A new approach on the oxygen isotope micro analysis of diatom silica with a laser-fluorination based mass spectrometry unit

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Introduction

The analysis of oxygen isotopes from diatom silica in sediment cores has reached importance for reconstructing the paleoclimate and is especially valuable in non-carbonate lakes of cold regions, where no other bioindicators such as ostracods and foraminifera are available. A new approach for samples in sub-mg range 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'gygytgyn (Center: N 67°30', E 172°5', core LZ 1024) will be analysed and a $\delta^{18}O$ curve of the last 280.000 years will be generated to add a strong climate proxy to the various analysis performed so far. The Lake lies inside a meteorite impact crater formed app. 3.6 million years ago and hence offers a unique option to fill the spatial gap of locations in the Arctic where paleoclimate reconstructions are rare.

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

Diatom extraction

The diatoms are extracted from sediment samples with various preparation steps. At first organic material and carbonates are removed with H_2O_2 and HCl. Second, after rinsing out the acid, the sample is dispersed with Na-hexametaphosphat. Third, sieves with mesh sizes of 5µm, 10 µm, 20 µm, 32 µm and 125 µm are used to receive the different sized fractions. For Lake El'gygytgyn the *cyclotella-ocellata complex* can be found mostly in the 5-10µm fraction whereas the species of *Pliocaenicus costatus* is predominant in the 10 µm to 20 µm fraction. Finally a heavy liquid separation is performed in a centrifuge by adding 2.1 sg Wolfram-polytungstate solution to the different fractions of the sample. A minimum of ~700 µg fine material from 5 g of wet sample is obtained after rinsing out the heavy liquid in another sieving process. A control slide is prepared to determine the degree of purity.

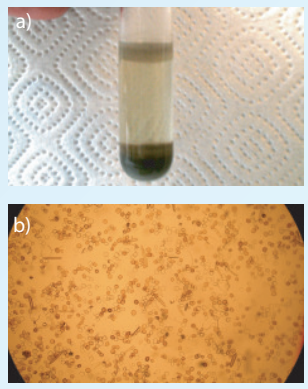

Fig. 2: Centrifuge tube after the heavy liquid searation: Diatoms float on top. (a) Control slide of the 10-20 µm fraction (b)

Melting powder to beads

Between 0.7 and 2 mg of standard (NBS 28, Campolungo) or diatom material is pressed into the holes of a Platinum plate. The prepared plate is arranged on a specially designed stand that fits into the conditioning chamber where the samples will be melted into beads. The pressure in the chamber has to be under 10^{-3}mbar before the CO_2 laser can be operated. It is adequate to direct the defocused beam over the sample at first with an increasing power of 0.5 W, 0.6 W and 0.7 W (Fig.3; 1). At each stage the move should follow a spiral starting from the center point to equally warm up the powder and evade parts spreading apart or a potential explosion of the sample. A light glow can be seen when 0.8 W are applied (Fig.3; 2). Then, the laser power is increased fast to 5-6 W with this power stable for about 5 to 10 seconds (Fig.3; 5). The power is then reduced to zero within 10 seconds. A bead is formed (Fig.3; 8) with a calculated mass loss between 4% (NBS 28) lacking any water and 20% (Radiolarians/Diatoms) due to chemically-bound water in the sample.

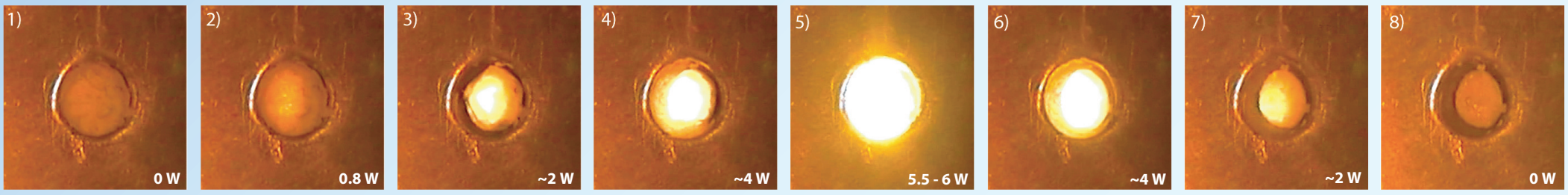

Fig. 3: The process of melting the powdered samples to beads takes about 5 to 10 seconds with a recommended laser power between 5.5W and 6W. Picture 1 to 8 show the different stages of the sample in this process: Picture 1 shows the powdered sample where as at Picture 8 the finished bead can be seen.

The process

The extracted diatom sample is melted into a bead (see above) and then heated with a CO_2 laser under BrF_5 atmosphere to release the O_2. The non-oxygen gas components are trapped in a -150°C cold trap, whereas oxygen passes on to the molecular sieve cooled with liquid nitrogen. It is then transferred to the mass spectrometer and compared with reference O_2 calibrated with several standards. By measuring the isotope ratio difference between sample and reference, the $\delta^{18}O$ value of the sample vs. VSMOW is determined.

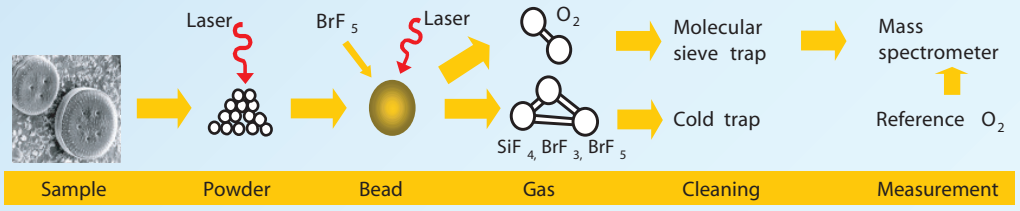

Fig. 4: Principle of the analysis from sample to measurement. After ground to powder and melted to a bead the sample is heated with a CO_2 laser under BrF_5 atmosphere to release the O_2. The non-oxygen gas components are trapped in cold trap, Oxygen passes to the molecular sieve cooled with liquid nitrogen and is transferred to the mass spectrometer for isotope measurement.

Rooms & Safety

Due to high safety regulation principles for toxic gases such as BrF_5 the instrument is arranged in two rooms: The reaction room (Fig. 5a) and the control room (Fig. 5b). The fluorination line is installed in the reaction room under a hood containing conditioning chamber and reaction chamber, laser, gas bottles, reagent reservoirs, pumps and cold traps. Additionally the chambers and the laser are located in a specially designed safety box to assure maximum security. Mass spectrometer and control unit are connected through a void in the wall and set up in the control room.

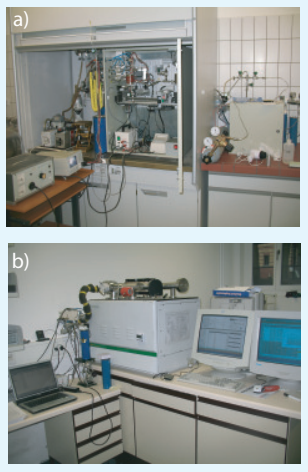

Fig. 5: The reaction room (a) is separated from the control room (b) and contains the fluorination line. The mass spectrometer and the work station are located in the control room.

Connections & Valve Chart

The whole system is assembled with 1/4 and 3/8 inch stainless steel tubing connected with fittings from Swagelok. Pneumatic valves can be switched on and off automatically (see „ The Software“ left) where as for more critical spots (release of BrF_5, etc.) manual valves are included. Pressure gauges are installed to secure an airtight system at all times. Temperature probes guarantee stable conditions in cold trap and molecular sieve.

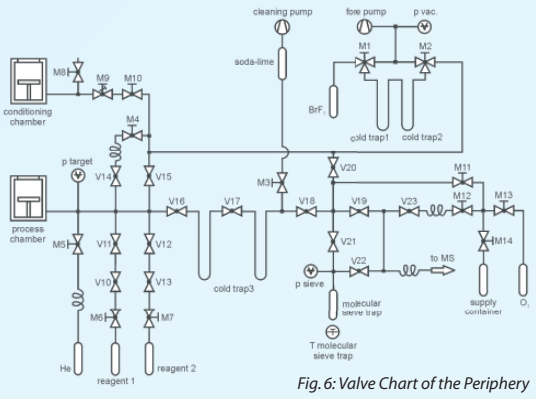

Fig. 6: Valve Chart of the Periphery

The Software

A Window-based software for a remotely-controlled fluorination line and mass spectrometer was developed. It allows the control of the mass spectrometer as well as of the pneumatic valves. A ‚Drag and drop' menu to compile a measurement procedure is integrated to measure the samples automatically.
The measured data are transferred to an Excel file where the $\delta^{18}O$ values of the sample are determined All parameters and the used measurement procedure are stored in the Excel file. A video camera is connected to a second computer to survey and record the process in the reaction chamber (see extracted images above).

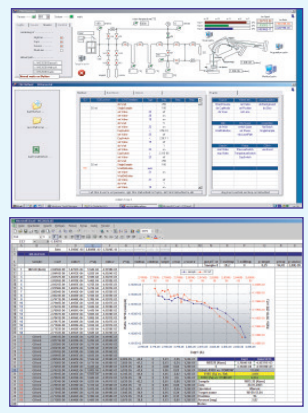

Fig. 7: Screenshots of the software windows (a) and the created Excel File (b). The software shows the clickable valve chart (for switching the valves on/off) and updated temperature and pressure information on top. On the bottom the measurement procedure window is opened.

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Summary of a Poster series concerning the analysis of $\delta^{18}O_{si}$ in Lake Sediments from EL'Gygytgyn Crater Lake with a laser-fluorination based mass spectrometry unit (PhD Thesis of Bernhard Chapligin)

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