Productivity Control of Fine Particle Transport to Equatorial Pacific Sediment

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Productivity control of fine particle transport to equatorial Pacific sediment

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Abstract. Accumulation rates of ³He (from cosmic dust), ²³⁰Th (produced in the water column), barite (produced in the water column during decay of organic matter), and Fe and Ti (arriving with wind-borne dust) all are positively correlated in an equatorial Pacific core (TT013-PC72; 01.1°N, 139.4°W; water depth 4298 m). These accumulation rates are also positively correlated with the accumulation rates of noncarbonate material. They are not significantly correlated to the mass accumulation rate of carbonate, which makes up the bulk of the sediment. The fluctuations in accumulation rates of these various components from different sources thus must result from variations in some process within the oceans and not from variations in their original sources. Sediment focusing by oceanic bottom currents has been proposed as this process [Marcantonio et al., 1996]. We argue that the variations in the accumulation rates of all these components are dominantly linked to changes in productivity and particle scavenging (³He, ²³⁰Th, Fe, Ti) by fresh phytoplankton detritus (which delivers Ba upon its decay) in the equatorial Pacific upwelling region. We speculate that as equatorial Pacific productivity is a major component of global oceanic productivity, its variations over time might be reflected in variations in atmospheric levels of methanesulfonic acid (an atmospheric reaction product of dimethyl sulfide, which is produced by oceanic phytoplankton) and recorded in Antarctic ice cores.

1. Introduction

The eastern equatorial Pacific Ocean has been speculated to have a major influence on global climate [e.g., Cane, 1998]. New productivity in that region is an important component of global oceanic productivity [e.g., Archer and Maier-Reimer, 1994; Shimmield and Jahnke, 1994]. Nutrient- and CO₂-rich waters well up in this region and are the largest natural source of CO₂ to the atmosphere because only a small fraction of the upwelled CO₂ is recycled biologically [Murray et al., 1994]. Fluctuations in productivity and burial efficiency of the organic matter in this region on short (annual) and longer (glacial-interglacial) timescales thus have the potential to have a major impact on the global carbon cycle [e.g., Hansell et al., 1997].

The sedimentary record of carbonate sedimentation over the last several glacial cycles in the equatorial Pacific has been studied for more than 45 years [e.g., Arrhenius, 1952; Hays et al., 1969; Thompson and Saito, 1974; Shackleton and Oddyke, 1976; Valencia, 1977; Chuey et al., 1987; Farrell and Prell, 1989; Rea et al., 1991; Lyle et al., 1988, 1992], but there is no agreement on its interpretation [e.g., Wei et al., 1995; LaMontagne et al., 1996]. Specifically, there is no agreement whether the fluctuations in carbonate percentage and carbonate accumulation rates reflect fluctuations in primary productivity [Archer, 1991], in dissolution [Farrell and Prell, 1989], or in sediment focusing by bottom currents [Marcantonio et al., 1996]. If these fluctuations are driven by dissolution, there is no agreement on the question whether the fluctuations in dissolution are caused mainly by changes in deep-water corrosiveness, thus in deep-water circulation patterns [Farrell and Prell, 1989], or by changes in supply of organic carbon (thus productivity) [e.g., Archer, 1991; Hagelberg et al., 1995].

If productivity fluctuations, such as the productivity increase by a factor of 2 postulated to have occurred during the last glacial at low latitudes [e.g., Pedersen, 1983; Herguera and Berger, 1991; Murray et al., 1993; Paytan et al., 1996], caused the carbonate fluctuations, we do not know what caused the changes in productivity. Different authors have invoked increased rates of upwelling [e.g., Berger and Weffer, 1991], increased rates of supply of limiting micronutrients such as iron [Coale et al., 1996], or more complex processes involving nitrate utilization [Farrell et al., 1995; Falkowski, 1997]. It is not clear whether any proxy (e.g., concentrations or mass accumulation rates of barite, opal, organic carbon, CaCO₃, or Al/Ti) reliably mirrors long-term productivity or at least delivery of organically produced material to the seafloor [e.g., McCorkle et al., 1994; Pisas et al., 1995], although primary production and particulate organic flux presently are well correlated in the equatorial Pacific [e.g., Betzer et al., 1984; Smith et al., 1997].

We evaluate published data on an equatorial Pacific core and suggest a mechanism (marine productivity and particle scavenging) by which all these different data sets can be explained in an internally consistent manner. We add a

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speculation over possible teleconnections between equatorial Pacific productivity and deposition of methanesulfonic acid (MSA) in the Antarctic ice cap.

Figure 1a. Core TT013-PC72. Age model derived from correlation of benthic oxygen isotope data [Marcantonio et al., 1996; A. Mix, personal communication, 1997] to the SPECMAP stack [Imbrie et al., 1984]; gray bars indicate glacial isotope stages 2 through 12. Accumulation rate of carbonate [Murray et al., 1995].

Table 1. Age Model of Core TT013-PC72

<table>
<thead>
<tr>
<th>Event</th>
<th>Boundary of Stages</th>
<th>Age, kyr</th>
<th>Depth in PC72, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1/2</td>
<td>12</td>
<td>35–40</td>
</tr>
<tr>
<td>3.0</td>
<td>2/3</td>
<td>24</td>
<td>75–80</td>
</tr>
<tr>
<td>4.0</td>
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<td>4/5</td>
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<td>165–170</td>
</tr>
<tr>
<td>6.0</td>
<td>5/6</td>
<td>128</td>
<td>235–240</td>
</tr>
<tr>
<td>7.0</td>
<td>6/7</td>
<td>186</td>
<td>368–373</td>
</tr>
<tr>
<td>8.0</td>
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<tr>
<td>12.0</td>
<td>11/12</td>
<td>423</td>
<td>742–747</td>
</tr>
</tbody>
</table>

a From Murray et al. [1995] and Marcantonio et al. [1996].

b Age (kyr) after Imbrie et al. [1984], names of isotope events and stage boundaries as listed by Prell et al. [1986].

2. Data Compared

Core TT013-PC72 (140°W, 0.1°N; water depth 4298 m) was recovered as part of the equatorial Pacific Joint Global Ocean Flux Studies (JGOFS). An age model for its sediments was derived from δ18O analysis of the benthic foraminifer Cibicidoides wuellerstorfi and correlation to the SPECMAP stack [Murray et al., 1995; Marcantonio et al., 1996; A. Mix, personal communication, 1997]. The benthic foraminiferal oxygen isotope record for core TT013-PC72 closely resembles the SPECMAP stacked record, with many of the subevents well represented. The depth of the stage boundaries is close to these in the late Quaternary reference section [Prell et al., 1986] (Table 1). Numerical ages of the samples and accumulation rates can thus be estimated with confidence within the SPECMAP age model.

There is a strong positive correlation between accumulation rates of Fe and Ti (wind-borne dust), 230Th (produced in the water column by radio-isotopic decay), 3He (carried by interplanetary dust particles), and barite (produced by decay in association with organic matter), as can be seen by comparing data by Murray et al. [1995], Marcantonio et al. [1995, 1996], and Paytan et al. [1996] (Figure 1a–j). All these accumulation rates are significantly and positively correlated to each other. There is no simple, significant correlation between these accumulation rates and the oxygen isotope record of benthic foraminifera, i.e., between these rates and global ice volume (Figure 2). The accumulation rates of these sediment compo-
between the accumulation rates of these noncarbonate components and that of CaCO₃, which determines the bulk accumulation rate. It is not probable that size-dependent winnowing only could have caused the differences in CaCO₃ and non-CaCO₃ accumulation rates because a large part of the carbonate is derived from nanoplankton in the same size range as the fine noncarbonate particles. Marcantonio et al. [1995] suggested that CaCO₃ dissolution caused this lack of correlation, because the peaks of ³He and ²³⁰Th accumulation occurred at minima in CaCO₃% (Figures 1a–j and 4). They thus implied that low CaCO₃% values are caused by dissolution. In order to evaluate whether low carbonate content is caused by dissolution, we need to compare the CaCO₃% data with an index of dissolution, such as the index for dissolution of planktonic foraminifera [e.g., Berger, 1973; Le and Shackleton, 1992; LaMontagne et al., 1996]. If we do this for core TT013-PC72, we see that there is no significant correlation between the CaCO₃% and the mass accumulation rates of CaCO₃ and between CaCO₃% and indices of dissolution such as the fragmentation of planktonic foraminifera (Figure 5).

If we assume an initial sediment composition of 85% carbonate, 15% noncarbonate (as usually done for equatorial Pacific sediments from depths of around 4200 m [Pisias and Prell, 1985]), a change to a carbonate percentage of 60% (about the lowest value observed) would require dissolution of ~75% of the original carbonate [Dean et al., 1981]. Such

3. Discussion

The positive correlation between accumulation rates of various components that have different sources indicates that all these particles (wind-borne, cosmic dust, biogenic) were concentrated within the water column and that the fluctuations in their accumulation rates must have been caused by a common concentrating process within the oceans. Fluctuations in accumulation rates of Fe, for example, may not be caused directly by fluctuations in wind-borne dust concentrations (in contrast to Murray et al. [1995]). Fluctuations in the accumulation rate of ³He are likewise probably not caused by fluctuations in the influx of cosmic dust (in contrast to Farley and Patterson [1995]).

We argue that sediment focusing may very well be a factor but that it cannot explain the correlations by itself alone: if there had been simple sediment focusing, there should have been a correlation between the accumulation rate of the noncarbonate components and that of bulk sediment. There is no such correlation (Figure 3) because there is no correlation...
with François et al. [1990] that sediment focusing is the most important factor in equatorial Atlantic sediments from a non-upwelling region but consider these observations not relevant to the interpretation of carbonate sedimentation and dissolution in an upwelling region in the Pacific. In the equatorial Atlantic cores from nonupwelling regions, for instance, carbonate productivity was lower during the last glacial [François et al., 1990], in contrast with most interpretations of the eastern equatorial upwelling region during the last glacial [e.g., Pedersen, 1983; Herguera and Berger, 1991; Murray et al., 1993; Paytan et al., 1996]. Others have argued that sediment trap data may not accurately reflect the spatial and temporal heterogeneity of the biogenic flux [Buesseler et al., 1994; Boyd and Newton, 1997; Beaulieu and Smith, 1998; Shaw et al., 1998].

JOGOFS data along 140°W [Honjo et al., 1995] demonstrate strong variability in space and time and demonstrate the occurrence of very short-term (less than 3 weeks) episodes of high-particle flux during the passage of tropical instability waves. We suggest specifically that the well-recognized overestimates of particle flux during low-productivity periods and underestimates at high-productivity periods may be more severe than suggested [François et al., 1993; Buesseler, 1998]. Shaw et al. [1998], for instance, document that the accumulation rate of Th nuclides is underestimated by a factor of 10 using sediment trap data in the northeastern Pacific.

Figure 1c. Same as Figure 1a, but for accumulation rate of Ti [Murray et al., 1995].

Severe dissolution does not agree with the observed indices of dissolution (Figure 5). Decoupling of CaCO₃% and dissolution intensity has been observed in many cores in the equatorial Pacific [e.g., Luz and Shackleton, 1975; Wei et al., 1995; LaMontagne et al., 1996].

We argue that the correlation between CaCO₃ minima and the excess deposition of ³He and ²³⁵Th can be seen as an indirect argument against sediment focusing as a cause of this excess deposition. The CaCO₃% minima have been widely correlated among many cores in the equatorial Pacific region [e.g., Arrhenius, 1952; Hays et al., 1969; Luz and Shackleton, 1975; Farrell and Prell, 1989]. If these minima are linked to sediment focusing, the excess deposition resulting from the focusing must have also occurred throughout the eastern equatorial Pacific “sediment bulge,” which leaves the place of origin from where the focused sediment must have been removed far outside this bulge. Such an outside source appears more probable if we envisage the material to have been moved (at least in part) toward the “equatorial bulge” by lateral advection toward the equator in surface to upper intermediate waters rather than by bottom currents.

Marcantonio et al. [1996] favored sediment focusing by bottom currents as the mechanism and cited sediment trap data [Lao et al., 1993; François et al., 1990] to argue that organically produced particle scavenging could not be the cause of the correlation between all the accumulation rates. We agree

Figure 1f. Same as Figure 1a, but for the ³He burial rate [Marcantonio et al., 1996].
We also conclude that sediment accumulated during these high-flux events may make up a significant part of the total sediment deposited [Kemp et al., 1995; Verity et al., 1996; Shaw et al., 1998]. On the basis of the above considerations we argue that fluctuations in the abundance of scavenging phytodetritus which is deposited rapidly to the seafloor may have caused the fluctuations in accumulation rates of all the various materials associated with fine, noncarbonate particles derived from different sources. JOGFS studies along 140°W document that presently, phytodetritus accumulates on the seafloor in a pattern reflecting overall productivity [Smith et al., 1996; Barber et al., 1996], with the highest accumulation rates close to the location of core TT013-PC72. This phytodetritus may largely be concentrated in dense mats containing needle-shaped diatoms [Kemp et al., 1995], which are concentrated during the passage of tropical instability waves [e.g., Kemp, 1994; Yoder et al., 1994; Smith et al., 1996]. Such long waves occur seasonally, are weak during El Niño events [Feely et al., 1994], but are strong just after its ending [Yoder et al., 1994; Smith et al., 1996].

In the present ocean, removal of Th isotopes from seawater column is strongly linked to biological activity [e.g., Lao et al., 1993; Shaw et al., 1998]. This phytodetrital scavenging is at present probably not a very important contributor to the sediment flux, but it might have been more important during earlier geological periods [e.g., Kemp, 1995]. We suggest that at times of higher equatorial Pacific upwelling rates, productivity was higher. At these times, phytoplankton blooms were more frequent and rapidly deposited phytodetrital matter contributed a larger fraction of the total sediment compared to the present [e.g., Ittekat, 1993; Verity et al., 1996; Buessler, 1998; Shaw et al., 1998]. We thus envisage that the strong enrichment in 234Th (more than can be derived from the water column directly over the site of the core) as caused by a combination of high and fluctuating productivity, scavenging of elements by organically produced particles, and concentration of such particles from a fairly large region by passage of tropical instability waves.

Accumulation rates of the various fine-grain particles associated components (such as cosmic He) and scavenged elements (such as Ti and Al) can therefore be used as a proxy for delivery of organically produced material to the seafloor. In the equatorial Pacific the particulate organic flux is linked to primary productivity [Betzer et al., 1984], and the vertical flux of biogenic particles has been shown to exert tight control on the nature and rates of benthic biological and chemical processes [Smith et al., 1997]. We therefore can use the accumulation rates of particles that are indirectly (by scavenging of dissolved elements or small particles) associated with organic matter flux as a proxy for primary productivity.

This conclusion is supported by the positive correlation with the barite accumulation rate because barite forms in microenvironments within decaying organic matter [e.g., Dehairs et al., 1996].

**Figure 1g.** Same as Figure 1a, but for accumulation rate of barite [Paytan et al., 1996].

**Figure 1h.** Same as Figure 1a, but for burial rate of excess 230Th [Marcantonio et al., 1995, 1996].
Figure 1. Same as Figure 1a, but for dissolution of carbonate in core TT013-PC72, using the percentage of whole planktonic foraminifera as an indicator (K. Y. Wei, unpublished data, 1999).

Barite accumulation rates are thus directly related to the organic matter export flux [Paytan et al., 1996] and to the accumulation rates of organic carbon in the sediments [Lyle, 1988, 1992]. Further support comes from a comparison of the accumulation rates of various fine-grain particle associated components with the record of combustion oxygen demand (COD) over the last 400 kyr at eastern equatorial Pacific Ocean Drilling Program (ODP) site 849 at 0°11'N, 110°34'W and a water depth of 3839 m [Perks, 1999]. This parameter provides a good approximation of the organic carbon content of sediments, which have such low-organic carbon content that it cannot be reliably measured. COD data [Perks, 1999] are available at higher time resolution than the data for core TT013-PC72, and we thus cannot compare the records sample by sample. There are, however, peaks in COD at site 849 and peaks in the fine-grain particle associated components in core TT013-PC72 at 20 kyr, 70 kyr, 150–185 kyr, 275 kyr, and 320 kyr.

This view implies that the calcium carbonate accumulation rate at the location of TT013-PC72 cannot be used as productivity proxy: at very high productivity the main primary producers are the Si-walled diatoms rather than the carbonate-walled nanoplankton [e.g., Dymond and Collier, 1988]. Calcite-secreting and silica-secreting plankton communities may alternate in dominating overall productivity [Lyle et al., 1988]. In the equatorial Pacific, high productivity could be reflected by low values of CaCO₃%, as a result of a combination of dilution by biogenic silica and increased dissolution caused by the larger supply of organic material [e.g., Theyer et al., 1985; Hagleberg et al., 1995]. The deposition of the various components linked to organic material does not necessarily imply high net accumulation rates of organic matter in the sediments because labile organic matter is quickly degraded on the seafloor by bacteria and protists, given an adequate oxygen supply [Gooday and Turley, 1990; Turley and Locht, 1990; Poremba, 1994].

We do not know whether the overall biological composition of the bulk phytoplankton (thus its biogenic silica and organic matter content) would have been constant over time. Probably, it fluctuated on glacial-interglacial timescales with fluctuations in the biological components [e.g., Lyle et al., 1988]. We can therefore not assume that rates of element concentrations within this phytoplankton have been constant over time. The ratio of scavenged material to organically produced material likewise may have fluctuated.

The peaks in accumulation rates of the above-mentioned indicators are to some extent but not completely related to glacial isotope stages: comparison of the records with the oxygen isotope data from core PC72 (Figure 1a) shows that they occurred in glacioclases 2, 4, 6, and 8 (but were much more short-lived than glacioclases 6 and 8) but also in interglacioclases 9 and 11, which are said to represent the warmest two interglacioclases [e.g., Hiddell, 1993]. There is no peak in accumulation rate in biogenic Ba apparent in interglacials 9, but this is probably caused by a lack of data points over the core interval with the

Figure 1j. Same as Figure 1a, but for percentage of CaCO₃ in core TT013-PC72 [Murray et al., 1995].
peak in mass accumulation rates of the other productivity indicators.

The linkage between fluctuations in CaCO₃%, CaCO₃ accumulation rates, and glacial-interglacial timing is complex [e.g., Luz and Shackleton, 1975; Farrell and Prell, 1989]. Productivity in tropical Pacific regions probably was not coupled to ice-volume fluctuations, the variance of which was dominated by the 100 kyr Milankovitch cycle during the last 900 kyr (Figure 2). Tropical productivity fluctuated dominantly at the periodicity of precessional forcing (19–23 kyr) in the equatorial Indian Ocean [Beaufort et al., 1997; Keeling et al., 1998], western equatorial Pacific [Perks and Keeling, 1998; Cane, 1998], and eastern equatorial Pacific [Perks, 1999]. Perks et al. [1999] records of COD (a productivity proxy, see above) show peaks at times of peaks in the mass accumulation rates of the productivity indicators observed in core TT013-PC72, although the time resolution of these records is not quite sufficient to resolve precessional periodicity.

Variability on timescales differing from the main glacial-interglacial 100 kyr periodicity in ice volume may explain that not all glacials at the location of TT013-PC72 were similar: during glacials 2, 4, and 6, peaks in carbonate and noncarbonate accumulation rates appear to be at least generally coeval, but during the earlier glacials and in interglacial 11, they are strongly decoupled. Carbonate mass accumulation rates are generally high in glacials but are not well correlated to the benthic foraminiferal oxygen isotope record on the same core (Figure 1a–j).
The correlation between CaCO3% values and glacial-interglacial stages (Figure 1a–j) is even less precise. There is no clear correlation between CaCO3% values and the transition between glacial and interglacial stages, in contrast with Broecker and Sanyal [1997]. These authors argued that dissolution events in core TT013-PC72 occurred at glacial/interglacial stage boundaries, but of the three events that they mentioned, only one (stage 7–6) occurred within a few thousand years of such a transition (Figure 1a–j). The earlier minima occur at about the middle of glacial stage 8 and interglacial stage 11; the latter of these can be correlated to the widely recognized carbonate minimum B9 [Hays et al., 1969; Farrell and Prell, 1989].

Understanding the coupling and decoupling of the accumulation rates of carbonate and noncarbonate is of importance for the understanding of glacial/interglacial changes in equatorial Pacific climate. It is evident that the last glacial was not typical of all earlier glacial periods (Figure 1a–j), possibly because the variability in precession and eccentricity bands interacts differently during different isotope stages [e.g., Beaufort et al., 1999].

Equatorial Pacific productivity is a large component of global oceanic productivity [Barber and Chavez, 1987], and productivity fluctuations in eastern and western Pacific appear to be correlated [Perks, 1999]. Therefore we argue that equatorial Pacific productivity fluctuations could be seen as an important factor of global oceanic productivity. If this is correct, we might see an impact of variations in equatorial Pacific productivity in global records of methanesulfonic acid (MSA), a reaction product of dimethyl sulfide which is produced by phytoplankton. Dimethyl sulfide (DMS) and its reaction products are indeed seen to be enriched across the high-produc-

Figure 3. (a) Comparison of the accumulation rates of Fe and bulk sediment in core PC72 [Murray et al., 1995]. (b) Comparison of bulk accumulation rates with accumulation rates of CaCO3 and non-CaCO3 [Murray et al., 1995].

Figure 4. Comparison of the percentage of CaCO3 [Murray et al., 1995] and the accumulation rates of (a) Fe and (b) Ti.

A relation between equatorial Pacific productivity and the Antarctic MSA record appears to exist in records over the last 150 kyr [LeGrand et al., 1991], as seen from the general agreement in accumulation rate of biogenic Ba in TT013-PC72 with that of MSA in the Antarctic Vostok ice core (Figure 6). Specifically, the peak in equatorial productivity at ~70 kyr (glacial isotope stage 4) corresponds to a peak in Antarctic MSA.

We do not think that these high concentrations in MSA in Antarctic ice cores during glacial times were derived from productivity close to the Antarctic continent, although LeGrand and Fenet-Saigne [1991] linked variations in MSA accumulation rates in Antarctic snow layers to strong El Niño events. They argued that the enrichments in MSA were produced close to the Antarctic continent, possibly as a result of El Niño–Southern Oscillation linked variations in sea ice cover because in the present ocean, high levels of DMS are produced during the Southern Hemisphere summer by Phaeocystis [DiTullio et al., 1998; Kettle et al., 1999]. Even during cold periods in the Holocene, however, productivity was low in the Antarctic [e.g., Leventer et al., 1996], and Antarctic productivity during the Last Glacial Maximum was depressed [e.g., François et al., 1993; Kumar et al., 1993]. We therefore argue that the shelf regions where relatively high productivity occurs in the Southern Hemisphere summer would have much more extensive ice cover during glacials, limiting seasonal phytoplankton productivity. The elevated MSA levels thus would have to be transported from a place with elevated productivity during glacial periods, such as the equatorial Pacific, although we do not know whether the apparent correlation is due primarily to changes in equatorial Pacific productivity patterns or to changes in the efficiency of atmospheric transport to Antarctica.

4. Conclusions

Accumulation rates of sediment components derived from interplanetary dust (³He), from radioactive decay in the water column (²³⁰Th), from biological activity in the water column (barite), and from wind-blown dust (Fe, Ti) are strongly correlated in an equatorial Pacific carbonate core. We suggest that this strong correlation results dominantly from concentration of all these components by particle scavenging of organically produced particulate matter (³He, ²³⁰Th, Fe, Ti) and decomposition of the organic matter (Ba). Both productivity and efficiency of scavenging may play a role. The accumulation rates of these components thus are proxies for productivity.

Figure 5. Comparison of the percentage CaCO₃ [Murray et al., 1995] with the percentage of whole foraminifera, an indicator of severity of dissolution.

Figure 6. Accumulation rates of Ba in equatorial Pacific core TT013-PC72 (open symbols [Murray et al., 1995]) compared to accumulation rates of MSA in the Antarctic Vostok ice core (solid symbols [LeGrand et al., 1991]). The correlation was made using the depths provided by LeGrand et al. [1991] for the Vostok ice core and calculating numerical ages according to Sowers et al. [1993].
We speculate that global oceanic productivity is strongly influenced by equatorial Pacific productivity and that this global signal might be present in the MSA records in Antarctic ice cores.

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