	7.58	0.0065	0.0256	13.8	0.00109	0.000072	295	0.252	0.0423	0.0028	0.551
NY01Dec-200	9.57	0.0097	0.0233	12.3	0.00093	0.000072	410	0.418	0.0401	0.0031	0.775
NY01Dec-195	7.64	0.0071	0.0271	14.3	0.00115	0.000076	282	0.261	0.0426	0.0028	0.535
NY01Dec-190	9.08	0.0069	0.0278	15.0	0.00119	0.000084	327	0.248	0.0429	0.0030	0.604
NY01Dec-188	19.2	0.0121	0.0488	24.3	0.00198	0.000134	393	0.247	0.0406	0.0028	0.789
NY01Dec-185	26.7	0.0204	0.0525	26.6	0.00191	0.000133	509	0.388	0.0365	0.0025	1.003
NY01Dec-185	22.2	0.0154	0.0562	28.7	0.00212	0.000121	395	0.274	0.0377	0.0022	0.773
NY01Dec-183	25.8	0.0195	0.0710	34.8	0.00275	0.000158	364	0.274	0.0388	0.0022	0.742
NY01Dec-180	27.9	0.0235	0.0646	30.1	0.00231	0.000157	432	0.364	0.0358	0.0024	0.926
NY01Dec-180	23.8	0.0193	0.0721	33.6	0.00266	0.000154	331	0.267	0.0368	0.0021	0.709
NY01Dec-178	22.5	0.0217	0.0797	34.7	0.00295	0.000175	283	0.272	0.0370	0.0022	0.650
NY01Dec-175	19.1	0.0219	0.0788	33.0	0.00282	0.000162	242	0.278	0.0358	0.0020	0.578
NY01Dec-175	23.0	0.0290	0.0712	29.9	0.00253	0.000169	323	0.407	0.0355	0.0024	0.771
NY01Dec-170	16.5	0.0224	0.0836	33.5	0.00304	0.000179	198	0.268	0.0364	0.0021	0.493
NY01Dec-165	14.3	0.0226	0.0778	30.2	0.00279	0.000159	183	0.290	0.0359	0.0020	0.473
Lake Monoun											
December 2001 (Plastic hose method)											
MN01Dec-95	9.0	0.0083	0.0356	16.7	0.00170	0.000144	252	0.234	0.0478	0.00405	0.537
MN01Dec-85	13.0	0.0097	0.0436	20.9	0.00203	0.000167	298	0.223	0.0465	0.00384	0.621
MN01Dec-70	11.3	0.0100	0.0394	18.7	0.00182	0.000150	287	0.253	0.0461	0.00380	0.606
MN01Dec-65	12.9	0.0106	0.0446	21.0	0.00210	0.000171	290	0.237	0.0471	0.00384	0.614
MN01Dec-60	13.4	0.0098	0.0430	20.4	0.00207	0.000168	311	0.228	0.0480	0.00390	0.657
MN01Dec-55	11.7	0.0102	0.0431	19.9	0.00199	0.000157	272	0.237	0.0461	0.00363	0.588
MN01Dec-45	63.1	0.5878	1.1414	361	0.03411	0.002048	55	0.515	0.0299	0.00179	0.175
MN01Dec-35	56.7	0.1538	0.3873	133	0.01379	0.000943	146	0.397	0.0356	0.00244	0.427
Air (Ozima and Podosek, 2002)	5.24	16.5	31.5	9303	0.649	0.0234	0.166	0.524	0.0206	0.00074	0.00056
Air saturated water (30°C water, Kipfer <i>et al.</i> , 2002)							0.050	0.178	0.0359	0.00230	0.00017

rors for the isotopic ratios are in one standard deviation including uncertainties for mass discrimination correction. Concentrations of noble gases in CO<sub>2</sub> gas exsolved from water are summarized in Table 2 and Appendix 2, together with the CO<sub>2</sub> concentrations in lake waters (Kusakabe *et al.*, 2008). Carbon isotopic ratios of CO<sub>2</sub> are also included in the tables.

The noble gas concentrations in CO<sub>2</sub> gas were calculated for each ampoule by dividing the measured absolute noble gas abundances (ccSTP) by the amount of CO<sub>2</sub> gas in the ampoule (ccSTP). The noble gas concentrations in CO<sub>2</sub> gas were converted to those in water in the unit of ccSTP/g-water using the CO<sub>2</sub> concentrations in

water (Kusakabe *et al.*, 2000, 2008). For two water samples NY99-35 and NY99-0, only isotopic ratios were shown in Appendix 1. Experimental uncertainties for the noble gas concentrations were estimated to be about 5–15% based on the fluctuation in sensitivity of the mass spectrometer observed by replicate measurements of standard gas.

Isotopic ratios of hydrogen and oxygen of waters from Lakes Nyos and Monoun are summarized in Table 5.

#### Evaluation of the sampling methods based on <sup>4</sup>He/<sup>20</sup>Ne and <sup>40</sup>Ar/<sup>36</sup>Ar ratios

<sup>4</sup>He/<sup>20</sup>Ne ratio is often used as a measure of atmos-

Table 2. (continued)

Sample name	<sup>4</sup> He	<sup>20</sup> Ne	<sup>36</sup> Ar	<sup>40</sup> Ar	<sup>84</sup> Kr	<sup>132</sup> Xe	CO <sub>2</sub> (water)	$\delta^{13}\text{C}_{\text{PDB}}$
	Concentration in water (10 <sup>-6</sup> ccSTP/g water)						ccSTP/g water	‰
Lake Nyos								
January 2001 (Flute de Pan method)								
NY01Jan-210	61.4	0.062	0.27	165	0.0107	0.000692	7.91	-3.42
NY01Jan-210								
NY01Jan-202	56.6	0.091	0.56	242	0.0214	0.001469	7.75	-3.36
NY01Jan-199	56.8	0.088	0.47	212	0.0168	0.001105	7.74	-3.38
NY01Jan-195	59.1	0.090	0.53	230	0.0198	0.001272	7.74	-3.37
NY01Jan-190	62.0	0.084	0.44	208	0.0161	0.001024	7.48	-3.37
NY01Jan-180	88.1	0.147	0.68	276	0.0228	0.001360	4.04	-3.32
NY01Jan-170	52.5	0.102	0.53	202	0.0182	0.001058	3.45	-3.34
NY01Jan-144	26.1	0.103	0.61	208	0.0224	0.001299	3.06	-3.32
NY01Jan-120	15.8	0.095	0.58	191	0.0198	0.001055	2.63	-3.30
NY01Jan-99	11.5	0.107	0.75	238	0.0255	0.001356	1.98	-3.27
NY01Jan-83	10.1	0.136	0.90	279	0.0298	0.001596	1.65	-3.24
December 2001 (Plastic hose method)								
NY01Dec-208	60.6	0.055	0.21	113	0.0102	0.000852	7.84	-3.46
NY01Dec-208	71.3	0.078	0.18	97	0.0070	0.000512	7.84	-3.38
NY01Dec-205	59.4	0.051	0.20	108	0.0085	0.000567	7.84	-3.35
NY01Dec-200	75.0	0.076	0.18	97	0.0073	0.000564	7.84	-3.35
NY01Dec-195	59.1	0.055	0.21	110	0.0089	0.000588	7.74	-3.36
NY01Dec-190	68.0	0.052	0.21	113	0.0089	0.000632	7.49	-3.35
NY01Dec-188	114.9	0.072	0.29	146	0.0119	0.000806	5.99	-3.35
NY01Dec-185	122.2	0.093	0.24	122	0.0088	0.000609	4.57	-3.31
NY01Dec-185	101.5	0.071	0.26	131	0.0097	0.000555	4.57	-3.36
NY01Dec-183	107.1	0.081	0.29	144	0.0114	0.000656	4.15	-3.41
NY01Dec-180	107.4	0.091	0.25	116	0.0089	0.000604	3.85	-3.32
NY01Dec-180	91.8	0.074	0.28	129	0.0102	0.000593	3.85	-3.36
NY01Dec-178	83.6	0.081	0.30	129	0.0109	0.000649	3.71	-3.36
NY01Dec-175	68.1	0.078	0.28	118	0.0101	0.000577	3.57	-3.34
NY01Dec-175	82.2	0.103	0.25	107	0.0090	0.000604	3.57	-3.38
NY01Dec-170	57.6	0.078	0.29	117	0.0106	0.000624	3.48	-3.35
NY01Dec-165	48.4	0.077	0.26	102	0.0095	0.000539	3.39	-3.37
Lake Monoun								
December 2001 (Plastic hose method)								
MN01Dec-95	33.5	0.031	0.133	62.3	0.00636	0.000538	3.74	-7.35
MN01Dec-85	46.1	0.035	0.155	74.3	0.00721	0.000595	3.56	-6.83
MN01Dec-70	40.2	0.035	0.140	66.2	0.00645	0.000531	3.55	-6.82
MN01Dec-65	45.8	0.037	0.158	74.6	0.00744	0.000607	3.55	-6.82
MN01Dec-60	47.4	0.035	0.152	72.2	0.00731	0.000595	3.54	-6.83
MN01Dec-55	38.7	0.034	0.142	65.8	0.00657	0.000517	3.30	-6.84
MN01Dec-45	81.4	0.758	1.472	466.2	0.04401	0.002642	1.29	-7.56
MN01Dec-35	56.3	0.153	0.385	132.0	0.01369	0.000937	0.99	-8.11
Air (Ozima and Podosek, 2002)								
Air saturated water (30°C water, Kipfer <i>et al.</i> , 2002)	0.044	0.156	0.874	259	0.0314	0.00201		

pheric contamination, because the ratio is generally much higher (>1000) than the atmospheric value of 0.32 in samples derived from deep interior of the earth such as volcanic gases (e.g., Kusakabe *et al.*, 2009), natural gases in

old continents (e.g., Ballentine and Sherwood Lollar, 2002; Cornides *et al.*, 1986; Ballentine *et al.*, 1991; Kotarba and Nagao, 2008, and see references therein), glassy basalts from mid oceanic ridges (e.g., Staudacher

Table 3. Comparison of  $^4\text{He}/^{20}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios for the deep water (>175 m) samples from Lake Nyos collected by different sampling methods

Method	$^4\text{He}/^{20}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$
Al-bag	132–318	337–359
SS-cylinder	419–757	497–535
Flute de Pan	598–994	407–604
Plastic hose	913–1588	466–541
Air (Ozima and Podosek, 2002)	0.32	296

*et al.*, 1989), and mantle xenoliths (e.g., Nagao and Takahashi, 1993).  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio is also seriously affected by addition of atmospheric Ar with  $^{40}\text{Ar}/^{36}\text{Ar} = 296$  because air contains high concentration of Ar (~1%).

$^4\text{He}/^{20}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios in deep water (>175 m) from Lake Nyos by different sampling methods are compared in Table 3. The  $^4\text{He}/^{20}\text{Ne}$  ratios by the “Al-bag method” and the “stainless steel cylinder (SS-cylinder) method” were 132–318 and 419–757, respectively, which were much lower than those for the samples obtained using the “Flute de Pan” and the “Plastic hose” methods.  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios by the Al-bag and SS-cylinder methods were also lower than those obtained by the Flute de pan and plastic hose methods. The atmospheric contamination of the Al-bag samples can be attributed to a small amount of air which remained unremoved in the Al-bag when attached to the Niskin sampler, because the concentrations of noble gases in  $\text{CO}_2$  gas in the lake are 2 orders of magnitude lower than those in atmosphere (Appendix 2). Only He was not seriously affected by such air contamination because of its high concentration in  $\text{CO}_2$  gas.

With the “Flute de Pan” method, the highest  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of 604 and a high  $^4\text{He}/^{20}\text{Ne}$  ratio of 994 were obtained for the sample from the bottom layer of Lake Nyos. However, since the gases from the Flute de Pan were collected by displacement in a glass bottle filled with surface water, contamination from atmosphere dissolved in the surface water was still suspected in this method. With the plastic hose method, bubbling gas was directly introduced into a sampling bottle. After thorough flushing of the bottle with the bubbling gas, stopcocks on both ends were closed. Advantage of this sampling method is demonstrated by high  $^4\text{He}/^{20}\text{Ne}$  (>1000) and  $^{40}\text{Ar}/^{36}\text{Ar}$  (>400) ratios as shown in Table 3. Thus, this method was found most suitable for collection of contamination-free gas and water samples. In the following discussion we will use the data from samples collected in January 2001 and December 2001 only, for they are almost contamination-free (Tables 1, 2 and 4). The noble gas data for samples col-

lected with the Al-bag and SS-cylinder methods are given in Appendixes 1 and 2.

#### Profile of noble gas concentration and chemical structure of lake water

Concentrations of  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  in different water depths in January 2001 and December 2001 were shown in Figs. 1 and 2 for Lakes Nyos and Monoun, respectively. The concentrations in air-saturated water at 30°C (Kipfer *et al.*, 2002) were shown by arrows for comparison (also see Table 2). Chemical structures of both lakes in 2001 were also presented in the figures as exemplified by the measured electric conductivity profiles (Kusakabe *et al.*, 2008).

In Lake Nyos, the concentrations of Ne, Ar, Kr and Xe in water were roughly constant with respect to depths between 100 m and bottom (Fig. 1b) though they are up to several times lower than those of air saturated water. They increased by 3–5 times higher at 70 m, just below the upper chemocline at 50 m. Only He is enriched in water by 3 orders of magnitude compared to that in air saturated water, implying its different origin.

The concentrations of Ne, Ar, Kr and Xe in Lake Monoun are almost constant below the depth of about 50 m (Fig. 2b). Their concentrations are similar to those in Lake Nyos, suggesting a similar origin for Ne, Ar, Kr and Xe. The maximum concentrations were observed at the depth of 45 m, just above the lower chemocline at 50 m. Then the concentrations appeared to decrease upward, although we do not have data for water shallower than 20 m.

Relative elemental abundances of noble gases, normalized to air composition, are presented in Fig. 3.  $F(^m\text{X})$  is defined as  $(^m\text{X}/^{36}\text{Ar})_{\text{sample}} / (^m\text{X}/^{36}\text{Ar})_{\text{air}}$ , where  $^m\text{X}$  stands for  $^{20}\text{Ne}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  (Ozima and Alexander, 1976). The  $F(^m\text{X})$  values for air saturated water (ASW) at 30°C (Kipfer *et al.*, 2002) are shown for comparison. Ne is depleted, while Kr and Xe are enriched compared with air composition at both lakes. In deep waters the relative abundances are similar to those of air-saturated water, suggesting that the noble gases except He are mainly supplied from groundwater.

#### $^3\text{He}/^4\text{He}$ ratios

Depth profiles of  $^3\text{He}/^4\text{He}$  ratio for Lakes Nyos and Monoun are presented in Fig. 4a. Those in deep waters of Lake Nyos (140–210 m in depth) are enlarged in Fig. 4b. The  $^3\text{He}/^4\text{He}$  ratios are much higher than the atmospheric value of  $1.4 \times 10^{-6}$ , confirming magmatic gas input to the lake water as already reported by Sano *et al.* (1987, 1990). The ratios are almost constant in the depth range of 80–210 m at Lake Nyos and 40–100 m at Lake Monoun. The  $^3\text{He}/^4\text{He}$  ratio approaches the atmospheric value of  $1.4 \times 10^{-6}$  in waters shallower than 80 m and 40 m for Lakes



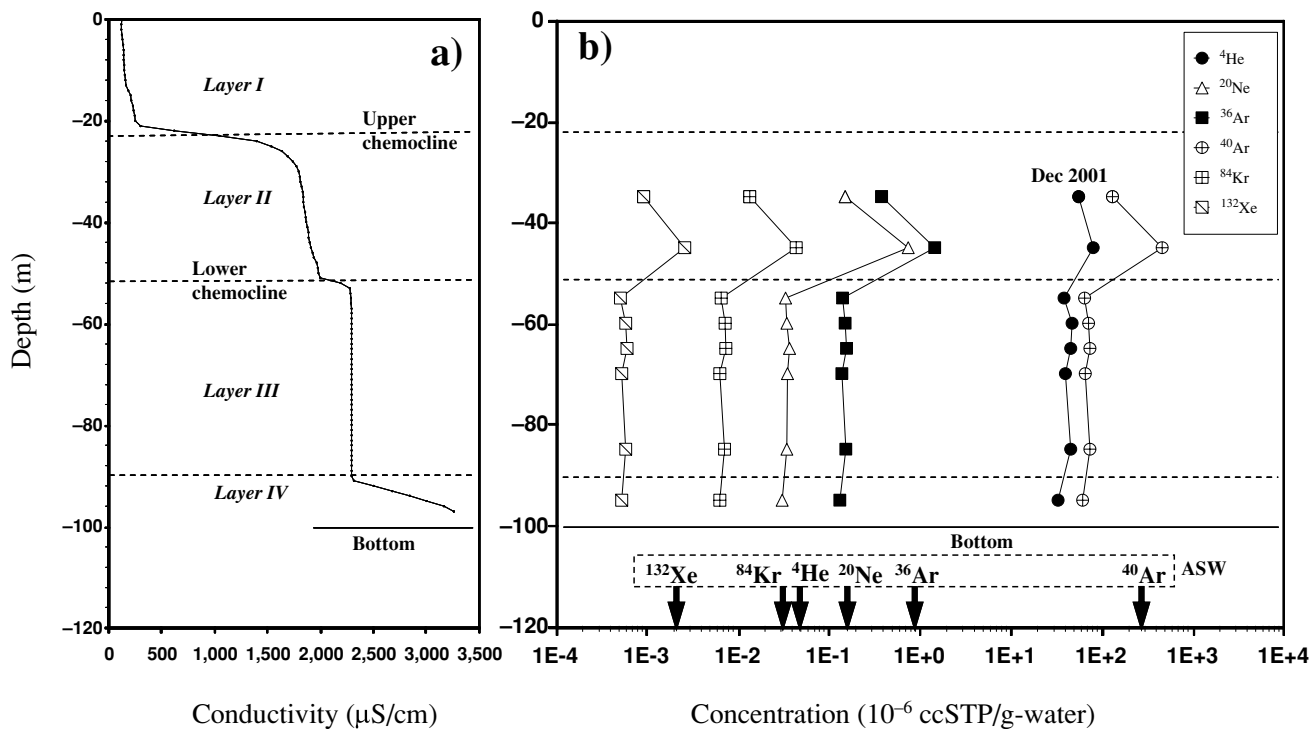


Fig. 2. a) Chemical structure of Lake Monoun as expressed by electric conductivity of water at 25°C. Two chemoclines and four stratified layers are defined (see Kusakabe *et al.*, 2008). b) Depth profiles of noble gas concentrations in water ( $10^{-6}$  ccSTP/g-water) for Lake Monoun. Noble gas concentrations in air saturated water (ASW) at 30°C (Table 2: Kipfer *et al.*, 2002) are also shown by arrows for comparison.

Nyos and Monoun, respectively. These depths are slightly deeper than the upper chemoclines (~50 m at Lake Nyos and ~25 m at Lake Monoun). No systematic differences were observed between the profiles at different times, i.e., November 1999, January 2001 and December 2001. This suggests that there was no temporal variation in  $^3\text{He}/^4\text{He}$  ratios of magmatic He being supplied to both lakes. The  $^3\text{He}/^4\text{He}$  ratios observed at these lakes clearly indicate a contribution of mantle-derived He. However, the ratios are distinctly lower than the values for MORB-like He of  $12 \times 10^{-6}$  as observed at the oceanic and continental sectors of CVL (Aka *et al.*, 2004b). Figure 4b shows that the  $^3\text{He}/^4\text{He}$  ratios increase from  $(7.8\text{--}7.9) \times 10^{-6}$  in the bottom water to  $(8.0\text{--}8.2) \times 10^{-6}$  above the lower chemocline that lies at ~180 m depth at Lake Nyos.  $^4\text{He}/^{20}\text{Ne}$  ratios for these samples are close to 1000. Such high  $^4\text{He}/^{20}\text{Ne}$  values indicate that we can ignore air contamination to the measured  $^3\text{He}/^4\text{He}$  ratios. The observation that  $^3\text{He}/^4\text{He}$  ratios of  $(8.0\text{--}8.2) \times 10^{-6}$  at ~180 m are slightly higher than those of bottom water ( $7.8\text{--}7.9 \times 10^{-6}$ ) may be explained by an idea that the recharge water is supplied to the lake at ~180 m depth. This possibility will be discussed later in more detail.

#### MORB-like Ne isotopic ratios

Ne isotopic ratios are presented in Fig. 5. Small excess in both  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios was observed compared with the values for atmospheric Ne. Most data points of both lakes lie on the MORB line that connects the atmospheric Ne and mantle Ne reported by Ballentine *et al.* (2005). The data clearly indicate the presence of mantle Ne in addition to the mantle-derived He in the lakes. The Nyos data points in January 2001 are plotted close to atmospheric Ne compared with other samples. This indicates that atmospheric contamination of the samples obtained by the “Flute de Pan” method is greater than those by the plastic hose method. Our Ne data are consistent with the conclusion by Barfod *et al.* (1999) that the CVL mantle contains MORB-like Ne, though the Ne isotopic variation in Lakes Nyos and Monoun is restricted ( $^{20}\text{Ne}/^{22}\text{Ne} \leq 9.9$  and  $^{21}\text{Ne}/^{22}\text{Ne} \leq 0.0303$ ) compared with the ranges ( $^{20}\text{Ne}/^{22}\text{Ne} \leq 11.87$  and  $^{21}\text{Ne}/^{22}\text{Ne} \leq 0.0508$ ) measured for xenoliths (Barfod *et al.*, 1999). This indicates that atmospheric Ne from groundwater has diluted the MORB-like Ne in magmatic fluid beneath the lakes.

In contrast to the samples lying on the MORB-line (Fig. 5), two samples collected at the bottom of Lake Nyos

Table 4. Concentrations of  $^3\text{He}$ ,  $^{21}\text{Ne}_{\text{excess}}$  and  $^{40}\text{Ar}_{\text{excess}}$ , and  $C/^3\text{He}$ ,  $^{21}\text{Ne}_{\text{excess}}/^4\text{He}$ ,  $^4\text{He}/^{40}\text{Ar}_{\text{excess}}$ ,  $^3\text{He}/^{40}\text{Ar}_{\text{excess}}$  and  $^3\text{He}/^{21}\text{Ne}_{\text{excess}}$  for deep water samples from Lake Nyos (>160 m) and Lake Monoun (>50 m) collected in 2001 by Flute de Pan and Plastic hose methods

Sample name	Depth (m)	$C/^3\text{He}^*$	$^3\text{He}$	$^{21}\text{Ne}_{\text{excess}}$	$^{40}\text{Ar}_{\text{excess}}$
		$10^{+10}$	$10^{-12}$ ccSTP/g	$10^{-12}$ ccSTP/g	$10^{-6}$ ccSTP/g
Lake Nyos					
January 2001 (>160 m)					
NY01Jan-210	-209.8	1.63	487 ± 7	5.6 ± 2.2	83.99 ± 0.34
NY01Jan-202	-201.62	1.73	448 ± 7	3.6 ± 2.5	76.79 ± 0.59
NY01Jan-199	-199.22	1.71	452 ± 8	4.4 ± 1.8	74.00 ± 0.44
NY01Jan-195	-195.04	1.66	467 ± 7	4.0 ± 2.6	74.92 ± 0.59
NY01Jan-190	-189.85	1.51	495 ± 9	5.4 ± 1.8	79.69 ± 0.45
Average		1.65 ± 0.08			
NY01Jan-180	-180.03	0.57	704 ± 11	5.1 ± 2.1	75.51 ± 0.57
NY01Jan-170	-170.04	0.82	422 ± 6	2.7 ± 1.7	45.39 ± 0.39
Average		0.70 ± 0.12			
December 2001 (all data)					
NY01Dec-208	-208	1.64	449 ± 4	5.3 ± 2.1	48.02 ± 0.19
NY01Dec-208	-208	1.39	528 ± 7	6.1 ± 3.5	40.17 ± 0.12
NY01Dec-205	-205	1.70	459 ± 5	5.6 ± 2.2	48.00 ± 0.13
NY01Dec-200	-200	1.32	593 ± 8	9.0 ± 2.0	42.60 ± 0.19
NY01Dec-195	-195	1.66	467 ± 5	6.6 ± 1.8	48.42 ± 0.11
NY01Dec-190	-190	1.42	528 ± 4	6.8 ± 1.4	51.03 ± 0.18
Average		1.52 ± 0.15			
NY01Dec-188	-187.5	0.66	912 ± 9	6.7 ± 2.6	58.92 ± 0.20
NY01Dec-185	-185	0.47	974 ± 12	9.7 ± 4.7	50.77 ± 0.12
NY01Dec-185	-185	0.56	815 ± 7	7.8 ± 1.9	55.27 ± 0.35
NY01Dec-183	-182.5	0.49	848 ± 6	8.4 ± 2.5	57.19 ± 0.17
NY01Dec-180	-180	0.46	843 ± 11	7.9 ± 1.9	42.37 ± 0.20
NY01Dec-180	-180	0.52	745 ± 6	6.1 ± 1.1	47.24 ± 0.18
NY01Dec-178	-177.5	0.56	659 ± 6	6.0 ± 1.2	41.07 ± 0.12
NY01Dec-175	-175	0.65	551 ± 5	5.0 ± 2.0	34.65 ± 0.14
NY01Dec-175	-175	0.55	653 ± 8	7.8 ± 2.2	31.34 ± 0.11
NY01Dec-170	-170	0.74	471 ± 5	3.5 ± 1.2	30.64 ± 0.21
NY01Dec-165	-165	0.86	393 ± 4	4.2 ± 0.9	24.18 ± 0.12
Average		0.59 ± 0.12			
Lake Monoun					
December 2001 (>50 m)					
MN01Dec-95	-95	2.24	167 ± 2	2.0 ± 0.9	22.99 ± 0.08
MN01Dec-85	-85	1.52	233 ± 3	2.9 ± 1.2	28.42 ± 0.08
MN01Dec-70	-70	1.75	202 ± 3	3.6 ± 0.8	24.81 ± 0.09
MN01Dec-65	-65	1.55	228 ± 3	2.2 ± 1.0	27.79 ± 0.14
MN01Dec-60	-60	1.46	243 ± 3	3.0 ± 1.4	27.09 ± 0.12
MN01Dec-55	-55	1.70	195 ± 3	3.1 ± 1.0	23.69 ± 0.09
Average		1.70 ± 0.26			

Table 4. (continued)

Sample name	$^{21}\text{Ne}_{\text{excess}}/^{4}\text{He}^*$		$^4\text{He}/^{40}\text{Ar}_{\text{excess}}^*$		$^3\text{He}/^{40}\text{Ar}_{\text{excess}}$		$^3\text{He}/^{21}\text{Ne}_{\text{excess}}$	
	$10^{-8}$				$10^{-6}$			
Lake Nyos								
January 2001 (>160 m)								
NY01Jan-210	9.1	± 3.5	0.731	± 0.003	5.80	± 0.09	87	± 33
NY01Jan-202	6.4	± 4.4	0.736	± 0.006	5.84	± 0.11	124	± 86
NY01Jan-199	7.7	± 3.1	0.768	± 0.005	6.11	± 0.11	103	± 42
NY01Jan-195	6.8	± 4.4	0.789	± 0.006	6.24	± 0.11	116	± 74
NY01Jan-190	8.7	± 2.9	0.778	± 0.004	6.21	± 0.11	91	± 30
Average	7.8	± 1.1	0.760	± 0.023	6.04	± 0.19	104	± 14
NY01Jan-180	5.8	± 2.4	1.166	± 0.009	9.33	± 0.16	138	± 57
NY01Jan-170	5.2	± 3.2	1.157	± 0.010	9.30	± 0.16	156	± 96
Average	5.5	± 0.3	1.162	± 0.004	9.32	± 0.01	147	± 9
December 2001 (all data)								
NY01Dec-208	9.3	± 3.6	1.184	± 0.005	9.34	± 0.09	85	± 33
NY01Dec-208	9.2	± 5.2	1.665	± 0.005	13.14	± 0.19	86	± 49
NY01Dec-205	9.5	± 3.7	1.229	± 0.003	9.55	± 0.10	82	± 32
NY01Dec-200	12.0	± 2.7	1.760	± 0.008	13.93	± 0.20	66	± 15
NY01Dec-195	11.2	± 3.0	1.221	± 0.003	9.64	± 0.10	71	± 19
NY01Dec-190	9.9	± 2.1	1.332	± 0.005	10.35	± 0.09	78	± 16
Average	10.2	± 1.1	1.40	± 0.23	11.0	± 1.8	78	± 7
NY01Dec-188	5.9	± 2.3	1.950	± 0.007	15.48	± 0.16	135	± 53
NY01Dec-185	8.0	± 3.9	2.406	± 0.006	19.18	± 0.25	100	± 49
NY01Dec-185	7.7	± 1.8	1.836	± 0.012	14.74	± 0.16	104	± 25
NY01Dec-183	7.8	± 2.4	1.873	± 0.006	14.84	± 0.12	101	± 30
NY01Dec-180	7.4	± 1.8	2.535	± 0.012	19.90	± 0.27	106	± 26
NY01Dec-180	6.6	± 1.2	1.943	± 0.007	15.78	± 0.15	122	± 23
NY01Dec-178	7.1	± 1.5	2.035	± 0.006	16.06	± 0.15	111	± 23
NY01Dec-175	7.3	± 2.9	1.967	± 0.008	15.89	± 0.15	110	± 44
NY01Dec-175	9.4	± 2.7	2.622	± 0.009	20.85	± 0.27	84	± 24
NY01Dec-170	6.1	± 2.1	1.879	± 0.013	15.37	± 0.18	135	± 46
NY01Dec-165	8.7	± 1.9	1.999	± 0.010	16.26	± 0.20	94	± 21
Average	7.5	± 1.0	2.10	± 0.27	16.8	± 2.0	109	± 15
Lake Monoun								
December 2001 (>50 m)								
MN01Dec-95	5.9	± 2.7	1.455	± 0.005	7.26	± 0.09	84	± 39
MN01Dec-85	6.2	± 2.6	1.623	± 0.004	8.21	± 0.12	81	± 34
MN01Dec-70	8.8	± 1.9	1.618	± 0.006	8.16	± 0.12	57	± 12
MN01Dec-65	4.9	± 2.2	1.646	± 0.008	8.22	± 0.12	102	± 45
MN01Dec-60	6.4	± 3.0	1.749	± 0.008	8.95	± 0.13	80	± 37
MN01Dec-55	8.1	± 2.7	1.633	± 0.006	8.22	± 0.12	62	± 20
Average	6.7	± 1.3	1.621	± 0.086	8.17	± 0.49	78	± 15

\*Concentrations of  $^4\text{He}$  and  $\text{CO}_2$  are presented in Table 2.

(210 m in depth) in January 2001 plot above the MORB-line. They plot close to a line for hot-spot Ne such as Loihi-type Ne (Graham, 2002). The  $^3\text{He}/^4\text{He}$  ratios of these samples (Fig. 4b) suggest an input of small amount

of radiogenic crustal  $^4\text{He}$  as noted previously. The highest  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of 604 and 599 (Fig. 6) were observed for these samples, which suggest contribution of radiogenic  $^{40}\text{Ar}$  to the bottom water along with crustal  $^4\text{He}$ . If

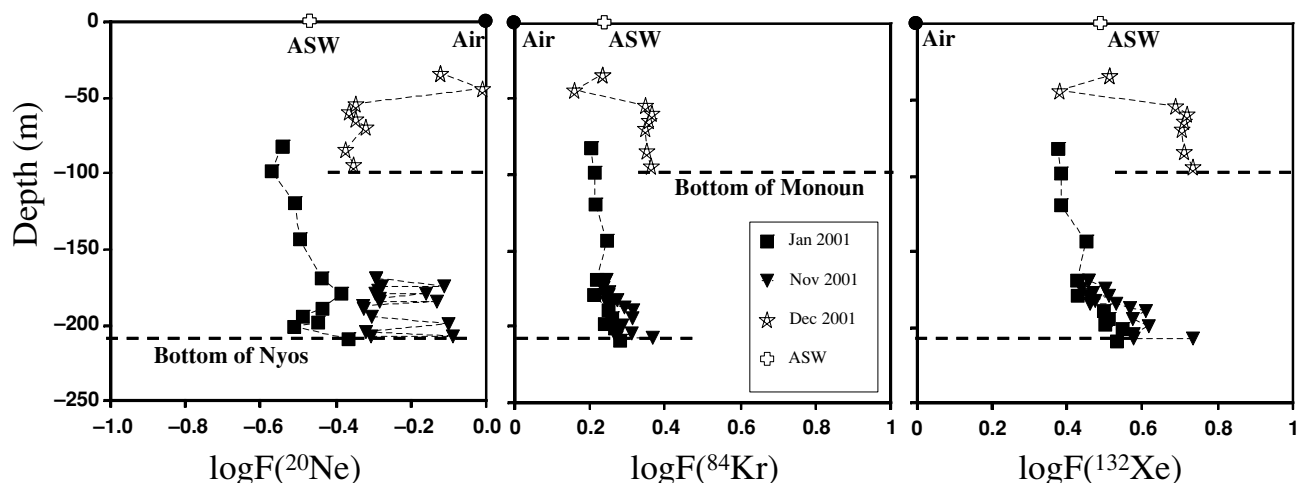


Fig. 3. Relative abundances of  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$ , normalized to air composition, defined as  $F(^m\text{X}) = (^m\text{X}/^{36}\text{Ar})_{\text{sample}} / (^m\text{X}/^{36}\text{Ar})_{\text{air}}$ , where  $^m\text{X}$  stands for  $^{20}\text{Ne}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  (Ozima and Alexander, 1976). The  $F(^m\text{X})$  values for air and air saturated water (ASW) at 30°C (Kipfer *et al.*, 2002) are shown for comparison.

nucleogenic  $^{21}\text{Ne}$  in crust also contributes to the observed MORB-like Ne, however, data point would have shifted to the right of the MORB-Ne line.

Though the Ne data points could be qualitatively explained by addition of nucleogenic  $^{21}\text{Ne}$  in the crust to mass fractionated atmospheric Ne, the nucleogenic  $^{21}\text{Ne}$  may not be sufficient to explain the observed concentration of excess  $^{21}\text{Ne}$  of  $(6 \pm 2) \times 10^{-12}$  ccSTP/g-water (Table 4). Based on production rate ratio of  $^4\text{He}/^{21}\text{Ne}$  of  $2 \times 10^7$  in crust (Ballentine and Burnard, 2002) and the addition of crustal  $^4\text{He}$  of  $<5 \times 10^{-6}$  ccSTP/g-water to the bottom water, concentration of nucleogenic  $^{21}\text{Ne}$  is estimated to be  $<3 \times 10^{-13}$  ccSTP/g-water, much smaller than the observed excess  $^{21}\text{Ne}$ . Moreover, it is difficult to imagine that two different types of magma sources such as hot-spot type and MORB-type exist in this small region of CVL. Thus, we believe that contribution of nucleogenic  $^{21}\text{Ne}$  to the observed MORB-like Ne is denied. Hence, most plausible explanation for the Ne isotopic ratios in the bottom-most water is mass fractionation of Ne from a common reservoir for other samples. A pass of fluid containing noble gases observed in the bottom samples NY01Jan-210 will be discussed later in a recharge model for Lake Nyos.

#### Ar isotopic ratios and concentrations

$^{38}\text{Ar}/^{36}\text{Ar}$  ratios for all samples agree with atmospheric value of 0.1880 within  $2\sigma$  error limits (Table 1). This indicates that no detectable fractionation effect on the  $^{38}\text{Ar}/^{36}\text{Ar}$  ratio was observed for the samples with high  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio as noted above. Small fractionation effect on  $^{38}\text{Ar}/^{36}\text{Ar}$  ratio, if any, would be easily masked by atmospheric Ar dissolved in groundwater, because solubility of

Ar is much greater than that of Ne.  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios for all samples are higher than the atmospheric value of 296 as shown in Fig. 6, but much lower than the estimated value of  $>1650$  for upper mantle beneath the CVL (Barfod *et al.*, 1999). This means atmospheric Ar was mixed with the mantle Ar in a sub-lacustrine fluid reservoir. This is consistent with the dilution of mantle-derived Ne by atmospheric Ne as shown in Fig. 5.

Of the samples collected in January 2001, just prior to the initiation of degassing operation at Lake Nyos, the highest  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio was about 600 at the bottom (210 m) of the lake. The ratio decreased to 433–455 between depths 202–195 m, increased again to 479 at 190 m, sharply decreased to 310 at 83 m, and then approached the atmospheric value of 296. At 190 m where  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio showed a maximum (Fig. 6),  $\text{CO}_2$  concentration in water stayed constant at  $\sim 7.8$  ccSTP/g-water and  $^3\text{He}$  concentration increased significantly as will be discussed later. Figure 6 shows that the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios between 190 and 208 m in December 2001, 10 months after the initiation of degassing operation, became almost constant in a narrow range of 527–541, and the high ratios of about 600 observed at the bottom layer in January 2001 disappeared when compared at the same depth. It may be noted, however, that the maximum ratios of  $^{40}\text{Ar}/^{36}\text{Ar}$  (541) and  $^4\text{He}/^{20}\text{Ne}$  (1320–1590) still remained at 188–190 m depth.

Almost uniform  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios between 190 m and 208 m in December 2001, and high  $^4\text{He}/^{20}\text{Ne}$  ratios ( $\sim 1100$ , Table 1) at the same depths, are quite a contrast to those in January 2001. This may have resulted from vertical mixing in the depth range caused by the degassing operation, because water was pumped out by the degassing pipe with the intake depth of 203 m. Such homogeniza-

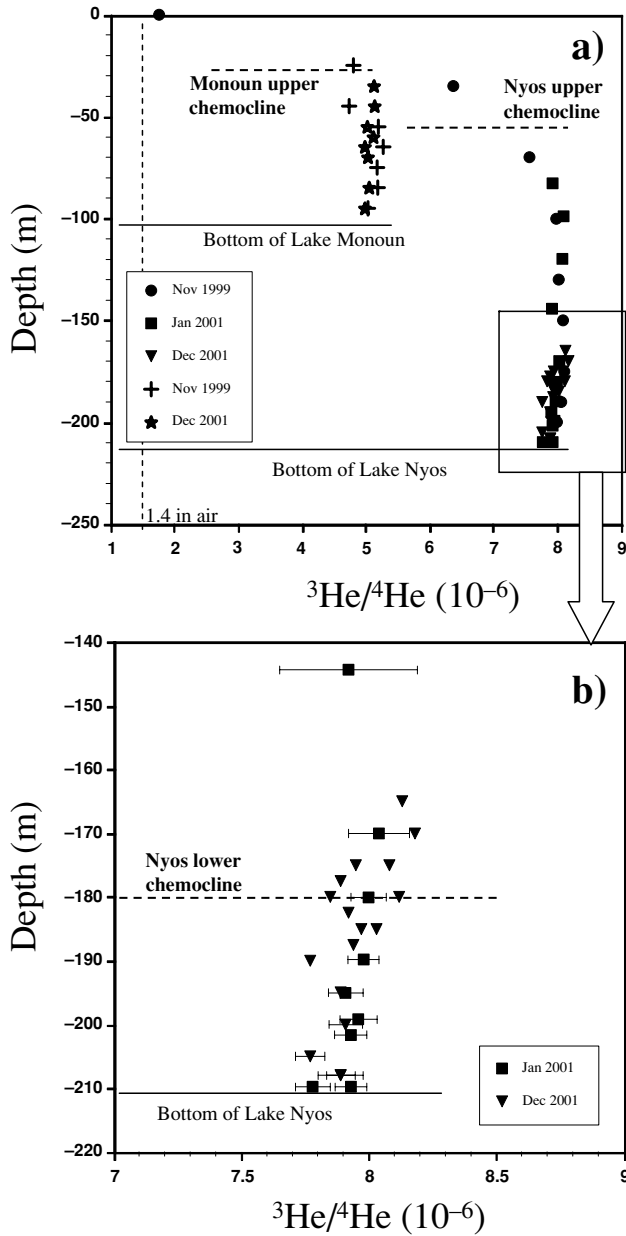


Fig. 4. a)  $^3\text{He}/^4\text{He}$  ratios as a function of depth at Lakes Nyos and Monoun during 1999 and 2001. b) A part of deep layer (140–210 m) of Lake Nyos is enlarged.

tion observed in the  $^4\text{He}/^{20}\text{Ne}$  and Ar isotopic ratios, however, was also observed in the water temperature and electric conductivity profiles at the corresponding depths, although they were less clear than the noble gas profiles (Kusakabe *et al.*, 2008).

At Lake Monoun, the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios were in a narrow range at about 470 between 60 m and 100 m (bottom) (Fig. 6). The ratios are lower than those in deep waters of Lake Nyos. This indicates that contribution of atmospheric Ar to the magma-derived gases at Lake

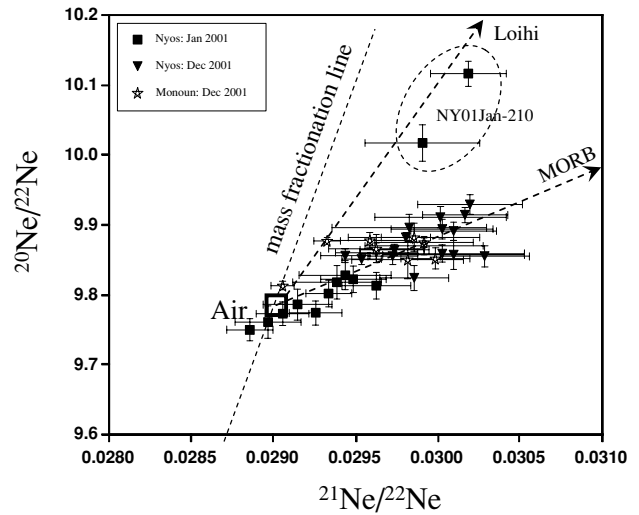


Fig. 5. Plot of  $^{20}\text{Ne}/^{22}\text{Ne}$  versus  $^{21}\text{Ne}/^{22}\text{Ne}$  for samples collected in January and December 2001 from Lakes Nyos and Monoun (see Table 1). The “mass fractionation line” indicates Ne isotopic ratios for mass fractionated atmospheric Ne; A dashed line heading to MORB represents a mixing line between atmospheric Ne and Ne in MORB or upper mantle (Ballentine *et al.*, 2005). A dashed line heading to Loihi represents a mixing line between atmospheric Ne and hot-spot type Ne such as Loihi (Graham, 2002).

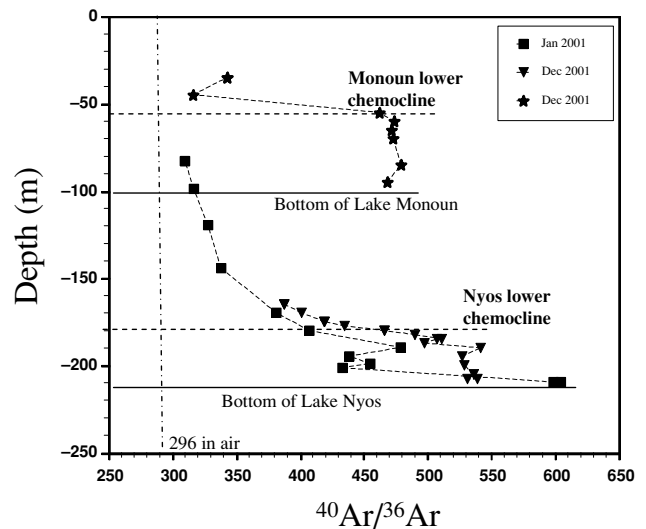


Fig. 6. Depth profiles of  $^{40}\text{Ar}/^{36}\text{Ar}$  in Lakes Nyos and Monoun. Chemoclines are from Kusakabe *et al.* (2008).

Monoun is greater than that at Lake Nyos. The ratio decreases sharply at depths shallower than 55 m, which corresponds to the depth of lower chemocline in 2001 (Fig. 6) (Kusakabe *et al.*, 2008).

Plots of  $^{40}\text{Ar}/^{36}\text{Ar}$  vs.  $1/^{36}\text{Ar}$  are presented in Fig. 7,

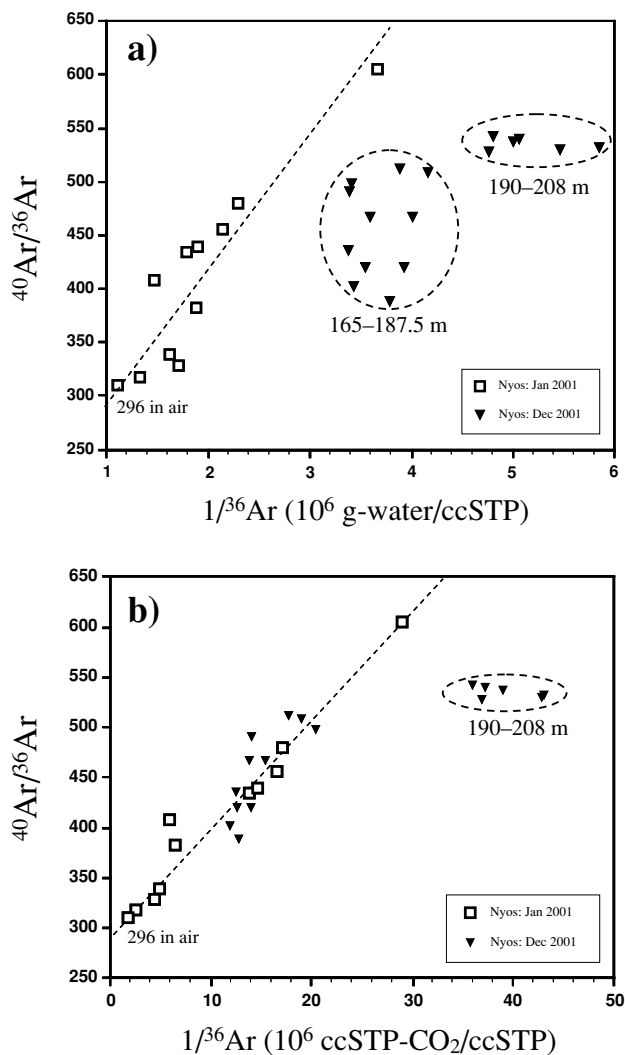


Fig. 7. (a)  $^{40}\text{Ar}/^{36}\text{Ar}$  versus  $1/^{36}\text{Ar}$  (concentration in water) and (b)  $1/^{36}\text{Ar}$  (concentration in  $\text{CO}_2$  gas) for the samples collected from Lake Nyoos in January and December 2001.

where the  $^{36}\text{Ar}$  concentrations in water (Fig. 7a) and in  $\text{CO}_2$  gas (Fig. 7b) are shown. If Ar in the lake is a simple mixture between atmospheric Ar and Ar from a magmatic source, the data points should plot on a straight line passing through the atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of 296 at  $1/^{36}\text{Ar} = 0$ . In both plots, the Ar data for January 2001 plot roughly on a single line, suggesting simple mixing between atmospheric Ar and magmatic Ar. On the contrary, the December 2001 data do not show linear correlation in Fig. 7a, but form two clusters for the samples from two layers of 165–187.5 m and 190–208 m. The December 2001 samples from the 165–187.5 m layer plot on the January 2001 line in Fig. 7b, but the samples from the 190–208 m layer show almost constant  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $1/^{36}\text{Ar}$  values, plotting away from the mixing line. The high

$1/^{36}\text{Ar}$  values correspond to low Ar concentrations in  $\text{CO}_2$  gas at 190–208 m in December 2001 (Fig. 7b).

#### Carbon, hydrogen and oxygen isotopic compositions of lake water

$\delta^{13}\text{C}$  values for Lake Nyoos of  $\approx -3.4\text{‰}$  (Table 2 and Appendix 2) are consistent with previously reported values (Kling *et al.*, 1987; Kusakabe *et al.*, 1989). The values are slightly higher than those for the nominal mantle values of  $-5\text{‰}$ – $-7\text{‰}$ . They are close to those reported for soda springs from islands along the CVL (Kusakabe and Sano, 1992), and may represent carbon from the CVL-mantle, where carbon from marine carbonate might have contributed. On the other hand the  $\delta^{13}\text{C}$  values of  $\approx -6.8\text{‰}$  for Lake Monoun are slightly lower than that for mantle. Contribution of organic carbon to the CVL-mantle carbon is conceivable. The  $\delta$ -values of D/H and  $^{18}\text{O}/^{16}\text{O}$  ratios of waters collected in 1998–2001 from Lakes Nyoos and Monoun (Table 5) were almost the same as those for waters collected in 1986 reported in Kusakabe *et al.* (1989). No magmatic isotope signature was detected. All data points lie close to the typical meteoric water line with Lake Nyoos waters being isotopically heavier than Lake Monoun waters. The results indicate that the lake waters were originated from surface meteoric water, though the water was subjected to evaporation with respect to the surface waters.

#### DISCUSSION

Table 4 lists  $^3\text{He}$ , excess  $^{21}\text{Ne}$  and  $^{40}\text{Ar}$  concentrations, and ratios of  $\text{C}/^3\text{He}$ ,  $^{21}\text{Ne}_{\text{excess}}/^4\text{He}$ ,  $^4\text{He}/^{40}\text{Ar}_{\text{excess}}$ ,  $^3\text{He}/^{40}\text{Ar}_{\text{excess}}$  and  $^3\text{He}/^{21}\text{Ne}_{\text{excess}}$  for the samples collected in 2001 from deep layers of Lake Nyoos ( $>160$  m) and Lake Monoun ( $>55$  m). The excess  $^{21}\text{Ne}$  and  $^{40}\text{Ar}$  concentrations are defined as;

$$[^{21}\text{Ne}_{\text{excess}}] = [(^{21}\text{Ne}/^{22}\text{Ne})_{\text{measured}} - 0.0290] \times [^{22}\text{Ne}], \text{ and}$$

$$[^{40}\text{Ar}_{\text{excess}}] = [(^{40}\text{Ar}/^{36}\text{Ar})_{\text{measured}} - 296] \times [^{36}\text{Ar}],$$

where 0.0290 and 296 are  $^{21}\text{Ne}/^{22}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios in atmosphere, respectively.

#### $\text{CO}_2$ and $^3\text{He}$ concentrations and $\text{C}/^3\text{He}$ ratios in deep water of Lake Nyoos

The  $\text{CO}_2$  and  $^3\text{He}$  concentrations and  $\text{C}/^3\text{He}$  ratios in water were compared for the bottom layer (160–210 m) of Lake Nyoos in Fig. 8. The  $\text{CO}_2$  and  $^3\text{He}$  concentrations were in the ranges of (3.3–7.8) ccSTP/g-water and  $(3.9\text{--}9.7) \times 10^{-10}$  ccSTP/g-water, respectively. The  $^3\text{He}$  concentrations are nearly constant at  $5 \times 10^{-10}$  ccSTP/g-water below the lower chemocline at around 187 m. However, the  $^3\text{He}$  concentration increases sharply toward the

Table 5.  $\delta D$  and  $\delta^{18}O$  values of Lakes Nyos and Monoun

	Lake Nyos			Lake Monoun		
	Depth (m)	$\delta D_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)	Depth (m)	$\delta D_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)
May 1998						
	-1.0	-8.7	-2.00	-1.0	-12.7	-2.42
	-15.0	-11.5	-2.42	-15.0	-20.2	-3.93
	-30.0	-12.9	-2.59	-45.7	-22.0	-4.26
	-50.0	-12.1	-2.48	-61.0	-22.0	-4.34
	-100.0	-12.0	-2.66	-68.6	-22.2	-4.26
	-150.0	-12.6	-2.76	-79.3	-22.4	-4.24
	-200.0	-12.4	-2.86	-95.4	-21.1	-4.09
	-208.0	-12.7	-2.87			
November 1999						
	-35.0	-14.3	-2.76	-0.5	-26.1	-4.70
	-70.0	-11.7	-2.77	-1.5	-25.8	-4.68
	-100.0	-11.5	-2.77	-3.0	-26.0	-4.73
	-130.0	-11.6	-2.88	-5.0	-28.6	-5.03
	-150.0	-11.2	-2.87	-10.0	-28.7	-5.06
	-175.0	-11.9	-2.83	-15.2	-29.2	-4.98
	-190.0	-14.0	-2.99	-20.0	-26.6	-4.57
	-200.0	-13.9	-3.05	-79.2	-23.3	-4.33
				-95.4	-23.3	-4.31
January 2001						
	-0.5	-14.2	-2.80	-0.5	-19.1	-3.62
	-10.0	-14.5	-2.78	-3.0	-19.6	-3.65
	-20.0	-14.7	-2.80	-7.0	-20.4	-3.98
	-30.0	-14.6	-2.84	-22.9	-21.7	-4.13
	-40.0	-14.7	-2.78			
	-50.0	-12.7	-2.63			
	-75.0	-12.0	-2.68			
	-125.0	-12.3	-2.76			
	-150.0	-12.2	-2.83			
	-198.1	-13.0	-2.99			
	-205.8	-13.0	-2.97			
December 2001						
	-165.0	—	-2.81	-35.0	—	-4.23
	-170.0	—	-2.84	-45.0	—	-4.12
	-175.0	—	-2.83	-55.0	—	-4.36
	-180.0	—	-2.82	-60.0	—	-4.35
	-182.5	—	-2.91	-65.0	—	-4.37
	-185.0	—	-2.86	-70.0	—	-4.35
	-187.5	—	-2.95	-85.0	—	-4.27
	-190.0	—	-2.95	-95.0	—	-4.35
	-205.0	—	-2.94			
January 2005						
	0.0	—	-2.65	-7.0	—	-3.69
	-20.0	—	-2.61	-22.9	—	-3.69
	-50.0	—	-2.62	-30.0	—	-4.42
	-70.0	—	-2.81	-35.0	—	-4.31
	-98.8	—	-2.84	-45.7	—	-4.27
	-136.9	—	-2.96	-50.0	—	-4.38
	-170.4	—	-2.95	-60.0	—	-4.38
	-180.0	—	-2.92	-80.0	—	-4.43
	-190.2	—	-3.04	-95.4	—	-4.47
	-197.8	—	-3.08			
	-205.5	—	-3.05			

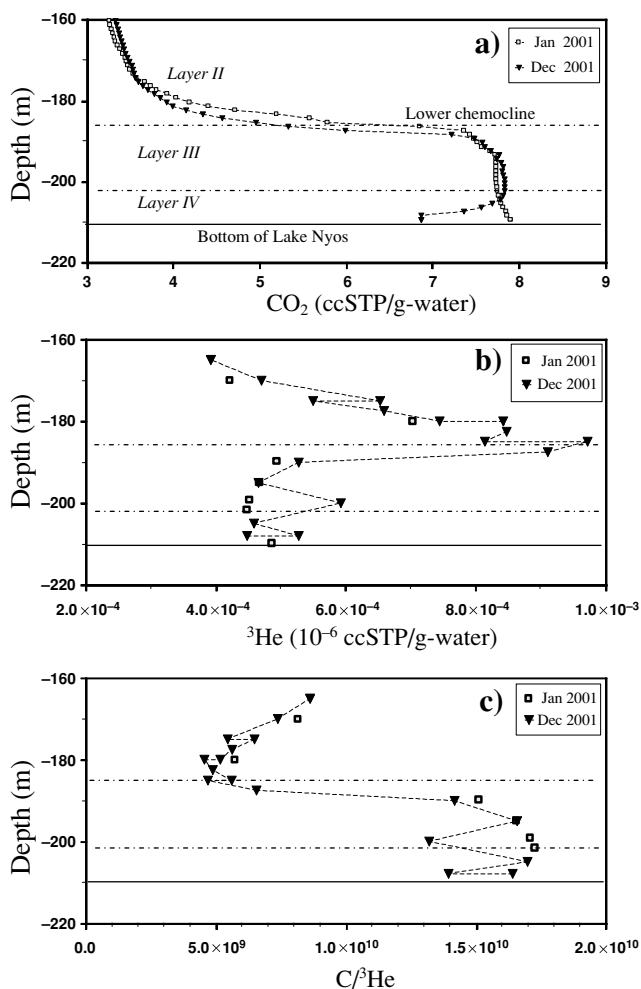


Fig. 8. Profiles of  $\text{CO}_2$  (a),  ${}^3\text{He}$  (b), and  $\text{C}^3\text{He}$  ratios (c) in deep water from 160 to 210 m at Lake Nyos. Refer to Kusakabe *et al.* (2008) for Layers II, III and IV and lower chemocline.

lower chemocline, followed by gradual decrease toward shallower water (layer II) (Fig. 8b). The change in  $\text{C}^3\text{He}$  ratios from  $(1.5 \pm 0.2) \times 10^{10}$  in layers III and IV to  $(0.6 \pm 0.1) \times 10^{10}$  above the lower chemocline reflects the different profiles of  $\text{CO}_2$  and  ${}^3\text{He}$  concentrations. The low  ${}^3\text{He}$  concentrations in the bottom layer (190–210 m) may be difficult to attribute to a selective removal of He from this layer by the degassing operation, because the concentrations are almost the same for the samples before and after the initiation of degassing operation. There may be a mechanism to accumulate He below the lower chemocline due to lowered diffusivity of gases across the density-stratified chemocline (Tietze, 1987) that will lead to accumulation of gases below the chemocline. The observation that  ${}^3\text{He}$  (and  ${}^4\text{He}$  as well) has a maximum concentration at 190 m whereas  $\text{CO}_2$  does not may reflect higher diffusivity of He ( $6.28 \times 10^{-5} \text{ cm}^2\text{sec}^{-1}$  at  $25^\circ\text{C}$ )

than  $\text{CO}_2$  ( $1.92 \times 10^{-5} \text{ cm}^2\text{sec}^{-1}$  at  $25^\circ\text{C}$ ) in water (Ferrell and Himmelblau, 1967). Another possible mechanism, which will be discussed later, is that gases with different  $\text{C}^3\text{He}$  ratios (e.g.,  $\sim 1.7 \times 10^{10}$ ) are added to the bottom layer. In this model, gases in shallower layer (above 190 m) are interpreted to represent a main magmatic fluid with  $\text{C}^3\text{He}$  of  $\sim 0.6 \times 10^{10}$ . These ratios are about 1/5 to 1/2 of the estimation of  $(3.0 \pm 1.5) \times 10^{10}$  by Sano *et al.* (1990) for the samples collected in 1986 and 1988. The  $\text{C}^3\text{He}$  ratio might have decreased with time.

The  $\text{C}^3\text{He}$  ratios at Lake Monoun were  $(1.7 \pm 0.3) \times 10^{10}$ , similar to the value in the Lake Nyos bottom water (Table 4). These ratios, however, are several times higher than the value of  $\sim 2 \times 10^9$  reported for mantle gases (Marty and Jambon, 1987) as pointed out by Sano *et al.* (1990). Relatively high  $\text{C}^3\text{He}$  ratios have been observed for gas samples from islands of São Tomé and Bioko, and mainland Cameroon along the CVL (e.g., Tanyileke *et al.*, 1996; Barfod *et al.*, 1999; Aka *et al.*, 2001). They were attributed to addition of  $\text{CO}_2$  derived from marine limestone and sedimentary rock (Aka *et al.*, 2001).

Based on the observed  $\text{C}^3\text{He}$  ratios, a flux of mantle-derived  ${}^3\text{He}$  can be calculated. Kusakabe *et al.* (2008) estimated a mean accumulation rate of  $\text{CO}_2$  in Lake Nyos as  $0.12 \pm 0.04 \text{ G mole/yr}$ , i.e.,  $(2.3 \pm 0.8) \times 10^{24} \text{ atom C/sec}$ , as an average over the period from November 1986 to January 2001 below the upper chemocline. Based on the  $\text{C}^3\text{He}$  ratios of  $1.5 \times 10^{10}$  at the bottom layer and  $0.6 \times 10^{10}$  at the 190 m layer (Fig. 8c), recharge rates of  ${}^3\text{He}$  to the lake waters were calculated as  $1.5 \times 10^{14}$  and  $3.8 \times 10^{14} \text{ atoms/yr}$  at the respective layers. The values correspond to average  ${}^3\text{He}$ -flux of  $2.9 \times 10^4$  and  $7.4 \times 10^4 \text{ atoms/cm}^2 \text{ sec}$ , if we adopt the bottom area below 183 m depth of  $5.16 \times 10^9 \text{ cm}^2$  (Kling *et al.*, 2005). The fluxes are 10–30% of the estimation of  $(2.4 \pm 0.4) \times 10^5 \text{ atoms/cm}^2 \text{ sec}$  based on data in 1988 by Sano *et al.* (1990). He flux from the magmatic gas reservoir beneath the lake might have decreased during the last 12 years.

#### Noble gas signatures in sub-lacustrine reservoirs of Lakes Nyos and Monoun

In contrast to  ${}^3\text{He}$ , part of  ${}^4\text{He}$  is radiogenic, though its source is difficult to identify. Excess  ${}^{21}\text{Ne}$  (Fig. 5) and excess  ${}^{40}\text{Ar}$  (Fig. 6) can be attributed to both mantle and crustal origins. MORB-type Ne with high  ${}^{21}\text{Ne}/{}^{22}\text{Ne}$  ratio (Fig. 5) and Ar with high  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratio ( $>20000$ ) are present in upper mantle, while in crustal rocks  ${}^{21}\text{Ne}$  is produced by nuclear reactions and  ${}^{40}\text{Ar}$  by  ${}^{40}\text{K}$ -decay. Hence, we can examine the sources from which the high  ${}^{21}\text{Ne}/{}^{22}\text{Ne}$  and  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratios have been derived.

A positive linear relationship is found between  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  and  ${}^{21}\text{Ne}/{}^{22}\text{Ne}$  ratios that pass through the atmospheric ratios (Fig. 9). There is no systematic difference between the two lakes as well as the different sampling



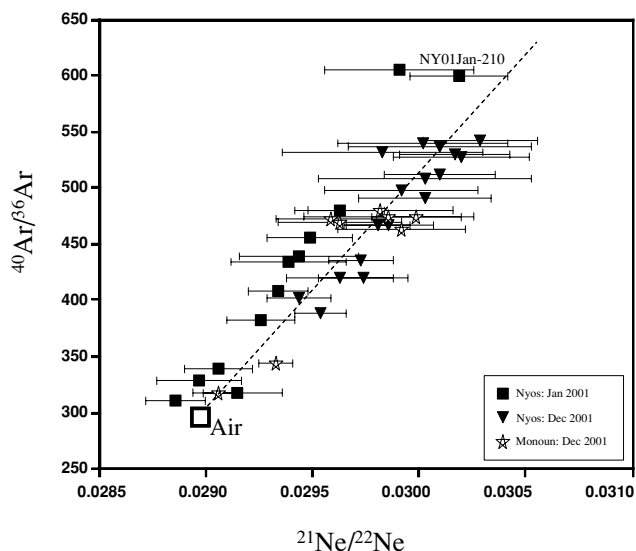


Fig. 9. Plot of  $^{40}\text{Ar}/^{36}\text{Ar}$  versus  $^{21}\text{Ne}/^{22}\text{Ne}$  for Lakes Nyos and Monoun.

dates. This implies a common source for these gases.  $^3\text{He}/^4\text{He}$  ratios versus  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios are presented in Figs. 10a and 10b together with a mixing line between the gases that derives from the sub-lacustrine reservoirs and atmosphere. Because He/Ne and He/Ar ratios are high in sub-lacustrine  $\text{CO}_2$  gas and low in atmosphere, the mixing lines are horizontal until atmospheric gas becomes dominant in the mixture. Both  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  data are plotted on the horizontal lines for both lakes, confirming the two component mixing. The isotopic compositions of gases from the sub-lacustrine reservoirs are  $^3\text{He}/^4\text{He} = 8 \times 10^{-6}$ ,  $^{21}\text{Ne}/^{22}\text{Ne} \sim 0.0305$ , and  $^{40}\text{Ar}/^{36}\text{Ar} \sim 550$  for Lake Nyos, and  $^3\text{He}/^4\text{He} = 5 \times 10^{-6}$ ,  $^{21}\text{Ne}/^{22}\text{Ne} \sim 0.03$ , and  $^{40}\text{Ar}/^{36}\text{Ar} \sim 500$  for Lake Monoun. The above estimated  $^{21}\text{Ne}/^{22}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios must be minimum, because atmospheric Ne and Ar dissolved in groundwater possibly contribute to the reservoirs, and groundwater is likely added to the fluid during ascent to the bottom of the lakes.

#### Relationship between $^3\text{He}$ , $^{21}\text{Ne}_{\text{excess}}$ and $^{40}\text{Ar}_{\text{excess}}$ in deep water

Figure 11a shows a positive linear correlation between  $^3\text{He}$  and  $^{21}\text{Ne}_{\text{excess}}$  at Lake Nyos. The  $^3\text{He}/^{21}\text{Ne}_{\text{excess}}$  ratio (slope of the regression line) was about 100, although the  $^3\text{He}/^{21}\text{Ne}_{\text{excess}}$  ratios of  $78 \pm 7$  in the bottom layer (190–208 m) were slightly lower than  $109 \pm 15$  in upper layer (165–188 m) (Fig. 11a' and Table 4). The low value corresponds to the low concentration of  $^3\text{He}$  in the bottom layer as indicated in Fig. 8. In contrast to the  $^3\text{He}$  vs.  $^{21}\text{Ne}_{\text{excess}}$  plot, the concentrations of  $^3\text{He}$  and  $^{40}\text{Ar}_{\text{excess}}$  in Lake Nyos plotted in Fig. 11b do not show such a simple

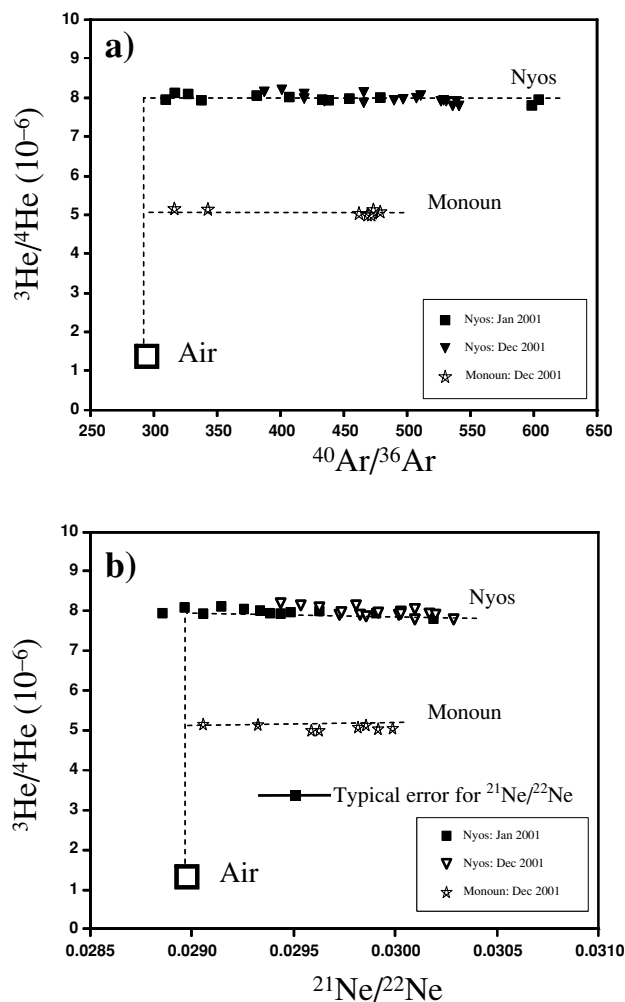


Fig. 10. (a)  $^3\text{He}/^4\text{He}$  versus  $^{40}\text{Ar}/^{36}\text{Ar}$ , and (b)  $^3\text{He}/^4\text{He}$  versus  $^{21}\text{Ne}/^{22}\text{Ne}$  for Lakes Nyos and Monoun. The dashed lines represent mixing lines between atmosphere and magmatic sources for Lakes Nyos and Monoun.

correlation. In January 2001, both  $^3\text{He}$  and  $^{40}\text{Ar}_{\text{excess}}$  concentrations in deep water (190–210 m) are nearly constant, i.e.,  $^3\text{He} \sim 5 \times 10^{-10}$  and  $^{40}\text{Ar}_{\text{excess}} \sim 80 \times 10^{-6}$  ccSTP/g-water. At 180 m  $^3\text{He}$  concentration increased to  $\sim 7 \times 10^{-10}$  ccSTP/g-water, while  $^{40}\text{Ar}_{\text{excess}}$  remained unchanged. In shallower depth both  $^3\text{He}$  and  $^{40}\text{Ar}_{\text{excess}}$  concentrations decreased with a constant  $^3\text{He}/^{40}\text{Ar}_{\text{excess}}$  ratio of  $\sim 9 \times 10^{-6}$ , though only two data were available (Fig. 11b' and Table 4). A similar trend was also seen for the samples collected in December 2001, i.e.,  $^3\text{He} \sim 5 \times 10^{-10}$  and  $^{40}\text{Ar}_{\text{excess}} \sim 50 \times 10^{-6}$  ccSTP/g-water below 190 m. At 188–185 m  $^3\text{He}$  concentration increased to  $\sim 10 \times 10^{-10}$  ccSTP/g-water (also shown in Fig. 8b), and decreased in shallower depth keeping roughly a constant  $^3\text{He}/^{40}\text{Ar}_{\text{excess}}$  ratio of  $\sim 17 \times 10^{-6}$  (Fig. 11b'). The concentrations of  $^{40}\text{Ar}_{\text{excess}}$  in deep water were about half of those

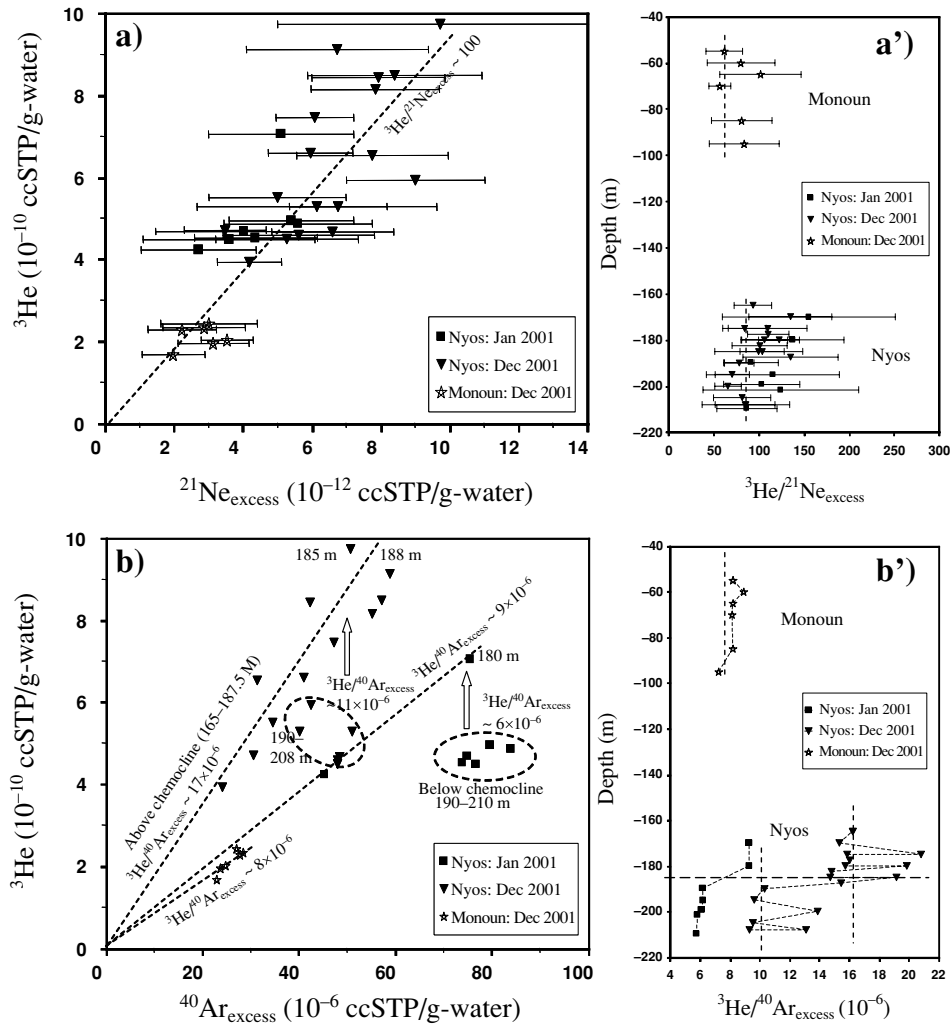


Fig. 11. (a) Plots of  $^3\text{He}$  concentration versus excess  $^{21}\text{Ne}$  concentration, and (b)  $^3\text{He}$  concentration versus excess  $^{40}\text{Ar}$  concentration of deep waters of Lakes Nyoos and Monoun. Samples were collected in January and December 2001 from depths deeper than 160 m at Lake Nyoos and deeper than 55 m at Lake Monoun.  $^3\text{He}/^{21}\text{Ne}_{\text{excess}}$  and  $^3\text{He}/^{40}\text{Ar}_{\text{excess}}$  ratios are also plotted against water depth in (a') and (b').

in January 2001. This indicates that  $^{40}\text{Ar}_{\text{excess}}$  supply from the sub-lacustrine reservoir to deep water decreased during the 10 months.

$^3\text{He}/^{40}\text{Ar}_{\text{excess}}$  for Lake Monoun is  $\sim 8 \times 10^{-6}$ , slightly lower than that in the Nyoos water, though it is still higher than that for bottom water of Lake Nyoos in January 2001. This is consistent with relatively low  $^3\text{He}/^4\text{He}$  of  $5 \times 10^{-6}$  of deep water at Monoun, suggesting greater contribution of radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$  in Lake Monoun than in Lake Nyoos.

#### Recharge of gases from magmatic source to Lake Nyoos

Characteristic features of noble gases observed at Lake Nyoos are summarized as follows: 1) Helium with  $^3\text{He}/^4\text{He}$  ratio of  $8 \times 10^{-6}$  observed in the lake water is not

supplied directly from mantle, because the  $^3\text{He}/^4\text{He}$  ratios of upper mantle beneath the area have been found to be  $(9.3\text{--}9.8) \times 10^{-6}$  in clinopyroxene and amphibole separated from mantle xenoliths collected at Lake Nyoos, and  $10 \times 10^{-6}$  in olivine from basalt collected at Lake Monoun (Aka *et al.*, 2004b). Approximately 20% of radiogenic  $^4\text{He}$  that accumulated in crustal rocks must have been admixed to the mantle-derived He, probably in sub-lacustrine region beneath the lake. 2)  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are in the range of 450–550 (Figs. 6 and 7), which cannot be produced by addition of radiogenic  $^{40}\text{Ar}$  to the mantle-derived Ar if  $^{40}\text{Ar}/^{36}\text{Ar}$  in the mantle is as high as 1650 (Barfod *et al.*, 1999). Both radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$  are produced from U, Th and  $^{40}\text{K}$  in local granitic rocks. Most likely source of Ar to reduce the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio is atmos-

pheric Ar ( $^{40}\text{Ar}/^{36}\text{Ar} = 296$ ) carried to the source region by groundwater. 3) Ne may be a mixture of atmospheric Ne and a small amount of MORB-like Ne from the mantle, because MORB-like Ne with maximum  $^{20}\text{Ne}/^{22}\text{Ne} = 11.87$  and  $^{21}\text{Ne}/^{22}\text{Ne} = 0.0508$  has been reported for the CVL mantle (Barfod *et al.*, 1999). 4) Non-uniform distribution of  $^3\text{He}$  (Fig. 8b), and  $^{40}\text{Ar}/^{36}\text{Ar}$  (Figs. 6 and 7) and  $^3\text{He}/^{40}\text{Ar}_{\text{excess}}$  (Fig. 11b) were observed in lake water, e.g., sharp increase in  $^3\text{He}$  concentration at 185~190 m may reflect higher recharge rate of magmatic He than in deeper water.

Relationships between the observed He, Ne and Ar isotopic ratios at the lake waters can be best explained by mixing between two noble gas reservoirs, i.e., air dissolved ground water and the sub-lacustrine reservoir (Fig. 10), where the mantle-derived gases meet radiogenic  $^4\text{He}$  from crustal rocks and atmospheric gases in ground water. The admixed gases must be homogenized in the sub-lacustrine reservoir.

Apart from the general features noted above, samples collected at the bottom (210 m) of Lake Nyos in January 2001 showed exceptional isotopic ratios; highest  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of 600 (Fig. 6) and anomalous Ne isotopic ratios (Fig. 5). A contribution of Loihi-type Ne to the samples is unacceptable to explain the observed isotopic ratios, because coexistence of MORB-type and Loihi-type mantle in a small area like Nyos–Monoun beneath CVL is unlikely. Another significant feature is  $^3\text{He}/^4\text{He}$  ratios in the deep layer. It is recalled that  $^3\text{He}/^4\text{He}$  ratios show a maximum at ~180 m at Lake Nyos (Fig. 4). These isotopic features observed in the bottom water can be explained by greater input of radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$  to the bottom water along with mass fractionated Ne.

The model illustrated in Fig. 12 may explain the above isotopic features in the Lake Nyos water. The volcanic vent immediately beneath the lake bottom, or diatreme, is filled by fractured rocks and covered by sediments. There may be a sub-lacustrine reservoir of fluid beneath the lake, to which noble gases and  $\text{CO}_2$  of upper mantle origin are supplied from magma. Isotopic signatures of the CVL mantle characterize such gases. Mixing of noble gases enriched in  $^4\text{He}$  and  $^{40}\text{Ar}$  from surrounding crustal rocks reduces the  $^3\text{He}/^4\text{He}$  ratios of mantle He from  $10 \times 10^{-6}$  to  $8 \times 10^{-6}$  at Lake Nyos. About 20% of total  $^4\text{He}$  is estimated to be of crustal origin. Similarly, if crustal Ar, therefore, radiogenic Ar is mixed, the resulting  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio would have increased from the mantle value ( $>1650$ ; Barfod *et al.*, 1999). However, the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios observed in the deep water were *ca.* 500, much lower than the mantle value. Thus, atmospheric Ar dissolved in ground water is an only candidate to reduce the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio without affecting the He isotopic ratio. This is due to a large difference between the concentrations of  $^4\text{He}$  and  $^{40}\text{Ar}$  in air saturated ground water ( $^4\text{He}/^{40}\text{Ar} = 1.7 \times$

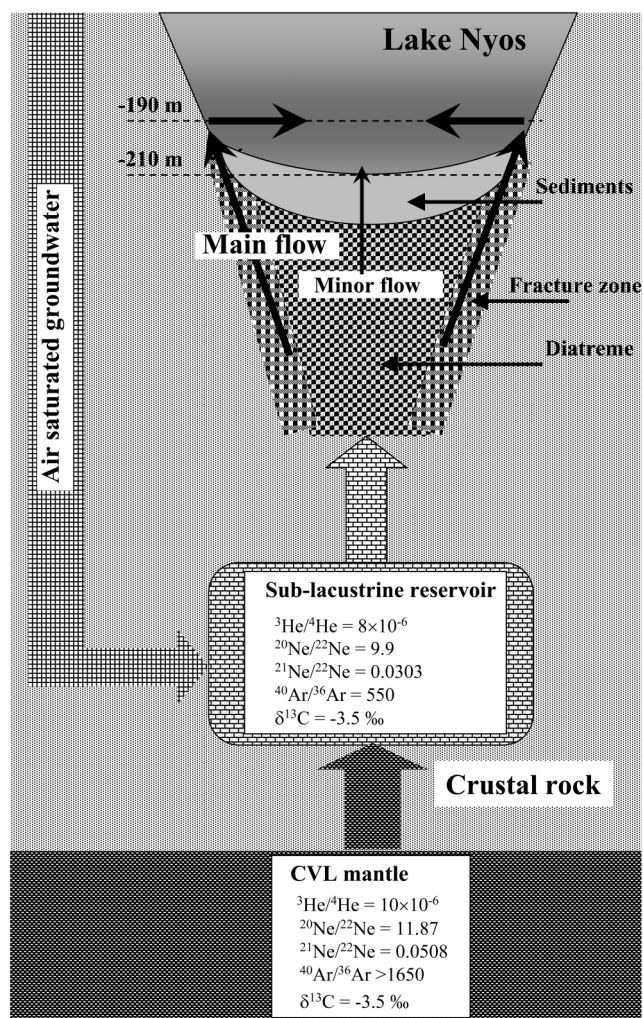


Fig. 12. A model of gas recharge for Lake Nyos. In the sub-lacustrine reservoir, gases from upper mantle are accumulated and mixed with radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$  from the crust and atmospheric noble gases dissolved in groundwater. Two recharge passes for the fluids from the reservoir to lake water may produce the layered structure in the water; most of fluids are supplied into the lake at depth of ~190 m. A smaller flux of the fluids may be supplied the lake bottom. The fluids gain radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$  and may also be subjected to mass fractionation as observed in Ne isotopic ratios.

$10^{-4}$  at  $30^\circ\text{C}$  in Table 2; Kipfer *et al.*, 2002) and those in the mantle gases with high  $^4\text{He}/^{40}\text{Ar}$  ratio of ~1.

The observed depth profiles of  $^3\text{He}/^4\text{He}$ ,  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^4\text{He}/^{20}\text{Ne}$  ratios and He concentration in deep water, which showed a maximum at around the lower chemocline (~190 m in depth), strongly suggest that fluids from the sub-lacustrine reservoir are supplied not from bottom but mainly from side wall of the lake at that depth. Figure 12 schematically illustrates the idea mentioned above. Since the sediments in the central part of the lake bottom would

consist of finer particles and be thicker than the sediments in the periphery, it would be easier for the fluids to find their way to the lake through the periphery. The peripheral sediments would be coarser than those in the central part of the lake, thus allowing easier input of the fluids from the periphery.

It has been suggested that high temperature fluids enriched in CO<sub>2</sub> containing mantle-derived He ascend along the wall of diatreme of Nigorikawa caldera, southwest Hokkaido, Japan (Nagao *et al.*, 1979; Yoshida, 1991). It is noted that the geological structure of the Nigorikawa basin is very similar to that of Lake Nyos with respect to the volcanic vent in that it is filled with fractured basaltic and granitic rocks. The Nigorikawa caldera may be said to be a fossil of Lake Nyos.

Another possible pathway of the fluids from the reservoir may be through the lake bottom. During ascent of the fluid it may acquire radiogenic <sup>4</sup>He and <sup>40</sup>Ar from surrounding crustal rocks. Then, it is finally supplied to the bottom of the lake. The highest <sup>40</sup>Ar/<sup>36</sup>Ar of 600 (Fig. 6) can be attributed to the addition of radiogenic <sup>40</sup>Ar of crustal origin. Isotopic mass fractionation of Ne that favors enrichment of lighter isotopes may take place during the ascent, resulting in the enhanced Ne isotopic ratios as observed for samples NY01Jan-210 (Fig. 5 and Table 1). In this case, only 2% enrichment in <sup>20</sup>Ne/<sup>22</sup>Ne and 1% enrichment in <sup>21</sup>Ne/<sup>22</sup>Ne ratios relative to Ne in the sub-lacustrine reservoir (which contains MORB-like Ne with <sup>20</sup>Ne/<sup>22</sup>Ne ~ 9.85 and <sup>21</sup>Ne/<sup>22</sup>Ne ~ 0.0295) may produce the observed Ne isotopic ratios (Fig. 5).

Similar recharge model seems to be applicable to Lake Monoun. Distribution of noble gases as well as CO<sub>2</sub> in both lake waters is very similar, although some differences such as <sup>3</sup>He/<sup>4</sup>He ratios and δ<sup>13</sup>C values are present (Tables 1 and 2) (<sup>3</sup>He/<sup>4</sup>He ratios are 8 × 10<sup>-6</sup> and 5 × 10<sup>-6</sup> (Table 1) and δ<sup>13</sup>C values are -3.4‰ and -6.8‰ for Lakes Nyos and Monoun, respectively.) The lower values of <sup>3</sup>He/<sup>4</sup>He and δ<sup>13</sup>C for Lake Monoun can be explained by a contribution of radiogenic <sup>4</sup>He and organic carbon enriched in crustal materials to the source reservoir of the lake. Slight increase in <sup>3</sup>He/<sup>4</sup>He ratio from bottom to shallower water in Lake Monoun suggests similar recharge pass ways for noble gases from the reservoir.

## SUMMARY

Noble gas isotopic compositions in water from different depths of Lakes Nyos and Monoun were investigated for samples collected in November 1999, January 2001 and December 2001.

1. Direct sampling of lake water by using a hose that was deployed to a desired depth was found to be the most suitable method to collect noble gas samples that are free

of atmospheric contamination.

2. Concentrations of Ne, Ar, Kr and Xe in the lake waters were very low, by factors of ~10 for Ne and ~3 for Xe compared with air saturated water (ASW). Moreover, their concentrations in CO<sub>2</sub> gas were 2 orders of magnitude lower than those in atmosphere. Only He was heavily enriched by more than three orders of magnitude compared with ASW.

3. The <sup>3</sup>He/<sup>4</sup>He ratios in the lakes were reduced by the addition of radiogenic <sup>4</sup>He from crustal rocks, because magmatic <sup>3</sup>He/<sup>4</sup>He ratio is about 10 × 10<sup>-6</sup> as reported for mantle-derived minerals collected around the lakes.

4. Ne with a MORB-like isotopic signature was detected in both lake waters, though the isotopic shift from air-Ne was as small as <2%. This means that part of Ne in the lake was derived from the CVL upper mantle, for which presence of MORB-like Ne has been indicated.

5. Noble gases in each lake are a simple two-component mixture; atmosphere and deep-seated reservoir beneath the lakes.

6. Anomalous isotopic ratios of Ne (plotted along Loihi line in Fig. 5) and Ar (highest <sup>40</sup>Ar/<sup>36</sup>Ar = 600) were observed at the bottom of Lake Nyos in January 2001, just before initiation of degassing operation. The anomalies disappeared 10 months later (in December 2001). <sup>40</sup>Ar/<sup>36</sup>Ar ratios were vertically homogenized between the depths of 210 (bottom) to 180 m.

7. Depth profile of <sup>3</sup>He concentration in Lake Nyos shows a maximum at the depth of ~190 m. In the deeper layer, <sup>3</sup>He concentration and <sup>3</sup>He/<sup>4</sup>He ratio decrease. C/<sup>3</sup>He ratios were 0.6 × 10<sup>10</sup> and 1.5 × 10<sup>10</sup> in upper and lower layers, respectively.

8. A gas recharge model to explain the observed layered structure of noble gases in Lake Nyos was presented. A sub-lacustrine fluid reservoir was assumed to exist beneath the lake, where gases from mantle with CVL noble gas signatures, radiogenic <sup>4</sup>He and <sup>40</sup>Ar from crustal rocks, and air saturated groundwater are homogenized. Main flow of gas and water from the reservoir is supplied to the lake either at a depth of about 190 m through the lake wall. In addition to the major flow(s), a minor flow to bottom water (210 m depth), which acquired radiogenic <sup>40</sup>Ar from the crustal rocks and mass fractionated Ne, would explain the anomalous Ne and Ar isotopic ratios observed in January 2001.

**Acknowledgments**—The authors thank J. V. Hell, director of the Institute for Geological and Mining Research (IRGM, Cameroon) and the IRGM staff for their technical and logistic support in this research. We are indebted to W. C. Evans and G. W. Kling who provided us with the SS-cylinder samples. T. Ohba is acknowledged for their help in the field work. The field surveys were made while M.K. was working for the Institute for Study of the Earth's Interior, Okayama University at Misasa, and supported by the fund to M.K. from the Grant-in-Aid for

Scientific Research from Japan Society for the Promotion of Science (No. 13573013, 2001–2002). We also thank the Japanese and U.S. Embassies in Cameroon. The manuscript has been improved by constructive suggestions from two anonymous reviewers.

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#### APPENDIX

Noble gas data for the samples collected by the Al-bag and the SS-cylinder methods are presented in Appendixes 1 and 2. Noble gases of these samples might have been affected by contamination from atmospheric noble gases (see text), and the data are not used in most discussion.

Appendix 1. Isotopic ratios of He, Ne and Ar in waters and gases collected from Lakes Nyos and Monoun, Cameroon

Sample name	Depth (m)	$^4\text{He}/^{20}\text{Ne}$	$^3\text{He}/^4\text{He}$ ( $10^{-6}$ )	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$	$^{38}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}/^{36}\text{Ar}$
<b>Lake Nyos</b>							
November 1999 (Al-bag method)							
NY99-200	-200	132	8.00 ± 0.06	9.748 ± 0.017	0.02867 ± 0.00026	0.1885 ± 0.0005	336.83 ± 0.33
NY99-190	-190	318	8.07 ± 0.07	9.763 ± 0.024	0.02885 ± 0.00029	0.1883 ± 0.0006	358.75 ± 0.38
NY99-175	-175	167	8.11 ± 0.06	9.811 ± 0.017	0.02889 ± 0.00010	0.1882 ± 0.0005	339.02 ± 0.44
NY99-150	-150	86.5	8.10 ± 0.07	9.810 ± 0.017	0.02891 ± 0.00008	0.1879 ± 0.0005	316.51 ± 0.27
NY99-130	-130	36.0	8.03 ± 0.07	9.830 ± 0.016	0.02894 ± 0.00007	0.1881 ± 0.0005	305.84 ± 0.35
NY99-100	-100	20.5	7.99 ± 0.06	9.813 ± 0.017	0.02896 ± 0.00011	0.1881 ± 0.0004	303.70 ± 0.33
NY99-70	-70	3.40	7.57 ± 0.07	9.807 ± 0.016	0.02901 ± 0.00007	0.1878 ± 0.0005	296.27 ± 0.45
NY99-35*	-35	0.906	6.37 ± 0.12	9.728 ± 0.017	0.02883 ± 0.00011	0.1886 ± 0.0003	297.73 ± 0.30
NY99-0*	0	0.427	1.76 ± 0.27	9.756 ± 0.017	0.02891 ± 0.00011	0.1886 ± 0.0004	297.93 ± 0.17
USA, November 1999 (Stainless steel cylinder method)							
NY99US-206	-205.7	461	7.60 ± 0.09	9.763 ± 0.024	0.02911 ± 0.00038	0.1885 ± 0.0004	534.74 ± 0.69
NY99US-191	-190.5	419	7.60 ± 0.06	9.799 ± 0.024	0.02929 ± 0.00037	0.1885 ± 0.0006	499.17 ± 0.59
NY99US-183	-182.9	757	7.70 ± 0.06	9.807 ± 0.019	0.02887 ± 0.00032	0.1880 ± 0.0005	496.90 ± 0.71
NY99US-53	-53.3	24.3	7.08 ± 0.07	9.845 ± 0.021	0.02865 ± 0.00013	0.1880 ± 0.0008	303.34 ± 0.36
<b>Lake Monoun</b>							
November 1999 (Al-bag method)							
MN99-95	-95	51.1	5.03 ± 0.04	9.807 ± 0.017	0.02898 ± 0.00010	0.1878 ± 0.0004	319.74 ± 0.25
MN99-85	-85	436	5.19 ± 0.04	9.816 ± 0.018	0.02912 ± 0.00025	0.1879 ± 0.0004	371.81 ± 0.41
MN99-75	-75	304	5.18 ± 0.04	9.812 ± 0.018	0.02895 ± 0.00015	0.1879 ± 0.0006	355.66 ± 0.54
MN99-65	-65	297	5.28 ± 0.06	9.822 ± 0.017	0.02894 ± 0.00015	0.1877 ± 0.0005	358.40 ± 0.52
MN99-55	-55	193	5.20 ± 0.05	9.818 ± 0.017	0.02889 ± 0.00014	0.1877 ± 0.0004	333.82 ± 0.46
MN99-45	-45	191	4.74 ± 0.04	9.719 ± 0.016	0.02896 ± 0.00013	0.1886 ± 0.0005	335.70 ± 0.49
MN99-25	-25	29.9	4.81 ± 0.05	9.646 ± 0.016	0.02879 ± 0.00007	0.1885 ± 0.0004	304.11 ± 0.41
USA, November 1999 (Stainless steel cylinder method)							
MN99US-95	-95.4	486	4.82 ± 0.04	9.787 ± 0.031	0.02876 ± 0.00026	0.1881 ± 0.0006	446.85 ± 0.70
MN99US-79	-78.5	412	4.92 ± 0.04	9.857 ± 0.022	0.02890 ± 0.00015	0.1877 ± 0.0007	448.06 ± 0.70
MN99US-61	-61.0	375	4.92 ± 0.04	9.866 ± 0.025	0.02868 ± 0.00019	0.1877 ± 0.0004	419.34 ± 0.72
MN99US-46	-45.7	179	4.88 ± 0.05	9.856 ± 0.023	0.02870 ± 0.00015	0.1879 ± 0.0004	332.74 ± 0.46
MN99US-23	-22.9	6.58	4.28 ± 0.04	9.760 ± 0.021	0.02857 ± 0.00013	0.1884 ± 0.0004	298.87 ± 0.41
Air (Ozima and Podosek, 2002)		0.32	1.40	9.80	0.0290	0.1880	296.0

\*Water samples.

Appendix 2. Concentrations of noble gases in CO<sub>2</sub> gas and in water, and elemental abundance ratios normalized to <sup>36</sup>Ar for the samples from Lakes Nyos and Monoun

Sample name	<sup>4</sup> He	<sup>20</sup> Ne	<sup>36</sup> Ar	<sup>40</sup> Ar	<sup>84</sup> Kr	<sup>132</sup> Xe	<sup>4</sup> He/ <sup>36</sup> Ar	<sup>20</sup> Ne/ <sup>36</sup> Ar	<sup>84</sup> Kr/ <sup>36</sup> Ar	<sup>132</sup> Xe/ <sup>36</sup> Ar	<sup>4</sup> He/ <sup>40</sup> Ar
Concentration in CO <sub>2</sub> gas (ppm)											
<b>Lake Nyos</b>											
November 1999 (Al-bag method)											
NY99-200	11.9	0.0902	0.245	82.8	0.00720	0.000415	48.6	0.368	0.0294	0.0017	0.144
NY99-190	10.9	0.0343	0.129	46.3	0.00483	0.000344	84.5	0.266	0.0374	0.0027	0.235
NY99-175	29.8	0.178	0.310	105	0.00841	0.000457	96.1	0.574	0.0271	0.0015	0.284
NY99-150	14.1	0.163	0.289	91.3	0.00739	0.000383	48.8	0.564	0.0256	0.0013	0.154
NY99-130	10.2	0.283	0.452	138	0.0111	0.000571	22.6	0.626	0.0246	0.0013	0.074
NY99-100	7.02	0.342	0.647	197	0.0168	0.000887	10.9	0.529	0.0260	0.0014	0.036
NY99-70	9.09	2.67	3.64	1080	0.0808	0.00364	2.50	0.734	0.0222	0.0010	0.0084
<b>USA, November 1999 (Stainless steel cylinder method)</b>											
NY99US-206	11.3	0.0245	0.0561	30.0	0.00213	0.000208	201	0.437	0.0380	0.0037	0.377
NY99US-191	11.1	0.0265	0.0514	25.6	0.00183	0.000118	216	0.516	0.0356	0.0023	0.434
NY99US-183	31.5	0.0416	0.116	57.9	0.00455	0.000377	272	0.359	0.0392	0.0033	0.544
NY99US-53	5.41	0.223	0.743	225	0.0266	0.00195	7.28	0.300	0.0358	0.0026	0.024
<b>Lake Monoun</b>											
November 1999 (Al-bag method)											
MN99-95	8.07	0.158	0.290	92.8	0.00849	0.000472	27.8	0.545	0.0293	0.0016	0.087
MN99-85	13.2	0.0303	0.108	40.3	0.00449	0.000326	122.2	0.281	0.0416	0.0030	0.328
MN99-75	17.6	0.0578	0.182	64.7	0.00678	0.000487	96.7	0.318	0.0373	0.0027	0.272
MN99-65	10.7	0.0360	0.133	47.5	0.00537	0.000406	80.5	0.271	0.0404	0.0031	0.225
MN99-55	19.3	0.100	0.247	82.4	0.00831	0.000554	78.1	0.405	0.0336	0.0022	0.234
MN99-45	29.6	0.155	0.688	231	0.0247	0.00150	43.0	0.225	0.0359	0.0022	0.128
MN99-25	18.7	0.625	2.56	779	0.0881	0.00513	7.3	0.244	0.0344	0.0020	0.024
<b>USA, November 1999 (Stainless steel cylinder method)</b>											
MN99US-95	10.6	0.0218	0.0839	37.5	0.00363	0.000282	126	0.260	0.0433	0.0034	0.283
MN99US-79	11.9	0.0289	0.0844	37.7	0.00373	0.000381	141	0.342	0.0442	0.0045	0.316
MN99US-61	11.0	0.0293	0.0749	31.4	0.00337	0.00030	147	0.391	0.0450	0.0040	0.350
MN99US-46	17.0	0.0952	0.274	90.7	0.0113	0.000848	62	0.347	0.0412	0.0031	0.187
MN99US-23	24.6	3.74	16.8	5040	0.657	0.0475	1.5	0.223	0.0391	0.0028	0.005
Air (Ozima and Podosek, 2002)	5.24	16.5	31.5	9303	0.649	0.0234	0.166	0.524	0.0206	0.00074	0.00056
Air saturated water (30°C water, Kipfer <i>et al.</i> , 2002)							0.050	0.178	0.0359	0.00230	0.00017



Sample name	<sup>4</sup> He	<sup>20</sup> Ne	<sup>36</sup> Ar	<sup>40</sup> Ar	<sup>84</sup> Kr	<sup>132</sup> Xe	CO <sub>2</sub> (water)	$\delta^{13}\text{C}_{\text{PDB}}$ ‰
	Concentration in water (10 <sup>-6</sup> ccSTP/g water)						ccSTP/g water	
Lake Nyos								
November 1999 (Al-bag method)								
NY99-200	93.4	0.708	1.92	650	0.0565	0.003258	7.85	
NY99-190	81.6	0.257	0.97	347	0.0362	0.002577	7.49	
NY99-175	98.6	0.589	1.03	348	0.0278	0.001513	3.31	
NY99-150	42.7	0.494	0.88	277	0.0224	0.001160	3.03	
NY99-130	29.2	0.809	1.29	395	0.0317	0.001633	2.86	
NY99-100	14.4	0.701	1.33	404	0.0344	0.001818	2.05	
NY99-70	13.6	4.005	5.46	1620	0.1212	0.005460	1.50	
USA, November 1999 (Stainless steel cylinder method)								
NY99US-206	90.2	0.196	0.45	239	0.0170	0.001660	7.98	
NY99US-191	83.5	0.199	0.39	193	0.0138	0.000887	7.52	
NY99US-183	166.0	0.219	0.61	305	0.0240	0.001987	5.27	
NY99US-53	6.7	0.277	0.92	279	0.0330	0.002418	1.24	
Lake Monoun								
November 1999 (Al-bag method)								
MN99-95	28.8	0.564	1.035	331.3	0.03031	0.001685	3.57	-7.50
MN99-85	47.0	0.108	0.384	143.5	0.01598	0.001161	3.56	-7.05
MN99-75	62.5	0.205	0.646	229.7	0.02407	0.001729	3.55	-6.83
MN99-65	38.0	0.128	0.472	168.6	0.01906	0.001441	3.55	-6.99
MN99-55	63.7	0.330	0.815	271.9	0.02742	0.001828	3.30	-7.29
MN99-45	38.2	0.200	0.888	298.0	0.03186	0.001935	1.29	-8.28
MN99-25	5.1	0.171	0.701	213.4	0.02414	0.001406	0.27	
USA, November 1999 (Stainless steel cylinder method)								
MN99US-95	37.8	0.078	0.300	133.9	0.01296	0.001007	3.57	
MN99US-79	42.4	0.103	0.300	134.2	0.01328	0.001356	3.56	
MN99US-61	39.1	0.104	0.266	111.5	0.01196	0.001054	3.55	
MN99US-46	22.4	0.126	0.362	119.7	0.01492	0.001119	1.32	
MN99US-23	0.8	0.115	0.517	155.2	0.02024	0.001463	0.031	
Air (Ozima and Podosek, 2002)								
Air saturated water (30°C water, Kipfer <i>et al.</i> , 2002)	0.044	0.156	0.874	259	0.0314	0.00201		