17. DISSOLUTION AND PRESERVATION OF DIATOMS IN THE SEA OF JAPAN AND THE EFFECT ON SEDIMENT THANATOCOENOSIS

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ABSTRACT

Sediments of Pliocene age from the Sea of Japan as well as the North Pacific frequently contain abundant remains of the centric diatom, *Coscinodiscus marginatus*, a species which is neither abundant in surface waters nor in surface sediments of those regions. To test whether these occurrences are a product of opaline silica dissolution, we selected several sediment samples from the Quaternary record of Hole 798A which had opaline silica concentrations ranging from less than 5% to approximately 16%. Laboratory-timed dissolution experiments using an alkaline solution (40 mL of 2 M Na2CO3) were carried out at 80°C on the three bulk samples. At the end of each time interval the samples were centrifuged and the supernatant prepared for microscopic examination. The two samples with less than 5% opaline silica contained no diatoms or highly fragmented forms after the first 5 min of the experiment had elapsed. The third sample (with 16% opaline silica), however, showed an increase in percent *C. marginatus* as dissolution progressed (from less than 5% to more than 35%). These data suggest that high abundances of *C. marginatus* in sediments may be due to silica dissolution rather than to any unique paleoceanographic signal.

INTRODUCTION

Several factors may compromise the utility of microfossils in time-stratigraphic and paleoceanographic reconstructions. Over longer time scales, microfossil first and last occurrences may be diachronous, particularly between high and low latitudes and between major ocean basins. Burckle and Opdyke (1985), for example, pointed out that the last occurrence of the diatom, *Actinocyclus inicus*, is early late Miocene in the equatorial Pacific and latest Miocene in the North Pacific and that the first occurrence of the diatom, *Neodenticulina kamtschatica*, ranges over an approximately million year interval in the North Pacific. In some cases, this diachrony may be considered trivial (i.e., although measurable, it falls within a zone or within the margin of error of biostratigraphic resolution) but it becomes non-trivial in light of the need to resolve time with greater resolution. Sorhannus et al. (1991), for example, noted that the first appearance of the diatom *Rhizosolenia praebuergeroni* in the Indian Ocean may be some 200 k.y. later than its first occurrence in the Pacific Ocean. Since this diachrony occurred during an interval of time which is now receiving some attention (early late Pliocene), it is important that it be recognized.

A second factor which may compromise the utility of microfossils, particularly diatoms, in paleoceanographic or paleoclimatic reconstructions is diagenesis, both post-depositional and within the water column. In considering diatoms in surface sediments Sancetta (1982), for example, noted that, in the absence of sediment trap data, a "predictive equation based on the relative abundance of species can yield incorrect values." Shemesh et al. (1989) showed that the sequence of dissolution of Antarctic diatoms in laboratory experiments is reflected in their spatial distribution in surface sediments of the Southern Ocean. The typical dissolution pattern in laboratory experiments of Antarctic diatom assemblages can be described by a decrease in percentage *Nitzschia kerguelensis*, an increase in percentage *Thalassiosira lentiginosa*, and a small increase in percentage *Eucampia antarctica*.

These data suggest that, in surface sediments, the *T. lentiginosa*-dominated assemblage is the product of dissolution and does not reflect the true diatom distribution in the overlying water masses. They concluded that "temperature transfer equations derived for the Southern Ocean from surface sediment cannot be used safely without considering dissolution-induced changes upon diatom assemblages." That diatom dissolution may affect assemblages to the extent that their true paleoceanographic message is blurred is only now becoming apparent (largely because of the increase in sediment trap studies). One of us (LHB) is presently working on a middle/late Miocene site from the south Atlantic in which two different microfossil groups (diatoms and coccolithophorids) give contrasting temperature estimates; the coccolithophorids suggest a warm water environment while the diatom assemblage, which is dominated by one dissolution resistant species (*Denticulopsis dimorpha*), indicates a cold water environment. Such data suggests that the *D. dimorpha*-dominated assemblage is likely an artifact of dissolution and is giving a misleading paleoceanographic message.

This paper considers diatom dissolution in the Sea of Japan and the northwest Pacific, and its role in blurring or distorting the paleoceanographic record based on diatoms. On Leg 128 (Sea of Japan) thick diatomaceous sections of Pliocene age were encountered in which the diatom, *Coscinodiscus marginatus*, appeared to be a principle sedimentary component. In some samples, the relative abundance of this species exceeded 60%. In the water column this species is found at mid-latitudes in all oceans although it can range into higher latitudes and is sometimes seen as a component, albeit minor, of low latitude upwelling systems. *Coscinodiscus marginatus*-rich assemblages have been described before in North Pacific and Sea of Japan Neogene sediments. Schrader (1973), for example, reported it from the northwest Pacific, and Burckle and Opdyke (1985) noted the presence of a *C. marginatus*-rich ooze ranging in age from late Miocene to Pliocene in a core from the north central Pacific. Specimens of *C. marginatus* showed visual evidence of dissolution before grading downward into an opal-poor interval around the middle of the late Miocene. In the Sea of Japan, Akiba (1982) reported the presence of an interval in the Pliocene with abundant *C. marginatus* and named it the *C. marginatus* zone. Similarly, he reported intervals of *C. marginatus*-rich sediments in continental marine sections from the west coast of Japan. Typically, such sediments were late Miocene to early Pliocene in age.

Kanaya and Koizumi (1966) reported that *C. marginatus* averages 10%–40% of the flora in subarctic surface sediment assemblages while Jouse (1962) noted that it is common, but not abundant, in the summer plankton of the central Sea of Okhotsk and that it has a similar distribution in underlying surface sediments. In the Sea of Japan,
Tanamura (1981) reported that it does not exceed 10% in surface sediments while in our surface sediment data set (LHB) from this region it does not exceed 8% and is usually less than 4%. Sancetta (1982) reviewed the taxonomy of this species as well as its spatial distribution in surface sediments of the North Pacific and concluded that it actually occurred in insignificant quantities, averaging less than 5% in Bering Sea basins and the North Pacific. She concluded that it usually occurred in higher abundances (3%-5%) in winnowed areas (Aleutian Arc or Bowers Ridge) or in the Gulf of Alaska where silica dissolution has biased assemblages toward more resistant forms. Our unpublished data set from the North Pacific tends to bear out this conclusion. Previous work on both in situ and laboratory dissolution experiments on marine diatoms is given in Shemesh et al. (1989).

In quantitative paleoceanography the presence of high percentages of C. marginatus in pre-Holocene sediments would be considered a no-analog condition. High percentages of C. marginatus have not been observed in modern relatively undisturbed (i.e., undissolved) surface sediments. Therefore, no present-day analog exists which allows us to use high percentages of C. marginatus to characterize pre-Holocene water mass distribution. Here we investigate whether increases in percent C. marginatus in Sea of Japan sediments is the result of dissolution or whether it records a unique paleoceanographic event in the late Miocene and Pliocene. Our protocol largely follows that of Shemesh et al. (1989) with some deviations dictated by sediment type (Miocene/Pliocene sediments above the Opal A/Opal CT boundary tend to be diatom oozes while Quaternary sediments are largely silty clay to silty diatomaceous clay).

**MATERIALS AND METHODS**

Three bulk samples were obtained from Quaternary sediments in Holes 798A (12H-5, 100–101 cm; 14H-CC; and 15H-CC). Two samples had an opal content of less than 5% while the third had an opal content of approximately 16% (Dunbar et al., this volume); all showed at least traces of diatoms in smear slide examination. Where possible, i.e., where more than a trace of diatoms was present, the percent abundance of C. marginatus was determined (in fact, this was only true for the sample with 16% opaline silica). Since these samples were recovered from Quaternary sediment, percent abundance of C. marginatus was always low (i.e., 0%-5%). In addition to the three bulk samples mentioned above we also took two samples from each section of the Quaternary and Pliocene parts of Holes 798A, 798B, and 799A. These samples were taken primarily for biostratigraphic and paleoenvironmental analysis, but the percent abundance of C. marginatus was also determined.

Laboratory-timed dissolution experiments using an alkaline solution were carried out at 80°C on the three Quaternary age bulk samples (Table 1). Five grams of each sample was macerated with mortar and pestle and dried at 65°C for 24 hr. For each timed interval of the experiment (5–60 min), a 20 mg split was weighed into a centrifuge tube. The alkaline solution (40 mL of 2 M Na₂CO₃) was introduced into the tubes at the experimental temperature and the tubes were placed in a thermostatic water bath (± 1°C). At the end of each time interval the samples were centrifuged and the supernatants were saved in precleaned vials. The residual solids were washed with deionized water and saved for diatom enumeration. Permanent diatom slides of all samples (bulk samples as well as samples for biostratigraphic determinations) were made using methods described by Schrader (1974). A minimum of 300 diatoms were counted for each sample and placed in one of two categories (C. marginatus or others). Only those specimens with one half or more of the valve present were included in the count.

In order to apply observations of laboratory-induced dissolution patterns to naturally occurring sediment assemblages, it is desirable to show that the laboratory procedure mimics the natural process. In choosing a suitable laboratory protocol, we want one that is expedient and that speeds up the dissolution process, but does not otherwise change the treated sediments. For example, an experiment using seawater at temperatures on the order of 15°–20°C closely represents the natural condition but would take a year or more to complete. We chose a more rapid procedure for our experiments: Na₂CO₃ at 80°C. Though less representative of the natural condition, the experiments were completed within 4 hr for each run.

Evidence supporting the assumption that the rapid dissolution procedure does not attack other components includes petrographic observation of untreated and treated sediments and chemical analysis of the leach fluid. Other than changes in diatom abundances, untreated and treated sediments appear identical when examined under the petrographic microscope. Dissolved aluminum in the leach solution, after sediment treatment, was less than 5 nM Al. Very low concentrations of dissolved aluminum in the post-treatment fluid indicate that aluminosilicates, such as clay minerals, were not dissolved by the leach process. However, in spite of our presumption that the 80°C leach procedure dissolves only biogenic amorphous silica, the results of these experiments should be considered preliminary, pending development of a dissolution process that more closely mimics nature.

**RESULTS**

Shemesh et al. (1989) point out that the rate of opal dissolution is a function of dissolution temperature and the geologic age of the sample. They found that Holocene samples completely dissolved after 60 min at 85°C while at 240 min and 60°C, only 80% had dissolved. The dissolution pattern of the three samples studied is a function of the original percent opaline silica content of the sample. In two samples with an opaline silica content of less than 5%, and with only traces of diatoms in smear slide examination, no diatoms were present after 60 min. Indeed, the sample was essentially barren of diatoms after the first 10 min of dissolution. Sample 798A-12H, 100–101 cm, differed, however, in that, in smear slide examination of the untreated sediment, common to abundant diatoms were observed, opal content exceeded 15% and the diatom count on the undissolved sample showed a percent abundance of C. marginatus of slightly less than 5%.

Results of the dissolution of this sample are shown in Figure 1. Its dissolution pattern is characterized by an increase in relative abundance of C. marginatus and a drop in relative abundance of Coscinodiscus spp. Accompanying this increase in C. marginatus is a modest increase in broken valve fragments of the genus Thalassionema. This genus, as well as Thalassiothrix spp., appears to have a variable response to laboratory and in situ dissolution, sometimes being high-graded by this process and, at other times, decreasing in relative abundance (Shemesh et al., 1989). Much of the increase in relative abundance of C. marginatus takes place in the latter stages of dissolution; after 35 min the relative abundance of C. marginatus rises to approximately 40% but drops to less than 35% at the end of the experiment (60 min). These numbers are within the margin of error of our counts and suggest that very little dissolution took place after 35 min to the end of the run (60 min).

Figures 2 and 3 show the results of the relative abundance count of C. marginatus in Holes 798A and B and 799A. To further resolve the chronostratigraphy we also included the magnetostatigraphy and biostratigraphy (i.e., diatom datum levels; Burckle, this volume).
These datum levels have previously been tied to the magnetostratigraphy in deep sea sediments of the northwest Pacific (Koizumi and Tanimura, 1985); the Last Appearance Datum (LAD) of *Rhizosolenia curvisirostris* has also been tied to the oxygen isotope record in the north Pacific at an age of 276 k.y. (Morley et al., 1982). We have made the unsubstantiated assumption that the diatom LAD levels in the northwest Pacific and the Sea of Japan are time-correlative.

Although percent abundance of this species is similar during the middle and late Quaternary of both Site 798 and 799 (usually less than 5%), it differs slightly between the two sites in the earliest Pleistocene. At Site 798 (the slightly more southerly site) percent *C. marginatus* increases to 6%–8% during the early Pleistocene before increasing to as much as 12% in the late Pliocene. Figure 2 shows that this increase is maintained down into the Gauss magnetic chron. Although percent determinations were not made in the lower part of Site 798, smear slide analysis indicates that percent *C. marginatus* also tends to be high in this interval (i.e., above the Opal A/Opal CT boundary). Site 799 has a somewhat different pattern in percent *C. marginatus*. Figure 3 shows that while percent abundance of this species increases to near 10% in the latest Pliocene, the major increase (to more than 30%) occurs earlier just below the Gauss/Matuyama magnetic chron boundary at about 2.5 Ma). Further downsection percent abundance increases to, at times, over 60% and increased relative abundance of this species persists down to the opal A/Opal CT transition (approximately 450 m; Fig. 3).

As noted above, late Neogene increases in relative abundance of *C. marginatus* have long been recognized in North Pacific and Sea of Japan sediments. Figure 4 shows late Neogene abundance of this species in core RC12-431 (43°38′N, 167°49′W) plotted against the paleomagnetic stratigraphy (data redrawn from Burckle and Opdyke, 1986). Although relative abundance counts were not made, *C. marginatus* so dominated the assemblage that, near the lower part of its range, there were few other floral elements; near the transition to a barren ooze, even though it is a remnant of a dissolved assemblage, represents high productivity, although such an assemblage does not reflect the true temperature/salinity regime that existed in surface waters at the time of deposition.

In our laboratory experiments to produce a *C. marginatus* ooze via timed dissolution, two basic observations are apparent. Such an ooze will not result if the original opal content is below 5% even when diatoms, and especially *C. marginatus*, are present in smear slide examination. On the other hand, when the opal percent is high (say, on the order of 15%–20%) *C. marginatus* is high-graded and will become one of the dominant components. We conclude from this that a *C. marginatus* ooze, even though it is a remnant of a dissolved assemblage, represents high productivity, although such an assemblage does not reflect the true temperature/salinity regime that existed in surface waters at the time of deposition.

In the two Sea of Japan ODP sites studied by us, *C. marginatus* abundance is high in the Pliocene (although the amplitude is greater in Site 799 than Site 798) but drops to near Quaternary abundance levels in the late Pliocene around the Gauss/Matuyama boundary. In both sites there is a modest abundance peak in the lowermost Matuyama while the Quaternary is characterized by abundance levels of 0% to less than 5% (indeed, frequently there were too few diatoms to be counted). In both the Sea of Japan and the northwest Pacific, glacial intervals are characterized by low biosiliceous productivity while interglacial levels in sea ice distribution appear to dictate productivity and, thus, changes in opal percent. In the Sea of Japan, increased opal content (and increased concentrations of diatoms and radiolarians) occurs during interglacial while low percent occurs during glacialas (Dunbar et al., this volume; LHB, unpubl. notes). This is likely due to the fact that transport of Tsushima Current water into the Sea of Japan (via the Tsushima Strait) during glacial is considerably restricted (Morley and Heusser, 1989). In our unpublished data set (Burckle, unpubl. data) from a radiocarbon dated deep sea core (RC12-379) taken from the southeastern part of the Sea of Japan, both diatom and radiolarian levels are consistent with the Last Glacial Maximum and high productivity during the Holocene.

**Figure 1.** Results of timed dissolution of *C. marginatus*. Percent is based upon a count of 300 specimens.
Figure 2. Percent abundance of *C. marginatus* for Hole 798A. Because of dissolution we are unsure of age control toward bottom of hole.
record on these two sites (Burckle, unpubl. data) closely parallels the results of Morley and Dworetzky (1991); i.e., relative abundance of C. marginatus increases in intervals of increased biosiliceous productivity. Implicit in this conclusion is the realization that highest productivity in the Sea of Japan occurred at a time when the southern gateway to the Sea of Japan (the Tsushima Strait) was closed. In data sets recovered by Leg 128 micropaleontologists, it was obvious that warm water microfossils first appeared in Sea of Japan sediments around the Pliocene/Pleistocene boundary; prior to that time this strait was closed and there was a more northerly gateway into the sea.

Although we conclude that C. marginatus-rich sediment in the Sea of Japan and the north Pacific represents higher relative productivity and is an artifact of dissolution, we cannot discern the agents of dissolution. The fact that such sediment persists down to the opal A/opal CT boundary suggests to us that dissolution may be related to the upward migration of this boundary. Similarly, the presence of a silica barren zone below a C. marginatus ooze in core RC12-431 and the fact that, in that core, individual diatom valves show increased dissolution toward the base of that ooze suggests a genetic relationship between the two.

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Figure 3. Percent abundance of *C. marginatus* for Hole 799A. Because of dissolution we are unsure of age control toward bottom of hole.
Figure 4. Relative abundance of *C. marginatus* in upper Miocene/Pliocene sediments of core RC12-431 from the North Pacific.
Figure 5. Percent abundance of *C. marginatus* in two DSDP sites from the North Pacific. Data from Site 581 are taken from Koizumi and Tanimura (1985); Site 433 data from Koizumi (1980).

Figure 6. Percent abundance of *C. marginatus* from the Aikawa section, western Honshu, Japan. Data are taken from Koizumi (1968).