

NEW APPROACHES FOR REMOVING THE Si-OH LAYER OF BIOGENIC SILICA BEFORE ANALYSING OXYGEN ISOTOPES – HELIUM FLOW DEHYDRATION (HFD) AND VACUUM BEAD MELTING (VBM) TECHNIQUE

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Background & Challenge

Oxygen isotopes of biogenic silica hold a great potential to reconstruct the paleoclimate. In marine and lacustrine environments where other paleoproxies are not available diatoms are used. Compared to the widely accepted relation of oxygen isotopes of carbonate origin to climate-relevant parameters, challenges still occur when using biogenic silica. Problems arise during the sample preparation stage as well as during the isotope analysis itself. These problems are often related to the removal of loosely bound oxygen of the hydrous layer. Diatoms consist of an isotopically homogenous inner Si-O-Si layer and a less dense, hydrous layer forming Si-OH bonds (Fig. 1). This layer has to be removed from the sample prior to isotope analysis as it can be isotopically exchanged and does not reflect the original isotopic water composition anymore.

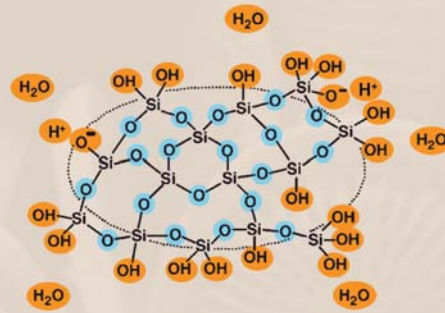


Fig. 1: Simplified sketch of a diatom $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ structure showing the siliceous part of the diatom cell wall. An SiO_2 skeleton (blue) is surrounded by loosely bound and, thus, exchangeable hydroxyl groups and chemically combined water (marked orange). Modified from Leng et al. (2008) original by Hecky et al. (1973)

Accepted Methods

Three methods have been accepted so far to perform the removal of exchangeable oxygen: Controlled Isotopic Exchange (CIE) followed by fluorination, Stepwise Fluorination (SWF) and inductive High-Temperature carbon Reduction (iHTR). A former method of vacuum dehydration (VD) proved to be unable to remove all exchangeable oxygen. CIE is both time-consuming and work-intensive while SWF is impractical for our setup due to the pressure increase during dehydration. Therefore, we developed a new, efficient and fast method to remove the hydrous layer prior to isotope analysis. Two new approaches were tested (see grey boxes to the right).

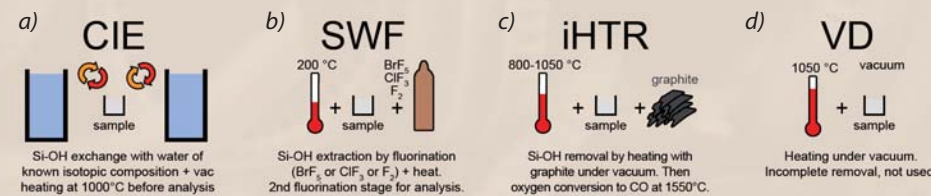


Fig. 2: Accepted methods for removing the OH-layer from biogenic silica: a) Controlled Isotopic Exchange (CIE), b) Step-Wise Fluorination (SWF) c) inductive High-Temperature carbon Reduction (iHTR), d) outdated Vacuum Dehydration (VD)

Samples used

Two diatom standards (BFC*, $\delta^{18}\text{O}_{\text{Si}} \sim 28.6 \text{ ‰}$; PS1772-8, $\delta^{18}\text{O}_{\text{Si}} \sim 43.0 \text{ ‰}$) were used to reproduce their known values with the two new methods. The target values are displayed in the figures (BFC — green —, PS1772-8 — red —). For all analysis between 0.7 mg and 2 mg were used.

* We kindly thank NERC Isotope Geosciences Laboratory (NIGL), British Geological Survey, Keyworth, Nottingham for supplying us with the BFC standard

Vacuum Bead Melting (VBM)

Method

The standard diatom material was pressed into the holes of a Platinum plate. The prepared plate was arranged on a stand that fits into the reaction chamber where the samples were melted into beads. A defocused CO_2 laser beam was directed over the sample with an increasing power targeting 5-6 W. A bead formed (Fig 3.8). The bead was then completely reacted under BrF_5 atmosphere with a focused laser beam.

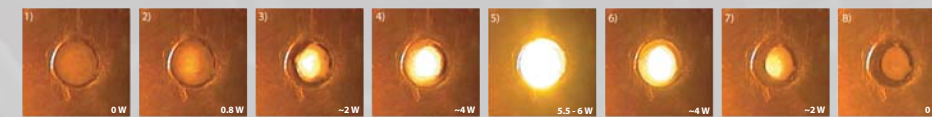


Fig. 3: The process of melting the powdered samples to beads took about 5 to 10 seconds with a recommended laser power between 5.5W and 6W. Picture 1 to 8 show the different stages of the sample in this process; picture 1 shows the powdered sample where as in picture 8 the finished bead is displayed. Variations in time have been tested as well as variations in laser power.

Results

VBM had difficulties to fully remove the hydrous layer, as shown by too low $\delta^{18}\text{O}$ values. After ten minutes of a constant laser beam the values roughly converged to the target values (Fig. 4a). However, fractionation occurred during the process (Fig. 4b): The longer the sample was exposed to the laser the higher the mass loss and heavier the isotopic composition. As this tendency continued even after the target value was reached, most likely not only the hydrous layer was removed, but accompanied by the preferential release of ^{16}O from the inner structure.

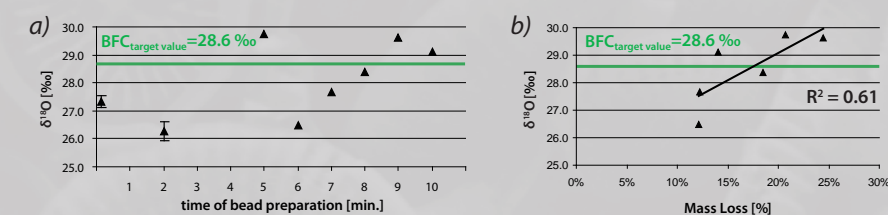


Fig. 4: a) Results from the VBM time series. A rough trend towards the reference values can be seen, however fractionation occurred. b) A continuous increase of the $\delta^{18}\text{O}$ value was observed with increasing mass loss. As this carried the results higher than the target value, ^{16}O from the structure itself has most likely been additionally removed during this process.

Conclusions

Two new approaches for the removal of exchangeable oxygen in biogenic silica were tested. VBM did not show the ability to remove all -OH groups from the biogenic silica. In addition a fractionation effect could be observed when comparing mass loss during the bead preparation with the measured $\delta^{18}\text{O}$ values. A possible conclusion would be a preferential removal of ^{16}O from the Si-O-Si structure itself. Hence, the VBM method is not suitable for removing the hydrous layer.

For HFD, our results give evidence that we were able to remove the hydrous layer as good

Helium Flow Dehydration (HFD)

Method

The standard diatom material was pressed into the holes of a Nickel plate (37 positions). The plate was moved into a horizontal oven in which a constant Helium flow kept air from the sample and transported away any removed OH-groups immediately. The oven was heated to 1050 °C within 1.5 hours, the temperature was held constant for app. 90 minutes. The cooling process took app. 3 hours until a temperature of 400 °C was reached. The plate was taken out, and transported to the reaction chamber of the mass spectrometer (Fig. 5).

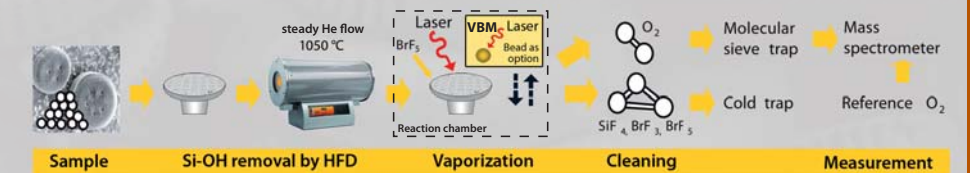


Fig. 5: The sample was heated at 1050°C under a He flow to remove the Si-OH layer by Helium Flow Dehydration (HFD). A different method to remove this layer was tested by producing a bead at 4 W with a defocused laser (VBM - see middle box). Through the use of a CO_2 laser, the sample is vaporized and under BrF_5 , the O_2 is released and the non-oxygen gas is trapped in a cold trap. The oxygen is transported to the molecular sieve and then transferred to the mass spectrometer for isotope measurement.

Results

The HFD generated $\delta^{18}\text{O}$ values with a high reproducibility and accuracy (Fig. 6) for both standard samples ($1\sigma < 0.25 \text{ ‰}$, $n=15$). The final values were within the standard error as compared to the reference values from a laboratory applying SWF.

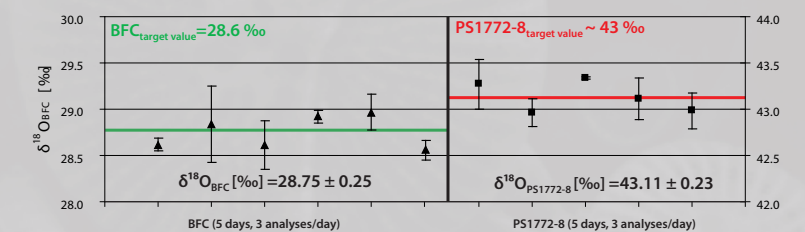


Fig. 6: HFD treatment of BFC and PS1772-8. This method provided results close to the reference values analysed with SWF in other labs. The repeatability is $< 0.25 \text{ ‰}$.

as the other accepted methods. The results showed a good repeatability for silica standards on a single day ($1\sigma < 0.2 \text{ ‰}$) and between different days ($1\sigma < 0.3 \text{ ‰}$). As this method is comparably easy and a lot faster when combining it with our semi-automated mass spectrometer settings (60-80 analyses per week) it has a good potential to be adopted by other laboratories. At the moment a laboratory comparison is carried out to directly compare all existing methods and to introduce for the first time new, amorphous standard material.