"compound" clusters to explain why the excess energy is not completely quenched in radiationless processes but may manifest itself in light emission from the separated fragments.

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Glacial to Interglacial Fluctuations in Productivity in the Equatorial Pacific as Indicated by Marine Barite

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An empirical correlation between marine barite ($BaSO_4$) accumulation rate in core-top sediment samples from two equatorial Pacific transects (at 140°W and 110°W) and the estimated primary productivity of the overlying water column were used to evaluate glacial to interglacial changes in productivity. Fluctuations in barite accumulation rates down-core indicate that during glacial periods of the past 450,000 years, the productivity in the central and eastern equatorial Pacific was about two times that during intervening interglacial periods. This result is consistent with other evidence that productivity was high in the eastern and central equatorial Pacific during the last glacial.

Ocean productivity influences organic carbon supply to the sediment and its burial efficiency, affecting the partitioning of CO_2 between the ocean and atmosphere, and thus climate (*1–3*). Large glacial to interglacial fluctuations in atmospheric CO_2 concentrations have been observed in ice cores and related to variations in ocean productivity (*4*, *5*). In order to discern the coupling between ocean circulation, productivity, and climate, it is important to be able to estimate past ocean productivity and thus to reconstruct its history from the record of marine sediments (*6*).

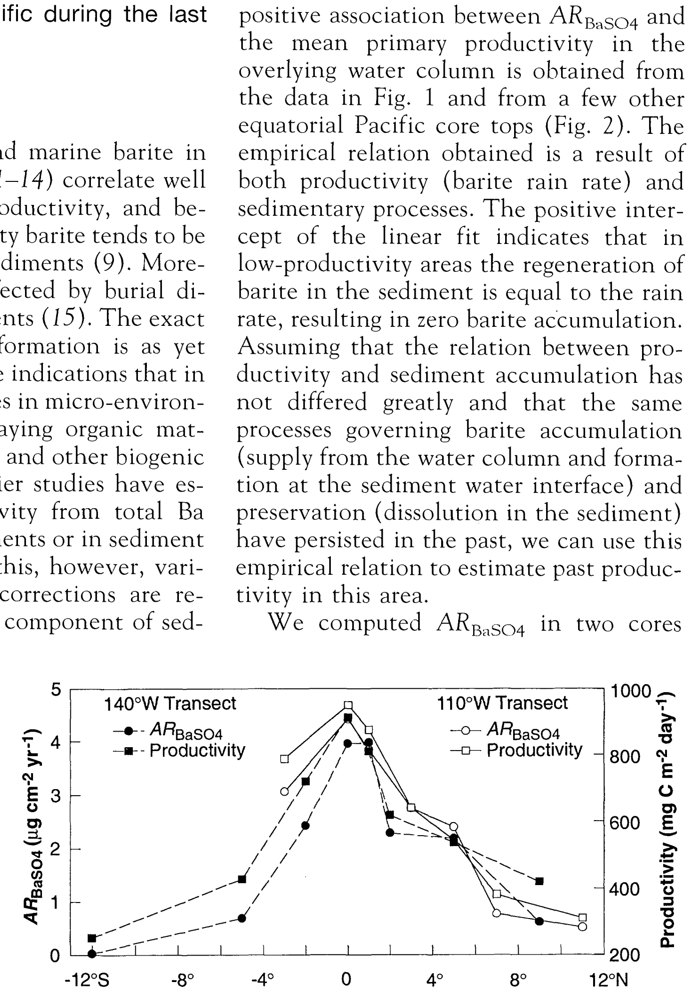
We use barite accumulation rate (AR_{BaSO4}) in sediments to reconstruct changes in productivity in the equatorial Pacific for the past 450,000 years and to relate these fluctuations to the climate record. The equatorial Pacific region is emphasized because upwelling of CO_2-rich waters in this region provides the largest natural source of CO_2 to the atmosphere (*7*, *8*).

Barite is a suitable proxy for oceanic productivity because biogenic Ba in sediment traps (*9*, *10*) and marine barite in deep-sea sediments (*11–14*) correlate well with the overlying productivity, and because of its low solubility barite tends to be preserved in pelagic sediments (*9*). Moreover, barite is not affected by burial diagenesis in oxic sediments (*15*). The exact mechanism of barite formation is as yet unknown, but there are indications that in the ocean it precipitates in micro-environments containing decaying organic matter, acantharian shells, and other biogenic remains (*16–18*). Earlier studies have estimated paleoproductivity from total Ba concentration in sediments or in sediment traps (*9*, *19–22*). For this, however, various assumptions and corrections are required because Ba is a component of sediment phases not directly related to biogenic productivity, such as windblown silicates and Fe-Mn oxyhydroxides (*9*). We measured, instead, only the concentration of barite grains, the dominant Ba-bearing phase related to biological productivity (*9–11*, *23*).

We separated barite from equatorial Pacific sediments using a sequential leaching method (*18*); yields were between 90 to 95% and the reproducibility was within ±5%. The cores selected are from two transects across a region of the equatorial Pacific (12°S to 11°N at 110°W and 140°W) where productivity in the overlying water columns varies greatly (*8*). We determined AR_{BaSO4} from weight percent barite, sedimentation rates, and sediment dry bulk densities (*24*). Gross primary productivity estimates were compiled from measurements made over the past 12 years (*25–28*). At both transects, the maxima in AR_{BaSO4} and productivity were centered at the equator (Fig. 1), at the 110°W transect however, this zone is somewhat wider. Other productivity indicators [abundance of $CaCO_3$ and organic carbon (*29*) and Al/Ti (*30*), Pa/Th, and Be/Th (*31*) ratios] show similar distributions. A positive association between AR_{BaSO4} and the mean primary productivity in the overlying water column is obtained from the data in Fig. 1 and from a few other equatorial Pacific core tops (Fig. 2). The empirical relation obtained is a result of both productivity (barite rain rate) and sedimentary processes. The positive intercept of the linear fit indicates that in low-productivity areas the regeneration of barite in the sediment is equal to the rain rate, resulting in zero barite accumulation. Assuming that the relation between productivity and sediment accumulation has not differed greatly and that the same processes governing barite accumulation (supply from the water column and formation at the sediment water interface) and preservation (dissolution in the sediment) have persisted in the past, we can use this empirical relation to estimate past productivity in this area.

We computed AR_{BaSO4} in two cores

Fig. 1. Barite accumulation rates (AR_{BaSO4}) (circles) and primary productivity (squares) in equatorial Pacific coretop sediments (0 to 5 cm) along the TT013 transect at 140°W (full symbols) and VNTR01 transect at 110°W (open symbols).



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from this region (VNTR01-08PC, 0°02.3′N 110°28.5′W, and TT013-PC72, 0°06.8′N 139°24.1′W). Sedimentation rates were determined from the slope of an age model computed from detailed $\delta^{18}O$ records of foraminifera based on the SPECMAP time scale (*32, 33*). The uncertainties in the SPECMAP time scale and in fitting the data to this time scale sum to about ±30%; thus the only significant fluctuations in AR_{BaSO4} are those larger than ±30%. Pronounced variations, of fivefold, in the AR_{BaSO4} with depth are evident (Fig. 3A). In general, during glacial periods AR_{BaSO4} was higher; the empirical correlation implies that primary productivity during glacial periods was about a factor of 2 higher than during the interglacials. Cross-spectral analyses (*34*) indicate that the maxima in AR_{BaSO4} are generally early in the glacial periods, suggesting that maximum productivity and export to the sediment occurred somewhat before the maximum glaciation, probably related to an increase in nutrients supply caused by change in the wind regime. Similar phase relations have been observed in benthic foraminifera accumulation and in $\Delta\delta^{13}C$ in this area (*35*). Calculated paleoproductivities are all within the range of present-day productivity levels in this area (400 to 1200 mg C m^{-2} day^{-1}). Both cores show a synchronous pattern of higher productivity during glacials than during interglacials, suggesting that the cause for these fluctuations in productivity has prevailed both in the eastern and central equatorial Pacific. These results agree with patterns of organic carbon and $CaCO_3$ accumulation in these cores (*29, 30*) and are consistent with other evidence that during glacial periods productivity was high in the eastern and central equatorial Pacific (*36, 37*).

The weight percent barite on a $CaCO_3$ free basis, provides an estimate of glacial to interglacial changes in equatorial Pacific productivity in the past 450,000 years that is independent of accumulation rate (Fig. 3B). The data are consistent with those of AR_{BaSO4} estimates and also show maxima during glacial periods. These maxima are, however, broader and extend throughout the glacial periods, and some start rising at the end of interglacials. Because this plot is influenced to a great extent by the abundance of opal it suggests that the sedimentation records of opal and barite do not respond identically to climate and productivity changes.

Sedimentation rates (and thus bulk sediment accumulation rates) estimated by the $^{230}Th_{exs}$ (initial excess ^{230}Th) normalization method in PC72 are much lower (about 40%) than those derived by ^{14}C or $\delta^{18}O$ chronologies (*38, 39*). In addition, the integrated sedimentary $^{230}Th_{exs}$ inventory exceeds the overlying water column ^{230}Th production by about a factor of 2 (*40*). It has recently been suggested that these differences can be attributed to regional focusing of the vertical particulate

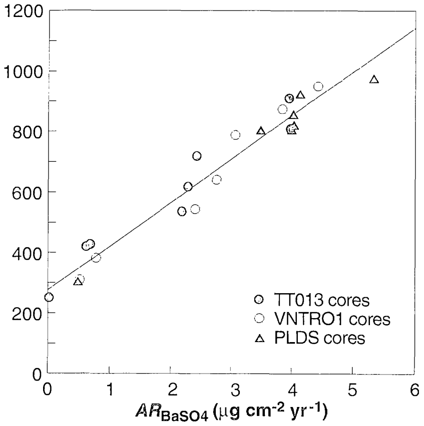

Fig. 2. Barite accumulation rates in core-tops versus productivity. Data from TT013 (full circles), VNTR01 (open circles) and PLDS expeditions (full triangles). AR_{BaSO4} was calculated from sedimentation rates (derived from ^{14}C where data are available and from $\delta^{18}O$ and carbonate stratigraphy where no ^{14}C data exist), for the TT013 cores by (*41, 42*), for the VNTR01 cores by (*32*), and for PLDS cores by (*43*). The DBD for the TT013 cores are from (*41*), for the VNTR01 cores from (*44*), and for the PLDS cores from (*43*). Primary productivity estimates were compiled from measurements made over the past 12 years (*26–28*).

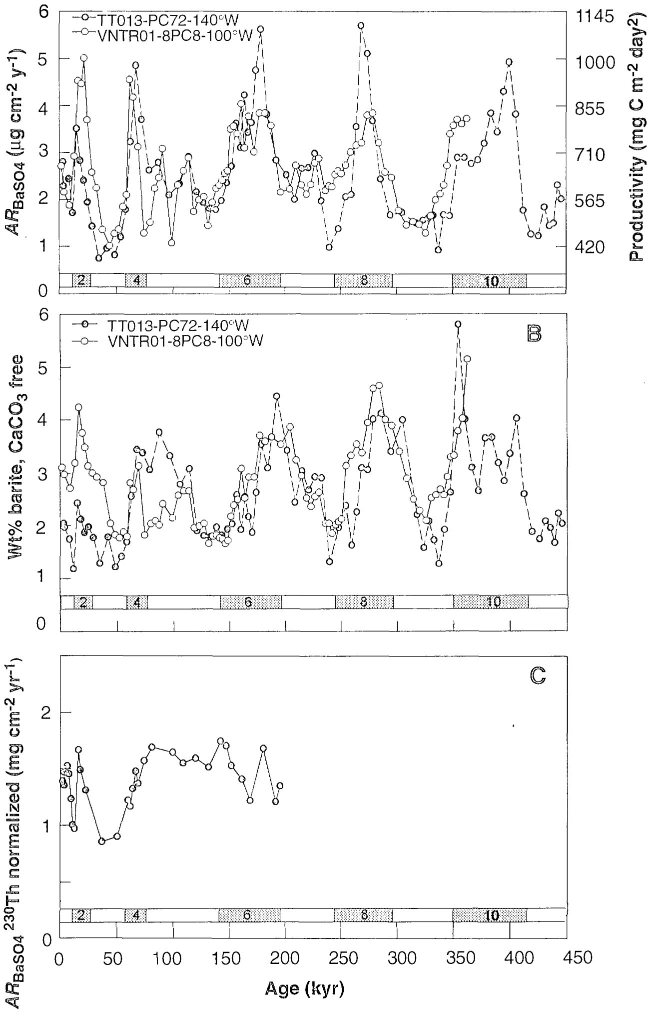

Fig. 3. (**A**) AR_{BaSO4} and productivity in the equatorial Pacific in the past 450,000 years; data from cores VNTR01-08PC at 110°W (open circles) and TT013-PC72 at 140°W (full circles). The age model and sedimentation rates used for TT013-PC72 are from (*32, 33*) and sedimentation rates for VNTR01-08PC are from (*29*). Dry bulk densities are calculated using weight percent $CaCO_3$ (*44, 48*) and the relationship obtained by (*44*). Productivity values are calculated from the relation in Fig. 2. (**B**) Weight percent barite, $CaCO_3$ free, in the past 450,000 years in cores VNTR01-08PC at 110°W [open circles, as in (A)], and TT013-PC72 at 140°W (full circles). $CaCO_3$ data for VNTR01-08PC are from (*44*), and for TT013-PC72 from (*48*). (**C**). AR_{BaSO4} calculated using ^{230}Th-normalized accumulation rates in TT013-PC72 at 140°W (*39*). Gray areas on age scale represent glacial periods (isotope stages 2, 4, 6, 8, and 10).

rain toward the equator (sediment focusing), enhancing accumulation rates there, and that this focusing effect displays a glacial-interglacial variation linked to periods of carbonate dissolution (40). If correct, this effect might introduce a glacial-interglacial bias into stratigraphically based accumulation rates. Indeed, barite accumulation rates in PC72 calculated by the $^{230}Th_{exs}$ normalized method (Fig. 3C) do not display coherent, systematic, and consistent variations with climate signals. Taken at face value, this would suggest that productivity in this region does not vary systematically with global climate changes. The coherent variations in stratigraphically based barite accumulation in the two equatorial Pacific sites we studied that are apart by 30° of longitude, at 140°W and 110°W (Fig. 3A), however, would then require that sediment focusing and its secular variations be remarkably uniform along the equator. More work will be required to evaluate the reasons for the excess (overproduction) inventories of $^{230}Th_{exs}$ in equatorial sediments and their temporal change. We thus assume here that sediment focusing in the equatorial Pacific is not an important factor in our barite accumulation records and that the stratigraphically based barite accumulation rates in PC72 and 8PC (Fig. 3A) are reliable proxies for late Pleistocene productivity variations in the equatorial Pacific Ocean.

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24. AR_{BaSO4} were calculated using sedimentation rates which were in most core tops derived from ^{14}C data (*32, 43*). These ^{14}C sedimentation rates in most cases agree well with $\delta^{18}O$ derived rates where both were determined in the same core and are consistent with values obtained by other workers (*44*). In cores for which no ^{14}C data exist sedimentation rates were determined from $\delta^{18}O$ and carbonate stratigraphy (*44*). For the TT013 cores from data in (*43, 44*), for the VNTR01 cores from *(32)* and for PLDS cores from (*45*). The dry bulk densities (DBD) for the TT013 cores are from (*43*), for the VNTR01 cores from (*46*), and for the PLDS cores from (*45*).
25. Although it would have been more appropriate to relate the AR_{BaSO4} to new production (all primary production associated with newly available nitrogen), we have chosen to use gross primary production data for the correlation. At present in this area direct measurements of new production are scarce, and the f ratios (the portion of new production from total production) *(47)* are not precisely known and tend to vary considerably in space and time *(48)*. With the Eppley and Peterson equation (*47*) the conversion of primary productivity (*PP*) to new production (*NP*) yields a positive association between *NP* and AR_{BaSO4}, and a greater difference (tenfold) between glacial and interglacial signals. Existing measurements of the f ratio by both ^{15}N uptake and C/N flux data *(49)* suggest that a rather small fraction of the total production is exported locally in the equatorial Pacific, consistent with low calculated f ratios of 0.1 to 0.3, that are considerably lower than the actual NO^{3-} concentrations suggest.
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49. We thank A. C. Mix and R. F. Anderson for sharing their data with us and P. Johnson for assistance in the laboratory. Comments from W. H. Berger and J. Dymond and reviews by P. Froelich and an anonymous reviewer improved this manuscript. This work was supported by funds from the National Science Foundation OCE#91-16010 and the American Chemical Society PRF#27886AC8. Sediment samples were provided by the OSU core repository supported by NSF grant OCE-9102881 and the URI core repository supported by NSF grant OCE-9102410.

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Stability of Perovskite ($MgSiO_3$) in the Earth's Mantle

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Available thermodynamic data and seismic models favor perovskite ($MgSiO_3$) as the stable phase in the mantle. $MgSiO_3$ was heated at temperatures from 1900 to 3200 kelvin with a Nd-YAG laser in diamond-anvil cells to study the phase relations at pressures from 45 to 100 gigapascals. The quenched products were studied with synchrotron x-ray radiation. The results show that $MgSiO_3$ broke down to a mixture of MgO (periclase) and SiO_2 (stishovite or an unquenchable polymorph) at pressures from 58 to 85 gigapascals. These results imply that perovskite may not be stable in the lower mantle and that it might be necessary to reconsider the compositional and density models of the mantle.

The Earth's lower mantle has been thought to consist of principally the iron-magnesium silicate perovskite with an average composition of 10 to 15 mole percent of the iron component and some magnesiowustite (*1*, *2*). Ito *et al.* (*3*) showed experimentally that