Estuarine, Coastal and Shelf Science 81 (2009) 83–93

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Iron geochemistry under mussel rafts in the Galician ria system (Galicia-NW Spain)

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A R T I C L E   I N F O

Article history:
Received 17 June 2008
Accepted 15 October 2008
Available online 1 November 2008

Keywords:
biodeposits
sediments
pyrite
reactive iron
anaerobic oxidation of methane
diagenesis
ria

A B S T R A C T

The intensive mussel culture carried out in the past 40 years in the Rias of Vigo and Arousa (Galicia-NW Spain) has led to substantial changes in the ecology and geochemistry of the seabed in these areas. Organic C enrichment of the seabed has generated strongly reducing conditions that directly affect the geochemistry of Fe and S. In the present study a total of six sediment cores were collected from the seabed under mussel rafts, and two different layers were distinguished: the biodeposit generated by the mussels, and the sediment situated immediately below this. Samples of each were analyzed to determine the pH, redox potential, sulphate and chloride in the interstitial water, as well as total percentage of organic C (TOC), N and S. Sequential extraction of the samples differentiated six fractions of Fe: exchangeable, carbonate, ferrihydrite, lepidocrocite, goethite and pyrite. The contents of total Fe, Fe associated with silicates, Fe soluble in 1 M HCl and AVS-Fe were also determined. In general, both the biodeposit and the sediment were anoxic ($Eh < 100$ mV) and there were no significant differences between the two in the total Fe or in the Fe associated with silicates, which appears to indicate that the input of Fe to the system did not vary greatly. However, there were significant differences between the sediment and the biodeposit in terms of the forms of Fe in each layer. The concentrations of pyrite in the biodeposit (0.37 ± 0.25 μmol g^{-1}) were high but significantly lower than in the sediment (1.10 ± 0.20 μmol g^{-1}), and there remained large quantities of reactive-Fe that were susceptible to pyritisation. In contrast, in the sediment, the reactive-Fe was intensively pyritised, and judging from the ratio of TOC–DOP, it limited synthesis of pyrite. Furthermore, a plot of the concentration of pyrite-S against TOC revealed an excess of ~15% of pyrite-S, which is explained by the partial decoupling of pyrite formation from organic matter accumulation, caused by the formation of pyrite from the H_2S generated by the anaerobic oxidation of methane. The latter process also appears to favour, although to a lesser extent, the precipitation of Ca carbonate, with incorporation of Fe.

1. Introduction

The forms of Fe present in marine sediments have been the subject of many studies, with special attention given to pyrite formation (see e.g. Berner, 1984; Raiswell and Berner, 1985; Oenema, 1988, 1990; Raiswell et al., 1994; Haese et al., 1997; Schenau et al., 2002; Poulton and Raiswell, 2005; Otero et al., 2005, 2006; Ferreira et al., 2007). However, very few studies have investigated the Fe forms in the special marine systems constituted by the seabed of the Galician rias, and even fewer have investigated the effects of deposition of biodeposits on these systems. From a geomorphological point of view, Galicia has one of the most complex littoral environments in the Iberian Peninsula, and the rias are the most unusual feature. The origin of the different rias is complex and has been the subject of many studies since they were first described in 1886 by Richthofen von, 1886 (for more detail see Vidal Romani, 1984; Evans and Prego, 2003). It is generally accepted that the rias are very special geological formations that exist in few parts of the world (Ireland, China, Great Britain). The rias were formed in the Tertiary era as a consequence of the reactivation of ancient hercinic faults, giving rise to tectonic sunken valleys that were later invaded by the sea (Torre, 1958). In the Rias Baixas the water depth ranges from 5 m in the inner part to 55 m in the outer zone; the mean tidal range is 2–3 m (García-Gil, 2003). From an economic point of view, the rias constitute a highly productive ecosystem as a result of coastal upwelling of deep, nutrient rich water, which generally occurs between May and September. Furthermore, Galicia is currently the main mussel producer in Europe and the second highest producer in the world after China, with a mean annual production of 250,000 tonnes (Figueiras et al., 2002). The high production is mainly concentrated in two rias, the Ria of Arousa (2282 mussel rafts) and the Ria of Vigo (~478 mussel

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doi:10.1016/j.ecss.2008.10.006

rafts) (for more detail see Figueiras et al., 2002). In these rias mussel culture is carried out on floating platforms of 500 m^2, from which some 500 ropes of 12 m length are hung, and to which the mussels attach. Previously reported alterations include an increase in sedimentation due to the trapping effect of the ropes, and also the metabolic activity of the mussels themselves, which may produce up to 129–190 kg (dry weight)/day/raft of faecal material (faeces, pseudofaeces) (Cabanas et al., 1979). Taking into account the composition of these biodeposits, this accounts for an annual input per raft of 69.3 tonnes of sediment, 5219 kg of C, 620 kg N and 979 kg of Fe to the seabed (Cabanas et al., 1979; Collazo and Pascual, 1997). Furthermore, intense changes are produced in the biogeochemical conditions of the sediments located below the rafts. Studies of the composition of the mussel biodeposits have shown that they comprise a material of fine texture, which is relatively rich in C and N. The presence of the biodeposits results in changes in the metabolism of the benthic community, and the seabed is transformed into an anoxic environment; mineralisation of organic matter is stimulated by sulphate reduction processes, and there is an increase in substances that are toxic to benthic organisms (e.g. H_2S); these cause significant changes in the benthic community (Tenore et al., 1982; Otero et al., 2006). Some authors therefore believe that mussel culture is the human activity that has the greatest impact on the natural cycling of elements and on the ecology of the rias, and modifies practically all of the seabed in the Rias of Arousa and Vigo (Tenore et al., 1982; Figueras, 1989; Otero et al., 2006).

These findings indicate that the conditions existing under the mussel rafts result in an unusual geochemical environment that provides a good opportunity to study the diagenetic processes involving C, S, Fe and trace metals. Despite this, very few studies have been made of these environments (Emiroglu et al., 2004; Otero et al., 2005, 2006; Prego et al., 2006). The aim of the present study was to provide further knowledge of the geochemical behaviour of Fe in relation to C and S. For this, the total content of these elements was analyzed and a sequential extraction of Fe was carried out, in which exchangeable, carbonate, easily reducible (ferrihydrite), reducible (lepidocrocite), and goethite and pyrite fractions were distinguished. The Fe-AVS and Fe associated with silicates were also determined.

2. Materials and methods

2.1. Sampling analysis

A total of 44 cores were obtained from the Rias of Vigo and Arousa in September 1999 and February 2000. For this, the rias were divided into three zones (inner, middle, outer zone) in terms of bathymetric characteristics and oceanographic processes (Macías and Mora, 2001; Otero et al., 2005, 2006). The cores were collected with a gravity corer and box core (for more details see Otero et al., 2005), transported in a vertical position, and once in the laboratory, cut into segments of 2 and 5 cm thickness and then frozen at −18 °C until analysis. Special care was taken to separate the surface layer comprising of the mussel biodeposits from the underlying sediment. X-ray analysis was used to distinguish the two layers, with the abundance of mussel shell fragments as an indicator of the biodeposit (see Emiroglu et al., 2004; Otero et al., 2005). Nonetheless, only the material that could be unequivocally identified as biodeposit was considered as such.

A total of six cores from different zones of the Rias of Arousa and Vigo were selected for a more detailed study of the Fe geochemistry (Table 1). The redox potential (Eh) was measured, at the same time as the cores were collected, with a platinum combination electrode, and the Eh values were recorded when the variation was less than 2 mV min^{-1}. The values were corrected to the standard hydrogen electrode by adding 244 mV to the measured values. The pH of fresh samples was determined in the laboratory with a Crisol micropH 2000 pH meter. Sulphate and chlorides were measured in the interstitial water (after extraction by centrifugation at 10,000 rpm under N_2 atmosphere) by ionic chromatography, with a Dionex 4500i apparatus. The contents of total organic carbon (TOC) and carbonates (TIC) were analysed with a Leco CNH-1000 apparatus, and the content of total S was determined with a Leco 100 S–C 144DR apparatus. The concentration of acid volatile sulphides (AVS) was determined in triplicate samples of 0.25–0.50 g of wet weight, according to the method described by Kostka and Luther (1994). Sulphide from AVS was liberated with 20 mL 6 N HCl previously de-aerated for 40–50 min. The sample was digested in a gas-tight reaction flask for 40–50 min under a continuous flow of nitrogen, which was bubbled through the flask at the slowest possible rate. The evolved H_2S was then received in a trap, which contained 25 mL of 3% Zn acetate, one mL of concentrated H_2SO_4 and 4 mL of diamine reagent, and precipitated as ZnS. Sulphide was then measured colorimetrically with a UV-VIS spectrophotometer (Vitatron model MCP), at a wavelength of 670 nm, by the methylene blue method of Cline (1969). The concentration of pyrite-S was determined from the pyrite-Fe (see below).

Table 1
Sampling characteristics of the stations. In each ría the stations were grouped in three areas (inner, middle and outer) according to their geographical position. Thickness of the biodeposit layer was estimated by X-ray (Macías and Mora, 2001).

Core	Sector of Ría	Coordinates	Thickness of biodeposit (cm)	Water depth (m)
Ria of Arousa				
AR-1	Inner	42°34.455′N, 8°50.516′W	42	14
AR-2	Inner	42°36.204′N, 8°53.440′W	35	17
AR-3	Inner	42°36.377′N, 8°54.844′W	26	16
Ria of Vigo				
VIG-3	Inner	42°17.729′N, 8°38.659′W	70	10
VIG-2	Middle	42°15.867′N, 8°43.763′W	15	18
VIG-8	Outer	42°14.354′N, 8°50.378′W	10	30

Partitioning of solid phase Fe was determined under N_2 atmosphere by the sequential extraction method of Huerta-Díaz and Morse (1990). Briefly, the method consists of the extraction of four operationally defined phased. (1) Reactive (essentially consisting of Fe associated with carbonates, amorphous and poorly crystalline Fe oxyhydroxides including ferrihydrite and part of the lepidocrocite, as well as part of the Fe associated with silicates: for more detail, see Raiswell et al., 1994), extracted with 20 mL of 1 M HCl during 16 h of continuous shaking; (2) silicate (essentially consisting of Fe clays and other aluminosilicates), extracted with 30 mL of 10 M HF during 16 h of continuous shaking; (3) organic (essentially consisting of Fe associated with organic matter), extracted with 10 mL of concentrated H_2SO_4, during 2 h of continuous shaking; and (4) pyrite (consisting of Fe associated with pyrite), extracted with 10 mL of concentrated HNO_3 during 2 h of continuous shaking (for further details on the methods see Huerta-Díaz and Morse, 1990, 1992).

In addition, the exchangeable, carbonate and oxyhydroxide fractions of Fe were determined by the combined use of the sequential extraction methods of Tessier et al. (1979) and Fortin et al. (1993). The first fraction (exchangeable Fe, fraction F1) was extracted by digesting 2 g of fresh biodeposit/sediment in 30 mL of a 1 M $MgCl_2$ solution at pH 7.0 for 30 min. with continuous shaking. The Fe associated with carbonates (fraction F2) was extracted after digestion in 30 mL of 1 M NaOAc at pH 5.0, with 5 h of shaking (Tessier et al., 1979). The different kinds of iron oxyhydroxides were extracted by the methods of Fortin et al. (1993): ferrihydrite or easily reducible Fe (fraction F3) with 30 mL