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A chemical weathering control on the delivery of particulate iron to the continental shelf

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Abstract

The delivery of potentially reactive iron minerals to the marine environment exerts a major control on ocean and marine sediment biogeochemistry, including the preservation and burial of organic carbon. One aspect of the global iron cycle that has received little attention concerns the phase partitioning of iron in highly chemically-weathered sediments from (sub)tropical mountainous regions, where the sediment is commonly deposited directly onto adjacent continental margins. Here, we report the phase partitioning of particulate iron in surface seafloor sediments deposited from oxic bottom waters along the east coast of China, including the Bohai Sea, Yellow Sea and East China Sea, in addition to the continental shelf region adjacent to the (sub)tropical mountainous island of Hainan in the northern South China Sea.

We document highly reactive (Fe_{HR}) to total iron (Fe_T) ratios for the Bohai Sea, Yellow Sea and East China Sea that are typical of global marine sediments deposited under oxic water column conditions. By contrast, Fe_{HR}/Fe_T ratios in Hainan offshore sediments are significantly elevated above normal oxic marine sediments. These Hainan offshore sediments display a strong positive correlation between Fe_{HR}/Fe_T ratios and the chemical index of alteration (CIA) weathering proxy, suggesting that the Fe speciation systematics are controlled by the intensity of chemical weathering. This observation is supported by additional geochemical data and Nd isotope analyses, which suggest a common source lithology for all the studied regions. The Hainan sediments thus document a specific scenario, whereby highly chemically weathered sediments from the mountainous Hainan region bypass the inner shore settings that commonly disproportionately trap Fe (oxyhydr)oxide minerals, depositing high concentrations of Fe_{HR} on the adjacent continental margin. Such enrichments likely aid in the preservation of organic carbon in marine sediments, suggesting that organic carbon preservation and burial may be enhanced by elevated Fe_{HR} in such settings. We also establish a set of essential criteria for potential recognition of chemical weathering-induced enrichments in Fe_{HR}/Fe_T ratios in ancient marine sediments.

Keywords

continental margin sediments; east China coast; Fe speciation; chemical weathering; highly reactive Fe

1. Introduction

The supply of potentially bioavailable iron to the marine environment exerts a major control on ocean biogeochemistry. Iron is an essential limiting nutrient for phytoplankton, and its supply exerts a significant impact on marine productivity in large areas of the world's oceans, which in turn influences the carbon cycle and hence climate dynamics (Mackenzie and Andersson, 2013). In addition, the supply of 'reactive' particulate iron exerts a major control on the preservation and burial of organic carbon (e.g., Lalonde et al., 2012), as well as the formation of pyrite in continental margin sediments (Berner, 1970; Canfield, 1989; Raiswell and Canfield, 1998). Thus, given the significance for the long term regulation of the global carbon, oxygen and sulfur cycles (Kump and Garrels, 1986; Berner, 2003; Canfield, 2005), controls on the delivery of particulate iron phases to the marine environment are critical to evaluate.

Particulate iron is delivered to the ocean by rivers, aeolian dust, icebergs and subglacial runoff, while hydrothermal processes and recycling from shelf sediments provide dissolved iron, which may subsequently precipitate in the water column (Poulton and Raiswell, 2002; Raiswell et al., 2006; Raiswell and Canfield, 2012). The precise contribution from each of these sources is difficult to quantify and will have evolved over Earth history, but transport by rivers provides the dominant source of chemically-weathered sediment, and hence particulate iron, to the global ocean (Milliman and Meade, 1983; Raiswell, 2006). Canfield (1997) quantified the Fe (oxyhydr)oxide content of major US rivers in relation to the intensity of chemical weathering, and found that the proportion of Fe (oxyhydr)oxide minerals (hereon termed highly reactive Fe, Fe_{HR}) relative to total Fe (Fe_T) increased with enhanced chemical weathering. Poulton and Raiswell (2002) subsequently produced a global budget for the delivery of Fe_{HR} (dominantly as Fe (oxyhydr)oxide minerals) to the marine environment, and found that the average Fe_{HR}/Fe_T ratio for global river particulates (0.43 ± 0.03, 1σ) is substantially elevated relative to the average for marine sediments (0.26 ± 0.08, 1σ; Raiswell and Canfield, 1998) deposited under oxic water column conditions (note that for marine sediments, Fe_{HR} includes Fe sulfide phases to account for sulfidation of Fe (oxyhydr)oxides during diagenesis). Indeed, the vast majority of modern oxic marine sediments have Fe_{HR}/Fe_{T} ratios below 0.38 (Raiswell and Canfield, 1998), and this discrepancy between the chemical composition of river particulates and marine sediments arises due to the preferential trapping of Fe_{HR} minerals in inner shore environments, such as flood plains, subsiding deltas, salt marshes and lagoons (Poulton and Raiswell, 2002).

Currently, however, there is a missing link in our understanding of the global Fe cycle, which relates to the delivery of Fe_{HR} to the ocean from (sub)tropical mountainous rivers, many of which bypass inner shore settings to deposit sediment directly onto active margins (Milliman and Syvitski, 1992). The relatively high intensity of chemical weathering expected in (sub)tropical mountainous regions, combined with a general increase in sediment discharge directly to the ocean, might be expected to result in an elevated supply of Fe_{HR} to adjacent marine settings, and hence may contribute to increased primary productivity and organic carbon burial (Lalonde et al., 2012; Tagliabue et al., 2017). However, this premise has not previously been tested.

The potential for local Fe_{HR}-enriched sediment delivery to the ocean from mountainous (sub)tropical catchments also has implications for the use of Fe_{HR}/Fe_{T} ratios as a water column paleoredox indicator (Poulton and Canfield, 2011; Raiswell et al., 2018; Poulton 2020). Enrichment in Fe_{HR}/Fe_{T} above the upper range for oxic marine sediment deposition (>0.38) commonly occurs in sediments deposited beneath an anoxic water column, due to mobilization and precipitation of Fe in the water column (Canfield et al., 1996; Raiswell and Canfield, 1998).

This Fe_{HR}/Fe_T threshold generally provides a robust indication of water column anoxia (Poulton and Canfield, 2011), despite the fact that the global riverine Fe_{HR}/Fe_T ratio is substantially elevated relative to marine sediments (Poulton and Raiswell, 2002). Clearly, however, there is potential for local sedimentary Fe_{HR} enrichments in oxic marine settings, in regions experiencing relatively high rates of chemical weathering, and where the inner shore trap for Fe_{HR} is circumvented (e.g., Schobben et al., 2020).

Here, we investigate the potential role of sub(tropical) mountainous regions in the supply of Fe_{HR} to local marine sediments. We report Fe_{HR}/Fe_T ratios (using both sequential extraction and single dithionite methods), major and trace elements, and neodymium isotope data for surface sediments deposited along the east coast of China (Fig. 1). This includes the Bohai Sea, Yellow Sea and East China Sea, which receive sediment from major low-lying rivers such as the Huanghe (Yellow River) and Chang Jiang (Yangtze River), as well as the northern South China Sea, in an area that receives sediment from the mountainous island of Hainan. We aim to better unravel the potential effects of chemical weathering and detrital provenance on local Fe_{HR}/Fe_T ratios in continental margin sediments, and in doing so, we provide new insight into the modern global Fe cycle. We additionally discuss criteria for the potential recognition of weathering-induced Fe_{HR} enrichments in ancient marine sediments deposited under oxic water-column conditions.

2. Geological setting and methods

Forty-four surface sediments (0–4 cm) were sampled from the Bohai Sea, Yellow Sea, East China Sea and the Hainan offshore area of the northern South China Sea (Fig. 1). The bulk sediments are mainly silty and argillaceous, consisting of clay minerals, quartz, feldspar and very small amounts of biogenic carbonate (a detailed description of locality, water-depth and mean grain size for the samples is presented in the Supplementary Materials). Previous studies have shown that these surface sediments were deposited beneath bottom waters with dissolved O_2 concentrations of least 30 μM (e.g., Li and Qu, 2006; Chen et al., 2007; Li et al., 2015; Zhao et al., 2017). Samples in this study were collected by a box corer, from which surface sediments were taken and stored in a cold repository. Before analysis, the bulk sediments were freeze-dried and sieved to avoid biotic carbonate components, and samples were then analyzed for Fe speciation, major and trace elements, and Nd isotopes. Since our samples were not immediately frozen and stored under oxygen-free conditions, oxidation of reduced phases is likely to have occurred. However, while oxidation may have affected the speciation of the Fe_{HR} pool, it will not have affected determination of Fe_{HR} concentrations or Fe_{HR}/Fe_T ratios, which are the primary focus of this study.

For major (except Fe_T) and trace element analyses (including Al, K, Na, Ca, Ti, Sc, Zr, La, Th), ~50 mg of sample was initially leached using 0.5 N acetic acid, in order to remove carbonate phases and adsorbed seawater K and Na from bulk samples. Residues were then fully digested using distilled HF–HNO_3–HCl, and diluted in 3% HNO_3. Total Fe was determined directly using a full digestion method (i.e., without the initial 0.5 N acetic acid leach) with distilled HF–HNO_3–HCl. Major elements were measured using a Thermo ICAP 6000 ICP-OES, and trace elements were measured on an Agilent 7900 Quadrupole ICP-MS at the MOE Key Laboratory of Surficial Geochemistry, Nanjing University. The RSD was <5% for all elements based on repeat analyses of the rock standard BHVO-2, and the IAPSO standard seawater solution was used to ensure accuracy.

Neodymium isotopes were analyzed on a Thermo Neptune Plus MC-ICP-MS at the State Key Laboratory for Mineral Deposits Research, Nanjing University, following the procedures outlined in Wei et al. (2019). The $^{143}Nd/^{144}Nd$ ratios were normalized to a $^{146}Nd/^{144}Nd$ ratio of 0.7219 in order to correct for mass drift. BHVO-2 and an in-house standard solution were repeatedly measured to monitor the long-term reproducibility of Nd isotope analyses ($^{143}Nd/^{144}Nd_{BHVO\text{-}2} = 0.512987 \pm 0.000002$ (SE); $^{143}Nd/^{144}Nd_{Inhouse} = 0.511699 \pm 0.000003$ (SE)).

The extraction procedures for determining Fe_{HR} in marine or riverine sediments have evolved over recent decades, and are summarized in Table 1. The most recent scheme (Poulton and Canfield, 2005) utilizes a sequential extraction approach and targets a variety of operationally-defined phases (Table 1). In this approach, ~100 mg of sample was first treated with a room temperature sodium acetate solution at pH 4.5 for 24 h (to extract Fe_{carb}). The residue was then reacted with a room temperature sodium dithionite solution at pH 4.8 for 2 h (to extract Fe_{ox}). Finally, the residue was reacted with a room temperature 0.2 M ammonium oxalate and 0.17 M oxalic acid solution for 6 h (to extract Fe_{mag}). In addition, we also performed a single sodium dithionite extraction (Table 1) to quantify non-sulfidized Fe_{HR} phases (termed Fe_D), to allow direct comparison with existing data for modern marine sediments which were analyzed in this way (Raiswell and Canfield, 1998). Extractions were performed at the State Key Laboratory for Mineral Deposits Research, Nanjing University.

After drying and re-dissolution in 3% $HNO_{3,}$ all Fe solutions were analyzed on a Thermo ICAP ICP-OES at the MOE Key Laboratory of Surficial Geochemistry, Nanjing University, with a relative standard deviation (RSD) of <5% for all steps. Acid volatile sulfide (Fe_{AVS}) and pyrite Fe (Fe_{Py}) concentrations were determined by the two-step Cr-reduction method of

Canfield et al. (1986), but concentrations were found to be below detection (<0.001 wt%) in all cases, and are given a value of zero when determining Fe_{HR} concentrations.

It should be noted that all of the extractions are operationally-defined, and while specific mineral groups are targeted in each step (see Table 1), the utility of the technique is not predicated on the precise phases that are extracted. Rather, it is quantification of the total Fe_{HR} pool, regardless of mineralogy (Alcott et al., 2020; Poulton, 2021), that has been calibrated in terms of its reactivity towards dissolved sulfide in marine sediments (Canfield et al., 2002; Raiswell and Canfield, 1998). We determined Fe_{HR} in two ways, whereby $Fe_{HR} = Fe_D + Fe_{py}$ and allows direct comparison with existing data for modern marine sediments (Raiswell and Canfield, 1998) and riverine particulates (Canfield, 1997; Poulton and Raiswell, 2002), and $Fe_{HR}^* = Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py}$, representing the latest approach for determining highly reactive Fe (Poulton and Canfield, 2005).

3. Results

Results of major/trace element concentrations, Fe speciation and radiogenic Nd isotopes (εNd) are presented in the Supplementary Materials. Sediments from the Bohai Sea, Yellow Sea and East China Sea have low Fe_{HR}/Fe_T ratios (0.24 ± 0.04, 1σ; ranging from 0.15 to 0.32), and higher Fe_{HR}^*/Fe_T ratios (0.34 ± 0.05, 1σ; ranging from 0.25 to 0.44) (Fig. 2). By contrast, sediments from the Hainan continental margin have systematically higher Fe_{HR}/Fe_T ratios (0.46 ± 0.06, 1σ; ranging from 0.36 to 0.59), and Fe_{HR}^*/Fe_T ratios (0.59 ± 0.07, 1σ; ranging from 0.45 to 0.70).

The higher Fe_{HR}^*/Fe_T ratios relative to Fe_{HR}/Fe_T are as expected, due to the additional extraction steps that are now performed to provide a more complete evaluation of phases that are considered highly reactive towards dissolved sulfide (Poulton and Canfield, 2005). However, a comparison of the two extraction procedures is instructive when considering the nature of the phases extracted in each step. In some cases, Fe dissolved by the single dithionite extraction (Fe_D) is similar to that dissolved by the sequential dithionite extraction (Fe_{ox}; Fig. 2). However, more often, Fe_D/Fe_T ratios (Bohai Sea, Yellow Sea and East China Sea = 0.24 ± 0.04; Hainan Island = 0.46 ± 0.06) are closer to the sum of Fe_{carb} and Fe_{ox} (i.e., $(Fe_{carb}+Fe_{ox})/Fe_T$) determined via the sequential extraction technique (Bohai Sea, Yellow Sea and East China Sea = 0.28 ± 0.04; Hainan Island = 0.49 ± 0.06). Since these sediments have low carbonate contents, these considerations suggest that the Fe_{carb} step is likely dominantly extracting dithionite-soluble Fe, with only minor Fe dissolved from other phases. The Fe_D phases that are also solubilized by the Fe_{carb} extraction may be in the form of surface-reduced Fe(II), which is commonly prevalent during early diagenesis in locally reduced sediments (e.g., Poulton, 2003; Xiong et al., 2019), or freshly-precipitated hydrous ferric oxide phases, formed either via in situ diagenetic recycling or oxidation of reduced Fe phases during sampling and storage. As such, these differences in the two extraction techniques are unlikely to be prevalent when applied to ancient marine rocks, since surface-reduced Fe phases and freshly precipitated hydrous ferric oxides ultimately age to more resistant phases during diagenesis, and hence would not be dissolved as part of the Fe_{carb} fraction (Poulton and Canfield, 2005).

Nevertheless, consistent with other studies that have applied the more recent Poulton and Canfield (2005) extraction technique to modern marine sediments (Hardisty et al., 2018), $Fe_{HR}*/Fe_T$ ratios are generally below the 0.38 threshold used to identify water column anoxia, which was defined using the less complete extraction procedure of Raiswell et al. (1994). By contrast, the Hainan continental margin sediments have Fe_{HR}/Fe_T and $Fe_{HR}*/Fe_T$ ratios that generally exceed global modern marine sediments (Fig. 2), suggesting that they are geochemically distinct, regardless of the precise Fe extraction technique utilized.

Chemical index of alteration (CIA) values were calculated as CIA = mol $Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O) \times 100$ (Nesbitt and Young, 1982). Values range from 52.3 to 62.4 for the Bohai Sea, Yellow Sea and East China Sea sediments, and from 62.8 to 79.1 for the Hainan offshore sediments. Sediment TiO_2, Zr, Sc, Th and La concentrations were relatively variable, and range from 0.40–1.73 wt% for TiO_2, 27.5–200.2 ppm for Zr, 2.9–22.9 ppm for Sc, 4.4–29.0 ppm for Th, and 9.8–68.4 ppm for La. All of the studied sediments show relatively uniform εNd values, ranging from -9.6 to -12.9.

4. Discussion

4.1 Geochemical characteristics

The studied sediments exhibit a strong correlation between Fe_T and Al concentrations ($R^2 = 0.80$, Fig. 3A), with the trend in Fe_T/Al ratios (0.56 ± 0.09, 1σ) being analogous to modern oxic marine sediments ($Fe_T/Al = 0.55 \pm 0.11$, 1σ; Clarkson et al., 2014) and slightly higher than continental detrital materials ($Fe_T/Al = 0.472 \pm 0.051$, 1σ; Cole et al., 2017), which is consistent with a dominant terrestrial source for the iron.

The linear relationships between both Fe_{HR} and $Fe_{HR}*$ as a function of Fe_T (Fig. 3B, C) support a continental chemical weathering control on the Fe speciation characteristics, since both Fe_T and highly reactive Fe increase as the intensity of chemical weathering increases (Canfield, 1997; Poulton and Raiswell, 2002; 2005). However, the much steeper trends for Hainan offshore sediments (Fig. 3B, C) demonstrate enhanced accumulation of highly reactive

Fe, relative to the other sites in this study and average oxic marine sediments (Raiswell and Canfield, 1998).

While the Fe speciation systematics imply a chemical weathering control on the geochemistry of the marine sediments deposited in the two broad regions (i.e., the Bohai Sea, Yellow Sea and East China Sea region, and the Hainan offshore region), it is also important to evaluate the provenance of the sediments, as markedly different source material may have different chemical weathering characteristics. Where the primary major element contents (e.g., Ca, Na, K) and mineralogy of silicate rocks are intensely altered during chemical weathering, the source rocks for fine grained marine sediments may still be constrained by conservative trace element systematics (e.g., TiO_2/Zr ratios, La–Th–Sc relationships) and Nd isotope compositions (McLennan et al., 1993; Fralick and Kronberg, 1997; Cullers and Podkovyrov, 2000; Li et al., 2003; Wei et al., 2012). Our sediments exhibit uniformly low εNd values (–11.2 ± 0.9, 1σ), and variable but low TiO_2/Zr ratios (from 56 to 114 ppm) (Fig. 4A), suggesting an intermediate–felsic source rock (cf. Fralick and Kronberg, 1997; Li et al., 2003).

We additionally examine the relationship between Th/Sc and Zr/Sc ratios (Fig. 4B), to consider the potential effects of sediment recycling on geochemical composition, which is based on the assumption that recycled sediments are preferentially enriched in zircon (giving higher Zr/Sc ratios relative to Th/Sc ratios) (McLennan et al., 1993). Our studied sediments align with the compositional trend of the parent rock (Fig. 4B), suggesting a more felsic provenance without appreciable sediment recycling. Furthermore, the La–Th–Sc distribution indicates that the sediments are more likely derived from granite- and granodiorite-type source rocks (Fig. 5A), which is consistent with previous provenance analyses for the sediments of these areas (Wei et al., 2012). In conclusion, the marine sediments analyzed in this study are dominantly derived from the chemical weathering of intermediate–felsic rocks, with no significant local control on the provenance of the sediments deposited in different regions off the east coast of China.

4.2 A link between chemical weathering and Fe_{HR} accumulation in Hainan offshore sediments

Based on the above provenance analysis, the significant enrichments in highly reactive Fe in Hainan offshore sediments are unlikely to be a consequence of different source rock types. We can also discount a water column redox control on the relative enrichments, as all sediments were deposited in bottom waters with $[O_2]$ >30 μM, despite seasonal seawater hypoxia in some areas off the east China coast (Chen et al., 2007; Zhao et al., 2017).

Continental margin sediments do, however, commonly display relative enrichments in Fe_{HR} in surface sediments, due to upwards diffusion of Fe^{2+} after mobilization in anoxic sediment porewaters, followed by precipitation as Fe (oxyhydr)oxides close to the sediment-water interface (Raiswell and Canfield, 1998; Poulton, 1998). Indeed, the database for modern oxic continental margin sediments (Raiswell and Canfield, 1998) gives an average increase of ~15% (with some increases at >50%) in Fe_{HR}/Fe_T ratios for surface sediments, relative to sediments from deeper in the same core section. Depth profiles were not analyzed in the present study, and thus it remains likely that the surface sediment Fe_{HR}/Fe_T ratios are inflated by upwards diffusion of Fe^{2+}. Thus, the steady-state Fe_{HR}/Fe_T ratios preserved in deeper sediment piles, and indeed in the average rock record, will likely be slightly lower than those of the surface sediments. For example, a 15% decrease for the Hainan offshore region lowers the range in Fe_{HR}/Fe_T ratios to 0.31–0.50. However, the global data-base of Raiswell and Canfield (1998) also included surface sediment samples, with a maximum Fe_{HR}/Fe_T ratio of ~0.38, and thus the measured Fe_{HR}/Fe_T ratios for Hainan region sediments (0.36 to 0.59) are clearly generally elevated relative to normal marine sediments.

Soils on Hainan Island are characterized by widespread formation of intensely weathered Fe-rich laterite and bauxitic laterite (e.g., Yu et al., 2019), consistent with a chemical weathering control on Fe_{HR}/Fe_T ratios. To further investigate this potential control, we utilize the chemical index of alteration (CIA) as a weathering proxy (Nesbitt and Young, 1982; McLennan, 1993; Fedo et al., 1995). During chemical weathering, labile cations (e.g., Ca^{2+}, Na^+, K^+) are preferentially dissolved and transported from the weathering profile, leaving the regolith enriched in less mobile elements, such as Al, Fe and Ti. Thus, utilizing an A–CN–K (i.e., Al–Ca+Na–K) ternary diagram, where primary silicate minerals tend to have CIA values around 50 (Fig. 5B), increased CIA values correspond to elevated degrees of chemical weathering, due to sequential loss of Ca, Na and K from primary minerals followed by the formation of secondary clays (e.g., feldspar–illite/smectite–kaolinite series) (Nesbitt and Young, 1982; Fedo et al., 1995).

Furthermore, since marine siliciclastic sediments comprise chemical weathering products and fine-grained rock debris from physical erosion, the CIA values of marine sediments also reflect the extent of chemical weathering in the source region (i.e., the relative proportions of chemical weathering products deposited in bulk sediments). Given a granodiorite–granite source rock type (Fig. 5A), changes in CIA values for the studied sediments reproduce a trend consistent with an increasing degree of chemical weathering of the source rocks (solid arrow in

Fig. 5B; McLennan, 1993), without any discernable effect on the CIA values from K metasomatism (dashed line in Fig. 5B; cf. Fedo et al., 1995).

Next, we investigate the relationship between highly reactive Fe (here, we focus on Fe_{HR} concentrations to allow direct comparison with previously published data for river particulates, but note that the same relationships are evident when considering Fe_{HR}*) and the CIA proxy, in order to document potential links between Fe_{HR} accumulation and chemical weathering (Fig. 6). Surface sediments from the east China coast exhibit a strong relationship between Fe_{HR}/Fe_T and CIA values ($R^2 = 0.85$). However, in more detail, sediments from Bohai Sea, Yellow Sea and East China Sea have relatively low CIA values (52–62) and Fe_{HR}/Fe_T ratios (0.15–0.32), indicating relatively weak chemical weathering. By contrast, the Hainan region sediments have significantly higher CIA values (63–79), coincident with the higher range observed in Fe_{HR}/Fe_T ratios (0.36–0.59). This clearly supports the chemical weathering control on the speciation of Fe in river particulates that has previously been documented for both individual US rivers (Canfield, 1997), and continental-scale river catchments (Poulton and Raiswell, 2002).

Indeed, the global riverine data also show a clear positive correlation between Fe_{HR}/Fe_T ratios and CIA values ($R^2 = 0.48$), and the marine sediments from the east coast of China overlap with the range of global river particulate data (Fig. 6). This suggests that the source rocks in the region weather in a manner that is typical of global scale weathering trends, specifically in terms of the generation of increased Fe_{HR}/Fe_T ratios as chemical weathering intensity increases. In this context, the observed enrichment in Fe_{HR} in the Hainan offshore sediments is consistent with the widespread formation of lateritic or bauxitic lateritic soils in sub-tropical and tropical regions, as found on both the southeastern mainland of China, and Hainan Island (Lan et al., 2003; Qiu et al., 2014; Yu et al., 2019), with both soil types commonly being enriched in Fe (oxyhydr)oxide minerals (Schwertmann, 1988; Widdowson, 2007).

4.3 Weathering-induced Fe_{HR} enrichments in modern and ancient marine sediments

Our data demonstrate that it is possible for enhanced chemical weathering to result in a locally high influx of Fe (oxyhydr)oxide minerals to the marine environment, which has implications for the local biogeochemistry of marine waters and sediments. However, enhanced chemical weathering is not sufficient, in isolation, to result in enrichments in highly reactive Fe relative to normal oxic marine sediments. As discussed above, global river particulates are also enriched in highly reactive Fe, but preferential trapping of Fe oxyhydr(oxide) minerals in inner-shore environments results in marine sediments that have significantly lower Fe_{HR}/Fe_T ratios on a more global scale (Poulton and Raiswell, 2002). Our data thus specifically document a missing factor in understanding of the modern global iron cycle, whereby the supply of Fe_{HR} from (sub)tropical mountainous regions (e.g., Hainan Island) may be transported directly onto active margins, thus supplying sediment to the marine environment that is relatively enriched in Fe (oxyhydr)oxide minerals.

We compare our data to other oxic and anoxic environments in Fig. 7, which shows a global compilation of both Fe_{HR}/Fe_T (Fig. 7A) and $Fe_{HR}*/Fe_T$ (Fig. 7B) ratios for different sediment types and localities, plotted as a function of Fe_T/Al ratios. It is clear from Fig. 7 that a very limited range of oxic environments record weathering-induced enrichments in Fe_{HR}. In addition to the (sub)tropical mountainous region represented by Hainan Island, these include restricted basins in (sub)tropical areas, such as the Gulf of Aqaba in the Red Sea. The defining characteristic of these settings, is that not only does the sediment originate from highly weathered (sub)tropical catchments, but the inner-shore trap for Fe_{HR} is bypassed, resulting in a direct influx of Fe_{HR}-enriched sediment.

The sediments off Hainan Island thus appear to be influenced by a ‘perfect storm’ of combining factors, whereby the source area was in a (sub)tropical locality, and the inner-shore trap for Fe_{HR} was bypassed due to the mountainous terrain that extends to the coast. These observations are consistent with the suggestion that significant enrichments in Fe_{HR} in ancient, open marine oxic settings are likely to be relatively rare through the geological record (Poulton, 2021). However, such enrichments remain a distinct possibility on a local scale at times when chemical weathering rates were particularly high (e.g., in the run-up to the Permian–Triassic boundary; Schobben et al., 2020). Given the common utility of Fe_{HR}/Fe_T ratios as a proxy for identifying local bottom water redox conditions (Poulton and Canfield, 2011), it is clearly important to attempt to recognize weathering-induced enrichments in Fe_{HR}/Fe_T in the rock record.

An important factor in identifying criteria for recognition of weathering-induced enrichments in Fe_{HR}/Fe_T concerns the differing behavior of Fe_{HR}/Fe_T and Fe_T/Al ratios during chemical weathering. While both proxies may increase under anoxic conditions, due to the transport and subsequent precipitation of Fe_{HR} minerals in the water column (Canfield et al., 1996; Raiswell and Canfield, 1998), only Fe_{HR}/Fe_T ratios are appreciably enhanced during chemical weathering (Canfield, 1997). This is because both Fe_T and Al behave conservatively during chemical weathering, to approximately the same degree (Martin and Meybeck, 1979; Canfield, 1997). Thus, as demonstrated in Fig. 7, all samples from the east China coast, as well as global river particulates and sediments from Gulf of Aqaba, plot in the average Fe_T/Al range characteristic of oxic depositional conditions (0.44–0.66; Clarkson et al., 2014), despite some of the samples having elevated Fe_{HR}/Fe_T ratios due to enhanced chemical weathering.

The above observations suggest that a combination of elevated Fe_{HR}/Fe_T (>0.38) and low Fe_T/Al may provide an initial indication of a possible chemical weathering, rather than water column anoxia, control on sedimentary Fe speciation characteristics. However, we stress here that the local Fe_T/Al ratio of sediments may be highly variable (Cole et al., 2017; Raiswell et al., 2018), and indeed, in settings where the Fe_T/Al ratio of terrestrial materials supplied to the marine environment is low, the addition of Fe_{HR} from anoxic water column precipitation may not be sufficient to increase Fe_T/Al ratios above the upper range that is typical of oxic marine sediments. This may give a false indication of a chemical-weathering control on Fe speciation characteristics. We demonstrate this likelihood in Fig. 7, where data from anoxic modern basins are also plotted. While some anoxic modern basins show the expected elevated Fe_{HR}/Fe_T and Fe_T/Al ratios diagnostic of anoxic depositional conditions, sediments from the anoxic Cariaco Basin, as well as some sediments from the anoxic Orca Basin, have relatively low Fe_T/Al ratios. Thus, wherever possible, a background oxic Fe_T/Al ratio should be defined for the particular setting of interest, to allow a more refined evaluation of potential enrichments in Fe_T/Al (Sperling et al., 2016; Cole et al., 2017; Raiswell et al., 2018; Poulton, 2021).

While it may be possible to define a local oxic Fe_T/Al ratio in some paleoenvironmental settings (e.g., Poulton et al., 2010; Sperling et al., 2016; Scholz et al., 2019a), in many cases this is not straightforward. However, it is increasingly the case that a multi-proxy approach is taken to reconstruct ancient water column redox conditions, whereby enrichments in redox sensitive trace metals may provide independent evidence for anoxic depositional conditions (for reviews see Robbins et al., 2016; Bennett and Canfield, 2020). In this context, however, we note that anoxic enrichments in Fe_{HR}/Fe_T may arise in two distinct ways. Firstly, Fe_{HR} enrichments may arise from precipitation in, and settling through, an anoxic water column (e.g., Canfield et al., 1996). Under such conditions, and notwithstanding possible diminished marine trace metal inventories when anoxia is widespread (e.g., Algeo, 2004; Scott et al., 2008; Goldberg et al., 2016), certain trace metals (dependent on the precise redox state) would be expected to be enriched in the deposited sediments, and as such would provide supporting evidence for an anoxic source for Fe_{HR} enrichments. However, Fe_{HR} enrichments may also arise through upwelling of dissolved Fe^{2+} into shallow oxic waters (e.g., Wood et al., 2015). Under such conditions, deposition occurs under oxic conditions, and Fe_{HR} enrichments actually reflect deeper water anoxia (Poulton and Canfield, 2011; Poulton, 2021). In this case, trace metal enrichments at the site of Fe_{HR} enrichment may therefore not necessarily occur, which adds an extra dimension of complexity that should be considered when attempting to distinguish chemical weathering-induced enrichments in Fe_{HR} from anoxic enrichments.

In addition, it is clearly important to have direct evidence for an enhanced degree of chemical weathering, as in the present study, when invoking a chemical weathering rather than water column anoxia control on Fe speciation systematics. Given that enrichments in Fe_{HR}/Fe_T ratios due to enhanced chemical weathering are likely relatively rare in the geological record, we propose that four principal criteria should be satisfied in order to invoke this control: 1. Sediments should display persistent (not fluctuating) enrichments in Fe_{HR}/Fe_T (>0.38); 2. Sediments should have low Fe_T/Al ratios, and where possible these ratios should be evaluated relative to the local ratio for oxic deposition; 3. The sediments should display no independent evidence for deposition under anoxic conditions, for example via additional consideration of trace element (noting the caveat to this discussed above) or biomarker systematics; 4. Independent evidence for a relatively high degree of chemical weathering should be provided, for example via use of the CIA weathering proxy, mineralogical considerations, or isotope systematics.

4.4 Implications for the modern oceanic Fe cycle

Our demonstration that (sub)tropical mountainous rivers may provide elevated fluxes of highly reactive Fe to adjacent shelves has implications for the modern oceanic Fe cycle. Recent work has demonstrated that the significance of glacial catchments has commonly been underappreciated in terms of supply of highly reactive Fe to the ocean, with such sites ultimately constituting an important source of potentially bioavailable Fe to fuel primary productivity (e.g., Raiswell et al., 2016). Similarly, elevated oceanic influxes of highly reactive Fe from (sub)tropical mountainous regions also constitute an additional source of potentially bioavailable Fe to the marine environment, which through subsequent mobilization from sediments may impact the global budget of bioavailable Fe and thus help to regulate global ocean primary productivity (e.g., Tagliabue et al., 2017; Homoky et al., 2021). In addition, Fe (oxyhydr)oxide minerals exert an important control on the preservation and burial of organic carbon (e.g., Lalonde et al., 2012), and thus enrichments in Fe_{HR} in continental margin sediments deposited adjacent to (sub)tropical mountainous regions may enhance regional rates of organic carbon burial.

5. Conclusions

Our new iron speciation data for surface seafloor sediments deposited from oxic bottom waters on the east coast of China, provide new insight into potential controls on highly reactive Fe accumulation in continental margin settings. Surface sediments from the Bohai Sea, Yellow Sea and East China Sea have low Fe_{HR} contents ($Fe_{HR}/Fe_T = 0.24 \pm 0.04$; $Fe_{HR}^*/Fe_T = 0.34 \pm 0.05$, 1σ), which are similar to those of typical oxic marine settings ($Fe_{HR}/Fe_T = 0.26 \pm 0.08$, 1σ; Raiswell and Canfield, 1998). However, surface sediments from the Hainan offshore area in the northern South China Sea have significantly elevated Fe_{HR} contents ($Fe_{HR}/Fe_T = 0.46 \pm 0.06$ and $Fe_{HR}^*/Fe_T = 0.59 \pm 0.07$, 1σ), despite deposition from oxic bottom waters.

Nd isotope compositions and TiO_2/Zr ratios demonstrate a similar dominant source rock composition for sediments deposited in the two regions, and Th/Sc and Zr/Sc ratios additionally suggest limited sediment recycling. Thus, based on a close relationship between Fe_{HR}/Fe_T ratios and the CIA weathering proxy, we suggest that the elevated Fe_{HR}/Fe_T ratios of the Hainan region are a direct result of an enhanced degree of chemical weathering, coupled with the mountainous terrain, which results in Fe (oxyhydr)oxide minerals bypassing the inner shore trap and depositing directly on the local continental margin. We propose that a carefully considered combination of high Fe_{HR}/Fe_T, low Fe_T/Al, no independent evidence for water column anoxia, and evidence for a high degree of chemical weathering, may be used to indicate a possible chemical weathering control on Fe_{HR} enrichments in marine sediments preserved in the rock record. The observed linkage between chemical weathering and enhanced terrestrial Fe_{HR} delivery from (sub)tropical mountainous regions provides new insight into the modern oceanic Fe cycle, with wider potential implications for a variety of biogeochemical elemental cycles in the ocean.

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Figure Captions

Figure 1. Location of the surface sediment samples from the Bohai Sea, Yellow Sea and East China Sea (A), and the Hainan offshore area (B). The dashed lines represent major rivers in the studied regions.

Figure 2. Iron speciation data shown as a proportion of total Fe for the Bohai, Yellow and East China Seas (A and B), and for Hainan offshore sediments (C and D). Data are reported for sequential extractions (A and C) using the method of Poulton and Canfield (2005), and for a single sodium dithionite extraction (B and D) using the method of Raiswell et al. (1994). See Table 1 for operationally-defined target phases. Blue lines in (A) and (C) represent $Fe_{HR}*$, calculated as the sum of Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py} (Fe_{py} were below detection). Blue lines in (B) and (D) represent Fe_{HR} determined via a single sodium dithionite extraction. Dashed lines represent the upper limit for normal marine sediments deposited under oxic conditions ($Fe_{HR}/Fe_T = 0.38$; Raiswell and Canfield, 1998), and the average value for oxic marine sediments ($Fe_{HR}/Fe_T = 0.26$ Raiswell and Canfield, 1998).

Figure 3. Cross-plots of (A) Fe_T vs. Al, (B) Fe_{HR} vs. Fe_T, (C) $Fe_{HR}*$ vs. Fe_T, and (D) $Fe_{HR}*$ vs. Fe_{HR}. The R^2 values represent the coefficient of determination for the correlations (2σ uncertainties, dashed lines). The red lines in (A) represent the overall trend for modern oxic marine sediments ($Fe_T/Al = 0.55$; Raiswell and Canfield, 1998; Raiswell et al., 2018) and average terrestrial materials ($Fe_T/Al = 0.472$; Cole et al., 2017). The red lines in (B) represent the overall trend for modern riverine sediments ($Fe_{HR}/Fe_T = 0.43$; Poulton and Raiswell, 2002) and oxic marine sediments ($Fe_{HR}/Fe_T = 0.26$; Raiswell and Canfield, 1998). The red line in (C) represents the upper threshold value for oxic depositional conditions ($Fe_{HR}*/Fe_T = 0.38$) (Poulton and Canfield, 2011).

Figure 4. Cross-plots of trace elements and Nd isotope values for the studied sediments. (A) εNd vs. TiO_2/Zr; (B) Th/Sc vs. Zr/Sc. The dashed lines in (B) represent varying trends for compositional changes in parent rocks and for sediment recycling (after McLennan et al., 1993).

Figure 5. Ternary plots of the studied sediments. (A) La–Th–Sc diagram; (B) A–CN-K (Al–Ca + Na–K) diagram with calculated CIA values. Red stars represent the distributions of molar Al_2O_3, $CaO+N_2O$, and K_2O for different primary silicate minerals and igneous rocks. The solid arrow represents the trend for increasing degree of chemical alteration of primary silicate minerals in this study. The dashed arrow denotes the chemical alteration process with effects of K addition via K metasomatism in sedimentary rocks or paleosols (after Fedo et al., 1995).

Figure 6. Relationship between the Fe_{HR}/Fe_T ratios and CIA values for the China east coast sediments analyzed in this study and global riverine sediments (modified from Canfield, 1997; Poulton and Raiswell, 2002). The division of different chemical weathering degrees is modified from Rieu et al. (2007), Schoenborn and Fedo (2011), and Wang et al. (2020). The R^2 values represent the coefficient of determination for the correlations (2σ uncertainty; dashed lines).

Figure 7. Compilation of Fe_{HR}/Fe_T (A) and $Fe_{HR}*/Fe_T$ (B) ratios as a function of Fe_T/Al for the studied sediments, modern riverine sediments, and published marine sediment data (presented as average values with 1σ uncertainty). The upper threshold Fe_{HR}/Fe_T value for recognition of oxic sedimentation (0.38) is shown in both A and B, since this value is currently used to identify anoxic deposition, regardless of the precise Fe extraction scheme used. The range in Fe_T/Al for average oxic modern marine sediments is 0.55 ± 0.11 (1σ) (Clarkson et al., 2014). The range in Fe_T/Al for terrestrial materials is 0.472 ± 0.051 (1σ) (Cole et al., 2017), and is shown as a gray area in (A) and (B). Data sources: China east coast sediments (this study), global riverine sediments (Canfield, 1997; Poulton and Raiswell,

2002), oxic marine sediments (average continental margin and deep sea; Raiswell and Canfield, 1998), dysoxic marine sediments (Raiswell and Canfield, 1998), tropical semi-enclosed bays (Praslin and Savannes Bay), Saint Lucia, Lesser Antilles (Ku et al., 2008), Gulf of Aqaba, Red Sea (Steiner et al., 2017; Boyko et al., 2019), FOAM, Long Island Sound (Hardisty et al., 2018), Black Sea, Orca Basin, Effingham Inlet (Andersen and Raiswell, 2004; Lyons and Severmann, 2006), Cariaco Basin (Lyons et al., 2003), Mediterranean sapropels (Benkovitz et al., 2020), Peru margin (Scholz et al., 2014), Lake Cadagno (Xiong et al., 2019). Note that basins influenced by strong hydrothermal activity (e.g., Guaymas Basin, Gulf of California; Scholz et al., 2019b) are excluded from the compilation.