ENHANCED SEDIMENT PURIFICATION TECHNIQUES FOR THE <10μm FRACTION OF DIATOM SILICA AND A COMPARISON OF CONTAMINATION ASSESSMENT BEFORE ANALYSING OXYGEN ISOTOPES

B. Chapligin, H. Meyer, U. Hoff, B.Diekmann, A. Eulenburg, H.-W. Hubberten

Alfred Wegener Institute for Polar and Marine Research, Research Unit Potsdam, Telegrafenberg A43, D-14473 Potsdam, Germany • bernhard.chapligin@awi.de

Background & Challenge

Sediment samples have to go through a long purification process before clean diatom samples can be obtained. This is particularly difficult in the <10 μm fraction containing clay particles. As the structure of contaminants e.g. organic material, carbonate, mineral particles contains oxygen, it is essential to assess the degree of contamination. If high impurities exist a correction factor has to be implemented (Fig. 1). We developed an updated protocol for purifing the <10 μm fraction and compared various methods of assessing the degree of purity to apply the fastest and most appropriate method for future analyses.
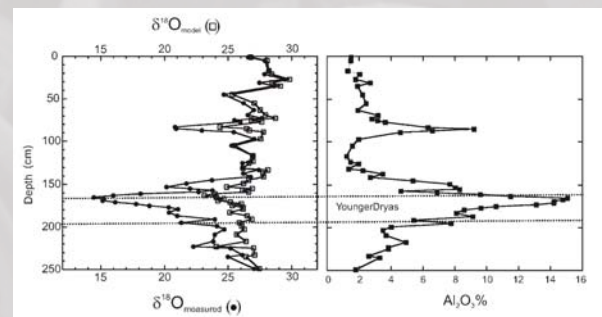

Fig. 1: Contaminants influencing the stable isotope composition of biogenic silica at Lake Baikal.
a) Measured and corrected δ18O values
b) Al2O3 percentage representing contamination, responsible for the corrected curve in a   by Brewer et al (2008)**

Preparation steps

To analyse the δ18O of diatom material, it is essential to purify the original sediment samples in various physical and chemical preparation steps. Figure 2 shows the purification process: The sample is freeze-dried to remove water. Then, organic material and cabrbonate are removed by adding H_2O_2 and HCl for more than 20h on a heating plate at 50°C. The sample is sieved to gain different size fractions (>10 μm, <10μm). The heavy liquid separation (HLS) using sodium-polytungstate (SPT) was repeated 4 times with different solutions of decreasing density (2.4 -2.3 g/cm³). A final acid cleaning is applied to remove micro organics. Several rinsing procedures ensured a neutral pH value as well as the complete removal of the SPT solution from the sample.
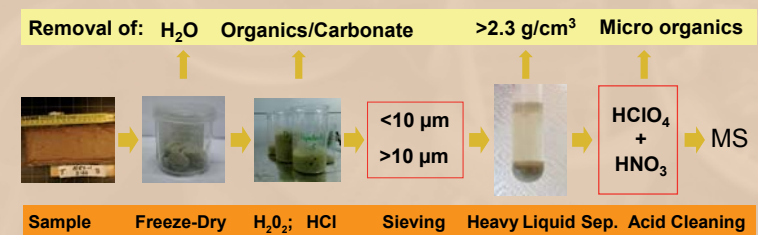

Fig. 2: Overview of the preparation steps to gain pure biogenic silica material of 0-10 μm and >10 μm fractions out of a sediment sample.

Effect of preparation steps

The effect of the different cleaning stages was assessed by using energy dispersive x-ray spectroscopy (see Box „contamination tool kit") operated under the SEM. The samples were sputtered with Carbon. This is why a quality increase of the sample by removing organic material cannot be observed. The original sediment samples have a SiO2 content of app. 72 %. As more contaminants are (high clay content) is left in the <10 μm fraction, the purity of the >10 μm fraction increases already by sieving. A final purity of >97 % (value shifts below the instrument's error) can be achieved in both fractions. The >10 μm fraction has a purity degree of >97 % already after the first heavy liquid separation, where as for the <10 μm fraction the four repetitions of this step are essential.
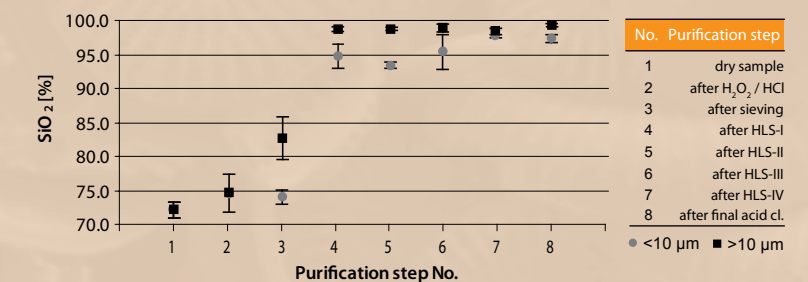

No.	Purification step
1	dry sample
2	after H_2O_2 / HCl
3	after sieving
4	after HLS-I
5	after HLS-II
6	after HLS-III
7	after HLS-IV
8	after final acid cl.

Fig. 3: The development of the SiO2 content throughout the different purification stages (left) was assessed with EDX (see Box „Contamination tool kit"). Both fractions (>10 μm, <10 μm) shows a final purity degree of >97 %. The resulting difference in the isotopic composition is within the analytical error. No correction factor due to contamination has to be applied.

Contamination „tool kit"

The analytical possibilities to assess the degree of purity are either by optical identification of contaminants or by chemical analyses determining the chemical composition. Optical methods are represented by light microscope (LM) or scanning electron microscope (SEM). The chemical composition can be either analysed by X-ray Fluorescence (XRF), energy-dispersive X-ray spectroscopy (XRD) under the SEM or inductively coupled plasma optical emission spectrometry (ICP-OES). To compare these methods the biogenic silica standard BFC* was used.

Assessment
- Light Mic
- SEM
- EDS
- ICP-OES
- XRF

Light Microscope & SEM

The degree of purity under the LM is assessed by chosing random screens and counting the amount of diatoms vs. contaminants. At least 200, (better 500) items were counted. Thus, LM is a time taking but precise procedure, as long as the <5 μm fraction (too small for identification) is excluded. The SEM is not limited by resolution as it is possible to zoom in to every spot not being clearly identified. Again, this is time taking and SEM should only be used as a quick overview or for detail shots.
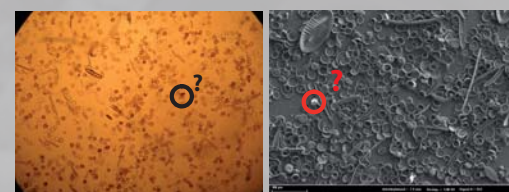

Fig. 4: a) Picture under the LM. Contaminants can be identified as particles without regular shape. The LM is limited, particles smaller than 2 μm cannot be identified.
b) Picture under the SEM. Similar particle detection. Zooming towards the contaminant supports the identification process. Not limited but slow detection. Convenient for a quick overview or one detailed view only.

ICP-OES

The preparation for ICP-OES is time-taking (2 weeks for 30 samples) as full HF, HNO3, HCl digestion has to be performed. As this analysis is normally operated with 100 mg no big advantage would have been achieved regarding the amount needed. Hence, it was attempted to use only 50 mg and 10 mg of sample to see whether this technique is capable of reproducing the known chemical composition. The results were compared to XRF analyses performed in Great Britain on 300 mg BFC*.

XRF by NERC, UK		set 100%		ICP-OES by AWI	50mg	10 mg
SiO2	91.91	97.22		SiO2	dissolved	dissolved
TiO2	0.07	0.07		TiO2	0.10	0.09
Al2O3	1.38	1.46		Al2O3	1.96	1.99
Fe2O3	0.39	0.41		Fe2O3	0.45	0.43
MnO	0.01	0.01		MnO	bdl	bdl
MgO	0.24	0.25		MgO	0.06	0.05
CaO	0.33	0.35		CaO	n.d.	n.d.
Na2O	0.14	0.15		Na2O	0.08	0.07
K2O	0.07	0.07		K2O	0.04	0.04
P2O5	0	0.00		P2O5	bdl	0.02
LOI: 5.46 %	94.54	100		SiO2 to 100%	97.47	97.31

Fig. 5 a) British XRF results on 300 mg BFC standard material. The loss of ignition is 5.46 %. It is segregated and values are normalized to 100%. The final SiO2 content is 97.22%. **
b) ICP-OES results with 50 mg and 10 mg are comparable between each other. The final SiO2 content is 97.47 % resp. 97.31 % and thus comparable to the XRF results.

XRF & EDX

XRF and EDX work with a similar principle of detecting the secondary x-rays after material has been exposed to x-rays. For XRF a high amount of sample material is needed for a reliable analysis (min. 300 mg). EDX is not as precise but needs lesser than 0.5mg as it is operated under the SEM. It provided the fastest results but with a higher mean standard deviation ($1\sigma_{SiO_2}$= 0.5 %). The detection limit for this analysis is comparably high (app. 0.1 %) but still suitable for this purpose. Again, the analysis (Fig. 6) was compared to the performed XRF of the BFC* standard (Fig. 5).
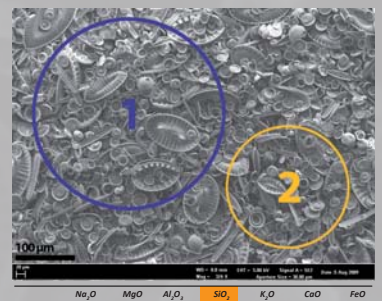

	Na2O	MgO	Al2O3	SiO2	K2O	CaO	FeO
AVERAGE	0.47	0.09	1.34	97.41	0.31	0.02	0.32
STDEV	0.58	0.02	0.28	0.61	0.05	0.02	0.05

Fig. 6: EDX analysis of a defined circular area ranging between 200 and 500 μm in diameter. The SiO2 content can be analysed with an average standard deviation of <0.5 % (n=5).

Conclusion

Purification

For sediment cores from Lake El'gygytgyn, NE Russia, we found a purification protocol to decrease the non SiO2 fraction to <3 % for the <10 μm as well as for the >10 μm fraction. The major improvement was made by introducing a multiple heavy liquid separation with varying densities. The final acid cleaning showed no further cleaning effect and can be disregarded in the future.

Method for Contamination assessment

If there is more time it is recommended to analyze the sample with ICP-OES taking longer in the preparation phase but giving results with a higher precision. The optical methods don't provide exact quantified results for the <10 μm fraction but SEM pictures should be used in addition to verify the degree of purity optically by providing detailed view. The EDX is the most recommended analysis after this comparison as it needs less than 0.5 mg. In addition it is the quickest technique (30/day, n=5) and its precision is good enough for the purpose of assessing degree of purity. Further tests on more biogenic standard material are carried out at the moment to undermine the usefulness of EDX for contamination assessment.

Method	Type	min. mass required [mg]	Precision	time consumption
Light microscope	optical count	~ 0.1	0	-
SEM microscope	optical count	~ 0.1	0	++[1]
EDX analysis	chemical analysis	< 0.5	+	++
ICP-OES	chemical analysis	10	++	--
XRF	chemical analysis	300	+++	-

[1] just for overview picture, or detailed shot

Fig. 7: Overview table of the various methods for assessing the degree of contamination and their efficiency quality criteria.