Structure-related oxygen isotopes in diatom frustules (Opal-A)

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Large amounts of silica dissolved in the oceans are precipitated as biogenic silica. Diatom phytoplankton is forming siliceous frustules during growth at the seawater surface. Most of silica frustules are resolved during sedimentation in the watercolumn, undersaturated by silica. Opal-A within the sediments was believed to reflect growing conditions (temperature and salinity) of the sea surface (Shemesh *et al.*, 1992; Juillet-Leclerc and Labeyrie, 1987).

Stable isotope measurements (Schmidt *et al.*, 1997) of silica-bound oxygen from phytoplankton samples showed isotope compositions much different from values measured for sedimentary opal-A. Moreover, a clear relationship to the growing temperature was not found. A non-isotope equilibrium of the diatom frustules was postulated and isotopic and structural reorganization during sedimentation had to be assumed.

TABLE 1. Results of isotopic and infrared measurements of marine diatom samples

Sample	Age (y)	I(800)/I(935)	$\delta^{18}O_{SiO}$ (‰)
phytoplankton-1	0.1	1.04	33.9
phytoplankton-2	0.1	1.08	32.8
phytoplankton-3	0.1	0.81	
culture-1	0.1	1.11	36.0
culture-2	0.1	1.27	36.1
culture-3	0.1	0.78	36.3
sediment trap-1	10	1.27	
sediment trap-2	20	1.24	
sediment trap-3	10	1.32	
sediment trap-4	10	1.29	
sediment trap-5	10	1.38	
surface sediment-1	5000	3.54	42.1
surface sediment-2	10000	4.50	43.5
surface sediment-3	10000	3.94	42.8
surface sediment-4	10000	4.11	
sediment-1	120000	5.93	44.1
sediment-2	4000000	9.27	46.8

The present study deals with the diagenesis of diatomaceous opal-A during sedimentation. Structural investigations of phytoplankton blooms, sediment traps and sediment core material were performed by X-ray diffraction and infrared analysis. Structural variations were related to stable oxygen isotope composition of the silica framework.

Sampling and methods

Phytoplankton blooms were sampled during several expeditions in the Norwegian-Greenland Sea and Antarctic (Bellingshausen Sea and Weddell Sea) from surface waters using 10–20 µm net or 25 µm filters. Diatom cultures (isolated from a phytoplankton sample collected from the Weddell Sea) were cultured in 10l bottles containing seawater enriched with nutrients.

Sediment trap material (BO1,PF3) was derived from the Weddell Sea at 450/2194m and 614/3196m, respectively.

Sedimentary Opal-A was sampled from several cores (0–6 m) taken during cruises in the Antarctic Ocean (Bellingshausen, Scotia and Weddell Sea) and North Atlantic.

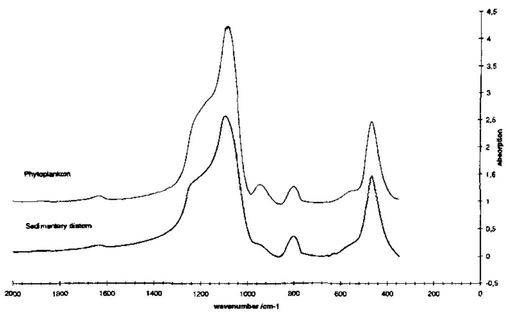

FIG. 1. Infrared absorption spectra of diatoms.

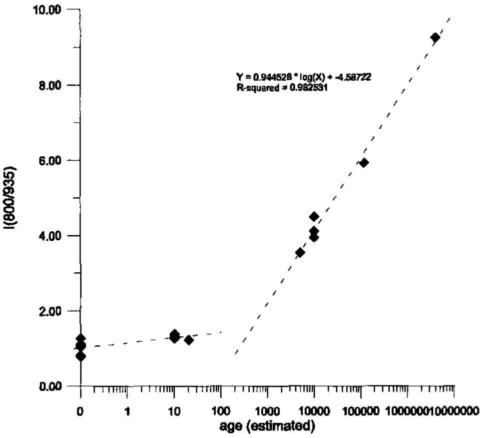

FIG. 2. Diagenesis of diatom opal-A during sedimentation.

Sediment samples were separated from detrital clay by differential settling. Diatom samples were oxidized by $HNO_3/HClO_4$. The organic-free frustules were washed with destilled water and dried at 60°C. Only pure (by means of XRD and SEM) diatomaceous opal-A was used for further experiments.

Stepwise fluorination and controlled isotope exchange experiments were performed inorder to determine the stable isotope composition of silica bound oxygen of opaline samples (Schmidt *et al.*, 1997).

Infrared spectra were taken with a FTIR (Bruker IFS 66v/S) in the MIR / NIR-range.

Results and discussion

Infrared absorption measurements of diatomaceous opal-A samples show structural differences in the 750–1000 cm^{-1} wavenumber range as shown in Fig. 1. The absorption band at 935 cm^{-1} which is assigned to Si-OH stretching mode is stronger in phytoplankton samples than in sedimentary samples. This band weakens as Si-OH condenses to form Si-OSi bonds assigned to the absorption band at 800 cm^{-1} (Farmer, 1974). Dissolution-/precipitation processes during sedimentation probably control this structural parameter.

A significant shift to higher I(800)/I(935)-ratios (I=integrated area of the absorption band) was detected with increasing estimated age of diatom samples (Table 1).

Moreover, this structural parameter appears to change during sedimentation (Fig.2). Minor changes in I(800)/I(935)-ratios from phytoplankton to sediment trap material indicate low structural changes in the silica framework (SiOSi/SiOH-ratio). Major changes were recorded for sedimentary diatoms with a good linear correlation against sample age in log-scale.

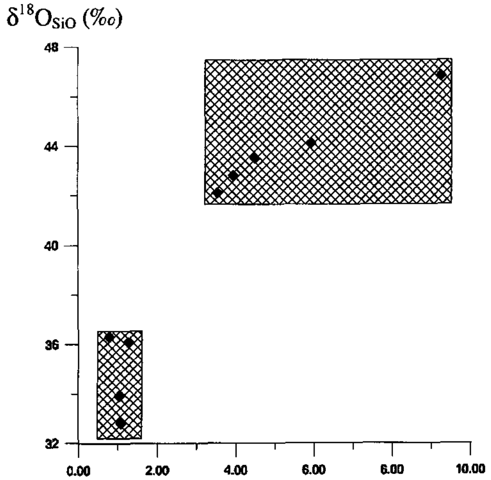

FIG. 3. Isotope composition of silica bound oxygen *vs* ratio of infrared bands (Si-OSi/Si-OH).

Structural characteristics, indicated by infrared absorption bands are compared with stable isotope composition of the silica-bound oxygen (Fig. 3). $\delta^{18}O_{SiO}$-values of the recent diatom samples (phytoplankton, cultures) plot in a range of low I(800)/I(935)-ratios (0.7–1.1) and low oxygen isotope values (32-36\$). Measured sedimentary diatoms have higher (3.5–10) infrared I(800)/I(935)-ratios and oxygen isotope compositions between 42 and 47\$.

More data, especially isotope data of sediment trap samples is needed and will be measured in the near future in order to classify diatom samples by infrared and isotopic parameters. This may lead to a better understanding of dissolution/precipitation processes of sedimenting diatomaceous opal-A.

References

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