Variations in Fe$_3$O$_4$ and CaCO$_3$ Contents in Deep-Sea Cores from the Western Equatorial Pacific

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An inverse correlation between the CaCO$_3$ and magnetic mineral contents was obtained from deep-sea sediment cores taken from the western equatorial Pacific, in which the predominant magnetic mineral is of bacterial origin. It is shown that the fluctuations of the relative concentration of magnetite over a period of time are caused solely by variations in CaCO$_3$ dissolution in the relatively deep sea bottom. This conclusion seems to explain the observed result that fluctuations in the intensity of saturation isothermal remanence are concordant in two adjacent cores with different sedimentation rates.

1. Introduction

Magnetic minerals contained in deep-sea sediments are not only a carrier of the natural remanent magnetization but also a good indicator of the paleoenvironment. Accumulation rate of magnetic minerals often depends upon supply of eolean dusts and terrigenous detritus correlatable to the climatic change (THOMPSON and OLDFIELD, 1986). Relative contents of magnetic minerals are also controlled by paleoenvironment through dilution by non-magnetic materials such as CaCO$_3$, which are sensitive to environmental factors. Cyclic variations in CaCO$_3$ contents with a periodicity similar to that of the Upper Pleistocene glacial-interglacial fluctuations have been observed in deep-sea cores (ARRHENIUS, 1952; BERGER, 1973; GARDNER, 1975).

The accumulation of CaCO$_3$ on the seafloor is largely determined by the balance between the biogenic production of CaCO$_3$ in the surface waters and its dissolution in the deep waters. Recent studies suggest that changes of the ocean circulation patterns associated with consequent variations of global oceanic geochemical inventories followed by changes in greenhouse gas concentration play an important role in the mechanisms through which global climate is tuned by solar insolation changes (BOYLE, 1988; DUPLESSY et al., 1988; BROECKER and DENTON, 1989; CHARLES and FAIRBANKS, 1992). It must be emphasized that changes in CaCO$_3$ dissolution derived from changes in the global inventories play the greater part in the content change (FARRELL and PRELL, 1989).

It has been shown that close correlation exists between two calcareous deep-sea sediment cores with different sedimentation rates in the variation patterns of saturation isothermal remanent magnetization (SIRM). These cores (KH 73-4-7 and KH 73-4-8) were collected from the western equatorial Pacific Ocean. On the basis of the SIRM correlation, long-term secular variations of both declination and intensity of the geomagnetic field in the range up to 0.1 My have been revealed by a comparison of the results from the cores (SATO and KOBAYASHI, 1989).

In this article we describe results of our investigation of magnetic minerals contained in deep-sea cores and their implications with cause of variation in the content of the magnetic minerals. The CaCO$_3$ content in the KH 73-4-7 core was measured in order to elucidate the role of the variations in CaCO$_3$. We propose that content of magnetic minerals in the seafloor sediment is independent of their sedimentation rates and depends upon environmental changes over a period amounting to at least a few million of years in the surveyed region.
2. Cores

Deep-sea sediment samples treated in this study were two 11 m long piston cores, KH 73-4-7 and KH 73-4-8, collected at sites 500 km apart in the Melanesia Basin, in the western equatorial Pacific Ocean (2°41’N, 164°50’E, 4,160 m deep and 1°33’S, 167°39’E, 4,000 m deep, respectively). Both cores are composed mostly of calcareous ooze. Sampling sites of the two cores are shown in Fig. 1, together with the locations of ODP drill holes, 804 and 806. Several horizons in these cores were dated by paleomagnetic correlation of the magnetic polarity boundaries and by a datum plane of the last appearance of P. lacunosa. Sedimentation rates between the two dated horizons are assumed to be constant. In addition their ages were measured by the ESR (Electron Spin Resonance), as already reported by SATO and KOBAYASHI (1989). It is remarkable that the sedimentation rates of KH 73-4-8 show large fluctuations in contrast with the almost constant sedimentation rates of KH 73-4-7, although water depths and other environmental factors appear to be roughly similar.

3. Variations in the Content of Magnetic Minerals

3.1 Correlation of variations in the SIRM intensity between two cores

Intensity of saturation isothermal remanent magnetization (SIRM) of the cores was measured using thin sliced sections of sediment magnetized in a static field of 0.90 T. Fluctuation of the SIRM intensity in each core ranges between 1 and 7 in units of 10^{-3} Amp²/kg with predominating periods of about 0.1 million years. Remarkably, the patterns of fluctuations are quite similar and peak to peak correlation seems to be possible between the two cores. In Fig. 2 we can see that SIRM intensity in both cores exhibits almost concordant variations, even for the interval around 0.6 Ma in which the sedimentation rate of KH 73-4-8 is about 3 times as fast as that of KH 73-4-7.

3.2 Rock magnetic studies of the sediment

It is usually agreed that the SIRM intensity corresponds to the content of magnetic minerals in the sediment, unless there is a significant grain size variation (OPDYKE et al., 1973). The content of magnetic minerals is a ratio of their sedimentation rate to that of the non-magnetic materials. Rock magnetic
experiments have shown that variations in magnetic grain size in the two cores are negligibly small (SUEISHI et al., 1979), and that the magnetic materials are mostly composed of single domain or pseudo-single domain-sized magnetite particles (YOSHIDA and KATSURA, 1985). Therefore, it can be concluded that the magnetite content of the sediments at the two coring sites has a similar variation in the past 2.2 million years, despite the different sedimentation rates.

3.3 Results of TEM observation

Recent studies of magnetic minerals contained in sediments deposited in detritus-poor aquatic systems have demonstrated that fossil bacterial magnetite plays an important role in magnetization of the sediments (KIRSCHVINK and LOWENSTAM, 1979; PETERSEN et al., 1986; STOLZ et al., 1986; CHANG and KIRSCHVINK, 1989). In order to test validity of this postulate in the present samples, we examined the magnetic minerals contained in the cores using a transmission electron microscope (TEM), a JEM 200 CX with a TN 2000 system. The extracts are classified into two groups according to their grain sizes. A coarse fraction has particle diameters in the range of 2 to 10 µm, with an average value of 5 µm. The other is an aggregate of submicron particles with a very restricted variation in size (Fig. 3). These are present in cumulated short chains or clusters. Particles with octahedral shapes, like those found previously in some living magnetotactic bacteria, are predominant in the sediment. Some grains have diffuse boundaries, which are probably due to the alteration as suggested by VALI and KIRSCHVINK (1989).

Chemical compositions of these magnetic minerals were also analysed by an analytical electron microscopy. The coarser fraction was composed of iron with varying titanium contents, whereas the submicron fraction was pure magnetite without titanium. Detailed results of both electron-microscopic examinations have been reported elsewhere (AKAI et al., 1991). On the basis of their shape, size distribution and chemical composition, we concluded that the submicron particles were bacterial in origin.

Quantitative proportions of submicron to coarser fractions were unable to be measured in these sediments, because the submicron fraction is much more difficult to extract than the coarser one. However, the rock magnetic diagnosis suggested that magnetite of submicron-sizes is a major magnetic constituent in the sediments (YOSHIDA and KATSURA, 1985). It can, therefore, be concluded that the majority of magnetic minerals contained in these deep-sea sediments are of bacterial origin.
4. Content of CaCO₃ and Its Correlation with SIRM

The weight percent of CaCO₃ in the bulk dry sediment of core KH 73-4-7 was determined at 31 horizons by measuring CO₂ gas pressure generated after stripping samples with phosphoric acid at Kanazawa University (Table 1). The carbonate record of core KH 73-4-7 shows large-scale fluctuations by up to 43%. There is a clear inverse correlation between CaCO₃ content and intensity of SIRM (Fig. 4). The relationship can be expressed as:

\[ J = k(1 - R) - \beta, \]

where \( J, R \) and \( \beta \) are of SIRM intensity, a content of CaCO₃ and a constant. The coefficient \( k \) depends on neither \( J \) nor \( R \), but shows some variations over time.

Recently the variations in CaCO₃ content in the ODP cores drilled from the Ontong Java Plateau close to the present coring sites have been reported (BERGER et al., 1991). The CaCO₃ record of core 804A (\( D = 3,862 \) m) shows long-term fluctuations by up to 15%, which are correlatable to the long-term Brunhes patterns of carbonate deposition postulated by FARRELL and PRELL (1989). In contrast, the amplitudes of fluctuations of hole 806B (\( D = 2,520 \) m) are only about 5%. In an adjacent region, a similarly small variation in the carbonate content has also been reported with shallow-water sediments (\( D = 1,963-2,256 \) m, TAUXE and WU, 1990). As their sampling sites are all close to one another, we concluded that the apparent fluctuation in the degree of CaCO₃ content mainly depends upon the rate of dissolution of CaCO₃ in sea water. Tentative results of measurement of the dissolution index, which is the ratio of fragmented to perfect tests of planktonic foraminifera (OBA and KU, 1977; KU and OBA, 1978), show harmonious fluctuations of the dissolution (OBA, personal communication). FARRELL and PRELL (1989) pointed out that degree of CaCO₃ dissolution has been fluctuated markedly in conjunction with the late Pleistocene climate cycle. On the other hand, CaCO₃ contents at deeper sites show smaller fluctuations in amplitude.

It is well known that CaCO₃ is dissolved faster in deeper water. In shallow water, CaCO₃ is dissolved so slowly that the influence of climatic factors is obscured. In very deep areas most of the CaCO₃ is completely dissolved, thereby also masking time variations in the dissolution rates. Only in moderately deep water can the fluctuations be distinctly revealed by examination of cores.

Our results show that the magnetic mineral content is a good indicator of the dissolution of CaCO₃ in the surveyed region which has water depths around 4,000 m.
Table 1. The weight percent of CaCO₃ in the bulk dry sediment and SIRM intensity for core KH 73-4-7.

<table>
<thead>
<tr>
<th>Depths from the sea floor (cm)</th>
<th>CaCO₃ contents (%)</th>
<th>SIRM ($\times 10^{-3}$ emu/gr)</th>
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<tr>
<td>4.5</td>
<td>76.4</td>
<td>1.36</td>
</tr>
<tr>
<td>15.4</td>
<td>74.5</td>
<td>1.06</td>
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<td>20.9</td>
<td>77.5</td>
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<tr>
<td>40.0</td>
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</tr>
<tr>
<td>48.1</td>
<td>67.7</td>
<td>1.24</td>
</tr>
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<td>460.3</td>
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</tr>
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</table>

Fig. 4. SIRM vs. CaCO₃ for KH 73-4-7.
5. Models of Bacterial Magnetite Concentration by Dissolution of CaCO₃ and Locally Discriminative Deposition

As shown previously, our sediment cores contain two groups of magnetic minerals. The coarser fraction is likely to be of terrigenous, authigenic, or diagenetic origin. This fraction of magnetic minerals was transported along with the non-CaCO₃ fraction. On the other hand, it is plausible that the productivity of the benthic magnetotactic bacteria is determined by the flux of organic matter (BLOEMENDAL et al., 1988). In most of the sea bottom the organic materials are brought from the sea surface together with the CaCO₃, which is wholly dependent on the surface sea biogenic productivity (LYLE, 1988).

We introduce a two-origin model in which the deposition of magnetic minerals is proportional to both the flux of non-CaCO₃, \( N \) and that of CaCO₃, \( C \). Where the original CaCO₃ content, \( R₀ \), decreases to \( R \) after CaCO₃ dissolution in the deep sea, and \( r \) represents a degree of CaCO₃ preservation, \( R₀ = C/(C+N) \) and \( R = C r/(C+N) \). Therefore, the SIRM intensity, \( J \), which is proportional to the magnetic mineral contents, can be expressed as:

\[
J = k₁N + k₂C = k₁(1-R) + k₂R₀(1-R)
\]

where \( k₁ \) and \( k₂ \) are constants independent of the CaCO₃ content. The linear relationship between \( J \) and \( R \) may be valid if \( k \) is constant. The scattering of observed data shown in Fig. 4 seems to be caused by changes in \( R₀, k₁, \) and/or \( k₂ \). At the present stage, it is difficult to estimate the variabilities of \( k₁ \) and \( k₂ \).

If variability of \( R₀ \) is assumed to be the degree of standard deviation of observed CaCO₃ content (=2.2%) as given by hole 806B, we can estimate the effect of the \( R₀ \) variation. If the first term of Eq. (2) is negligibly small and \( R₀ \) is nearly 1, even a small variation of \( R₀ \) greatly affects \( k \). Variations of \( R₀ \) from the average value (0.87 in 806B hole) amounting to 4% are sufficient to cause variability of \( k \). Large variations in biological productivity, which would influence long-term atmospheric CO₂, have been estimated using planktonic foraminifera species data (Mix, 1989). These productivity variations would seem to affect \( k \) if both variations are not synchronous. A possible origin of the 3rd term, \(-β \) in Eq. (1), seem to be dissolution of magnetic minerals as assumed from the TEM observation.

If sedimentation rates, \( d \) partially depend on circumstances such as topography of the ocean floor and deep-sea currents, sedimentation rates, \( d \) would be expressed as:

\[
d = (Cr + N)f
\]

where \( f \) is a non-dimensional parameter related to the changes in the sea floor over time and of geographical position. The SIRM correlation between two cores can then be interpreted using (3), if the composition and quantity of the initial flux are unchanged over time and the same in two sites.

6. Discussion

The theoretical relationship between the normalized contents of magnetic minerals (\( J' \)) versus the degree of CaCO₃ dissolution (\( L \)) calculated from the model is shown in Fig. 5. This leads to the following conclusions;

1. the ratio of the maximum to the minimum value is \( 1/(1-R₀) \). If \( R₀ \) is 0.87, the ratio is only about 8.

2. the intensity of SIRM is kept small as long as the degree of dissolution does not exceed 0.8, whereas it becomes abruptly large if it exceeds 0.8.
Fig. 5. Theoretical relationship of normalized contents of magnetic minerals ($J'$) versus degree of CaCO$_3$ dissolution. The effects of the variability of $R_0$ assumed to be the degree of the standard deviation of observed CaCO$_3$ content (=2.2%) in hole 806B are drawn with dashed lines.

Fig. 6. Histogram of the SIRM for KH 73-4-7.

A histogram of the SIRM intensity for KH 73-4-7 corresponds well to the model (Fig. 6), as is seen by the following characteristics:

1. the ratio of the maximum to the minimum values is only 8.
2. the lower SIRM values appear more frequently than higher SIRM values except for a narrow range of the low SIRM.

A general feature of the SIRM variations shown in the lower column of Fig. 2 is that peaks in the SIRM are steeper and sharper than troughs, like a suspension bridge. These types of curves can be interpreted in terms of concentration of magnetic minerals resulting from the CaCO$_3$ dissolution.

No sign of changes in the grain size of magnetic minerals was indicated from the ratio of ARM/SIRM for KH 73-4-7 (SUEISHI et al., 1979) in spite of the large variations in the CaCO$_3$ content. It is thus concluded that a dominant factor controlling the intensities of SIRM and ARM is the degree of CaCO$_3$ dissolution. Recent rock-magnetic experiments conducted with piston cores from the Ontong Java Plateau (TAUXE and WU, 1990) exhibited fairly different features, although the magnetite grains in the cores are classified into two groups according to grain size in a similar manner to KH 73-4-7. While little change exists in the CaCO$_3$ content, the magnetic susceptibility, $\chi$, varied significantly by a factor of about 2 to 10 in each core. They did not observe bacterial magnetite. Large variations in the ratio of ARM/$\chi$ were also observed with their cores, indicating substantial variations in the grain sizes of magnetic minerals. Various different sources of magnetic minerals may therefore have to be considered along with their coring sites.

Mass accumulation rates (MAR) calculated from sedimentation rates from age profiles of each core have been used in many paleoceanographic studies to examine vertical flux of sediments onto ocean floor quantitatively. We found that there is a mechanism in which sedimentation rate varies locally without changes in the ratios of the components presumably because of lateral transport of the sediment. Deep-sea sediment transport storms (GROSS et al., 1988) seem to be one of the phenomena whose relation to the mechanism deserves consideration. At least locality and variability of the lateral transport should be considered when estimates variations of mass fluxes onto the deep-sea floor.

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