Lake Kivu – A Multi-Methodological Approach Tackeling Questions on Age, Dynamics and Gas Concentrations

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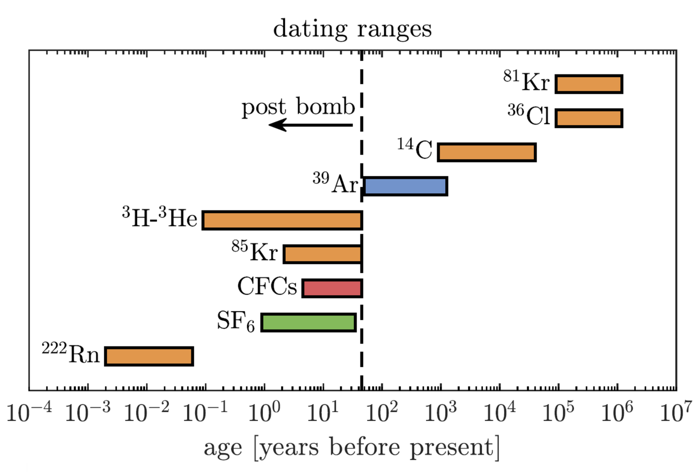
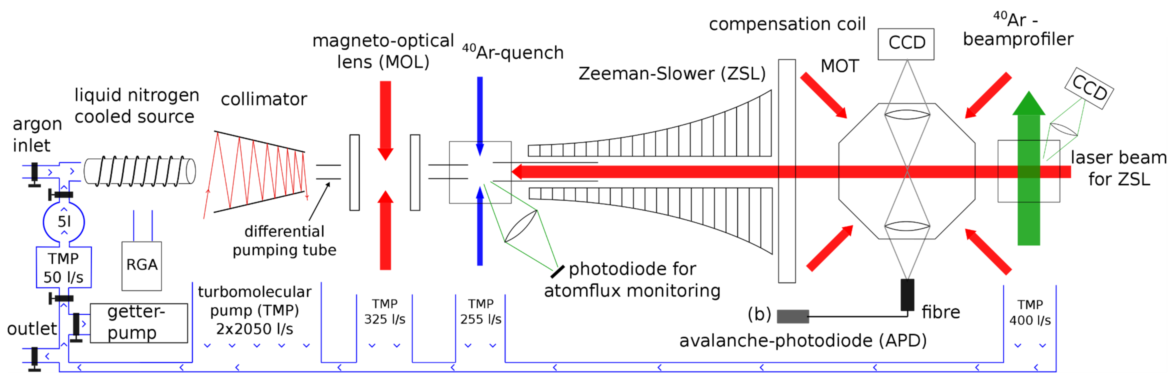
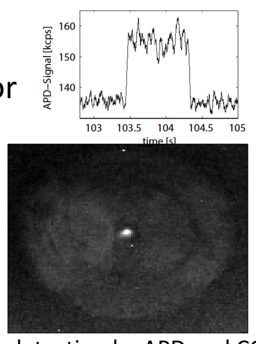
Argon Trap Trace Analysis – ArTTA

^{39}Ar is a cosmogenic radioisotope with a halflife of 269 years. Its chemical inertness and quasi constant input function makes it a very powerful dating tracer covering ages in between 50 and 1000 years corresponding to timescales important in hydrological systems. ^{39}Ar has long been restricted to groundwater studies due to its long lifetime ($\tau_{1/2} = 269\ y$) and its extremly low abundance of $^{39}Ar/Ar = 8 \cdot 10^{-16}$ requiring sample sizes about 1000 L for low level counting. ArTTA makes the transition from decay counting towards direct atom counting and thus reducing required sample sizes down to 0,5 ml_{STP} pure Argon, which corresponds to about 1L of water or 5 – 10 kg of glacier ice.





Setup of our current ArTTA machine. A liquid nitrogen cooled plasma discharge source provides meta stable 39Ar necessary for optical cooling. A Collimator and a 2D magneto optical trap (MOT) collimate and narrow the atom beam, an increasing B-field Zeeman-slower slows the atoms down, before they are trapped and detected in a 3D MOT.
Our most resent campaigns you can find here [1] and here [2]

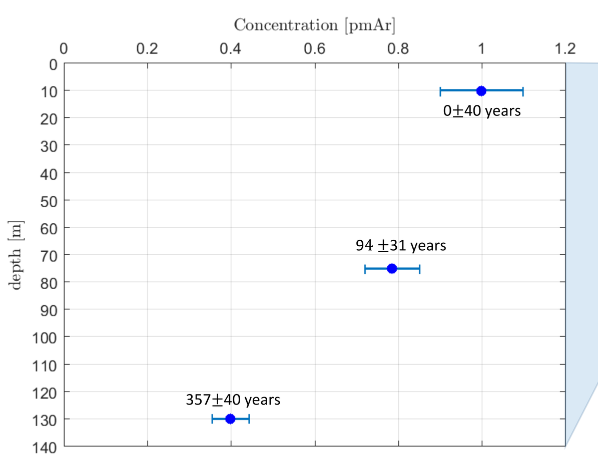


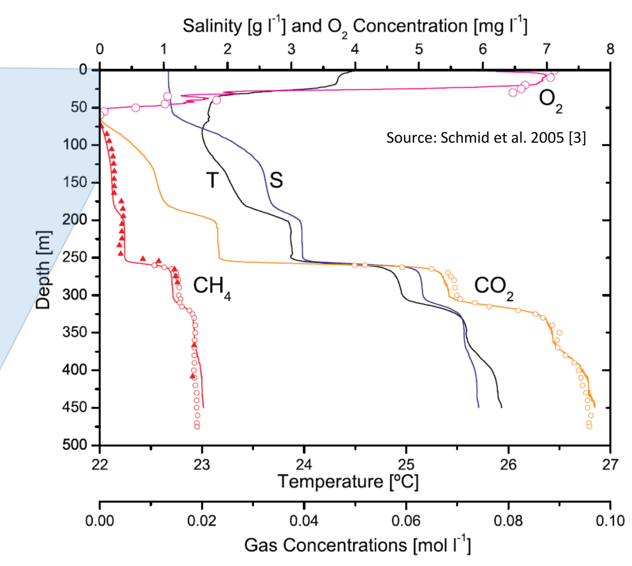
Single Atom detection by APD and CCD-Camera

ArTTA relies on the quantum optical method of laser cooling commonly used in atomic physics. Due to an isotopic shift and nuclear spin effects the resonance frequency of ^{39}Ar is shifted about 0,001 nm in respect to other Ar isotopes. The necessity of the consecutive scattering of $> 10^6$ resonant photons for laser cooling and trapping leads to the distinguishability from 39Ar against its huge background by utilising single atom detection. The detection rate of ^{39}Ar atoms and comparison to artificial reference samples then leads to the relative ^{39}Ar content and thus the tracer age.

Lake Kivu Residence Times

Lake Kivu is an meromictic East African Rift Lake between Rwanda and the Democratic Republic of Congo with a maximum depth of 485m and a mixed layer of 60 – 80 m. Lower layers are very stable and deep layers contain extremely high amounts of methane and carbon dioxide. The large storage of methane is aimed to be used as an energy ressource but potential limnic eruptions may be a fatal threat to residents [3]. 39Ar dating with ArTTA offers the possibility to date the different layers and might give valuable input to flow model calculations.
In spring 2018 and in summer 2019 we were able to gather gas and water samples from lake Kivu and present now the first 39Ar dating of lake water using ArTTA.

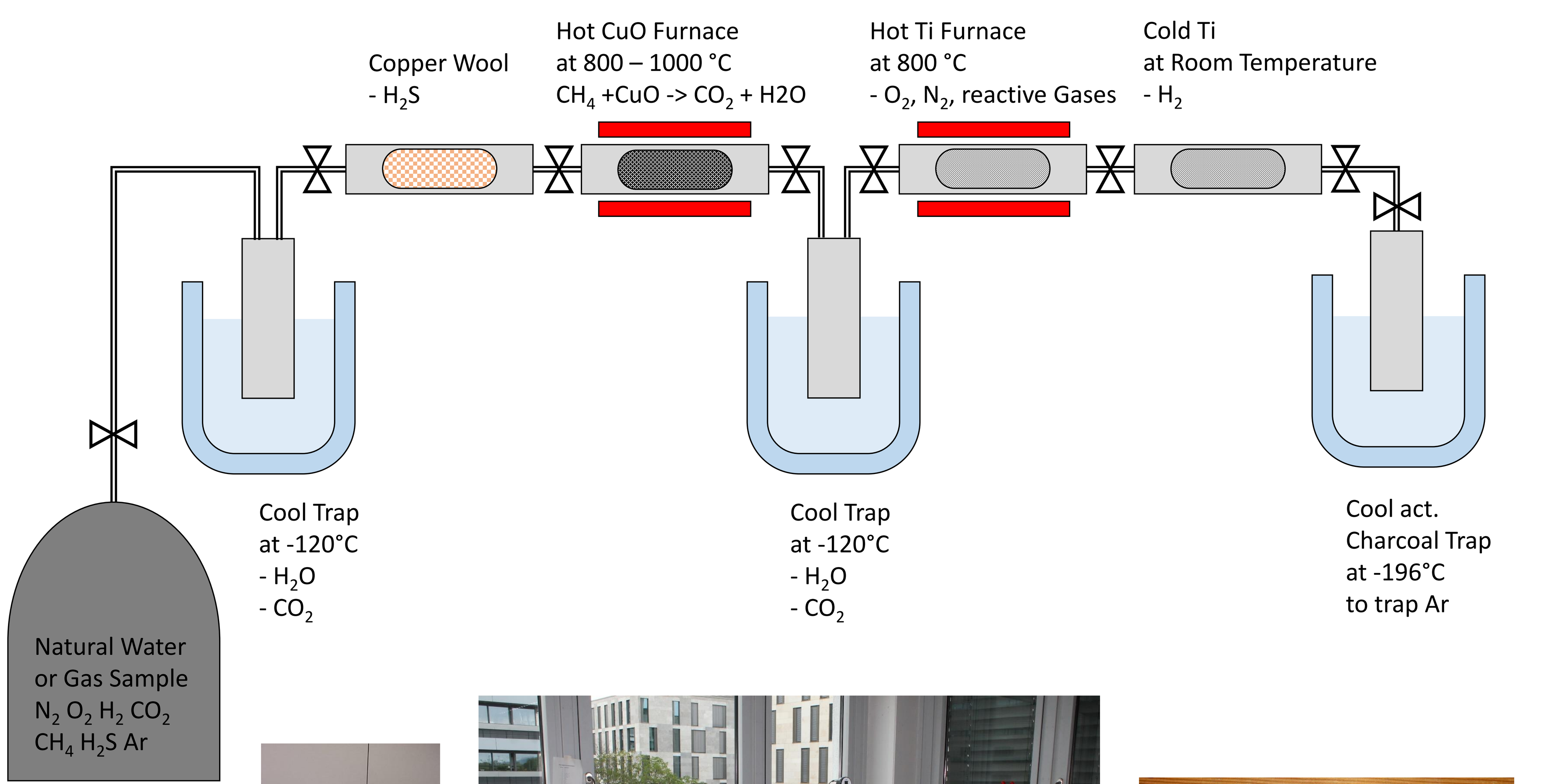




Lake Kivu on the border between Rwanda and DRC.
The red cross indicates the sampling location.

This project is in cooperation with M. Schmid and F. Bärenbold from EAWAG Aquatic Research Institute, Luzern

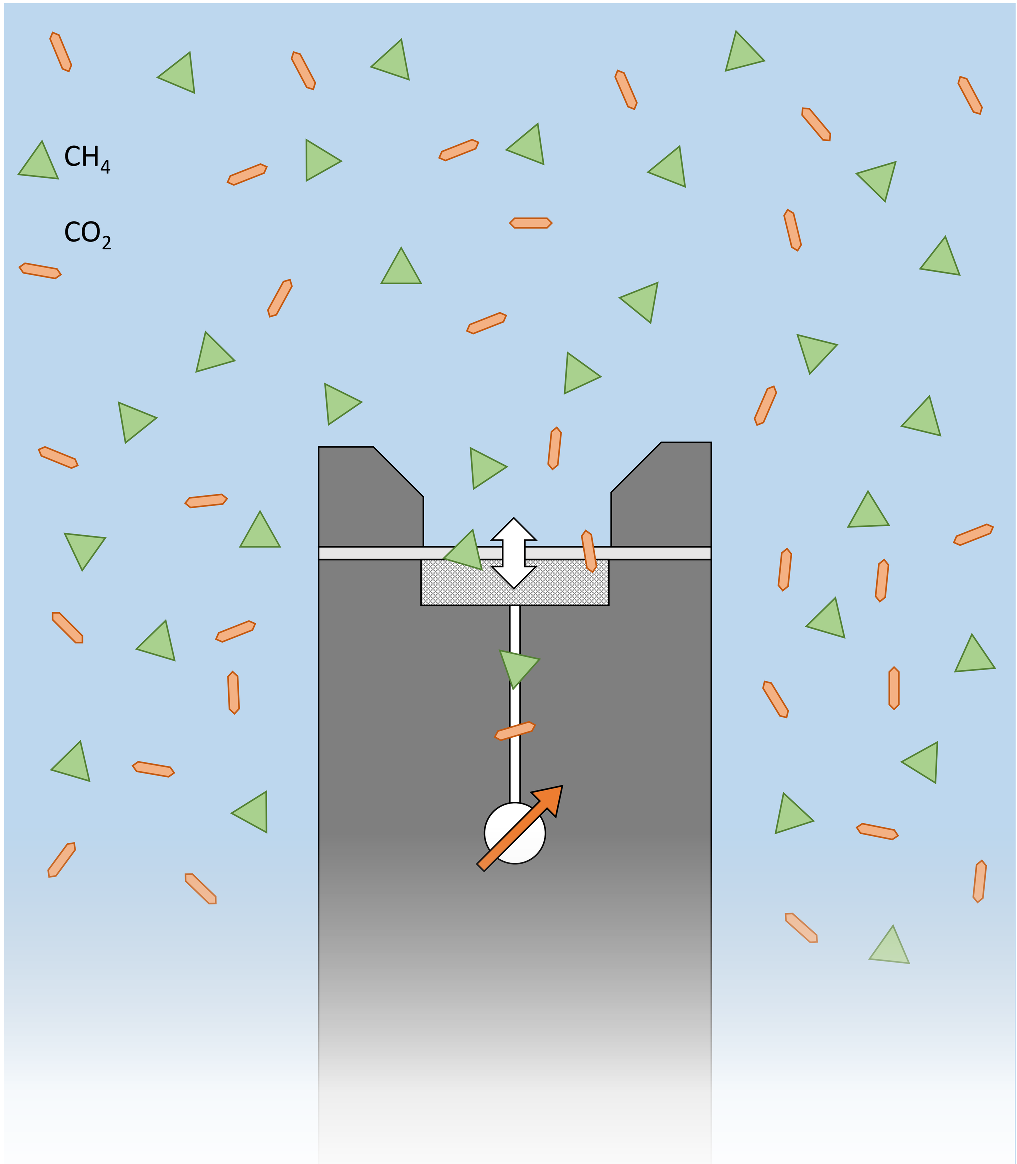
Lake Kivu Sample Preparation and Handling



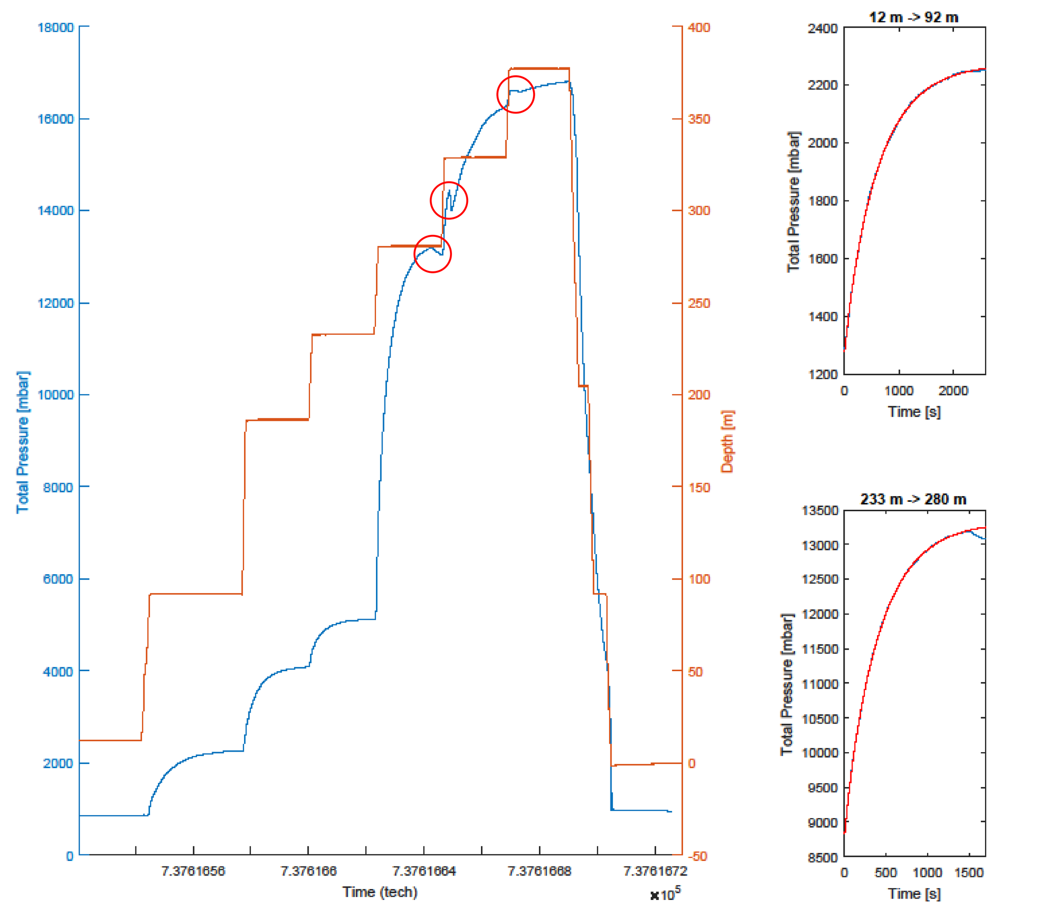
For the preparation of the water and gas samples from lake Kivu we use a slightly adapted preparation line to isolate Argon: The principle of the preparation lies in the chemical inertness of argon, passing the gas through two hot and cold titanium-sponge getters, where all reactive gases are bound and the noble gases remain. In addition to this standard procedure we need to handle high amounts of CO_2, CH_4 and H_2S. For this purpose we are reacting H_2S with pure copper, binding it via the production of coppersulfite, we guide the gas through hot CuO to react CH_4 to CO_2 and H_2O and trap CO_2 in cold traps resublimating it to dry ice. Consequent treatment of the remaining gas mixture leads to Argon purities around 99%, perfectly suitable for ArTTA. Our typical standard sample sizes range from 0,5 – 20 L of water or 5 – 10 kg of ice achieving argon volumes of typically 0,5 – 10 ml_{STP}

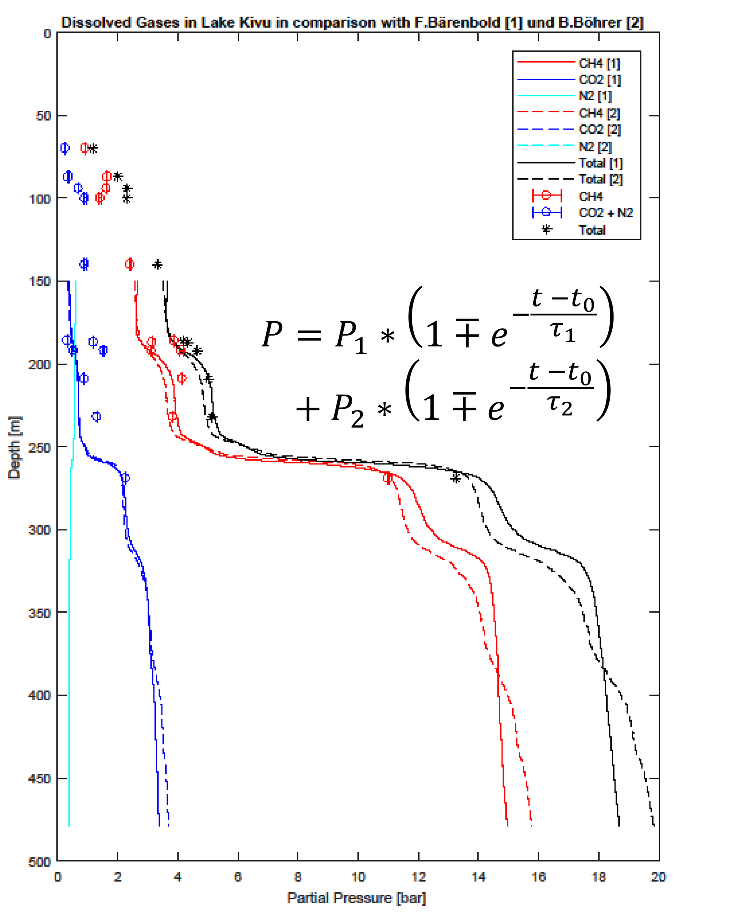
Investigating a quick (and dirty?) Method to Measure Partial Dissolved Gas Pressures

Modified Pro Oceanus Mini TDGP Probe with Sea & Sun CTD Probe



Our measurement device is a modified total dissolved gas sensor by Pro Oceanus. It has been modified to be capable of measuring the very high total dissolved gas pressures in Lake Kivu, which are lying far beyond normally occurring values. During a measurement the dissolved gases (here mainly CO_2 and CH_4) are diffusing through a semi-permeable membrane, through a metal sinter mesh into a total pressure gauge, which is independent in gas composition.





Typical data from a pressure measurement run. The probe is submerged into the lake and halts at specific depths in order to wait for the pressure to equilibrate. This equilibration time now is the key to our approach. Assuming different migration times for different gas species one can expect for the measured total pressure to develop over time like a sum of bounded exponential growth functions, one for each gas species weighted by thei respective partial pressure and their specific migration time constants.

Resulting partial pressures in comparison to data by F. Bärenbold and B. Böhrer [4] gathered by equivalent methodologies. One can observe, that our obtained partial pressures are in good correspondence although showing some fluctuations especially in the range of low pressures. The data shown are reduced to the steps, where the pressure develops like in the described model. Obvious casualties (e.g. as marked with red circles) can't be explained by now, showing the need of further investigations.

Our first results of investigating this method to measure the partial pressure of gases using only a total dissolved gases pressure probe are showing us, that this method can offer the possibility for a very easy measurement routine for an otherwise absolutely non trivial problem. The very high gas pressures occuring in this lake are causing immense problems e.g. for gathering samples and finding appropriate equipment and thus are demanding highly educated scientist and strong economical possibilities. Regarding Lake Kivu's location on the border between Rwanda and the Democratic Republic of Kongo one sees the need for a cheap and easy to use alternative for the governments programs monitoring the lake's gases for economic and risk management purposes. If we might be able to refine this method improving reliability and accuracy it could bear the possibility to give these countries a quick and easy - and hopefully not so dirty anymore - tool.

This project is in cooperation with B. Böhrer from Umweltforschungszentrum UFZ Magdeburg

References:

1) Ebser et al., 39Ar dating with small samples provides new key constraints on ocean ventilation. *Nature Communications* (2018)9:5046
2) Feng et al., Dating glacier ice of the last millennium by quantum technology, *PNAS April 30, 2019 116 (18)*
3) Schmid et al., Weak mixing in Lake Kivu: New Insights indicate increasing risk of uncontrolled gas eruption,*Geochem. Geophys. Geosyst., 6,* Q07009
4) Bärenbold et al., Updated dissolved gas concentrations in Lake Kivu from an intercomparison project, *in review 2019 Limnology and Oceanography*