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Geochemistry of Cretaceous Oceanic Red Beds — A synthesis

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ABSTRACT

This paper summarizes the geochemistry of Cretaceous Oceanic Red Beds (CORBs), their depositional conditions and their significance in reconstructing marine environments. We report major and minor element compositions of carbonate, clayey, and siliceous CORBs and compare these with average element compositions of carbonates, deep sea carbonates, deep sea clays, and average shale compositions. Element distributions in carbonate CORBs are mostly similar to average carbonate compositions. In particular, Sr concentrations are more comparable to average carbonates than deep sea carbonate Sr concentrations. Clayey CORBs are high in Al, Ti, K, and Fe. Their minor element compositions are more similar to average shale than deep sea clay, which generally has higher values in minor elements. In comparison, siliceous CORBs have at least two times lower Al but higher Si concentrations than clayey CORBs. We further speculate on possible reactions involved in iron mobilization and CORB formation.

1. Introduction

The Late Cretaceous was a greenhouse period with considerable sea level changes and tectonic compression in the Tethyan belt that resulted in opening and closing of ocean basins (Stampfli et al., 2002; Wagreich and Faupl, 1994). A major characteristic of the Late Cretaceous global change was the evolution from anoxic to predominantly oxic conditions in the oceans which took place after the last global oceanic anoxic event OAE 2 (Hu et al., 2005).

This global climate change was a result of variations in the operating mode of various earth processes such as changes in palaeoceanography and palaeocirculation (e.g. Friedrich et al., 2008; Hay, 2008, 2009; Puceat et al., 2005), changes in palaeoproductivity (nutrient distribution, e.g. Neuhuber et al., 2007), tectonic processes (opening and closing of major seaways, migration of continental plates and subduction or expansion of ocean basins, e.g. Friedrich and Erbacher, 2006; Wagreich and Faupl, 1994), and climatic variations (change from greenhouse to icehouse conditions, e.g. Bice et al., 2006; Miller et al., 2005).

Periods of high primary production resulted in Oceanic Anoxic Events (OAEs) when vast amounts of organic material were buried in oceanic sediments (Larson, 1991; Pedersen and Calvert, 1990; Schlanger and Jenkyns, 1976). OAEs resulted in significant CO_2 fixation in marine sediments in the form of organic matter and can be correlated worldwide. In contrast to anoxic events, oceanic red beds were deposited under oxic conditions and are widespread and diachronous (Hu et al., 2005; Wagreich and Krenmayr, 2005) and therefore reflect a state of the ocean system rather than a distinct and short stratigraphic level like OAEs.

The most significant worldwide change from anoxia to oxic deposition with the formation of CORBs (Cretaceous Oceanic Red Beds, Hu et al., 2005; Wang et al., 2009) deposition started after the global oceanic anoxic event OAE 2 in the early Turonian (Hu et al., 2006; Neuhuber et al., 2007; Wagreich et al., 2009). In the Santonian–Campanian a peak episode of worldwide enhanced CORB deposition is recognized globally (Wang et al., 2009, 2011). These changes in the deep sea recorded by pelagic sediments are more likely to reflect an overall climatic change as opposed to shallow seas where regional and seasonal influences may be more pronounced.

New ideas on oceanic circulation proposed by Hay (2008, 2009) for the Cretaceous differ fundamentally from modern ocean circulation. Thermohaline circulation drives the sea today whereas the Cretaceous sea – due to reduced deep water formation at largely ice free poles – was probably characterized by slow vertical water exchange. The vertical and latitudinal temperature gradient was smaller compared to the modern ocean and resulted in large regional eddies (Hay, 2008).

This paper investigates the geochemistry of CORBs in detail. Based on a review of published data (Bak, 2007; Baltuck, 1982; Hikoroa et al., 2009; Jiang et al., 2009; Neuhuber and Wagreich, 2009; Neuhuber et al., 2007) we classify CORBs according to their chemical composition.

2. Material, methods and data

Cretaceous Oceanic Red Beds cover a wide range of lithologies that range from shallow water deposits (Wiese, 2009) to deposits below CCD (Wagreich et al., 2009). The sedimentology of these deposits was

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elucidated by Hu et al. (2005, 2006), Wagreich and Krenmayr (2005) and Wagreich et al. (2009), among others. Geochemical studies dealing with element distribution in CORBs include studies from Italy (Calderoni and Ferrini, 1984; Hu et al., 2009), from the Alps (Neuhuber et al. 2007; Neuhuber and Wagreich, 2009; and XRF data presented in this paper), New Zealand (Hikoroa et al., 2009), the Polish Flysch Carpathians (Bak, 2007; Jiang et al., 2009) and siliceous sediments from the Pindos Zone (Baltuck, 1982).

This paper compiles X-ray fluorescence spectrometry (XRF) data from the literature (authors previously mentioned) in different palaeogeographic settings as well as some data points from an Austroalpine Profile (Brandenberg, Austria). Table 1 gives an overview of the number of samples in each profile and their main element composition. Minor element distributions are given in Tables 2 and 3. Austrian and Italian CORBs contain significant amounts of calcium carbonate ranging between 50% and 98%. Samples from New Zealand (Manganotone section, Hikoroa et al., 2009), from the Polish Flysch (Trzemesnia section, Bak, 2007 and Mazak section, Jiang et al., 2009) are free of biogenic carbonate.

2.1. Lithology and age constraints of discussed profiles

Four profiles are set in the Tethys ocean: Vispi (Italy), Rehkogelgraben (Austria, Ultrahelvetics), Buchberg (Austria, Ultrahelvetics) and Brandenberg (Austria, Austroalpine). The Vispi section (Fig. 1) contains Scaglia Rossa limestones of Turonian age. Sediments from Buchberg and Rehkogel (Ultrahelvetics) are red marl — limestone cycles of Turonian (Buchberg) and Santonian (Rehkogelgraben) age. Brandenberg was situated at the active margin of the Austroalpine microplate (Fig. 1). Both sections at Karpenision and Plaka from the Pindos ocean cover red marlstones of Santonian age. The Manganotone section consists of Turonian mudstone deposited on a passive continental margin. The variegated shales from the Polish Flysch Carpathians in Trzemesnia are of early Turonian age and those of the Mazak section of Cenomanian age.

2.2. Data presentation

Wagreich et al. (2009) and Wang et al. (2009) introduced a classification of CORBs with three end members: siliceous CORBs, carbonate CORBs, and clayey CORBs (Fig. 2A). This scheme is based on the classification of recent pelagic-hemipelagic sediments as calcareous ooze, siliceous ooze, and red pelagic clays (Hay et al., 1984). We plot geochemical data in a similar fashion with the end members Ca (for carbonate production) assuming negligible amounts of feldspar, Si, and Al. This representation is not directly comparable to the classification of CORBs introduced by Wagreich et al. (2009), because it characterizes CORBs according to their chemical composition.

3. Compilation and discussion of geochemical data

3.1. CORB geochemistry worldwide

The comparison of bulk XRF was fit to the three end members: calcium, silica, and aluminium. Al concentrations never reach the average shale value (Turekian and Wedepohl, 1961) of 50% but range around 25%. The average composition of deep sea carbonates (Turekian and Wedepohl, 1961, DC, Fig. 2) lies below the values of the Vispi Quarry (Hu et al., 2009). Average values from Manganotone (New Zealand) and from the Pindos Zone (Greece) plot a little above 75% Si but samples from the Pindos are higher in Ca (Fig. 2). Three sections are virtually free of Ca: Manganotone (New Zealand), Trzemesnia (Polish Flysch) and the Mazak section (Flysch, Czech Republic). Deposition below CCD of these siliceous clays and the distal deposition without any Ca-bearing minerals such as plagioclase is the reason for this depletion. These three sections plot in the vicinity of

Table 1
Bulk composition: average main element distribution in CORBs.

Section	Author(s)		n	Al		Ca		Si	
				Avg	Stdev	Avg	Stdev	Avg	Stdev
Manganotone	Hikoroa et al., 2009	Clayey CORB	7	119.3	6.6	9.3	7.7	304.0	4.3
Trzemesnia	Bak, 2007		13	90.8	7.1	5.3	0.5	305.3	7.8
Mazak	Jiang et al., 2009		16	101.5	7.3	3.6	1.4	315.9	7.2
Karpenision	Baltuck, 1982	Siliceous CORB	2	46.2	16.2	77.0	96.5	248.2	36.1
Plaka	Baltuck, 1982		4	4.8	3.2	89.3	167.8	343.7	180.2
Vispi	Hu et al., 2009	Carbonate CORB	20	0.3	0.1	379.4	8.3	16.2	6.2
Rehkogel	Neuhuber and Wagreich, 2009		4	45.8	4.6	234.8	18.2	122.7	12.9
Buchberg	Neuhuber et al., 2007		7	46.2	10.3	225.3	30.4	133.9	22.3
Brandenberg	this work		4	55.1	6.0	192.9	22.6	124.8	9.6
Avg shale	Turekian and Wedepohl, 1961	Al end member		80		22.1		73	
Avg carbonate		Ca end member		4.2		302.3		24	
Deep sea carbonate		Ca end member		20		312.4		32	
Deep sea clay		Si end member		84		29		250	

Section		n	Fe		K		Mg		Mn		Na		P		Ti	
			Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev
Manganotone	Clayey CORB	7	66.9	10.9	53.1	5.2	12.4	0.4	0.5	74.3	26.3	1.0	1.0	0.1	4.1	0.5
Trzemesnia		13	47.0	13.8	37.4	4.0	9.8	0.6	0.3	0.3	3.5	0.4	0.4	0.1	3.2	0.3
Mazak		16														
Karpenision	Siliceous CORB	2	53.6	33.4					1.7	0.1					2.9	1.7
Plaka		4	3.7	2.0					0.6	0.6					1.4	2.2
Vispi	Carbonate CORB	20	1.8	1.0	1.9	0.5	2.3	0.2	0.5	0.1	0.3	0.1	0.2	0.1	0.1	0.0
Rehkogel		4	22.0	2.9	12.2	1.7	7.0	0.8	0.4	0.0	1.7	0.4	0.3	0.0	1.9	0.2
Buchberg		7	19.5	6.9	10.9	3.4	7.7	1.2	0.3	0.1	1.9	1.1	0.5	0.2	2.0	0.5
Brandenberg		4	35.8	4.5	30.8	2.1	28.2	7.8	0.7		3.5	1.2	0.3	0.1	1.8	0.3
Avg shale	Al end member		47.2		26.6		15		0.85		9.6		0.7		4.6	
Avg carbonate	Ca end member		3.8		2.7		47		1.1		0.4		0.4		0.4	
Deep sea carbonate	Ca end member		9		2.9		4		1		20		0.35		0.77	
Deep sea clay	Si end member		65		25		21		6.7		40		1.5		4.6	

n = number of samples.
All data are XRF data in mg/g.