

# LIMNOLOGY and OCEANOGRAPHY: METHODS

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## An improved method for the analysis of dissolved noble gases in the porewater of unconsolidated sediments

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### Abstract

We developed a new and improved method for the extraction of dissolved noble gases from the porewater of unconsolidated lacustrine sediments. The new method relies on the separation of the porewater from the sediment matrix by centrifugation of the bulk sediment within the closed copper tubes being used as sampling containers. After centrifugation, the porewater liberated from sediment matrix is completely separated from the dewatered sediment by applying and closing a metal clamp between the two phases. After separation, the noble-gas abundances are determined only in the porewater phase by applying the standard protocols used for noble-gas analysis in water samples, which allows simpler, faster and more reliable measurements. The new method overcomes known experimental difficulties encountered by our former method, such as the release of He from sediment grains, and incomplete extrusion of the bulk sediment from the copper tube used as a sample container. It follows that the determination of the He concentrations and isotope ratios in the sediment porewater is less affected by He locally produced in sediment minerals. The new method is less operator-sensitive and the noble-gas extraction efficiency (especially for heavy noble-gas species) has, in general, improved. As only bulk porewater is used for analysis, the new method can easily be adopted by other noble-gas laboratories. Also, the new method can be used to determine the abundance of other dissolved gases such CH<sub>4</sub>, N<sub>2</sub>, or CO<sub>2</sub>.

In recent years, the analysis of noble gases in meteoric waters has become a powerful tool for studying mixing dynamics in lakes, oceans, and groundwaters, and for reconstructing past climate conditions (Kipfer et al. 2002; Schlosser and Winckler 2002). Noble-gas concentrations in sediment porewater have been shown to reflect past noble-gas concentrations in the overlying water body (Brennwald et al. 2003, 2004), and can provide information on transport and gas-exchange processes within the sediment (Brennwald et al. 2005; Strassmann et al. 2005; Holzner et al. 2008).

Until now, the method developed by Brennwald et al. (2003) was the only method available for the quantitative analysis of the concentrations of noble gases dissolved in the porewater of lacustrine sediments. This method was successfully used to study the noble-gas abundance in the sediments in various lakes (Brennwald et al. 2003, 2004, 2005; Strassmann et al. 2005), and in the Black Sea (Holzner et al. 2008). Gas extraction is achieved by connecting the bulk sediment sample container to an evacuated extraction vessel. The sample container is then rapidly heated to 150°C, which results in a pressure increase in the sample container. The bulk sediment is then extruded explosively into the extraction vessel (“blow-out”), and the sediment grains are dispersed over the interior surface of the extraction vessel. The porewater is liberated from the sediment matrix and is degassed in the extraction vessel. Chaduteau et al. (2007) recently proposed an extraction method based on flushing the sediment samples with degassed water. However this method was only applied to determine the concentrations of He isotopes, requires a dedicated extraction apparatus, and is time-consuming.

Although the analytical protocol of Brennwald et al. (2003) allows noble-gas concentrations to be determined reliably, it

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also has several shortcomings. Heating the sediment may cause the gas sample to be contaminated with radiogenic  $^4\text{He}$  released from the sediment grains, and may also induce chemical reactions that produce large amounts of gases such as  $\text{CH}_4$  that interfere with the analysis of noble gases in the porewater sample (see Brennwald et al. 2003). Furthermore, in the specific case of Lake Van (Turkey), quantitative extraction of some sediment samples could not be achieved because part of the bulk sediment remained in the sample container after blow-out, and quantitative degassing of the porewater in this sediment is therefore not possible. In addition, it emerged that the blow-out step needs to be performed by experienced specialists to minimize the number of incompletely degassed sediment samples. The experimental difficulties encountered with the Lake Van sediments are probably the result of the very fine texture of the laminated sediments of this lake.

To overcome the shortcomings of the blow-out method, we developed a new and improved method to extract the noble gases dissolved in sediment porewater, which is based on the centrifugation of the bulk sediment samples.

## Materials and procedures

### Concept overview

The sediment cores are collected using a gravity corer, as described in Brennwald et al. (2003). Bulk sediment samples are transferred into sample containers (copper tubes) in the field immediately after sediment coring by squeezing the sediment core with two pistons inserted into both ends of the plastic core liner. The copper tubes, which are attached to the side of the core liner by Swagelok fittings at the chosen sampling depths, are filled with bulk sediment and closed off airtight using two special metal clamps to avoid the contamination and degassing problems that might result if the sediment were to come in contact with air. For further details on sampling, refer to Brennwald et al. (2003).

In the laboratory, the separation of the porewater from the sediment matrix within the still closed sampling containers is achieved by centrifugation. The original sample is split into two aliquots. After centrifugation, one aliquot is opened to determine the position of the sediment–water interface. The second aliquot is split at the position of the sediment–water interface with a third clamp. Thereafter, the porewater and the compressed sediment phase are completely separated from each other. The pure porewater phase of the second aliquot is analyzed as a normal water sample following well-accepted protocols for the analysis of noble gases in water samples (Beyerle et al. 2000).

Here we describe and discuss only our new and improved method of extracting the dissolved gases from the sediment porewater.

### Centrifugation

To separate the porewater from the bulk sediment, the copper tube containing the bulk sediment sample is split into two aliquots of the same length (~20 cm each, Fig. 1A). Both aliquots are centrifuged at 2300 rpm, resulting in the release

of 1–3 g porewater from the sediment matrix (Fig. 1B). To avoid deformation of the copper tubes during centrifugation, they are held in place by a polypropylene support. The maximum length of copper tube that fits our currently used centrifuge (Heraeus UJ3S) is ~20 cm. Of this, 3 cm must remain empty, as this is needed for later connection to the vacuum extraction system. The sediment-filled copper tube between the two sealing clamps of each aliquot has a length of ~11 cm.

### Separation of porewater and sediment phases

The position of the sediment–water interface depends on the type of sediment (e.g., grain size, porosity) and therefore needs to be determined for each sample or each sediment core individually. To this end, the copper tube containing one sample aliquot is cut open at the end containing the released porewater. The tube is then cut successively shorter in a stepwise manner to determine the position of the sediment–water interface (Fig. 1C). The tube holding the other sample aliquot is then pinched off close to the expected sediment–water interface (Fig. 1D), but shifted about 5–10 mm toward the water phase to avoid the inclusion of residual sediment grains in the water sample.

### Noble-gas analysis

Noble gases dissolved in the porewater separated from the sediment matrix are then extracted and analyzed following our standard protocol for noble-gas analysis in water samples (Beyerle et al. 2000), which is based on static mass spectrometry. The only exception to this standard protocol is made necessary by the fact that the connection part of the copper tube (see Fig. 1) is too short to be joined to the UHV extraction line using the standard cutting-edge mechanism (Beyerle et al. 2000; Brennwald et al. 2003). We, therefore, use a rubber O-ring connector to establish a gas-tight connection between the copper tube and the extraction line.

To determine the water mass of the sample, the part of the copper tube that contained the analyzed porewater is vacuum dried. The water mass is then given by the difference of the mass of the tube plus sample before analysis and that of the dry tube after analysis.

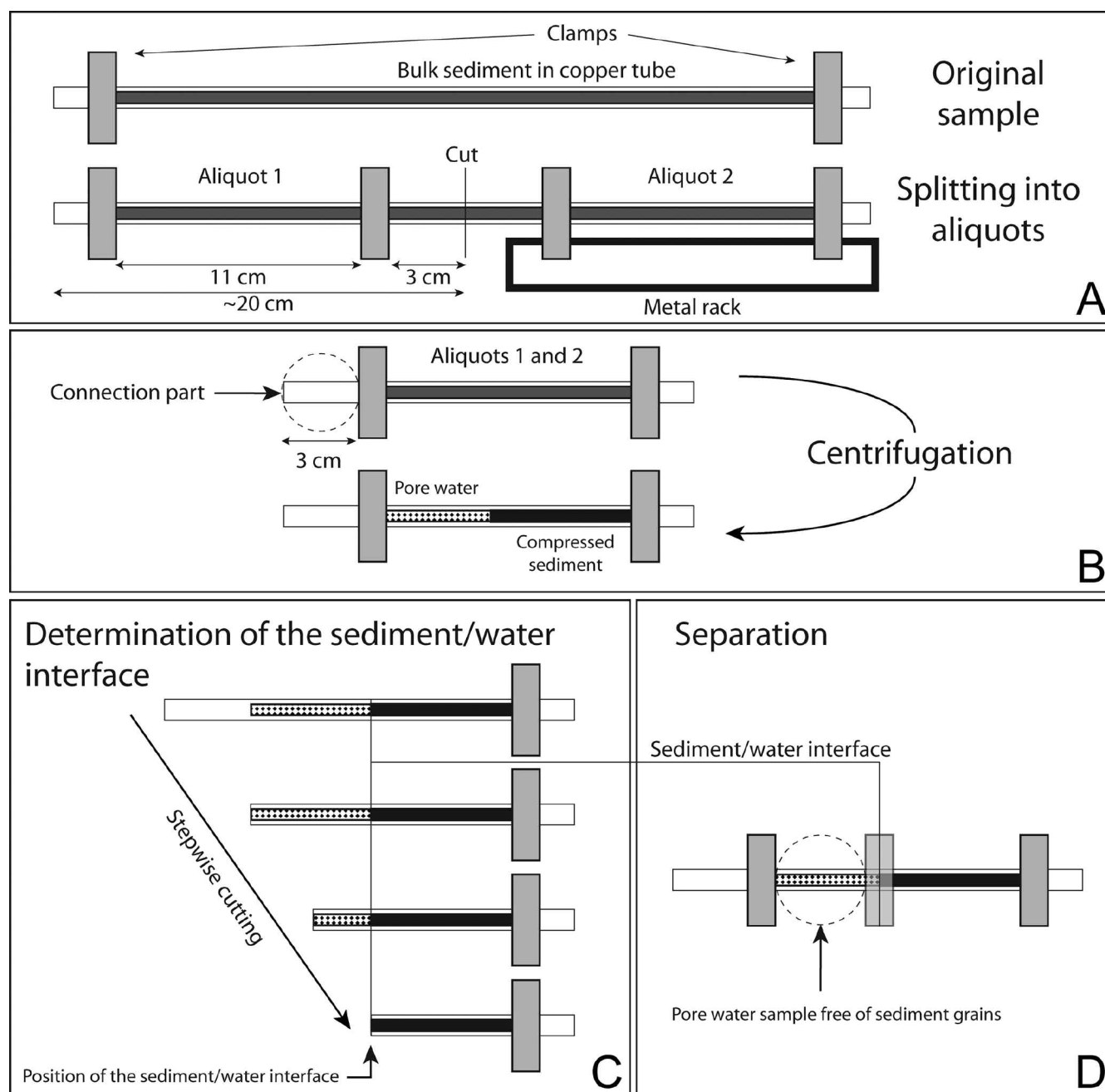
### Assessment

We assessed the performance of our new method to determine noble-gas concentrations from unconsolidated sediments in two stages:

- Overall performance and leak test using standard water samples.
- Comparison of the new centrifugation method with the previously used blow-out method as applied to lacustrine sediments.

### Performance and leak test

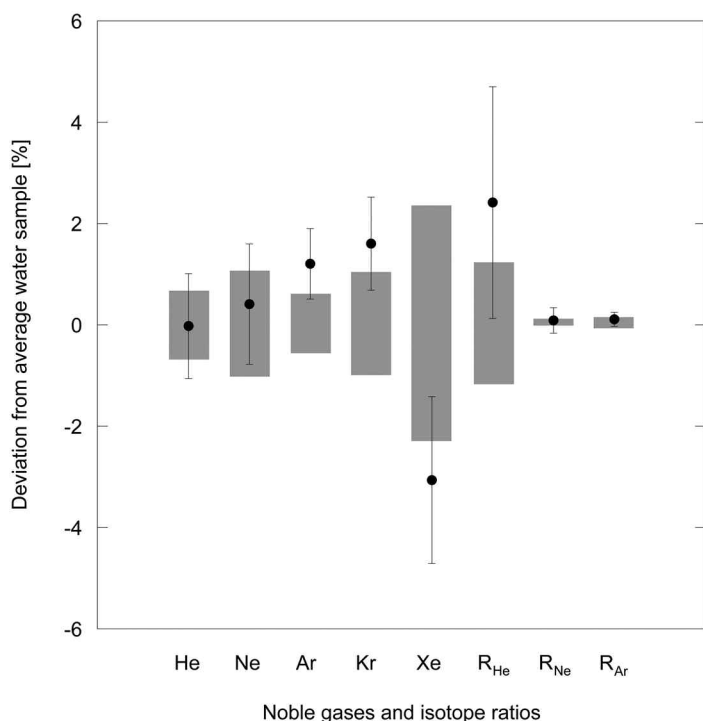
We evaluated the performance of the centrifugation method using water samples from Lake Lucerne (Switzerland), which are used as an internal laboratory standard for the routine analysis of water samples. The noble-gas concentrations in these water samples are therefore very well known and pro-



**Fig. 1.** Preparation of sediment samples for centrifugation. (A) A copper tube containing a bulk sediment sample is split into two aliquots of the same length with the help of a tailor-made metal rack, leaving a length of about 3 cm on at least one side of each aliquot that is later used to connect the sample to the extraction line. (B) The two aliquots are centrifuged to separate a pure porewater phase from the sediment phase. (C) One aliquot is used to determine the position of the sediment–water interface. (D) The other aliquot is pinched off at the sediment–water interface, yielding a porewater sample free of sediment grains.

vide a well-defined reference. We applied our new centrifugation protocol to three of these internal standard water samples. The concentrations and isotope ratios of the noble gases measured in these centrifuged water samples agree with the expected concentrations and isotope ratios within the analytical  $1\sigma$  error (Fig. 2; Table 1). The slight He excess relative to

the expected equilibrium concentration can be explained either by the accumulation of terrigenous He in the water body or by the presence of excess air related to wave formation at the surface of the lake. The results indicate that the copper tubes and sealing clamps remain airtight during the centrifugation process. Further, centrifugation does not result in a sig-



**Fig. 2.** Comparison of mean noble-gas concentrations and isotope ratios in three centrifuged standard water samples (black dots) with mean concentrations and isotope ratios in water standards analyzed in the same way as normal (noncentrifuged) water samples (gray-shaded areas).  $R_{He}$ ,  $R_{Ne}$ , and  $R_{Ar}$  are the isotope ratios  $^3He/^4He$ ,  $^{20}Ne/^{22}Ne$ , and  $^{40}Ar/^{36}Ar$ , respectively. The mean concentrations and isotope ratios of the normal water samples (i.e., samples Li-N in Table 1, where  $i = 1, 2, 3$ ) is set to zero on the y-axis, and their standard deviations are given by the gray areas. The data from the centrifuged samples (i.e., samples Li-C in Table 1, where  $i = 1, 2, 3$ ) are represented as relative deviations from the corresponding normal water sample data, and the black error bars indicate the standard deviation of the mean. The concentrations and isotope ratios measured in the centrifuged water samples agree with those of the standard samples within the analytical error.

nificant elemental or isotopic fractionation of noble gases in the water.

#### Comparison of new and old methods

A comparison of the overall experimental performance of the new method of determining noble-gas concentrations in unconsolidated sediments with the standard “blow-out” protocol of Brennwald et al. (2003) was carried out on samples from two sediment cores acquired from Lake Van in May 2005 (cores V1 and V2, see Fig. 3 and Table 1).

Lake Van is located at 1640 m above the sea level in a tectonically active zone in eastern Anatolia. The lake is about 450 m deep and accumulates terrigenous helium from a depleted mantle source (Kipfer et al. 1994). The sediments of Lake Van are homogeneous and fine-textured, and the first 10–15 m of the sediment column are annually laminated (Landmann et al. 1996; Wick et al. 2003; Reimer et al. 2008). The porosity in

the upper few meters is 60% to 70%. The sediment samples were taken from the sediment cores using the standard procedure described by Brennwald et al. (2003).

The two sediment cores for noble-gas sampling were taken from different locations within Lake Van (see Fig. 3). From each of the cores, two replicate samples for each sediment depth were taken for noble-gas analysis. One replicate was split into two sub-samples, which were analyzed using the blow-out method of Brennwald et al. (2003). The other replicate was analyzed using the new centrifugation method.

Various aliquots of samples from other sediment cores from Lake Van were used in centrifugation experiments to assess how well the position of the sediment–water interface could be determined after centrifugation. Inspection of the prepared aliquots showed that the bulk water contained no residual sediment grains. Based on our experience, knowledge of the position of the sediment–water interface in a few centrifuged aliquots is sufficient to define an empirical relationship between the position of the sediment–water interface in the copper tube and the sediment depth. In the case of Lake Van, we were able to determine the position of the sediment–water interface reliably from such an empirical relationship. It should be noted, however, that the latter may only apply in the case of homogeneous and fine-textured sediments like those from Lake Van. We, therefore, suggest that the position of sediment–water interface always be determined experimentally for each sample using an aliquot of the same sample.

In the case of Lake Van the available water mass becomes very small in samples taken at depths greater than 1.5 m. This poses practical difficulties in setting the third clamp to separate water and sediment (see Fig. 1D). Because space within the centrifuge is limited, the maximum sample length (i.e., the distance between the clamps) is about 11 cm (Fig. 1A). This defines the maximum available water mass after centrifugation as ~2 g (at least with the copper tubes used in our experiments, which have an inner diameter of ~7 mm).

Comparison of the noble-gas concentrations determined by the blow-out extraction method of Brennwald et al. (2003) and our new centrifugation method shows that, in the case of the Lake Van sediment, the former method has a lower extraction efficiency for noble gases with mass greater than He (Table 2). This is probably due to incomplete blow-out of the fine-grained sediments of Lake Van.

With the blow-out method, the discrepancy between the noble-gas concentrations measured in the porewater and in the overlying bulk water increase with increasing atomic mass (Table 2). The greatest discrepancy is found in the case of Xe (21%, sample V1-B1). It seems that the blow-out method extracts light noble gases from the sediments of Lake Van more efficiently than heavier ones, whereas the new method does not fractionate noble-gas species (or not appreciably). Brennwald et al. (2003) successfully analyzed sediment samples from two Swiss lakes using the standard blow-out method with a mean extraction efficiency for Xe of ~98% for Lake

**Table 1.** Noble-gas concentrations and isotope ratios for sediment and water samples from Lake Lucerne and Lake Van. L1, L2, and L3 define 3 bulk water samples from Lake Lucerne, which are divided each into 2 subsamples, one for standard water analysis (Beyerle et al. 2000) and one to be analyzed by the presented method, respectively. STP = standard temperature (0°C) and pressure (1 atm). Method used (indicated in the sample name): N = bulk water samples measured using the standard protocol for analyzing noble gases in water samples (i.e., noncentrifuged: Beyerle et al. 2000); B1, B2 = sediment samples measured using the blow-out method (Brennwald et al. 2003); C = sediment samples measured using the centrifugation method. *L-Weg*: calculated equilibrium concentrations for Lake Lucerne water samples. *V1-Wm*, *V2-Wm*: measured concentrations for Lake Van water samples.

Sample	z (m)	He ( $10^{-8}\text{cm}^3_{\text{STP}}/\text{g}$ )	Ne ( $10^{-7}\text{cm}^3_{\text{STP}}/\text{g}$ )	Ar ( $10^{-4}\text{cm}^3_{\text{STP}}/\text{g}$ )	Kr ( $10^{-8}\text{cm}^3_{\text{STP}}/\text{g}$ )	Xe ( $10^{-8}\text{cm}^3_{\text{STP}}/\text{g}$ )	$^3\text{He}/^4\text{He}$ ( $10^{-6}$ )	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$
Lake Lucerne (36.9 m water depth, temperature 3.2°C, salinity ~0‰)									
<i>L-Weg</i>		4.49	1.98	3.99	0.96	1.42	1.36	9.78	294.9
L1-N		4.74	1.95	3.92	0.92	1.42	1.34	9.80	294.5
L2-N		4.96	2.03	4.04	0.95	1.41	1.33	9.79	296.0
L3-N		4.77	1.99	4.03	0.96	1.44	1.33	9.80	294.5
L1-C		4.80	1.98	4.03	0.95	1.36	1.34	9.81	296.2
L2-C		4.80	1.99	4.04	0.96	1.36	1.37	9.76	296.1
L3-C		4.86	2.02	4.07	0.97	1.43	1.38	9.80	293.6
Lake Van–Core V1 (250 m water depth)*									
<i>V1-Wm</i>		4.05	1.49	3.02	7.17	1.07	2.61	9.76	295.7
V1-B1	0.20	4.15	1.39	2.54	0.57	0.85	3.57	9.78	295.8
V1-B2	0.20	4.05	1.38	2.56	0.59	0.90	3.19	9.76	295.4
V1-C	0.20	4.08	1.51	3.09	0.73	1.05	2.77	9.76	297.1
Lake Van–Core V2 (196 m water depth)†									
<i>V2-Wm</i>		3.98	1.49	3.03	7.23	1.10	2.33	9.79	294.7
V2-B1	0.26	4.11	1.40	2.63	0.62	0.97	5.53	9.82	295.7
V2-B2	0.26	4.18	1.46	2.87	0.67	1.08	3.14	9.82	295.4
V2-C	0.26	4.13	1.52	3.09	0.73	1.11	6.36	9.65	296.0
Error B‡ (%)		1.0	1.3	1.1	1.9	2.6	1.0	0.2	0.1
Error C§ (%)		1.9	1.9	1.9	2.0	2.5	1.7	1.6	0.2

\*The water sampling station was located in the Ahlat sub-basin about 9 km east of sediment sampling station V1 (Fig. 3).

†The water sampling station was located in the main basin of Lake Van about 10 km west of sediment sampling station V2 (Fig. 3).

‡Relative standard error for the blow-out extraction method of Brennwald et al. (2003) for a single noble-gas analysis.

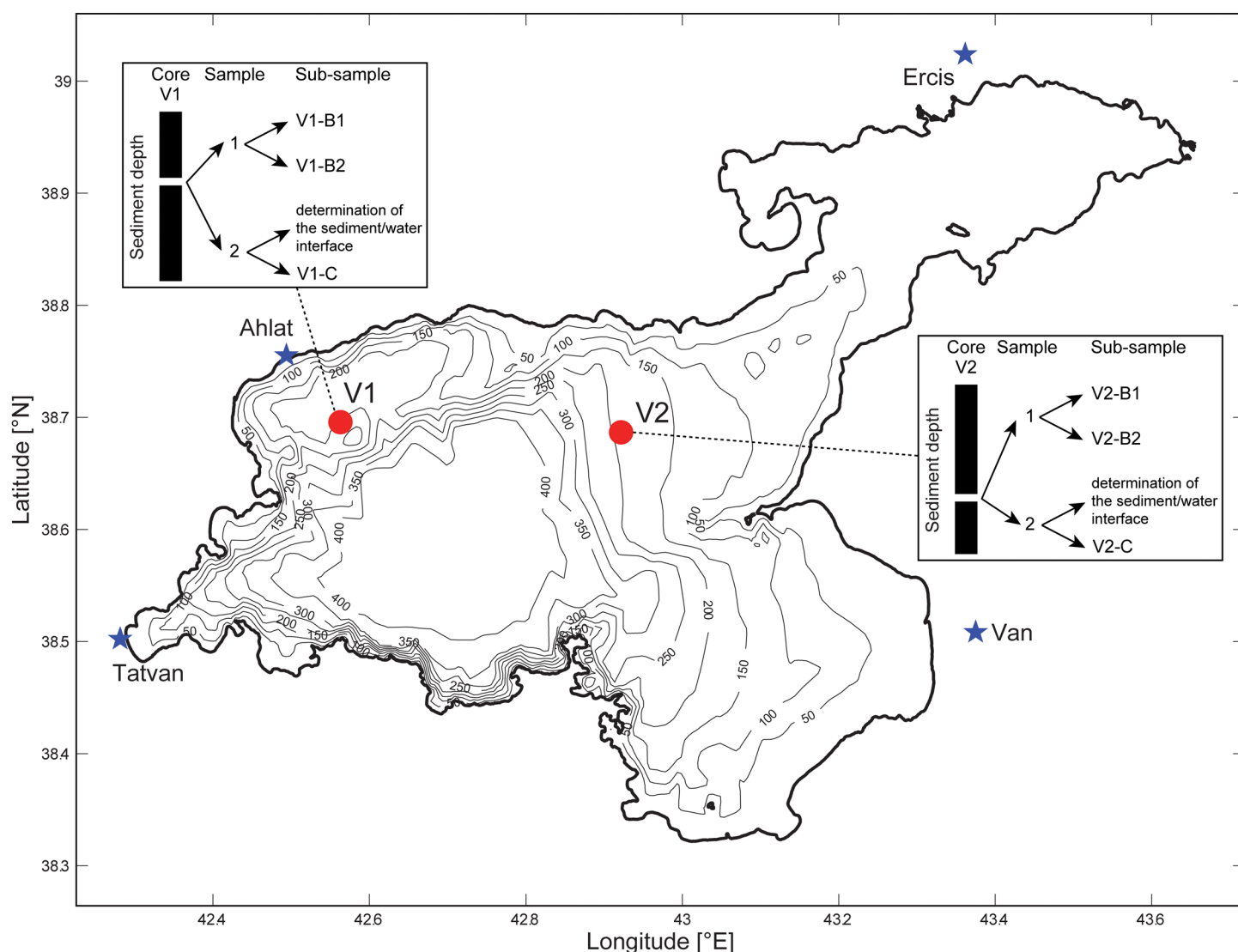
§Relative standard error for the centrifugation method for a single noble-gas analysis.

Lucerne and ~94% for Lake Zug. However, incomplete extrusion of the sediment sample significantly reduces the extraction efficiency of the standard method. A very fine-grained sediment matrix may hamper gas extraction in the blow-out method, as the effective diffusivity is significantly attenuated by an increase in tortuosity that prevents the noble gases from being released from the sediment.

We, therefore, conclude that the strong depletions of about 10% to 20% in the concentrations of the heavy noble gases (Ar, Kr, and Xe) measured in the samples that were extracted using the blow-out method are related to something specific to the matrix of the analyzed sediments that either hindered complete extrusion of the gases from the copper tube, or generated large sediment clumps during the extrusion step. In both cases, the sediment structure was apparently able to form a diffusive barrier that hindered complete degassing of the heavier dissolved noble gases from the sample during the extraction process.

For all noble gases, the samples analyzed using the centrifugation method show concentrations that agree with those in the overlying water to within 4% (Table 2), indicating that the textural problem encountered by the blow-out method is completely bypassed by the new extraction procedure. For He, the agreement is not as good as that for the heavier noble gases, and  $^3\text{He}/^4\text{He}$  ratios in the sediment, especially at sampling station V2, are much higher than in the overlying bulk water (Table 2). However, this is to be expected because of the accumulation of mantle He enriched in  $^3\text{He}$  at the bottom of Lake Van (Kipfer et al. 1994). He in the sediment column, in contrast to He in the overlying bulk water, cannot be dispersed by strong horizontal turbulent transport.

The measured  $^4\text{He}$  concentrations agree with those of the standard method to within 1%; however, the  $^3\text{He}/^4\text{He}$  ratios deviate considerably from those of the standard method. As already pointed out by Brennwald et al. (2003), the standard blow-out method tends to result in an uncontrolled release of



**Fig. 3.** Map of Lake Van showing the locations of the sediment sampling stations in 2005 (red dots) and the major cities in the vicinity of the lake (blue stars). For each station, a schema of the respective samples and aliquots is shown.

He from the sediment matrix in response to the heat applied. A direct comparison of the two methods based on  $^3\text{He}/^4\text{He}$  ratios from the porewater of Lake Van is therefore not feasible.

### Discussion

The results from the centrifuged sediment samples from Lake Van show that centrifugation yields a bulk porewater sample that is free of residual sediment grains. The procedure is experimentally straightforward, and results are reproducible. The optical determination of the geometrical position of the sediment–water interface within the centrifuged samples could be achieved in a robust manner. The position of this interface needs to be precisely known to obtain the maximum amount of water for the subsequent noble-gas analysis, as the mass of water liberated by centrifugation determines the over-

all error of the noble-gas determination. Otherwise, if the position is only vaguely defined, the third clamp that separates the sediment from the water has to be set at a safe position near the water end of the sample to keep the water phase clear of sediment. Under such unfavorable conditions, our geometrical setting does not always guarantee that the separated water mass is large enough ( $>2$  g) to allow adequate determination of the noble-gas concentrations.

The centrifugation method described here represents a significant step forward in the analysis of noble gases in the porewater of unconsolidated sediments. First, the uncontrolled release of He from the sediment grains, which affects the  $^3\text{He}/^4\text{He}$  isotope ratios determined by the blow-out method (Brennwald et al. 2003), is completely avoided by separating the pure porewater from the compressed sediment phase. The

**Table 2.** Comparison of noble-gas concentrations and isotope ratios in the sediments of Lake Van (stations V1 and V2, see Fig. 3) as determined by the standard method of Brennwald et al. (2003) (B1 and B2) and by the centrifugation method (C). The data of a single noble-gas analysis are expressed as the percentage deviation from the measured concentrations and isotope ratios in the overlying water column.  $\Delta V1$  and  $\Delta V2$  denote the difference between the two extraction methods at each station:  $\Delta Vi = (Vi\_C) - [(Vi\_B1) + (Vi\_B2)]/2$  where  $i = 1, 2$ . It should be noted that the extraction efficiency for light noble gases is the same for both methods whereas the new method has a higher extraction efficiency for heavy noble gases.

Sample	He (%)	Ne (%)	Ar (%)	Kr (%)	Xe (%)	$^3\text{He}/^4\text{He}$ (%)	$^{20}\text{Ne}/^{22}\text{Ne}$ (%)	$^{40}\text{Ar}/^{36}\text{Ar}$ (%)
V1-B1	2	-7	-16	-20	-21	37	-0.3	0.1
V1-B2	0	-7	-15	-18	-16	22	0.0	-0.1
V2-B1	3	-6	-13	-15	-12	137	-0.3	0.3
V2-B2	5	-2	-5	-7	-2	34	-0.3	0.2
V1-C	1	1	2	2	-2	6	-0.1	0.5
V2-C	4	2	2	1	1	172	1.5	0.5
$\Delta V1$	-1	8	18	21	17	-23	0.1	0.5
$\Delta V2$	0	7	11	12	8	87	1.8	0.2

pure porewater sample is extracted like a common water sample under normal ambient temperature conditions.

Second, the new centrifugation method is more reliable, as it is less operator-sensitive. Also, the formation of gases such as  $\text{CH}_4$  as the result of heating that can interfere with the noble-gas measurements is avoided. Moreover, the time needed for gas extraction is considerably shorter, as the extrusion/heating procedure (~30 min) is avoided and drying the sample (which contains only water instead of a water/sediment mixture) after extraction is much faster.

Finally, the new experimental protocol is much easier to handle from both an experimental and a conceptual point of view, making it feasible for other laboratories to apply the method. The centrifugation of the bulk sediment samples intended for noble-gas analysis can be accomplished using commercially available equipment.

## Comments and recommendations

### Sample containers

The available volume in the cylinders of the centrifuge can severely limit the amount of water that can be separated within the copper tubes during centrifugation, which leads to the occurrence of larger overall errors in the noble-gas analysis because of the limited water mass. The use of larger volumes (by increasing the diameter of the copper tube or the capacity of the centrifuge) would overcome this limitation. This might be of key importance in the case of low-porosity sediments.

### Centrifuge

By using a centrifuge with a higher angular velocity, it might be possible to separate even samples of low porosity into a water phase and a sediment phase. Large centrifuges rotating at 12,000 rpm are available that produce a force about three times that of the centrifuge used in the present work.

### In situ noble-gas analysis in aquifers

Our method could also easily be applied to bulk sediments from aquifers to determine  $^3\text{H}$ - $^3\text{He}$  water ages and atmospheric

noble-gas concentrations with the aim of reconstructing past climate conditions. Because groundwaters are commonly sampled by pumping water from an observation well, the resulting forced water flow may follow preferential pathways from the aquifer to the borehole. Such preferential flow will bias the sampling, because the pumped water may not belong to the local groundwater in which the well is embedded under natural flow conditions. Moreover, it is time-consuming and expensive to sample groundwater from specific depths or aquifers using multi-screen ground-water monitoring wells. The adaptation of the sampling technique of Brennwald et al. (2003) to aquifer materials would allow sediments to be acquired from a drilled core. Our experimental protocols also allow the centrifugation method to be applied to aquifer sediments and hence allow the real noble-gas concentrations present in the aquifer at a precise spatial position to be determined. Such exact spatial information is often ultimately needed to validate state-of-the-art numerical groundwater models.

### Analysis of other dissolved gases

As the most commonly used techniques for sampling other gases dissolved in sediment porewaters (e.g.  $\text{CH}_4$ ,  $\text{N}_2$  or  $\text{CO}_2$ ) are subject to experimental artifacts—e.g., degassing during sampling by syringes or peeper plates—reliable, quantitative determination of the concentrations of these gases still poses an experimental challenge. As the physical properties (solubility, diffusivity, etc.) of most common dissolved gas species lie within the range of those of the noble gases, the centrifugation method is expected to allow the determination of their concentrations also.

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