

Exploring Physical Indicators for Carbonate Contents in Deep Sea Sediments^{*}

Huang Wei Liu Zhifei Chen Xiaoliang Wang Pinxian

Laboratory of Marine Geology, Tongji University, Shanghai 200092

ABSTRACT: To determine carbonate contents of deep sea sediments using physical properties is an enjoyable and efficient paleoceanographic way, which has been processed successfully in many studies based on a low resolution, but rather than a high one. A series of mathematical methods including the least square method were used in this study to build multiple regression equations between color reflectance and carbonate content, and between magnetic susceptibility and carbonate content, based on the data of color reflectance and magnetic susceptibility collected via the ODP Leg 184 cruise, as well as measured carbonate contents. We found that percent carbonate estimated with diffuse reflectance is closer to the measured one than that estimated with magnetic susceptibility, and the multiple regression equation is varied in different sites.

KEY WORDS: carbonate, color reflectance, magnetic susceptibility, South China Sea, ODP Leg 184.

INTRODUCTION

The deep sea carbonate sediment is one of the largest carbon warehouses on the earth surface as it almost covers a half of the ocean floor in the world (Sundquist and Broecker, 1985). Therefore, it is very important to understand the distribution of deep sea carbonate sediments for investigating the variation of CO₂ concentration with the fluctuation of marine carbon-carbonate system (Norris and Röhl, 1999). As we know, carbonate content is nearly parallel to the oxygen isotope in Atlantic Ocean, with higher contents at interglacial stages but lower contents at glacial stages (Curry and Lohmann, 1986), but it is reversed in Pacific Ocean (Andersson, 1998). Now, the deep sea carbonate sediments can be used in the fields such as deep sea stratigraphic correlation (Ortiz et al., 1999; Wang et al., 1995), biologic productivity (Naidu and Malmgren, 1999) and ocean-atmosphere circulations (Howard and

Prell, 1994). However, those kinds of applications need high-resolution quantitative analysis from enough carbonate sediments, implying that it must be efficient and economical. Now, physical property analysis is found more and more useful just for the fact that it fits the high-resolution environment research with long core (Schmieder et al., 2000).

Physical property data were collected at small sampling intervals (a few centimeters), such as magnetic susceptibility, color reflectance, gamma-ray density and natural gamma radiation, and were applied for core-to-core and hole-to-hole correlation and for correlating core data to wireline log data. These correlation procedures are essential for stratigraphic studies, and some of the most important ocean drilling projects are unthinkable without the high-performance acquisition of physical property data. Physical properties of rocks and sediments are indicators of composition, formation and environmental conditions when they deposited. Some physical properties can be measured rapidly and easily at high spatial resolution (core logging) and serve as proxies for processes, such as paleoclimatic changes (Balsam et al., 1999; Hounslow and Maher, 1999; Mix et al., 1995). Physical property data are usually well de-

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finer and quantitative, which helps constrain the complex mineralogical and fluid systems in rocks and sediments. They are more frequently used by a wide scientific community for various scientific objectives. In this paper, we use the color reflectance and magnetic susceptibility to estimate the carbonate contents of site ODP1148, and try to find out the dubious factors and its feasibility.

PHYSICAL BACKGROUND

Color Reflectance

Color is the human eye perception of reflected radiation in the visible region of the electromagnetic spectrum (400–700 nm). One of the most objective ways to measure color is to use diffuse-reflected spectrophotometry. Light reflected from the material is collected in an integration sphere, normalized to the source light of the reflectance, and calibrated with the measurement of a pure white standard (100 % reflection) and a black box (zero reflection) over the entire wavelength spectrum of visible light. Several color spaces have been defined based on the tristimulus values X , Y , Z , such as the $L^* a^* b^*$ system. The $L^* a^* b^*$ system is adopted by ODP, because its use is recommended for sediment and rock color analyses. The $L^* a^* b^*$ system is referred to as the CIELAB system. It can be visualized as a cylindrical coordinate system in which the axis of the cylinder is the lightness variable L^* , ranging from 0 to 100 %, and the radii are the chromaticity variables a^* and b^* . Variable a^* is the green (negative) to red (positive) axis, and variable b^* is the blue (negative) to yellow (positive) axis. The two most common uses of color reflectance data are (1) color parameters, such as $L^* a^* b^*$ provides detailed time series of relative changes in the composition of the bulk material and are frequently used to correlate sections from core to core or hole to hole and to analyze the cyclicity of lithologic changes, and (2) spectral data can be used to estimate the abundance of certain compounds. Spectral analysis of visual light spectra can provide quantitative estimates of carbonate, opal, organic matter, chlorite and some combinations of clay minerals (Ortiz et al., 1999). Results from many ODP legs have shown that the correlation between L^* and carbonate content is usually the best and most obvious one and also is similar at many sites (Balsam, 1999; Ortiz et al., 1999; Mix et al., 1995). Parameters a^* and b^* do not seem to yield much character-

istic information or cyclic variations. So we can generate a kind of stepwise, multiple linear regression to estimate proxy percent carbonate from percent carbonate measurements and reflectance measurements, this has been successfully applied in the ODP Leg 162.

Magnetic Susceptibility

Magnetic susceptibility is the ratio of induced magnetization to the intensity of the magnetizing field. The bulk magnetic susceptibility cumulates ferromagnetic (κ_{fer}) (e. g. magnetite), imperfect antiferromagnetic (κ_{ifer}) (e. g. hematite, goethite), paramagnetic (κ_{para}) (e. g. Fe-bearing silicates), and diamagnetic (κ_{dia}) (e. g. calcium carbonate, quartz) contributions (Schmieder et al., 2000; Hounslow and Maher, 1999). The susceptibility of ferromagnetic minerals (up to $\sim 57 \times 10^6 \text{ m}^3/\text{kg}$) is orders of magnitude larger than that of imperfect antiferromagnetic ($\sim 0.5 \times 10^6 \text{ m}^3/\text{kg}$), paramagnetic ($\sim 0.4 \times 10^6 \text{ m}^3/\text{kg}$) or diamagnetic ($\sim 0.005 \times 10^6 \text{ m}^3/\text{kg}$) minerals for the Quaternary sediments (Maher, 1998). Thus, ferrimagnets often dominate the magnetic susceptibility of sediments. However, in ferromagnet-deficient sediments, shifts in magnetic susceptibility can reflect changes in the other mineral components. In particular, the content of diamagnetic carbonate can vary greatly in deep sea sediments, as a consequence of changes of the total susceptibility due to "dilution effects" (Hounslow and Maher, 1999). Therefore, an experiential equation could be determined based on the negative relationship between magnetic susceptibility and carbonate content, and be allowed to calculate the carbonate content for deep sea sediments using their magnetic susceptibility. The magnetic susceptibility of deep sea sediments is usually obtained on board by a convenient way. This method was firstly used successfully during the cruise Meteor to South Atlantic (Schmieder et al., 2000).

MATERIAL AND METHODS

We generated stepwise, multiple linear regression equations from measured carbonate contents and shipboard data of color reflectance and magnetic susceptibility of the ODP Leg 184 site 1143 (9°21.72' N, 113°17.11' E, 2 772 m) and site 1148 (18°50.17' N, 116°33.94' E, 3 294 m) (Wang et al., 2000) with the least square method.

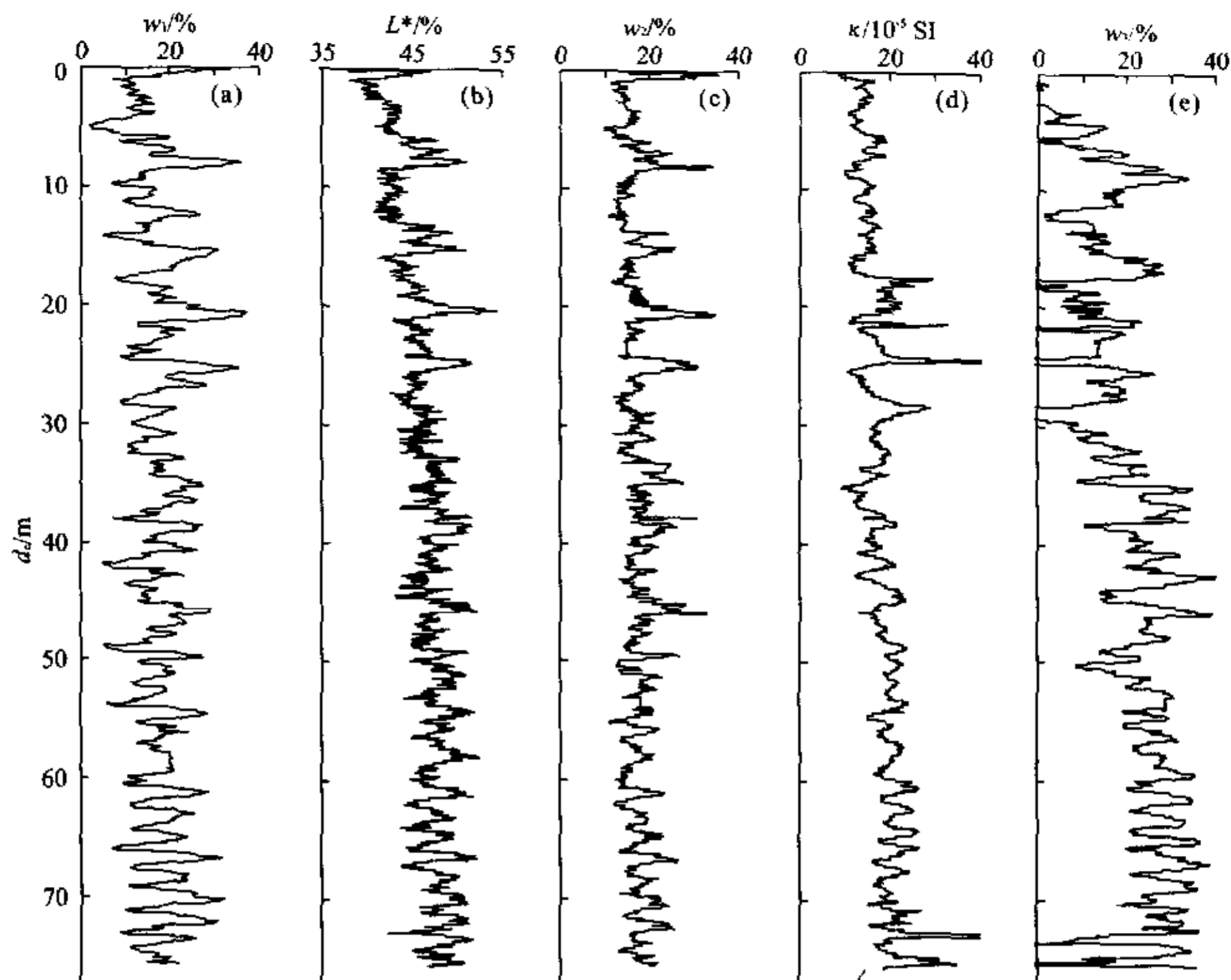


Figure 1. Measured carbonate contents (after Frederiches et al. (1999)), percent carbonate estimated using color reflectance (after Wang et al. (2000)) and magnetic susceptibility (after Wang et al. (2000)), proxy of site 1143 ODP Leg 184 (all of the source data had been smoothed with 5-point). w_1 , measured carbonate content; L^* , color reflectance; w_2 , proxy carbonate derived from L^* ; κ , magnetic susceptibility; w_3 , proxy carbonate derived from magnetic susceptibility; d_c , composed depth.

Determine Carbonate Contents Using Color Reflectance

Sediment color reflectance was measured onboard during the cruise ODP Leg 184 using the Minolta Photospectrometer CM-2002, with a resolution of 2 cm for site 1143 and 4 cm for site 1148 (Shipboard Scientific Party, 2000). The standard output for the ODP database includes the full 31-channel spectra of 10 nm length between 400–700 nm and L^* a^* b^* parameters. Since carbonate exhibits its maximum diffuse reflectance at the wavelengths towards the blue end of the visible spectrum (470, 530, 550 nm) (Mix et al., 1995), we generated the multiple linear regression equations using these reflectance bands and the square of them which are also based on the measured carbonate contents in laboratory. The equations have following forms

$$\text{ODP site 1143: } w(\text{CaCO}_3) = 1.406 R_{470} - 0.724 R_{530} - 0.278 R_{470}^2 + 0.256 R_{550}^2 - 0.027 \quad (1)$$

$$\text{ODP site 1148: } w(\text{CaCO}_3) = -10.17 R_{470} + 11.96 R_{530} + 0.0538 R_{470}^2 - 0.0582 R_{550}^2 - 16.65 \quad (2)$$

where R_λ represents the 10 nm reflectance band centered on wavelength λ .

Determine Carbonate Contents Using Magnetic Susceptibility

Magnetic susceptibility was measured onboard during the cruise ODP Leg 184 using Bartington MS2C with a resolution of 5 cm (Shipboard Scientific Party, 2000). In marine sediments, κ_{fer} and κ_{para} are typically subordinate and proportional to κ_{fer} . κ_{dia} is a constant background signal and can be subtracted from κ using an average value for carbonate (Schmieder et al., 2000).

$$\kappa_{\text{fer}} = \kappa - \kappa_{\text{dia}} \approx \kappa + 15 \times 10^{-6}$$

κ_{fer} expresses sedimentary magnetite content or can at least be converted into a magnetite equivalent. It can be written as following form

$$\kappa_{\text{fer}} = \varphi_{\text{mag}} \cdot \kappa_{\text{mag}} = \rho \cdot w_{\text{mag}} \cdot \chi_{\text{mag}}$$

where φ_{mag} is magnetite volume fraction; κ_{mag} is magnetite volume susceptibility (value is 3.1); ρ is dry bulk density; w_{mag} is magnetite mass fraction, χ_{mag} is magnetite mass susceptibility (value is $6 \times 10^{-4} \text{ m}^3/\text{kg}$). Under favorable sedimentation conditions (no reductive magnetite dissolution, largely terrigenous origin of magnetite, absence of siliceous fossils),

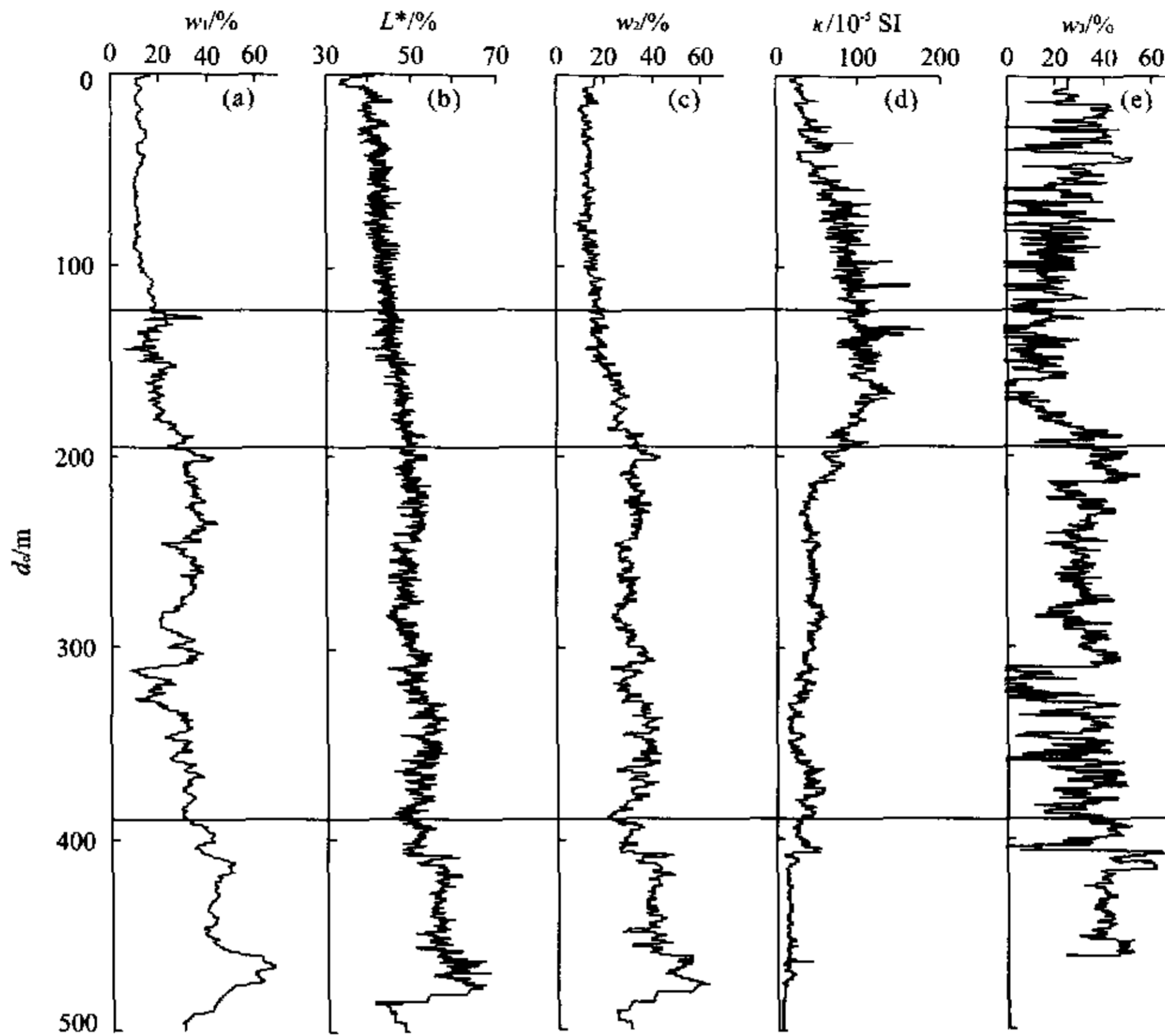


Figure 2. Measured carbonate contents, percent carbonate estimated using color reflectance and magnetic susceptibility proxy of site 1148 ODP Leg 184. w_1 , measured carbonate contents; L^* , color reflectance; w_2 , proxy carbonate derived from L^* ; κ , magnetic susceptibility; w_3 , proxy carbonate derived from magnetic susceptibility.

magnetite mass fraction (w_{mag}) is a linear measure of the terrigenous fraction and therefore anticorrelated with carbonate

$$w_{mag} \approx c \cdot w_{ter} \approx c \cdot (1 - w_{car})$$

where w_{ter} is terrigenous mass fraction and w_{car} is carbonate mass fraction. The c is regionally valid calibration coefficients. Then we can get the carbonate using magnetic susceptibility

$$w_{car} \approx 1 - \kappa_{ter} / (c \cdot \rho \cdot \chi_{mag}) \tag{3}$$

The data of magnetic susceptibility and dry bulk density can be downloaded from Ocean Drilling Program database. Comparing with measured carbonate contents, we can determine the c . In the top 75 m of site 1143, c is equal to 0.000 1, and because site 1148 is too long, we determine c in six sections that are presented in Table 1.

Carbonate Measurement

Carbonate contents of sites ODP1143 and 1148 were determined using the standard gasometric techniques, which have a precision of better than 2 %. A

total of 760 samples from the upper 76 m at site ODP1143 were measured, with a resolution of 10 cm. Likewise, 1 707 samples from upper 500 m at site ODP1148 were processed, with a 30 cm resolution.

Table 1 Coefficient c for site ODP1148

depth /m	c
0-213.44	0.000 19
213.49-310.09	0.000 10
310.44-359.89	0.000 06
359.94-376.99	0.000 10
377.04-416.64	0.000 075
416.69-461.94	0.000 050

RESULTS AND DISCUSSION

The carbonate contents, color reflectance, magnetic susceptibility and proxy carbonate contents are shown in Figs. 1 and 2. The carbonate contents of site 1143 indicate the obvious cyclicity with its maximum value of 40 % and minimum 5 %, averaged at

10 %–25 % (Fig. 1a). The color reflectance curve is parallel to the carbonate content curve, implying a better correlation between them. The color reflectance varies among 40 %–55 %, with its majorities at 40 %–50 % (Fig. 1b). The proxy carbonate contents determined using equation (1) is very close to the measured values. The correlation coefficient is 58.5 % and the average error is 20.6 %. The magnetic susceptibility curve mirrors the carbonate content curve, with a higher value corresponding to a lower one for the carbonate content. The magnetic susceptibility of this site is in $(10-40) \times 10^{-5}$ SI and mainly in $(15-25) \times 10^{-5}$ SI, which is increased when the depth becomes more deep, but is very high in the depth of 16–30 m and 72–75 m (Fig. 1d). The proxy carbonate contents calculated using equation (3) with $c=0.0001$ is in $(-10\%) - 40\%$ (Fig. 1e). It has low correlation coefficient (26.2 %) and high average error (more than 50 %, especially in the top 30 m and bottom 5 m, there is negative value) compared with the measured carbonate.

The carbonate content of site 1148 is in 10 %–60 %. We made it into three sections: (1) 0–120 m, the carbonate content is stable, in 10 %–15 %; (2) 120–410 m, percentage carbonate is cyclicity and increases while the depth deepening, and the average is 25 %; (3) 410–500 m, percentage carbonate is in 40 %–60 % and even higher (Fig. 2a). The color reflectance (L^*) curve is parallel to the carbonate contents curve too. The L^* is in 35 %–60 %, and also has three sections: 42 % in upper part (0–120 m), 50 % in middle part (120–410 m) and 55 % in bottom part (410–500 m) (Fig. 2b). The

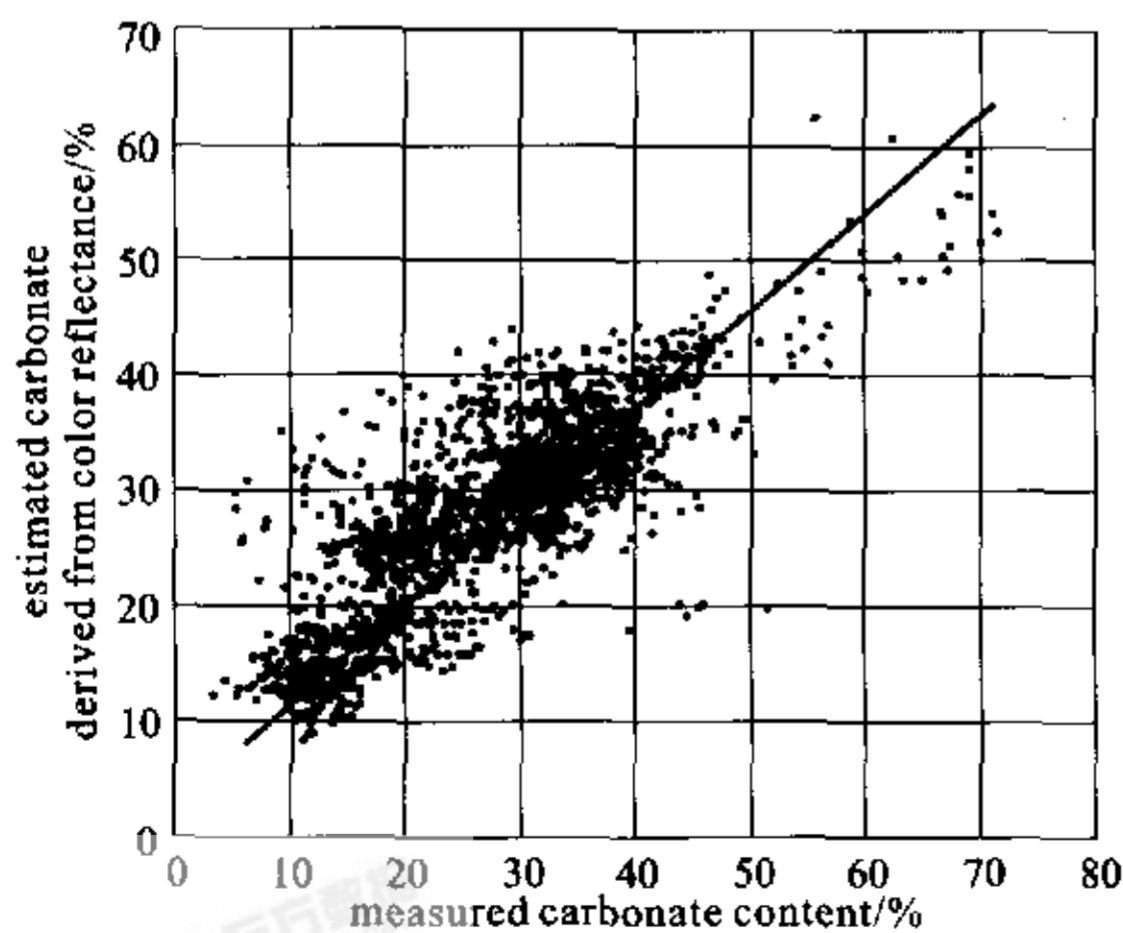


Figure 3. Correlation between measured carbonate contents and estimated ones derived from color reflectance data.

measurement interval of color reflectance is 2–4 cm, so it has much higher resolution than the measured carbonate contents. Calculated with equation (2), the proxy carbonate content is very coherence with the measurement, the correlation coefficient is 82.7 % (Fig. 3) and the average error is 10 %. The magnetic susceptibility of site 1148 has another character, which is negative correlation to the carbonate contents. The magnetic susceptibility of this site is in $(20-150) \times 10^{-5}$ SI, and also has three sections: (1) 0–200 m, the magnetic susceptibility increases from 20×10^{-5} SI to 150×10^{-5} SI at 180 m, then decreases to 80×10^{-5} SI at 200 m, and has high frequency cycle during this procedure; (2) 200–410 m, the magnetic susceptibility decreases cyclically, and the average is $(40-50) \times 10^{-5}$ SI; (3) 410–500 m, the magnetic susceptibility is very low as 20×10^{-5} SI (Fig. 2d). The proxy carbonate contents calculated with equation (3) and the c in Table 1 is between -10% and 60% . This result just agrees with the measurement in 200–300 m and 410–500 m, and has very large error in the other parts. The average error of this site is more than 85 %.

The positive or negative correlation among carbonate contents and color reflectance and magnetic susceptibility provides the feasibility to calculate the proxy percentage carbonate using physical properties. It has shown from our study that we can get ideal results using color reflectance with the average error 20 % in site 1144 and 5 % in site 1148. This is mainly because that the color reflectance is controlled by the carbonate, and the contents of other sediment component (such as opal, organic matter and clay minerals) are stable or vary synchronously with carbonate contents. But the error of proxy percentage carbonate gotten from magnetic susceptibility is very large, sometimes even more than 100 %. Because the carbonate is a kind of diamagnetic mineral, which changes the magnetic susceptibility of whole samples through the “dilution effect”, the magnetic susceptibility is mainly controlled by ferromagnetic mineral which is supplied by terrigenous sediments. The “dilution effect” is quite locally, for example, it is very high in the western tropic Pacific Ocean (such as GeoB site 1523) (Dobeneck and Schmieder, 1999; Rühlemann et al., 1999), and much in the eastern tropic Pacific Ocean, such as V22-196 (Bloemendal et al., 1988) though they are all negative correlation with carbonate contents. The ferromagnetic mineral in sediments of South China Sea is mainly terrigenous

origin, which must have different contents during the geo-history. So if we use the calibration coefficients constant c , it is inevitable that the error is very large.

CONCLUSIONS

Multiple regression equations were generated based on the comparing diffuse reflectance and magnetic susceptibility records from site 1143 and site 1148 of ODP Leg 184 with carbonate contents measured in our laboratory. The proxy percentage carbonate calculated from the multiple linear regression equations using the blue end reflectance bands of visible spectrum (470, 530, 550 nm) and the square of them is very close to the measured data with the error 20.6 % for site 1143 and 10 % for site 1148. But the results are not well calculated by using magnetic susceptibility for the large error more than 50 %. If the other components are stable, we can get reliable results. The equations were based on some measurements in laboratory and can be used only for the right site. It is a valuable chance for us to improve efficiency on the deep sea carbonate research.

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