



# Constraining the colouration mechanisms of Cretaceous Oceanic Red Beds using diffuse reflectance spectroscopy



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## ABSTRACT

We have used diffuse reflectance spectroscopy to investigate the colouration mechanisms of hematite in Cretaceous Oceanic Red Beds (CORBs). Data for samples of CORBs from the Chuangde section in Tibet, Vispi Quarry section in Italy, and Core 12X of Ocean Drilling Program Hole 1049C in the North Atlantic were compared with calibration datasets obtained for hematite in different crystalline forms (kidney and specular hematite) and calcite matrix. Spectra for hematite in either pure form or in calibration datasets show that the centre of the reflection peak shifts to a longer wavelength and depth ( $D$ ) decreases as the crystallinity of the hematite increases. Compared with specular hematite, the presence of just 0.5% of kidney hematite can cause a much deeper absorption peak and greater redness value, which indicates that kidney hematite has a higher colouration capacity than specular hematite. However, both kidney and specular hematite exhibit a good correlation between the redness value for each calibration dataset and the absorption peak depth. In all three studied sections, hematite is the main iron oxide mineral responsible for colouration. Spectral features such as absorption peak depth and peak centre reveal that hematite crystallinity gradually decreases from red shale to limestone to marl. Based on a spectral comparison of red shale in the Chuangde section before and after citrate–bicarbonate–dithionite (CBD) treatment, we found that two forms of hematite are present: a fine-grained and dispersed form, and a detrital form. The former is relatively poorly crystalline hematite, which has a much stronger colouration capacity than the detrital form. In the Vispi Quarry section and Core 12X of ODP Hole 1049C, a good correlation between the absorption peak depth of hematite and redness value indicates that the red colouration is caused by hematite of similar crystallinity in each section.

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## 1. Introduction

Sediment colour is one of the main physical properties that can easily be observed with the naked eye. It is generally acknowledged that sediment colour is controlled by iron-bearing minerals, such as iron oxides or oxyhydroxides, iron-bearing sulphides, and iron-rich clay minerals (Potter et al., 1980). Other minor constituents may also have a secondary or local influence on sediment colour (Balsam and Deaton, 1996; Giosan et al., 2002a; Li et al., 2011; Lyle, 1983; Mix et al., 1995). In some cases, sediment colour has been linked to a prominent geological event, such as the organic-rich black shale that was widely distributed in the Cretaceous global ocean

and has been attributed to Oceanic Anoxic Events (OAEs) (Arthur et al., 1990; Jenkyns, 1980, 2010). The origin of Cretaceous Oceanic Red Beds (CORBs) has also been deduced from the red colour of the beds (Cai et al., 2012; Hu et al., 2005, 2012; Wagreich et al., 2011; Wang et al., 2005).

The term CORBs was defined by Wang et al. (2004, 2005). CORBs are red coloured sedimentary rocks of Cretaceous age, which were mainly deposited in a (hemi-) pelagic environment (Hu et al., 2005, 2012; Scott, 2009). The nature of CORBs has been attributed to the presence of iron oxides and, in particular, hematite in these rocks (Cai et al., 2009, 2012; Eren and Kadir, 2001; Hu et al., 2006a, 2009, 2012; Li et al., 2009, 2011). However, the colouration mechanisms of hematite in CORBs have not been studied in detail.

Iron oxides in CORBs, soils, and loess–paleosol sequences are often fine-grained, relatively poorly crystalline, and present at low concentrations. Hence, the techniques commonly used to study iron oxides, such as X-ray diffraction (XRD) and Mössbauer

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spectroscopy, are constrained by their respective detection limits. For example, in the Upper Cretaceous Scaglia Rossa limestone from the Vispi Quarry section in central Italy, the average  $\text{Fe}_2\text{O}_3$  content is only 0.22 wt.% (Hu et al., 2009) and no hematite was detected by XRD prior to the elimination of calcite (Cai et al., 2009).

Compared with other analytical techniques, diffuse reflectance spectroscopy (DRS) is a rapid and non-intrusive tool for identifying the constituents of sedimentary rocks and their abundances. Recently, DRS in the visible band (Vis-DRS) has increasingly been used for the identification of iron oxides in soils (Fontes and Carvalho, 2005; Scheinost et al., 1998; Scheinost and Schwertmann, 1999; Torrent et al., 1983), deep sea deposits (Balsam and Deaton, 1996; Balsam and Damuth, 2000; Giosan et al., 2002a,b; Harris and Mix, 1999; Mix et al., 1995; Zhang et al., 2007), aerosol particles (Arimoto et al., 2002; Shen et al., 2004, 2006), and loess–paleosol sequences (Balsam et al., 2004; Ji et al., 2001, 2002, 2004; Zhou et al., 2010). Vis-DRS is extremely sensitive to the presence of iron oxides and is approximately one order of magnitude more sensitive than XRD, with a limit of detection of ca. 0.01 wt.% for free iron oxides in soils and sediments (Barranco et al., 1989; Deaton and Balsam, 1991). The successful application of DRS to identify iron oxides makes it feasible for identifying the minerals responsible for the colouration of CORBs (Hu et al., 2009, 2012; Li et al., 2011). In previous studies of CORBs, we have reported the application of DRS to the detection of iron oxides (particularly hematite and goethite) in CORBs and performed a quantitative analysis of iron oxides in red beds of ODP Hole 1049C in the North Atlantic using multiple linear regression techniques based on DRS (e.g., Li et al., 2011). Compared with hematite, goethite is bright yellow (8.1YR–1.6Y, Munsell hue) and imparts a bright yellow colour to sediments (Deaton and Balsam, 1991; Torrent et al., 2006). The yellow colour of goethite is easily masked by the presence of red hematite (Torrent et al., 1983). Furthermore, goethite is unstable and may gradually transform to hematite during late diagenesis. Therefore, in this paper, we focused on the methodology exploration using DRS combined with CR during the study the colouration mechanisms of hematite in CORBs. Kidney and specular hematite were taken as examples of relatively poorly and well-crystalline hematite, respectively, and were mixed with calcite to obtain calibration sample sets. CORBs from the Chuangde section in Tibet, Vispi Quarry section in Italy, and Core 12X of ODP Hole 1049C in the North Atlantic were chosen for study, as these CORBs represent three different lithologies (shale, limestone, and marl, respectively).

## 2. Geological setting and sampling

During the Cretaceous, the Chuangde section, Vispi Quarry section, and site of ODP Hole 1049C were located in the eastern Tethys, western Tethys, and Atlantic Tethys, respectively (Fig. 1).

The Chuangde section is situated near Chuangde Village, which is ca. 10 km to the east of Gyangze City, southern Tibet, China. This area was tectonically part of the northern subzone of the Himalayan Tethys zone and contains widely developed Cretaceous oceanic strata. Wang et al. (2000) revised the stratigraphy in this section and divided it in ascending order into the Gyabula, Chuangde, and Zongzhuo formations. The Berriasian–Coniacian Gyabula Formation comprises black shale with pyrite nodules that is intercalated with sandstone beds. The overlying Chuangde Formation comprises violet–red shale that is intercalated with thinly bedded marlstone. The overlying upper Campanian to Palaeocene Zongzhuo Formation predominantly comprises dark grey to black shales that enclose various olistoliths of sandstone, limestone, and bedded chert (Hu et al., 2006a; Liu and Aitchison, 2002). Thirty red shale samples collected from the Chuangde Formation were studied (Fig. 1). According to Geological Society of America (GSA) Rock-

Colour Chart, their Munsell colour were 10R2/2, 5YR2/2, 5Y3/2, respectively (Table 1).

The Vispi Quarry section crops out on the eastern slope of the Contessa Valley about 2 km west of the town of Gubbio in Italy. This section is composed of the Scaglia Bianca and Scaglia Rossa formations (Hu et al., 2006b). The Scaglia Bianca Formation is mainly yellowish to greyish limestones that are intercalated with sparse pink to reddish limestone beds and several green to grey–black marlstones and shales (Bonarelli Level). The Scaglia Rossa Formation predominantly comprises pink to reddish marly limestone beds that generally contain 65–92 wt.%  $\text{CaCO}_3$ , with the exception of rare shale interbeds. The details of this section have been described by Arthur and Fischer (1977) and Alvarez and Montanari (1988). We studied the section above the Bonarelli (OAE2) Level from 9.8 m in the Scaglia Bianca Formation to 10.9 m in the Scaglia Rossa Formation. Up to the point that the limestone succession becomes completely reddish, two transitional beds (at 10.35–10.55 and 10.63–10.83 m) are present. Both of the transitional beds are a whitish colour at the base with a gradually increasing pinkish colour towards the top. Above these two transitional beds (>10.83 m), the limestone is completely pink to red in colour (e.g., Hu et al., 2009; Fig. 2). We collected 10 red limestone samples from the two transitional beds for DRS analysis (Fig. 1). According to Geological Society of America (GSA) Rock-Colour Chart, their Munsell colour were 10GY7/2, 5Y8/1, respectively.

ODP Leg 171B drilled mid-Cretaceous unconsolidated sediments in the western North Atlantic off the coast of Florida. According to a compilation of magnetic poles, Site 1049 was located at 23°N during the Cretaceous and represents a pelagic sedimentary environment above the carbonate compensation depth (CCD) (Norris et al., 1998). Core 12X of Hole 1049C was drilled at depths of 139.3–148.1 m below sea floor (mbsf). The sediments are late Aptian to early Albian in age and clayey, calcareous, nannofossil-bearing chalk and claystone, which are rich in planktic foraminiferal assemblages and have high-frequency colour variations between red (brown/orange), white, and green beds. These rhythmic colour changes are interrupted by a 46-cm-thick layer of laminated black shale that correlates with OAE 1b, which is a black shale sequence identified in equivalent European sections (Erbacher et al., 2001). In a previous study, we divided these sediments into eight cycles of red–white beds, based on colour changes and magnetic susceptibility (Li et al., 2011). In this study, only 24 red marl samples from Core 12X of Hole 1049C were chosen for DRS analysis (Fig. 1). According to Geological Society of America (GSA) Rock-Colour Chart, their Munsell colour were 5YR5/6, 10YR 7/4, 10YR 7/5, 10YR 8/2, respectively.

## 3. Sample treatment and reflectance measurements

Samples were analysed using a Perkin–Elmer Lambda 6 spectrophotometer with a diffuse reflectance attachment, which is capable of measuring sample reflectance in the near-ultraviolet (190–400 nm), visible (400–700 nm), and near-infrared (700–2500 nm) bandwidths, at the Institute of Surficial Geochemistry at Nanjing University, China. Sample preparation and analysis followed the procedures described in Balsam and Deaton (1991) and Ji et al. (2002). Powder specimens were made into slurries with distilled water on glass slides, smoothed, and dried slowly at <40 °C. Data are presented as the percent reflectance relative to the Spectralon™ (reflectance = 100%). Data processing was restricted to the visible spectrum (400–700 nm), which is the region most sensitive to iron oxide minerals (Deaton and Balsam, 1991). To better understand the colouration mechanisms of hematite, kidney hematite (as an example of relatively poorly crystalline hematite) was mixed with calcite matrix to obtain a calibration sample set

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