# 23. REGIONAL AND STRATIGRAPHIC PATTERNS IN COLOR REFLECTANCE OF SEDIMENTS FROM LEG 175<sup>1</sup>

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## **INTRODUCTION**

During Leg 175, color reflectance was routinely measured downcore at all sites (1075–1087). These measurements allow determination of the light reflectance from the sediment surface in the visible wavelength band (see "Explanatory Notes" chapter, this volume). Previous studies have shown that the ratio between reflectance values of the red and blue wavelengths is closely related to diagenetic redox conditions in the sediment, reflected in the presence of iron oxyhydroxides or sulfides (Mix et al., 1992; Schneider et al., 1995). Reflectance data can be a suitable proxy for reconstructing high-resolution changes in carbonate sedimentation (see Curry, Shackleton, Richter, et al., 1994).

Leg 175 drilled a north–south transect along the southwest African margin (5°S to 31°S, 10°E). The sediments consist of different lithologies, ranging from carbonate-poor sediments with varying amounts of biosiliceous and terrigeneous material in the north to carbonate-rich sediments at the southernmost sites (see Wefer et al., Chap. 16, this volume). This chapter briefly summarizes the regional and stratigraphic patterns in color reflectance of sediments recovered during Leg 175. First, we show the relationship between lithology and color reflectance and, second, how stratigraphic changes in the color data can be used to obtain clues to climate forcing in the different sedimentary environments drilled during Leg 175.

## **METHODS**

On board color reflectance was measured for each core in the visible wavelength band between 400 and 700 nm in increments of 10 nm. Before measuring each core, the spectrophotometer was calibrated for the white color reflectance by attaching a white cap. The reflectance values of the white calibration cap were constant throughout the measurement period. The color data were corrected for "outliers" resulting from small voids. In addition, color data of the first and last measurements of each section were omitted when the resolution was 2 cm because of the proximity to the plastic cap at the ends of each section.

The analysis and interpretation proceeds from the percentage reflectance values as a function of wavelength (*reflectance*), the ratio between reflectance values of the red (650 nm) and blue (450 nm) wavelengths (*r/b ratio*) and the lightness expressed in percent of a white surface (*total reflectance*).

The downcore reflectance records of the dark-colored sediments from the Congo Basin display an overall small range in the total reflectance values and are dominated by high-frequency variability (see "Lithostratigraphy" sections, "Site 1075," "Site 1076," and "Site

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1077" chapters, this volume). To consider the analytical variations, one section from Site 1077 was selected and measured four times over a 12-hr shift and was therefore exposed to changing temperature and light conditions (Fig. 1A). The comparison of the 4-run measurements shows that the analytical variation is about 15% of the total variability in the dark-colored section from Site 1077, which defines the reproducibility of the spectrophotometer measurements for this type of sediment (Fig. 1A). This suggests that even subtle color changes often not visible to the eye mostly reflect lithologic changes. A better reproducibility is obtained for light-colored sediments, as shown from a 3-run measurement of a section from Hole 1083A (Fig. 1B).

#### **REFLECTANCE VS. LITHOLOGY**

The aim of this synthesis is to explore the underlying lithologic control for the color of sediments recovered during Leg 175. At Sites 1075, 1076, and 1077, the major lithologic component is clay with very low calcium carbonate contents (on average <4 wt%). South of the Walvis Ridge, the sediments consist of calcareous oozes with clay abundances ranging between 10% and 30%. In this area, the calcium carbonate contents range between 40 and 70 wt%. Generally, the lithologic changes at each site were mostly gradual regarding the amounts of diatoms, nannofossils, and foraminifers. The largely continuous presence of authigenic minerals, such as pyrite and glauconite, downhole at all sites suggests reducing diagenetic conditions, which are typical for high-productivity areas (Wefer et al., Chap. 16, this volume). Iron oxyhydroxides were observed only at Sites 1085 and 1087 at the base of the cores near the Miocene/Oligocene boundary. The different lithologic environments encountered during Leg 175 enable us to evaluate the reflectance pattern of specific wavelengths in the visible band for each lithologic type and to compare the color data with preliminary shipboard measurements of calcium carbonate and organic carbon contents and magnetic susceptibility. To explore these relationships, individual reflectance patterns were selected based on carbonate contents.

## Low-Carbonate Environments

Environments with carbonate contents <10 wt% were encountered at Sites 1075–1080. Here, sediments consist mostly of darkcolored terrigeneous clay with varying abundances of diatoms, nannofossils, and authigenic minerals, with very low calcium carbonate contents (<6 wt%) and relatively high organic carbon contents (4 wt% on average). The selected sediments have low reflectance levels and slightly enhanced reflectance values in the green-to-red spectrum (550–700 nm; Fig. 2A). In general, the r/b ratios are low. This pattern could be related to traces of reduced iron minerals such as glauconite and pyrite (see Wefer et al., Chap. 16, this volume). Relative changes in the biogenic component are not detectable; this is a possible consequence of the clay dominance, which leads to overall low reflectance values.



Figure 1. Reflectance values (in percentages) from a dark-colored section at (A) Hole 1077A, measured four times, and from a light-colored section at (B) Hole 1083A, measured three times. The standard deviation for each section is indicated.



Figure 2. Reflectance spectra (400–700 nm) characteristic of distinctive lithologies of sediments from Leg 175. A. Clay with various amounts of diatoms, nannofossils, and authigenic minerals at Holes 1075A, 1076A, and 1077A. B. Organic-rich clay with abundant diatoms at Hole 1084A.

The reflectance intensity for individual wavelengths of the socalled "black" layers at Site 1084 (see "Lithostratigraphy" section, "Site 1084" chapter, this volume) was studied in greater detail. The major lithologic component of these layers is organic-rich clay with varying amounts of diatoms and nannofossils. Calcium carbonate contents are low (<10 wt%), whereas organic carbon contents are high (as much as 18 wt%). The black layers show low reflectance values, with highest values in the red spectrum (Fig. 2B). The reflectance spectrum shows an inflection point at 650 nm (Fig. 2B). This feature has also been observed in the reflectance spectrum of diatom oozes and siliceous clay (Mix et al., 1992). The authors related this reflectance pattern to the presence of biogenic silica or to the associated organic matter. Although the clay component is dominant in the black layers at Site 1084, smear-slide analyses indicate that diatoms are common to abundant. On the other hand, reflectance spectra from the Congo Basin sediments, where diatoms are common, do not show any inflection point at 650 nm (Fig. 2A). This characteristic seems to be typical for sediments containing abundant diatoms and high organic carbon contents. The color of these sediments is varying from olive, dark olivegray, to black on the Munsell color chart. The same black layers were encountered at Site 1082 and also have high organic carbon contents (>10 wt%), but higher calcium carbonate contents (>10 wt%) and lower diatom abundances compared with Site 1084. The response to individual wavelengths is similar to that at Site 1084 and is characterized by an inflection point at 650 nm and a relatively high r/b ratio (Fig. 2C). At Site 1082, the diatom component is only minor, suggesting that the inflection point at 650 nm is related to high organic carbon contents.

#### **Carbonate-Rich Environments**

For sediments with high carbonate contents (>20 wt%), the color reflectance is high regardless of the individual wavelength bands, but still shows a pronounced difference between the blue and green-tored spectra (Fig. 2D). The diatom ooze interval at Site 1084 shows an inflection point at 650 nm. There are no organic carbon content measurements available for this layer. However, this site is characterized by overall high organic carbon contents (see "Geochemistry" section, "Site 1084" chapter, this volume). There is no clear explanation for the high r/b ratio characteristic of the nannofossil ooze. At Site 1085, the presence of pyrite throughout the core does not appear to influence the reflectance spectrum, for example, by lowering reflectance values in the red spectrum. The reflectance spectrum is flat at wavelengths from 500 to 700 nm in accordance with the study of Gaffey (1984).

## Comparison Between Color Data and Shipboard Measurements (Calcium Carbonate and Organic Carbon Contents)

Lithologic changes in sediments with low calcium carbonate contents and dominated by clay cannot be distinguished by relative differences in the reflectance of individual wavelengths (Fig. 2A). Also, crossplots of total reflectance and r/b ratio with calcium carbonate contents do not show any correlation that would suggest control on the color changes observed downcore (Fig. 3A, C). Comparison between organic carbon contents and total reflectance shows a weak



Figure 2 (continued). C. Organic-rich clay with high carbonate contents at Hole 1082A. D. Carbonate-rich sediments (oozes) from Holes 1081A, 1084A, and 1085A.



Figure 3. Relationship between color measurements (total reflectance and red/blue ratio) and calcium carbonate and organic carbon contents for (A-D) Holes 1075A, 1077A, and 1076A, respectively; (E-F) Holes 1082A and 1084A, respectively (solid triangles = measurements for levels with high amount of diatoms, defined as diatomaceous clay; open squares = nannofossil clay and nannofossil ooze); and (G) Holes 1083A and 1085A.

negative correlation (Fig. 3B) and a weak positive correlation when compared with the r/b ratio (Fig. 3D). Despite the small number of measurements, the influence of organic carbon on the color reflectance (r/b ratio) is supported by the study of the black layers, which show high r/b ratios (Fig. 2B). Layers with high organic carbon contents have low percentage reflectance values even when calcium carbonate contents are >20 wt%, such as at Site 1082 (Fig. 2C), suggesting the control of organic carbon on total reflectance. Nevertheless, in such environments, in addition to the clay and organic matter components, the biogenic silica component has to be considered to understand the changes in total reflectance.

For sediments with calcium carbonate contents >10 wt%, such as at Sites 1082, 1083, and 1085, total reflectance correlates positively with calcium carbonate, indicating that the color changes are controlled by the changes in carbonate contents (Fig. 3E, G). A similar relationship is observed between total reflectance and calcium carbonate at Site 1084, although some differences exist between the lithologic subunits (Fig. 3F). The crossplots show larger scatter at Site 1084 than at Site 1082, especially for subunits containing diatomaceous clays. This may be because of the higher biogenic opal and organic carbon contents at Site 1084. Shore-based measurements of biogenic opal contents are required to quantify the biosiliceous component and to determine the competing influences of opal and carbonate on total reflectance.

#### REGIONAL AND STRATIGRAPHIC PATTERNS: CONGO AND CAPE BASINS

Downcore variations in total reflectance and r/b ratio show cyclicities regardless of depth or age. However, the underlying lithologic controls for the observed variations in the color data are poorly known and differ between the Congo and Angola Basins and south of the Walvis Ridge.

#### **Congo Basin**

Stratigraphic variations of the color data from the dark green-colored sediments from Site 1077 show periodic cycles. Moreover, the periodicities of the total reflectance and the r/b ratio appear to be different (Fig. 4A). Because clay dominates at this site, underlying lithologic changes of the other sediment components are only subtle. Spectral analysis from the spliced records for total reflectance and the r/b ratio was performed only for the first 120 meters composite depth (mcd) because some poor-recovery intervals occur between 130 and 200 mcd. Results from the spectral analysis reveal that the main peaks in the variance power of the color data are not related to the lengths of the sections. Sections were, on average, 1.5 m long. This corresponds to a peak at ~0.66 on the frequency scale (Fig. 4B, C). For the r/b ratio, the variance power is concentrated at 8, 4, and 2.3 mcd periodicities and at 5.5, 3.2, and 2 mcd periodicities for total reflectance (Fig. 4B, C). These periodicities can be interpreted in terms of age, assuming a mean sedimentation rate of 100 m/m.y. at Site 1077 (see Giraudeau et al., Chap. 19, this volume). Both the total reflectance and r/b ratio records display cycles that are close to the orbital periods. The most striking feature is the dominance of the near-23-k.y. periodicity in the r/b ratio, which is observed for different depth intervals (Fig. 4B). Spectral analysis of the total reflectance reveals a more complicated picture showing a larger number of competing cycles in accordance with spectral analysis performed for Site 1075 color data (see Berger et al., Chap. 22, this volume).

Although the relationship between the r/b ratio and organic carbon contents is weak, the dominance of the precession cycle in the r/b ratio suggests a strong influence of productivity variation. The close tie between precession and productivity has been evidenced in this area for late Quaternary sediments (Schneider et al., 1997a). The r/b ratio may be used as an indicator of oceanic productivity in the Congo Basin—at least for the last million years.

Cyclicities obtained for total reflectance are not easily interpreted in terms of climate forcing (Berger et al., Chap. 22, this volume). Further comparison with other parameters is required to deconvolute the influence of the different climate components (oceanic or continental). At Site 1077, total reflectance data show a weak positive correlation with magnetic susceptibility measurements (see "Lithostratigraphy" section, "Site 1077" chapter, this volume). In this area, variations in the magnetic susceptibility have been interpreted to result from the dilution with biosiliceous material, which is stronger during glacial periods and would therefore result in lower magnetic susceptibility values (Schneider et al., 1991, 1997a; Thiessen, 1993). This suggests that biogenic opal and the associated organic matter might influence variations in total reflectance. Additional studies will explore opportunities for detecting climatic effects on land and at sea, based on color reflectance.

## Northern and Southern Cape Basins

For sediments with calcium carbonate contents >20 wt%, total reflectance is a suitable proxy for reconstructing changes in carbonate sedimentation. The spliced records for total reflectance were selected from Sites 1082, 1083, 1084, and 1085, located along a north-south transect from the Walvis Bay to the Southern Cape Basin. The color data exhibit high-frequency-scale variability. Total reflectance may be used as an additional stratigraphic tool between biostratigraphic and paleomagnetic tie-points (Fig. 5A). High total reflectance values are observed between the biostratigraphic ages of 0.46 and 0.26 m.y. and at the Brunhes/Matuyama boundary (0.78 m.y.). These periods of high total reflectance values, occurring in the upwelling-influenced areas (Sites 1082 and 1084) and also in more oceanic-influenced areas (Sites 1083 and 1085), indicate either high carbonate productivity or better carbonate preservation. The carbonate proxy records from upwelling-influenced areas (Sites 1082 and 1084) support a switch from siliceous to carbonate production during these periods.

The total reflectance records vs. age from two high sedimentation-rate sites (1082 and 1083) show that the transition to high reflectance values occurs between 0.6 and 0.55 m.y., close to the Milankovitch/Croll boundary, which marks the boundary to the dominance of the 100-k.y. cycles in the climate records. The transition is sharp at Site 1083 and gradual at Site 1082. Similar changes in the carbonate sedimentation have been observed from color measurements on deep-sea gravity cores from the same area (22°S-35°S; Schneider et al., 1997b). Superimposed on this high-reflectance pattern between 0.5 and 0.26 m.y., fluctuations in the carbonate proxy are observed. The magnitude of these changes appears to be small compared with carbonate records from the Southern Ocean for this time interval; for example, at the transition from marine isotope Stages 12 to 11 (Howard and Prell, 1994; Howard, 1997). Ongoing paleontological studies will improve the stratigraphy for these sites and will allow a more detailed assessment of the history of carbonate sedimentation in this area.

## CONCLUSIONS

 Shipboard measurements were used to determine the lithologic control on the color data in low-carbonate environments. Preliminary results suggest that the r/b ratio is controlled by the amount of organic carbon in the sediment and that organic matter and biosiliceous sedimentation influence total reflecSite 1077



Figure 4. Stratigraphic variations in (**A**) the total reflectance and the red/blue ratio at Site 1077. Spectral analysis of (**B**) the r/b ratio and (**C**) total reflectance (color data) for three depth intervals. The spectra are computed using the Blackman-Tukey method with a Barlett-type window. The variance power has been normalized to 100% on the frequency range of 0 to 3. The square root of the amplitude is shown. Frequency is given as cycles per meter composite depth.

tance. Further measurements of the terrigeneous component and the biogenic component, such as opal contents, are necessary to establish the threshold value for carbonate control on the total reflectance. 2. Spectral analysis of the color data of undisturbed intervals indicates that cycles have orbital scale periods regardless of depth or age. In the Congo Basin, variations in the r/b ratio may reflect productivity changes. 3. Carbonate contents in sediments from the Walvis and Cape Basins strongly influence the total reflectance data. Highreflectance values are especially observed between 0.55 and 0.26 m.y. and may be caused by enhanced carbonate accumulation.

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Figure 5. A. Total reflectance vs. meters composite depth at Sites 1082, 1083, 1084, and 1085. The positions of the biostratigraphic (gray boxes) and paleomagnetic (black boxes) events are indicated. (Continued on next page.)

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Figure 5 (continued). B. Total reflectance records vs. age at Sites 1082 and 1083 compared with an ice-volume index (Bassinot et al., 1994).