Cretaceous oceanic red beds (CORBs): Different time scales and models of origin

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Abstract

The Cretaceous oceanic red bed (CORB) is a newly opened window on global oceanic and climate changes during the Cretaceous greenhouse world. As a result of the International Geoscience Programmes 463, 494 and 555 (2002–2010), CORBs have been documented in many places by numerous publications. The principle goal of this paper is to summarize scientific advances on CORBs including chronostratigraphy, sedimentology, mineralogy, elemental and isotopic geochemistry, and their relationship to oceanic anoxic events (OAEs), palaeoecology and palaeoceanography.

We propose a new geochemical classification of the CORBs using CaO, Al₂O₃ and SiO₂ values, which lithologically refer to marly, clayey, and cherty CORBs respectively. Detailed mineralogical studies indicate that hematite, goethite and Mn²⁺-bearing calcite are the minerals imparting the red color of CORBs. Hematite clusters of several to tens of nanometers in the calcite structure are the main cause of the red coloring of limestones, and the Mn²⁺-bearing calcite gives additional red color. Goethite was thought to form originally with hematite, and was subsequently transformed to hematite during late diagenesis.

Chronostratigraphic data allow the distinction of two groups of CORBs by their durations. Short-term CORBs are generally less than 1 myr in duration, and seem to be on the scale of Milankovitch cycles. During the deposition of Cretaceous reddish intervals from ODP cores 1049 and 1050, low primary productivity and relatively high surface temperature resulted in low organic carbon flux into the sediments which reduced oxygen demand and produced oxidizing early diagenetic conditions. In such an oxic environment, iron oxides formed imparting the reddish color. The long-term CORBs’ depositional events lasted longer than 4 myr, and may be a possible consequence of the OAEs. Enhanced amounts of organic carbon and pyrite burial during and after the OAEs would have resulted in a large and abrupt fall in atmospheric CO₂ concentration, which probably induced significant global climatic cooling during and after the OAEs. Global cooling would have enhanced formation of cold deep water, increasing its oxidizing capacity due to the greater content of dissolved oxygen and would promote formation of oceanic red beds.

Sedimentological, mineralogical and geochemical data indicate that CORBs were deposited under highly oxic, oligotrophic conditions probably at a low sedimentation rate. The Cretaceous red and white limestones from Italy have similar compositions of terrestrial input-sensitive elements (Al, Ti, K, Mg, Rh, Zr), higher contents of Fe₂O₃ and depleted redox-sensitive elements (V, Cr, Ni, and U) and micronutrient elements Cu, Zn, indicating similar provenance sources but red limestones were deposited under more oxic conditions at the sediment–water interface than white limestones. The Cretaceous red shales such as those from the North Atlantic and Tibet have similar mineralogy and geochemistry as the Late Cenozoic red clays in the Pacific Ocean and the environment where both are formed was well-oxygenizing at a very low sedimentation rate. We compiled seventeen published stratigraphic examples of Phanerozoic oceanic red beds including the Late Cenozoic red clays in the Pacific. Different hypotheses explain the origin of red pigmentation of limestones and shales including (1) detrital origin of iron derived from continental weathering; (2) iron-bacterial mediation at the time of sedimentation; and (3) iron oxidation in oligotrophic, highly oxic environment. Additional research on Phanerozoic oceanic red beds is needed in order to better document their origin and palaeoceanographic and palaeoclimatic significance.

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1. Introduction

Cretaceous marine red beds have been known for at least 150 years, since Stur (1860) and Gümbel (1861) first described them from the Puchov beds in the Carpathians and the Nierental beds in the Eastern Alps. A few biostratigraphic and sedimentological studies followed, particularly in European countries. During late 1990s Chinese colleagues (Chengshan Wang and Xiuxian Hu) discovered and studied the Upper Cretaceous marine red beds in the Chuangde section, southern Tibet that were deposited in the Eastern Tethys Ocean. Following studies of well-known Cretaceous chalks (see Hay, 2008) and black shales (Schlanger and Jenkyns, 1976; Jenkyns, 1980), Cretaceous oceanic red beds (CORBs) became a study focus since the 2000s within the framework of the International Geoscience Programme (IGCP) projects. Transnational interdisciplinary research was conducted on their global distribution, correlation, and significance of the oxidation of these
deposits for palaeoceanographic reconstructions. Their relationships were contrasted to the distinctly different, interbedded mid-Cretaceous black shales.

The term CORB was born in 2001 discussions in Lhasa, Tibet and Chengdu when Luba Jansa, Massimo Sarti, Chengshan Wang and Xiumian Hu meet together to revise IGCP463 proposal. The term CORB was first published by Wang et al. (2004, 2005) and Hu et al. (2005), and became widely used in global correlation. CORBs are reddish to pinkish to brownish sedimentary rocks (generally limestone, marl, shale, and/or chert), of Cretaceous age, deposited in pelagic marine environments (Hu et al., 2005; Scott et al., 2009). A number of publications were published both in international and regional journals during the past years as achievements of IGCP projects, including the IGCP 463 “Upper Cretaceous Oceanic Red Beds: Response to Ocean/Climate Global Change” (2002–2006 led by Chengshang Wang, Massimo Sarti, Robert Scott, and Luba Jansa), the IGCP 494 “Dysoxic to oxic change in ocean sedimentation during mid-Cretaceous: a study of the Tethyan realm” (Young Scientists Project, 2003–2006 led by Xiumian Hu, Krzysztof Bak, Jens Wendler and Nataliya Tur), and the IGCP555 “Rapid Environmental/Climate Change in the Cretaceous Greenhouse World: Ocean-Land Interactions” (2007–2010 led by Chengshang Wang, Robert Scott, Hugh Jenkyns, Michael Wagreich, William Hay and Yuri D. Zakharov). Papers related to CORBs were mainly published in four special volumes: two in the journal “Cretaceous Research” (Wan and Sarti, 2005; Hu et al., 2012a), one in the journal “Sedimentary Geology” (Wagreich et al., 2011), and another in the Society of Sedimentary Geology (SEPM) Special Publication 91 (Hu et al., 2009b). Wang et al. (2009) summarized the results of the IGCP studies, including temporal–spatial distribution, biostratigraphy, and sedimentology. Several papers summarized CORBs in several regions including the Northern Atlantic (Jansa and Hu, 2009), the Eastern Alps (Wagreich et al., 2009) and the Romanian Carpathians (Melinte-Dobrinescu and Roban, 2011). Neuhuber and Wagreich (2011) discussed the inorganic geochemistry of the CORBs.

Here we propose a new geochemical classification of the CORBs, using CaO, Al2O3 and SiO2 values and the mineral composition and element geochemistry of different types of CORBs. The relationships with OAEs and orbitally controlled oceanic red beds (ORBs) are considered. Finally, we discuss the geological history and different origins of oceanic red beds.

2. Geochemical classification of CORBs

The CORBs are generally classified into three end members mainly based on types of sedimentary petrology (Wagreich et al., 2009; Wang et al., 2009): (1) red hemipelagic and pelagic carbonates (Fig. 1A and B); (2) deep-water red claystones deposited below the carbonate compensation depth (CCD) (Fig. 1C); and (3) red cherts and radiolarites deposited below the CCD (Fig. 1D). In this paper, we use geochemical CaO, Al2O3 and SiO2 values to classify the CORBs based on the compiled data of CORBs (Table 1, Figs. 2 and 3).

2.1. Ca-CORBs

The CaCO3 contents of the Ca-CORBs vary from 48% (Brandenberg, Austria) to 50% (Chuangde, Tibet) and up to the highest at 95% (Vispi, Italy) (Table 1). The Al2O3 values range from 1% (Vispi, Italy) to 10% (Brandenberg, Austria). The SiO2 value varies from 3% (Vispi, Italy) to 30% (Chuangde, Tibet), except for one sample from DSDP 417D which has 58% SiO2, and can be classified as siliceous limestone. Ca-CORBs are mainly pelagic limestones like the Italian Scaglia Rossa. Biogenous
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**Table 1**

Average contents of CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> in different types of CORBs.

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**Notes:**

1. Calculated from the CaO values using an oxide conversion factor of 1.7751.

2. Indicated in Fig. 2.
carbonate is mainly derived from calcareous nannofossils and planktonic foraminifera.

2.2. Al-CORBs

The CaCO₃ contents of the Al-CORBs are generally lower than 10%, ranging from 1% (Marzak, Czech Republic) to 21% (Albian ODP1049C, North Atlantic). The Al₂O₃ values range from 7% (Pindos, Greece) to 20% (Audia Nappe, Romania). The SiO₂ values vary from 42% (Albian ODP1049C, North Atlantic) to 70% (Tarcău Nappe, Romania). Terrigenous clay and silt-sized quartz are the main grain types of the Al-CORBs and are mainly derived from continental erosion and transported either by ocean currents or wind.

2.3. Si-CORBs

The CaCO₃ contents of the Si-CORBs are extremely low (0.2 to 1.4%) except the samples from Baergang (Tibet) with 17% (Table 1). The Al₂O₃ values are from 1% (Pindos, Greece) to 4% (Baergang, Tibet). The SiO₂ values vary from 86% (ODP site 800A, Pacific) to 96% (ODP legs 20, 30, 32, Pacific), except the samples from Baergang (Tibet) which have 72% of SiO₂. The cherts from the Baergang (Tibet) are associated with red limestones and deposited on the northern Indian continental margin, above the CCD (Hu et al., 2006a). Other examples are all pelagic red cherts in open oceanic environments including those from the Pacific ODP sites, Xialu section in Tibet and Pindos in Greece (Wang et al., 2009). This is the reason why the cherts from Baergang have relatively low SiO₂ and high CaCO₃ contents. Si-CORBs consist of biogenous SiO₂, which is mainly from radiolaria.

Depositional environments of most CORBs were pelagic, deep water in oceanic basins where they were generally far from shorelines (Wang et al., 2009; Fig. 4). Outer shelf to upper/middle bathyal CORBs comprise mainly red pelagic limestones and marlstones (Ca-CORBs) characterized by high amounts of planktonic foraminifera, and constitute a widespread facies type in low palaeolatitudes, especially in the Tethyan palaeogeographic realm (e.g. Spain, Italy, Switzerland, Austria, Poland, Greece, Turkey, Indian Himalaya). Towards deeper bathyal depths, carbonate content decreases as the depositional area approaches the calcite lysocline. Red pelagic limestones and cyclic CORBs become scarce, and marls and marly shales become the dominant lithology/facies type. Below the CCD, in abyssal depths, either red claystones and carbonate-free shales (Al-CORBs) or red cherts (Si-CORBs) were deposited, depending on the proportion of terrigenous input. Such lithologies are widely distributed in the North Atlantic Ocean (Jansa et al., 1979). The sediment input of Al-CORBs and Si-CORBs is controlled largely by aeolian transport or oceanic bottom currents, and siliceous biogenic production, which is comparable to siliceous oozes in modern oceans, respectively.
3. Chronostratigraphy of CORBs

The ages and rates of sediment accumulation of the CORBs provide constraints on hypotheses of origin of these deposits. Bimodal distribution of CORB durations based on numerous sections suggests two groups (Fig. 5A–C; Scott, 2009). Short-term CORBs generally are less than 1 myr in duration and range up to 3 myr. Some short-term CORBs approximate the duration of Milankovitch cycles. Long-term CORB deposition was longer than 4 myr (Fig. 5B and C) and the red intervals may be composed of composite short-term CORB cycles.

3.1. Long-term CORB deposition

Long-term CORBs are several to tens of meters thick and have variable beddings. Long-term CORB deposition in the Tethys began during the Late Aptian very soon after deposition of the organic beds of OAE 1a (Hu et al., 2005, 2006a). The Upper Aptian ORB 1 at Gorgo a Cebara (Italy) is 15 m thick and composed of cyclically interbedded red calcareous marls (Hu et al., 2006a). ORB 1 is 2.6 m above the Selli Level and overlies gray limestone; and deposition began about 890–500 kyr after the Selli bed and ORB duration was about 5.12 myr (Fig. 6A). At Ouzon, Switzerland Upper Aptian pelagic red beds that interbedded with gray limestone are 8.4 m thick and span at least 2.3 Ma in duration (Hable, 1997). In the deep-water Pindos Basin of Greece, siliceous CORBs 25 to 100 m thick extend from Valanginian to Coniacian (~50 myr in duration).

Late Cretaceous ORB deposition began in the Tethys and North Atlantic basins soon after the Cenomanian/Turonian black shale of OAE 2 (Hu et al., 2005, 2006a; Scott, 2009; Yilmaz et al., 2010). CORB depositional durations ranged from about 2 to 26 Ma from Early Turonian to Maastrichtian. In the Umbria–Marche basin, ORB 9 (Turonian), ORB10 (Coniacian to Santonian) and ORB 11 (Campanian to Maastrichtian) are about 19 m, 63 m and 147 m thick, respectively, with durations of ~2 myr, ~5 myr and ~15 myr, respectively (Cocconi and Premoli Silva, 2012). Along the western Atlantic margin close to North America in DSDP 385, 386 and 603B, thin bedded yellowish red to brown clay alternates with greenish gray clay and dark red zeolitic clay extending from Turonian to Maastrichtian (Jansa and Hu, 2009). In the middle of the North Atlantic basin on the proto-Mid-Atlantic ridge, thin bedded, dark brown to red brown clay is interbedded with volcaniclastics in DSDP 382 where CORB deposition lasted about 4 myr during the latest Campanian and earliest Maastrichtian. On the eastern margin of the North Atlantic near the coast of Iberia in ODP 641A lower Turonian brown clay overlies black clay at the Cenomanian/Turonian boundary, and the Upper Turonian to Santonian CORBs are brown clays interbedded with calcareous oozes. In DSDP 398 Turonian red to yellow brown mudstone is interbedded with rhythmic thin silt intercalations and is overlain by Campanian–Maastrichtian red to brown marly chalk, marl and claystone. These sections indicate that for most of the Late Cretaceous oxic bottom waters were long lasting throughout the North Atlantic and periodic influx of coarse siliciclastic and calcareous nanofossil oozes interrupted marine red bed deposition. Meanwhile, in the equatorial Atlantic and parts of the Caribbean Sea organic-rich strata were deposited during the Coniacian–Santonian, which was interpreted as OAE 3 (see Jenkyns, 1980; Wagreich, 2009).

Other examples of long-term CORB deposition are on the northern Indian shelf and in Alpine basins. For example, the Santonian to Campanian Chuandge Formation in Tibet was deposited on the northern margin of the Indian plate and is composed of homogeneous red shale interbedded with red limestones deposited near the base of the continental shelf below the CCD (Hu et al., 2006b; Chen et al., 2011). West of the Indian plate CORBs were deposited in the small partly isolated Penninic Ocean basin (Wagreich and Krenmayr, 2005; Wagreich et al., 2009), where pelagic and hemipelagic and turbiditic red beds were deposited beginning in the Early Turonian and continued at different places into the Maastrichtian. At Plagersflue, Switzerland, Turonian–Santonian CORBs are red, thin bedded pelagic limestones (Guillaumé, 1986). In the Carpathian Mountains of the Czech Republic and Romania, CORB deposition began in the Late Albian and continued into the Early Palaeocene (Melinte and Jipa, 2005; Melinte-Dobrinescu et al., 2009; Skupien et al., 2009). In the Sakarya Zone of northwestern Turkey Upper Cenomanian–Upper Turonian red beds alternate with black shales and bracket OAE2 strata (Yilmaz et al., 2010). In the Pontide of Turkey, the CORBs of the Late Santonian Unaz Formation are 5 to 20 m thick (Tüysüz et al., 2012).

3.2. Short-term ORB deposition

Short-term ORBs 1–7 are precisely dated as the Upper Aptian–Albian in the Piombico core, the Monte Petrano section and the Vispi Quarry section in central Italy (Hu et al., 2006a; Fig. 6A–C).

Correlation of these ORB intervals with the Albian stage boundaries is based on traditional biozones of planktonic foraminifers and calcareous nanofossils defined in the ORB sections and on graphic correlation to the CRET1 Database (Scott, 2009). Both methods result in a degree of
imprecision and uncertainty. The recognition of zones assumes that the first and last appearances of species are synchronous, although species ranges relative to each other differ in various sections so zone boundaries tend to be diachronous.

The CRET1 Database is composed of the ranges of nearly 3500 taxa and chronostratigraphic events in 161 globally distributed outcrops and cored sections (Scott, 2009). CRET1 integrates the ranges of planktonic and benthic foraminifera, nannofossils, dinoflagellates, ammonites, inoceramids, magnetochrons, radiometric dates, geochemical events, and selected sequence stratigraphic markers defined in published reference sections. Stage boundaries as defined by Ogg et al. (2004) were integrated into this database using the same criteria and calibrated to the new age scale except for the base of the Cenomanian. The age of the base Cenomanian is interpolated at 99.6 Ma by Ogg et al. (2004) and at 97.13 Ma by Scott et al. (2009) based on chronostratigraphic data from two different basins. The ages of ORB strata defined by Hu et al. (2006a) are interpolated from the Piobbico core, Monte Petrano and Vispi Quarry sections (Fig. 6A–C).

Kennedy et al. (2000) proposed that the base of the Albian stage can be defined by the first occurrence of the ammonite Leymeriella tardefurcata in the Col de Pré-Guittard section of the Vocontian Basin (France) at 66.5–66.9 m (Fig. 6D) and Niveau Paquier laminated black shale at 66.5–68 m. The first occurrence of L. tardefurcata was also used by Hoedemaeker et al. (2003) and Rebourlet et al. (2009) as the basal Albian zone, but no Global Boundary Stratotype Section and Point (GSSP) for the Aptian/Albian boundary has been accepted. This criterion, however, was rejected by Owen (2002), as being of local value and not associated with any microfossil or chronostratigraphic events. He supported the first occurrence of the geographically widespread nannofossil Prediscosphaera columnata as the base of the Albian stage (Owen, 2002). The first occurrence of L. tardefurcata projects into the Vispi Quarry section at 6.1 m by graphic correlation to the CRET1 Database (Fig. 6C).

The Albian/Cenomanian boundary is defined at its GSSP at Mont Risou (France), by the first occurrence of Rotalipora globotruncanoides (Gale et al., 1996; Kennedy et al., 2004). The first occurrence of R. globotruncanoides in the Monte Petrano section (Fiet et al., 2001) (Fig. 6B) projects into the Vispi Quarry section between 58.4 and 74.5 m (Fig. 6C). The numerical ages of ORB intervals in the Piobbico core, the Monte Petrano and Vispi Quarry sections are interpolated by the lines of correlation, which are constrained by the bioevents and eccentricity cycles (Fig. 6A–C).

The Piobbico core cuts seven ORB beds (Fig. 6A) and yields a diverse assemblage of Lower Aptian to Upper Albian planktonic foraminifers and calcareous nannofossils (Erba, 1988; Tornaghi et al., 1989). These biozones correlate ORBs 1–7 with Upper Aptian through the Upper Albian substages (Hu et al., 2006a). The base of the Albian as approximated by the first occurrence (FO) of P. columnata is between ORBs 2 and 3 in eccentricity cycle 1. The Albian/Cenomanian boundary was above the core top and above ORB 7 (Fig. 6A). Secondary correlation

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**Fig. 5.** CORB durations. (A) Durations in millions of years of stratigraphic and geographic occurrences of Tethyan CORB. (B) Number of CORBs in one million year increments showing the difference in durations of orbital-cycle control and long-term CORB deposition. (C) Chronostratigraphic succession of ORBs in Italian sections and their chronologic relation with oceanic anoxic events and the Aptian/Albian, and Albian/Cenomanian stage boundaries. Arrows mark positions of minor black shale beds. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.) Panel A and Panel B data are from Hu et al. (2005); Scott (2009).
ties are the Selli Level in the lower part of the core (Erba, 1988) and the Urbino bed. Cyclostratigraphy is a third tool. The rhythmically interbedded marl, marly limestone and limestone of the Scisti a Fucoidi Formation were deposited with orbital-cycle controlled eccentricity frequencies at about 406 ka and 95–100 ka, an obliquity frequency of about 41 ka, and a weak precession signal of about 19–23 ka is also recorded (Fischer et al., 1991; Grippo et al., 2004; Huang et al., 2010).
The Monte Petrano section records continuous pelagic deposition from Late Aptian to earliest Cenomanian and spans ORBs 3 through 7 (Fig. 6B) (Hu et al., 2006a). The biostratigraphy is calibrated by planktonic foraminifera, calcareous nannofossils, dinoflagellates, and the Urbino bed. Fiet et al. (2001) correlated the Albian base at the base of the measured section by the FO of the nannofossil P. columnata and the dinoflagellate Hystrichosphaeridium ataliesenae, and above the last occurrence (LO) of the foraminifer Ticinella bejouaenensis, which is slightly below the base of ORB 3. The Albian/ Cenomanian boundary based on foraminifera was correlated with , which is slightly below the base of ORB 3. The Albian/ Cenomanian boundary based on foraminifera was correlated with the FO of Rotalipora brotzeni (Kennedy et al., 2004). ORB 7 is just below this boundary. Twenty-nine marl–limestone bundles represent the two eccentricity frequencies of about 400 ka and 100 ka (Fiet et al., 2001) and support the correlation of Monte Petrano with the Piobico core.

The Vispi Quarry section is composed of limestone interbedded with ORBs 3 to 6. The limestones yield low diversity, moderately preserved calcareous nannofossil assemblage diagenetically altered (Appendix Table 1). The most abundant species is Watznaueria barnesiae, and Eprolithus floralis, Zeugrhabdoton embegeri, R. asper and R. angustus are consistently present. Correlation of this section with the Albian stage and substages is based on new analyses of calcareous nannofossils (Fig. 6C; Appendix Table 1). ORB 3 at the base of the section is in the basal Albian stage, which is approximated by the FO of P. columnata, the nannofloral event at the base of NCBa zone (Sissingh, 1977; Brawerler et al., 1993, 1995). This event is followed by the FO of the nannofossil Hayesites albiensis, which marks the base of the NCBB subzone (Brawerler et al., 1993, 1995) also in the Early Albian. The top of ORB 4 is just below the base of the Middle Albian as defined by the FO of the nannofossil Tranolithus orionatus, which defines the base of Subzone NCRC (Brawerler et al., 1993, 1995). In the Middle Albian, the FO of Axopodorhabdus albianus defines the base of NC9A nannofloral subzone (Brawerler et al., 1993, 1995), which is between ORBs 4 and 5. The top of ORB 6 is slightly below the base of the Upper Albian defined by the base of subzone NC9B and the FO of Eiffellithus monechieae. At Col de Palluel, Hautes-Alpes, France, the FO of E. monechieae is in the lower part of the Upper Albian coincident with the last occurrence of H. albiensis (Gale et al., 2011).

The graphic interpretation of the Albian interval in the Vispi Quarry section is constrained by the nannofossil ranges and the positions of ORB 3–6 (Fig. 6C). The age at the base of the section is interpolated at 113.96 Ma, slightly younger than the FOs of P. columnata and H. albiensis; the latter species defines NCBB Zone. So, the oldest part of NC8 Zone, Subzone NC8 is not sampled. The base of Subzone NC8 at the FO of T. orionatus is at 13.5 m and here projected at 108.85 Ma at the base of the Middle Albian. An unconformity or normal fault is posited at 36.01 m because the age of the FO of E. monechieae is slightly offset above the termination of ORB 6. The age of this bioevent is projected at 101.97 Ma in the lower part of the Upper Albian. The uppermost interval from 36.01 m to 90 m is poorly constrained and two interpretations are proposed. The base of the interval is pinned on the FO of E. monechieae and the top of the steeper line of correlation (LOC) is at the LO of E. monechieae and the alternative LOC is at the LO of A. albianus. The position of the Albian/Cenomanian boundary defined by the FO of R. globotruncanoideas at 97.2 Ma in the CRET1 Database is projected into the Vispi Quarry section between 58.4 m and 76.6 m. Additional data are needed to constrain this interpretation more narrowly.

The ages of the ORBs 3–6 in the Vispi Quarry section appear to be coeval with those beds in the Piobico core and the Petrano section. The numerical ages are projected from the database by the correlation lines and the ORBs are correlated with the Albian ammonite zones by the same lines. ORB 3 at 111.73–110.61 Ma is within the range of Early Albian Douvilleiceras mammillatum at 111.60 to 110.26 Ma. ORB 4 at 109.11–108.67 Ma is slightly older than the FO of the Middle Albian marker Hoplitites dentatus at 107.60 Ma. ORB 5 at 105.48–104.94 Ma is within the age range of Dipoloceras cristatum from 105.54 to 104.16 Ma, which is the basal zone of the Upper Albian. ORB 6 at 103.97–103.21 Ma is about the same age as the Upper Albian Hysteroceras varicosum ammonite subzone at 103.03 to 102.27 Ma. Within this ammonite subzone, included in the Mortoniceras inflatum Zone (Owen, 1999), Bown et al. (1999) reported the FO of E. monechieae.

The co-occurrence of the Upper Aptian–Albian ORBs and eccentricity cycles defined by lithology suggests that ORBs may be related to eccentricity cycles. The duration of ORBs is clearly highly variable and not an obvious climatic cycle frequency (Appendix Table 2). But do they begin on a Milankovitch beat or are they composites of multiple cycles? To test these hypotheses the Upper Aptian to Upper Albian ORB beds are plotted with the eccentricity cycles on a time scale (Fig. 7). The ages of the eccentricity cycles are interpolated by plotting their positions in the Piobico core and the Monte Petrano section to the CRET1 Database by means of the pelagic microfossils (Fig. 6). The ages of the ORBs in the same sections are interpolated in the same manner. The ages of ORB onset vary relative to eccentricity cycles. In the Piobico core ORB 3 began near the end of cycle 31 and ended at the end of cycle 29. ORB 4 coincided with but was shorter than cycle 25, but ORBs 5, 6, and 7 straddle cycle boundaries. The thicknesses of ORBs 1–7 range from 17.5 to 0.6 m and the durations range from 5.51 to 0.14 myr. In the Piobico core the Albian ORBs 3 to 7 are either shorter or somewhat longer than the eccentricity cycles but are not composites (Gripp et al., 2004; Huang et al., 2010). So no direct relationship is evident between the Upper Aptian to Upper Albian ORBs and eccentricity cycles.

4. Mineralogical composition and color origin of CORBs

The origin of the red color is one of the keys to understanding the formation of CORBs. In this section, we discuss mineral compositions, iron oxides and spectral features of the CORBs in three areas: Tibet of China, Italy and the Atlantic ODP1049C, in order to interpret the origin of the CORBs’ colorations.

4.1. Mineral composition of CORBs

Based on the qualitative analysis, we use the whole-pattern fitting technique under the support of a general structure analysis system program (Larson and Von Dreele, 2004) based on Rietveld refinement to calculate the weight fraction of every X-ray diffractometry (XRD)-detected mineral for limestones from Italy and shales from Tibet. The red limestone in Scaglia Rossa Formation from the Vispi Quarry section is mainly composed of calcite, quartz and boehmite (Fig. 8), with minor hematite, illite, montmorillonite, and albite in the residues after the removal of carbonates (Cai et al., 2009). The quantitative analysis shows that the calcite weight fraction ranges from 92 to 99%; boehmite is 0.1 to 0.9%; and the quartz ranges from 0.5 to 6.5% (Fig. 8).

The red shales from the Chuande section are composed of chlorite, illite and kaolinite, quartz, albite, calcite, and hematite. They differ from red limestone in the same section by the higher contents of hematite and chlorite (Fig. 9). The weight fractions of chlorite, illite and kaolinite vary in the range of 6–23%, 26–57% and 3–13%, respectively (Fig. 9). The weight fractions of quartz, albite and calcite are in the range of 3–30%, 5–24% and 0–33%, respectively (Fig. 9).

The Upper Albian–Lower Turonian red shales of the Eastern Carpathian inner Moldavides nappes are dominated by around 50% ililitc folowed by up to 11% kaolinite and around 3% each of chlorite and hematite, and quartz and chaledony together make around 25% (Papiu et al., 1983; Melinte-Dobrinescu et al., 2009). Dolomite and calcite are up to 1%. In the outermost part of the Eastern Carpathians Outer Moldavides, quartz and chaledony together are
43.4%, followed by illite (35.6%); other components (kaolinite, chlorite, hematite, calcite, and feldspar) are in minor amounts, each representing less than 6%, and combined amounting up to 15%.

According to the XRD analyses, the less than 2 μm grain-size fraction of the Aptian–Albian red beds in ODP Hole 1049C in the North Atlantic mainly consists of quartz, albite and clay minerals, which are mainly illite, with subordinate chlorite, minor kaolinite and montmorillonite or mixed-layer illite–montmorillonite (Han et al., 2008). The well crystallized illite and chlorite were mainly included in the larger than 2 μm grain size fractions. The weight fractions of chlorite, illite and kaolinite vary in the range of 0–30%, 15–75% and 0–20%, respectively (Fig. 10). The weight fractions of quartz and albite are in the range of 0–40% and 0–48%, respectively (Fig. 10).

4.2. Iron oxides in CORBs

Species and amount of iron oxides, which are key issues in evaluating the redox condition, can be determined by XRD, diffuse reflectance spectroscopy (DRS), transmission electron microscopy as well as sequential leaching of the sediments. When the iron oxide content is over its lowest detection limitation, the XRD method is one of the most efficient and frequently used. Compared to the XRD method, the DRS is considered to be a useful, rapid and effective detection tool that can detect the presence of iron oxide as low as 0.01% (Deaton and Balsam, 1991). The transmission electron microscopy is extremely effective in identifying the very fine (nanno-scale) mineral grains.

4.2.1. Quantitative analysis of iron oxide with XRD

The XRD fitting results suggest that the content of hematite in the red shales from the Chuangde section varies from 3.81 to 12% wt.% (Fig. 9) (Li et al., 2009; Cai, unpublished).

4.2.2. DRS data of the CORBs

The DRS data of red limestones from the Vispi Quarry section suggests that hematite was composed of different crystalline types (Cai et al., 2008). A broad spectral band is present in the range of 520–620 nm of first derivative spectra and is centered at 560 nm.
with a shoulder present at 574 nm and/or 587 nm (Fig. 11). The greater the wave-length, the higher is the crystallinity. For example, the peak centered at 587 nm suggests the presence of well-crystalline hematite, such as specularite and mica hematite (Cai et al., 2008). The peak centered at 575 nm was assigned to weakly-crystalline hematite and rhodochrosite (Cai et al., 2008).

Two DRS spectra in red shales from the Chuandge section were measured in bulk rock and residual after the CBD (citrate–bicarbonate–dithionite) treatment (Fig. 12C and D). Only a single hematite peak was present in the first derivative spectra of both bulk rock and samples with CBD treating (Fig. 12C; Hu et al., 2006b; Li et al., 2009). Three DRS spectra (Fig. 12A, and B) were collected for each sample from ODP Hole
1049C before and after CBD treating, and from a synthetic mixture with different fractions of hematite and goethite, respectively. Two peaks, centered at 435 and 565 nm, were present in the spectra of samples with brown and orange colors (Fig. 12A) (Han et al., 2008; Li et al., 2011). After treatment by CBD, the brown and orange samples changed to green or white, and the peaks assigned to hematite and goethite disappeared in the first derivative spectra (Fig. 12B). Then, with the different hematite and goethite contents that were added to the CBD treated samples, the DRS analysis suggests the restoration of brown and orange colors (Fig. 12B). This indicates that the stain minerals in these brown and orange sediments are hematite and goethite (Li et al., 2011).

4.2.3. Quantitative analysis of iron oxide concentrations in ODP Hole 1049C

To obtain the absolute contents of iron oxides in these sediments, Li et al. (2011) performed a quantitative analysis using DRS with multiple linear regression (see Fig. 23). The results suggest that the hematite content in the Albian brown samples ranges from 0.13 to 0.82% and averages 0.51%, and the goethite content is in the range...
of 0.22–0.81% and averages 0.58% (see Fig. 23). The content of hematite in Aptian orange samples is in the range of 0.19–0.46% and averages 0.35%, and the content of goethite is in the range of 0.29–0.67% and averages 0.50% (see Fig. 23).

4.3. Origins of the red color of CORBs

4.3.1. Determination of staining minerals

Different stain minerals such as hematite and goethite behave differently in terms of determining the color of sediments. Hematite appears blood-red in color (3.5R–4.1YR, Munsell hue), imparting a red color to sediment. In contrast, goethite is bright yellow (8.1YR–1.6Y, Munsell hue), imparting a bright yellow color to sediment (Torrent and Schwertmann, 1987; Deaton and Balsam, 1991; Li et al., 2011). Mn$^{2+}$-doped calcite can be excited to radiate visible red light by means of thermal, cathodoluminescent, ultraviolet or laser energy sources (e.g. Macedo et al., 1999; Cai et al., 2008). However, the color was significantly lighter after it had been ground to a powder than before it had been in the crystals, which suggests that Mn$^{2+}$-bearing calcite may only give the limestone a light red tinge (Cai et al., 2008). Dyeing of kidney-red hematite is 10 times greater than rhodochrosite, which has a similar coloring mechanism to Mn$^{2+}$-doped calcite (Cai et al., 2008).

For hematite minerals, different degrees of crystallinity may cause different redness of sediments. Cai et al. (2008) showed that crystallinity of specularite is best, mica hematite is middle and kidney-red hematite is the poorest of crystallinity. The DRS peak of hematite was centered at 577, 585 and 586 nm for kidney hematite, mica hematite, specularite, respectively, which suggests that the DRS peak shifts to a longer wave-length when its crystallinity increases. DRS data showed that the dyeing ability decreased as the degree of hematite crystallinity increased, with the order of kidney-red hematite, mica hematite and specularite.

4.3.2. Red coloring mechanism of red limestone

Hematite originates in red Turonian limestone of the Vispi Quarry section in two ways. The first is continental origin by seasonal winds together with boehmite and quartz, and the other is authigenic hematite origin which is precipitated from sea water (Cai et al., 2009). The grain size of continentally-derived hematite is more than several microns and is heterogeneously distributed in the limestone. Autogenic hematite is in very low concentrations but homogenously distributed within the interstices of the calcite microlites, calcite grains, holes of the microfossils, and entrapped in the calcite structure. The continentally-derived hematite cannot be the major cause that imparts the red color to limestone because of its heterogeneous distribution and low proportion (Cai et al., 2009, 2012).

High resolution transmission electron microscopy (Cai et al., 2012) suggests that the nanometer-sized hematite grains are in the interstice of calcite grains. This is verified by selected areal electron diffraction patterns. The hypothesis is that iron was originally trapped in the calcite structure in two forms, the first was ferrous iron in the calcite lattice, and the second was iron in the interstices of the calcite structure, which replaces the oxygen from the CaO$_6$ octahedron to form Fe$_2$O$_3$ clusters. These clusters were then oxidized to form hematite clusters by releasing the electron to dissolve O$_2$ in groundwater. These hematite clusters grow to several tens of nanometers in the calcite structure, and was a major factor imparting the homogeneous red limestone color (Cai et al., 2009).

The electron-spin resonance spectra of limestones from the Vispi Quarry clearly show that manganese is present as octahedral cations in the calcite structure (Cai et al., 2009) and was incorporated during calcite formation (Calderoni and Ferrini, 1984). This suggests that the calcite in the red limestone is a type of manganese-bearing calcite, which may give additional red color to those limestones.

DRS work suggests that both goethite and hematite are present in the brown and orange beds (Fig. 11), but are not found in black and
white beds from ODP 1049C (Han et al., 2008; Li et al., 2011; Fig. 11). The CBD treatment of brown and orange samples recovered synthetic hematite and goethite (Fig. 12) suggesting that ferric oxide is in the form of nanograins of poorly crystallized or amorphous hematite and goethite. Consider the following facts: (1) goethite is not found in red limestone from the Vispi Quarry section, and (2) red limestones from the Vispi Quarry are lithified and have experienced considerable diagenesis (Arthur and Fischer, 1977), whereas the red marls in ODP 1049C are largely unaffected by diagenesis (Erbacher et al., 2001). Therefore we propose that goethite originally formed together with hematite. Subsequently, the goethite was transformed to hematite during late diagenesis, as already documented in other sedimentary rocks (Berner, 1969; van Houten, 1973; Channell et al., 1982).

Fig. 13. Enrichment factors (relative to the Average Shale of Wedepohl, 1971) of major and trace elements of the Ca-CORBs. Numbers refer to Table 1. (A) Major elements; (B) trace elements. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.) Data source is listed in Table 3 of the Appendix.

Fig. 14. Enrichment factors (relative to the Average Shale of Wedepohl, 1971) of major and trace elements of the Al-CORBs. Place number refers to Table 1. (A) Major elements; (B) trace elements. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.) Data source is listed in Table 3 of the Appendix.
Fig. 15. Enrichment factors (relative to the Average Shale of Wedepohl, 1971) of major and trace elements of the red limestones, white limestones and black shales of Bonarelli level from the Vispi Quarry section of Italy. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.) Data source is listed in Table 4 of the Appendix.

Fig. 16. Enrichment factors (relative to the Average Shale of Wedepohl, 1971) of major and trace elements of the red shales and non-red shales from (A) Albian ODP1049C of the North Atlantic; (B) Chuangde section of Tibet; and (C) Marzak section of the Czech Republic. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.) Data source is listed in Table 4 of the Appendix.
4.3.3. Red coloring mechanism of red shale

Red shales from the Chuangde section have 3.81 to 12% in weight hematite which is much higher than that of the limestones from Vispi Quarry (~0.1–0.2%, Hu et al., 2009a). Hematite in the Albian red shale in ODP1049C is no more than 0.13–0.82% (Li et al., 2011). Hematite grain size ranges from several tens of nanometers to several tens of microns in red shales based on scanning electron microscopy. The red color of shales in the Chuangde section is imparted by both nanograin hematite and larger size (tens of microns) of hematite based on CBD treatment (Fig. 12).

4.4. Summary

1. Hematite, goethite and Mn$^{2+}$-bearing calcite impart the red color of CORBs. Hematite imparts a red color; goethite imparts a bright yellow color; Mn$^{2+}$-bearing calcite gives a light red tinge. The red color decreases when either the degree of hematite crystallinity or grain size of hematite mineral increased.

2. Both hematite and goethite are responsible for the brown and orange colors of the Albian–Aptian sediments from ODP 1049C. Hematite clusters of several to tens of nanometers in the calcite structure are the main cause of the red coloring of limestones, and manganese-bearing calcite may give additional red color to limestones in the Vispi Quarry section. Goethite was suggested to be originally formed together with hematite, but was subsequently transformed to hematite during late diagenesis.

3. The red color of shales in the Chuangde section resulted from hematites of different grain sizes, ranging from several tens of nanometers to several tens of microns in size.

5. Elemental geochemistry

5.1. Data source and method

Elemental geochemical data of CORBs are available from numerous publications. In this study, we compiled elemental geochemical data of both Ca-CORBs (red limestones/marls) and Al-CORBs (red shales) in the world (Appendix Tables 3–6). Geochemical data from the Si-CORBs (red cherts) are rare and not discussed in this paper.

Elemental values were normalized to Al in order to account for dilution effects by potential biogenic components such as carbonates, silica, and phosphorites. Concentrations are compared to the average values of the Average Shale (Wedepohl, 1971) and expressed as relative enrichment factors ($EF_{Element}$). Enrichment factors were calculated using:

$$EF_{Element} = \left( \frac{\text{Element}}{\text{Al}} \right)_{\text{sample}} / \left( \frac{\text{Element}}{\text{Al}} \right)_{\text{average shale}}$$

where $n$ is the shale-normalized concentration.

5.2. Ca-CORBs (red carbonates)

5.2.1. Major elements

Major elements Fe, Mg, K, and Ti from red limestones and marls are relatively similar to the Average Shale (Wedepohl, 1971) with $EF_{Fe}$, $EF_{Mg}$, $EF_{K}$, $EF_{Ti}$ ranging from 0.62 to 1.47, 0.86 to 4.16, 0.58 to 1.65, 0.62 to 1.42 respectively (Fig. 13A, Appendix Table 4). Mn is enriched in red limestones from Tibet ($EF_{Mn}$ is 7.14 in Chuangde, 25.65 in Baergang, and 8.89 in Tianba) and Italy ($EF_{Mn}$ is 6.48 in Pia da Stua and 15.67 in Vispi Quarry). Mn values of red limestone/marl in Austria and Atlantic ODP1049C site are comparable to the Average Shale (Wedepohl, 1971) with $EF_{Mn}$ ranging from 0.67 to 4.71 (Fig. 13A, Appendix Table 4). P is enriched in red limestones from Pia da Stua and Vispi Quarry of Italy with $EF_{P}$ of 9.15 and 5.90, respectively. Na is depleted from red shales in Austria with $EF_{Na}$ ranging from 0.28 to 0.47.

In comparison with Bonarelli black shales (Turgeon and Brumsack, 2006), the white limestones and red limestones in the Vispi Quarry are enriched in Mg and Mn, and depleted in Na (Fig. 15). $Fe_{2O3}$ in the red limestones are from 0.12 wt.% to 0.41 wt.% with an average of 0.22 wt.%, which is significantly higher than in the white limestones, where $Fe_{2O3}$ values range from 0.02 wt.% to 0.19 wt.% with an average of 0.12 wt.% (Hu et al., 2009a; Fig. 15).

Shale (Wedepohl, 1971) with $EF_{P}$ ranging from 0.67 to 4.71 (Fig. 13A, Appendix Table 4). P is enriched in red limestones from Pia da Stua and Vispi Quarry of Italy with $EF_{P}$ of 9.15 and 5.90, respectively. Na is depleted from red shales in Austria with $EF_{Na}$ ranging from 0.28 to 0.47.

In comparison with Bonarelli black shales (Turgeon and Brumsack, 2006), the white limestones and red limestones in the Vispi Quarry are enriched in Mg and Mn, and depleted in Na (Fig. 15). $Fe_{2O3}$ in the red limestones are from 0.12 wt.% to 0.41 wt.% with an average of 0.22 wt.%, which is significantly higher than in the white limestones, where $Fe_{2O3}$ values range from 0.02 wt.% to 0.19 wt.% with an average of 0.12 wt.% (Hu et al., 2009a; Fig. 15).

Shale (Wedepohl, 1971) with $EF_{Mn}$ ranging from 0.67 to 4.71 (Fig. 13A, Appendix Table 4). P is enriched in red limestones from Pia da Stua and Vispi Quarry of Italy with $EF_{P}$ of 9.15 and 5.90, respectively. Na is depleted from red shales in Austria with $EF_{Na}$ ranging from 0.28 to 0.47.

In comparison with Bonarelli black shales (Turgeon and Brumsack, 2006), the white limestones and red limestones in the Vispi Quarry are enriched in Mg and Mn, and depleted in Na (Fig. 15). $Fe_{2O3}$ in the red limestones are from 0.12 wt.% to 0.41 wt.% with an average of 0.22 wt.%, which is significantly higher than in the white limestones, where $Fe_{2O3}$ values range from 0.02 wt.% to 0.19 wt.% with an average of 0.12 wt.% (Hu et al., 2009a; Fig. 15).
Fig. 19. Chemostratigraphic correlation by stable carbon isotopes of the Aptian interval from OAE 1a to ORB1 of Gorge a Cerbara, Italy (Stein et al., 2011 and this study) with the Yenicesihlar section, Turkey (Hu et al., 2012b), the Roter Sattel section, Switzerland (Menegatti et al., 1998), and the La Bédoule section, France (Kuhnt et al., 2011). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
Fig. 20. Chemostratigraphic correlation by stable carbon isotopes of the Turonian interval from OAE 2 to ORB9 of the Buchberg section, Austria (Wendler et al., 2009) with the Vispi Quarry section, Italy (Stoll and Schrag, 2000; Tsikos et al., 2004), and the Halle-Oerlinghausen/Culver Cliff section, Germany (Voigt et al., 2007), compared to the Upper Cretaceous carbon isotopic curve from the English Chalk (Jarvis et al., 2006). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
5.2.2. Trace elements

The element V is depleted in red limestones from Baergang (EF\textsubscript{V} = 0.31) and Rehkogel (Austria) (EF\textsubscript{V} = 0.08; Fig. 13B), but it is close to the Average Shale (Wedepohl, 1971) in other places. The elements Cr, Co, Ni are similar to the Average Shale (Wedepohl, 1971) with EF values ranging from 0.6 to 3.2 (Fig. 13B). The element Cu is enriched at Baergang (Tibet) (EF\textsubscript{Cu} = 0.38) and depleted at Buchberg (Austria) (EF\textsubscript{Cu} = 0.38). The element Zn is enriched at the Vispi Quarry with EF\textsubscript{Zn} = 5.94. The element Rb is depleted from Tianba (Tibet) (EF\textsubscript{Rb} = 0.45) and from Marzak (EF\textsubscript{Rb} = 0.46). The element Sr is depleted from Tianba (EF\textsubscript{Sr} = 0.45) and from Marzak (EF\textsubscript{Sr} = 0.46). The element Zr is highly depleted from Rehkogel (Austria) with EF\textsubscript{Zr} = 0.46 and at Buchberg (Austria) with EF\textsubscript{Zr} = 0.46. The element Mo is enriched at the Vispi Quarry with EF\textsubscript{Mo} = 0.47. The element Ba is comparable with the Average Shale (Wedepohl, 1971) with EF\textsubscript{Ba} ranging from 0.51 to 4.71, with one exception at the Vispi Quarry where Ba is highly enriched with EF\textsubscript{Ba} = 19.75. The element U varies from place to place, being enriched at Pia da Stua, Italy (EF\textsubscript{U} = 6.90) and depleted at Tianba, Rehkogel, Brandenberg, and ODP1049C with EF\textsubscript{U} ranging from 0.05 to 0.38.

In comparison with the Bonarelli black shales (Turgeon and Brumsack, 2006), the white limestones and red limestones in the Vispi Quarry are enriched in Co, depleted in V, Zn and U (Fig. 15). Detrital input-sensitive elements (Al, Ti, K, Mg, Rb, Zr) show no significant difference between red and white limestones. However, the redox-sensitive elements V, Cr, Ni, and U, and the micronutrient elements Cu, Zn are slightly enriched in the white limestones (Fig. 15 and Appendix Table 4).

5.2.3. Rare earth elements

The \textit{ΣREE} in the red limestones average 24.19 ppm (17.02–41.07 ppm, n = 9) in the Vispi Quarry section, 71.23 ppm (66.57–76.58 ppm, n = 4) in the Aptian ODP1049C, and 177.56 ppm in the Chuangde section (94.23–299.64 ppm, n = 6; Appendix Table 6). The \textit{ΣREE} are strongly negatively correlated (\(R^2 = 0.876\)) with carbonate content (Fig. 17), because the marine carbonate phase generally contains significantly less REE than detrital clay and heavy minerals (Piper, 1974). The differences in the \textit{ΣREE} between red and white limestones are minor (Hu et al., 2009a).

Overall, the PAAS-normalized REE patterns of studied limestones exhibit seawater-like REE distribution patterns characterized by small enrichments in heavy REE (HREE) relative to light REE (LREE) with negative Cerium anomalies (Fig. 18).

Red limestones have 0.35 of averaged \(\delta^{13}C\) (Appendix Table 6). The \(\delta^{13}C\) values of Cretaceous red limestones are very similar to those of typical oceanic seawater (\(\delta^{13}C\) values ranging from <0.1 to 0.4, Elderfield and Greaves, 1982). Also, in the Vispi Quarry section, the red limestones show very similar REE pattern and \(\delta^{13}C\) values to those of the white limestones (Hu et al., 2009a).

5.3. Al-CORBs (red shales)

5.3.1. Major elements

The major elements Fe, K, and Ti from red shales are relatively similar to the Average Shale (Wedepohl, 1971) with EF\textsubscript{Fe}, EF\textsubscript{K}, EF\textsubscript{Ti} (Fig. 14, Appendix Table 4). Mg is enriched in red shales from Pacific ODP 800A. Na is depleted in red shales from the Silesian Nappe of Poland and Marzak of the Czech Republic. Mn is depleted in red shales from the Silesian Nappe of Poland and Albian ODP1049C.

The red shales at Marzak have about two times higher Fe\textsubscript{2}O\textsubscript{3} content than the gray shales, and Mn concentration tends to be higher in the gray shales than in the red shales (Jiang et al., 2009; Fig. 16). Similar trends can be found in the gray and red calcareous shales from the Albian ODP1049C with about three times higher Mn concentration in the gray shales than in the red shales (Chen, 2008; Fig. 16).

5.3.2. Trace elements

The element Cu is depleted in the red shales from Chuangde (Tibet) (EF\textsubscript{Cu} = 0.45). The element Sr is depleted in the red shales from the Silesian Nappe (EF\textsubscript{Sr} = 0.02) and from Marzak (EF\textsubscript{Sr} = 0.26). The element Mo is depleted at Baergang and Chuangde with EF\textsubscript{Mo} of 0.36–0.39.
Fig. 22. Moving average curves of elemental abundance (Ca, Fe, Ti), mineralogic composition variation, and stable carbon and oxygen isotopic results of foraminifera and fine fraction from the section 16R-2 (Maastrichtian) in ODP Hole 1050C. Note abrupt changes at reddish intervals. Revised from Macleod et al. (2001). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Fig. 23. Comparison of magnetic susceptibility and CaCO₃ content (data from Han et al., 2008) from the Aptian–Albian ODP1049C with concentrations of hematite and goethite minerals (data from Li et al., 2011) and element values of Al₂O₃, SiO₂ and element ratio of Ba/Al (data from Chen, 2008). MS: magnetic susceptibility. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
The element U is strongly depleted in the red shales compared to the gray shales (Fig. 16). The element Ba is more enriched in the gray shales than in the red shales from the Albian ODP1049C and Chuanqde (Fig. 16).

5.3.3. Rare earth elements

The ΣREE in the red shales averages 450.22 ppm at Chuanqde, 127.46 ppm in the Albian ODP1049, and 125.87 ppm at Marzak (Appendix Table 6). The PAAS-normalized REE patterns of the Cretaceous red shales exhibit seawater-like REE distribution patterns, similar to those of the red limestones (Fig. 18). Cretaceous oceanic red shales show negative δCe excursions with an average of 0.69 of δCe, ranging from 0.54 to 0.77 (Appendix Table 6). However, the red shales from Marzak show positive δCe excursions with an average of 1.34 of δCe (Appendix Table 6).

5.4. Summary

(1) Compared to the Average Shale (Wedepohl, 1971), the redox-sensitive element V is depleted in the red limestones from Baergang and Rehkogel. The elements Mn, Ba, P, and Mo are highly enriched at the Vispi Quarry, probably indicating a higher paleoproductivity compared to the Average Shale (Wedepohl, 1971). Compared with the white limestones, the red limestones have a higher Fe₂O₃ content. Detrital input-sensitive elements (Al, Ti, K, Mg, Rb, Zr) show no significant difference between the red and white limestones. Redox-sensitive elements (V, Cr, Ni, and U) and micronutrient elements Cu, Zn are depleted in the red limestones indicating a more oxic condition at the sediment–water interface.

(2) Red shales are similar to the Average Shale (Wedepohl, 1971) in terms of major and trace elements. Compared to the gray shales, the red shales from the Marzak section and Albian ODP1049C have higher Fe₂O₃, lower Mn and lower Ba contents (Chen, 2008; Jiang et al., 2009). The element U is strongly depleted in the red shales compared with the gray shales. Detrital input-sensitive elements (Al, Ti, K, Mg, Rb, Zr) show no significant difference between the red and gray shales indicating a stable terrigenous input. The color change between the gray or white and red shales was caused most probably by the variation of redox bottom conditions in the deep ocean (Wang et al., 2005; Hu et al., 2006a; Jiang et al., 2009).

(3) The differences in the ΣREE, δCe values as well as the PAAS-normalized REE patterns either between the red and white limestones or between the red and gray shales are minor (Hu et al., 2009a; Jiang et al., 2009).

6. OAE–ORB transition and stable carbon isotopes

Temporal–spatial distribution shows that CORBs experienced two palaeogeographical expansions (Wang et al., 2009): (1) in the Aptian nannofossil zone CC7 shortly after OAE1a and (2) in the Turonian zone CC11 after OAE2, respectively. To better understand the relationship between OAEs and CORBs, we have studied two stratigraphic intervals in the Tethys realm in detail. First we will summarize the OAE 1a–ORB1 transitions at the Gorgo a Cerbara section (Italy) and the Yenicesihlar section (Turkey) and second the OAE 2–ORB9 transitions in the Vispi Quarry (Italy) and the Buchberg section (Austria).

6.1. OAE 1a–ORB1 transition

6.1.1. Gorgo a Cerbara section, Italy

In the Gorgo a Cerbara section, OAE 1a (the Selli Level) is approximately 1.92 m thick and consists of laminated to bioturbated gray to black mudstones and shales, with 20 thin (1 to 3 cm) grayish silty/sandy layers (Coccioni et al., 1992); and total organic carbon (TOC) contents are 0.74–7.28% (Baudin et al., 1998). A 2.5 m thick stratigraphic interval separates the Selli Level and ORB 1a (Fig. 19) and is lithologically characterized by bioturbated gray cherty limestones and marly limestones. ORB1 is over 15 m thick and is dominated by dark red marlstones and marly limestones with subordinate gray marlstones and marly limestones, in beds 1–30-cm-thick. The gray beds are locally interbedded with red beds in a cyclical manner. If we apply the 2.6 m/Ma sedimentation rate for the interval from the base of M0 (35.6 m) to the top of Chiastrzygus litterarius nannofossil zone (40.8 m) of Coccioni et al. (1992), it took about 0.95 Ma for the change from the top of the Selli Level to the deposition of the first reddish limestone of the ORB1 (Hu et al., 2006a).

We compiled our analyzed data with those of Stein et al. (2011) from the Gorgo a Cerbara section (Fig. 19 and Appendix Table 7). The Selli Level is equal to the carbon isotopic stages of C3 to C6 of Menegatti et al. (1998) (Fig. 19). The transitional interval from OAE 1a to ORB1 is within the carbon isotopic stage C7 (Appendix Table 7). The first occurrence of ORB1 is also within the C7 stage but a few meters above the base of ORB1, where the carbon isotopic values start to decrease as represented by the C8 stage.

6.1.2. Yenicesihlar section, Turkey

The Yenicesihlar section documents the stratigraphic and palaeoenvironmental changes from OAE 1a to ORB1 during the Aptian (Yilmaz, 2008; Hu et al., 2012b) (Fig. 19). The OAE 1a interval is approximately 2.1 m thick and consists of black to dark gray shales with gray marlstones. TOC values of the black shales are up to 2.05%. The high organic carbon content and pyritization in the black shales of OAE 1a indicate an anoxic environment. The OAE 1a–ORB1 transitional interval (~20.3 m thick) displays an alternation of light gray limestones with very thin-bedded gray marls. ORB1 is approximately 3.5 m thick and consists of pinkish to light brownish limestones, which were deposited in an oxic environment, as indicated by hematite in the reddish limestones (Hu et al., 2012b).

The carbon isotopic record shows several perturbations in the OAE 1a–ORB1 transitional interval including a negative excursion (C3, 0.58 m) in the lower part of the Selli-equivalent black shales, a stepwise positive excursion (C4 to C6, 1.52 m) in the Selli-equivalent black shales, a positive carbon isotopic plateau (C7, up to 9.48 m) in the lower part of the transitional interval, and a carbon isotopic decrease in the upper part of the transitional interval (C8, up to 10.86 m; Fig. 19; Hu et al., 2012b). The OAE 1a to ORB1 transition interval corresponds to carbon isotope stages C7 and C8, which lasted approximately 1.3 Ma (Hu et al., 2012b). This duration is very close to the duration of the OAE 1a (1.1 to 1.3 myr). The C7 stage of positive carbon isotopic plateau persisted for ~650 kyr, and the negative carbon isotopic shift of the C8 stage also lasted for ~650 kyr (Hu et al., 2012b).

6.2. OAE 2–ORB 9 transition

6.2.1. Umbria–Marche, Italy

In the Vispi Quarry and Moria sections, about 10.35 m above the Bonarelli bed, white limestones of the Scaglia Bianca grade into a sequence of predominantly pinkish–reddish limestones and marls of the Scaglia Rossa Formation (Hu et al., 2006a; Trabucho-Alexandre et al., 2011; and references within) (Fig. 20). Below the reddish limestone succession are two transitional beds, the lower at 10.35–10.55 m and the higher at 10.63–10.83 m. Both transitional beds are whitish in color at the base and gradually become increasingly pinkish color towards the top. The strata above 10.83 m are pinkish, to reddish. If we apply the 7.4 m/myr sedimentation rate of the Helvetoglobotruncana helvetica zone of Premoli Silva and Sliter (1994), it took about 1.5 myr for the change from the top of the Bonarelli Level to the predominantly red colored limestones of the Scaglia Rossa Formation (ORB9) (Hu et al., 2006a).
Near the Cenomanian–Turonian boundary, a positive $\delta^{13}C$ excursion was documented globally (Jenkyns, 1980; Schlanger et al., 1987; Tsikos et al., 2004). From the Early to Middle Turonian, the $\delta^{13}C$ values stay relatively flat in a so-called carbon isotopic plateau with several slight positive or negative excursions including the Holywell, Lulworth, Round Down, and Low-woollgari events (Jarvis et al., 2006; Fig. 20). Just above the Low-woollgari event (Middle Turonian), the $\delta^{13}C$ values fall steeply becoming the Glynde event at the minimum value (Fig. 20). In the Vispi Quarry section, red limestones occur around the Round Down event (Fig. 20). The steeply falling $\delta^{13}C$ values start about 2.5 m above the Low-woollgari event (Fig. 20).

### 6.2.2. Buchberg section, Austria

The Buchberg section exposes a Cenomanian–Turonian succession of limestones, marly limestones and marlstones with Cenomanian strata being not fully exposed (Neuhuber et al., 2007; Wagreich et al., 2009; Wendler et al., 2009). Light gray limestones with dark gray mottles alternate with medium and dark gray spotty marlstones at the base of the section. They are overlain by gray and red limestones and marlstones of Turonian age; pink marl is 2 to 3 m above beds of OAE 2 and red limestone is 5 m above (Wagreich et al., 2009). This interval represents a duration of approximately 1.1–1.5 myr (Neuhuber et al., 2007; Scott, 2009; Wendler et al., 2009). In the lower part of the profile, the red color is restricted to marl beds whereas in the upper part of the section both marl and limestone beds are red (Wendler et al., 2009). The sediment accumulation rate of the red beds was about 3 m/myr (Scott, 2009).

The stable carbon isotopes from the Buchberg section display a broad plateau in the interval of 0–4.8 m with maximum values of +2.7% and decrease to a minimum of +1.9% at 5.4 m (Wendler et al., 2009; Fig. 20). where the general shape of the stable carbon isotopes is comparable to the Early to Middle Turonian isotope records in the other regions (Fig. 20).

### 6.2.3. Onset of the ORB9: an Early to Middle Turonian global event?

The ORB9 occurred after the OAE2 black shales in a time span of 1.1–1.5 Ma in Italy and Austria (Hu et al., 2006a; Neuhuber et al., 2007). In detail, the first reddish or pinkish beds occur at 590 kyr in Italy (Hu et al., 2006a) or about 700 kyr in Austria following OAE 2 (Wagreich et al., 2009). In the eastern Atlantic, CORB deposition began about 670 kyr following OAE 2 in ODP 641A (Scott, 2009). Wagreich et al. (2009) suggested that the coeval onset of Turonian red oxic sedimentation both in deep-ocean like the North Atlantic and in the basinal and slope environments above the CCD of the Tethys may indicate a widespread or even global change in the climate–ocean system following the OAE2 event.

### 6.3. Summary on the stable carbon isotopes during the OAE–ORB transition

The stable carbon isotope signature of the OAE 1a–ORB1 transition shares some similar characters with the OAE 2–ORB9 transition (Fig. 21). The $\delta^{13}C$ values show a prominent carbon positive excursion during the OAEs, they either stay in an isotopic plateau (the C7 stage of Menegatti et al., 1998 or Low-woollgari–Glynde transition of Jarvis et al., 2006), or return to the pre-OAE values (Fig. 21). The abrupt decrease of $\delta^{13}C$ above OAE 2 is about 2.5 m stratigraphically above the first occurrence of the ORBs at the Vispi Quarry section. In the Buchberg section, the occurrence of the ORBs correlates to the onset of the abrupt $\delta^{13}C$ decrease (Fig. 20). The abrupt $\delta^{13}C$ decreases after OAE 1a occurs a few meters above the first occurrence of the oceanic red beds at the Gorge a Cerbara section. At the Venicesihlar section, the ORBs correlate to the C9 stage with carbon isotopic minimum values (Fig. 19). A scientific question is: Does the occurrence of the ORBs contribute to the abrupt $\delta^{13}C$ decrease following the OAEs? We believe that during the formation of the ORBs, when the sediment–water interface regains oxic conditions due to either greater content of dissolved oxygen or low productivity, organic carbon burial during the ORBs would greatly decrease. The gradual diminishing of organic carbon burial could result in a gradual decrease in carbonate $\delta^{13}C$ values, as more $^{12}C$-bearing organic matter was delivered to the hydrosphere–atmosphere reservoirs and was not preserved in the sediments, which would be recorded in the coeval carbonates.

### 6.4. Model for the OAE–ORB transitions

Wang et al. (2011) proposed a hypothesis that deposition of the CORBs was a possible consequence of Cretaceous OAEs. Enhanced amounts of organic carbon and pyrite burial during the OAEs would have resulted in a large and abrupt fall in atmospheric CO$_2$ concentration (Arthur et al., 1988). For example, the OAE 2 would lead to a profound decrease (26% to 40–80%) in atmospheric pCO$_2$ (Kuyper et al., 1999; Barclay et al., 2010). The decrease in pCO$_2$ probably induced significant global climatic cooling. But, it is still not known for how long the decrease in pCO$_2$ and global climatic cooling would last as a result of enhanced burial of organic carbon. Recently, a remarkable large cooling (5–11 °C) was discovered within OAE 2 interval, which was interpreted to be a response to the associated pCO$_2$ drop (Sinninghe Damsté et al., 2010). They argued that the response of pCO$_2$ drop and climatic cooling to enhanced burial of organic carbon during OAEs are probably concurrent and relatively short in time. Another view focused on the relatively long time after the OAEs. For example, the Late Aptian after the OAE 1a and the Middle to Late Turonian after OAE 2 are in fact considered two cold snaps during the greenhouse Cretaceous. Direct evidence for the Late Aptian global cooling is indicated by occurrences of glendonites and ice-rafted debris in the Canadian Sverdrup Basin, the West Svalbard Basin and in southeast Australia (Frakes et al., 1995). Isotopic evidence for a cool Late Aptian includes data from south temperate belemnites, glendonites (De Lurio and Frakes, 1999) and carbon isotopes (Weissert and Lini, 1991).Recently, the Late Aptian global cooling was suggested by a decline of Tethyan calcareous nanofossils and a subsequent biogeographic expansion of species of high latitudinal affinities (Mutterlose et al., 2009). Another “cool” period during the Cretaceous is the Middle to Late Turonian, with evidence from a positive oxygen isotopic excursion in marine limestones (Voigt and Wiese, 2000), brachiopods (Voigt et al., 2004) and foraminifers (Bornemann et al., 2008). An incursion of boreal faunas (ammonites, echinoids and inoceramids) into lower latitudes (Wiese and Voigt, 2002), together with data from organic geochemical proxy (TEX$_86$) (Forster et al., 2007), and data from the Late Turonian sequence on the eastern U.S. continental shelf and elsewhere represent sea level fall of 25–30 m that may be related to glacio-eustasy (Miller et al., 2003). Moreover, Bornemann et al. (2008) suggested that short periods of glaciation existed during Middle Turonian, with ice sheets of about half the size of the modern Antarctic ice cap. However, other factors such as tectonics could have lead to sea-level fall. We also note that one of the possible mechanisms for global cooling after the OAEs would be the general reduction in seafloor volcanic activity (Larson, 1991).

Global cooling would have enhanced formation of cold deep water, increasing its oxidizing capacity due to the greater content of dissolved oxygen. Furthermore, enhanced organic carbon burial during the Cretaceous OAEs would result in an equal addition of O$_2$ to the atmospheric oxygen reservoir, assuming a CO$_2$–to-O$_2$ photosynthetic ratio of 1:1 (Arthur et al., 1988, p.716). This would also have increased the oxidation potential of oceanic deep water. Therefore, an increase in pCO$_2$ and global climate cooling with increased cold deep-water formation resulting from organic carbon burial during the OAEs would have increased the oxidizing capacity of oceanic deep water and promoted formation of the ORBs. As stated above,
the transition from OAE 1a to ORB1 during the Aptian took a relatively short time of 0.95–1.2 Ma in western Tethys (Italy), and 1.3 Ma in the Middle Tethys (Turkey). The transition from OAE 2 to ORB9 took about 1.1 Ma in western Tethys (Italy and Austria). This model provides an effective mechanistic explanation for the development of CORBs, but it remains speculative pending further data collection.

7. Orbital-cycle control CORBs on Blake Nose, North Atlantic

Besides long-term CORB deposition such as in the Scaglia Rossa, highly cyclic ORBs have received less attention. In recent decades, high-frequency cycles consisting of CORBs have been widely recognized in the Tethyan Ocean, North Atlantic, South Atlantic, Indian Ocean, and Pacific Ocean (MacLeod et al., 2001; Hu et al., 2006a; Neuhuber and Wagreich, 2009; Wang et al., 2009; Wendler et al., 2009; Li et al., 2011). Below we describe this type of CORB cored on the Blake Nose of the North Atlantic as an example.

7.1. Data

Cycles 30–50 cm thick in ODP1050C (Blake Nose) Maastrichtian core (Core 16-2R) are defined by gradational color alternations between light grayish green and reddish brown (Fig. 22), which were interpreted as representing the ~21 kyr precessional signal (Norris et al., 1998), MacLeod et al. (2001) found that high planktonic δ18O values in the green intervals are correlated with high planktonic but low benthic δ18O values (Fig. 22), indicating that cooler and/or more saline surface waters were associated with higher productivity. The green intervals with higher productivity are also characterized by high CaCO3 concentration, as well as enrichment in feldspar and kaolinite (Fig. 22). Conversely, the reddish intervals are interpreted to have low-productivity, and together with low planktonic δ18O values indicate warm and/or less saline surface waters, high Fe and Ti concentrations, and enrichment in quartz, illite, and chlorite (Fig. 22). Potential forcing mechanisms for covariation of these properties found in the Maastrichtian ODP1050C include cyclic variation in water column stratification, variation in continental nutrient and detrital fluxes, and changes in the intensity of upwelling (MacLeod et al., 2001).

The Albann sediments encountered on the Blake Nose in ODP 1049C (Core 12X) in the Microhedbergella rischi planktonic foraminiferal zone (e.g. Huber and Leckie, 2011) are characterized by high-frequency cycles consisting of oceanic, brown and white calcareous claystone. This interval is composed of five cycles of brown and white beds that are based on magnetic susceptibility (Li et al., 2011). The thicknesses of the cycles (from top to bottom) were 580, 420, 650, 320, 310 mm, which correspond to cycle durations of 99, 71, 111, 54, 53 ka, respectively. These durations are based on a sedimentation rate of 5.88 mm/ka for the Albann part, which is derived from palaeomagnetic data and astronomical cycles (Ogg et al., 1999). The lowest durations are comparable to the 53.6 ka cycle of the weak obliquity of the Earth's axis, and the highest are comparable to the 85–140 ka cycle of the short eccentricity of Milankovitch cycles.

Based on the study of the Albann sediments in the Core 12X of Hole 1049C by Han et al. (2008) and Li et al. (2011), we summarized characteristics of the brown–white cycles as follows (Table 2): (1) clay mineral contents as well as Al2O3 and SiO2 contents are higher in red than in white beds (Fig. 23). This may indicate that terrigenous input was stronger in the brown beds than in the white beds. (2) Albann brown beds contain an average hematite value of 0.51% and an average goethite value of 0.58% (Fig. 23). The white beds contain neither hematite nor goethite. The color of ORBs from the Albann ODP1049C is mainly controlled by hematite that imparts a red color to sediment and goethite that imparts a bright yellow color (Li et al., 2011). (3) CaCO3 contents are higher in the white beds (58% on average) than in the brown beds (21% in average. Fig. 23). The Ba/Al value is considered to be a palaeoproductivity proxy (e.g. Dymond et al., 1992), and is higher in the white beds than in the red beds. Thus the brown beds may have resulted from low primary productivity that may have produced anoxic environment during deposition.

7.2. Model

During the deposition of brown beds, low primary productivity would result in low organic carbon flux into the sediments, which would reduce oxygen demand and produce an oxidizing early diagenetic condition (Fig. 24A). In such anoxic environment, iron oxides will form. Low primary productivity is expected to be associated with low CaCO3 production and low Ba content, as well as high contents of clay minerals and the terrigenous-related elements of Al, Si, K, and Na, which represent high terrigenous input. During the deposition of white beds, low terrigenous input and relatively high primary productivity are expected to be associated with high CaCO3 and Ba contents and low contents of clay minerals (Fig. 24B). In such a condition, organic carbon flux into the sediments would be relatively high, which would result in relatively reducing conditions, thus neither hematite nor goethite would form.

8. CORBs and the Cretaceous ocean and climate

Lower Cretaceous (Berriasian–Barremian) ORBs are known from rare outcrops (Greenland, Northern Calcareous Alps of Austria, Cismon of northern Italy, and in the eastern Indian Ocean only from site DSDP 261). Generally, the Early Cretaceous was regarded as a relatively cool climate possibly with transient glaciations (Price et al., 2000). Recently, the TEX86 palaeotemperature proxy suggested that Early Cretaceous sea-surface temperatures exceeded 32 °C at 15°–20°N, 26 °C at 53°S (Littler et al., 2011) and 26°–30 °C at 60°–70°S (Jenkyns et al., 2011). These temperatures substantially exceed modern temperatures at equivalent latitudes, and are incompatible with the notion of cooler conditions in the earliest Cretaceous.

Mid-Cretaceous (Aptian–Cenomanian) ORBs are well exposed in the remnants of the Tethys Ocean, Atlantic Ocean and Pacific Ocean as well as in the Indian Ocean (Wang et al., 2009). After the Early Aptian OAE1a, red or brown clays, marls, and limestones became more geographically widespread. Consequently Late Aptian is thought to mark the onset of global CORB deposition. Mid-Cretaceous CORBs commonly occur as discrete thin beds (named ORB1 to ORB8) with short durations of hundreds of thousands years (Hu et al., 2006a), except for ORB1, which was 5.12 myr in duration in central Italy. The greenhouse climate of the mid-Cretaceous was likely related to major global volcanism and associated outgassing of CO2. OAEs may be recognized as a negative feedback in response to sudden warming episodes preventing further acceleration of warming through the removal of organic carbon from the ocean–atmosphere (CO2), via increased productivity cycle, with organic carbon being buried in the deep ocean. However, the presence of oxic sediments (CORBs) in transition zones between individual OAEs indicates development of longer cooling-climate periods, and therefore sharp swings in the mid-Cretaceous climate. Hay (2008) proposed that the ocean structure would be very different during the Cretaceous if there were no ice at the poles. He stated that the only steady ocean currents would have been those of the equatorial systems, forced by the constant easterly wind. At mid and high latitudes the ocean would have been filled with eddies. Without polar ice, about half of the entire ocean surface would have almost the same density, and that the density of the ocean surface would approximately be the same as the density of the deeper ocean. Under these conditions, storm and wind-generated eddies could pump water up and down. Through the changes in ocean salinity by evaporation and precipitation in different climate modes, the ocean circulation may be changed accordingly, which could explain the frequently changing redox conditions during the mid-Cretaceous as...
evidenced by the repeated changes from black shales to red beds in the deep ocean.

The Upper Cretaceous (Turonian to Maastrichtian) ORBs were globally deposited in the Tethyan, Indian, Atlantic and Pacific oceans, even much wider than the mid-Cretaceous CORBs. The global occurrence of the Upper Cretaceous ORBs indicated that bottom waters were well-oxygenated with high dissolved oxygen, as supported by morphologic characteristics of benthic foraminifera in the global ocean (Kaiho, 1994). Besides well-oxygenated deep water, several other processes may have contributed to the formation of CORBs. During the Late Cretaceous, bio-available phosphorus was at a low level (Follmi, 1996), which may have resulted in lower productivity. Most of the organic carbon exported from the photic zone to the deeper waters was oxidized and only a small amount was buried. The oxic, lower productivity ocean can be further explained by the global climatic–oceanic change that occurred during the Late Cretaceous Epoch. With global cooling (Huber et al., 2002) from a “hot” to a “cool-” greenhouse climate during Turonian to Campanian (Clarke and Jenkyns, 1999), the equator-to-pole temperature gradient increased, progressively favoring the formation of large volumes of deep water at high-latitudes, particularly along the Antarctic margin (Otto-Bliesner et al., 2002), and increasing the turnover rates of the ocean. Opening of the deep connection between the North and South Atlantic Oceans in the Campanian allowed deep waters generated in the southern hemisphere to circulate throughout the Atlantic basin (Poulsen et al., 2001). Furthermore, widening and deepening of the passages between Antarctica, Africa, and India, and between India and Australia allowed deep waters generated along the Antarctic margin to enter the Eastern Tethys Ocean (Hay et al., 1999). The cooler high latitude deep waters introduced more oxygen to the deep ocean, so that more organic matter was oxidized, and iron oxides formed at the sediment–seawater interface. However, in some basins organic-rich muds and chalks were deposited and are now important source rocks, e.g. Austin Chalk, Niobrara Chalk, Eagle Ford/Boquillas Shale, and Maastrichtian in the Gulf of Suez, among others.

9. Perspective: Phanerozoic oceanic red beds

9.1. Distribution of oceanic red beds in the Phanerozoic Eon

Oceanic red beds have been found in nearly every period from the Cambrian to the Quaternary as mentioned as early as Galloway (1922). We compiled the distribution of the ORBs (Ca- and Al-rich oceanic red beds) mainly based on the published data and our own field investigation from China (Fig. 25 and Table 3).

9.1.1. Red shales

(1) Rhythmically bedded red and green claystones, siltstones, sandstones and conglomerates in a Cambrian flysch in Quebec Appalachians of Canada (Lajoie and Chagnon, 1973) are 12–90 m thick. The green hemi-rhythms are 7–150 m thick, and are composed of claystone with minor siltstone and sandstone beds.

(2) The Lower Cambrian marine Caerfai Bay Shale is a volcanlastic red-bed horizon in Dyfed, Wales (Turner, 1979). The red coloration was suggested to have been produced entirely by a diagenetic alteration of iron-silicates and volcanic ash in an oxidizing diagenetic environment (Turner, 1979).

(3) Lower Silurian (Middle Llandovery to Lower Wenlock) red shales and siltstones are widely distributed in the UK, Norway, Ireland, Estonia, Latvia, and Appalachian basin (Ziegler and McKerrow, 1975) where they were mainly deposited in offshore shelf marine environments. In south China (Rong et al., 2012) red shales were deposited in shallow marine environments. Ziegler and
McKerrow (1975) suggested that the red oxidized material is probably second-cycle, derived through coastal erosion of soil or alluvial complexes during marine transgression. They concluded that “the sediments are red because they were derived from oxidized source materials and were buried rapidly in quiet marine environments before they could be reduced.” Obviously this statement needs to be re-evaluated by further investigation especially in light of modern integrated provenance analysis.

(4) The Upper Devonian (mainly Famennian) red mudstones are a conspicuous facies type of the Variscan basins in Europe (Germany and England) (Franke and Paul, 1980). The environment was interpreted to be pelagic based on the study of fossils and trace fossils.

9.1.2. Red carbonates

Up to now, at least twelve stratigraphic levels of oceanic red limestones are known in the Phanerozoic Eon (Table 3).

(5) Red Lower Cambrian carbonate buildups in the Flinders Ranges are composed of two facies: low-energy, archaeocyath-sponge-spicule mud mounds, and high-energy, archaeocyathocalcimicrobe (calcified microbial microfossil) bioherms (James and Gravestock, 1990). Mud mounds are composed of red carbonate mudstone and floatstone with stromatactis and abundant sponge spicules that form structures up to 150 m wide and 80 m thick. Bioherms are either red or dark gray limestone forming isolated small structures 2–20 m in width.

Fig. 25. Field photos of Phanerozoic Eon oceanic red beds. (A) Red limestone of the Gunian Formation, Middle Ordovician, Shitai County, Anhui Province, China; (B) red nodular limestone of the Podona Formation, Upper Ordovician, Jiange County, Sichuan Province, China (photo by Prof. Dr. Mingcai Hou); (C) red limestone with stromatolites (sponge cavities), Frasnian (Upper Devonian), Les Bulants quarry, Neuville, Belgium (photo by Prof. Frédéric Boulvain); (D) red nodular limestone in the Nanlinghu Formation, Olenekian (Lower Triassic), Caohu, Anhui Province, China (photo by Dr. Kuidong Zhao); (E) red nodular limestone of the Ammonitico Rosso Formation (Upper Jurassic) near Gubbio, Italy. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
Phanerozoic oceanic red beds other than the Cretaceous oceanic red beds.

Table 3

<table>
<thead>
<tr>
<th>Lithology</th>
<th>No</th>
<th>Period</th>
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<td>to Eocene</td>
<td>Central Italy</td>
<td>Note</td>
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<td>Oligotrophy, iron oxidation</td>
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<td>Nodula</td>
<td>Pelagic</td>
<td>in oxic environment</td>
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<td>Northern Spain–Baleas Lm</td>
<td>Stromatactis</td>
<td>Shallow to carbonate slope</td>
<td>Iron–bacterial mediation</td>
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<td>Quebec Appalachians</td>
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<td>Stromatactis</td>
<td>Shelf</td>
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<td>Offshore marine;</td>
<td>Marine transgression;</td>
<td>Marine transgression;</td>
<td>Ziegler and McKerrow (1975); Tong et al. (2012)</td>
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<td>Early</td>
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<td>Marine</td>
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<td></td>
<td>Canadian Quebec Appalachians</td>
<td>Flysch type</td>
<td>Deep marine</td>
<td>Rapid resedimentation</td>
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(6) The Middle to Upper Ordovician reddish nodular limestones are widely distributed in the south China Yangtze area, from Sichuan to Zhejiang provinces and are over 1500 km long (Zhang, 1996; Zhan and Jin, 2007) (Fig. 25A). The Guniutang Formation consists of reddish to purple and gray nodular and bedded limestones about 20 m thick (Zhang, 1996). The Pagoda Formation is about 10–20 m thick and dominated by light purple–reddish thin-to-thick bedded limestones (Fig. 25B). One of its typical characters is the polygonal reticulate structure that is widely developed in the Pagoda Formation, and its origin is greatly debated. These Upper Ordovician red limestones also crop out near Prague, Czech Republic. Normally they are lenses-shaped and deposited in an inner ramp environment (see van der Kooij et al., 2007). A total of seven red muddy, or peloidal patches or well-developed layers, rich in organic material are present on the slope of the Sierra del Cuera platform (van der Kooij et al., 2007).

(10) Carboniferous red limestones are distributed in Austria and Spain and were interpreted to be deposited in an outer ramp environment (see van der Kooij et al., 2007). A total of seven red muddy, or peloidal patches or well-developed layers, rich in organic material are present on the slope of the Sierra del Cuera platform (van der Kooij et al., 2007).

(11) In the Sanandaj–Sirjan Province of Iran, the 18 m thick uppermost Permian is reddish argillaceous limestones with characteristically nodular texture and pelagic ammonites and conodonts (Heydari et al., 2003). These red limestones were deposited in pelagic, deep-water, below storm wave base.

(12) The Lower Triassic (Olenekian stage, Spathian substage) red thin bedded and partly nodular limestones are 10–20 m thick in the Anhui Province, southeastern China (Tong et al., 2001) (Fig. 25E). In southwestern Tibet along the Yarlung Zangbo suture zone Lower Triassic red nodular limestone (Fig. 25D) is over 100 m thick and was deposited in a deep-water environment (Guo et al., 1991).

(13) Lower Jurassic red stromatactis limestone in Switzerland (Neuweiler and Bernoulli, 2005) forms a massive sublithofacies and is enclosed in a mold–shaped, brachiopod–rich bioclastic limestone. The thickness ranges from several tens of centimeters to several meters and limestone patches are lense–to–mound-shaped with gradational contacts.

(14) A Middle Jurassic red stromatactis mud-mound is in the Czorsztyn Unit of the Pieniny Klippen Belt (Western Carpathians, Slovakia) (Aubrecht et al., 2002).

(15) Perhaps the most famous red limestone is the Jurassic Ammonitico Rosso, which is well known for its nodular
structure, the presence of ammonites and the world-wide distribution as an ornamental stone. The Ammonitico Rosso facies are widely distributed in Tethys, such as in Spain, Italy, Switzerland, Austria, Czech, Poland, Yugoslavia, Hungary, Bulgaria, Romania, Morocco, Algeria, Greece, Turkey (Cecca et al., 1992), as well as in the central Atlantic. The Ammonitico Rosso is a stratigraphically condensed pelagic facies and consists of the Middle to Upper Jurassic to basal Cretaceous red pelagic limestones, commonly nodular and rich in ammonites (Martire et al., 2006) (Fig. 25f). The Ammonitico Rosso was deposited in a pelagic deep-marine environment probably near the CCD, which resulted in the formation of the nodular structure at the early diagenetic stage (Jenkyns, 1974). Martire (1996) suggested that sediments accumulated at a very slow sedimentation rate (−3 mm/ka, even after decomposition and taking into account multiple hiatuses). However, Prêat et al. (2006, 2011) reported calcite and ferruginous microfilaments of different shapes and sizes from the Ammonitico Rosso in Italy and they attributed the red color to the presence of hematite (former iron oxo-hydroxides), which resulted from the mediation of iron bacteria at the poorly dysoxic–anoxic sediment–water interface. The isotope δ56Fe (Prêat et al., 2008) is systematically lighter in the red facies than in the gray facies.

(16) It is important to point out that many of the CORBs extend into the Palaeogene, such as in central Italy where the reddish facies of the Scaglia Rossa range from the Cretaceous to as young as Late Eocene. Therefore, Palaeogene ORBs are present.

9.2. Late Cenozoic red clays

Late Cenozoic red clays, one example of the ORBs, were discovered during the Challenger Expedition (1872–1875) and cover approximately 31% of the world’s ocean basins or about 20% of the total surface of the Earth (Bryant and Bennet, 1988). Red clays constitute up to 49%, 26%, and 25% of the sediments of the Pacific, Atlantic, and Indian Oceans, respectively (Anderson, 1986). The red clays in the Pacific Ocean were studied in detail, being often used as a model for other marine red sedimentsary deposits. Generally, the red clays represent the residual sediment type formed in deep-sea areas of low biological productivity occurring below the CCD where terrigenous input is low. Red clay generally has a grain size of about 1 μm, a CaCO3 biogenic content <15%, net bulk density of 1.35–1.40 g/cm^3, water content of 125%, porosity of 75–80%, and sedimentation rate of <1 mm/ka (McCoy and Sancetta, 1985; ~0.45 mm/ka by Gleason et al., 2002). The most abundant mineralogical components of red clays from the North Pacific Ocean are authigenic and detrital smectite, aeolian shale clasts of ilite, kaolinite, and chlorite, and in variable proportions, quartz, feldspar, zeolite, and authigenic metal oxides (Bryant and Bennet, 1988). The average mineralogical composition of pre-Miocene red clays in the northwest Pacific is illite 25%, smectite 55%, kaolinite and chlorite 9%, quartz 5%, feldspar 1.5%, pyrolusite 0.5%, and amorphous material 4% (Bryant and Bennet, 1988).

The most important contribution to the allgenic fraction of modern red clays in the Pacific is aeolian dust, which is mainly derived from Asia, Australia, and Central America (Glasby, 1991). Besides aeolian input, authogenic aluminosilicates and volcanic debris were found in the chemically post-extraction, residual component in the Late Cenozoic red clays in the central Pacific (Ziegler et al., 2007). A number of elements are enriched in the Pacific red clays including Mn, Co, Cu, Ni, and Fe, which occur as authigenic fractions such as Fe and Mn oxides (Glasby, 1991). Red clays form in regions of low sedimentation rates where rates of organic matter deposition are very low (Lyle, 1983). In such circumstances, where bottom water is under well-oxidizing conditions, diffusion of oxygen into the sediments exceeds its consumption during the degradation of organic matter (Glasby, 1991). Iron is therefore present in the sediments dominantly in the trivalent state and reduction of nitrate in the pore waters by organic carbon does not occur (Sawlan and Murray, 1983). The sediments therefore remain brown throughout the length of the sediment column, and elements such as Mn, Co, Cu, and Ni are enriched in the authigenic fraction of the sediment (Glasby, 1991).

9.3. Origin of Phanerozoic marine red beds

During the past decades, numerous authors dealt with continental red beds and concluded that the red coloration commonly is due to breakdown and oxidation of iron-bearing minerals (e.g., van Houten, 1973). However, the origin of the ORBs and their geological significance remained a great debate. Galloway (1922) thought that some marine red beds resulted by telogenic (post-sedimentary) superficial alteration. He stated that “red limestones were not originally red, but in all cases are due to atmospheric weathering”. A good example is the Lower Carboniferous Redwall Limestone in the Grand Canyon, USA in which the overlying Pennsylvanian red arenites provide iron oxides that superficially cover the face of the outcrops (McKee and Gutschick, 1969). Obviously this origin model cannot apply to the ORBs. Up to now, three different hypotheses have been proposed to explain the origin of red pigmentation of limestones and shales with the following possible scenarios.

9.3.1. Detrital origin of the iron derived from continental weathering

Lajoie and Chagnon (1973) studied rhythmically red and green claystones in a Cambrian flysch sequence, Quebec Appalachians of Canada, and suggested that the red detritus was derived from an oxidizing, paralic environment, and was directly and rapidly transported into the basin. Similarly, Ziegler and McKerrow (1975) suggested that a plentiful supply of oxidized iron from land into sea was the main origin for the red color of Silurian marine red beds in Western Europe and in the Appalachian Basin. They related this process to the Llandovery marine transgressions. Franke and Paul (1980) suggested that hematite enrichment of the clay fraction was derived from land and imparted a red coloration to the Devonian red shales in Germany. They stated: “As nearly all fine-grained terrigenous sediments contain several percentages of ‘free’ ferric iron, the minimum of 1.5% hematite required for red coloration is easily achieved. Hence, all claystones and silty claystones are potentially red.” However, as documented from the Cretaceous deep-water red shales intercalated with turbiditic beds in the Gosau Group in Austria, the red shales represent as a normal background sedimentation with relatively low sedimentation rates, while the gray shales would be the results of turbiditic currents with high sedimentation rates (Wagreich and Krenmayr, 2005).

9.3.2. Iron-bacterial mediation at the time of sedimentation

This hypothesis involves the mediation of iron bacteria near the water–sediment interface during sedimentation and is applicable to a number of marine limestones of different ages (see review by Mamet and Prêat, 2006 and reference therein). Iron (II)–oxidation occurs in microaerobic or anoxic environments as a result of the activity of microorganisms that oxidize Fe(II) to generate energy for growth (Mamet and Prêat, 2006). The products of biologically oxidized iron are highly insoluble ferric oxide minerals (normally hematite), which are sub-micrometric and occur in the matrix of limestones (Mamet and Prêat, 2006; Prêat et al., 2011).

9.3.3. Iron oxidation in oligotrophic, highly oxic environment

The reddish limestones of Cretaceous Scaglia Rossa in Italy were suggested to be deposited over several decades in an oxic environment (Arthur and Fischer, 1977). The reddish Scaglia Rossa strata are regularly bedded and are in conformable contact with the underlying whitish-colored strata. Within a single red limestone bed the red color of individual limestone beds is generally uniform, but in other beds the color changes from white to pink and red.
from bottom to top (Hu et al., 2006a). These characters indicate that the red color of the Scaglia Rossa most probably resulted from synsedimentary or early diagenetic processes. Furthermore, the red Scaglia Rossa limestones are enriched in hematite and depleted of redox-sensitive and nutrient-like trace elements, but the terrigenous fraction is nearly the same as in white limestones (Hu et al., 2009a). These factors indicate that the Scaglia Rossa red limestones were deposited under highly oxic, oligotrophic, and probably low-productivity conditions (Hu et al., 2006a, 2009a, 2009b). Palaemagnetic properties of the Upper Cretaceous Scaglia Rossa red pelagic limestones support this interpretation (Channell et al., 1982). The boundaries of palaeomagnetic reversals defined by hematite are a few tens of centimeters below those of magnetite. Therefore, they interpreted that hematite grains were magnetized in the post-reversal field, which demonstrates that growth of hematite crystals occurred over ~10^5 years during early diagenesis.

Hematite platelets of the Upper Cretaceous pelagic red sedimentary rocks in Turkey are hexagonal in shape and grew epitaxially on the grains, strongly suggesting an early diagenetic origin (Eren and Kadir, 1999). A similar origin was suggested for CORBs in other areas (see Hu et al., 2005; Wagreich et al., 2009; Wang et al., 2009).

Field investigations confirmed that CORBs are not the products either of superficial alteration or detrital origin derived from land (see Hu et al., 2009a; Wagreich et al., 2009; Wang et al., 2009). The consistent interlamination of red and gray facies in some CORBs on a meter-to-centimeter scale is incompatible with post-sedimentary weathering. As stated by Wang et al. (2009), CORB sedimentation was in opposition to clastic deep-water sedimentation. The general rule is that the greater the clastic input, the higher the sedimentation rate, and thus the decreased probability for CORB deposition (Wagreich and Krenmayr, 2005; Wagreich et al., 2009). Clearly some CORBs such as the Scaglia Rossa are not the products of iron-bacterial mediation because no evidence was found. However, we are very careful to say that iron-bacterial mediation may occur in some CORBs, and more work needs to be done before we can answer this question more surely.

10. Conclusion

CORBs are reddish to pinkish to brownish sedimentary rocks deposited in pelagic marine environments (Hu et al., 2005; Wang et al., 2009). Geochemically, the CORBs can be classified into three end members: Ca-CORBs, Al-CORBs, and Si-CORBs by CaO, Al2O3, and SiO2 values. Ca-CORBs have CaCO3 contents of 48–95%, Al2O3 values of 1–10% and SiO2 values of 3–30%. Al-CORBs have CaCO3 contents of 1–22%, Al2O3 values of 7–20%, SiO2 values of 42–70%. Si-CORBs have CaCO3 contents of 0.2–1.4%, Al2O3 values of 1–4%, SiO2 values of 86–96%. Outer shelf to upper/middle bathyal CORBs are mainly red pelagic limestones (Ca-CORBs). Towards deeper bathyal depths, red marls and marly shales become the dominant lithology/facies type. Below the calcite compensation level, in abyssal depths, either red marls and marly shales become the dominant lithology/facies red pelagic limestones (Ca-CORBs). Towards deeper bathyal depths, the Milankovitch cycles.

Hematite, goethite and Mn2+—bearing calcite are the minerals that impart the red color to CORBs. Hematite and goethite are responsible for brown and orange colors from the Albanian–Aptian sediments from the ODP 1049C. Hematite clusters in several to tens of nanometers in the calcite structure is the main reason for the red coloring of limestones, and manganese-bearing calcite may give additional red color to limestones in the Visp Quarry. Goethite was suggested to be originally formed together with hematite, but was subsequently transformed to hematite during late diagenesis. The red color of shales from the Chuangde section resulted from hematites of a different grain size, ranging from several tens of nanometers to several tens of microns in size.

Elemental geochemical data indicated that red limestones have a similar composition of detrital input-sensitive elements (Al, Ti, K, Mg, Rb, Zr), higher content of Fe2O3, and depleted redox-sensitive elements (V, Cr, Ni, and U) and micronutrient elements Cu, Zn compared to white limestones, indicating a similar provenance source and a more oxic condition at the sediment–water interface. Red shales are comparable to the Average Shale (Wedepohl, 1971) in terms of elements. Compared to the gray shales, the red shales have higher Fe2O3, lower Mn and lower Ba contents, with similar detrital input-sensitive elements indicating a stable terrigenous input. The color change between the gray or white and red shales was caused most probably by the variation of redox bottom conditions in the deep ocean.

Detailed studies of the stratigraphic transitions from OAE1a–ORB1 and OAE2–ORB9 lead to the hypothesis that deposition of the CORBs was a possible consequence of the Cretaceous OAEs (Wang et al., 2011). Enhanced amounts of organic carbon and pyrite burial during the OAEs would have resulted in a large and abrupt fall in atmospheric CO2 concentration, which probably induced significant global climatic cooling after the OAEs. Global cooling would have enhanced formation of cold deep water, increasing its oxidizing capacity due to the greater content of dissolved oxygen and would promote formation of the ORBs. As we stated above, the transition from OAE1a to ORB1 during the Aptian took a relatively short time from 0.95 to 1.2 Ma in western Tethys (Italy), and 1.3 Ma in Middle Tethys (Turkey). The transition from OAE2 to ORB9 took about 1.1 Ma in western Tethys (Italy and Austria). The stable carbon isotope signature of the OAE1a–ORB1 transition shares some similar characters with the OAE2–ORB9 transition. Generally, the δ13C values show a prominent carbon positive excursion during the OAEs, they either stay in an isotopic plateau, or return to the pre-OAE values. We suggest that the occurrence of the ORBs would contribute to the abrupt δ13C decrease following the OAEs, as in oxic conditions during the formation of the ORBs, organic carbon burial would be greatly decreasing.

Data from the ODP Leg 171B (Holes 1049C and 1050C) indicate that during the deposition of the Albanian and Maastrichtian reddish intervals, low primary productivity and relatively high temperature would result in low organic carbon flux into the sediments, which would reduce oxygen demand and produce an oxidizing early diagenetic condition. In such an oxic environment, iron oxides will form. Low primary productivity is expected to be associated with low CaCO3 production and low Ba contents, as well as high contents of clay minerals and the terrigenous-related elements of Al, Si, K, and Na, which represent high terrigenous input.

ORBs were found in nearly every period from Cambrian to Quaternary. We compiled the distribution of the known ORBs (5 localities of red shales including the Late Cenozoic red clays and 12 localities of red limestones, to our knowledge), which indicated that the ORBs are not only found in the Cretaceous, but the whole Phanerzoic. Different hypotheses can be considered to explain the origin of the red pigmentation of limestones and shales including (1) detrital origin of the iron derived from continental weathering; (2) iron-bacterial mediation at the time of sedimentation; and (3) iron oxidation in oligotrophic, highly oxic environment. Abundant field and laboratory evidence support the conclusion that CORBs were deposited under highly oxic, oligotrophic conditions with probably a low sedimentation rate.

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References


