Chemical Geology 389 (2014) 48–59

Contents lists available at ScienceDirect

Chemical Geology

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

On the isotope composition of reactive iron in marine sediments: Redox shuttle versus early diagenesis

Florian Scholz [a,*], Silke Severmann [b], James McManus [a,c], Anna Noffke [d], Ulrike Lomnitz [d], Christian Hensen [d]

[a] College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, 104 Ocean Admin. Bldg., Corvallis, OR 97331-5503, USA
[b] Institute of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ 08901, USA
[c] Department of Geosciences, University of Akron, Akron, OH 44325–4101, USA
[d] GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstraße 1-3, 24148 Kiel, Germany

ARTICLE INFO

Article history:
Received 19 February 2014
Received in revised form 1 September 2014
Accepted 6 September 2014
Available online 28 September 2014

Editor: Michael E. Böttcher

Keywords:
Reactive iron
Iron isotopes
Shuttle
Diagenesis
Authigenic minerals
Paleo-redox

ABSTRACT

The isotope composition of reactive iron (Fe) in marine sediments and sedimentary rocks is a promising tool for identifying Fe sources and sinks across ocean basins. In addition to cross-basinal Fe redistribution, which can modify Fe isotope signatures, Fe minerals also undergo diagenetic redistribution during burial. The isotope fractionation associated with this redistribution does not affect the bulk isotope composition, but complicates the identification of mineral-specific isotope signatures. Here, we present new Fe isotope data for Peru margin sediments and revisit previously published data for sediments from the California margin to unravel the impact of early diagenesis on Fe isotope compositions of individual Fe pools.

Sediments from oxic California margin sites are dominated by terrigenous Fe supply with Fe release from sediments having a negligible influence on the solid phase Fe isotope composition. The highly reactive Fe pool (sum of Fe bound to (oxyhydr)oxide, carbonate, monosulfide and pyrite) of these sediments has a light isotope composition relative to the bulk crust, which is consistent with earlier studies showing that continental weathering shifts the isotope composition of Fe (oxyhydr)oxides to lighter values. Ferruginous sediments within the Peruvian oxygen minimum zone are depleted in Fe relative to the lithogenic background, which we attribute to extensive Fe release to the water column. The remaining highly reactive Fe pool has a heavier isotope composition compared to California margin sediments. This observation is in agreement with the general notion of an isotopically light benthic Fe efflux. Most of the reactive Fe delivered and retained in the sediment is transferred into authigenic mineral phases within the topmost 10 to 20 cm of the sediments. We observe a first-order relationship between the extent of pyritization of Fe monosulfide and the isotope composition of authigenic pyrite. With increasing pyritization, the isotope composition of authigenic pyrite approaches the isotope composition of the highly reactive Fe pool. We argue that the isotope composition of authigenic pyrite or other Fe minerals that may undergo pyritization may only be used to trace water column sources or sinks if the extent of pyritization is separately evaluated and either close to 100% or 0%. Alternatively, one may calculate the isotope composition of the highly reactive Fe pool, thereby avoiding isotope effects due to internal diagenetic redistribution. In depositional settings with high Fe but low sulfide concentrations, source and sink signatures in the isotope composition of the highly reactive Fe pool may be compromised by sequestration of Fe within authigenic silicate minerals. Authigenic silicate minerals appear to be an important burial phase for reactive Fe below the Peruvian oxygen minimum zone.

1. Introduction

1.1. Scientific rationale

An increasing number of studies use the concentration and speciation of reactive iron (Fe) within marine sediments or sedimentary rocks to infer past processes related to Fe biogeochemical cycling and the ocean's redox structure (e.g., Raiswell and Canfield, 1998; Poulton et al., 2004, 2010; Canfield et al., 2008; Poulton and Canfield, 2011; März et al., 2012). Reactive Fe is defined as the fraction of Fe in marine sediments (chiefly Fe (oxyhydr)oxides) which readily reacts (or has already undergone reaction) with hydrogen sulfide to form Fe sulfide minerals such as Fe monosulfide (FeS) and eventually pyrite (FeS_2) (Berner, 1970, 1984; Canfield, 1989). To assess these operationally defined species, various sequential extraction techniques have been developed and applied to bulk sediments and rocks (Canfield, 1989; Huerta-Diaz and Morse, 1990; Kostka and Luther, 1994; Raiswell et al., 1994; Poulton and Canfield, 2005). Reactive Fe is typically calculated

---

* Corresponding author at: GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstraße 1-3, 24148 Kiel, Germany. Tel.: +49 431 600 2114.
E-mail address: fscholz@geomar.de (F. Scholz).

http://dx.doi.org/10.1016/j.chemgeo.2014.09.009

as the sum of Fe extracted by dithionite (or equivalent) and Fe present as pyrite (Raiswell and Canfield, 1998, 2012; Raiswell and Anderson, 2005; Lyons and Severmann, 2006). An alternative approach to sequential extractions uses total Fe to aluminum ratios (Fe_T/Al) to assess reactive Fe enrichments (Lyons et al., 2003; Lyons and Severmann, 2006). The advantage of this latter approach is that elevated Fe_T/Al (over lithogenic background) is preserved even when some of the reactive Fe has been transferred to the silicate fraction through diagenetic or metamorphic processes, i.e., it is independent of the specific reactive phases (Lyons and Severmann, 2006).

Generally speaking, enrichments of reactive Fe occur when Fe is transferred from an area of high Fe solubility (e.g., with reducing but non-sulfidic conditions) to an area of low Fe solubility (e.g., with oxic or sulfidic conditions). If this transfer operates on the scale of ocean basins it is typically referred to as a redox shuttle. Prominent examples of areas where a redox shuttle has been observed are anoxic and sulfidic (i.e., euxinic) basins (e.g., the Black Sea and Baltic Sea Deeps), where Fe is mobilized from reducing shelf sediments and scavenged from the euxinic water column through syngenetic pyrite formation (Canfield et al., 1996; Wijsman et al., 2001; Anderson and Raiswell, 2004; Lyons and Severmann, 2006; Dellwig et al., 2010; Fehr et al., 2010; Scholz et al., 2013). This euxinic Fe shuttle is identified in sedimentary records by a high proportion of reactive Fe to total Fe (or high Fe_T/Al) coupled to a high proportion of pyrite in the reactive Fe pool (i.e., a high extent of pyritization) (Raiswell et al., 1988; Raiswell and Anderson, 2005; Lyons and Severmann, 2006; Raiswell and Canfield, 2012). In contrast to euxinic settings, a high ratio of reactive Fe to total Fe coupled to a low extent of pyritization has been attributed to ferruginous settings, i.e., those with abundant dissolved Fe but no hydrogen sulfide (H_2S) in the water column. This kind of environment is limited to isolated lakes today (e.g., Lake Matano, Indonesia; Crowe et al., 2008) but was likely dominant in the ocean during the Archean and much of the Proterozoic (Canfield et al., 2008; Poulton et al., 2010; Poulton and Canfield, 2011). Findings from a recent study (Scholz et al., 2014) suggest that shuttle-related Fe enrichments may also occur in association with contemporary oxygen minimum zones (OMZs). Scholz et al. (2014) reported elevated Fe_T/Al ratios in sediments underneath the lower boundary of the Peruvian OMZ and attributed this observation to a net lateral transfer of Fe from reducing sediments within the OMZ.

In addition to sequential extraction techniques, Fe isotope systematics have been suggested as a potentially powerful tool for constraining Fe transport across basinal redox gradients. Fe that is mobilized through reductive dissolution has a low δ^{56}Fe relative to lithogenic Fe (Bergquist and Boyle, 2006; Rouxel et al., 2008; Severmann et al., 2010; John et al., 2012). Depending on the efficiency of the Fe trapping mechanism within the basin and the extent of isotope fractionation during re-precipitation, the sediment-derived Fe may be traceable within the sedimentary bulk Fe pool (i.e., $\delta^{56}Fe_T \neq \delta^{56}Fe_{lithogenic}$) (Scholz et al., 2014). A highly efficient sink is characteristic of isolated euxinic basins where the mobilized Fe is quantitatively trapped within basin sediments (Fehr et al., 2008, 2010; Severmann et al., 2008). In many open-marine settings, however, the trapping efficiency and proportion of shuttle-derived Fe in the sediment are small and deviations in $\delta^{56}Fe_T$ from $\delta^{56}Fe_{lithogenic}$ cannot be resolved analytically (Scholz et al., 2014). Analyzing the isotope composition of specific authigenic Fe mineral phases, which are part of the reactive Fe pool, could be an appropriate solution to identifying primary signatures. However, interpreting the isotope composition of authigenic Fe minerals is complicated by early diagenetic processes such as, e.g., reductive dissolution of Fe (oxyhydr)oxides, partial loss of dissolved Fe across the sediment-bottom water interface and re-precipitation of Fe as carbonate, monosulfide and pyrite (e.g., Berner, 1970; Canfield, 1989, 1993; Haese et al., 1997; Pakhomova et al., 2007). Unless all of the trapped reactive Fe is transferred into one single mineral phase prior to burial, these processes are likely to result in a variable isotopic offset among different authigenic Fe fractions (Severmann et al., 2006; Staubwasser et al., 2006). Extracting information on water column Fe cycling from the isotope composition of individual authigenic Fe pools therefore requires a more complete understanding of Fe isotope fractionation during early diagenesis. Here we continue the discussion on how and under what circumstances an open-marine Fe shuttle may be tracked in sedimentary archives (cf. Scholz et al., 2014). Specifically, we evaluate how a shuttle-related isotopic fingerprint in the reactive Fe pool may be distinguished from fractionation effects inherited during early diagenesis. Our findings provide useful constraints on the interpretation of Fe isotope variability in reactive Fe minerals in the geological record.

1.2. Prior work and open questions

This study is based on samples that were taken on a sediment core transect across the Peru upwelling area at 11°S (Figs. 1 and 2A). Previous work on benthic Fe fluxes as well as bulk Fe concentrations (Fig. 2B) and isotope data (Fig. 3A) for the same sediment cores (Noffke et al., 2012; Scholz et al., 2014) suggests that terrigenous reactive Fe undergoes a redox-dependent lateral relocation across the Peruvian continental margin. The findings of these previous studies will be briefly summarized in the following paragraphs, followed by an outline of the major goals of the present study.

The physical environment and general biogeochemistry of the Peruvian continental margin have been discussed extensively within the literature (Brink et al., 1983; Reimers and Suess, 1983; Strub et al., 1998; Levin et al., 2002; Böning et al., 2004). Briefly, off the Peru coast upwelling of oxygen-depleted and nutrient-rich water leads to a near-complete oxygen drawdown in the water column overlying the upper slope and shelf. The OMZ ($[O_2] \leq 0.5$ ml $L^{-1} \approx 22$ µM; definition after Levin et al., 2002) resulting from this mechanism extends from less than 100 m to roughly 700 m water depth (Fuenzalida et al., 2009). Where the OMZ comes into contact with the seafloor, Fe reducing conditions prevail close to the sediment–bottom water interface. Because of the high mobility of Fe under anoxic but non-sulfidic conditions, Fe dissolved in pore water may escape into the water column without being immobilized while transiting the sediment-bottom water interface (Noffke et al., 2012). Sediments within the permanent OMZ (~300–700 m water depth) are characterized by Fe_T/Al below the regional lithogenic background (Fig. 2B), which has been attributed to long-term Fe loss to the water column inferred from benthic flux data (Scholz et al., 2011). Sediments underneath the lower boundary of the OMZ display Fe_T/Al above the lithogenic background (Fig. 2B) indicating that they are enriched in Fe relative to the lithogenic background

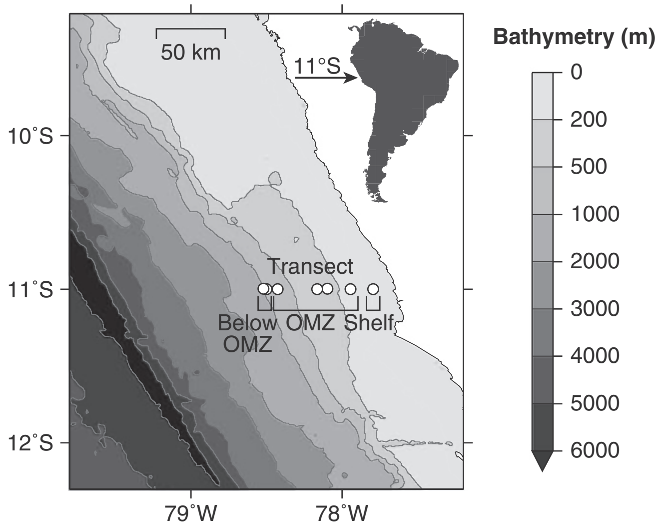

Fig. 1. Location map showing the sediment core transect (bathymetric data from GEBCO). The transect is subdivided into three domains corresponding to sediment cores from the shelf, from within the OMZ and from below the OMZ.