

Oxygen isotope micro analysis of diatom silica from El'gygytyn Crater Lake, NE Russia

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Introduction

In non-carbonate lakes of cold regions, where no other bioindicators are available the analysis of oxygen isotopes from diatom silica in sediment cores has reached importance for reconstructing the paleoclimate. A new instrumental approach for samples has been developed to provide a better chronological resolution and to expand the method to periods where less biogenic silica is available. Sample material from Lake El'gygytyn (Center: N 67°30', E 172°5', core LZ 1024) will be analysed and a $\delta^{18}\text{O}$ curve of the last about 280.000 years will be generated. The Lake is situated inside of a meteorite impact crater formed app. 3.6 million years ago (Melles, 2007) and hence offers a unique option to fill the spatial gap of locations in the NE Siberia where paleoclimate reconstructions are rare.

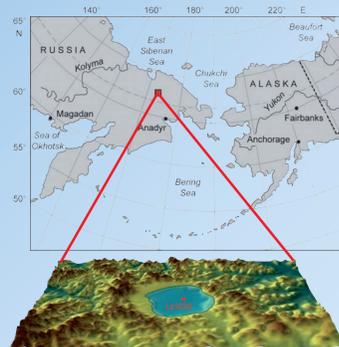


Fig. 1: Geography and Digital area model of the Surrounding area of Lake El'gygytyn (Courtesy: C. Kopsch).

Expeditions & expectations

Three expeditions to the lake were carried out in 1998, 2000 and 2003. In 1998 the first two 13m long sediment cores were recovered and revealed a promising chronology and paleoclimate record (Brigham-Grette et al., 2005 and 2007). It is expected that El'gygytyn Crater Lake potentially contains the longest, most continuous terrestrial record of past climate change in the entire Arctic back to the time of impact (Brigham-Grette et al., 2007). The processes taking place in Lake El'gygytyn basin lead to changes in limnogeology and biogeochemistry that reflect robust changes in the regional climate and paleoecology over a large part of the western Arctic (Nolan et al., 2007).

The analysis aims on the core LZ1024 drilled in 2003. The 13m long core was dated to max. about 280.000 years. The planktonic *Cyclotella ocellata-complex* is persistent through a variety of climate conditions and present throughout the core (Cherapanova et al., 2007; Cremer et al. 2003). Around 200 samples will be analysed for oxygen isotopes to add a strong record for reconstructing the palaeoclimate change.

Process I - Diatom extraction

To gain a pure diatom sample H_2O , organic material, carbonate, grain sizes bigger than $20\ \mu\text{m}$ and heavier than $2.1\ \text{sg}$ are removed with various chemical and physical separation steps (Fig. 2). For Lake El'gygytyn the *Cyclotella-ocellata complex* can be found mostly in the $0\text{-}10\ \mu\text{m}$ fraction whereas the species of *Pliocenicus costatus* is predominant in the $10\ \mu\text{m}$ to $20\ \mu\text{m}$ fraction, but only in the Holocene.

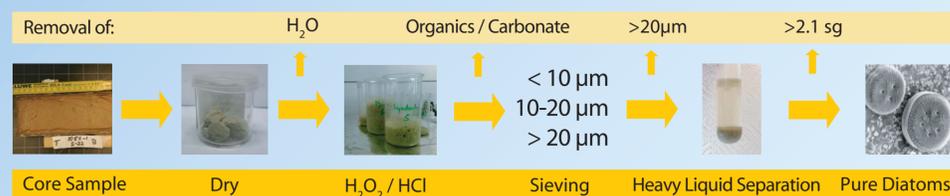


Fig. 2: Principle for the preparation of a pure diatom sample. After drying the sample, organic matter and carbonate is removed by adding H_2O and HCl . The wet sample is rinsed with deionised water until it is neutral and sieved over $10\ \mu\text{m}$ and $20\ \mu\text{m}$. A heavy liquid separation with Sodium-polytungstate is performed several times and possible micro-organic contamination is removed by a final cleaning step with perchloric acid and salpetric acid.

Process II - $\delta^{18}\text{O}$ Analysis

The bead formed by the extracted diatom sample is heated with a CO_2 laser under BrF_5 atmosphere to release the O_2 . The non-oxygen gas components are trapped, whereas oxygen passes on to the molecular sieve. It is then transferred to the mass spectrometer and compared with reference O_2 . The $\delta^{18}\text{O}$ value of the sample vs. VSMOW is then determined.

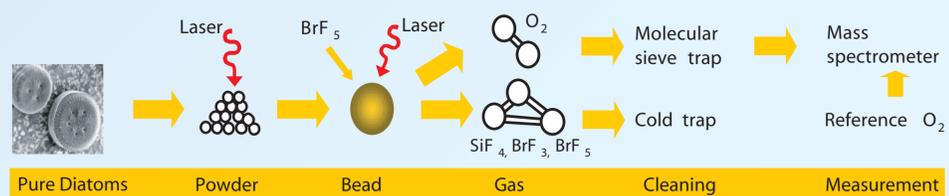


Fig. 3: Principle of the experimental procedure. After ground to powder and melted to a bead the sample is heated with a CO_2 laser under BrF_5 atmosphere to release the O_2 . The non-oxygen gas components are trapped in cold trap, Oxygen passes to the molecular sieve cooled with liquid nitrogen and is transferred to the mass spectrometer for isotope measurement.

Melting powder to beads

Standard or diatom material of 0.7 to $2\ \text{mg}$ is pressed into the holes of a Platinum plate and melted into beads. It is adequate to direct the defocused beam over the sample at first with an increasing power of $0.5\ \text{W}$, $0.6\ \text{W}$ and $0.7\ \text{W}$ (Fig. 4; 1). At each stage the move should follow a spiral starting from the center point to equally warm up the powder and evade parts of the sample spreading apart or a potential explosion of the sample. A light glow can

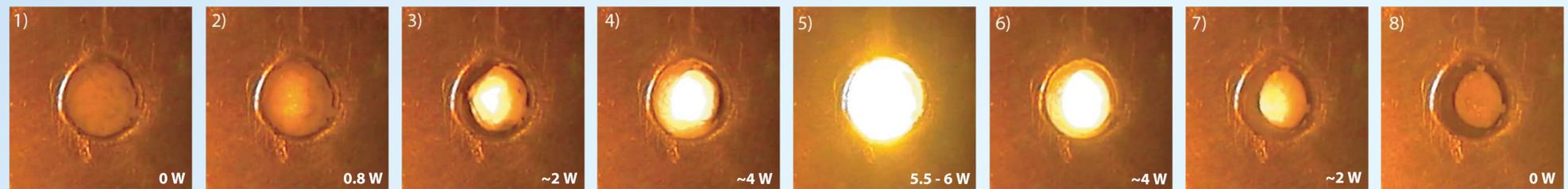


Fig. 4: The process of melting the powdered samples to beads takes about 5 to 10 seconds with a recommended laser power between $5.5\ \text{W}$ and $6\ \text{W}$. Picture 1 to 8 show the different stages of the sample in this process: Picture 1 shows the powdered sample where as in Picture 8 the finished bead can be seen.

be seen when $0.8\ \text{W}$ are applied (Fig. 4; 2). Then, the laser power is increased fast to $5.5\text{-}6\ \text{W}$ with this power stable for about 5 to 10 seconds (Fig. 4; 5). The power is then reduced to zero within 10 seconds. A bead is formed (Fig. 4; 8) with a calculated mass loss between 4% (NBS 28) lacking any water and 15% (Radiolarians/ Diatoms) due to chemically-bound water in the sample.

Preliminary Results

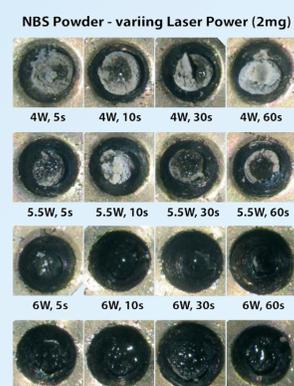


Fig. 5: Melting quartz standard (NBS 28) to beads with a varying in laser intensity and duration.

The IRMS was calibrated and optimised and the reproducibility of the reference O_2 tested ($< 0.1\ \text{‰}$). A heating device was constructed for the cold trap to hold the temperature at -150°C (formerly -196°C) since significantly better results could be achieved ($< 0.1\ \text{‰}$ as compared to $< 0.25\ \text{‰}$ before the change).

Focusing on the bead preparation the best beads were produced with the procedure described above. Figure 5 shows the different results for a variety of laser intensities and durations. No fractionation occurred with a laser power between $5.5\ \text{W}$ and $6\ \text{W}$.

As the O_2 reference itself is of unknown isotopic composition different masses of powdered and melted standard ($0.5\ \text{mg}$ to $3\ \text{mg}$) were analysed for $\delta^{18}\text{O}$. The two standards were used to calibrate the reference gas. Between $1.5\text{-}2.0\ \text{mg}$ (chosen interval) the standard deviation was $0.134\ \text{‰}$ ($n=20$) higher and lower mass intervals showed a significantly higher standard deviation (Fig. 6).

First tests on diatoms from Lake El'gygytyn show $\delta^{18}\text{O}$ values between $19\ \text{‰}$ and $23\ \text{‰}$ for surface sediments and the samples from the Holocene. The reproducibility is good when performing double measurements ($< 0.2\ \text{‰}$). This indicates that climate variations can be traced by analysing the $\delta^{18}\text{O}$ in diatoms. Next samples from Lake El'gygytyn are in the preparation phase and need to be analysed before drawing scientific conclusions.

However, the values in general seem to be slightly too low. Therefore tests with various preparation methods will be performed. Additionally, further tests to establish an internal diatom standard and ring tests with other laboratories are planned.

$\delta^{18}\text{O}$ (reference O_2) calibrated with NBS 28 and Campolungo		
0,5 bis 1,0 mg	Average	13,394
n= 8	Std. dev.	0,316
1,0 bis 1,5 mg	Average	13,66
n= 13	Std. dev.	0,23
1,5 bis 2,0 mg	Average	13,825
n= 20	Std. dev.	0,134
2,0 bis 2,5 mg	Average	13,794
n= 2	Std. dev.	0,001
2,5 bis 3,5 mg	Average	13,94
n= 15	Std. dev.	0,374

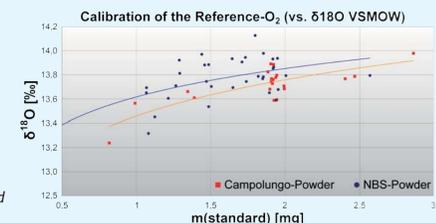


Fig. 6: Calibration of the O_2 reference with two standards (NBS 28 and Campolungo). A dependency between mass $\delta^{18}\text{O}$ and is observed.