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Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates

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Abstract

The development of a sequential extraction procedure for iron in modern and ancient sediments is presented. The scheme recognizes seven operationally derived iron pools: (1) carbonate associated Fe (Fe_{carb}), including siderite and ankerite; (2) easily reducible oxides (Fe_{ox1}), including ferrihydrite and lepidocrocite; (3) reducible oxides (Fe_{ox2}), including goethite, hematite and akaganéite; (4) magnetite (Fe_{mag}); (5) poorly reactive sheet silicate Fe (Fe_{PRS}); (6) pyrite Fe (Fe_{py}); and (7) unreactive silicate Fe (Fe_U). As such, this is the first extraction scheme specifically developed to allow the separate identification of magnetite, and the first to allow a complete evaluation of Fe carbonate phases such as siderite and ankerite. The scheme was developed following tests on pure mineral phases to evaluate the minerals solubilized by each technique and to determine optimum extraction times. Further tests on mixtures of pure minerals and on grain-size separated sediments from two major US rivers and two glacial meltwaters validate the specificity of the scheme for different pools of iron minerals, and demonstrate a high degree of reproducibility for each analytical stage. The data obtained for the riverine and glacial sediments are additionally discussed in relation to the dominant modes of transport of different iron minerals in fine-grained continental sediments.

Keywords: Iron; Extraction; Magnetite; Siderite; River particulates; Glacial sediments

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1. Introduction

The availability and speciation of sediment iron has been demonstrated to exert a major control on syngenetic and diagenetic pyrite formation in many modern depositional settings (e.g. Berner, 1970; Canfield, 1988, 1989; Canfield et al., 1992, 1996; Raiswell and Canfield, 1996, 1998). These studies have set the framework for the development of water column redox indicators based on the speciation of iron (e.g. Berner, 1970; Raiswell et al., 1988, 2001). The initial redox proxy based on iron speciation was the degree-of-pyritization (DOP; Berner, 1970; Rais-

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well et al., 1988). This parameter determines the extent to which the iron minerals potentially reactive towards dissolved sulfide have been transformed into pyrite, and is commonly used to distinguish deposition beneath oxic and anoxic bottom waters in both modern and ancient settings (e.g. Raiswell and Al-Biatty, 1989; Gagnon et al., 1995; Raiswell and Canfield, 1998; Poulton et al., 1998; Muller, 2002; Schenau et al., 2002; Lyons et al., 2003). In this case, 'reactive' iron is extracted by a boiling 12 N HCl extraction (DOP=Pyrite Fe/[Pyrite Fe+HCl-extractable Fe]). The HCl extraction removes a variety of Fe phases, including Fe (oxyhydr)oxides such as ferrihydrite, lepidocrocite, goethite and hematite, and some Fe from sheet silicates. These different Fe phases display a broad degree of reactivity towards sulfide, ranging from hours for ferrihydrite and lepidocrocite to 10^5–10^6 years for Fe-containing silicates (Canfield et al., 1992; Raiswell and Canfield, 1996; Poulton, 2003; Poulton et al., 2004a).

More recently, refined techniques identify three 'reactive' iron pools (Canfield, 1989; Raiswell et al., 1994; Raiswell and Canfield, 1998); highly reactive iron (Fe_{HR}), poorly reactive iron (Fe_{PR}), and unreactive iron (Fe_U). Highly reactive iron includes dithionite-soluble (oxyhydr)oxides such as ferrihydrite, lepidocrocite, goethite and hematite, in addition to iron which has been transformed to pyrite (Fe_{py}). The poorly reactive fraction refers to iron solubilized by the boiling 12 N HCl technique minus that soluble in dithionite. In addition to iron-bearing sheet silicates, this operationally defined fraction includes magnetite and ferrous carbonate phases such as siderite and ankerite (Raiswell et al., 1994). Finally, the Fe_U fraction consists of residual silicate iron, which is essentially unreactive towards dissolved sulfide.

The ratio Fe_{HR}/total Fe (FeT) has been successfully applied to modern (e.g. Canfield et al., 1996; Raiswell and Canfield, 1998), Phanerozoic (e.g. Raiswell et al., 2001; Poulton and Raiswell, 2002) and Mesoproterozoic (Schen et al., 2002, 2003) sediments to demonstrate or infer deposition beneath an anoxic water column. However, the ratio Fe_{HR}/FeT is limited as it does not distinguish between deposition beneath an anoxic, non-sulfidic (potentially Fe(II)-containing) water column and a sulfidic water column. Furthermore, the extraction scheme operationally includes the ferrous-containing minerals magnetite, siderite and ankerite as part of the poorly reactive iron fraction. At present, no extraction schemes allow either the separate identification of magnetite, or the inclusion of siderite and ankerite as part of the total Fe_{carb} pool. The separate identification of these minerals would be advantageous to many modern and ancient sediment studies, firstly because they are in fact likely to be 'highly reactive' towards dissolved sulfide (Canfield and Berner, 1987; Poulton et al., 2004a), and secondly because they may occur at elevated concentrations in marine sediments as a result of deposition beneath an Fe(II)-containing water column. Thus the development of such an extraction scheme may ultimately enable anoxic Fe(II)-containing depositional conditions to be distinguished from sulfidic conditions (e.g. Poulton et al., 2004b).

In this study we develop a sequential extraction procedure aimed at providing detailed information on the speciation of iron in both modern and ancient sediments. Seven operationally defined sediment iron fractions are characterized: (1) carbonate-associated Fe (Fe_{carb}), including siderite and ankerite; (2) easily reducible oxides (Fe_{ox1}), including ferrihydrite and lepidocrocite; (3) reducible oxides (Fe_{ox2}), including goethite, hematite and akaganéite; (4) magnetite (Fe_{mag}); (5) poorly reactive sheet silicate Fe (Fe_{PRS}); (6) pyrite Fe (Fe_{py}); and (7) unreactive silicate Fe (Fe_U). We start by evaluating the effectiveness of a range of extractants for the dissolution of pure Fe-bearing minerals. Based on these results, a sequential extraction scheme was developed and tested on mixtures of pure Fe-bearing minerals. Finally, the extraction scheme was applied to a series of grain-size separates of sediments from two major US rivers and two glacial meltwaters, and these data are discussed in relation to recent studies on the continental transport of reactive iron fractions to marine settings (Poulton and Raiswell, 2002, in review).

2. Methods

2.1. Preparation of iron minerals

Synthetic ferrihydrite, lepidocrocite, goethite, akaganéite, hematite and magnetite were prepared according to the standard methods of Cornell and Schwertmann (1996). All chemicals were Analytical Reagent grade and all solutions were prepared in MilliQ water. Ferrihydrite was prepared by titrating a 50 mM solution of $Fe(NO_3)_3 \cdot 9H_2O$ to pH 6.5 with 1 M KOH. After hydrolysis the ferrihydrite was washed thoroughly to remove traces of nitrate, and then freeze dried. Lepidocrocite was prepared by precipitation of a 0.06 M $FeCl_2$ solution to pH 7 with NaOH. The precipitate was then oxidized with oxygen while maintaining the pH at 7 by the addition (via a pH-stat) of NaOH, and the final product was then washed and dried. Goethite was prepared by adding 180 ml of 5 M KOH to 100 ml of 1 M $Fe(NO_3)_3$. The resulting suspension was diluted to 2 l, and heated at 70 °C for 60 h. The final precipitate was then washed and dried at 50 °C. Akaganéite was precipitated from a 0.1 M $FeCl_3$ solution heated at 70 °C in a closed vessel for 48 h. The precipitate was then washed and dried. Hematite was prepared by adding $Fe(NO_3)_3 \cdot 9H_2O$ (to give a 0.02 M solution) to a preheated (98 °C) 0.002 M HCl solution. This solution was heated at 98 °C for 7 days, and the precipitate was then washed and dried. Magnetite was prepared by the slow addition of 240 ml of a 3.33 M KOH/0.27 M KNO_3 solution to a 0.3 M $FeSO_4$ solution (560 ml) preheated to 90 °C. The suspension was heated for 1 h with constant stirring, and the resulting precipitate was washed and dried. All synthetic oxide minerals were characterized with a Phillips PW1050 XRD with Cu Kα radiation.

Ferrous carbonate ($FeCO_3$) was synthesized by adding 0.5 mol of Na_2CO_3 to an anoxic solution of 0.5 M $FeCl_2$. The solution was stirred continuously under oxygen-free N_2, and the resulting precipitate washed in anoxic MilliQ water. The precipitate was then freeze-dried and stored under N_2. Natural, crystalline siderite was obtained from Roxbury Iron Mines, Connecticut, and from a sideritic layer of the Biwabik Iron Formation, N. Minnesota (see Pfleider et al., 1968). Natural ankerite was obtained as a crystalline sample from Mt. St. Hilaire, Quebec. For the siderite and ankerite samples, fresh mineral surfaces were exposed and then the sample was obtained by drilling. Natural magnetite and nontronite were obtained from the G.J. Brush Mineral Collection (Yale, Peabody Museum). All natural minerals were crushed to <63 μm prior to analysis.

2.2. Sediments

The sequential extraction procedure developed in this study was tested on grain-size separates of bed sediment from the Mississippi and Tombigbee rivers (USA), and glacial meltwater sediment from the Tsanfleuron and Tsijiore Novue glaciers (French Alps). These samples represent two diverse weathering environments. Thus, bulk glacial sediments generally contain significantly lower concentrations of iron (oxyhydr)oxide minerals relative to riverine sediments, due to the enhancement of physical weathering over chemical weathering in the glacial environment (Poulton and Raiswell, 2002, in review). Furthermore, the Tsanfleuron sediment was chosen specifically because of a relatively high carbonate content, thus allowing the relationship between inorganic C and carbonate-associated iron (Fe_{carb}) to be determined for this sample. Mississippi and Tombigbee river bank sediments were sampled in June 1986 (see Canfield, 1997). Mississippi river sediment was collected at Pointe a la Hache, LA, and Tombigbee river sediment at Jackson, AL. Glacial meltwater samples were collected in July 1996. The samples were immediately filtered (0.45 μm), and then air-dried. Particles were carefully removed from the filters with a scalpel. The river and glacial sediments were grain-size separated by wet-sieving, followed by density settling in water for the finer fractions (<25 μm), according to Stoke's law. All sediments were crushed to <63 μm prior to analysis.

2.3. Iron extractions

All iron extractions were performed under oxic conditions in constantly agitated centrifuge tubes, with the exception of the boiling HCl and total Fe techniques which were performed in glass test tubes. The extractant volume was 10 ml except where otherwise noted. Sediment extractions were performed with a sample size of 100–200 mg. The following extractions were used during this study:

(a) *Magnesium chloride*: River and glacial sediments were subjected to a 1 M $MgCl_2$ extraction at pH 7 for 2 h. Both $MgCl_2$ and $CaCl_2$ are commonly used to extract exchangeable metals, including Fe (see Tessier et al., 1979; Heron et al., 1994). In a test of the efficiency of this method, Heron et al. (1994) obtained complete recovery of adsorbed Fe(II).

(b) *Sodium acetate*: Several different versions of the standard acetate extraction for carbonate dissolution (see Tessier et al., 1979) were applied to evaluate the most suitable extraction conditions for siderite and ankerite, while leaving other phases relatively unaffected. These included 1 M sodium acetate adjusted (with acetic acid) to pH 5.0, pH 4.5 and pH 4.0 at room temperature and at 50 °C. Extractions at 50 °C were performed in a temperature-regulated water bath.

(c) *Hydroxylamine–HCl*: A 1 M hydroxylamine–HCl solution in 25% v/v acetic acid (Chester and Hughes, 1967) was tested for suitability as an extractant of 'easily reducible' oxides (ferrihydrite and lepidicrocite).

(d) *Sodium dithionite*: A sodium dithionite solution (50 g l^{-1}) buffered to pH 4.8 with 0.35 M acetic acid/0.2 M sodium citrate (Mehra and Jackson, 1960; Lord III, 1980) was tested for the selective extraction of 'reducible' oxides (goethite, hematite and akaganéite). The dithionite solution was always used immediately after preparation.

(e) *Ammonium oxalate*: A 0.2 M ammonium oxalate/0.17 M oxalic acid solution (pH 3.2; McKeague and Day, 1966; Phillips and Lovley, 1987) was evaluated for suitability as an extractant of magnetite.

(f) *Concentrated HCl*: A 1 min boiling 12 N HCl (5 ml volume) extraction was applied to the river and glacial sediments. This technique has been extensively tested (Raiswell et al., 1994) and has been shown to quantitatively extract Fe (oxyhydr)oxides, siderite and ankerite, in addition to some Fe from certain sheet silicate minerals (e.g. nontronite, chlorite, glauconite, biotite).

(g) *Total Fe extraction*: Ashed samples (450 °C for 8 h) were subjected to a near boiling 6 N HCl extraction for 24 h (Aller and Mackin, 1986). This technique removed >96% of the Fe from the PACS1 international sediment standard, with a reproducibility of <4%.

2.4. Iron, carbon and surface area analyses

All Fe analyses were performed by atomic absorption. Carbonate C was determined as the difference between total C and organic C (after treatment with 10% HCl at room temperature for 24 h). Carbon measurements were performed on a Carlo Erba 1106 Elemental Analyzer. Surface area was determined by the multi-point BET method (using a Beckman/Coulter SA 1300 analyzer with a Beckman/Coulter SA-PREP outgasser).

3. Results

3.1. Single extractions

Table 1 details the concentrations of iron removed by the different extraction techniques for a range of Fe minerals. The data shown relate to the optimum extraction times determined for each technique. Tests of the effectiveness of various acetate extractions for the dissolution of crystalline siderite were complicated by the fact that natural siderite rarely occurs in pure form. XRD analyses indicated the presence of hematite in the Roxbury siderite sample, and a significant proportion of the Fe-rich sheet silicate, stilpnomelane, in the Biwabik siderite sample. Therefore, the total siderite Fe content of these samples was estimated as the difference between a 24-h 1 N HCl extraction (which quantitatively dissolves siderite and Fe (oxyhydr)oxides; Raiswell et al., 1994) and a 2 h dithionite extraction (which dissolves Fe (oxyhydr)oxides but not siderite; see below and Raiswell et al., 1994). Furthermore, oxidation of siderite may result in surface coatings of Fe (oxyhydr)oxides, which can prevent dissolution by acetate. Therefore siderite samples were ground (to <63 µm) immediately prior to analysis to minimize oxidation, and this approach should be adopted for all studies aimed at determining the siderite content of sediments.

The standard acetate extraction at pH 5 (Tessier et al., 1979) was ineffective at dissolving both freshly precipitated $FeCO_3$ and crystalline siderite (Table 1; see also Heron et al., 1994). The room temperature acetate extractions at pH 4 and pH 4.5 quantitatively solubilized synthetic $FeCO_3$ and ankerite, but only partially solubilized the crystalline

Table 1
A comparison of the concentrations of iron (in wt.%) removed by different extraction techniques (for optimum extraction times)

Mineral	Total	Na acetate pH 4, 24 h	Na acetate pH 4.5, 24 h	Na acetate pH 5, 24 h	Na acetate pH 4.5, 48 h, 50°C	Hydr.–HCl 48 h	Dithionite 2 h	Oxalate 6h
$FeCO_3$ (syn.)	46.2	46.1	46.2	32.8	46.1	ND	ND	ND
Roxbury siderite	28.9[a]	24.8	24.4	22.4	28.1	ND	ND	ND
Biwabik siderite	22.3[a]	14.5	12.3	4.1	21.3	ND	ND	ND
Ankerite	13.9	13.6	13.6	13.2	13.2	ND	ND	ND
Ferrihydrite	54.7	6.31	0.95	0.27	1.72	54.2	54.7	54.2
Lepidocrocite	62.8	5.97	0.85	0.24	0.71	61.9	62.9	62.8
Akaganéite	63.1	0.16	0.08	0.06	0.07	2.44	63.2	2.37
Goethite	62.8	0.14	0.02	0.01	0.05	0.05	62.8	0.60
Hematite	69.8	<0.001	<0.001	<0.001	<0.001	0.05	65.7	0.30
Magnetite (syn.)	72.3	0.33	0.01	0.006	0.19	0.34	5.1	72.3
Magnetite (nat.)	72.3	ND	0.01	0.008	0.17	0.41	4.1	72.0
Nontronite	22.7	0.09	0.003	0.04	0.004	0.34	3.5	0.24

ND=not determined.

[a] Total siderite Fe determined as the difference between a 24-h 1 N HCl extraction and a 2-h dithionite extraction (see text for details).

Roxbury and Biwabik siderites. In addition, the pH 4 extraction resulted in significant dissolution of ferrihydrite and lepidicrocite. For many studies, particularly of modern sediments where crystalline siderite may not be a significant component, a 24-h, room temperature acetate extraction at pH 4.5 appears sufficient for the complete dissolution of ankerite and poorly crystalline $FeCO_3$, and for the determination of trace Fe associated with carbonate phases. For studies where crystalline siderite is likely to be an important component, a 48-h, pH 4.5 extraction at 50 °C is more appropriate. This extraction resulted in the dissolution of >95% of the crystalline siderite, while leaving most Fe (oxyhydr)oxides relatively unaffected (Table 1). Furthermore, the slight dissolution of ferrihydrite evident with this extraction technique (Table 1) is unlikely to be a major concern in studies of ancient sediments, due to the relatively rapid environmental transformation of ferrihydrite to geothite (e.g. Schwertmann, 1966) or hematite (e.g. Torrent and Cabedo, 1986). Many modern sediments may also contain significant concentrations of Fe in the form of acid volatile sulfides (AVS). In an additional test, the pH 4.5 acetate extraction gave complete recovery of AVS from a fine-grained coastal sediment from Young Sound, N.E. Greenland (determined relative to an acid distillation; Cornwell and Morse, 1987).

A 48-h hydroxlamine–HCl extraction effectively solubilized both ferrihydrite and lepidocrocite, while removing only a minor amount of akaganéite and leaving the remaining minerals relatively unaffected (Table 1). A 48-h extraction time is necessary to adequately extract both ferrihydrite and lepidocrocite; after 24 h 100% of the ferrihydrite, but only ~64% of the lepidocrocite, had been solubilized. The dithionite extraction has been extensively tested (Mehra and Jackson, 1960; McKeague and Day, 1966; Canfield, 1988; Raiswell et al., 1994), and the results presented in Table 1 are in close agreement with these previous studies. Thus, a single dithionite extraction (for 2 h) effectively results in the quantitative dissolution of the ferric (oxyhydr)oxides ferrihydrite, lepidocrocite, akaganéite, goethite and hematite. The technique also dissolved 5–7% of the magnetite and 15% of the nontronite. Raiswell et al. (1994) found that nontronite was the only silicate mineral of a range tested which was significantly affected by this treatment.

It is well-established that acid oxalate extractions are efficient at dissolving poorly crystalline ferric oxides, in addition to crystalline oxides such as magnetite (e.g. Chao and Zhou, 1983; Canfield, 1988). Table 1 shows that for a 6-h oxalate extraction, ferrihydrite, lepidocrocite and magnetite were quantitatively extracted, while other Fe minerals were not extensively dissolved. These data alone suggest that a hydroxylamine–HCl extraction followed by an oxalate extraction may give an indication of the concentrations of magnetite present in sediments. Such a scheme for determining magnetite would appear preferable to a sequential hydroxylamine–HCl, dithionite, oxalate extraction scheme, due to the release of 5–7% of the magnetite in association with the dithionite extraction (Table 1). However, the presence of dissolved Fe(II) during oxalate extractions has been demonstrated to result in the catalytic dissolution of crystalline ferric (oxyhydr)oxides (e.g. Suter et al., 1988; Phillips et al., 1993), the extent of which depends on the concentration of Fe(II) present (Suter et al., 1988). Dissolved Fe(II) may be produced during oxalate extractions on modern and ancient sediments from the dissolution of magnetite and/or acid volatile sulfides. Thus a series of experiments were performed in which magnetite/goethite mixtures were subjected to the 6 h oxalate extraction, in order to determine whether the catalytic effect of Fe(II) caused significant dissolution of crystalline ferric (oxyhydr)oxides at concentrations of magnetite likely to be encountered during typical sediment extractions.

Fig. 1 highlights the significant catalytic effect of Fe(II) release from even relatively low concentrations of magnetite on the dissolution of goethite. The data are expressed in terms of the maximum concentration of Fe(II) expected in solution, assuming complete dissolution of magnetite during the course of each experiment. For example, a concentration of 5 mg l^{-1} Fe(II) would be equivalent to a magnetite Fe concentration of 0.075 wt.% for a 10 ml extraction on 200 mg of sediment. Thus the oxalate extraction is likely to cause significant dissolution of crystalline oxides other than magnetite when applied to natural sediments (cf. magnetite concentrations in the continental sediments reported later). Therefore the sequential dithionite extraction should be performed before the oxalate extraction, even though this may slightly underestimate magnetite Fe (by around 5%).

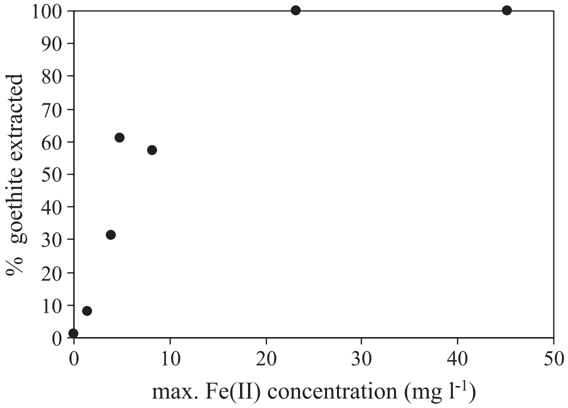

Fig. 1. Extent of goethite dissolution during oxalate extractions on goethite/magnetite mixtures. Data are expressed in terms of the maximum concentration of dissolved Fe(II), assuming complete dissolution of magnetite during the course of each experiment. Initial goethite concentration=80 mg l^{-1}.

Table 2

Details of the developed extraction scheme, with target phases and the reproducibility of each stage (based on replicate sequential extractions of international standard PACS1)

Extraction	Target phases	Terminology	RSD (%)
(1) Na Acetate, pH 4.5, 24 h[a]	Carbonate Fe, including siderite and ankerite	Fe_{carb}	5.4
(2) Hydroxylamine–HCl, 48 h	Ferrihydrite, lepidocrocite	Fe_{ox1}	4.4
(3) Dithionite, 2 h	Goethite, akaganéite, hematite	Fe_{ox2}	4.4
(4) Oxalate, 6 h	Magnetite	Fe_{mag}	4.4
(5) Boiling 12 N HCl	Poorly reactive sheet silicate Fe	Fe_{PRS}	6.3
Chromous chloride distillation[b]	Pyrite Fe	Fe_{py}	ND
Total Fe	Unreactive silicate Fe (Total Fe—sum of first 5 stages plus pyrite Fe)	Fe_U	7.5

RSD=relative standard deviation.

[a] For samples likely to contain significant concentrations of crystalline siderite, a 48-h extraction at 50 °C is recommended (see text for details).

[b] See Canfield et al. (1986).

Table 3

Recovery of Fe from a mixture of pure minerals during the first four sequential extraction stages

Fe fraction	Minerals tested	Actual individual mineral wt.% Fe	Actual total wt.% Fe	Measured wt.% Fe
Fe_{carb}	$FeCO_3$	3.3	3.3	3.2
Fe_{ox1}	Ferrihydrite	10.4	17.6	16.8
	Lepidocrocite	7.2		
Fe_{ox2}	Goethite	5.2		
	Hematite	6.3	13.5	14.0
	Akaganéite	2.0		
Fe_{mag}	Magnetite	23.6	23.6	24.1
Totals			58.0	58.1

3.2. Sequential extractions

Based on the results presented above, the extraction scheme detailed in Table 2 was developed. The first five stages are performed sequentially, and unreactive Fe is determined as the difference between total Fe and the sum of the first five stages plus pyrite Fe. Replicates of the PACS1 international sediment standard were carried through the procedure (this sample contains no pyrite and thus the separate chromous chloride extraction was not applied). The reproducibility of each stage is reported in Table 2.

Several mixtures of pure minerals were subjected to the first four stages of the sequential extraction procedure, and the results of a typical experiment are shown in Table 3. The recovery of Fe varied between 95% and 104% for each stage (generally within analytical errors; Table 2), with a close agreement

Table 4

Surface area, inorganic C, and the partitioning of Fe in the river and glacial grain size suites

Sample	SA (m^2 g^{-1})	Inorg. C (wt.%)	Fe$_{carb}$ (wt.%)	Fe$_{ox1}$ (wt.%)	Fe$_{ox2}$ (wt.%)	Fe$_{mag}$ (wt.%)	Fe$_{PRS}$ (wt.%)	Fe$_U$ (wt.%)	FeT (wt.%)
Mississippi									
<2 μm	ND	0.65	0.124	3.102	1.233	0.148	0.857	1.966	7.43
2–6 μm	25.7	0.42	0.067	1.429	0.826	0.102	0.784	1.682	4.89
6–15 μm	17.0	0.27	0.029	0.795	0.602	0.070	0.598	1.086	3.18
15–25 μm	13.5	0.19	0.015	0.477	0.392	0.048	0.538	0.710	2.18
25–40 μm	8.1	0.07	0.012	0.283	0.265	0.051	0.453	0.616	1.68
40–63 μm	6.5	0.23	0.013	0.234	0.213	0.061	0.389	0.560	1.47
63–80 μm	6.8	0.33	0.010	0.233	0.208	0.062	0.402	0.555	1.47
80–125 μm	3.7	0.26	0.010	0.179	0.161	0.038	0.330	0.372	1.09
Tombigbee									
<2 μm	70.8	0.24	0.020	2.495	2.152	0.101	0.804	1.888	7.46
2–6 μm	32.4	0.29	0.010	1.693	1.541	0.096	0.764	1.516	5.62
6–15 μm	28.9	0.29	0.003	1.311	1.298	0.095	0.644	1.459	4.81
15–25 μm	25.9	0.02	0.003	1.103	1.138	0.075	0.570	1.171	4.06
25–40 μm	21.6	0.20	0.003	0.834	0.916	0.049	0.424	1.064	3.29
40–63 μm	12.8	0.23	0.003	0.607	0.666	0.040	0.436	0.948	2.70
63–80 μm	6.6	0.29	0.001	0.318	0.339	0.030	0.309	0.833	1.83
80–125 μm	6.1	0.13	0.001	0.251	0.262	0.040	0.219	0.497	1.27
Tsanfleuron									
<2 μm	ND	1.06	0.040	0.634	1.093	0.048	0.247	0.747	2.81
2–6 μm	32.4	2.84	0.092	0.497	0.970	0.035	0.225	0.472	2.29
6–15 μm	9.2	4.75	0.143	0.363	0.762	0.021	0.110	0.529	1.93
15–25 μm	5.6	5.17	0.149	0.278	0.585	0.014	0.097	0.426	1.55
25–40 μm	4.6	5.04	0.141	0.254	0.532	0.010	0.101	0.479	1.52
40–63 μm	6.5	4.39	0.119	0.270	0.527	0.018	0.110	0.416	1.46
63–80 μm	3.6	4.27	0.130	0.144	0.332	0.010	0.203	0.310	1.13
80–125 μm	2.8	4.47	0.135	0.123	0.304	0.011	0.210	0.101	0.88
Tsijiore									
<2 μm	20.1	<0.01	0.072	2.786	0.194	0.233	0.795	1.977	6.06
2–6 μm	10.4	<0.01	0.022	1.433	0.106	0.149	0.503	3.257	5.47
6–15 μm	3.8	<0.01	0.004	0.737	0.069	0.077	0.694	2.635	4.22
15–25 μm	2.9	<0.01	0.002	0.453	0.056	0.052	0.381	2.349	3.29
25–40 μm	2.4	<0.01	<0.001	0.367	0.069	0.039	0.388	1.860	2.72
40–63 μm	1.4	0.05	<0.001	0.227	0.069	0.030	0.360	1.254	1.94
63–80 μm	1.6	0.03	<0.001	0.221	0.084	0.033	0.459	1.078	1.88
80–125 μm	1.3	0.03	<0.001	0.234	0.147	0.042	0.488	1.214	2.13

Fe$_{carb}$ was determined by a room temperature, 24 h extraction at pH 4.5.

between the actual and measured total Fe concentrations, indicating that the sequential procedure may be successfully used to assess the partitioning of iron in sediments.

The results from the application of the extraction procedure to the river and glacial suites, in addition to surface area and inorganic carbon measurements, are presented in Table 4. Pyrite Fe is not a significant component of the river and glacial sediments (Poulton and Raiswell, 2002), and was thus not measured. Exchangeable Fe (extracted by 1 M $MgCl_2$) was also measured on these sediments, but was below detection (<0.001 wt.%) in all cases. As an additional check on the experimental procedure, samples were subjected to a non-sequential, boiling 12 N HCl extraction for 1 min. The relationship between this single extraction and the sum of the first five extractions (see Table 4) is shown in Fig. 2. The amount of Fe extracted in both cases should be equivalent, and the close agreement between these two data-sets further validates the extraction scheme and implies that the sequential procedure does not result in the dissolution of any 'unreactive' Fe.

Concentrations of Fe_{carb} were generally low for the Tombigbee and Tsijiore data-sets, consistent with low inorganic C contents (Table 4). By contrast, the higher concentrations of inorganic C in Mississippi and Tsanfleuron sediments resulted in relatively increased concentrations of carbonate-associated Fe (these sediments do not contain appreciable siderite or ankerite and thus Fe_{carb} dominantly consists of trace Fe within the carbonate). As a result, Fe_{carb} contents correlate closely with inorganic C for these two data-sets (Fig. 3). It should be noted that the inorganic carbon contents of these sediments do not directly correlate with decreasing grain size (particularly in the case of the Tsanfeuron sediments; Table 4). Thus the relationships in Fig. 3 do not result from the relatively increased dissolution of (oxyhydr)oxide Fe from the finer grain size fractions. These observations support the data obtained for single extractions on pure mineral phases (Table 1), and suggest that the room temperature, pH 4.5 acetate extraction is effective at dissolving carbonate-associated Fe (but not crystalline siderite) while essentially leaving Fe (oxyhydr)oxides unaffected.

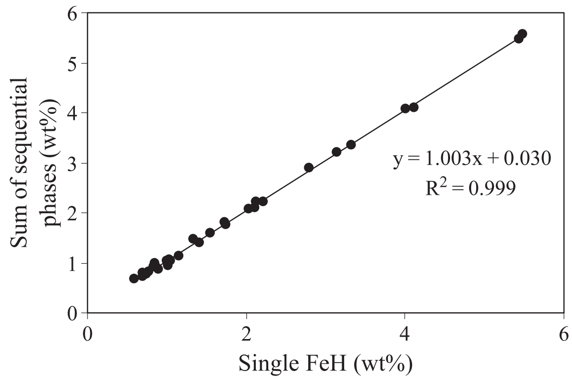

Fig. 2. Comparison of the sum of the first five sequential extraction stages with a single boiling 12 N HCl extraction for all river and glacial data.

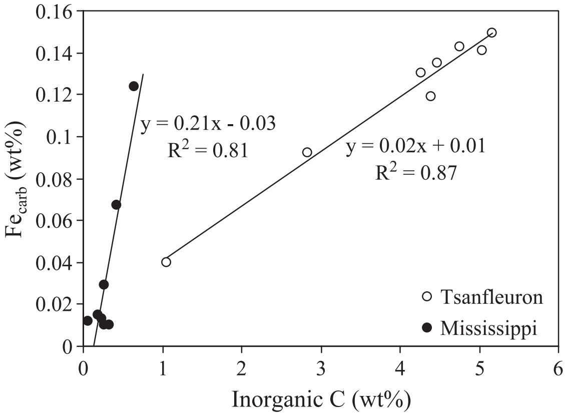

Fig. 3. Fe_{carb} as a function of inorganic C for Tsanfleuron and Mississippi sediments.

The Fe_{ox1} and Fe_{ox2} fractions show enrichments in the finer grain-size fractions of all the sediments explored (Table 4), and as a result display a strong association with surface area (Fig. 4). Magnetite Fe, Fe_{PRS}, and Fe_U are all also enriched in the finer grain-size fractions (Table 4), but magnetite additionally shows smaller enrichments in the medium-coarse grain-size fractions (Fig. 5).

4. Discussion

4.1. Application to modern and ancient sediments

The results presented above suggest that the sequential extraction scheme detailed in Table 2 may be successfully used (in full or in part) to assess Fe partitioning in modern and ancient sediments. The

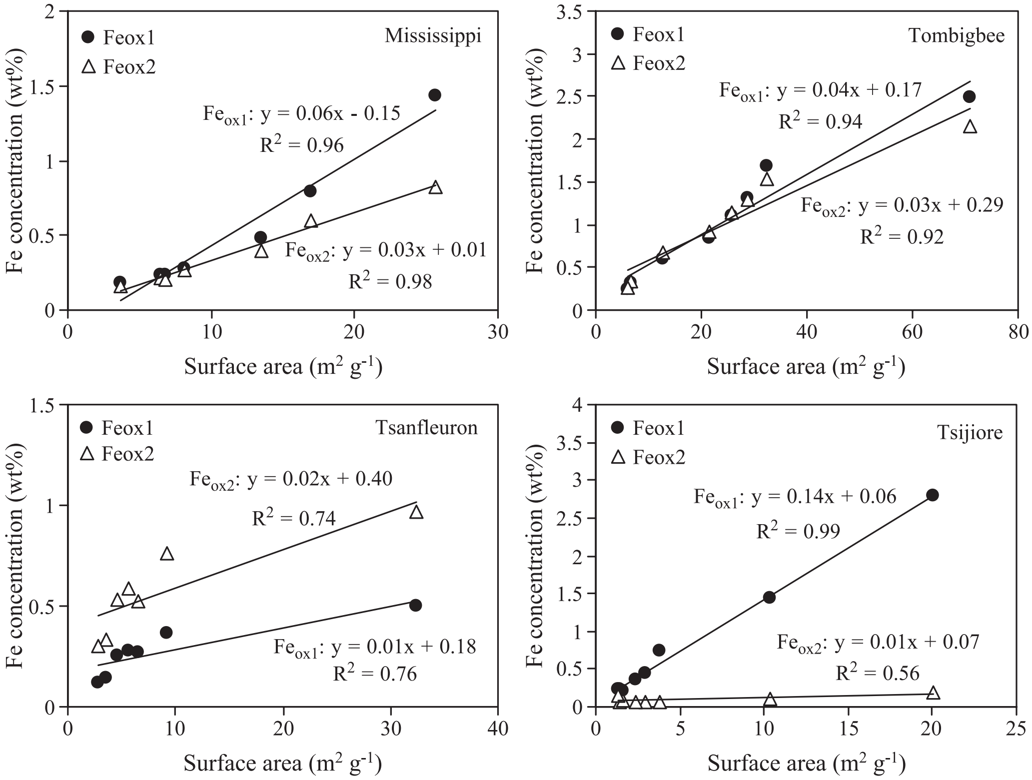

Fig. 4. Fe$_{ox1}$ and Fe$_{ox2}$ as a function of surface area for the river and glacial suites.

scheme is flexible and adaptable to different sediment types. Thus, the precise details of the acetate extraction will depend on the nature of the sediments and the objectives of the study. In general, the room temperature, pH 4.5 extraction for 24 h is recommended for sediments where crystalline siderite is not expected to be a significant component, while the 50 °C, 48 h extraction is recommended for sediments likely to contain crystalline siderite.

The concentrations of Fe sulfides will need to be assessed in many sediment types. Where pyrite is the only significant Fe sulfide, the concentration is determined on a sub-sample via the chromium reduction method (Canfield et al., 1986). Pyrite is not solubilized by any of the sequential extraction stages (see Lord III, 1982; Cornwell and Morse, 1987), and thus unreactive Fe can be determined as the difference between total Fe and the first five sequential stages plus pyrite Fe (Table 2). The presence of AVS may be determined on a sub-sample by an acid distillation (Cornwell and Morse, 1987). Since AVS is quantitatively solubilized by the pH 4.5 acetate extractions (see earlier), the Fe$_{carb}$ content of sediments containing AVS can be determined as the difference between the acetate and AVS extractions. In cases where AVS is of interest, samples should be preserved in a ZnCl$_2$ solution (e.g. Canfield et al., 1993) to avoid sulfide oxidation.

4.2. Iron partitioning in riverine and glacial sediments

One important application of the extraction scheme relates to the partitioning of iron in sediments which are ultimately transported to marine settings. The partitioning of iron in such sediments may influence the amount of sulfide fixed (as pyrite) during sediment diagenesis (e.g. Canfield, 1989; Canfield et al., 1992), and will exert a strong control on the transport of trace metals, organics, and ligands such as phosphate (e.g. Tipping, 1981; Salomons and Forstner, 1984; Poulton and Raiswell, 2000). The close relationship between

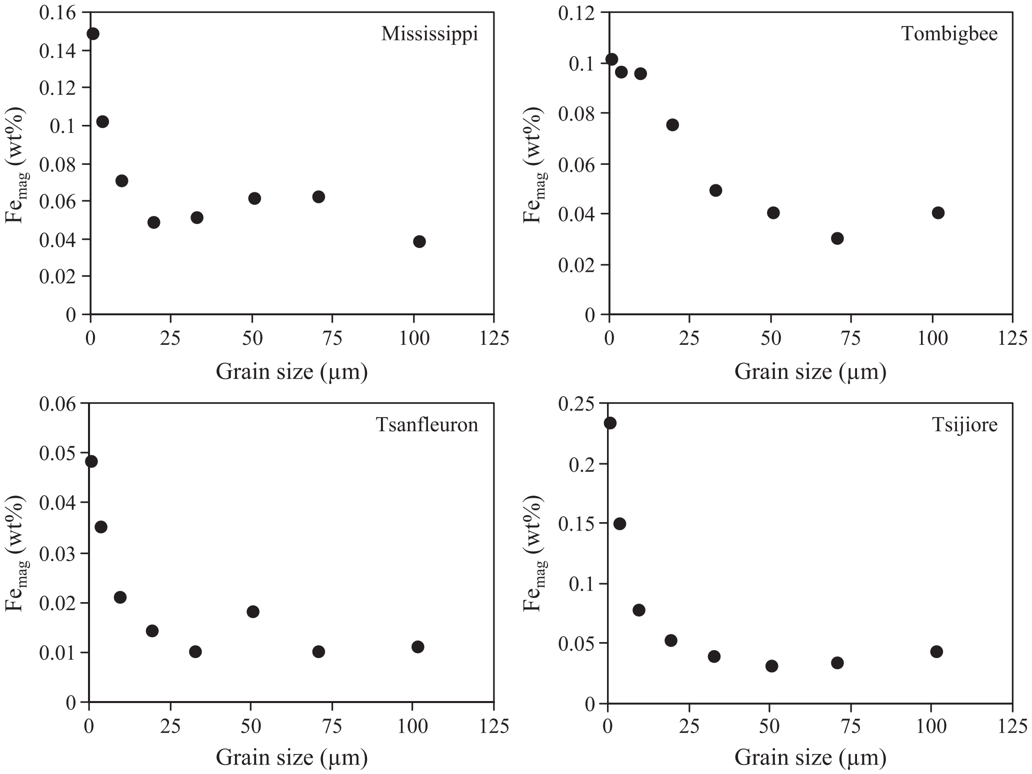

Fig. 5. Grain size distribution of magnetite Fe in the river and glacial suites.

surface area and Fe (oxyhydr)oxides (Fig. 4) is well-documented (e.g. Gibbs, 1977; Horowitz and Elrick, 1987), and implies an association with mineral surfaces (Gibbs, 1977; Horowitz and Elrick, 1987). However, Fe (oxyhydr)oxides do not occur as uniform surface coatings in river sediments. Electron microscope observations indicate three main modes of occurrence of Fe (oxyhydr)oxides in relatively fine-grained (<125 μm) river sediments (Poulton and Raiswell, in review): (1) small spheres (commonly 10–20 nm) associated with the edges of clay minerals in fine-grained fractions; (2) crystalline (oxyhydr)-oxides infilling mesopores in medium-coarse fractions; and (3) discrete crystalline (oxyhydr)oxides in medium-coarse fractions.

The application of the sequential extraction procedure to the river and glacial suites yields further insights into the partitioning of different Fe minerals in river and glacial environments. While it is clear that both the Fe$_{ox1}$ and Fe$_{ox2}$ fractions are dominantly associated with mineral surfaces (Fig. 4), the ratio Fe$_{ox1}$/Fe$_{ox2}$ varies as a function of surface area (and hence grain size; Fig. 6). Thus, finer-grained fractions contain relatively higher proportions of minerals in the Fe$_{ox1}$ pool. These observations imply different dominant modes of transport for poorly crystalline (i.e. ferrihydrite in the Fe$_{ox1}$ pool) and crystalline (i.e. Fe$_{ox2}$) Fe (oxyhydr)oxides, although there is also likely to be considerable overlap between the two groups. It is likely that poorly crystalline Fe (oxyhydr)oxides are commonly associated with the edges of fine-grained clay minerals, where small spheres appear to be the dominant Fe (oxyhydr)oxide morphology (see Poulton and Raiswell, in review). By contrast, the infilling of mesopores in medium-coarse fractions appears to be of increased importance for crystalline Fe (oxyhydr)oxides. Clay minerals supply a large proportion of the total surface area in fine-grained sediments (e.g. Mayer and Rossi, 1982), while mesopores may supply a large proportion of the surface area in medium-coarse fractions (Mayer, 1994). The strong relationships evident between

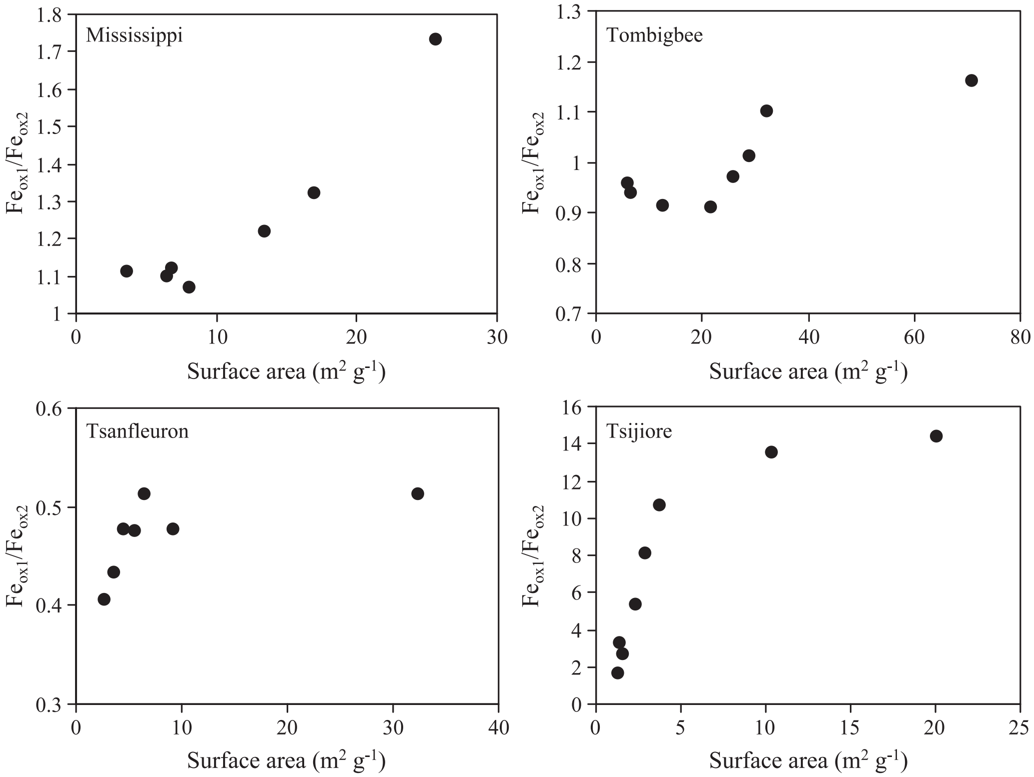

Fig. 6. Fe_{ox1}/Fe_{ox2} as a function of surface area for the river and glacial suites.

surface area and both the Fe_{ox1} and Fe_{ox2} pools (Fig. 4) are not, therefore, necessarily due to the simple presence of surface coatings, but are more likely due to the specific association of different iron minerals with the physical and mineralogical parameters that supply the majority of the surface area in different grain-size fractions.

Magnetite Fe also shows a significant relationship with grain size (and surface area) in finer fractions, but this relationship appears to be decoupled in coarser fractions (Fig. 5). This implies a relatively increased occurrence of magnetite as discrete mineral grains in coarser fractions, and is consistent with observations on the nature of magnetite in continental margin sediments (Canfield and Berner, 1987). The increased concentrations of Fe_{PRS} and Fe_U in finer fractions (Table 4) likely occurs due to a simple mineralogical control. In general, silicate minerals with significant concentrations of Fe tend to be clay minerals and other alumino-silicate minerals, which are often the more fine-grained components of rocks and soils.

5. Conclusions

The sequential extraction procedure developed during this study provides greater information on the partitioning of sediment iron than has previously been possible. In particular, the ability to estimate concentrations of carbonate Fe (particularly siderite and ankerite) and magnetite Fe in ancient sediments may help for the interpretation of paleoenvironmental depositional conditions.

The application of the extraction procedure to river and glacial particulates provides insight into the dominant modes of occurrence of different iron minerals in the modern environment. Poorly crystalline (i.e. ferrihydrite in the Fe_{ox1} pool) and crystalline (i.e. Fe_{ox2}) Fe (oxyhydr)oxides are largely associated with mineral surfaces. However, our data additionally suggest that the Fe_{ox1} pool may have a greater propensity to be associated with the edges of clay minerals in finer-grained fractions, while the infilling of mesopores in medium-coarse fractions may be relatively more important for the Fe_{ox2} pool. The minerals of the Fe_{ox1} fraction are considerably more reactive towards dissolved sulfide than those of the Fe_{ox2} fraction (Canfield et al., 1992; Poulton et al., 2004a). Thus fine-grained sediments are likely to be rich in Fe which is particularly reactive towards sulfide.

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