

# Noble gases as tracers for the gas dynamics in methane supersaturated lacustrine sediments

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## Abstract

The commonly observed heterogeneous and erratic emissions of methane from lacustrine sediments are difficult to quantify. The combined analysis of methane and noble gas concentrations in the pore water opens a novel route to analyse and quantify such emissions and was used in this work to explore the gas dynamics in the sediments of two lakes with different hydro-geochemical settings. In the hypertrophic Lake Rot the microbial activity in the sediment pore water results in a virtually continuous gas bubble formation and emission. By determining noble gas concentration gradients and the maximum methane supersaturation, the minimum methane emission from the sediment was quantified. The gas evolution in the pore water of the sediments of artificial Lake Lungern is strongly affected by annual lake level variations of up to 20 meters. Noble gas concentrations allow past gas dynamics at different lake levels to be traced back. At “hot spots” of bubble emission microbial methane from deeper sediments was released in response to the decreasing hydrostatic pressure, i.e. man-induced lake level drop.

Within zones of the sediment that seasonally fall dry, the oxygen supply to the sediment was inferred from the noble gas excess observed in the pore water, which is due to dissolving air bubbles which entered the sediment during the dry period.

These case studies demonstrate the potential of the combined analysis of noble gas and

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CH<sub>4</sub> concentrations for exploring the gas dynamics in lacustrine sediments. The feasibility of this method under different conditions calls for an application in other aquatic environments, such as wetlands and oceans.

*Keywords:* ebullition, lake water level variation, methane bubble emission, oxygen input, excess air, dry falling

## 1. Introduction

Methane ( $\text{CH}_4$ ) in the pore water of lacustrine sediments often results from anthropogenically induced eutrophication. Eutrophication affects lakes, reservoirs, ponds and rivers on a global scale (Smith, 2003; Downing et al., 2008) and is associated with elevated primary production in the lake water, high sedimentation rates and hypoxic or even anoxic conditions in the bottom water and sediments. Under such conditions, microbially produced  $\text{CH}_4$  can accumulate in the pore water (Lovley et al., 1982; Sobek et al., 2009). If the sum of the partial pressures of gases dissolved in the pore water exceeds the total in situ hydrostatic pressure, bubbles can be formed in the sediment (e.g., Boudreau, 2012). In the following these conditions are referred to as supersaturation. Gas supersaturation in the pore water of lacustrine sediments and subsequent bubble formation can result, for example, from enhanced microbial production, from rising water temperatures, or can be triggered by a hydrostatic pressure decrease, i.e. a change in the total in situ hydrostatic pressure. Such pressure unload might be caused by shear stress in the sediments induced by bottom currents, by wind events (i.e. wind pumping, see Precht et al., 2004; Hofmann et al., 2010), by variations in atmospheric pressure (Joyce et al., 2003) or by decreasing water level (Beaulieu et al., 2017; Harrison et al., 2017). The effect of such changes of the water level on the gas dynamics in lacustrine sediments has received little scientific attention so far, although the few available observations lend support to the argument that the resulting ebullition might foster the  $\text{CH}_4$  emission significantly (Varadharajan et al., 2012; Maeck et al., 2014; Beaulieu et al., 2017; Harrison et al., 2017).

If the bubbles formed in the sediment pore space reach a critical size, they tend to escape from the sediment. The free gas phase in the sediments is generated by the gases that were present in the surrounding pore water during gas bubble formation, e.g.  $\text{CH}_4$ ,  $\text{CO}_2$  and noble gases. The physical processes related to the formation of a free gas phase in the sediment and to the emanation of bubbles from the sediment are of interest for understanding the importance of gas ebullition with respect to the overall gas budget in the sediment column and in the lake.

The biogeochemically inert noble gases are ubiquitously present in the terrestrial environment, e.g. in lake sediments. Noble gas concentrations dissolved in the pore water of lacustrine sediments commonly agree with the equilibrium concentration of air and water, i.e. air saturated water (ASW). This is because noble gases enter the lake through exchange at the lake

surface during air water partitioning and are transported within the lake and finally incorporated in the sediment. In the case of strong microbial  $\text{CH}_4$  production in the sediment and local  $\text{CH}_4$  supersaturation in the pore water, the bubbles formed initially mainly contain  $\text{CH}_4$  and thus are not in equilibrium with the surrounding pore water. This non-equilibrium induces a diffusive transport of other gas species (e.g. noble gases) into the bubble, depending on the respective gas diffusion coefficient and on the difference in partial pressure. This exchange between gases in the bubble and gases dissolved in the pore water continues until solubility equilibrium between the free gas phase and the surrounding pore water is attained. Such in-situ re-equilibration leaves a characteristic depletion pattern against ASW of the hardly soluble noble gases in the surrounding pore water. Noble gas depletion patterns persist over long time scales e.g. in the case of strongly suppressed diffusive transport in the pore water such patterns can remain since the sediment deposition and pore water entrapment (Tomonaga et al., 2015). Noble gas depletion patterns have been used to reconstruct past gas bubble ( $\text{CH}_4$ ) emissions from highly eutrophic lakes (Brennwald et al., 2005). Gas ebullition from the sediment often occurs heterogeneously in time and space, as a single erratic event and over short periods of time and therefore is likely to be missed by conventional sampling strategies which commonly cover only a limited time period. Therefore, noble gases that record past emission events are ideal to trace gas ebullition from the lacustrine sediments. Furthermore, noble gases are ideal tracers due to their stability, their inertness. Noble gases dissolved in the pore water of lacustrine sediments can be determined with high precision in a robust and reliable manner (Brennwald et al., 2003; Tomonaga et al., 2011). Further recent technical advances in sampling (see Tyroller et al., 2016) now make it possible to quantify reliably the  $\text{CH}_4$  concentration in the sediment pore water, even in strongly supersaturated sediments where  $\text{CH}_4$  is present both in dissolved and in free gaseous form.

This study assesses the potential of the combined analysis of noble gas and  $\text{CH}_4$  concentrations to trace and analyse the gas dynamics in response to gas bubble formation in unconsolidated sediments. Noble gas and  $\text{CH}_4$  concentrations determined in the uppermost meter of the sediment (i.e., commonly the most active zone of  $\text{CH}_4$  production and emission) of Lake Rot and Lake Lungern are discussed, with the aim of further expanding the application of trace gas geochemistry in aquatic systems and adding to the understanding of the gas dynamics in unconsolidated lacustrine sediments. The two Swiss lakes investigated were chosen due to their

different conditions to generate gas bubbles in the sediments. At Lake Rot  $\text{CH}_4$  emissions are primarily driven by the high trophic level of the lake. In contrast, mesotrophic Lake Lungern is subject to extreme artificially induced lake level variations that may trigger degassing and gas release.

## 2. Study sites

**Lake Rot** (Canton Lucerne) is characterized by frequent algae bloom and considerable  $\text{CH}_4$  production in the sediment owing to the extremely high nutrient content in the lake. The lake is stratified during the warm season (May to November) and in the cold season (January to February). During spring and autumn the lake is completely mixed. The sediments of Lake Rot are known to emit  $\text{CH}_4$  as bubbles (Schubert et al., 2010; Naeher et al., 2012, 2014; Tyroller et al., 2016). Bubbles leaving the water column in the littoral zone can be observed by eye. The anthropogenic nutrient input, e.g. the sewage load of the city of Lucerne from 1850 to 1978, lead to strong eutrophication of Lake Rot, although the lake has been “naturally” eutrophic throughout the Holocene but at a lower level than today (Jüttner, 1990). Fig. 1 shows the location of sediment coring in the center of Lake Rot at a water depth of 16 m. The sediment cores, retrieved in three sampling campaigns in 2008, 2011 and 2013, were taken within a radius of 5 m from the position indicated in Fig. 1.

Figure 1: Bathymetric maps of Lake Rot and Lake Lungern (with inflowing rivers and contour lines in m.a.s.l.; Data source: Swisstopo DV 5704 000 000, reproduced by permission of swisstopo / JA100119). The sampling sites are marked with a cross. In Lake Lungern, samples **A**, were sampled in the late summer: **Sample A1** where no active bubble emission was observed and **Sample A2** where bubble emission from the sediment was observed by eye and by side scan sonar. **Sample C** was taken in the winter and **Sample D** in spring.

**Lake Lungern** (Canton Obwalden) is a mesotrophic reservoir and is subject to artificially-induced water level variations of up to 20 m as its water is used for hydropower production. Most of the littoral sediments originate from crop land being flooded when the lake was dammed in 1921. An earlier study on Lake Lungern suggested that  $\text{CH}_4$  emitted and

dissolved in the deep water during summer stagnation might originate from a deep natural gas reservoir ((Bossard et al., (1981): “fossil methane penetrating the sediment from below”). However, recently  $\text{CH}_4$  emission from Lake Lungern was found to be in a similar range as for other comparable Swiss reservoirs (Diem et al., 2012). A hydroacoustic survey (Ostrovsky, 2009) reported the emission of very small bubbles in the littoral zone (at a water depth of less than 7 m) and oxygen supersaturation in the overlying water column of Lake Lungern. Echosounding during our study identified active bubble emission in the southern part of the lake. For gas analysis seven sediment cores were taken in the area of these spots of active bubble emission and in the littoral zone of the southern part of Lake Lungern at different seasons (spring and autumn, see positions indicated in Fig. 1).

### 3. Methods

Sediment cores were retrieved in plastic liners using a gravity corer and were processed immediately after recovery according to the sampling protocol developed and optimised for noble gas sampling and analysis in lacustrine sediments (Brennwald et al., 2003; Tomonaga et al., 2011). In short, the whole sediment was squeezed through pre-drilled holes along the liner into copper tubes used as sampling containers ( $\sim 50$  cm length, 3/8 inches diameter), which were attached to the pre-drilled holes of the liner with modified Swagelock-fittings to avoid contamination (see Brennwald et al., 2003; Tomonaga et al., 2011). After flushing the copper tubes with sediment, the copper tubes were closed airtight with clamps, as it is standard procedure for free water samples (for further details refer to Brennwald et al., 2003, 2013).

The length of the copper tubes was chosen such that it could be split into three aliquots by adding and closing additional airtight clamps. The first aliquot was used to determine the geometrical position of the sediment/water interface within the copper tube after the separation of the pore water from the matrix by centrifugation (Tomonaga et al., 2011). The second aliquot was used to determine noble gas concentrations in the porewater (Brennwald et al., 2003; Tomonaga et al., 2011, 2014, 2015) and the third aliquot for the determination of the total  $\text{CH}_4$  abundance (Tyroller et al., 2016).

The analysis of noble gases in the second aliquot was performed connecting the copper tube containing the free water phase to the extraction line of a custom-built static-vacuum

sector-field mass spectrometer at the rare gas laboratory of ETH Zurich (Beyerle et al., 2000). The gases in the water were extracted and were separated into a He-Ne fraction and an Ar-Kr-Xe fraction using a series of cryogenic traps (Brennwald et al., 2003; Tomonaga et al., 2011). These gas fractions were then purified using additional cryogenic traps, zeolite traps and getter traps, which removed any reactive gases. The purified noble gases were then analysed in the static-vacuum sector-field mass spectrometer and their amounts determined by means of mass-spectrum-peak-height-comparison against a well-known air standard processed exactly as the gas of the water sample.

For CH<sub>4</sub> analysis a CH<sub>4</sub> free headspace (containing pure N<sub>2</sub>) was attached to the copper tube containing the third aliquot. After equilibration of the headspace and the sample, the headspace was connected by a gas-tight injector to a gas chromatograph flame ionisation detector (GC-FID, Agilent HP6890GC, with a 30 m Supelco Carboxen 1010 column x 530  $\mu$ m inner diameter x 3  $\mu$ m film thickness, and a carrier gas He) for final CH<sub>4</sub> analysis. The detector signal was converted into CH<sub>4</sub> amounts by calibration against gas standards with known CH<sub>4</sub> concentrations (for more details see Tyroller et al., 2016).

An Isoprime isotope ratio mass spectrometer (IRMS, instrumental precision  $\sim 0.5\%$ , see Zhou et al., 2005) was used to measure the stable carbon isotope composition of the CH<sub>4</sub> gas samples gathered by funnels being used for continuous bubble counting (see Maeck et al., 2014) at Lake Lungern.

A downward-looking Simrad split-beam echosounder (Kongsberg Maritime AS, Norway, EK60, 7° beam angle, 120 kHz transducer), modified for bubble search in aquatic systems according to Del Sontro (2011), was used to locate bubbles being emitted from the lake sediment, allowing the gravity corer to be precisely positioned at spots of active and ongoing bubble emission.

## 4. Results and Discussion

### 4.1. Noble gas data from Lake Rot

Fig. 2 shows the depth profiles of CH<sub>4</sub> concentrations (data from Tyroller et al., 2016), of noble gas concentrations normalized to ASW concentration and of <sup>36</sup>Ar/<sup>40</sup>Ar ratios normalized

to the air saturated water ratio ( $R_{ASW}$ ) determined in the sediment pore water of Lake Rot. Throughout the whole sediment core noble gases (Ne, Ar, Kr, Xe) show distinct and systematic elemental fractionation with sediment depth (depleted relative to ASW), whereby the light noble gas concentrations are more depleted than the heavy noble gases ( $\Delta Ne < \Delta Ar < \Delta Kr < \Delta Xe$ , with  $\Delta i$  being the relative deviation from the ASW concentrations; Fig. 2). Such a depletion pattern has been shown to be characteristic for the stripping of dissolved noble gases by gas bubbles (e.g.  $CH_4$ ) formed in the sediment (Ballentine et al., 2002; Holzner et al., 2004; Brennwald et al., 2005). He concentrations are also depleted throughout the sediment core, but He is less depleted relative to the other noble gases, e.g. it is less depleted than Ne, although being lighter. Such He enrichment relative to the other noble gases dissolved in the sediment pore water can be caused by the accumulation of terrigenous He (e.g. *in situ* production and/or accumulation of terrigenous He ascending from deeper strata; for review see Brennwald et al 2013).

From 0 to 25 cm sediment depth noble gas concentrations decrease with increasing sediment depth. Between 25 and 45 cm sediment depth noble gas depletion in the sediment reaches its maximum and a pronounced peak concentration of  $CH_4$  is observed. Below 45 cm for Ne - Xe depletion remains constant. Based on these observed trends of the  $CH_4$  and noble gas concentrations with sediment depth, the sediment is conceptually subdivided in three layers (0 - 25 cm, 25 - 45 cm, below 45 cm):

Figure 2: **E**  $CH_4$  concentration profiles in Lake Rot, determined in sediment cores sampled in 2011 and 2013 (see also Tjallingii et al., 2016). ASW concentrations and  $CH_4$ -local (intermitted line) were calculated according Henry's law (Eq. 3; Sander, 1999) and the presumed water temperature (4 °C), whereby for the latter a pure  $CH_4$  gas phase was assumed. **F** Noble gas concentrations in the pore water of Lake Rot with sediment depth. Mean values from three sediment cores obtained in 2008, 2011 and 2013 at Lake Rot at a depth of 16 m, the lowest two samples (0.65 and 0.7 cm) were determined in only one sediment core. Noble gas concentrations are presented in percent relative to ASW (100%). A linear regression was fitted to the concentrations of Ne, Ar, Kr and Xe in the upper 40 centimetres of the sediment of Lake Rot. **G**  $^{36}Ar/^{40}Ar$  isotope ratio profiles with sediment depth determined in the sediment pore water of Lake



Rot. The isotope ratios are mean values of the results determined in two sediment cores and normalized to the  $^{36}\text{Ar}/^{40}\text{Ar}$  ratio of ASW (solid line; Beyerle et al., 2000). The dotted line is the fractionation of Ar isotopes according the square root relation (e.g.  $\left(\frac{^{36}\text{Ar}}{^{40}\text{Ar}}\right)_{\text{ASW}} \cdot \sqrt{\frac{36}{40}}$ , Tyroller et al., 2014). **H** Chart of the gas dynamics in the different layers of the sediment. The grey shaded area indicates the zone of  $\text{CH}_4$  supersaturation and hence the zone where  $\text{CH}_4$  is present in gaseous phase. The error on the sediment depth is about  $\sim 0.05$  m due to sediment displacement upon sediment squeezing (see Tomonaga et al., 2015); the error of  $\text{H}_2$  (ranging between 10 - 50%) is not shown for reasons of clearness.

*0 - 25 cm sediment depth:* In this layer noble gas concentrations virtually linearly decrease with increasing sediment depth. The  $\text{CH}_4$  concentrations determined are close to the in situ saturation concentration, i.e. the local  $\text{CH}_4$  partial pressure agrees with the in situ hydrostatic pressure (further referred to as  $\text{CH}_4$ -local; see Fig. 2). Such a steadily decreasing noble gas profile can be interpreted to indicate diffusive transport of noble gases from the sediment/water interface (ASW concentration) downward to the zone of maximum noble gas depletion and as operating at steady state. The  $^{36}\text{Ar}/^{40}\text{Ar}$  ratios in this layer are not fractionated and agree with the  $R_{\text{ASW}}$  (determined e.g. by Beyerle et al., 2000) within the error of the measurements. This indicates that bubbles formed in this layer reach equilibrium before leaving the sediment. As the  $\text{CH}_4$  concentrations are close to  $\text{CH}_4$ -local, a prominent free  $\text{CH}_4$  gas phase seems not to be present in this zone.

*25 - 45 cm sediment depth:* The maximum noble gas depletion and largest  $\text{CH}_4$  supersaturation are observed in this layer (grey area in Fig. 2), with  $\text{CH}_4$  concentrations exceeding  $\text{CH}_4$ -local by one order of magnitude. This  $\text{CH}_4$  peak was determined in two independent sampling campaigns (i.e. 2011 and 2013; see Tyroller et al., 2016). The strong  $\text{CH}_4$  supersaturation indicates that  $\text{CH}_4$  is present in the dissolved and in the gaseous phase. Noble gas concentrations are strongly depleted relative to ASW concentrations. As mentioned previously, such fractionation pattern indicates that noble gases have been stripped out of the sediment pore water by escaping gas bubbles formed in

the sediment. The peak in  $\text{CH}_4$  supersaturation and the maximum noble gas depletion both indicate that this is the layer of most active  $\text{CH}_4$  production. We note that our study focusses only on the upper meter of the sediment and therefore the gas dynamics in deeper sediment layers of Lake Rot cannot be accessed. Up to a sediment depth of 45 cm the  $^{36}\text{Ar}/^{40}\text{Ar}$  ratios in the pore water are not significantly fractionated relative to  $R_{\text{ASW}}$  (Fig. 2, panel G), indicating that bubbles formed in this sediment layer attain equilibrium with the surrounding pore water before leaving the sediment.

*Below 45 cm:* In this lower layer,  $\text{CH}_4$  concentrations were found to be in the range of  $\text{CH}_4$ -local. Again, the noble gas concentrations are strongly depleted relative to ASW. The  $^{36}\text{Ar}/^{40}\text{Ar}$  ratios at a sediment depth of 45 - 55 cm are lower than  $R_{\text{ASW}}$ , i.e. indicating depletion of light isotopes. This isotopic fractionation might point to secondary gas exchange of dissolved noble gases with gas bubbles that escaped before reaching an equilibrium with the surrounding pore water (diffusion controlled noble gas stripping; see Brennwald et al., 2005).

However, as no free  $\text{CH}_4$  gas phase can be identified in this zone, the isotopic fractionation is more likely to be caused by diffusion of noble gases from deeper sediment layers to the zone of active  $\text{CH}_4$  bubble formation. Alternatively and analogously to Lake Soppen (Brennwald et al., 2005), it might point to more intensive  $\text{CH}_4$  ebullition from the sediment of Lake Rot in the past, which produced the noble gas depletion in the deeper sediments. The concentrations in the lowest two samples (65 and 70 cm sediment depth) are elevated (close to ASW concentration), which might indicate a contamination with air during sampling. During core retrieval and squeezing, the lower end of the sediment core is exposed to the atmosphere and air can enter the sediment column. However, the heavier noble gases in the lowest two samples seem not to be affected by contamination. In the case of air contamination during sampling slower diffusion of the heavier noble gases seem to allow the pore water to keep its original Ne - Xe composition. But the deviation of the  $^{36}\text{Ar}/^{40}\text{Ar}$  in the lowest sample (70 cm sediment depth) might be explained by the atmospheric contamination, e.g. Ar diffusing into the sample. However, as the determined noble gas concentrations below 45 cm are similar to the concentrations determined in the active layer (25 - 45 cm), the observed elemental and isotopic fractionation in the

lower layer (45 - 50 cm) does not influence the quantification of CH<sub>4</sub> emissions from the active layer: because there is no concentration gradient (noble gas concentrations are depleted but constant) there is no upward transport.

#### 4.1.1. Quantification of the methane emission

The CH<sub>4</sub> emissions from Lake Rot were quantified by means of a mass balance, combining the results of noble gas and CH<sub>4</sub> analysis.

During 2008 and 2013 very similar profiles of CH<sub>4</sub> and noble gas concentrations were observed in the sediment pore water of Lake Rot (see Tyroller et al., 2016). Therefore, noble gas and CH<sub>4</sub> concentrations are assumed to be virtually stable over a time scale of a few years, and the associated CH<sub>4</sub> and noble gas fluxes are assumed to operate at steady state. Thus, the concentration gradient of noble gases observed in the upper sediment layer is interpreted to be the result of the continuous (i.e. steady state) noble gas diffusion from the lake water at the sediment/water interface (e.g. ASW concentration) to the zone of maximum CH<sub>4</sub> supersaturation (e.g. depleted relative to ASW). This assumption appears realistic as the sediment near the sediment/water interface is unconsolidated (“fluffy”) and the diffusive transport of solutes in the pore water of such sediments is known to be similar to that of free water (Jähne et al., 1987; Cussler, 2009). Furthermore, it is assumed that gas bubbles containing noble gases are virtually continuously degassing from this zone of CH<sub>4</sub> supersaturation (25 - 45 cm) as a result of continuous CH<sub>4</sub> production. The continuous diffusive flux of noble gases from the sediment/water interface to the zone of active CH<sub>4</sub> bubble formation ( $F_{NG}^{diff-in}$ ) is assumed to be equal to the continuous flux of noble gases stripped out of the sediment ( $F_{NG}^{ebu-out}$ ) in response to the gas bubbles leaving the zone of maximum CH<sub>4</sub> concentration in the sediment:

$$F_{NG}^{diff-in} = F_{NG}^{ebu-out} \quad (1)$$

where  $F_{NG}^{diff-in}$  is the downward noble gas flux from the sediment/water interface to the zone of active CH<sub>4</sub> production and  $F_{NG}^{ebu-out}$  the upward noble gas flux in response to bubble emission from this zone. The downward noble gas flux to the zone of active CH<sub>4</sub> production  $F_{NG}^{diff-in}$  was calculated from Fick’s first law of diffusion (e.g. Crank, 1975):

$$F_{NG}^{diff-in} = -\phi D_{NG}^{eff} \frac{\Delta C_{NG}}{\Delta x} \quad (2)$$

whereby the molecular diffusivity  $D_{NG}^{eff}$  of the respective noble gas in the sediment pore water was calculated for the bottom lake water temperature of approximately 6 °C (e.g. see Jahne et al., 1987) and adjusted for tortuosity ( $D_{NG}^{eff} = D_{NG}^{free} / \tau$ , where  $D_{NG}^{free}$  is the diffusion coefficient in free water and  $\tau$  the tortuosity  $\sim 1.02^{-0.81}$ , see Maerki et al., 2004),  $\phi$  accounts for the sediment porosity,  $C_{NG}$  is the concentration of the noble gases and  $x$  the characteristic distance, which is given by the sediment depth of maximum  $CH_4$  concentrations (i.e. the mean sediment depth of the two  $CH_4$  peaks measured:  $\sim 35$  cm, see Fig. 2).

The concentration gradient of the respective noble gas species in the sediment pore water was obtained by linear regression to the respective noble gas profiles (Fig. 2). Strong and continuous  $CH_4$  production is expected to lead to supersaturation of the pore water with gases and hence to frequent bubble formation and emission from the sediment. In such sediments  $CH_4$  is assumed to be present mainly in the gas phase as it is hardly soluble (Chanton et al., 1989). Equilibrium between the gas phase and the surrounding pore water is assumed to be established before bubbles leave the sediment. The equilibrated free gas phase escapes continuously from the  $CH_4$  production zone and, as a result, strips gases from the sediment pore water (e.g. noble gases).

Due to the strong  $CH_4$  production in the sediment of Lake Rot, the partial pressure of  $CH_4$  in the gas bubbles formed in the sediment is assumed to virtually agree with the total gas pressure in the bubble ( $P_{tot} = P_{atmospheric} + P_{watercolumn}$ ) at the respective sediment depth (i.e. the total ambient pressure in the sediment). The partial pressure of the noble gases ( $P_{NG}$ ) in the gas bubbles was calculated with Henry's law:

$$P_{NG} = H_{NG}(T,S) \cdot C_{NG,x} \quad (3)$$

Whereby  $C_{NG,x}$  is the determined noble gas concentration in the pore water at sediment depth  $x$  and  $H_{NG}$  denotes the Henry coefficient of the respective noble gas, which depends on temperature (T) and salinity (S; as recommended by Kipfer et al., 2002). The flux ratio of  $CH_4$  and noble gas species ( $F_{CH_4}^{ebu-out} / F_{NG}^{ebu-out}$ ) during steady state agrees with the respective partial

pressure ratio of  $\text{CH}_4$  and noble gases ( $P_{\text{CH}_4} / P_{\text{NG}}$ ; in accordance with Fick's first law of diffusion the flux is proportional to the concentration, see Eq. 2):

$$\frac{F_{\text{CH}_4}^{\text{ebu-out}}}{F_{\text{NG}}^{\text{ebu-out}}} = \frac{P_{\text{CH}_4}}{P_{\text{NG}}} \quad (4)$$

By combining Eq. 1 and Eq. 4, the  $\text{CH}_4$  flux via ebullition from the sediment to the overlying water column is calculated as follows:

$$F_{\text{CH}_4}^{\text{ebu-out}} = \frac{P_{\text{CH}_4}}{P_{\text{NG}}} \cdot F_{\text{NG}}^{\text{diff-in}} \quad (5)$$

Tab. 1 shows the  $\text{CH}_4$  fluxes calculated from the respective concentration gradient observed for each noble gas (Ne, Ar, Kr, Xe; Fig. 2). Given the assumption made (see Eq. 4) underestimating the noble gas fluxes to the active zone does result in an underestimation of the  $\text{CH}_4$  flux. Our determined noble gas fluxes might be underestimated as they do not account for: (1) noble gas fluxes from the lower layer, (2) enhanced noble gas transport resulting from interaction with a free gas and (3) incomplete equilibration of  $\text{CH}_4$  bubbles.

Regarding the noble gas fluxes from layers below the active zone, (1) we again note that noble gas concentration gradients in low layers are absent and thus noble gas fluxes from the lower layer to the zone of active  $\text{CH}_4$  production are negligibly low.

(2) In principle, a free gas phase could result in an elevated noble gas flux from the water/sediment interface to the layer of maximum  $\text{CH}_4$  emission, as larger bubbles in the sediment pore space have been found to enhance the gas transport through the sediment pore water significantly (Flury et al., 2015). Conversely, microscopic gas bubbles in the sediment can trap noble gases permanently (Tomonaga et al., 2015; Brennwald et al., 2013). In Lake Rot a free gas phase is only expected at the zone of maximum  $\text{CH}_4$  concentrations ( $z > 35$  cm, see Fig. 2), and above this zone the  $\text{CH}_4$  concentrations are not significantly over-saturated relative to the local saturation concentration, thus elevated noble gas transport that results from interaction with a free gas phase can be expected not to take place.

(3) In case of incomplete equilibration of the free gas phase the partial pressure ratio between  $\text{CH}_4$  and noble gases ( $P_{\text{CH}_4} / P_{\text{NG}}$ ) might be higher than the ratio at equilibrium. Hence assuming an equilibrium ratio would result in an underestimation of the  $\text{CH}_4$  flux. However, the

gas composition of bubbles leaving the sediment before attaining equilibrium with the surrounding pore water is subject to kinetic isotopic fractionation, i.e. in the case of Ar the  $^{36}\text{Ar}$  would be enriched relative to  $^{40}\text{Ar}$  in the gas phase ( $\text{CH}_4$  bubble) but being depleted with regards to the concentrations in the surrounding pore water. Such an Ar isotope fractionation, in favour of the heavier  $^{40}\text{Ar}$  isotope is not observed in the pore water phase in the upper layer of the sediment. We conclude that the free gas phase and the pore water attains a partitioning equilibrium before the bubbles escape from the sediment.

Another point which might lead to underestimating the  $\text{CH}_4$  flux is the different properties of heavy and light noble gases. The  $\text{CH}_4$  flux calculated based on the Ne concentrations is found to be considerably lower than the flux calculated for the heavier noble gases (Ar, Kr and Xe). The lower flux is the consequence of the less pronounced concentration gradient of Ne in comparison to the heavier noble gases. If the Ar - Xe concentrations measured in the pore water are extrapolated to the sediment/water interface, the calculated concentrations reasonably agree with the ASW concentrations of the overlying water. In contrast, the back extrapolated Ne concentrations are significantly lower than ASW concentration (0.6 ASW, see Fig. 2). This indicates that other unknown processes affect the Ne concentrations which we cannot account for. Therefore, we decided to exclude the Ne results to calculate  $\text{CH}_4$  emission in Lake Rot.

The  $\text{CH}_4$  fluxes calculated based on concentration gradients of Ar, Kr and Xe, agree with each other within the error. The mean calculated  $\text{CH}_4$  flux<sub>Ar-Xe</sub> ( $3.8 \pm 0.3, \text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1} \pm 1\sigma$  deviation) represents a minimum value as Ne is not considered.

Table 1:  $\text{CH}_4$  emissions from the sediment pore water of Lake Rot calculated from the concentration gradient of the respective noble gas.

Noble gas	$\text{CH}_4$ ebullition flux
	$[\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}]$
Ne	$1.6 \pm 0.4$
Ar	$4.1 \pm 0.7$
Kr	$3.6 \pm 0.6$

Xe	$3.7 \pm 0.7$
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In the literature the  $\text{CH}_4$  flux from the sediment to the lake water are often quoted as total  $\text{CH}_4$  flux, which is the sum of the  $\text{CH}_4$  flux via diffusion and the  $\text{CH}_4$  flux via ebullition (e.g. Bastviken et al., 2008). To compare our results of the exchange via ebullition with some available studies, the diffusive  $\text{CH}_4$  flux at the sediment/water interface of Lake Rot was estimated from the  $\text{CH}_4$  concentration gradient in the upper cm of the sediment. Roughly approximating this gradient with the  $\text{CH}_4$  concentration difference in the lake water and determined at 10 cm sediment depth, the diffusive flux is in the range of  $1.3 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ ,  $\sim 1/3$  of the observed  $\text{CH}_4$  flux via ebullition. However, it is noted that this is a minimum estimate as the exact distribution of  $\text{CH}_4$  between pore water and bubbles in the sediment pore space is unknown.

The total  $\text{CH}_4$  flux from Lake Rot calculated by adding up the estimated diffusive flux and the mean  $\text{CH}_4$  flux<sub>Ar-Xe</sub> via ebullition is  $4.5 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ . The total  $\text{CH}_4$  flux agrees with the range of  $\text{CH}_4$  fluxes through the sediment/water interface in North American lakes ( $4.5 - 6.1 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ , Bastviken et al., 2008). In the Swiss Lake Wohlen higher  $\text{CH}_4$  fluxes from the sediments were reported ( $\sim 9.3 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ , Del Sontro et al., 2010). In a previous study on Lake Rot (Schubert et al., 2012)  $\text{CH}_4$  fluxes through the water/atmosphere interface were determined during peak emissions in wintertime when the water column is mixing. Although this “atmospheric”  $\text{CH}_4$  flux of  $\sim 4 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$  is not directly comparable to our results, due to the unknown  $\text{CH}_4$  amount within the water column of Lake Rot prior to mixing, the two estimates reasonably agree.

As the noble gas distribution within the sediment column of Lake Rot virtually remains constant on the time scale of several years, we are tempted to interpret our  $\text{CH}_4$  flux estimate from three sediment cores as being representative for the entire lake, particularly as its sediments are rather homogeneous in space.

## 4.2. Noble gas data from Lake Lungern

Lake Lungern is characterized by an elevated trophic status and is subject to extreme water level variations due to its utilization as a hydropower reservoir. This water level varies seasonally, whereby the water level is high in summer and low in wintertime ( $\sim 15 - 20$  m annual amplitude).

Figure 3: Gas dynamics in Lake Lungern at the different sampling sites (A1, A2, C, D; see Fig. 1). Graphs showing the determined noble gas concentrations versus sediment depth, are combined with a conceptual drawing of the bubble dynamics in Lake Lungern (lake water is presented in dark grey, the sediment in light grey and the position of sampled sediment cores are marked as black rectangle): **Sample A1** During summer the water level is at its highest and virtually stable from June to September. **Sample A2** At some locations  $\text{CH}_4$  is emitted virtually continuously. **Sampling period B** During lake level lowering the pressure release in the sediment results in bubble formation and emission. Note no cores were taken during lowering the water level in the reservoir. **Sample C** The lake level is at its lowest in winter and early spring, when part of the sediment is falling dry and is exposed to the atmosphere, i.e. air partly enters the sediment producing an unsaturated zone. **Sample D** With rising water level air gets entrapped in the sediment.

In summer, during a period of stable high water level, an echosounder survey (e.g. Del Sontro et al., 2010) of the lake bed of Lake Lungern was conducted. During this survey active gas bubble emission was observed in the southern part of the lake in the region of two inflowing rivers (see Fig. 1). This zone of river/lake transition has often been reported to be the zone of most active  $\text{CH}_4$  emission (e.g. Del Sontro et al., 2011; Harrison et al., 2017; Beaulieu et al., 2017). Sediment samples from different sites (see Fig. 1) were taken to study the gas dynamics related to the observed active  $\text{CH}_4$  ebullition in the southern part of Lake Lungern and to infer possible seasonal variability of  $\text{CH}_4$  emissions in response to seasonal lake level changes.

The characteristics of sampling sites are described in the following (see Figs 1, 3 and 4):

- **Sample A1/A2** taken during high water level in summertime. At the site where A1 was recovered no bubbles were detected, but at the sites where A2 samples were recovered active bubble emission was observed.



- **Sampling period B** Note: no sediment cores were taken during lowering the reservoir water level. However, during this phase strong gas ebullition ( $\text{CH}_4$ ) was observed at the water/air interface.
- **Sample C** taken during low water level in wintertime, only 5 cm of water was overlying the sediment.
- **Sample D** taken during rising water level from a site that had been fallen dry during winter.

In the following the results of the noble gas analyses at each sampling point are discussed:

**Sample A1:** As no bubbles were detected at the site where sample A1 was recovered, it was chosen to be representative for the “background” noble gas concentration in the sediments of the southern part of Lake Lungern. Although no bubbles could be observed by eye in the retrieved sediment core, noble gas concentrations in the uppermost 10 cm of the sediment are depleted relative to ASW. Most likely, and in analogy with Lake Rot, such depletion results from past secondary gas exchange between noble gases dissolved in the pore water with gas bubbles formed in the sediment and subsequent bubbles emission.

**Sample A2:** In the southern part of Lake Lungern the sediments are composed of a complex interlayering of sands and fine grained loam (see Fig. 4, panel J). The sand layers are expected to be characterised by a larger permeability for gases while loam layer are expected to be a barrier for gas transport. During low water level in the winter a partial erosion of the dry sediment was observed. The inflowing rivers carved trenches in the sediment (see Fig. 4, panel J and K). In summer, during high water level, these trenches were easily detectable by echo-sounding and an active and continuous bubble emission was observed from the bottom of these trenches (see Fig. 4, panel K). These spots of continuous gas emission were detected in several sampling campaigns in different years (2012, 2013). Three sediment cores were taken at such active spots by precisely positioning the gravity corer with the aid of the echosounder. In addition, gas bubbles were collected with a funnel, which was also precisely placed over the active site using a side scan sonar.

Noble gas concentrations in the sediment pore water were found to be strongly depleted relative to the expected ASW concentration throughout all sediment cores taken from A2. Noble gas depletion at A2 is more pronounced and depletion is observed up to deeper layers of the

sediment than at A1. This indicates that the gas emissions from A2 are significantly stronger than at the background position A1. The gas collected in the funnel consisted mainly of CH<sub>4</sub> gas and did not contain any detectable amounts of noble gases. The absence of noble gases indicates that the CH<sub>4</sub> gas might derive from a sediment layer where noble gases are strongly depleted due to the virtually continuous stripping by gas bubbles leaving the sediment. The composition of noble gases argues for a biological origin of the CH<sub>4</sub> gas, as elevated He abundance would be expected in deep terrigenous gas (e.g. Etiope et al., 2002). Indeed the captured CH<sub>4</sub> was found to be isotopically light ( $\delta^{13}\text{C} \approx -63 \text{ ‰}$ ). These results contradict the earlier interpretation suggesting that the emitted CH<sub>4</sub> might migrate in from deeper fossil depots in the crust (Bossard et al., 1981).

Figure 4: **I** Dry sediments of Lake Lungern in winter 2015 during low water level (pictures: Tyroller, 2018). **J** Inflowing river and sediment layers in winter 2015 excavated by the inflowing river during low water level. **K** Side scan sonar image with spots of active bubble emission near site A2 (see Fig. 1 and 3) in Lake Lungern (2012). Rising bubbles appear as parallel sloped stripes.

We hypothesize that the virtually continuous bubble flux emitted from the trenches in the southern part of Lake Lungern (see Fig. 4 panel J and K) originates from a reservoir of microbial CH<sub>4</sub> gas that accumulated beneath the hardly permeable clay layer. If this low permeable layer is “missing”, due to erosion of the inflowing river, CH<sub>4</sub> can escape along preferential pathways forming the continuous gas emission observed.

**Sample C:** Similar to A1 no active bubble emission was observed at the site where sample C was recovered during high water level in summer. The sediments were sampled during wintertime when the lake water level was at its lowest, with only 5 cm of overlying water column. Due to the low winter temperatures (between + 4 and - 5 °C) the biological activity in the sediment was assumed to be negligible (see e.g. Duc et al., 2010). The CH<sub>4</sub> concentrations in the sediment were found to closely agree with the local saturation concentration, i.e. the ambient partial pressure in the sediment. Such elevated CH<sub>4</sub> concentrations are interpreted as remaining from the production in the warmer season, whereas it is assumed that excess CH<sub>4</sub> had escaped as

bubbles during water level lowering. Noble gas concentrations were found to be depleted with regard to the ASW concentration up to a sediment depth of 40 cm. The depletion pattern is interpreted to be a result of enhanced  $\text{CH}_4$  bubble formation caused by the pressure release during lowering of the lake level. Compared to A1, the noble gas concentrations in sample C are more depleted. This pronounced depletion of noble gases might result from lake level lowering, since water drawdown is expected to enhance the  $\text{CH}_4$  emission and noble gas stripping. Even acknowledging that our data set (one core at high and one core at low lake level) is very limited and not really representative for the lake, the results tend to indicate that water level lowering and enhanced gas ebullition from the sediment are linked. This finding is in accordance with a recently published study using passive gas traps to determine  $\text{CH}_4$  flux from North American reservoirs which found that emissions increase by up to  $\sim 80\%$  during lake level lowering (Beaulieu et al., 2017). It is noted that the continuous monitoring of the  $\text{CH}_4$  emissions upon lake level drawdown with common methods (Beaulieu et al., 2017; Harrison et al., 2017) is time consuming and labour intensive. Thus, noble gas analysis in the pore water of lacustrine sediments at different lake levels (e.g. before and after reservoir drawdown) opens a novel experimental route to study the dynamics of gas ebullition in response to lake level changes.

**Sample D:** Sediment cores were taken in June 2015 in the littoral zone ( $< 9$  m water depth) in an area that had fallen dry in winter time. Due to the highly compacted texture, only the uppermost 15 centimetres of the sediment column could be sampled by gravity coring. In all samples a surplus of atmospheric gases were observed. Such noble gas excess could indicate a contamination with air. However, such contamination is expected to affect single samples in a rather erratic manner but not to occur systematically in all samples from a particular site. Therefore, we are tempted to interpret the atmospheric noble gas concentrations and the corresponding air excess in the sediments as a real signal in the pore water of D sampling site. We note, that the method used here for the determination of noble gases dissolved in sediment pore waters has been proven to be very robust against air contamination (Brennwald et al., 2013).

The pore waters are not only supersaturated with atmospheric gases, but the noble gases are elementally fractionated in favour of light noble gases ( $\Delta\text{He} > \Delta\text{Ne} > \Delta\text{Ar} > \Delta\text{Kr} > \Delta\text{Xe}$ ). Such enrichment of light noble gases is characteristic for excess-air resulting from re-dissolution

of air bubbles entrapped in porous media upon a rising hydrostatic pressure (e.g. excess-air formation in groundwater, for reviews see Kipfer et al., 2002; Klump et al., 2007; Aeschbach-Hertig and Solomon, 2013, and references therein).

The fact that the site where sample D has been recovered had fallen dry in the winter season suggests that the noble gas excess observed might result from air, that entered the sediment pore space during exposure to the atmosphere. The subsequently rising water level results in part of this air being entrapped. As a consequence of the rising water level, the in situ hydrostatic pressure in the sediment pore space increases (e.g. 0.1 atm per meter of overlying water column) and the entrapped air bubbles (partly) redissolve, causing the observed noble gas excess in the surrounding pore water.

Although the given interpretation is rather speculative, it seems to be supported by the results from a hydroacoustic survey on Lake Lungern in July 2006 (Ostrovsky, 2009). This study reports very small bubbles to be emitted from the littoral zone ( $< 7$  m water depth). There, the surrounding lake water was found to be extremely oversaturated with oxygen (160 to 170 %). As strong microbial  $\text{CH}_4$  production in the sediment pore water is unlikely in such an  $\text{O}_2$ -rich environment, we suggest that the bubbles observed might not consist of  $\text{CH}_4$ , but of air escaping from the recently submerged sediment being loaded with entrapped air during times of rising reservoir level. During the ascent of such small bubbles, air exchanges with the gases dissolved in the surrounding water producing the observed oxygen excess (see Holzner et al., 2012).

Oxygen is rapidly consumed by micro-organisms in the sediment pore water and thus its dynamics cannot easily be determined directly. In reservoirs like Lake Lungern, which are subject to strong lake level variations, noble gases are an excellent tool to trace the amount of oxygen entering the sediment pore water by means of the direct injection of air in the sediments as a result of falling dry during low water level periods. The “winter-dry” sediments of Lake Lungern receive a significant load of oxygen entering the sediment pore water in response to the entrapped air dissolution during the rising lake level.

Accepted methods to interpret the occurrence of atmospheric noble gases in aquatic systems were used to convert the noble gas concentrations into different components (e.g. ASW and injected amount of air, for details refer to Kipfer et al., 2002; Aeschbach-Hertig and Solomon, 2013). The excess-air ( $A$  [ $\text{cm}^3 \text{ STP/g}$ ]), that was injected into the sediment by the partial dissolution of entrapped air was quantified by applying the closed system equilibrium model (CE,

see Aeschbach-Hertig et al., 2000) and our well accepted code noble 90 (Aeschbach-Hertig et al., 1999, 2000; Kipfer et al., 2002). The dissolved  $O_2$  concentrations in response to such excess air formation were estimated to range between 4 and 25 mg/l  $O_2$  per litre of pore water, an amount which is comparable with the expected atmospheric equilibrium concentration ( $\sim 12$  mg/l ( $O_2$ ), 4 °C, 687,5 m.a.s.l.).

Thus, this study makes the case that noble gas analysis in pore water of sediments might facilitate the quantification of the  $O_2$  input to the sediment pore water as a result of excess air formation in response to seasonal water level variation in a reservoir.

## 5. Conclusions

The noble gas concentrations in the sediments of Lake Rot and Lake Lungern reflect the interaction of the porewater with a free gas phase. In the hypertrophic sediments of Lake Rot, gas formation is mainly driven by the microbial activity in the sediment pore water, whereby the layer from 25 to 45 cm sediment depth shows maximum activity (i.e. maximum  $\text{CH}_4$  production). A pronounced concentration gradient of noble gases ranges from ASW concentrations at the water/sediment interface to a strong depletion of noble gases relative to ASW concentrations in the zone of maximum microbial activity. Such depletion indicates stripping of dissolved gases by escaping gas bubbles. The gradient of increasing noble gas depletion with sediment depth can be interpreted to reflect the noble gas flux through the pore water and into the gas bubbles formed in the zone of maximum microbial activity. The repeated determination of very similar noble gas gradients and the  $\text{CH}_4$  peaks in different years indicates the overall gas dynamics operate at steady state and allows the  $\text{CH}_4$  flux from the sediment to the lake water to be calculated. The determined  $\text{CH}_4$  flux,  $5.1 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ , falls well in the range of available  $\text{CH}_4$  fluxes from other lakes ( $4.5 - 6.1 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ , see Bastviken et al., 2008) and agree with the range of  $\text{CH}_4$  emissions measured at the lake surface of Lake Rot ( $4 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ , Schubert et al., 2012).

In Lake Lungern noble gas results indicate the gas dynamics to be mechanistically linked to the seasonal variation of the lake water level. The decreasing lake level appears to trigger  $\text{CH}_4$  bubble emission as a result of the reduced hydraulic pressure. In parts of the lake gas, mainly  $\text{CH}_4$ , seems to accumulate beneath a clay layer and was observed to be emitted from trenches and other morphological structures in the sediment floor and to form a virtually continuous stream of bubbles. At shore sites that had fallen dry during periods of low water level, atmospheric noble gases were found to be in excess. This noble gas surplus is interpreted to result from air being entrapped and partly dissolved in the pore water when the water level rises again. Excess air formation also leads to  $\text{O}_2$  being in excess during air/water partitioning. Excess air formation in lake sediments in response to lake level variations is identified as an additional process in aerating lake sediments and might thus influence the lacustrine carbon cycle.

Overall, the combination of  $\text{CH}_4$  and noble gas analysis was shown to be a promising tool to trace gas dynamics in sediments and to analyse the physical exchange of reactive species such as

CH<sub>4</sub> and O<sub>2</sub>.

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Novel approach to quantify gas ebullition from CH<sub>4</sub> supersaturated lake sediments

Combined determination of CH<sub>4</sub> and noble gas concentrations reveals past gas dynamics

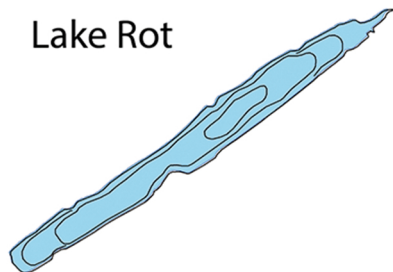
Lake level drops cause degassing in the benthal zone

Noble gas concentrations indicate entrapped air in seasonally dry littoral sediments



0 100 km

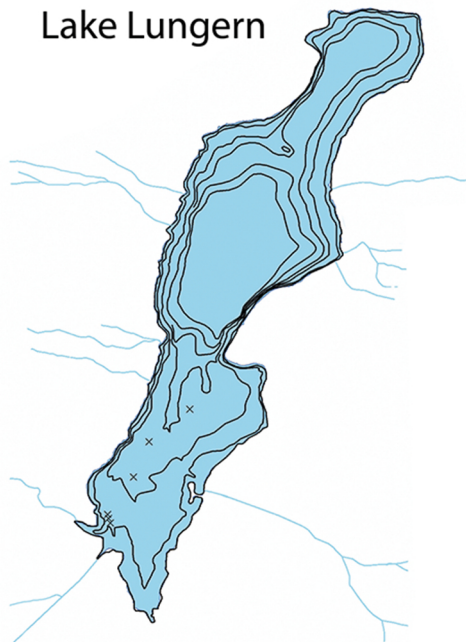
## Lake Rot



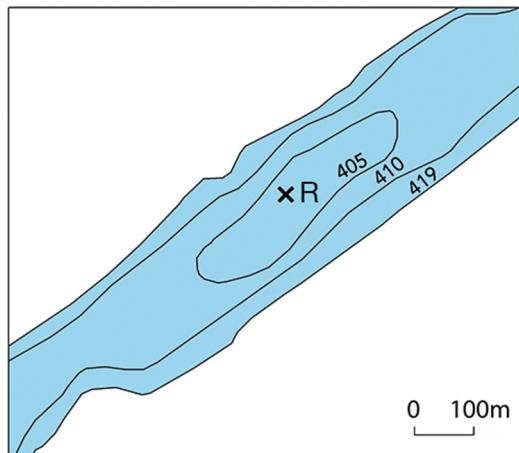
0 0.5 1 km



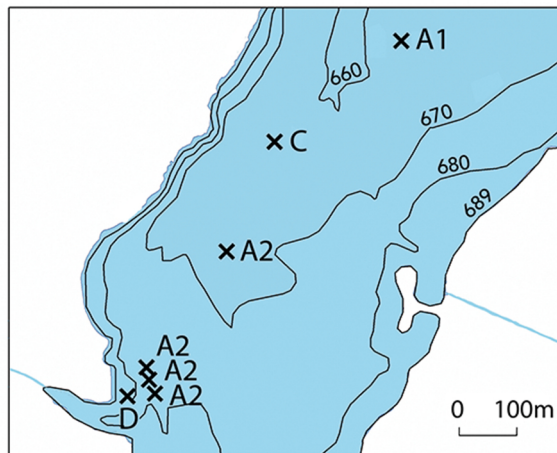
## Lake Lungern



0 0.5 1 km



0 100m



0 100m

Figure 1

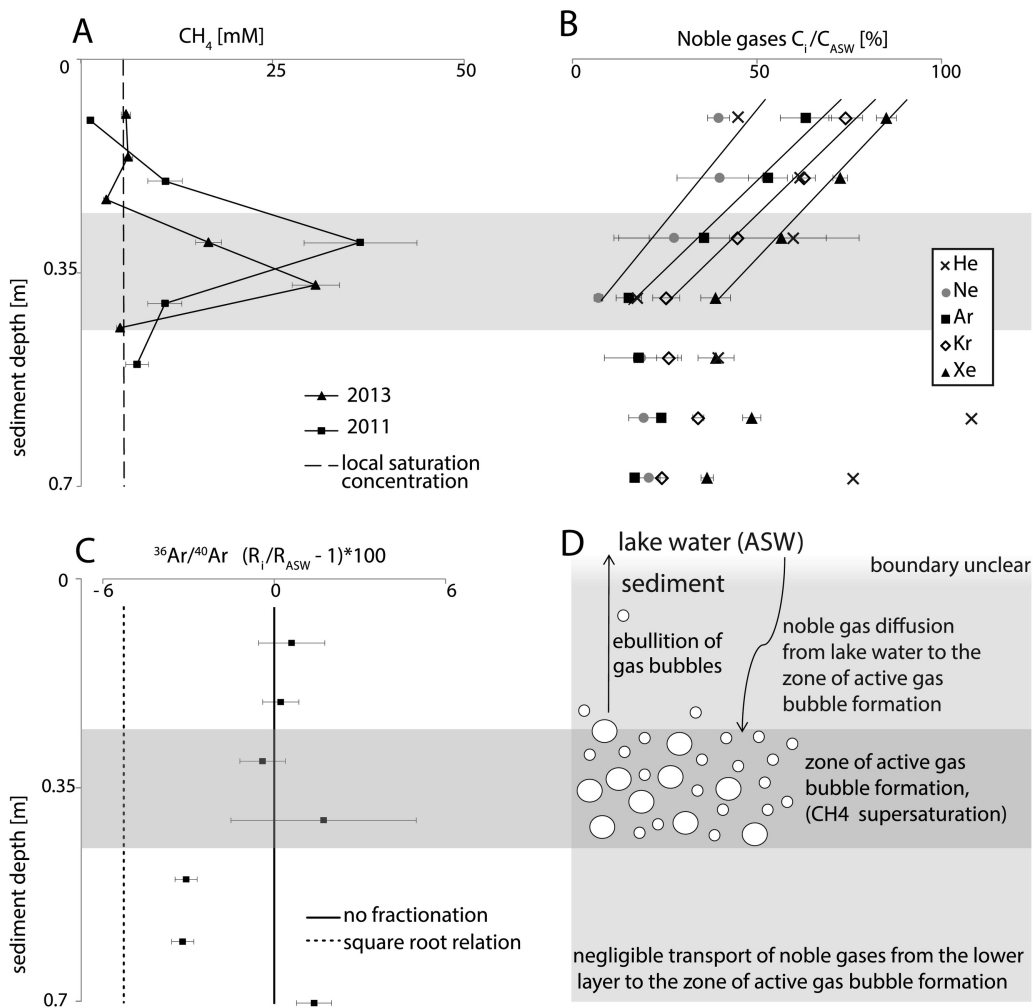


Figure 2

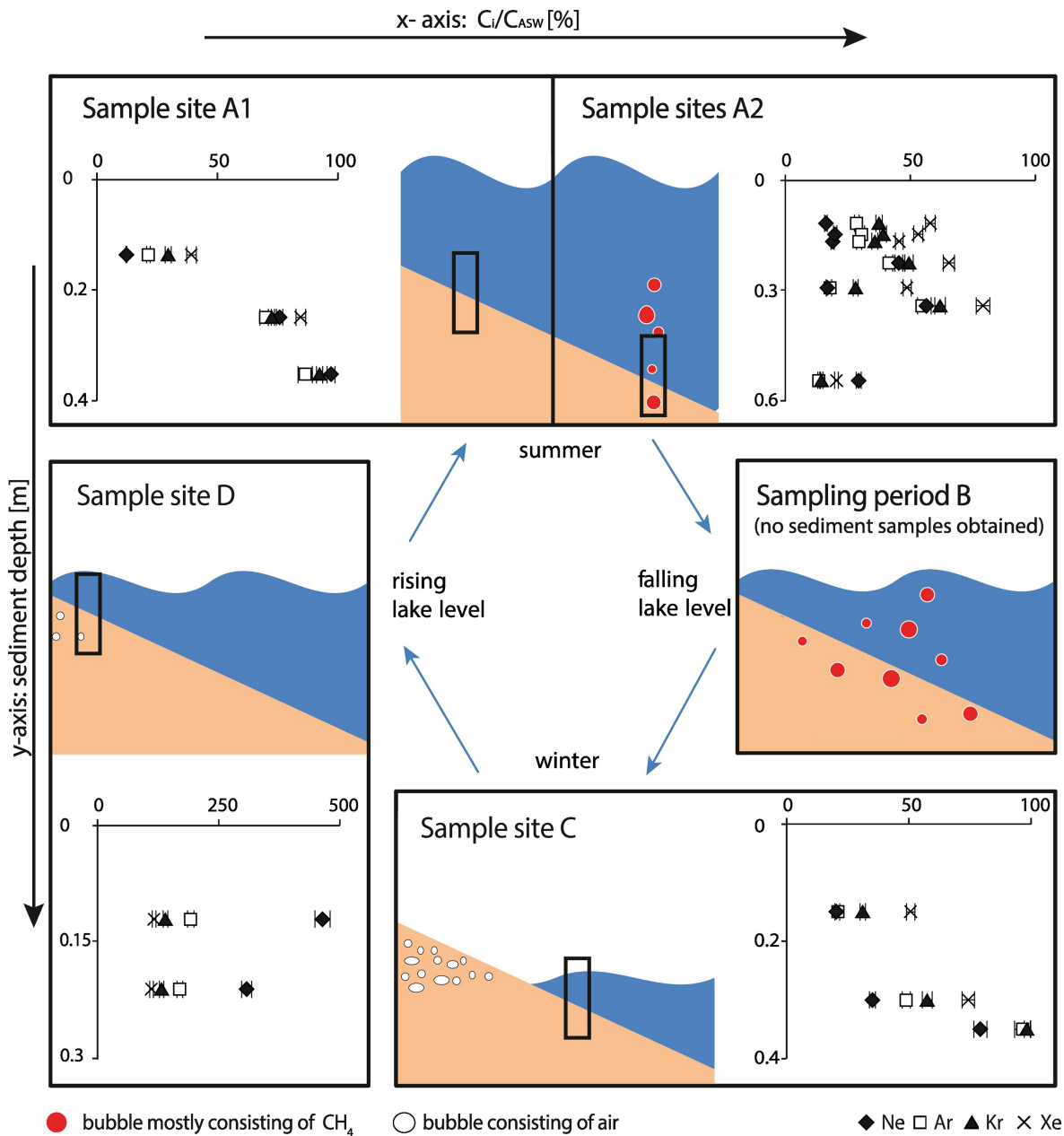


Figure 3



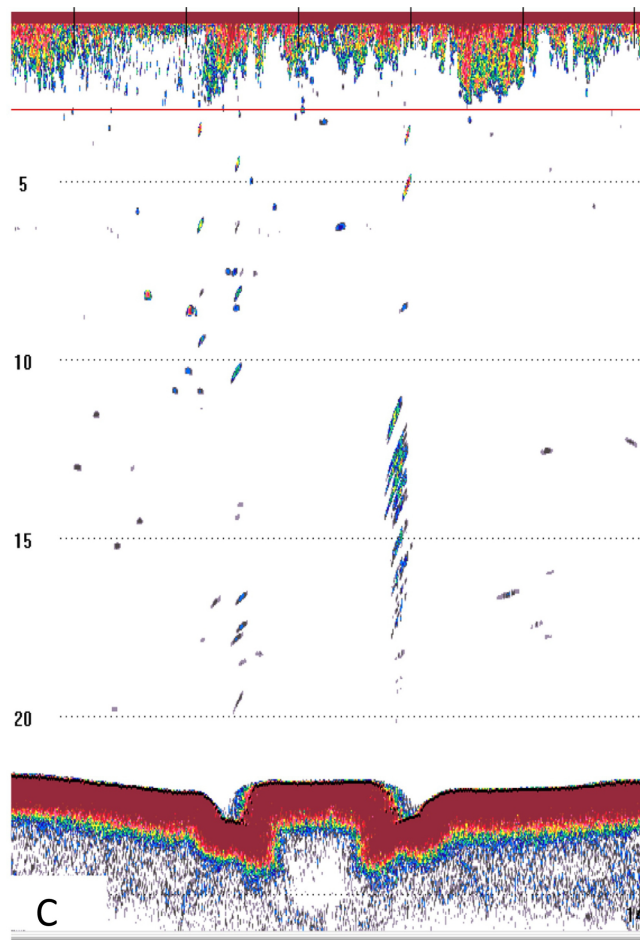
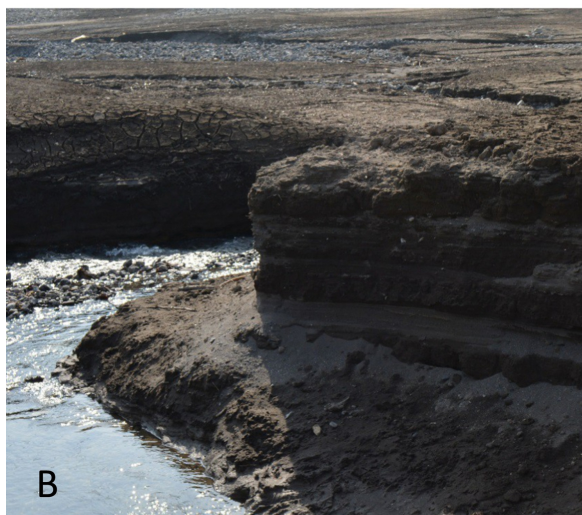
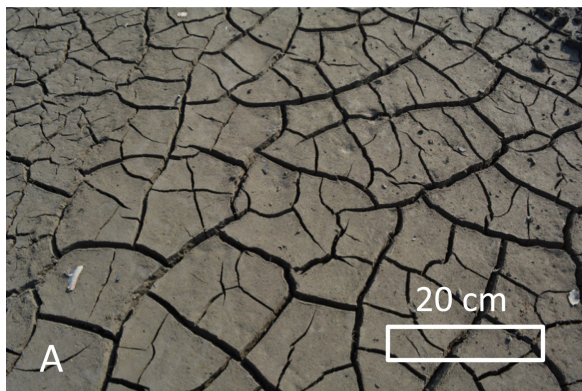


Figure 4