Sensitivity of biogenic silica oxygen isotopes to changes in surface water temperature and palaeoclimatology

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[1] Oxygen isotope ratios of biogenic silica derived from planktonic diatoms living in the pelagial of a freshwater lake are used to determine the temperature effect on the isotope fractionation between water and biogenic silica under ecosystem conditions. Our data show a deterministic relation between seasonally changing water temperatures (4°C–22°C) and the oxygen isotope fractionation during valve formation. The temperature dependent fractionation appears to be independent of diatom cell sizes indicating a mere physical control of this process. The isotopic change induced per degree centigrade, the temperature coefficient, amounts to a value of −0.2‰/°C. This implies that previous studies have overestimated the temperature relationship of this proxy by using coefficients of up to −0.5‰/°C for climate reconstructions. **Citation:** Moschen, R., A. Lücke, and G. H. Schleser (2005), Sensitivity of biogenic silica oxygen isotopes to changes in surface water temperature and palaeoclimatology, *Geophys. Res. Lett.*, *32*, L07708, doi:10.1029/2004GL022167.

1. Introduction

[2] Temperature reconstructions using palaeoclimate archives are of high priority in current palaeoclimate research. According to Northern Hemisphere temperature reconstructions [e.g., *Mann et al.*, 1999] the amplitudes of past variations were much smaller than the presently measured increase in temperature which in part is supposed to be anthropogenically driven. In contrast, global circulation models suggest that the amplitudes of past climate variations may have been larger than previously thought [e.g., *Von Storch et al.*, 2004]. In the context of this controversial subject, it is of prime importance to evaluate how precise and reliable, with respect to uncertainties and amplitude, estimates of past temperature variations from common proxy parameters are.

[3] The use of the oxygen isotope composition of biogenic silica as a possible palaeothermometer has increased ever since the relation between water temperature and oxygen isotope fractionation for diatoms was shown [*Labeyrie*, 1974]. Since diatom skeletons are often well preserved even within long sediment records their oxygen isotope composition can be seen as a powerful palaeotemperature proxy; particularly in sediments that lack the commonly used calcareous microfossils [*Shemesh et al.*, 1995].

[4] However, quantitative palaeoclimate applications are frequently not only limited by the unknown isotopic composition of ambient water in the past but also by uncertainties about the nature and the magnitude of the temperature influence on the oxygen isotope fractionation during formation of the diatom silica [e.g., *Shemesh et al.*, 1992; *Barker et al.*, 2001; *Leng et al.*, 2001; *Hu and Shemesh*, 2003; *Jones et al.*, 2004]. Obviously, all evidence drawn from $\delta^{18}O_{opal}$ values, either with respect to thermal or hydrological changes, must remain weak as long as the magnitude of the temperature-dependent fractionation between biogenic silica and water is not precisely known.

[5] Calibration studies with marine and freshwater diatoms have so far provided contradictory results and published values of the isotopic change per degree centigrade range from zero to −0.5‰ [*Labeyrie*, 1974; *Juillet Leclerc and Labeyrie*, 1987; *Matheney and Knauth*, 1989; *Shemesh et al.*, 1992; *Schmidt et al.*, 1997; *Brandriss et al.*, 1998]. Laboratory experiments by *Brandriss et al.* [1998] with two single freshwater diatom species revealed a temperature dependent fractionation of −0.19‰/°C. However, these results were not unambiguous for temperatures above 10°C and laboratory studies always bear the risk of a bias against natural conditions. Studies on diatomaceous silica from marine surface sediments resulted in temperature coefficients of −0.26‰/°C [*Labeyrie*, 1974] and −0.29‰/°C [*Juillet Leclerc and Labeyrie*, 1987]. For low temperatures, *Shemesh et al.* [1992] deduced a temperature coefficient of −0.49‰/°C making use of the low-temperature data points from *Juillet Leclerc and Labeyrie* [1987], thus, postulating a strong nonlinearity of the temperature-dependent fractionation. Contrary to these studies marine planktonic diatoms directly harvested from the photic zone showed no temperature-dependent fractionation at all [*Schmidt et al.*, 1997]. In summary, the true value of the temperature coefficient for biogenic silica oxygen isotopes is still controversial.

[6] In this contribution we report results of the first calibration study dedicated to the investigation of the temperature-dependent oxygen isotope fractionation between diatom silica and water directly in an ecosystem. Our approach avoids problems of former studies and, therefore, should contribute to the clarification of contradictory temperature coefficients.

2. Study Site

[7] The study was carried out in Lake Holzmaar, situated in the West Eifel Volcanic Field, Germany. The lake developed in a small maar crater, is mainly groundwater fed, has a limited surface inflow and outflow, a diameter of

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250–315 m and a maximum depth of 20 m. The small catchment area of 2.06 km^2 is drained by the Sammetcreek which flows in and out of the lake. Daily mean air temperatures recorded at Lake Holzmaar show a seasonal variation between $-7°C$ in January and about $25°C$ in July. Variations of the isotopic composition of precipitation (-4.0 to $-12‰$) were in accordance with air temperature variations. These variations of $\delta^{18}O$ in precipitation could not be traced in the Sammetcreek and a small spring, directly discharging into the lake (see auxiliary material[1]).

[8] The seasonal cycle leads to a stable summer stratification in the lake's water body, resulting in a thermocline at a depth of 7 to 8 m and a seasonal succession of various diatom communities [*Raubitschek et al.*, 1999]. Growth of the diatom phytoplankton occurs mainly in the lake's epilimnion and is exposed to a strong thermal gradient throughout the season allowing the direct observation of temperature effects on the oxygen isotope fractionation during formation of the diatom opal under natural conditions.

3. Materials and Methods

[9] Water temperatures were recorded biweekly from the surface to the lake bottom at intervals of 2 m depth and samples for the determination of $\delta^{18}O_{water}$ were taken accordingly. To harvest fresh diatom matter, we deployed sediment traps at a water depth of 7 m. The traps thus integrated the settling matter from the upper 7 m of the lake's water body, the main growth zone of planktonic algae (epilimnion) and were emptied every month from August 2000 to February 2002. The collected sediments were cleaned and sieved into the size fractions of 5 to 10 μm, 10 to 20 μm and 20 to 80 μm to investigate possible size effects (species-specific effects) on the oxygen isotope fractionation. The fractions chosen contained almost all diatom frustules representing more than 50 species. Ideally, evaluation of species-specific effects on the oxygen isotope fractionation would require samples of single species. The used SPLITT technique [*Rings et al.*, 2004], currently the most advanced method available to separate diatoms from minerogenic particles did not, however, lead to pure mono-species samples. Nevertheless, the diatom species composition of each size classes was basically unlike from those of other size classes (see auxiliary material).

[10] The diatom opal of each size class was treated as an independent sample for determination of the oxygen isotope composition and taken as representative of different diatom associations. The oxygen isotope composition of the opal was determined using inductive high-temperature carbon reduction (iHTR) (see auxiliary material). This novel method is based on the reduction of SiO_2 at a temperature of 1,550°C immediately following a multi-step thermal dehydration procedure [*Lücke et al.*, 2005].

4. Results

[11] The oxygen isotope composition of the diatom frustules, grown in the epilimnion of Lake Holzmaar, varies significantly with season (Figure 1c). The lowest $\delta^{18}O_{opal}$
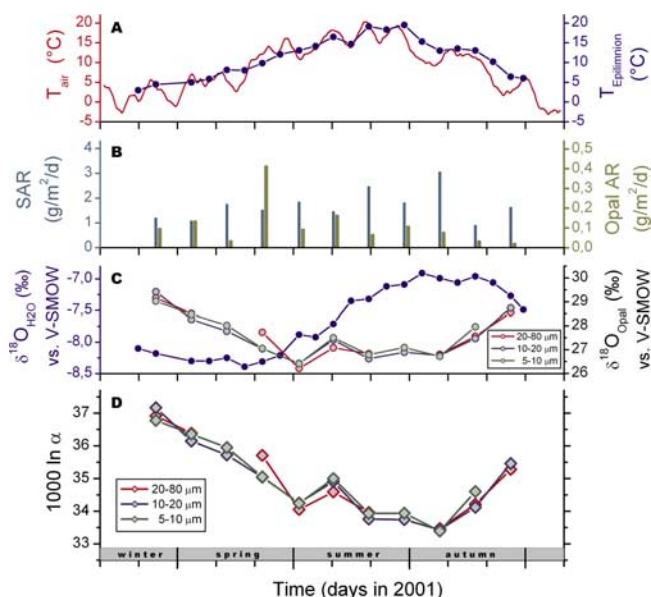

Figure 1. Ecosystem development and oxygen isotope behaviour in Lake Holzmaar during the annual cycle of 2001. (a) Five days running mean of daily air temperature one metre above the water level and biweekly temperature of the epilimnic water body, (b) monthly sediment accumulation rates (SAR) in the central part of the lake and corresponding opal accumulation rates (Opal AR), (c) biweekly oxygen isotope composition of epilimnic water body ($\delta^{18}O_{H2O}$) and monthly oxygen isotope composition of diatom opal from three different size classes, (d) oxygen isotope fractionation for three different diatom size classes calculated using the mean epilimnic $\delta^{18}O_{H2O}$ value of the diatom sampling period (see auxiliary material).

values coincide with the highest epilimnic water temperatures (see auxiliary material) during the summer months (Figure 1a). However, the relation is progressively obscured by successive evaporation from the lake surface. This evaporative enrichment increased the $\delta^{18}O$ value of surface water (see auxiliary material) by almost 1.5‰ in late summer/autumn (Figure 1c) and, thus, counterbalanced the reduced fractionation at higher temperatures.

[12] The respective oxygen isotope fractionation $\alpha_{silica-water} = (1000 + \delta^{18}O_{silica})/(1000 + \delta^{18}O_{water})$ determined for the various size classes (Figure 1d) reveals a very regular inverse behaviour ($1000\ln\alpha_{silica-water}$) compare to the water temperature. A similar relation appears with air temperature (Figure 1a). Overall diatom productivity, as revealed by opal accumulation rates (Figure 1b) as well as by diatom blooms (as in May 2001) with enhanced demand for dissolved silica, does not indicate any detectable influence on the oxygen isotope fractionation.

[13] Irrespective of variations in the seasonal abundance of larger and smaller taxa, of nutrient supply or of the degree of competition with other classes of algae, a linear relation between water temperature and fractionation ($1000\ln\alpha$) emerges for all size classes (Figure 2). The temperature coefficients for oxygen isotope fractionation according to size class appear to be $-0.216‰/°C$, $-0.194‰/°C$ and $-0.195‰/°C$, respectively. The coefficients for the three different size classes are identical within their uncertainties ($p < 0.05$). Taking these facts as tentative evidence for
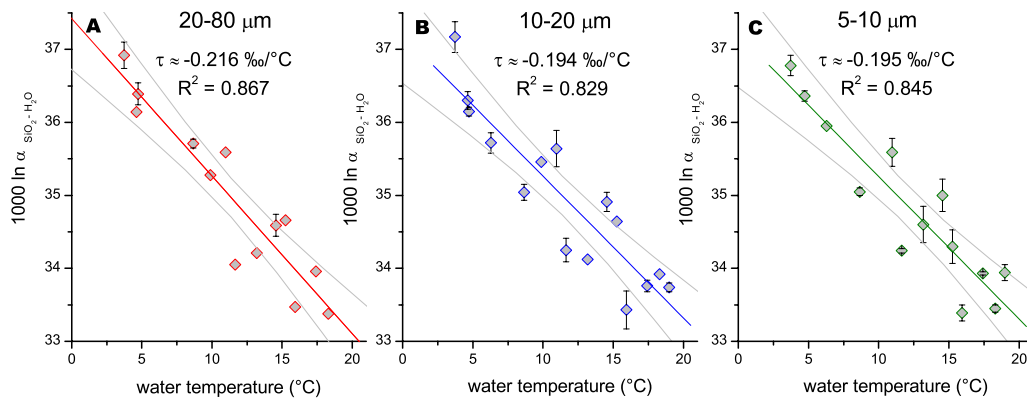
Figure 2

Figure 2. Dependency of the oxygen isotope fractionation in biogenic opal on temperature for three different size classes of freshwater diatoms from Lake Holzmaar. Each symbol represents the average of up to 4 measurements. Error bars represent 1σ. Centre lines are regression lines; neighbouring curves express 95% confidence intervals. Regression coefficients are identical at $p < 0.05$.

the absence of species-specific effects points to a pure physical temperature controlled fractionation process for oxygen in biogenic opal.

[14] Determination of the weighted mean oxygen isotope compositions of total opal (mean of $\delta^{18}O_{opal}$ from all size fractions of a single sampling date weighted by the respective mass of extracted opal) allows the calculation of the overall relation between water temperature and fractionation. This relation is also strictly linear for the complete temperature range from 4 to 22°C and has a slope of −0.198‰/°C (Figure 3). The functional relationship between water temperature which prevailed during valve formation and the fractionation can be expressed as $t\ (°C) = 190.07 - 5.05\ (\delta^{18}O_{opal} - \delta^{18}O_{water})$ were t is the water temperature and $\delta^{18}O_{opal}$ and $\delta^{18}O_{water}$ are the isotopic compositions of opal and water, respectively.

5. Discussion

[15] Based on identical results for three different diatom size fractions we propose a value of −0.2‰/°C as the most realistic temperature coefficient for oxygen isotope fractionation between diatom silica and water. The uncertainties related with our temperature coefficient are rather small with ±0.05‰ (95% confidence level). This temperature/fractionation relation derived from the lacustrine ecosystem of Lake Holzmaar is in good agreement with experimental data available from laboratory studies [*Brandriss et al.*, 1998]. Contrary to other studies [e.g., *Shemesh et al.*, 1992] no evidence could be found to justify the application of different temperature coefficients for different water temperature intervals in the range between 4 and 22°C. The identical results found for opal from the three different diatom size fractions also support a purely physical fractionation effect. Therefore, the linear relation with a slope of −0.2‰/°C also might be valid for other types of biogenic silica and, thus, also applicable for marine diatoms, sponge spicules and phytoliths [e.g., *Webb and Longstaffe*, 2003].

[16] As already described above, different results for the temperature dependent oxygen isotope fractionation were found in most of the earlier studies (Figure 3a). The cause of
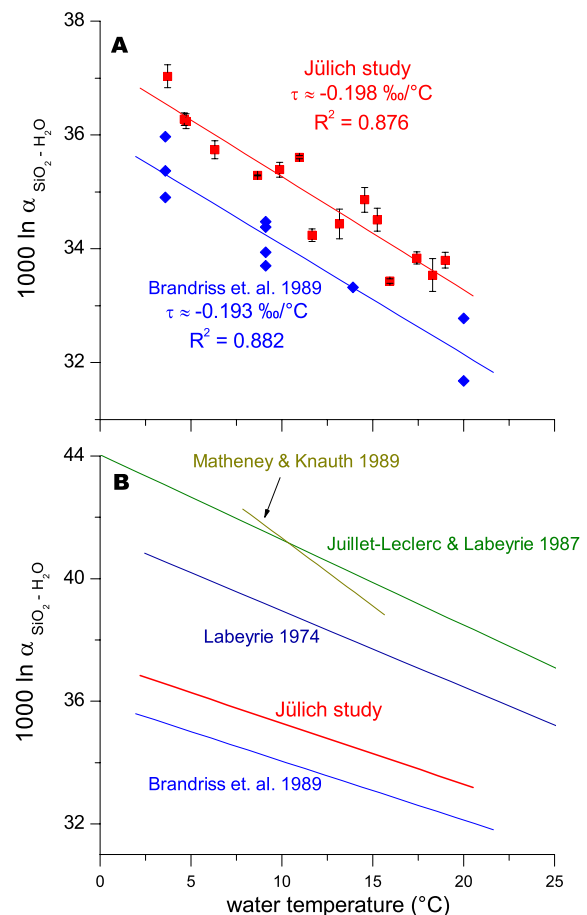

Figure 3. Comparison of our oxygen isotope fractionation investigations with results of earlier studies. (a) temperature dependence of fractionation for the weighted average of all diatom size classes of this study in comparison with results of laboratory studies by *Brandriss et al.* [1998]. (b) all calibration studies performed so far. Only the Jülich study and the Brandriss et al. investigation compare well with each other.

these discrepancies remains unclear, however, the pioneering works of *Juillet Leclerc and Labeyrie* [1987] and *Matheney and Knauth* [1989] were based on marine surface sediment samples. Therefore, recent seasonal or annual mean ocean temperatures had to be used as estimates of diatom growth temperatures and only approximations of the $\delta^{18}O$ values of ambient waters were possible. This could have easily caused higher uncertainties for the determined temperature dependent fractionation.

[17] The use of different techniques for oxygen isotope analysis of biogenic silica, namely controlled isotope exchange, stepwise fluorination and inductive high-temperature carbon reduction (*iHTR*), most likely have also contributed to these discrepancies [e.g., *Juillet Leclerc and Labeyrie*, 1987; *Schmidt et al.*, 2001]. Especially the problem of separating contaminating and probably exchanging oxygen containing compounds or molecular groups attached to or absorbed by the biogenic silica before silica decomposition is of great importance [*Labeyrie and Juillet*, 1982]. In this respect, it is remarkable that the similar dehydration techniques as were used by *Brandriss et al.* [1998] and our study led to reduced differences between the fractionation as well as between the respective temperature coefficients. The rather similar magnitudes of fractionation as given by our investigation and *Brandriss et al.* [1998] are promising and may open the chance for estimates of absolute temperature changes from biogenic silica oxygen isotopes in the future.

[18] With respect to the application of the temperature relation for oxygen isotope values of biogenic opal from sub-fossil and fossil diatoms caution seems to be, nevertheless, appropriate. For example, from a study in a marine environment it was concluded that in the course of settling through several hundreds of meters and final sedimentation, diatom opal may be subjected to an exchange of silica-bound oxygen [*Schmidt et al.*, 2001]. This would possibly change the primordial oxygen isotope signature if it affected substantial amounts of the opaline SiO_2. Due to shallower water depth and more rapid burial such an effect should be absent or inferior in lacustrine environments. However, further studies are needed to clarify this question for both freshwater and marine environments.

[19] Furthermore, evaporative enrichment of surface waters in the epilimnion of stratified lakes might lead, at least on short time scales, to an underestimation of the temperature change if the latter can only be inferred from $\delta^{18}O_{opal}$ values. This has clearly been documented by our study. Similarly, variations of the source value of ambient water on longer time scales due to changes of the $\delta^{18}O$ value in precipitation may obscure the temperature signal imposed on the oxygen isotope values of the diatom frustules. This might explain some of the variances of $\delta^{18}O_{opal}$ values already determined for sedimentary records but which could not only be ascribed to temperature changes [e.g., *Rioual et al.*, 2001].

References

Barker, P. A., F. A. Street-Perrott, M. J. Leng, P. E. Greenwood, D. L. Swain, R. A. Perrott, R. J. Telford, and K. J. Ficken (2001), A 14,000-year oxygen isotope record from diatom silica in two alpine lakes of Mt. Kenya, *Science*, *292*, 2307–2310.

Brandriss, M. E., J. R. O'Neil, M. B. Edlund, and E. F. Stoermer (1998), Oxygen isotope fractionation between diatomaceous silica and water, *Geochim. Cosmochim. Acta.*, *62*, 1119–1125.

Hu, F. S., and A. Shemesh (2003), A biogenic-silica $\delta^{18}O$ record of climatic change during the last glacial-interglacial transition in southwestern Alaska, *Quat. Res.*, *59*, 379–385.

Jones, V. J., M. J. Leng, N. Solovieva, H. J. Sloane, and P. Tarasov (2004), Holocene climate of the Kola Peninsula; evidence from the oxygen isotope record of diatom silica, *Quat. Sci. Rev.*, *23*, 833–839.

Juillet Leclerc, A., and L. Labeyrie (1987), Temperature dependence of the oxygen isotopic fractionation between diatom silica and water, *Earth Planet. Sci. Lett.*, *84*, 69–74.

Labeyrie, L. (1974), New approach to surface seawater palaeotemperatures using $^{18}O/^{16}O$ ratios in silica of diatom frustules, *Nature*, *248*, 40–42.

Labeyrie, L. D., and A. Juillet (1982), Oxygen isotopic exchangeability of diatom valve silica; interpretation and consequences for palaeoclimatic studies, *Geochim. Cosmochim. Acta*, *46*, 967–975.

Leng, M., P. Barker, P. Greenwood, N. Roberts, and J. Reed (2001), Oxygen isotope analysis of diatom silica and authigenic calcite from Lake Pinarbasi, Turkey, *J. Palaeolimnol.*, *25*, 343–349.

Lücke, A., R. Moschen, and G. H. Schleser (2005), High temperature carbon reduction of silica: A novel approach for oxygen isotope analysis of biogenic opal, *Geochim. Cosmochim. Acta*, *69*, 1423–1433.

Mann, M. E., R. S. Bradley, and M. K. Hughes (1999), Northern Hemisphere temperatures during the past millennium: Inferences, uncertainties and limitations, *Geophys. Res. Lett.*, *26*, 759–762.

Matheney, R. K., and L. P. Knauth (1989), Oxygen-isotope fractionation between marine biogenic silica and seawater, *Geochim. Cosmochim. Acta*, *53*, 3207–3214.

Raubitschek, S., A. Lücke, and G. H. Schleser (1999), Sedimentary patterns of diatoms in Lake Holzmaar, Germany (on the transfer of climate signals to biogenic silica oxygen isotoep proxies), *J. Palaeolimnol.*, *21*, 437–448.

Rings, A., A. Lücke, and G. H. Schleser (2004), A new method for the quantitative separation of diatom frustules from lake sediments, *Limnol. Oceanogr. Methods*, *2*, 25–34.

Rioual, P., V. Andrieu-Ponel, M. Rietti-Shati, R. W. Batterbee, J.-L. Beaulieu, R. Cheddadi, M. Reille, H. Svoboda, and A. Shemesh (2001), High-resolution record of climate stability in France during the last interglacial period, *Nature*, *413*, 293–296.

Schmidt, M., R. Botz, P. Stoeffers, T. Anders, and G. Bohrmann (1997), Oxygen isotopes in marine diatoms: A comparative study of analytical techniques and new results on the isotope composition of recent marine diatoms, *Geochim. Cosmochim. Acta*, *61*, 2275–2280.

Schmidt, M., R. Botz, D. Rickert, G. Bohrmann, S. R. Hall, and S. Mann (2001), Oxygen isotopes of marine diatoms and relation to opal-A maturation, *Geochim. Cosmochim. Acta*, *65*, 201–211.

Shemesh, A., C. D. Charles, and R. G. Fairbanks (1992), Oxygen isotopes in biogenic silica: Global changes in ocean temperature and isotopic composition, *Science*, *256*, 1434–1436.

Shemesh, A., L. H. Burckle, and J. D. Hays (1995), Late Pleistocene oxygen isotope records of biogenic silica from the Atlantic sector of the Southern Ocean, *Paleoceanography*, *10*, 179–196.

Von Storch, H., E. Zorita, J. M. Jones, Y. Dimitriev, F. González-Rouco, and S. F. B. Tett (2004), Reconstructing past climate from noisy data, *Science*, *306*, 679–682.

Webb, E. A., and F. J. Longstaffe (2003), The relationship between pytolith- and plant-water $\delta^{18}O$ values in grasses, *Geochim. Cosmochim. Acta*, *67*, 1437–1449.

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