17. RELATIONSHIP BETWEEN GRAIN DENSITY AND BIOGENIC OPAL IN SEDIMENTS FROM SITES 658 AND 6601

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INTRODUCTION

At Site 658, and especially at Site 660, sediments rich in biogenic opal were recovered. The fractions of biogenic silica, biogenic carbonate, and terrigenous material vary throughout the entire sequence at these sites (see chapters for Sites 658 and 660, this volume).

At Site 660, biogenic-opal contents up to 100% are common in Eocene sediments. In studying these opal-rich sediments, a rapid method for estimating biogenic opal published by Mann and Müller (1980) was found useful. These authors applied an X-ray method which measures the height of a broad, diffuse reflection band of opal extending from about 15° to 32° 2θ , with a maximum at about 22° 2θ (i.e., 4.04Å) (Fig. 1, IB).

Furthermore, this paper describes another method for estimating variations in the biogenic-opal content by using grain density. Grain density (ρ) can easily be determined by measuring the weight (G) and the volume (V) of the dry sediment, where ρ $= G/V(g/cm^3).$

METHODS

In this study the Mann and Müller (1980) method was slightly modified as follows. The absolute height of the background reflection (h) at

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 $22^{\circ} 2\theta$ may also be influenced by other (clay) minerals such as montmorillonite and mixed layers (Fig. 1, III). Thus, the height (h'), instead of h at 22° 2 θ , was used as an improved measure of opal content. The height (h') was determined by constructing line ABC, where A is the point on the base line at 15° 2θ , B the point on the X-ray-diffraction (XRD) diagram at about 19° 2θ , and C a point at 22° 2θ on a line extension of straight line AB (defining the height, h'). The line ABC coincides with the base line if the opal content is less than 10% (Fig. 1, II and III). This implies that the Mann and Müller (1980) method may not be useful only if the biogenic-opal content has values greater than 10%. Thus, for a more detailed investigation of biogenic opal in the Neogene sections at Sites 658 and 660, other methods may have to be used (e.g., Leinen, 1977; Koopmann, 1979; Bohrmann, 1986).

The calibration curve for estimating biogenic-opal content was determined by using mixtures of known biogenic-opal content. Because a pure biogenic-silica standard was not available on board JOIDES Resolution, Sample 108-660A-15H-4, 104-106 cm, was chosen as an endmember with 100% biogenic silica (Fig. 1, I). This assumption is based on (1) the XRD data, (2) the very low grain density of this sample, which is about 1.5 g/cm³ (accuracy ± 0.02 g/cm³, 1.7-2.05 g/cm³ density is typical for biogenic opal, Hurd and Theyer, 1977), and (3) optical determinations. Sample 108-658A-10H-1, 120-122 cm, was taken as the biogenic-opal-free end-member. In the X-ray diffractogram of this sample, no broad reflection band was recorded (Fig. 1, II). From both samples, standards of known biogenic-opal content were mixed. These standards, as well as all other samples, were measured by XRD using the following conditions: (1) generator settings, 40 kV, 35 mA; (2) step size, 0.020° ; (3) count time, 1.00 s; and (4) angle range (2 θ), 2.00° to 40.00°.

The XRD diagrams of these measurements indicate the increasing height of the broad reflection band between 15° and 33° 2θ with increasing content of biogenic opal (Fig. 2). The resulting calibration curve is shown in Figure 3 as a plot of percentages of biogenic opal vs. height (h') of the reflection band.

For the grain-density method the samples were dried for 8 hr in the freeze drier and an additional 8 hr in the oven at 110°C. Afterward they were weighed on a motion-compensated Scitech electronic balance. The accuracy of the measurements is ± 0.02 g, which was determined from 10 measurements of a calibration weight of 20 g. Immediately after a sample was weighed, its volume was measured with a pycnometer. This method uses helium gas inserted into a defined volume, in which the difference between the empty cell and the cell containing the sediment determines the volume of the sediment sample. From volume and weight measurements, we calculate grain-density values. The estimated accuracy is about ± 0.02 g/cm³.

Changes in grain density mainly reflect changes in the content of biogenic silica, biogenic carbonate, and terrigenous material. Because biogenic silica has a significantly lower grain density than other sedimen-tary components (1.7 to 2.05 g/cm³; Hurd and Theyer, 1977; Mayer, 1979), and both biogenic carbonate and terrigenous material have a similar high density of about 2.6 to 2.75 g/cm3, changes in grain density of the total sample can be used as a rough estimate of changes in biogenicopal content.

Clay minerals such as montmorillonite also may contribute significantly to lower grain-density values. However, according to the XRD data (e.g., Fig. 1), the relatively low amount of montmorillonite is assumed to have only minor influence on large-scale grain-density variations.

RESULTS AND DISCUSSION

Based on the calibration curve shown in Figure 3, most of the samples from Site 658 have biogenic-opal contents of less than 10% (Fig. 4A). By using a sample interval of 1.5 m, 7 upper Pliocene and 2 middle Pleistocene samples are characterized

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Figure 1. X-ray diffractograms of bulk sediment samples. IA. Sample 108-660A-15H-4, 104-106 cm, which is assumed to consist of about 100% biogenic opal. IB. Biogenic opal from an opal mine in Australia (Bulla Creek, Queensland; Mann and Müller, 1980). II. Sample 108-658A-10H-1, 120-122 cm, which contains no opal. III. Section 108-660A-11H, CC, which also contains no opal but does contain clay minerals such as montmorillonite (*mon*) and kaolinite (*kao*). The height, h', of the reflection band was measured at 22° 2 θ (point C) in centimeters above the base line, b. See text for further explanations.

by distinctly higher opal values of 10% to 50% (Fig. 4A). These peaks correlate with low grain-density values of 2.2 to 2.4 g/cm³ and low carbonate values of 15% to 25% (Fig. 4B and 4C).

also have low carbonate values of about 10% to 20% but high grain-density values of 2.5 to 2.85 g/cm³ (Fig. 4B and 4C) and thus reflect a high siliciclastic component.

In contrast, the older samples from the upper and lower Pliocene (i.e., between 230 and 300 m below the seafloor, mbsf) At Site 660 the Pliocene-Pleistocene interval is characterized by low biogenic-opal contents, except for one middle Pleisto-



Figure 2. Diffractograms of mixtures of standards, showing increasing height of the reflection band above the base line with increasing biogenic-opal content.

cene sample with an opal content of about 20% (Fig. 5A). A similar event of biogenic-opal enrichment was also recorded at Site 658 from middle Pleistocene sediment.

In contrast to this event, the biogenic opal reaches values up to 100% in middle Eocene radiolarian ooze (30% to 100%, Fig.

5A). During that time, Site 660 lay underneath the equator (cf. Sclater et al., 1977); that is, it was influenced by equatorial upwelling. Thus, high oceanic productivity may have resulted in deposition of biogenic-opal-rich sediments in this area. Since then, Site 660 has drifted northward out of the high-productiv-



Figure 3. Calibration curve plotted as percentages of biogenic opal vs. height, h', of the reflection band above the base line at 22° 2 θ .

ity belt. A similar evolution of depositional environments also was recorded at Sierra Leone Rise, at DSDP Site 366 (Stein, 1985) and at Site 667 (Site 667 chapter, this volume).

The accumulation of almost pure (and moderately well-sorted) radiolarian ooze at Site 660 may require further processes, such as bottom-current activity, to explain the extreme enrichment of radiolarians (Site 660 chapter, this volume). The samples with high biogenic-opal contents correlate with low grain-density values ranging from 1.5 to 2.2 g/cm³ and low carbonate values ranging from 0% to 36% (Fig. 5). A distinct peak of very high grain density of 3.21 g/cm³ occurs at 126 mbsf, possibly caused by significant amounts of manganite (Site 660 chapter, this volume).

In general, samples with grain-density values of 1.4 to 2.4 g/ cm³ are characterized by high biogenic-opal contents of 10% to 100% (Fig. 6). Because quartz and carbonate sediments have densities between 2.65 and 2.75 g/cm³, samples characterized by biogenic-opal contents of less than 10% and relatively low grain densities of about 2.4 to 2.65 g/cm³ (Fig. 6) must contain additional components with distinctly lower grain-density values, such as montmorillonite.

SUMMARY AND CONCLUSIONS

Biogenic-opal content determined by a slightly modified Mann and Müller method (1980) shows large-scale variations in biogenic opal between 0% and 100%. Three major events of biogenic-opal deposition were recorded: (1) middle Eocene at Site 660, (2) late Pliocene at Site 658, and (3) middle Pleistocene at Sites 658 and 660. However, changes in opal content in the range of 0% to 10% cannot be resolved by this method.

If changes in the content of montmorillonite are of minor importance, the compilation of grain-density and carbonatecontent records allows us to distinguish between intervals of relatively increased supply of terrigenous matter and intervals of relatively increased input of biogenic opal. Such records can help to reconstruct the history of climate-controlled sedimentation and the paleoenvironment.

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Figure 4. A. Biogenic-opal content at Site 658, based on XRD data. Hatched area indicates biogenic-opal content of less than 10%. B. Grain-density values (g/cm³) at Site 658. C. Carbonate content at Site 658.



Figure 5. A. Biogenic-opal content at Site 660, based on XRD data. Hatched area indicates biogenic-opal content of less than 10%. B. Grain-density values (g/cm³) at Site 660. C. Carbonate content at Site 660.



Figure 6. Correlation between biogenic-opal content and grain density, Sites 658 and 660.