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# Evaluating optical lightness as a proxy for carbonate content in marine sediment cores

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# Abstract

Optical lightness is increasingly being used as a proxy for the carbonate content of marine sediment. We compared three measurements of optical lightness, gray scale, brightness and  $L^*$ , to carbonate content to test the reliability of these measurements as carbonate content proxies. In five piston cores from isotope stages 1 though 6 (0- ~ 130 ka), all measures of optical lightness are reasonable proxies of relative, but not absolute, changes in carbonate content. In contrast, in the upper sediments of ODP Hole 997A, which are Holocene to Pliocene in age, lightness values in only the top 10 m of the 180 m analyzed exhibit a strong correlation to carbonate content. To better understand which factors control the optical lightness of sediments, we analyzed samples in which carbonate content remained constant while the composition of three common clay minerals — chlorite, illite and kaolinite was varied. Kaolinite, even at a concentration of 20%, did not significantly change optical lightness. However, 20% illite reduced optical lightness by 30%, and 20% chlorite reduced lightness by 20%. We conclude that regional and temporal changes in the composition of the non-carbonate sediment fraction may significantly alter the relationship between lightness and carbonate content. We recommend that care must be taken when applying these measures to sediment sequences which span long time intervals, or to sediment samples taken over a broad geographical areas. © 1999 Elsevier Science B.V. All rights reserved.

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# 1. Introduction and background

During the last several years, marine geologists and paleoceanographers have been investigating longer sediment cores (primarily from the Ocean Drilling Program) at increasingly finer sample intervals. Quantitative analysis of sediment properties at these increasingly finer intervals requires methods that are rapid and relatively inexpensive. One measure that has become increasingly common as an analytical tool for deep-sea core stratigraphy is variation in the optical lightness of sediment (see for example, Herbert and Fischer, 1986; Herbert and D'Hondt, 1990; Bond et al., 1992; Cortijo et al., 1995; Mix et al., 1995; Bodén and Backman, 1996). In this paper, we use optical lightness (hereafter referred to as lightness) as a general term to describe the amount of light in the visible (VIS) region of the

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electromagnetic spectrum (400–700 nm) reflected from a surface. Typically, sediment lightness is determined by one of three techniques — (1) visual examination and possible comparison to a color chart, (2) gray scale measurements either from photographs or directly from a core's surface, or (3) spectrophotometric analysis.

Visual analysis is rapid, but qualitative, Lightness has been recorded in marine cores at least since the 1940s when cores were visually examined and their color and lightness described by comparison to color charts such as the Munsell Color Chart or its derivative, the GSA Rock Color Chart (Goddard et al., 1948). In the Munsell color system, lightness is value and is numerical. Although value is numerical. it is determined by an imprecise instrument, the human eve. In addition to the imprecise nature of the human eve, lightness measures are also a function of the type of illuminant used: i.e., sunlight imparts one value to a sample, whereas incandescent or fluorescent lights impart other values. Despite the imprecise nature of lightness changes as interpreted by the human eye, early workers, especially in the North Atlantic (see for example Ericson et al., 1961, and references therein), successfully correlated lightness with changes in carbonate content. They observed that interglacial intervals were characterized by light, high carbonate sediments, whereas glacial intervals correlated with darker, lower carbonate sediment.

Gray scale analysis includes data gathered by a number of different techniques. Herbert and Fischer (1986) and Herbert and D'Hondt (1990) used a microdensiometer to determine transmission through photographic slides of rock and core samples. Bond et al. (1992) and Hagelberg et al. (1994) used digitized photographs (both color and black and white) of cores and related lightness to the intensity value of a pixel or group of pixels in the digitized photograph. The diagrams of Bond et al. (1992) clearly demonstrate a good inverse correlation between gray level and carbonate content; as carbonate content increases, gray level decreases, indicating lighter sediment.

Fresh core surfaces have also been subjected to gray scale analysis by obtaining a digital image of the core surface, generally from an RGB camera, and extracting from the digital information a measure of lightness such as luminance or intensity value of a pixel or group of pixels (Merrill and Beck, 1995; Schaaf and Thurow, 1995; Cortijo et al., 1995; Hughen et al., 1996). Bodén and Backman (1996) also used gray scale values, but instead of identifying carbonate, they identified laminated diatom ooze (LDO). Clearly, not only carbonate, but any light colored material (e.g., siliceous ooze), will produce low gray scale values. Gray scale is advantageous because the analysis can be done at a very fine scale and can be done on photographs (Bond et al., 1992) or stored digital images, rather than actual sediment. Thus, the technique can be applied to older cores that have essentially been consumed through sampling or have disintegrated through time.

Unlike gray scale, spectrophotometer analysis obtains a total reflectance spectrum either directly from a core's surface or from a sediment sample of the core. Lightness, which in this paper will be termed brightness when applied to reflectance data from a spectrophotometer, is calculated as the area under the spectral curve in the VIS. Although spectrophotometric analysis is a direct measure of optical lightness, it is limited by the aperture of the spectrophotometer, commonly 2-8 mm, or by the dexterity of the person sampling the core. Balsam et al. (1986) employed a diffuse reflectance spectrophotometer to examine 171 core top samples in the North and South Atlantic Oceans and noted a positive correlation between sample brightness and carbonate content. Later, Balsam and Deaton (1991) factor analyzed the first derivative of the spectral values from these 171 Atlantic core tops and identified a factor that appeared to be related to carbonate content. However, a regression of factor scores vs. carbonate content produced a correlation coefficient of only 0.44 suggesting that this factor was controlled by not only carbonate content, but additional constituents. To obtain an understanding of which wavelengths are related to carbonate content from reflectance spectra, Balsam and Deaton (1996) regressed the near ultra-violet, visible and near-infrared (NUV/VIS/NIR) spectra from 356 core-top (i.e., ~ Holocene) and Last Glacial Maximum (~21 ka) samples from the Atlantic Ocean cores against carbonate content. The resulting multiple linear regression equation had 13 terms from 290 to 850 nm, a correlation coefficient of 0.97, and a root mean square error (RMSE) of  $\pm 11.6\%$ . This study clearly

showed that even when a large calibration data set and a multi-termed equation is used, the errors associated with estimating carbonate content from spectra, as shown by the RMSE, are considerable.

Another color description system, the CIE/ L\*a\*b\* system overcomes many of the disadvantages of the Munsell system by specifying illuminant and quantifying color descriptors. In this system,  $L^*$ is luminance or lightness. Many modern photometers and spectrophotometers are capable of calculating and recording  $L^*$  and other related measures of lightness. Deployment of a portable spectrophotometer, a Minolta CM-2002, aboard the ODP drillship JOIDES Resolution in the early 1990s has given shipboard scientists an instrument capable of measuring lightness directly. In most cases, ODP shipboard parties have used  $L^*$  as a proxy for carbonate (see, for example, Schneider et al., 1995). As with sample brightness,  $L^*$  is a measure of area under the spectral curve and as  $L^*$  values increase, carbonate content is expected to increase.

The purpose of this paper is threefold. First, to compare and assess the fidelity of the three measures of optical lightness — gray scale, brightness and  $L^*$  — for estimating carbonate content. Second, because the comparison between lightness measures and carbonate content is less than perfect, we examine other factors that can affect sediment lightness and the relationship between lightness and sediment composition. Third, we investigate the significance of a correlation between lightness and carbonate content. In addition, we provide some caveats regarding the gathering of lightness data and the use of lightness measures as a proxy for carbonate content.

## 2. Methods and material

To accomplish the objectives of our study, we compared carbonate content to lightness measures in five piston cores from Lamont–Doherty Earth Observatory core collection, and all cores from the top 180 m of sediment recovered at ODP Hole 997A (Table 1). All samples were dry and both ground sediment and cleaned core surfaces were analyzed. We also conducted experiments in which we held carbonate content constant and varied mineralogy to

Table 1
Materials analyzed and data collected

Core #	% Carbonate	Gray scale	Brightness	L* values
V15-168	X <sup>a</sup>		X <sup>c</sup>	
V17-178	$X^a$		X <sup>c</sup>	
V25-26	$X^{a}$		X <sup>c</sup>	
V29-178	$X^b$	$X^b$	$X^d$	$X^d$
V30-97	$X^b$	$X^b$	$X^d$	$X^d$
ODP 997	$X^a$		X <sup>c</sup>	Xe

<sup>&</sup>lt;sup>a</sup> Determined by the gasometric technique of Jones and Kaiteris (1983)

demonstrate the effect of changing sediment composition on measures of optical lightness. In addition, we investigate the relationship between water content and lightness. Two diffuse reflectance spectrophotometers were used to obtain lightness data a Perkin-Elmer Lambda 6 and a portable, hand-held, Minolta CM-2002. Each of these spectrophotometers is equipped with diffuse reflecting integrating spheres, allowing total reflectance measurements to be made. The Lambda 6 is capable of analyzing wavelengths from 250 to 850 nm, whereas the CM-2002 only operates in the VIS, from 400 to 700 nm. A Perkin-Elmer white BaSO<sub>4</sub> plate was used to set the 100% reflectance level for each of the spectrophotometers. The spectrophotometric techniques utilized in this study are the same as previously reported for the Perkin-Elmer Lambda 6 (Balsam and Deaton, 1991; Deaton and Balsam, 1991) and Minolta CM-2002 (Balsam et al., 1998).

For the Perkin-Elmer Lambda 6 spectrophotometer, where the sample has to be held vertically, sample preparation followed the procedures described by Balsam and Deaton (1991). That is, samples were ground to < 38  $\mu$ m, made into a thick slurry on a glass microslide with distilled water and slowly dried either in air or on the warm setting of a hot plate. With the exception described below, all brightness values were determined with the Perkin-Elmer Lambda 6.  $L^*$  values and brightness values

<sup>&</sup>lt;sup>b</sup>From Bond et al., 1992.

<sup>&</sup>lt;sup>c</sup> Determined from spectral analysis of dry, ground samples with a Perkin-Elmer Lambda 6 diffuse reflectance spectrophotometer.

<sup>&</sup>lt;sup>d</sup>Determined from spectral analysis of dry core surfaces with a Minolta CM-2002 diffuse reflectance spectrophotometer.

<sup>&</sup>lt;sup>e</sup>Determined from spectral analysis of dry ground samples with a Minolta CM-2002 diffuse reflectance spectrophotometer.

for cores V29-178 and V30-97 were determined with the Minolta CM-2002 spectrophotometer by taking readings directly from the split surface of the dried cores. The surface was prepared by removing any oxidation and dirt which had accumulated during storage and smoothing the resulting surface. Previous studies have shown that direct measurement of a core surface (both wet and dry) with the Minolta and ground marine sediment samples measured with the Perkin-Elmer produce similar spectral results and down-core trends (Balsam et al., 1997). L\* values from ODP 997 were determined on the same slurry slides used for the determination of brightness. Grav scale values and carbonate content for both V29-178 and V30-97 are from Bond et al. (1992); carbonate values for V15-168 and V25-56 are from Damuth (1975). Carbonate content for the remaining cores was determined using the vacuum gasometric technique of Jones and Kaiteris (1983).

# 3. Comparison of measures of lightness down cores

There are many statistical methods for comparing curves. When deciding which method to use it is important to keep in mind how those curves will be used. For example, carbonate curves are used primarily for stratigraphy and stratigraphic correlation is done by comparing general trends in curves and by peak to peak correlation. Our comparison, therefore, will concentrate on trends and peak to peak correlations.

For two cores, V29-178 and V30-97, we have a complete set of data that includes weight percent carbonate and the three lightness measures (Figs. 1 and 2). Both of these cores are from the eastern North Atlantic; V29-178 was taken at 42.85°N, 25.15°W from a water depth of 3448 m and V30-97 was taken at 41.00°N, 32.93°W from a water depth

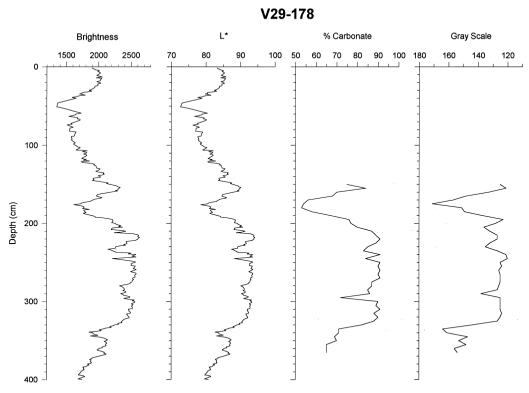


Fig. 1. Carbonate content and three measure of sample lightness in piston core V29-178 from the subpolar North Atlantic. Carbonate and gray scale values are from Bond et al. (1992);  $L^*$  and brightness were determined from data recorded by analyzing the core surface with the Minolta CM-2002 spectrophotometer. Gray scale was determined in a smaller section of core than  $L^*$  and brightness.

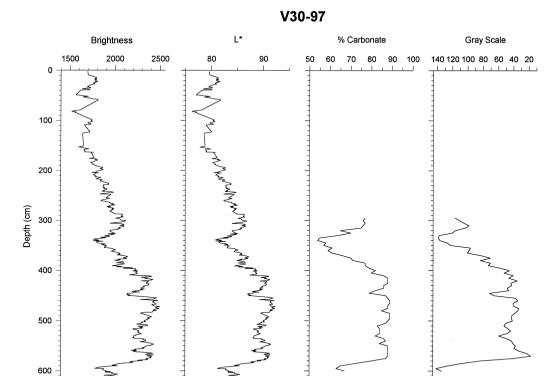


Fig. 2. Carbonate content and three measure of sample lightness in piston core V30-97 from the subpolar North Atlantic. Carbonate and gray scale values are from Bond et al. (1992);  $L^*$  and brightness were determined from data recorded by analyzing the core surface with the Minolta CM-2002 spectrophotometer. Gray scale was determined in a smaller section of core than  $L^*$  and brightness.

of 3371 m. Both cores contain latest Quaternary sediments extending back into isotope stage 6, about 130 ka. The visual correlation between general carbonate trends and all the lightness values in both the cores is good, and any of the three lightness measures could be used confidently as a proxy for carbonate. Most striking in these cores is the similarity of  $L^*$  and brightness. These indices of lightness appear identical in both cores despite differences in they way the two indices are calculated. In contrast, gray scale exhibits some subtle differences from  $L^*$  and brightness.

In V29-178 gray scale has a prominent peak at 195 cm that is not present in the carbonate curve or either the  $L^*$  or brightness measures (Fig. 1). In addition, gray scale values do not record the two minor carbonate lows at 235 and 245 cm, which are clearly exhibited in both  $L^*$  and brightness curves. On the other hand, the larger carbonate low at 295

cm is substantially reduced in both  $L^*$  and brightness and offset slightly upward in the gray scale curve. On average,  $L^*$  and brightness appear to be slightly better proxies for carbonate in this core.

In V30-97, as in V29-178, there are subtle differences between the gray scale curve and  $L^*$  and brightness (Fig. 2). The carbonate low at 340 cm appears to be shifted up about 10 cm in the gray scale curve (330 cm) in relation to the carbonate,  $L^*$  and brightness curves, which all show an increase at this level. Likewise, the small carbonate low between 440 and 450 cm seems to be offset slightly downward in the  $L^*$  and brightness curves. This slight offset down core may be the result of finer sampling for  $L^*$  and brightness. Finally, the presence of a small carbonate high between 535 and 575 cm is recorded by all three measures, but none of these measures records the shape of the high particularly well. Gray scale exhibits a peak at 570 cm not shown

in the carbonate and both  $L^*$  and brightness have a low at 565 cm not shown in the carbonate. In summary, all the measures of lightness do a credible job as proxies for carbonate in this core.

We have data on both carbonate content and brightness for cores V15-168, V17-178 and V25-56 (Figs. 3 and 4). V15-168 was taken from 0.2°N, 39.9°W at a water depth of 4219 m on the lower continental rise off northeast Brazil (Guiana Basin) and V25-56 was taken from 3.55°S, 35.23°W at a water depth of 3512 m from the mid-continental rise near a seamount in the Guiana Basin. Both V15-168 and V25-56 extend back to isotope stage 6 (Damuth, 1975, 1977). V17-178 was taken from the Laurentian Fan in the North Atlantic at 43.38°N, 54.87°W from a water depth of 4006 m. Two radiocarbon dates from this core indicate that carbonate content began to increase about 14 ka and that the core goes back about 30 ka (Balsam, 1981). For all three of these

cores, there is good agreement between trends in the carbonate curves and brightness.

In V15-168 most of the major peaks correlate, a few may be offset several centimeters by differences in sampling depth (Fig. 3). One exception is the carbonate peak at 600 cm, which appears shifted 20 cm downward in the brightness record. In addition, the brightness record exhibits some minor differences from the carbonate record from 210-350. 440-620 and 730-800 cm. In V25-56 brightness trends and peaks, even minor peaks, also correlate very well with the carbonate curve (Fig. 3). Minor differences in trends occur from 140 to 160 cm and from 270 to 300 cm and the minor carbonate high at 380 cm is not present in the brightness curve. These minor offsets of peaks and valleys between the carbonate and brightness curves in V15-168 and V25-56 are, in part, attributable to the fact that a 2 cm thick section of core was removed for carbonate analysis

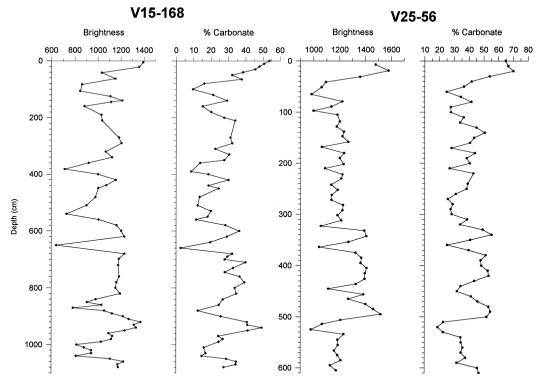


Fig. 3. Carbonate content and brightness curves for piston cores V15-168 and V25-56 from the continental rise off northeastern Brazil. Carbonate values are from Damuth (1975; 1977) whose stratigraphy indicates that the Y/Z boundary is at 70 cm and X/Y boundary at 1000 cm in V15-168 and at 40 and 505 cm, respectively, in V25-56.

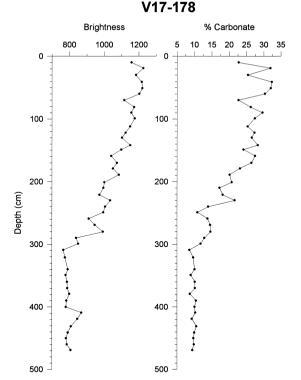


Fig. 4. Carbonate content and brightness curves for piston core V17-178 from the Laurentian Fan off the Cabot Straits, the mouth of the St. Lawrence River. Carbonate values are from Balsam (1981).

in the late 1960s and brightness was measured in 1997. In the intervening 30 years, these cores have probably shrunk through drying and been disturbed by handling in the repository. This makes precise measurement of sample location impossible. Sampling problems are not a concern for V17-178 because carbonate and brightness were determined on the same sample. For V17-178 most of the brightness trends and peaks, even minor peaks, correlate directly with the carbonate curve (Fig. 4). However, three minor peaks at 90, 160 and 190 cm have the opposite sense. These data clearly show that for stratigraphic purposes, brightness is a reasonable proxy for carbonate in these cores.

Based on the data from the five piston cores described above, we cautiously conclude that in any one core that encompasses only a short span of geologic time, optical lightness is a reasonable proxy

for relative changes in carbonate content. However, for cores that span much longer periods of time, such as ODP drill cores, it is possible that temporal variations in sediment composition could alter the relationship between lightness and carbonate content seen for short, Late Quaternary time spans. To determine if using lightness as a proxy for carbonate holds for sediments representing longer time spans. we analyzed samples from ODP Hole 997A on the crest of the Blake Outer Ridge (31.89°N; 75.47°W). In the top 180 m of this hole, which spans an interval from the present back into the upper Pliocene (Shipboard Scientific Party, 1996), we determined carbonate, L\* and brightness values on identical samples (Fig. 5). The comparisons of lightness to carbonate values, therefore, are direct. As with the previous examples from piston cores (Figs. 1-4),  $L^*$  and brightness show identical patterns and peaks down hole at 997A.

In this hole, the correlation between the two optical lightness measures and carbonate content is less impressive. In about the top 10 m of the hole, the lightness measures and carbonate content exhibit a good peak-to-peak correlation. However, below ~ 10 m, the correlation deteriorates (Fig. 5). While it is possible to correlate specific carbonate peaks to peaks in  $L^*$  and brightness below  $\sim 10$  m, the trends in high and low carbonate generally are not present in the lightness measures. The carbonate low from 35 to 46 m, the carbonate high from 46 to 61 m, and the distinct carbonate low from 61 to 69 m are not recorded by the lightness measures. Although the general decrease in carbonate content below about 100 m is recorded by  $L^*$  and brightness, peaks in these spectral measures do not always coincide with peaks in carbonate content. The lack of correlation between carbonate content and lightness measures in ODP Hole 997A suggests care must be exercised when using lightness as a proxy for carbonate over longer periods of geological time.

# 4. Discussion — factors that affect measures of lightness

The comparisons we make between gray scale, brightness,  $L^*$  and carbonate curves test the ability

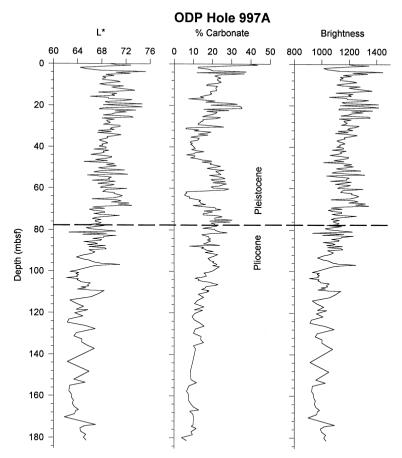


Fig. 5. Carbonate content,  $L^*$  and brightness curves for sediments in cores recovered from the top 180 m of ODP Hole 997A from the Blake Outer Ridge on the continental margin off South Carolina.

of the lightness measures to act as a proxy for down-core changes in carbonate content and particularly the application of optical lightness to stratigraphy. In the five piston cores described above, any of the spectral measures would be a reasonable proxy for carbonate stratigraphy. However, trends and peak to peak correlation are not necessarily indicative of the ability to predict absolute concentrations of carbonate. One indication of the ability of these measures to estimate the actual weight percent carbonate is the number of gray scale, brightness or  $L^*$  units per percent carbonate. From the work of Bond et al. (1992), it is evident that the number of gray scale units per percent carbonate varies by more than a factor of three (Table 2). Similarly, in our data, the number of brightness units per percent carbonate

also exhibits substantial variability, by more than a factor of 4 (11.7 to 49.7; Table 3). Regardless of how sediment lightness is measured, the lack of a

Table 2 Variations in gray level as a function of carbonate content

Core #	Bulk carbonate range (%)	Gray scale range	Gray scale/ % carbonate
DSDP 609	10-85	5-100	1.3
V27-116	5-80	0-240	3.2
V28-82	10-85	10-200	2.9
V29-178	53-91	121 - 171	1.3
V29-179	20-95	95-180	1.1
V30-97	54-89	17 - 148	3.7

Table 3
Variations in brightness as a function of carbonate content

Core #	Bulk carbonate range (%)	Brightness range	Brightness units/ % carbonate
V15-168	3-54	642-1391	14.7
V17-178	9-32	765-1225	20
V25-56	19-70	980-1579	11.7
V29-178	53-91	1621-2631	26.6
V30-97	54-89	759-2498	49.7

consistent relationship in the number of lightness units per percent carbonate from core to core (Tables 2 and 3) indicates that a complex relationship must exist between lightness and carbonate content.

# 4.1. The effect of sediment composition on lightness

For the dry samples we analyzed in this study the primary factor affecting optical lightness is changes in sediment composition. We have previously noted that small amounts of iron oxides and oxyhydroxides (Deaton and Balsam, 1991) or organic matter (Bal-

sam and Wolhart, 1993) may have a major effect on spectra and sediment lightness. These effects are rather obvious for metal oxides and oxyhydroxides which produce highly colored sediment, and for organic material or metal sulfides which color sediments gray and black. In the present study, we conducted a preliminary investigation of three common clay minerals in marine sediments — chlorite, kaolinite and illite — whose effect on sediment lightness and color is less obvious.

To demonstrate how lightness is affected by changing the abundances of these three clay minerals, we analyzed a series of samples in which carbonate content was held constant (80%) while the other minerals in the sample varied. Eighty percent reagent grade CaCO<sub>3</sub> and varying amounts of reagent grade SiO<sub>2</sub> (quartz) were used as a base in which to mix other minerals. CaCO<sub>3</sub> and SiO<sub>2</sub> were used as a base mixture because they and their combinations have similar lightness values (Fig. 6). Natural samples of chlorite, illite and kaolinite in concentrations of 1%, 2%, 10% and 20% by weight were mixed with 0.8 g of carbonate and sufficient silica to pro-

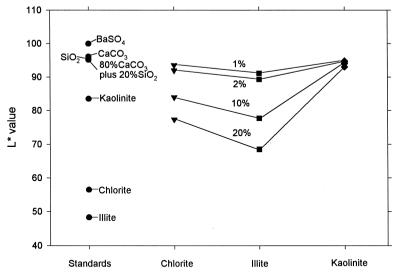


Fig. 6. Variations in  $L^*$  value as a function of mineralogy. The column labeled standard illustrates the  $L^*$  value for the minerals used in the mixture study and for the calibration standard, BaSO<sub>4</sub>. For the columns labeled chlorite, illite and kaolinite all samples contain 80% carbonate. The lines connect samples with the same concentration of one of the three minerals. For the 1%, 2% and 10% concentration, silica was mixed in to bring the weight percent up to 20% of the entire sample; the 20% mineral concentration contained no silica. CaCO<sub>3</sub> and SiO<sub>2</sub> are reagent grade chemicals; chlorite, kaolinite, and illite are natural samples. The chlorite (ripidolite) is Clay Minerals Repository sample CCA-2 from El Dorado County, CA; kaolinite is API #9 (Wards 48E-0290) from Mesa Alta, NM; illite is API #35 (Wards 46E-4100) from Fifthian, IL.

duce a 1 g sample. These samples were then made into slurry slides and analyzed with the Minolta CM-2002. The resulting  $L^*$  values were recorded and plotted for the base material, the natural mineral samples, and the mixtures (Fig. 6).

 $L^*$  values for the reagents and natural samples show a range of values from 48 to 100 (Fig. 6). As expected, the  $L^*$  value for BaSO<sub>4</sub>, which was used to set the 100% level, is 100.  $L^*$  values for CaCO<sub>3</sub>, SiO<sub>2</sub>, and the mixture of 80% CaCO<sub>3</sub> and 20% SiO<sub>2</sub> are all high ( $\sim$ 95). The three natural mineral samples, kaolinite, chlorite, and illite have  $L^*$  values of 83, 56 and 48, respectively. Mixtures with 1% or 2% of these minerals lower the  $L^*$  values, but only slightly. A sample composed of even 20% kaolinite by weight does not significantly lower the  $L^*$  value. However, samples composed of 10% and 20% chlorite or illite had substantially lower  $L^*$  values (e.g., 68 for 20% illite; Fig. 6).

# 4.2. Matrix effects

These relationships clearly illustrate that given a constant percentage of CaCO<sub>3</sub>, L\* values may exhibit substantial reduction by the addition of either illite or chlorite. Darker minerals such as pyrite and dark, refractory organic matter would be expected to have a correspondingly larger effect as would minerals like hematite or goethite, which have an absorption band through much of the VIS (Deaton and Balsam, 1991). These variations in the reflectivity of carbonate with changes in matrix composition may be thought of as the 'matrix effect'. The matrix effect results from a number of factors including spectral masking, internal reflection and refraction, and the density-volume effect. Deaton and Balsam (1991) demonstrated spectral masking of hematite by illite and chlorite. Hematite is easily distinguished at concentrations as low as 0.01% by weight in matrices with 1% illite and no chlorite, but with 32% illite and 16% chlorite added to the matrix, hematite could only be identified at a concentration of 0.03%. Internal reflection and refraction are beyond the scope of this study, but the density-volume effect requires explanation. The reason the density effect is important is that spectrophotometers do not analyze weight percent of a substance, but rather the proportion of surface area covered by substance and a few microns

beneath the surface. Hence, it is probably more accurate to interpret the results of spectral analysis in terms of volume percent. Thus, a sediment component with a very low density takes up a proportionately larger area of the sample surface than a similar weight of a denser material. Low density material, therefore, may have a larger spectral weight simply because of its density. If this particular low density sediment component also has a very large spectral signature, it will dominate the reflectance. The density-volume effect is especially important for organic matter which has a very low density relative to most minerals present in samples. Hence, even a small amount of organic matter by weight occupies a large volume and is capable of significantly darkening a sample (Balsam and Wolhart, 1993). The density-volume effect may also account for the non-linearity reported in use of lightness measures to estimate carbonate content (Herbert et al., 1997).

# 4.3. Lightness and sediment provinces

It is perhaps surprising that lightness is a reasonable proxy for relative changes in carbonate content in our piston cores given that matrix effects and/or changes in sediment composition described above have the potential to alter the relationship between lightness and carbonate. The fact that lightness is a reasonable proxy for relative changes in carbonate content over short periods of geologic time indicates that although the absolute amount of carbonate changes down core, the relative proportions of other light and dark minerals in the non-carbonate fraction remains relatively constant. For example, if kaolinite or some other white substance such as opaline silica increases as carbonate decreases, then the lightness measures would exhibit minimal change with decreasing carbonate content (Fig. 6). Likewise, changes in the composition of dark minerals in the non-carbonate fraction may cause lightness curves to show substantial deviations. An increase in illite relative to chlorite (Fig. 6) or the addition of a small amount of hematite, pyrite or organic matter would cause lightness measures to indicate darker sediment which could be misinterpreted as lower carbonate content, even though the carbonate content has not changed. The fact that in our piston cores lightness measures faithfully track carbonate at a single site

suggests that although carbonate content has changed, the relative proportions of materials in the non-carbonate fraction deposited at these sites has not changed dramatically. Similar lightness values per percent carbonate from cores which are near each other (V15-168 and V25-56 for example) suggests that much of the variation in lightness (Tables 2 and 3) results from local or regional differences in the composition and delivery of the non-carbonate component, that is, the provenance of the sediment.

## 4.4. ODP cores

As noted above, in the cores from ODP Hole 997 lightness is not a good proxy for carbonate. The probable cause for the lack of correlation between lightness and carbonate is temporal changes in non-carbonate mineral composition. If the composition of the non-carbonate sediment component remains constant over time than a reasonable correlation between lightness and carbonate should be possible in ODP holes. Clearly, using lightness as a proxy for carbonate in ODP holes assumes that changes in the composition of the non-carbonate component can be recognized.

Another major concern with respect to measuring lightness on ODP cores is that aboard the JOIDES Resolution cores are measured wet. Darkening of sediment by water is well known, although the exact reasons remain somewhat obscure (Ångstrom, 1925 in Planet, 1970; Twomey et al., 1986; Lekner and Dorf. 1988). Balsam et al. (1998) conducted a detailed study of the effects of water content on reflectance spectra from marine sediments which demonstrated how sample brightness changed as a function of both carbonate content and time as samples dried. To make the data of Balsam et al. (1998) more useful with respect to carbonate content, we have recast these data to illustrate changes in  $L^*$  as a function of water content (Fig. 7) for different carbonate contents. These data clearly indicate that if water content is held constant, L\* increases with increasing carbonate content (Fig. 7). The highest  $L^*$ values (lightest sediment) are for dry powder, followed by sediment that has been wet and then dried. such as cores that are stored dry at repositories. As water saturated sediments (> 35% water by weight) begin to dry, L\* values decrease and reach a minimum (darkest sediment) at a water content of about 22% by weight. Fully saturated sediments with water contents greater than 22% exhibit slightly higher L\*

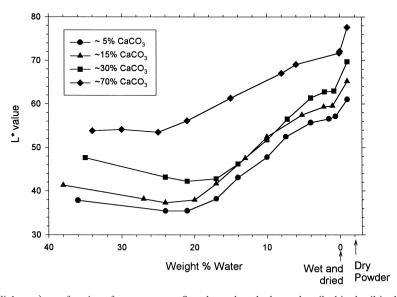


Fig. 7. Changes in  $L^*$  (lightness) as a function of water content. Samples and methods are described in detail in the work of Balsam et al. (1998).

values because the grains are forced apart by the water (Balsam et al., 1998). The curves in Fig. 7 illustrate that water can have a dramatic effect on  $L^*$  values. The difference in  $L^*$  values between a dry sample and the same sample with 20% water by weight is greater than the difference between dry samples containing 70% and 5% carbonate. When water content decreases to less than 5%, its effect on sediment lightness levels off. Clearly, caution must be exercised when applying lightness proxies to wet sediments or core photographs that were taken while the cores are still wet.

### 5. Conclusions

- (1) Measures of optical lightness (gray scale, brightness and  $L^*$ ) are reasonable proxies for relative changes in carbonate content over short spans of geologic time; the five piston cores we examined go back no further than isotope stage 6 ( $\sim$  130 ka).
- (2) For longer spans of geologic time, such as the top 180 m of ODP Hole 997A, which spans from the present back into the late Pliocene, the relationship between lightness values and carbonate content is not well defined. Therefore, the use of lightness measures as proxies for carbonate content for longer periods of geologic time should proceed with caution.
- (3) Lightness measures are strongly affected by the composition of the non-carbonate fraction. If the non-carbonate fraction is dominated by light materials, such as kaolinite, lightness would show little change as carbonate content decreased. On the other hand, the addition of dark material such as illite could substantially decrease sediment lightness. When considering how the non-carbonate fraction affects lightness measures the density–volume effect must also be considered.

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