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# Paleoceanographic significance of sediment color on western North Atlantic drifts: I. Origin of color

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### Abstract

Reflectance spectra collected during ODP Leg 172 were used in concert with solid phase iron chemistry, carbonate content, and organic carbon content measurements to evaluate the agents responsible for setting the color in sediments. Factor analysis has proved a valuable and rapid technique to detect the local and regional primary factors that influence sediment color. On the western North Atlantic drifts, sediment color is the result of primary mineralogy as well as diagenetic changes. Sediment lightness is controlled by the carbonate content while the hue is primarily due to the presence of hematite and  $Fe^{2+}/Fe^{3+}$  changes in clay minerals. Hematite, most likely derived from the Permo-Carboniferous red beds of the Canadian Maritimes, is differentially preserved at various sites due to differences in reductive diagenesis and dilution by other sedimentary components. Various intensities for diagenesis result from changes in organic carbon content, sedimentation rates, and H<sub>2</sub>S production via anaerobic methane oxidation. Iron monosulfides occur extensively at all high sedimentation sites especially in glacial periods suggesting increased high terrigenous flux and/or increased reactive iron flux in glacials. © 2002 Elsevier Science B.V. All rights reserved.

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# 1. Introduction

Color, which is a readily observable physical property of rocks or sediments, has long been considered of diagnostic and correlative value in geology. It has been acknowledged that the sediment chromatic characteristics are generally given by its iron-rich minerals: oxyhydroxides, sulfides, iron-rich clay minerals (e.g., Potter et al., 1980). Carbonate and opal increase the sediment brightness while organic matter decreases it (e.g., Balsam and Deaton, 1991, 1996; Mix et al., 1995). Other mineralogical constituents may also exert secondary or local influence on color reflectance (e.g., Mix et al., 1995; Balsam and Deaton, 1996). In fresh sediments, color is an ephemeral characteristic, changing rapidly after exposure to oxidizing conditions, and due to drying after recovery.

For geological studies, the Munsell Color system has been traditionally used to describe sedi-

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ment color. The system is a qualitative ordinal color scale dependent on visual comparison of the sample to color chips (Goddard et al., 1948). The color chips describe a three-dimensional space of hue, value, and chroma. The hue characterizes the property of being yellow, red, green, blue, purple, or any binary mixture thereof. The value describes the color lightness relative to a gray scale ranging from white to black, while the chroma corresponds to the degree of difference between a color and a gray of the same value or lightness. Data recorded in this system cannot be easily manipulated mathematically and vary in quality as observers and observational conditions change. Also color differences are too subtle and abundant for detailed work to be accomplished only by visual inspection.

Alternative quantitative approaches to the Munsell system that have been used to describe the sediment color include CIE La\*b\* chromaticity space (e.g., Nagao and Nakashima, 1992; Saito, 1995; Weber, 1998) and CIE x-y-Y color space (e.g., Merrill and Beck, 1996), which are both reductions of the reflectance spectra taken in the visible wavelength domain. The CIE  $La^*b^*$ , used frequently in ODP color estimation, is a three-dimensional color space which approximates a cylinder (Billmeyer and Saltzman, 1981). Its vertical axis L (lightness) is similar to the Munsell value, while  $a^*$  and  $b^*$  are the Cartesian coordinates that define a quasi-circular hue-chroma space (i.e., a normal section of the cylinder) at any given L. If one uses polar coordinates for the  $La^*b^*$  space, the hue (H) is more naturally defined as an angle measured counterclockwise from east, while chroma (C) is the length of the radius within a section of the cylinder. In this presentation, an angle of 45° corresponds roughly to a red hue, 90° to yellow, 180° to green, and 240° corresponds to blue. Chroma increases to the exterior of the cylindrical color space. Simple transforms are used to convert  $La^*b^*$  coordinates to LCH coordinates:

$$C = ((a^*)^2 + (b^*)^2)^{1/2}$$
  
H = tan<sup>-1</sup> (b<sup>\*</sup>/a<sup>\*</sup>) (degrees),0°≤H≤360°

Other geological applications utilized directly

the reflectance spectrum data in the visible range (sometimes extended to near-ultraviolet and nearinfrared; e.g., Balsam and Deaton, 1991; Mix et al., 1995; Harris et al., 1997; Ortiz et al., 1999). By using the spectral signatures of iron oxides, calcium carbonate, opal, clay minerals, organic matter, and other sedimentary components, it is possible in some cases to empirically quantify their presence in sediments (e.g., Balsam and Deaton, 1991; Mix et al., 1995). Factor analysis and multiple regression have been employed in deconvolving the sediment reflectance spectra. The possibility of rapid estimation of sediment composition at a high resolution is the main advantage of using sediment reflectance spectra in paleoceanographic studies. However rigorous quantitative calibrations are difficult to obtain since the spectral characteristics of individual components are subjected to a matrix effect (Balsam and Deaton, 1991). Also the original color of the sediments at the time of deposition is likely to differ from their color after the early diagenesis or the final color of the lithified rock.

In this paper, we present results from a study that investigated the origin of color in sediments drilled on two sediment drifts in the western North Atlantic: Blake-Bahama Outer Ridge and Northeast Bermuda Rise (Fig. 1; referred to as BBOR and BR in following discussion). Knowledge of processes responsible for setting the color in sediments is necessary in order to evaluate color as a potential paleoceanographic proxy (see the companion paper of Giosan et al., 2002). Sediments recovered during Leg 172 in the western North Atlantic had a variegated colorful character. Similar to other sites in the Atlantic basin (e.g., Schneider et al., 1995), a strong correlation between luminance (L) and carbonate content has been observed for the entire column of Pliocene to recent sediments. The presence of hematite (and possibly other iron hydroxides) imparted a reddish hue to sediments occurring mostly in glacial-deglacial intervals especially at deeper sites on BBOR and BR. They are the so-called 'brick red lutites' (Fig. 1), which are considered to be characteristic tracers of northern sediment sources (Hollister and Heezen, 1972; Piper et al., 1994). Thought to originate in the Canadian Maritime



Fig. 1. Location map for sites drilled during the ODP Leg 172 cruise with the generalized surface and deep water circulation scheme for the western North Atlantic (after Schmitz and McCartney, 1993) and the distribution of red lutites in the latest Pleistocene in the western North Atlantic. Circulation: WBUC – Western Boundary Undercurrent; AABW – Antarctic Bottom Water; GSRF – Gulf Stream Return Flow. Large circles indicate sites at which red lutites comprise more than 50% of the latest Pleistocene sediments and small circles for less than 5% (after Hollister and Heezen, 1972). Occurrences of red beds of Permo-Carboniferous age (depicted by R) and other ages (depicted by +) in the eastern Canada and US (after Dott and Batten, 1988) are indicated. The limit of the Laurentide Ice Sheet for the last glacial maximum and the main conduits to the deep western North Atlantic are shown (LC – Laurentian Channel; HC – Hudson Canyon; WCS – Wilmington Canyon System; and HCS – Hatteras Canyon System).

Provinces, which have extensive Permo-Carboniferous red beds exposed (Fig. 1), the red lutites were one of the first direct pieces of evidence for the existence of a deep western boundary current along the eastern continental margin of North America (Needham et al., 1969). Other sediments exhibited a greenish hue suggesting that iron is present in a reduced state in clay minerals (e.g., König et al., 1999). Also related to reduction, bluish-black metastable iron monosulfides occurred at Leg 172 deep sites (Keigwin et al., 1998). Therefore in order to understand the color variations at Leg 172 sites and interpret them as paleoceanographic changes, we need to know both the role of the primary detrital and pelagic sediment delivery on sediment color as well as the role of diagenesis in promoting secondary changes in sediment color.

#### 2. Methods

# 2.1. Color data acquisition and statistical treatment

Sediment reflectance spectra over the visible domain (400–700 nm) were measured on wet sediments immediately after the cores were split aboard JOIDES Resolution using a Minolta CM-2002 hand-held spectrometer (Keigwin et al., 1998). Technical characteristics of the Minolta spectrophotometer and the methods for acquiring the reflectance spectra are those presented by Balsam et al. (1997). Measurements were taken at intervals varying from 2 to 5 cm (Keigwin et al., 1998). Data from Site 1055 through Site 1063 are used in this study because they have been least affected by downslope mass transport phenomena and they have more detailed age models (Grützner et al., 2002).

Identifying the main chromatic characteristics of a substance requires the recognition of dominant, persistent absorption features within its reflectance spectra (see Clark, 1999 for a review). Absorption bands in minerals resulting from various processes overlap greatly in the visible range (Hunt, 1977); therefore one has to rely on subtle changes in the spectrum to identify them in reflec-

tance spectra. Because the raw reflectance spectra of deep-sea sediments are smooth and featureless they are usually pre-treated to increase their variance (Balsam and Deaton, 1996). Pre-treatments include computing the first or second derivative or applying various functions (logarithm, polynomials, etc.) to the raw spectra. We chose to use the first derivative of the spectra because several characteristic peaks have been successfully detected previously for various mineralogical components (e.g., Balsam and Deaton, 1991). Of special interest in this study are the reddish crystalline iron oxides hematite and goethite. Hematite is characterized by its unique peak in the first derivative situated between 555 and 575 nm, the exact position of the peak varying with the hematite content (Barranco et al., 1989; Deaton and Balsam, 1991). Goethite has a principal peak at 535 nm and a secondary one at 435 nm (Deaton and Balsam, 1991). First derivatives of the spectral data from each site (computed as a first-difference derivative between each two successive reflectance values and plotted at the midpoint of the 10-nm interval between the two values; Balsam et al., 1997) have been studied through factor analysis to identify the main chromophores (i.e., minerals responsible for setting the color in sediments). Factor analysis (Jöreskog et al., 1976) identifies the least number of patterns that explain the variance in a large number of variables (in our case the first derivative at 30 wavelengths from 405 to 695 nm) over a large population of samples (in our case the Minolta color measurements at a given site). The method of principal components was used and rotation was done with a VARIMAX procedure using the SPSS 7.5 software package. Color data from the oxic-suboxic zone, operationally defined here as the bright reddish-tan zone (Lyle, 1983; König et al., 1999) at the top of the first core at each site (less than 1.5 m in thickness), were eliminated from the factor analysis. Preliminary investigation showed that their reflectance spectra differ radically from the spectra taken below the zone.

# 2.2. Wet chemistry analytical techniques

A set of 25 samples collected at sites 1062 and

1063 were used to evaluate the relationships between the chemistry of iron solid phases and sediment color. The chemical measurements for this set, referred to as the color end-member sample set, are reported in Table 1. Reflectance spectra were taken, as previously described, at the time the cores were collected as well as onshore after the samples were oven-dried. The onshore color measurements were necessary to estimate the effect of drying and oxidation on the samples. The color of the dried samples was measured at UT Arlington by Bill Balsam using a Perkin-Elmer Lambda 6 spectrophotometer (see Balsam et al., 1998, for methodology and an assessment of differences between Minolta and Perkin-Elmer spectrophotometers).

After collection, the samples were immediately frozen in a nitrogen atmosphere in plastic bags.

Selective dissolution schemes were used to estimate several sediment iron pools with different degrees of reducibility during diagenesis. We chose to estimate (1) a hydroxylamine-leached iron pool (FeH) consisting mostly of pore water Fe, iron monosulfides, and amorphous oxyhydroxides following the procedure of Canfield (1988); (2) a dithionite-leached iron pool (FeD) composed mainly of crystalline oxides beside the easily reducible iron pool extracted by hydroxylamine (following the procedure of Lord, 1980); and (3) total iron content (FeT; following the procedure of Aller, 1980). Additionally, we measured iron oxidation state within the easily reducible iron pool (i.e., similar to the pool extracted by hydroxylamine; following the procedure of Aller and Blair, 1996) on eight trimmed un-oxidized samples. Preservation of the initial color ascertained

Table 1 Fe-C-S chemistry and carbonate content of the color end-member sample set

Sample I.D.	L	С	Н	F1	F2	F3	Carb.	OC	S	FeH	FeD	Fe <sup>2+</sup>	Fehr	FeT
ł			(°)				(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
1062 E 5 H 6–87	42.06	4.3	156	-0.16	-0.75	-1.66	24.2	0.40	0.30	0.17	0.28	n/a	n/a	4.52
1062 E 5 H 6–84	51.13	4.3	122	1.04	-1.10	-1.40	31.8	0.00	0.21	0.15	0.34	n/a	n/a	3.75
1063 A 16 H 6-115	43.59	3.4	109	-0.15	0.54	-1.81	35.1	0.31	0.00	0.22	0.30	n/a	n/a	2.72
1062 E 3 H 5-10	47.73	4.8	109	0.49	-1.18	-0.86	27.2	0.00	0.45	0.24	0.56	0.33	0.06	4.55
1062 E 3 H 3-70	43.58	4.8	102	0.00	-0.81	-0.86	17.0	0.45	0.05	0.23	0.56	0.13	0.04	4.03
1062 E 4 H 4–80	48.45	4.2	98	0.10	-0.18	-1.21	29.0	0.18	0.03	0.21	0.35	n/a	n/a	3.57
1063 A 4 H 2–70	43.61	4.4	83	-0.80	0.50	-1.11	7.9	0.13	0.18	0.26	0.40	n/a	n/a	4.23
1062 E 5 H 6–64	55.48	8.9	78	1.17	-1.86	0.92	46.7	0.04	0.00	0.14	0.31	0.04	0.01	2.71
1063 A 4 H 2–140	51.48	7.6	75	0.24	-0.50	0.05	32.6	0.16	0.01	0.16	0.38	n/a	n/a	3.06
1062 D 1 H 1–110	44.48	8.5	74	0.00	0.12	-0.42	19.7	0.37	0.08	0.28	0.64	0.26	0.03	4.28
1062 E 3 H 2-142	50.59	11.8	73	0.97	-1.21	1.02	36.9	0.00	0.07	0.14	0.49	0.19	0.04	3.53
1062 E 5 H 6–94	44.52	7.4	72	-0.55	-0.11	-0.19	22.1	0.34	0.01	0.21	0.39	n/a	n/a	3.55
1063 A 1 H 3-60	40.09	10.5	71	-0.32	-0.06	-0.03	10.5	0.68	0.21	0.25	0.67	n/a	n/a	4.01
1063 A 1 H 1–90	50.50	13.8	70	1.39	-0.27	0.79	33.5	0.33	0.03	0.15	0.56	n/a	n/a	3.15
1062 E 4 H 1–80	42.13	7.9	70	-0.74	0.25	-0.35	10.1	0.29	0.04	0.35	0.58	n/a	n/a	4.95
1063 A 1 H 1–80	52.20	16.7	67	2.00	1.30	0.50	33.4	0.34	0.05	0.23	0.72	0.19	0.01	3.3
1063 A 1 H 1–50	47.95	16.0	66	0.73	-0.12	1.24	31.0	0.26	0.04	0.13	0.67	0.23	0.03	3.5
1062 D 1 H 1–25	50.62	19.2	64	1.76	3.22	-0.20	36.5	0.23	0.04	0.30	0.71	n/a	n/a	3.29
1063 A 1 H 1–64	45.11	18.2	62	0.03	0.80	1.18	19.3	0.11	0.05	0.29	1.12	0.38	0.004	4.11
1063 A 1 H 3-80	41.54	13.9	62	-0.92	0.15	0.87	10.5	0.42	0.16	0.24	0.76	n/a	n/a	4.09
1063 A 4 H 5–58	41.55	14.9	61	-0.91	0.12	1.05	20.4	0.17	0.02	0.17	0.62	n/a	n/a	3.48
1062 E 8 H 4–114	42.32	12.5	60	-1.16	0.01	0.92	8.3	0.17	0.01	0.33	0.70	n/a	n/a	4.96
1063 A 4 H 2–34	45.92	11.7	60	-1.08	0.00	1.02	14.1	0.06	0.02	0.21	0.68	n/a	n/a	4.65
1062 D 3 H 3–117	42.11	6.2	60	-1.64	1.21	-0.71	36.3	0.37	0.06	0.13	0.40	n/a	n/a	3.3
1063 A 13 H 6-80	42.98	12.7	58	-1.49	-0.06	1.23	13.1	0.13	0.02	0.85	1.07	n/a	n/a	4.92

Sample I.D. – (Site Hole Core Type Section)–(position in cm); F1, F2, F3 – factors 1, 2, and 3 respectively, Carb. – carbonate content. Predicted carbonate content for all studied sites along with the Fe–C–S chemistry and carbonate content of the 200–400-ka sample set at sites 1057, 1061, 1062, and 1063 are not presented in the text and they will be archived at NOAA Paleoclimatology WDC-A archive (http://www.ngdc.noaa.gov/paleo/data.html).

that the center of each of these eight samples was not affected by oxidation during collection, storage, and/or subsampling. The  $Fe^{2+}$  ( $Fe^{2+}_{HR}$ hereafter) as well as the FeT content of the highly reactive iron pool (Fe<sub>HR</sub>) were measured from leachate by ferrozine colorimetry (Stookey, 1970). Carbonate content (Giosan et al., 2001), total organic carbon and sulfur content were also measured for all 25 samples in the set as well as for an additional 83 samples collected post-cruise from the interval between 200 and 400 ka at sites 1057, 1061, 1062, and 1063. Total carbon and sulfur content were measured using a Carlo Erba 1106 CHNS analyzer while the carbonate content was determined by coulometry. Organic carbon was taken as the difference between the total carbon and the inorganic carbon representing the carbonate content. The degree of pyritization (DOP; Berner, 1970), the ratio of iron already reduced to pyrite to the total reactive iron that existed initially in the sediment, was calculated for 20 samples from the set collected postcruise. The samples were chosen to be representative for the color range of all sediments in each site for the time interval analyzed. The reactive iron present initially in sediment was calculated as the sum of iron in pyrite and the FeD which was taken to represent the reactive iron still remaining in sediment (Raiswell et al., 1994). The pyrite content was computed stoichiometrically from the total sulfur content, which was assumed to come entirely from pyrite.

# 3. Results

Iron pools measured by wet leaching indicate that the bimodality in sediment color measured by hue (i.e., red vs. green) is the result of the iron mineralogy and chemistry (Fig. 2; Table 1). The reddish hue is given to the sediments by reddish crystalline iron oxides, i.e., goethite and hematite. The iron content in these crystalline oxides can be quantified as the difference between the FeD and the FeH pool. Magnetite, the other common oxide in deep-sea sediments, in contrast, has a black color and it is not leached substantially by the dithionite method used here (Can-



Fig. 2. Relationships between iron chemistry and sediment hue (reddish sediments are represented by circles; grayish sediments by diamonds; and greenish sediments by squares): (A) hue changes from red to green as the reductive stress in sediment (i.e.,  $Fe_{HR}^{2+}/Fe_{HR}$  in the highly reactive iron pool) increases; (B) higher content of red oxides (i.e., expressed as Fe in oxides) corresponds to reddish hues in sediments.

field, 1988). Examination of the first derivatives of the reflectance indicates that hematite, rather than goethite, is the dominant oxide. However, in the upper brown-tan layer of sediments at each site, which generally ranges from 1 to 3 m in thickness, goethite has been identified as well. At Site 1062 on Bahama Outer Ridge traces of goethite occur even deeper. A near-surface change in sediment color from brown-tan to gravishgreen is related to the base of the oxic-suboxic diagenetic zone (i.e., where nitrate is totally exhausted; Lyle, 1983; König et al., 1999). The presence of this oxic-suboxic zone, situated above a peak in solid-phase Mn and, in most cases, extending only in Holocene sediments, has been previously described in BBOR piston cores by Schwartz et al. (1997). High dithionite-, oxalate-, and hydroxylamine-reduced iron pools, as well as rock magnetic data indicate that the near surface brown color is not due to hematite (hematite content actually decreases in Holocene sediments) but to some other iron oxyhydroxide, most likely goethite (Schwartz et al., 1997). A peak in FeD indicates that goethite might be actively precipitating in situ at the  $Fe^{2+}/Fe^{3+}$  redox boundary

(Schwartz et al., 1997). However, other oxyhydroxides such as ferrihydrite, lepidocrocite, and/or amorphous forms are likely to be present as well. The average reflectance of the sediments in the oxic-suboxic zone is up to 25% higher than anywhere below it, although one would predict that increased organic matter and water content in this zone would darken the sediments (Balsam and Deaton, 1991; Balsam et al., 1998). However it is known that the presence of amorphous oxyhydroxides (e.g., Dematte and Garcia, 1999) or a decrease in size of the oxide grains (e.g., Haese et al., 1998) can be responsible for an increase in reflectance. We attribute the increase in reflectance to one or both of these mechanisms.

As the sediments become progressively reduced, as indicated by the  $Fe_{HR}^{2+}/Fe_{HR}$  ratio in the highly reactive iron pool (Fig. 2), the sediments tend to get progressively greener. This is most likely due to a change in the  $Fe^{2+}/Fe^{3+}$  ratio in the lattice of iron-rich clay minerals (König et al., 1999; König et al., 2000). In the yellowish sediments (Fig. 2) there is incomplete oxide reduction (i.e., the hematite peak is still relatively prominent). Reduction phenomena in the clay mineral lattice and possibly the formation of black iron sulfides (assumed to be present in sediments from an increase in sulfur content in gray sediments; Table 1) promote darkening of the sediments, which become gray. These gray sediments are found mostly in the first 10-20 m below the oxic-suboxic layer at most Leg 172 sites suggesting again that they are an expression of partial reductive diagenesis.

Factor analysis of the first derivative of the reflectance spectra collected at each site has produced three principal factors. The loadings of these three factors were essentially identical for all studied sites (Fig. 3) except for Site 1055 where only factors 1 and 3 are evident. The factor analysis revealed that the first derivative values at all sites had high communalities (>0.7 for all wavelengths and >0.9 for most wavelengths) over the entire visible range indicating that the factors capture well the spectral variance in these bands. The cumulative variance explained by these three factors at each site (except at Site 1055) accounted for more than 90% with each factor accounting



Fig. 3. Loadings of the three most important factors extracted for the first derivative of the sediment reflectance spectra at Leg 172 sites. Factor 1 is due to carbonate, Factor 2 to hematite, while Factor 3 has been tentatively ascribed to the ratio of  $Fe^{2+}$  to  $Fe^{3+}$  in iron-rich clay minerals.

for 25–35%. At Site 1055 over 60% of variance was explained by factors 1 and3. The three factors have been interpreted by (1) assessing the correlation between the factor scores to directly estimated sedimentary components; (2) by comparing their loadings in the visible range to first derivative curves of sediments of known composition (Balsam and Deaton, 1991); or (3) by comparing directly to reflectance spectra of minerals (Hunt, 1977; King and Clark, 1989; Kostka et al., 1999).

Comparisons of factor scores with direct measurements indicate a nearly linear correlation between carbonate and Factor 1 (Fig. 4A,E), which has the largest loadings in the blue band (i.e., the lower third of the visible spectrum). However, the correlation coefficient is low  $(r^2 = 0.6)$  because other components have high reflectance in the same region of the visible domain (the matrix effect; Balsam and Deaton, 1991; Harris et al., 1997; Balsam et al., 1998, 1999; Giosan et al., 2001). Better estimates of carbonate content  $(r^2 > 0.9)$  come from the multiple linear regression of reflectance spectra (Giosan et al., 2001), a technique able to reduce the effect of the matrix by using all the available data in the visible domain (see Giosan et al., 2002).

The loadings of Factor 2 (Fig. 3) are very sim-



Fig. 4. Relationships between sediment color factors and sediment mineralogy and chemistry: (A) Factor 1 vs. carbonate content (see Table 1); (B) Factor 2 vs. Fe content in oxides (see Table 1); (C) Factor 3 vs.  $Fe_{HR}^{2+}/Fe_{HR}$  in the highly reactive iron pool (see Table 1); (D) Factor 2 vs.  $Fe_{HR}^{2+}/Fe_{HR}$  in the highly reactive iron pool (see Table 1); (E) Factor 1 vs. carbonate content in the 200–400-ka sample set from sites 1057, 1061, 1062, 1063; (F) Factor 3 vs. organic carbon content in the 200–400-ka sample set from sites 1057, 1061, 1062, 1063; (F) Factor 3 vs. organic carbon content in the 200–400-ka sample set from sites 1057, 1061, 1062, 1063; (F) Factor 3 vs. organic carbon content in the 200–400-ka sample set from sites 1057, 1061, 1062, 1063; (F) Factor 3 vs. organic carbon content in the 200–400-ka sample set from sites 1057, 1061, 1062, 1063; (F) Factor 3 vs. organic carbon content in the 200–400-ka sample set from sites 1057, 1061, 1062, 1063; (F) Factor 3 vs. organic carbon content in the 200–400-ka sample set from sites 1057, 1061, 1062, 1063; (F) Factor 3 vs. organic carbon content in the 200–400-ka sample set from sites 1057, 1061, 1062, 1063; (F) Factor 3 vs. organic carbon content in the 200–400-ka sample set from sites 1057, 1061, 1062, 1063.

ilar to the pattern exhibited by the first derivative of hematite spectra. This relationship is also emphasized by the direct correlation between the 'crystalline oxide' content in the color end-members sample set and Factor 2 scores (Fig. 4B). Goethite when present can contribute to the same crystalline oxide pool and in some cases other iron minerals could contribute small amounts of iron to this fraction (Canfield, 1989; Giosan et al., in preparation). We noted that within the color end-member set, the hematite peak is smaller in samples measured wet when compared to the same samples when reflectance was measured after drying. The same phenomenon was observed for the all wavelengths and it is attributed to the presence of water which tends to darken the sediments (Balsam et al., 1998), hence a quantitative estimate of hematite content from wet sediment reflectance spectra is more difficult. However, a rough estimate of its range of variation can be made by taking into account that water decreases the hematite peak by about 1/3 from the dry peak value. Published curves for the first derivative of spectral reflectance in various matrices (Barranco et al., 1989; Deaton and Balsam, 1991) allow us to estimate by comparison that the hematite content is generally less than 0.5% in the studied sediments. This value agrees with estimates of Barranco et al. (1989) for the period since the last glacial maximum for the red lutites in most of the western North Atlantic (except for the St. Lawrence Trough and Fan and their immediately adjacent areas where hematite content can be higher).

Factor 3 has proven to be the most elusive: it has the highest loadings in the red band (600– 700 nm; Fig. 3) similar to refractory organic matter (Balsam and Deaton, 1991), but factors with similar loadings have been previously interpreted as reflecting the carbonate content (e.g., Balsam et al., 1998) or terrigenous content (e.g., Harris and Mix, 1999). This apparent contradictory interpretation is possible due to a competition for the same wavelength range in different sediment matrices (i.e., variation in mineralogical composition within deep-sea sediments). In our case, Factor 3 probably represents the content in green clay minerals with a high  $Fe^{2+}/Fe^{3+}$  ratio in their struc-

tural iron. Minima in Factor 3 are indicative of green sediments which display absorbance in the red band of the reflectance spectrum (i.e., negative values of the first derivative in the red band). An absorbance band extended in the red band and centered in the near-infrared at about 750 nm, where a locus for a  $Fe^{3+}-Fe^{2+}$  charge transfer occurs, is typical for many green minerals (e.g., Hunt, 1977). Some common deep-sea clay minerals are affected by this phenomenon (e.g., Karrickhoff and Bailey, 1973; Anderson and Stucki, 1979; King and Clark, 1989; Kostka et al., 1999). We have observed that this absorbance band disappeared in the reflectance spectra taken on oxidized (i.e., oven or open air dried) samples, which become yellowish. Moreover, the absorbance band was also attenuated in the spectra of samples stored in a damp but oxidative environment (i.e., samples whose reflectance was measured 2 months post-cruise at the core repository). Significant oxidation of iron in the silicate fraction was also detected within 6 months of core storage by König et al. (2000). Therefore, it is likely that Factor 3 corresponds to the  $Fe^{2+}/Fe^{3+}$  ratio in the clay minerals structure. Although it is believed that structural iron in clay minerals does not leach easily (e.g., Canfield, 1989), the direct covariation between Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio in clay minerals and the  $Fe_{HR}^{2+}/Fe_{HR}$  ratio in the easily reducible iron pool is indicative of increased reduction in sediments (Fig. 4C). Factor 3 might also be affected by other components in sediments that increase or decrease reflectance in the red band such as refractory organic matter (Fig. 4F; Balsam and Deaton, 1991) or water content (Balsam et al., 1998). Also, Factor 3 is a secondary factor in the sense that it becomes dominant only when iron oxyhydroxide content decreases to zero. The deconvolution of the effects of these individual components on the absorption in the red and near-infrared bands deserves further study.

#### 4. Discussion

The variegated, colorful appearance of the Neogene sediments in the western North Atlantic is due to the presence of hematite, which imparts a reddish color in otherwise yellow-green sediments. Permo-Carboniferous red beds of the Canadian Maritime Provinces are one of the possible source areas for this hematite. Outcrops of red beds occur in New Brunswick, Nova Scotia, and Prince Edward Island (Fig. 1; see Piper et al., 1990 and references therein). The Permo-Carboniferous also extends below the Gulf of St. Lawrence (Sanford and Grant, 1990). Sediments of the last glacial recovered from the Laurentian Channel and the Laurentian Fan contain abundant hematite-rich red detritus (e.g., see Stea et al., 1998 for a review of the region). Hollister and Heezen (1972) and Barranco et al. (1989) have shown that red lutites are ubiquitous in the last glacial maximum sediments along the North American margin from south of Newfoundland down into the Caribbean and extending directly south of the Laurentian Fan onto the Sohm Abyssal Plain (Fig. 1; see also Vilks et al., 1985). The distribution of red lutites was interpreted to result from the transport of sediment from the Gulf of St. Lawrence area to the southwest by bottom currents and to the south by turbidity currents. Indeed, the dispersal of red sediment to the southwest along the American continental margin was taken as evidence for the southward-flowing Western Boundary Undercurrent in the western North Atlantic (Heezen et al., 1966; Needham et al., 1969). Several mechanisms have been proposed to deliver the red sediment to the deep sea: ice-rafted detritus, turbidity currents, surface glacial plumes and/or nepheloid layers (see Barranco et al., 1989; Piper et al., 1994; Piper and Skene, 1998; Keigwin and Jones, 1995). Red sediments previously delivered to the deep basin can also be reintroduced to bottom currents through resuspension by benthic storms (Hollister and McCave, 1984; McCave and Tucholke, 1986). Once in the deep ocean water, either from direct delivery or by resuspension by benthic storms, red sediments will be redistributed along with other material by bottom circulation. Deposition of Wisconsinan red lutites in the Gulf of St. Lawrence region has been correlated with the history of ice sheet areal variation in the Maritime Canada (Stea et al., 1998) demonstrating that the primary input of red sediment is related to glacial action and lowered sea level. Red lutites have been described on the J-Anomaly Ridge (Fig. 1) in glacial sediments as old as Stage 12 (Piper et al., 1994) and possibly older (i.e., about 1 Myr old; Hall, 1990; Piper et al., 1994) suggesting that the Gulf of St. Lawrence has been a source of red sediments through the Pleistocene at least. Deep Sea Drilling Program Leg 11 recovered red lutites in Pleistocene sediments but the coring was not continuous to estimate their distribution in time (Hollister et al., 1972). ODP Leg 164 drilled on the Blake Outer Ridge at water depths as deep as 2800 m and red lutites were found sporadically in the Pleistocene sediments (Paull et al., 1996). If hematite in sediments recovered during Leg 172 originated in the Canadian Maritimes, the range for the occurrence of red lutites in the western North Atlantic would be extended at least to the Pliocene-Pleistocene boundary (~1.8 Ma; Keigwin et al., 1998) or possibly even to late Pliocene ( $\sim 2.5$  Ma; see Giosan et al., 2002).

Red detritus should have been preserved near a continental hematite source on the North American shelf just as it is preserved on the St. Lawrence shelf. In addition, turbidites originating from such a source must be hematite-rich just as on the Laurentian Fan. Hematite has been described in Hudson Strait originating from a Proterozoic bedrock unit in northern Hudson Bay (Kerwin, 1996) but no significant hematite-rich sediments in Pliocene to Recent sediments have been detected upcurrent of the St. Lawrence shelf in the Labrador Sea (e.g., Josenhans et al., 1986; Srivastava et al., 1987). Also, although red beds of various ages are common in the Appalachians (Fig. 1), no red sediments have been recovered from the shelf or slope along the U.S. margin south of Maine (see Poag, 1978 for a review on the drill sites in the region). Indeed, south of 40°N parallel, red lutites in the latest Pleistocene-Holocene sediments are confined primarily below the 4000 isobath (Barranco et al., 1989). The Gulf of Maine is the only shelf region where red sediment was observed; red sediments there ultimately originate also in the Permo-Carboniferous red beds in the Bay of Fundy and environs (Bacchus, 1993). No red turbidites have been described at the

mouths of the main canyon systems south of Maine (Fig. 1; e.g., Hollister et al., 1972; Cleary and Conolly, 1974; Cleary et al., 1977; Ayers and Cleary, 1980), although some of the hemipelagic sediments sandwiched between turbidites are red (Hollister et al., 1972; Cleary et al., 1977). This would suggest that the source of the hematite is upcurrent, not upslope. Moreover, Upper Carboniferous spores that characterize these red beds appear to increase significantly in hematiterich sediments of late Pliocene-early Pleistocene that were studied at sites 1063 and 1062 (Giosan et al., 2002). All these facts show that we can take as a starting point that red sediments on BBOR and BR originate in the Gulf of St. Lawrence region.

For the last 800 kyr, there is a broadly similar downhole hematite pattern at all deep sites on both BBOR and BR (Fig. 5; for the depth to age conversion we used the age model of Grützner et al., 2002) but important differences occur at shallower sites 1055, 1056, 1057, and 1058. During Leg 172 it was noticed that hematite from red lutites can be reduced locally around burrows (Keigwin et al., 1998). To test if differential preservation might be one factor responsible for the variability in downhole hematite patterns between sites, we studied the C-S-Fe chemistry of the sediments. Iron oxyhydroxides (including hematite) are reduced by dissimilatory Fe reduction during suboxic diagenesis (reaction 1; e.g., Lovley, 1991) as well as by sulfide during anoxic sulfidogenic diagenesis (reaction 2; e.g., Berner, 1970).

$$8FeOOH + CH_3COO^- \rightarrow 8Fe^{2+} + 2HCO_3^- +$$
$$15OH^- + 5H_2O \tag{1}$$

$$2\text{FeOOH} + 3\text{HS}^{-} \rightarrow \text{FeS} + \text{FeS}_{2} + \text{H}_{2}\text{O} + 3\text{OH}^{-}$$
(2)

While the hematite reduction during dissimilatory reaction should be negligible due to preferential consumption of other, more reactive, iron oxyhydroxides (Roden and Zachara, 1996) which are abundant in the oxic-suboxic zone (Schwartz et al., 1997), experimental results suggest that hematite has only a 30-day half-life in the presence of sulfide (Canfield et al., 1992). However, the exact reactivity of hematite will depend on factors such as surface area, crystallinity, and minor element composition.

In slowly accumulating deep-sea sediments (i.e., sedimentation rates on the order of 0.01 m/kyr and organic carbon content around 0.1%), the availability of sulfide from sulfate reduction is seldom high enough to pyritize completely the iron oxyhydroxides (Canfield et al., 1992), but the high sedimentation rates on a sedimentary drift would theoretically increase the rates of sulfate reduction by shortening the residence time of the organic carbon in the oxic-suboxic zone and therefore increasing the flux of organic matter to the sulfate reduction zone (e.g., Stein, 1990). However, when compared to other oceanic environments, the organic matter is relatively low at the BBOR and BR sites (ranging from 0.0 to 0.62%; Cagatay et al., 2001). At sedimentation rates typical for these sites during glacials (i.e., between 0.14 and 0.40 m/ kyr) we would typically expect significantly higher organic carbon contents (i.e., 0.7-1.2%; Stein, 1990). This low organic carbon content could be attributed to dilution by carbon-poor terrigenous detritus of glacial origin. Moreover, organic carbon tends to be more refractory during glacials (i.e., C/N ratio increases; Haskell, 1991). Shallower sites 1056 through 1058 on BBOR are richer in organic carbon than deeper sites 1059 through 1061 due to their different average sedimentation rates ( $\sim 0.2$  m/kyr vs.  $\sim 0.3$  m/kyr). Site 1055 on Carolina Rise is apparently not affected by dilution: the average organic carbon of 0.86-1.25% for average glacial sedimentation rates of 0.2 m/kyr falls in the field typical for open-marine oxic environments. The organic matter content and composition may therefore have limited hematite reduction by limiting the suboxic and anoxic diagenesis that affects iron minerals.

Hematite preservation might have also been affected by the peculiar diagenetic environment typical to the BBOR and BR. Relatively thin sulfate reduction zones (Fig. 5) with linear sulfate profiles and large sulfate gradients at most sites are indicative of localized sulfide production via anaero-



bic methane oxidation by sulfate (Borowski et al., 1996, 1999; Keigwin et al., 1998). Sulfate consumption at the interface between sulfate and methane accounts for at least 35% of the entire sulfate reduction (Borowski et al., 1997). The high sedimentation rates during glacials when most hematite is delivered may have limited the residence time that hematite-rich sediments spend in this thin sulfide-rich zone, but on the other hand the localized sulfide production might have drastically increased hematite consumption at the methane-sulfate interface during low sedimentation rate periods. Site 1062 illustrates these effects because it has a very low upward methane flux (Borowski et al., 1999). It presents a thick, convex-up sulfate reduction zone (Keigwin et al., 1998). Hematite preservation is higher here than in shallower BBOR sites and goethite is apparently found deeper than the oxic-suboxic zone (see above), which would suggest decreased reduction of iron oxides. This in turn would indicate that focused sulfide production via anaerobic methane oxidation has a distructive rather than protective effect at sites where it occurs. However, the lower dilution of hematite by other terrigenous materials due to the low sedimentation rate at Site 1062 might also help explain the increased average hematite content there.

Relationships between organic carbon content (C) on one hand, and sulfur content (S) and the DOP on the other hand, indicate also that hematite preservation is likely to have been different at various sites (Fig. 6; see also Çagatay et al., 2001). However, the samples analyzed in the present study are situated below the depth of no sulfate and therefore should show terminal C–S and C–DOP relationships. Most samples in the C–S diagram plot below the 'normal marine' line (Goldhaber and Kaplan, 1974; Berner, 1982) indicating a deficit in sulfidation. However, three out of five samples from Site 1057 show increased sulfur content above the levels supported by the organic matter in the sediments. This might indicate that sulfur is added to the sediments, most likely from below via pore fluid migration or by anaerobic methane oxidation. The C–DOP diagram also indicates that sediments at the shallow Site 1057 are more intensely sulfidized. This phenomenon might be related, as discussed above, to both a lesser dilution of the organic matter by terrigenous detritus as well as increased sulfide production via anaerobic methane oxidation.

Differential diagenesis among sites, implied by the C-S-Fe relationships discussed above, suggests that hematite distribution patterns should be interpreted with caution. However, a general pattern of hematite variation, common to the deep sites on both BBOR and BR, indicate that the main pulses in hematite supply are still recorded in the sedimentary sequences at these sites. Records of hematite content on deep Blake Outer Ridge are spikier than on BR suggesting a lesser role for diagenesis at the later location. As discussed before, hematite preservation is highest on Bahama Outer Ridge (i.e., Site 1062). For the shallow sites 1055-1058 on the Carolina Slope and Blake Outer Ridge, hematite is clearly present in stages 6 and 1-4 pointing to the existence of a shallower transport system. Isolated hematite peaks occur in Stage 12 at Site 1058 and in Stage 16 at sites 1058 and 1056.

The occurrence of black metastable iron monosulfides during glacials, at high sedimentation rate sites only, is also a witness of diminished and localized sulfidation at deeper sites on BBOR (Fig. 5). Two factors seem to be essential in the iron monosulfide preservation. First, although depending on the absolute values of the sedimentation rates, iron-rich sediments would tend to move more quickly through the oxic–anoxic boundary where intermediate sulfur species are

Fig. 5. Variation of Factor 2 (hematite) and Factor 3 in the last 800 kyr for the studied sites. The age model used is from Grützner et al. (2002). Depths of no sulfate (black vertical lines) as well as the intervals of iron monosulfides occurrence (dark gray vertical bars) are shown at each site. The bottom curve at each site is Factor 2 (hematite) while the curve at the top at each site is Factor 3. Note the inverted scale for Factor 3. Only Factor 3 is plotted for Site 1055. Marine isotope stages are represented by gray (interglacials) and white (glacials) bands.



Fig. 6. Organic C–S and organic C–DOP plots for sediments at sites 1057, 1061, 1062, and 1063. The 'normal marine' line is also drawn on the C–S diagram. Note that sediments from Site 1057 are the most sulfidized among the studied sites (i.e., highest S and DOP values).

generated during periods of high sedimentation rate. These are necessary in the transformation of the iron monosulfides to pyrite (e.g., Berner, 1984). As a result, the iron monosulfides that do form remain arrested and do not convert to pyrite (Hurtgen et al., 1999). Second, the iron monosulfide transformation to pyrite may be hampered by the low levels of H<sub>2</sub>S in pore fluids. Another pathway for the transformation of iron monosulfides into pyrite is the direct reaction with H<sub>2</sub>S resulting from either sulfate reduction by organic matter or via anaerobic methane oxidation. However, the H<sub>2</sub>S will be rapidly buffered to low levels by the production of more iron monosulfides in the presence of excess reactive iron (e.g., Hurtgen et al., 1999).

As discussed above, Factor 3 is a negative factor. Minima occur mostly in high carbonate intervals and they are more extensive at sites of intermediate water depths (sites 1058–1057). This variation pattern of Factor 3 might be related to either a change in the types of the primary clay input or more likely to a more extensive anoxic diagenesis in these interglacial, high carbonate intervals related to an increased organic matter content. Diagenesis would destroy iron oxyhydroxides, which are strong chromophores (usually reddish), and would promote an increase in the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio in iron rich clay minerals (König et al., 2000).

# 5. Summary and conclusions

Sediment studies at ODP Leg 172 sites have emphasized that changes in color are the result of changes in mineralogy as well as chemical variations within minerals. These variations could be primary, due to differences in composition of the detrital sedimentary input, or secondary, due to diagenesis. In the western North Atlantic, lightness is primarily a function of the carbonate content while the hue is a function of the presence of iron oxides and Fe<sup>2+</sup>/Fe<sup>3+</sup> changes in clay minerals. Factor analysis has proved a valuable and rapid technique to detect the local and regional primary factors that influence sediment color. A distinctive reddish hue is imparted to sediments especially during glacial and deglacial periods by hematite that is most likely derived from the Permo-Carboniferous red beds of the Canadian Maritimes. Hematite is differentially preserved at various sites due to differences in reductive diagenesis. However, a general pattern of hematite variation, common to the deep sites on both BBOR and BR, indicate that the main pulses in hematite supply are still recorded in the sedimentary sequences at these sites.

Various intensities for diagenesis are the result of varying sedimentation rates, organic carbon content, and  $H_2S$  production via anaerobic methane oxidation. Once red iron oxides, that are strong coloring agents, have been consumed via reductive diagenesis, changes in the redox state of the iron in clay minerals might take the lead in setting the sediment color to various shades of green. It is important to underline that any study attempting to quantify reduction phenomena in iron-rich green clay minerals by using their color should assemble a first color data set immediately after core collection. Also due to reducing conditions, iron monosulfides occur extensively at depth in all high sedimentation rate sites where the sulfate reduction zone is thin. They coincide with glacial periods and suggest increased high terrigenous flux and/or increased reactive iron flux in glacials.

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