

From method development to climate reconstruction - $\delta^{18}\text{O}$ analysis of biogenic silica from Lake El'gygytyn, NE Siberia

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Abstract

Especially in climate-sensitive areas such as the Arctic, longer drilling records for paleo-climate reconstructions are rare (BRIGHAM-GRETTE et al., 2007). Therefore, in 2003, a 16.50 m sediment core was drilled at Lake El'gygytyn (Lake E), NE Russia (dating back to app. 340 ka) in an area of the Northern Hemisphere which has not been glaciated at least during the last five glacial/interglacial cycles. In regions of high latitude, where carbonates are absent, the oxygen isotope composition from lacustrine biogenic silica, i. e. diatoms, is the best proxy for reconstructing past climate changes such as air temperatures as well as the isotope composition of precipitation (LENG and MARSHALL, 2004). In this study, the preparation of the samples as well as the contamination assessment had to be revised due to the peculiarity (only small diatoms < 10 μm available) of the material. In addition, a new approach for the dehydration/dehydroxylation process and for a high performance (fast, precise) oxygen isotope analysis was developed. The reliability of the method has been verified by analysing quartz and biogenic standards with a standard deviation < 0.2 ‰. Preliminary results of 50 samples from Lake E show variations in $\delta^{18}\text{O}$ that reflect glacial-interglacial cycles throughout the whole core, ranging between $\delta^{18}\text{O} = 18.6$ ‰ and $\delta^{18}\text{O} = 23.0$ ‰. This is the first proxy record from an Arctic lake sediment core dating back more than 300 ka directly responding to paleo-precipitation changes.

Method development

For the analysis of $\delta^{18}\text{O}$ Si very pure (>97 %) diatom samples are needed. Former studies included different purification techniques (MORLEY et al., 2004; RINGS et al., 2004; SHEMESH et al., 1995). However every sediment core has to be treated individually according to the specific material involved (LENG et al., 2009). Various preparation steps treatment have been performed in order to gain a most clean diatom sample from the original sediment: (1) drying, (2) $\text{H}_2\text{O}_2/\text{HCl}$ treatment, (3) wet sieving, (4-7) heavy liquid separation and (8) $\text{HClO}_4/\text{HNO}_3$ treatment. For the Lake E record the <10 μm fraction had to be selected as only this fraction contained enough purified sample material (>3 mg) throughout the whole core.

The degree of purity was verified under light microscope and by Energy Dispersive X-ray Spectroscopy (EDS) under the Scanning Electron Microscope (SEM) as any contamination can significantly change the $\delta^{18}\text{O}$ values (BREWER et al., 2008). The percentage of contamination was surveyed for all preparation steps 1-8 in Lake samples. Figure 1 shows the change in SiO_2 [%] after each step analysed by EDS. The dried, uncleaned sample contains app. 70 % SiO_2 . The SiO_2 content increases throughout the purification process to a percentage of > 96 % (which was our target value). Out of 115 samples, app. 90% show a final content of $\text{SiO}_2 > 96$ % and $\text{Al}_2\text{O}_3 < 3$ % (Al_2O_3 being an indicator for clay minerals).

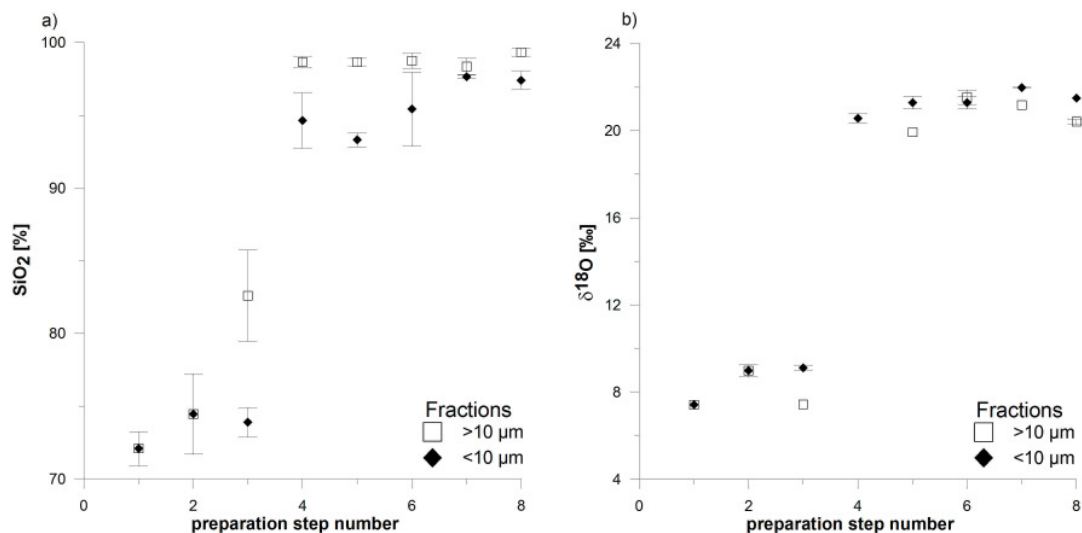


Figure 1: The development of the SiO_2 content (a) and the isotopic composition (b) throughout the different purification stages was assessed. Both fractions (>10 μm , <10 μm) show a final purity degree of >97 %, the last four purification steps are only essential for the <10 μm fraction. The $\delta^{18}\text{O}$ values reach a plateau after the 5th purification step. The final acid cleaning with $\text{HClO}_4/\text{HNO}_3$ slightly lowers the values.

Amorphous silica contains OH groups within the SiO₂ skeleton as well as chemically-combined water. The OH groups and chemically-combined water have to be removed prior to isotope analysis as their oxygen is easily exchanged and, thus, may not reflect the original isotopic composition of the water. Various methods have been established in the past 20 years for the dehydration and dehydroxylation of amorphous silica (ALEXANDRE et al., 2006; LABEYRIE and JUILLET, 1982; LÜCKE et al., 2005; SCHMIDT et al., 1997; SHARP, 1990), including Controlled Isotopic Exchange (CIE) followed by fluorination, Stepwise Fluorination (SWF) and inductive High-Temperature carbon reduction (iHTR).

Here, we present a new method we called Helium Flow Dehydration (HFD) which removes the “hydrous layer” by exposing the sample to an increased temperature (maximum 1100°C) within app. 7h in an oven with a continuous Helium stream leading away all exchangeable oxygen (Fig. 2).

The isotope analysis was performed with a PDZ-Europa 2020 mass spectrometer. The oxygen was liberated from the sample by laser-fluorination under BrF₅ atmosphere. The whole procedure is shown in Figure 2. Specially designed software and a video camera were used to survey and record the process in the reaction chamber and allowed a quick, half-automated, remote operation. This guaranteed maximum safety as the mass spec was installed in a different room than the reagent (BrF₅), the reaction chamber, and the laser unit arranged under a hood. The fluorination periphery is directly coupled to the mass spectrometer, making an online analysis possible. In addition, a direct comparison of oxygen was enabled omitting the intermediate step of reacting oxygen to CO or CO₂. Tests on standard material (Quartz: NBS 28, Campolungo, biogenic silica: BFC, PS1772-8) showed a standard deviation <0.2 ‰ (Fig. 3).

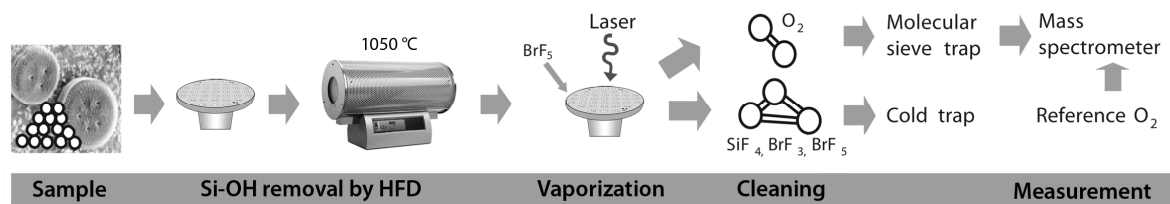


Figure 2: The sample was heated at 1100°C under a He flow to remove the Si-OH layer by Helium Flow Dehydration (HFD). Through the use of a CO₂ laser, the sample is vaporized and under BrF₅, the O₂ is released and the non-oxygen gas is trapped in a cryogenic trap. The oxygen is transported to the molecular sieve and then transferred to the mass spectrometer for isotope measurement.

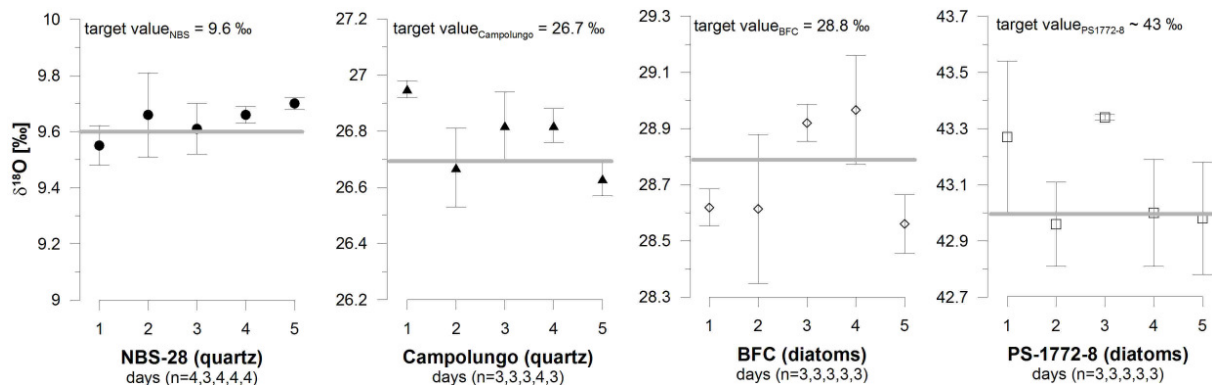


Figure 3: Verification of the method with quartz (filled symbols) and pure diatom standards (open symbols). The target values originate from IAEA (NBS-28), University of Bonn (Campolungo) and the National Environment Research Council (UK, BFC and PS1772-8). The daily standard deviation is <0.2‰ apart from BFC (2) and PS1772-8 (1). The reproducibility between the days is similar: NBS-28 (Avg: 9.64 ‰; SD:0.09 ‰; n=19), Campolungo (26.78 ‰; 0.14‰; 16), BFC (28.73‰; 0.22‰; 15) and PS1772-8 (43.11‰, 0.11‰; 15).

Core analysis

In 2003, a 16.50 m sediment core (Lz-1024) was drilled at Lake El'gygytgyn, NE Siberia which dates back to app. 340 ka. Preliminary studies have shown that mainly two diatom species are present in the lake: *Cyclotella ocellata* which occurs throughout the whole core and *Pliocaenicus costatus* mainly existing in the Holocene (CHERAPANOVA et al., 2007). In total, 115 samples were purified and the contamination was assessed according to the developed procedures described above. As *Pliocaenicus costatus* is of a size >10 μm, the purified samples <10 μm almost exclusively consist of a single species (*Cyclotella ocellata*). This is important as there are still a few discrepancies regarding the existence of species-dependent isotope fractionation in diatoms (BRANDRISS et al., 1998; MOSCHEN et al., 2005; SCHMIDT et al., 2001; SCHMIDT et al., 1997).

By now, around 50 different samples were measured (N=2-4) with a special emphasis on the time periods between 0-30 ka BP (resolution ~ 1k) and 100-170 ka BP (resolution ~ 3 k). The mean standard deviation between the repetitions was 1σ < 0.3 ‰. The downcore variations of δ¹⁸O show that glacial-interglacial cycles are present throughout the whole core (Figure 4) including the Holocene Thermal Maximum (HTM; δ¹⁸O = 21.5 ‰), the Last Glacial Maximum (LGM; δ¹⁸O = 18.6 ‰) and the Eemian interglacial period (δ¹⁸O = 23.0 ‰) By the time of the conference, more samples will be analysed and presented for the first time.

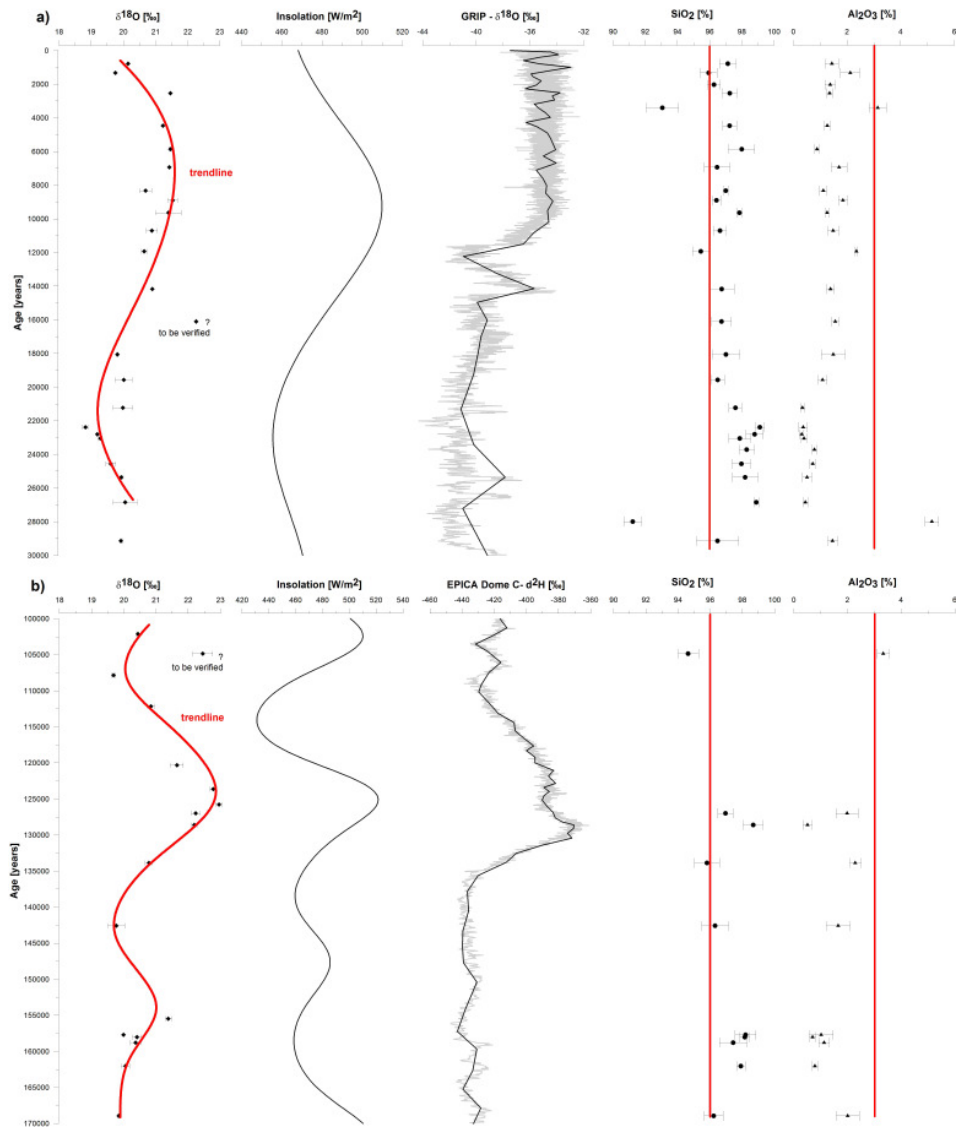


Figure 4: Preliminary $\delta^{18}\text{O}$ results from time intervals 0-30ka (a) and 100-170 ka (b). The trendline clearly shows climate-related isotope variations e.g. HTM and LGM (both in a) and further downcore an isotope maximum during the Eemian interglacial (b). The local insolation and ice core data from GRIP ($\delta^{18}\text{O}$ for 0-30ka) as well as EPICA Dome-C (dD for 100-170ka) were plotted for comparison (grey: all data, black: spline smoothing to 50 points). The EDS results from the contamination assessment of the purified samples show SiO_2 percentages of mostly $>96\%$ and $\text{Al}_2\text{O}_3 <3\%$. No corrections are applied to the isotope data so far, as not all samples have yet been analysed for both, EDS and $\delta^{18}\text{O}$.

Conclusions

A fast and precise approach was developed to analyse the oxygen isotope composition of biogenic silica: up to 15 samples per day can be analysed with a $\text{SD} < 0.2\%$. Novelties include a remote and half-automated analysis by new software development, a safe approach by installing the instrument in two different rooms and a new method to remove the “hydrous layer” by heating the sample at 1100°C in a Helium flow (Helium Flow Dehydration). All different applied methods are part of an on-going inter-laboratory comparison of eight laboratories coordinated by AWI.

The first 50 samples from the 16.50 m sediment core (dating back to app. 340 ka) drilled at Lake El’gygytyn (NE Russia) were analysed and show variations of the $\delta^{18}\text{O}$ values that reflect glacial-interglacial cycles. The Holocene Thermal Maximum, the Last Glacial Maximum as well as the Eemian interglacial and the interglacial period corresponding to MIS 7 are clearly visible. Further analyses will increase the resolution, close the gaps between the time intervals analysed up to now and allow a better interpretation of the paleo-climate variations. This work can be expanded to the long lake sediment core (dating back to about 3.6 Ma), which was drilled within the ICDP program at Lake El’gygytyn in early 2009.

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