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Oxygen Isotopes in Biogenic Silica: Global Changes in Ocean Temperature and Isotopic Composition

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A record of oxygen isotopes in biogenic silica from a deep-sea sediment core from the Southern Ocean reveals that marine diatoms retain their primary isotopic composition after burial. As a result, the marine diatom record can be combined with data on coexisting planktonic foraminifera to monitor past surface temperature and isotopic composition of seawater. The coupling of these two records allows the solution of two paleotemperature equations for each core interval. Data from a South Atlantic core show that the average $\delta^{18}O$ during the glacial period at this site was higher by about 1.3 per mil than average Holocene values, and that average glacial-age temperatures were not significantly different from average Holocene values.

The oxygen isotopic composition of foraminiferal calcite ($\delta^{18}O_c$) depends on the temperature and the isotopic composition of seawater ($\delta^{18}O_w$) from which it was deposited (*1*). Differentiation between these two components of the Pleistocene marine $\delta^{18}O$ record has been a long-standing problem because shifts in both temperature and mean oceanic $\delta^{18}O_w$ (a function of the amount of isotopically light water stored on continents in the form of ice caps) are crucial boundary conditions for climate models. One approach has been to estimate global ice volume by analysis of benthic foraminifera recovered from deep-sea sediments, with the assumption that the temperature of the bottom waters in which these foraminifera grew remained relatively constant (*2–4*). However, on the basis of ice sheet dynamics (*5*) and detailed comparisons between the deep-sea record and the elevation of coral terraces, it has become clear that the benthic $\delta^{18}O_c$ record does not trace ice volume accurately (*6–8*). Another, less inferential approach is to measure the isotopic composition of a coexisting phase in which oxygen isotopes are fractionated with a different temperature dependency. In this report we show that marine biogenic silica may be a suitable phase for such a comparison and describe a record of sea-surface temperature (SST) and $\delta^{18}O_w$ from the South Atlantic.

Marine biogenic silica is composed primarily of diatoms (marine algae) that deposit internal silica frustules. Silicification occurs only in the uppermost layer of the ocean, because of the light requirements for photosynthesis. Therefore, unlike planktonic foraminifera, which have the capacity to migrate through the water column, diatoms represent an ideal recorder of SST and the isotopic composition of seawater, provided that they deposit their silica with a known isotopic fractionation. Early attempts to measure the isotopic composition of biogenic silica ($\delta^{18}O_{Si}$) for paleoceanographic purposes (*9–12*) were hampered by difficulties in obtaining a clean diatom fraction, poor reproducibility due to isotopic exchange of oxygen between silica and hydration water during laboratory preparations, and initial results which suggested that the slope of the $\delta^{18}O_{Si}$-temperature relation was similar to that for carbonate.

More recent studies have suggested that these problems have been overcome. Diatoms in sediment may now be cleaned efficiently by differential settling and sieving combined with acid cleaning (*13*). Juillet-Leclerc and Labeyrie reported (*14*) an isotopic exchange technique that allows control and accurate calculation of the isotopically unstable (exchangeable) fraction of oxygen atoms in the silica structure. Measurement of diatoms from surface sediments with the use of this technique led to calibration of a paleotemperature equation (*14*):

$$t = 17.2 - 2.4(\delta^{18}O_{Si} - \delta^{18}O_w - 40) - 0.2(\delta^{18}O_{Si} - \delta^{18}O_w - 40)^2 \quad (1)$$

where t is temperature in degrees celsius. The slope of this equation is significantly different from that of the carbonate paleotemperature equation. This equation was calibrated between 1.5° and 24°C, based on samples from the Gulf of California for the high-temperature range. However, because effects of local upwelling were ignored in the tropical core sites, the equation yields temperatures that are too high for more polar sites. For example, measured $\delta^{18}O_{Si}$ in the top of core RC13-269 (South Atlantic) predicts a silicification temperature of 8.8°C, whereas the observed SST over the core site has never exceeded 4°C. The same applies for the top of the nearby core RC13-271. Therefore, we suggest that for high-latitude cores, it is preferable to use a calibration based only on the low-temperature data points reported in (*14*):

$$t = 11.03 - 2.03(\delta^{18}O_{Si} - \delta^{18}O_w - 40) \quad (2)$$

The slopes of Eqs. 1 and 2 are similar, and the recalibration changes primarily the intercept. The effect of temperature variability on $\delta^{18}O_{Si}$ is roughly twice that for carbonate, although more data points are needed to refine the $\delta^{18}O_{Si}$ paleotemperature equation. The difference in slopes suggests that it is possible to obtain a past record of both $\delta^{18}O_w$ and SST from diatom silica and planktonic foraminifera in a deep-sea core provided that both plankton groups deposited their solid phase at the same depth and time of year.

This condition is apparently satisfied in the Southern Ocean. Data from South Atlantic core tops suggest that the $\delta^{18}O$ of the planktonic foraminifer *Neogloboquadrina pachyderma* is close to equilibrium with surface water (*15*), and sediment trap studies indicate that the primary flux of *N. pachyderma* occurs within the seasonal bloom of diatoms (*16*). Therefore, the present diatomaceous ooze belt south of the Antarctic Polar Front (APF) is an appropriate region for paired time series of diatom and foraminiferal $\delta^{18}O$. We chose to analyze the siliceous core RC13-271 (51°59′S 04°31′E; water depth, 3634 m) for $\delta^{18}O_{Si}$ because it contains sufficient numbers of *N. pachyderma* for isotopic analysis and extends through the last glacial period with high resolution.

The 20- to 60-μm fraction of diatoms from 34 levels of core RC13-271 were cleaned and inspected with a microscope to ensure the absence of contaminant phases. The isotopic exchange procedure for $\delta^{18}O_{Si}$ analyses followed that in (*14*) with one modification: we used water with $\delta^{18}O$ of 39 per mil, close to the solid silica value, in the exchange reaction. This procedure eliminates the uncertainty involved with varying amounts of exchangeable oxygen in the silica structure. Fluorination was performed at the Weizmann Institute, and the

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results are calibrated versus the NBS-28 standard with a long-term reproducibility of ±0.14 per mil for diatom samples. Measurements of the $\delta^{18}O$ of *N. pachyderma* in RC13-271 were reported in (*15*). Diatom assemblages are well preserved throughout the core and consist mainly of *Thalassiosira lentiginosa*, *Nitzschia kerguelensis*, *Thalassiothrix*, and *Eucampia antarctica*. Generally, the sieving at 20 μm reduced the proportion of *N. kerguelensis* in the cleaned assemblage but there was no isotopic effect as a result of this bias (*14*). The similarity of the uppermost values for RC13-271 to those measured for the nearby core RC13-269 (*14*) suggests that the interlaboratory calibration is good.

The $\delta^{18}O_{Si}$ data from core RC13-271 (Fig. 1) clearly show that conditions for the Last Glacial Maximum (LGM) are recorded. Two lines of evidence indicate that the diatom opal silica has maintained its primary isotopic composition after burial, at least on time scales of about 80,000 years. The first is the alternation of $\delta^{18}O_{Si}$ between light and heavy values, regardless of burial depth. The second is the high $\delta^{18}O_{Si}$ values encountered in the deepest part of the core (44.59 and 44.61 per mil at 1850 and 2000 cm, respectively), which has an estimated age of about 80×10^3 years. Any postdepositional exchange with surrounding seawater or pore water would have severely smoothed the values with depth and altered the deepest samples toward low $\delta^{18}O_{Si}$. Thus, we are confident that the $\delta^{18}O_{Si}$ record from core RC13-271 is free of diagenetic artifacts.

Coupling of the silica data with the foraminiferal measurements and use of the linear form of the carbonate paleotemperature equation allow the change in isotopic composition of seawater (ΔW) and temperature over specific core intervals to be calculated:

$$\Delta t = t_1 - t_2 = 3.85[(\delta^{18}O_{Si_2} - \delta^{18}O_{Si_1}) - (\delta^{18}O_{c_2} - \delta^{18}O_{c_1})] \quad (3)$$

$$\Delta W = \delta^{18}O_{w_1} - \delta^{18}O_{w_2} = 0.89(\delta^{18}O_{Si_2} - \delta^{18}O_{Si_1}) - 1.9(\delta^{18}O_{c_2} - \delta^{18}O_{c_1}) \quad (4)$$

where the subscripts 1 and 2 refer to the lower and upper data points of the interval, respectively. We prefer this method to calculate changes in temperature and $\delta^{18}O_w$ rather than absolute values, because the intercept of the silica paleotemperature equation is uncertain. Using the core top values for the upper constraint, we generated curves of Δt and ΔW (with respect to the present) for the last 30,000 years (Fig. 2). In this calculation we interpolated $\delta^{18}O_c$ data for depths where only $\delta^{18}O_{Si}$ were available and ignored possible seasonality or isotopic disequilibrium effects in both diatoms and *N. pachyderma*. The Δt and ΔW curves show substantial cyclic variability. The cause of the large fluctuations remains unclear, but it could be the migration of the APF, across which both temperature and $\delta^{18}O_w$ decrease abruptly today. On the basis of the chronology developed previously for the core, the temperature variations for the last 30,000 years are roughly in phase with local summer insolation (*17*), with no mean glacial-interglacial shift.

In addition to these cycles, which represent a more local phenomenon, the ΔW curve also records longer term glacial-interglacial variations. The average ΔW values for the entire Holocene period (0 to 700 cm) and for the last glacial period (850 to 1200 cm) differ by 1.3 per mil. This value is close to that calculated for the change in global ice volume on the basis of the sea level record of Barbados coral (*18*) and deep-sea foraminifera (*3*, *19*). The corresponding temperature change that might be attributed to local effect of SST is only 1°C. The same conclusion is reached by taking the ^{14}C ages at face values. In this case, the interval of 945 to 930 cm represents the LGM level and the corresponding values of $\delta^{18}O_{Si}$ and $\delta^{18}O_c$ are 44.55 and 4.31 per mil, respectively. Recent values of $\delta^{18}O_{Si}$ and $\delta^{18}O_c$ are 42.41 and 2.70 per mil, respectively (aver-

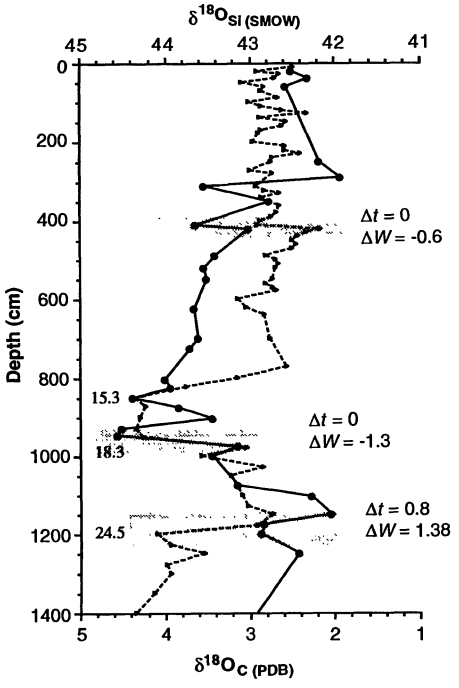

Fig. 1. Down-core variations of oxygen isotopic composition of diatoms ($\delta^{18}O_{Si}$, solid line) and foraminifera ($\delta^{18}O_c$, dashed line) in core RC13-271. The numbers next to the stippled areas correspond to the change in temperature (Δt) and isotopic composition of seawater (ΔW) in the interval. ^{14}C ages (*20*) (at 850, 925, and 1200 cm) are indicated to the left of the curves. SMOW, standard mean ocean water; PDB, Pee Dee belemnite.

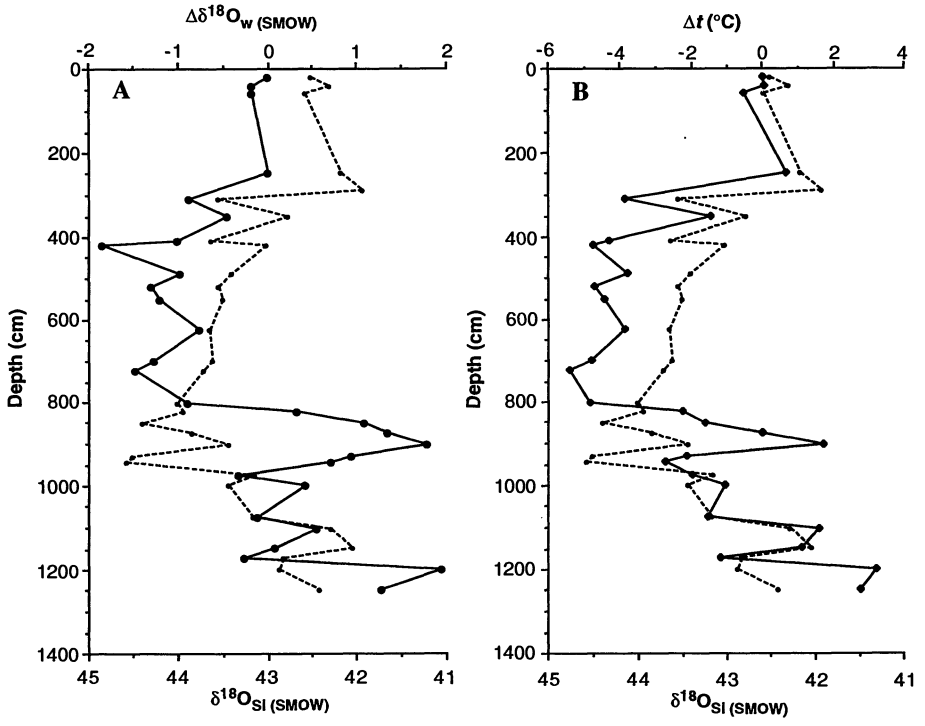

Fig. 2. Calculated variation in seawater isotopic composition (**A**) and temperature (**B**) in core RC13-271. The solid curves represent the difference between the calculated value at each depth and the calculated value at the top. The dashed lines connect the measured $\delta^{18}O_{Si}$ data points.

age of the upper 40 cm of the core). The calculation shows that in the transition from full glacial conditions to the Holocene, the $\delta^{18}O$ value of seawater decreased by 1.15 ± 0.18 per mil (1σ) while SST increased by 2.0° ± 0.8°C. Because we averaged data from intervals that represent about 1000 years, time longer than the mixing time of the ocean, the calculated change in $\delta^{18}O_w$ is the global effect and not a local feature of the APF zone. This observation suggests that, in the absence of local variability, the coupling of silica and carbonate $\delta^{18}O$ can be used to predict the global ice volume effect. If so, the method represents one possible means for resolving ice volume changes over intervals poorly constrained by coral reef terraces.

Short-term fluctuation can be analyzed similarly by taking segments of the curve. The sharp transition into the LGM corresponds to an enrichment of 1.3 per mil in seawater $\delta^{18}O$ composition. The same applies for the transition of 0.6 per mil in $\delta^{18}O_w$ at 420 cm. The shift around 1200 cm corresponds to a cooling of 0.8°C and a negative shift of 1.38 per mil in $\delta^{18}O_w$. The migration of the APF north of its present position and the presence of meltwater would generate such a change in isotopic composition of silica and carbonate. Such an effect cannot be deduced from analysis of a single phase and requires the simultaneous measurement of two phases.

More $\delta^{18}O_{Si}$ records from other Southern Ocean cores are needed to assess the significance of the local variability recorded in core RC13-271. In order for the coupled $\delta^{18}O_{Si}$-$\delta^{18}O_c$ approach to be generally useful, the relation between diatom blooms and the seasonal growth of surface-dwelling planktonic foraminifera must be established in other regions of the ocean. Our results provide the basis for extending research to regions of the ocean floor void of carbonate, and isotope stratigraphies may be constructed for records where previously they seemed impossible.

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Sexually Antagonistic Genes: Experimental Evidence

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When selection differs between the sexes, a mutation beneficial to one sex may be harmful to the other (sexually antagonistic). Because the sexes share a common gene pool, selection in one sex can interfere with the other's adaptive evolution. Theory predicts that sexually antagonistic mutations should accumulate in tight linkage with a new sex-determining gene, even when the harm to benefit ratio is high. Genetic markers and artificial selection were used to make a pair of autosomal genes segregate like a new pair of sex-determining genes in a *Drosophila melanogaster* model system. A 29-generation study provides experimental evidence that sexually antagonistic genes may be common in nature and will accumulate in response to a new sex-determining gene.

Sexually antagonistic genes (SA genes) are those that are favored by selection in one sex but disfavored in the other. Such genes have been hypothesized to play an important role in the evolution of karyotypes, sexual dimorphism, sex chromosomes, and genetic polymorphisms (*1–5*), but there is little evidence for an adequate pool of SA genes in nature.

One of the major problems that interferes with a search for SA genes is that theory predicts only a very narrow range of circumstances under which they are expected to be maintained in the polymorphic state (*2, 3*). As a consequence, SA genes may be rare at individual loci despite their potential abundance when summed over whole genomes or populations.

One circumstance where the level of polymorphism is expected to be high is that of primitive sex chromosomes, where a single Mendelian gene (or cluster of tightly linked genes) determines gender. Theoretical work predicts that the chromosomal region located within a few centimorgans (cM) of a sex-determining gene will be a "hot spot" for the accumulation of SA genes favoring the heterogametic sex, even when the disadvantage to the homogametic sex is large (*2, 4*).

The rationale for the theoretical prediction is intuitively straightforward. First consider the requisite conditions for an SA gene to accumulate at an ordinary autosomal locus. A new SA mutation favoring females will be transmitted with equal frequency to sons and daughters. When in females (males) it experiences a gain (loss) in gene frequency due to the action of sex-specific selection. To accumulate in the gene pool, gain must exceed loss, requiring the mutation to have a net advantage when averaged across the sexes. A similar SA mutation introduced at a position 1 cM away from a female-determining gene will be transmitted 99% (1%) of the time to daughters (sons) where it is favored (disfavored). This sex-specific gene transmission will permit virtually any female-benefit–male-detriment mutations to accumulate when rare, even when highly harmful to males. The constraint for the accumulation of SA genes is far less stringent at loci near a sex-determining locus, hence the SA "hot spot" prediction.

Our experiments take advantage of this prediction by creating a new sex-determining locus in a *Drosophila melanogaster* model system and then testing for the accumulation of SA genes in response to this experimental treatment. Details of the stock construction and protocol for maintaining the flies are given in Fig. 1. The basic strategy was to use artificial selection to make a dominant eye-color gene segregate as if it were a new female-determining gene. In each generation, artificial selection

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