THE LOW-TEMPERATURE GEOCHEMICAL CYCLE OF IRON: FROM CONTINENTAL FLUXES TO MARINE SEDIMENT DEPOSITION

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ABSTRACT. Suspended sediments from 34 major rivers (geographically widespread) and 36 glacial meltwater streams have been examined for their variations in different operationally-defined iron fractions; Fe_{HR} (iron oxides soluble in dithionite), Fe_{PR} (iron soluble in boiling HCl but not in dithionite) and Fe_U (total iron less that soluble in boiling HCl). River particulates show a close association between Fe_{HR} and total iron (FeT), reflecting the effects of chemical weathering which derive oxide iron from, and retain it in close association with, total iron. Consistent with this, continental-scale average Fe_{HR}/FeT ratios vary with runoff ratios (average river runoff per unit area/average precipitation per unit area). By contrast, the diminished effects of chemical weathering produce no recognizable association of Fe_{HR} with FeT in glacial particulates, and instead both Fe_{PR} and Fe_U are closely correlated with FeT, reflecting essentially pristine mineralogy. A comparison of the globally-averaged compositions of riverine particulates and marine sediments reveals that the latter are depleted in Fe_{HR}, Fe_{PR} and FeT but enriched in Fe_U. The river and glacial particulate data are combined with estimates of authigenic, hydrothermal, atmospheric and coastal erosive iron fluxes from the literature to produce a global budget for Fe_{HR}, Fe_{PR}, Fe_U and FeT. This budget suggests that the differences between riverine particulates and marine sediments can be explained by; (i) preferentially removing Fe_{HR} from the riverine particulate flux by deposition into inner shore reservoirs such as floodplains, salt marshes and estuaries; and (ii) mixing the resulting riverine particulates with Fe_{HR}-depleted glacial particulates. Preliminary measurements of inner shore sediments are consistent with (i) above. Phanerozoic and modern normal marine sediments have similar iron speciation characteristics, which implies the existence of a long-term steady state for the iron cycle. This steady state could be maintained by a glacioeustatic feedback, where Fe_{HR}-enriched riverine particulates are *either* more effectively trapped when sealevel is high (small ice masses, diminished glacial erosion), *or* are mixed with greater masses of Fe_{HR}-depleted glacial particulates when sealevel is low (large ice masses, enhanced glacial erosion). Further important controls on the steady state for Fe_{HR} operate through the formation of euxinic sediments and ironstones, which also provide sealevel-dependent sinks for Fe_{HR}-enriched sediment.

INTRODUCTION

Valuable insights into the nature and magnitude of oceanic removal processes for major and trace elements have been gained from examining the mass balance relationships between elemental riverine fluxes, and concentrations in seawater and oceanic sediments (see for example Garrels and Mackenzie, 1971; Martin and Meybeck, 1979; Drever and others, 1988; Martin and Windom, 1991). However, previous attempts to examine such mass balance relationships have usually been based on total element fluxes and concentrations whereas the geochemical cycles of many elements, and in particular iron (Wollast and Mackenzie, 1983; Martin and Windom, 1991; Haese, 2000), may be strongly affected by their solid phase speciation. Thus the purpose of this paper is to present a more detailed approach to the low temperature geochemical cycle of iron, by quantifying the major continental fluxes and marine sediment sinks in terms of solid phase speciation.

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The global iron cycle is unique for a combination of three reasons. Firstly, iron is one of the few major elements capable of undergoing redox transformations under surface (or near-surface) conditions. Secondly, iron exhibits markedly non-conservative behavior in estuaries (where it is preferentially flocculated and/or precipitated), such that dissolved fluxes to the ocean basins are typically depleted in iron by approximately 90 percent with respect to riverine supply (Boyle and others, 1974; Holliday and Liss, 1976; Sholokovitz, 1976; Boyle and others, 1977; Sholokovitz and others, 1978). Thirdly, iron is overwhelmingly transferred from the continents to the ocean in particulate rather than dissolved phases (Martin and Meybeck, 1979; Drever and others, 1988; Martin and Windom, 1991). These factors all involve to some extent the formation, transport and aggregation of iron as oxides, and thus emphasize the significant role that solid phase speciation plays in the iron cycle (Haese, 2000).

Our approach is based on the findings of Trefry and Presley (1982) who compared the solid phase speciation of suspended sediment samples from the Mississippi River and delta, with bottom sediments from the delta. The total Fe/Al ratio remained roughly uniform in suspended sediment through the salinity gradient, but changes did occur in the amounts of iron extracted by citrate-buffered dithionite (mainly iron oxides; see later) such that riverine suspended sediment was enriched in oxide iron (2.4 percent Fe) relative to delta suspended sediment (2.2 percent Fe) and delta bottom sediments (1.8 percent Fe). The ratios of oxide iron to Total Fe were 0.52, 0.47 and 0.43 for riverine suspended, delta suspended and delta bottom sediments respectively. The main thrust of the Trefry and Presley (1982) study was towards changes in Mn speciation through the delta and the iron data were not discussed in detail, although they clearly suggest that there may be differences in the solid phase iron speciation of riverine suspended sediment compared to marine sediments.

We will present comparable iron speciation data for suspended sediment from a selection of 34 world rivers, which will be used to quantify the global riverine input flux in terms of different solid phase iron fractions. Additionally we report the solid phase speciation of rock flour collected from 36 glacial meltwater streams and of Saharan atmospheric dust. Raiswell and Canfield (1998) have reported solid phase iron speciation data for modern marine sediments from different depositional settings, and these data are here supplemented by analyses for a suite of deep-sea red clays. The riverine data will be compared to this marine sediment data to ascertain whether the changes observed by Trefry and Presley (1982) are evident on a global scale. The analyses presented here will be supplemented by literature data in order to derive values for other iron fluxes (glacial, atmospheric, hydrothermal, coastal erosive and authigenic), and to examine their impact on the riverine/marine sediment comparison. Finally we will construct a preliminary partial geochemical cycle for iron species on a global scale, and examine how this cycle has operated through the Phanerozoic.

<p style="text-align:center">SAMPLING METHODS</p>

The Raiswell and Canfield (1998) database includes 46 samples of aerobic Continental Margin sediments from depths < 1000 m and 56 Deep Sea samples from depths > 1000 m. The continental margin sediments are muds and sands, and the Deep Sea samples include carbonate and siliceous oozes and clays. Thus the main sediment types are well represented, but pelagic red clays are possibly an important omission. Hence 9 deep-sea red clays have been analysed (table 1), comprising 5 samples from the eastern and northwestern Atlantic Ocean (Thomson and others, 1984; Colley and others, 1984) and 4 from the ODP sites 135 and 195 in the Pacific Ocean (Parson and others, 1992; Salisbury and others, 2001). New data are also presented for a suite of Saharan dust samples (table 1), collected on four occasions in 2001 on a clean glass impactor sampler located at Bet Herut, on the Mediterranean coast of Israel (Herut and others, 2001).

TABLE 1

Solid phase iron speciation in deep sea red clays and atmospheric particulates

	Fe_{HR}	Fe_{PR}	Fe_U	FeT	$Fe_{HR}/$ FeT
RED CLAYS					
E. Atlantic (25°42.4'N 30°57.7'W)[1]					
Core 10400 69-71 cm	2.26	0.99	2.80	6.06	0.37
Core 10400 173-175 cm	1.86	0.88	2.67	5.41	0.34
NW Atlantic (23°41.3'N 59°40.9'W)[2]					
Core 10163 40-42 cm	1.58	1.46	2.58	5.60	0.28
NW Atlantic (26°49'N 60°24.7'W)[2]					
Core 10164 24-26 cm	1.65	1.45	2.61	5.71	0.28
NW Atlantic (21°43.6'N 65°30.5'W)[2]					
Core 10170 20-22 cm	1.30	1.59	2.10	4.99	0.26
S Pacific (18°34.0'S 177°51.7'W)[3]					
ODP Site 135-834 0-5 cm	1.94	-	-	2.81	0.69
S Pacific (22°13.2'S 175°44.9'W)[3]					
ODP Site 135-840 0-5 cm	0.42	-	-	3.13	0.13
N Pacific (13°47.0'N 146°0.17'E)[4]					
ODP Site 195-1201A 0-5 cm	1.24	-	-	5.58	0.22
ODP Site 195-1201B 0-5 cm	1.89	-	-	5.23	0.36
Mean	1.57	-	-	4.95	0.33
Standard Deviation	0.54	-	-	1.16	0.16
SAHARAN DUST					
Bet Herut, Israel, 30/4/01	0.96	0.60	1.42	2.98	0.32
Bet Herut, Israel, 1/5/01	1.07	0.57	1.81	3.45	0.31
Bet Herut, Israel, 13/5/01	0.98	0.47	1.55	3.00	0.33
Bet Herut, Israel, 20/10/01	1.29	0.40	2.10	3.79	0.34
Mean	1.08	0.51	1.72	3.30	0.33
Standard Deviation	0.15	0.09	0.30	0.39	0.01

Superscripts identify further details: [1]Thomson and others (1984), [2]Colley and others (1984), [3]Parson and others (1992), [4]Salisbury and others (2001).

Suspended riverine particulates were collected from 25 rivers, which discharge directly into the ocean, and these data are combined with literature analyses of 9 additional rivers (table 2). Suspended sediments were collected from the mid-point of the main channel at approximately mid-depth. Rivers were sampled whenever possible at downstream locations but always in regions remote from any tidal influence (that is, where there is generally downstream, unidirectional flow; GESAMP, 1987). In order to minimize the effects of unrepresentative sample collection, sufficient volumes of water were sampled to allow the collection and analysis of several grams of sediment from each river. Samples were pressure-filtered through either 0.40 μm polycarbonate filters or 0.45 μm nitrocellulose filters, then air-dried and carefully removed from the filters using a scalpel (see Poulton and Raiswell, 2000). Samples were collected at various times from 1995 to 1997, with individual rivers being sampled on only one occasion. The glacial samples consist of meltwater suspended sediments collected from many of

TABLE 2

Characteristics of the riverine data set

River	Sediment discharge (Tg/yr)	Runoff (mm/yr)	Precipitation (mm/yr)	Date sampled	Locality
Amazon	1200	1067	2228	7/96	Macapa, Brazil
Huanghe	1100	72	501	7/97	N. China (37°52'N, 118°42'E)
Brahmaputra	540	378	2030	6/97	Bangladesh (25°14'N, 89°36'E)
Changjiang	480	510	1164	7/97	Shishou, China (29°44'N, 112°24'E)
Mississippi	400	151	895		See Canfield (1997)
Magdalena	220	843	2225	1/97	Colombia (07°30'N, 73°05'W)
Mekong	160	544	2225	3/96	My Tho, Vietnam
Colorado	120	134	500	6/96	Arizona, USA (37°56'N, 110°22'W)
Nile	120	48	816	4/96	Atbara, Sudan (17°38'N, 33°56'E)
Danube	67	259	889	11/95	Tuttlingen, Germany
Yukon	60	249	502		See Gibbs (1997)
Rhone	31	559	1131	10/95	Loyettes, France
Rio Grande	20	8.3	380		See Canfield (1997)
Brazos	16	63	630		See Canfield (1997)
Han	10	590	NA	1/97	Seoul, Korea
Burdekin	3	7.6	NA	1/96	Queensland, Australia, (19°05'S, 145°41'E)
Garonne	2.2	359	1079	8/96	Toulouse, France
Tombigbee	2.2	510	1510		See Canfield (1997)
Yodogawa	1.9	NA	NA	6/97	Osaka, Japan
Loire	1.5	246	969	10/95	Nevers, France
Seine	1.1	130	NA	10/95	Marney S. Seine, France
Rhine	0.72	462	1215	11/95	Schaffhausen, Switzerland
Connecticut	0.56	575	1130		See Canfield (1997)
Severn	0.44	380	NA	3/96	Worcester, UK
Colorado, Texas	0.42	25	880		See Canfield (1997)
Wye	0.20	630	NA	3/96	Hereford, UK
Tyne	0.13	680	NA	11/95	Newcastle, UK
Clyde	0.11	430	NA	12/96	Hamilton, Scotland
Neuse	0.08	360	1260		See Canfield (1997)
Ouse	0.03	NA	NA	2/96	York, UK
Avon	0.02	NA	NA	3/96	Stratford, UK
James	0.01	380	1130		See Canfield (1997)
Aire	0.01	NA	NA	2/96	Skipton, UK
Tees	0.006	NA	NA	2/96	Barnard Castle, UK

Discharge, runoff and precipitation data from Milliman and Syvitski (1992). NA = not available. Sample dates and localities are given only for those rivers sampled during the present study.

the world's major glacial localities (table 3). The sampling procedure was essentially the same as for river particulates, with samples being filtered (0.4 or 0.45 μm) either immediately or within a few hours of collection.

Table 2 shows the sediment discharges for all the rivers, which together represent approximately 23 percent of the annual global riverine sediment flux, based on the estimate of 20000 Tg/yr (see later) for pre-dam sediment discharge to the ocean (Milliman and Syvitski, 1992). Milliman and Syvitski (1992) subdivide this discharge flux on a continental-scale and on this basis our river particulate data represent 46 percent of the sediment flux from North America, 73 percent from South America, 45 percent from Europe, 36 percent from Asia, 19 percent from Africa and 5 percent from Australia. We have no data from Central America or the Oceanic Islands. Thus there is good coverage for many of the important sediment-discharging regions, however certain areas are under-represented by the current data set (see later).

TABLE 3

Chemical characteristics of the glacial sediment samples. All concentrations in wt%

Sample	Fe_{HR}	Fe_{PR}	Fe_U	FeT	$Fe_{HR}/$ FeT	Org. C
Argentiere (The Alps)	0.07	0.63	0.32	1.02	0.069	0.04
Arolla-upper (The Alps)	0.19	0.63	1.90	2.72	0.070	0.07
Arolla (The Alps)	0.78	1.61	2.57	4.96	0.16	0
Astrolabe (Antarctica)	0.24	0.89	0.35	1.48	0.16	0.03
Austerdalsbregn (Norway)	0.03	0.99	0.29	1.31	0.023	0.04
Austre Broggerbreen (The Alps)	0.54	1.11	0.11	1.76	0.31	0.69
Black Rapids (Alaska)	0.76	3.29	0.76	4.81	0.16	0.55
Boverdal (Norway)	0.85	2.74	2.96	6.55	0.13	0.98
Campbell (Antarctica)	0.24	1.85	0.37	2.46	0.10	0.08
Crary Ice Rise (Antarctica)	0.14	1.14	1.08	2.36	0.059	0.11
Finsterwalder (Norway)	0.52	0.59	1.13	2.24	0.23	0.94
Glomaga (Norway)	0.76	3.49	0.80	5.05	0.15	4.69
Gulkana (Alaska)	0.30	2.11	3.89	6.30	0.048	0.18
Helm (Canada)	0.74	1.79	0.89	3.42	0.22	0.37
Hvita (Iceland)	0.64	3.09	3.78	7.51	0.085	0.08
Jakobshaven Isbrae (Greenland)	0.05	0.45	1.02	1.52	0.033	0.02
John Evans (Ellesmere Island)	0.17	0.18	0.14	0.49	0.35	0.50
Leverett (Greenland)	0.11	0.69	2.25	3.05	0.036	0.04
Markarfljot (Iceland)	0.89	2.42	6.60	9.91	0.090	0
Mattevispa (Switzerland)	0.55	1.70	2.92	5.17	0.11	1.11
Noyes (Alaska)	0.41	2.32	2.37	5.10	0.080	0.70
Peters (Alaska)	1.01	2.48	1.21	4.70	0.22	0.37
Place (Canada)	0.13	0.96	1.87	2.96	0.044	0
Pre De Ba (Italy)	0.12	0.08	0.39	0.59	0.20	0.06
Quissertaq (Greenland)	0.23	1.25	2.17	3.65	0.06	0.04
Robertson (Canada)	0.48	0.31	0.02	0.81	0.59	1.10
Russell (Greenland)	0.17	0.84	2.86	3.87	0.044	0.03
Saint Soilin (The Alps)	0.97	1.84	1.31	4.12	0.24	0.56
Scott Turnerbreen (Svalbard)	1.72	1.19	0.88	3.79	0.45	3.29
Skattafelljokui (Iceland)	0.71	4.55	2.39	7.65	0.093	0
Solheimajokull (Iceland)	0.17	5.63	6.40	12.0	0.014	0.14
Storglacieren (Sweden)	0.20	0.53	7.71	8.44	0.024	0.24
Svart (Norway)	0.38	2.22	3.26	5.86	0.065	0.85
Tsanfleuron (The Alps)	1.04	0.16	0.52	1.72	0.61	0.26
Tsijiore (The Alps)	0.17	0.53	3.22	3.92	0.043	0.05
Variegated (Alaska)	0.41	2.79	5.50	8.70	0.047	0.15
Mean	**0.47**	**1.64**	**2.12**	**4.22**	**0.11**	
Standard Deviation	**0.37**	**1.28**	**1.95**	**2.78**	**0.11**	

The sampling of riverine suspended particulates in order to estimate annual fluxes of sediment mass and associated elements is a complex matter (see Walling and others, 1992; de Vries and Klavers, 1994; Olive and Rieger, 1992). Such estimates require measurements of water discharge, suspended sediment concentration and

suspended sediment composition, which are all subject to temporal and spatial variations (Walling, 1983; Horowitz and others, 2001). Horowitz and others (2001) point out that there can be more than order of magnitude variations in the site-specific measurements of discharge and suspended sediment concentrations (on an intra- or inter-annual basis), but compositional variations rarely exceed a factor of 2. Consistent with this, compositional variations between rivers tend to be higher than those found for repeat analyses of sediment from single rivers, particularly for major elements (Konovalov and Ivanova, 1970; Martin and Meybeck, 1979).

The present study further seeks to constrain compositional (also mineralogical and grain-size) variations by mainly focusing on ratios of iron species to total iron. There are no literature values on sources of variation in ratios of iron species to total iron, but there is good evidence from several major river systems to show that major element ratios of suspended riverine particulates show relatively little variation with discharge. Trefry and Presley (1982) found that the Fe/Al ratio of suspended particulates from the Mississippi remained constant $(0.53+/-0.01)$ through an annual discharge cycle. Similarly riverine particulates from the Scheldt (Zwolsman and van Eck, 1999) showed little seasonal variation in Fe/Al $(1.02+/-0.06)$. Longer term variations have been examined by Horowitz (personal communication), who recorded the following mean and standard deviations for Fe/Al ratios in suspended sediment collected at approximately monthly intervals from autumn 1995 to spring 2002 in the Ohio $(0.55+/-0.03)$, Mississippi $(0.46+/-0.05)$, Missouri $(0.42+/-0.06)$, Atchafalaya $(0.48+/-0.05)$, Willamette $(0.71+/-0.06)$ and Columbia $(0.57+/-0.06)$ rivers in the United States. The Fe/Al ratio of suspended sediment (Tuominen, personal communication) from the Fraser River, Canada, collected twice monthly (spring 1991 to spring 1995) also showed only a limited variation $(1.47+/-0.20)$. In all these studies the coefficient of variation of the mean Fe/Al ratio lay in the range 5 to 13 percent. Somewhat larger variations (Walling, personal communication) have been found in some United Kingdom rivers with high Fe/Al ratios (Ouse $3.3+/-0.7$, Swale $3.6+/-0.8$), but overall the data indicate that single sampling episodes can provide a reasonable first approximation of major element ratios in suspended particulates.

<center>ANALYTICAL METHODS</center>

A variety of extraction procedures have been used to determine the speciation of metals in sediments (see for example Chester and Hughes, 1967; Gibbs, 1977; Tessier and others, 1979; Forstner and others, 1981). These procedures commonly provide a measure of the metals associated with five phases (adsorbed, associated with oxyhydroxides, organic matter or carbonates, or present in residual silicate minerals). However, organic matter, carbonate and adsorbed phases tend to be relatively insignificant in terms of the total transport of iron (Gibbs, 1973, 1977; Trefry and Presley, 1982; Zhang and others, 1990; Baruah and others, 1996). Thus we have adopted a three stage extraction procedure for our river particulates, based on techniques used to determine the speciation of iron in marine sediments (see Berner, 1970; Canfield, 1989; Raiswell and others, 1994). The techniques used to determine iron speciation in our riverine sediments in table 4 are therefore identical to those adopted for the marine sediments to which they will be compared.

The chosen extraction scheme for iron allows the recognition of three operationally defined fractions commonly used to define the reactivity of sediment iron towards dissolved sulfide. Amorphous and crystalline iron oxides (with the exception of magnetite; Canfield, 1988; Raiswell and others, 1994) were solubilised by a citrate-buffered (pH = 4.8) sodium dithionite solution (Canfield, 1989; Raiswell and others, 1994). This method additionally removes the generally lower proportions of iron present in exchange sites (see above). A boiling 12N HCl extraction quantitatively extracts the same oxides but, in addition, removes iron present as magnetite and some

TABLE 4

Chemical characteristics of the river suspended sediment. Concentrations in wt%

River	Fe_{HR}	Fe_{PR}	Fe_U	FeT	$Fe_{HR}/$ FeT	$Fe_{PR}/$ FeT	$Fe_U/$ FeT	Organic C
Amazon	2.60	0.38	2.61	5.59	0.47	0.07	0.47	3.13
Huanghe	0.96	1.43	1.20	3.59	0.27	0.42	0.33	1.25
Brahmaputra	0.62	2.17	0.27	3.06	0.20	0.71	0.09	0.83
Changjiang	1.86	1.72	1.34	4.92	0.38	0.35	0.27	0.78
Mississippi[1]	1.27			4.19	0.30			1.83
Magdalena	3.00	0.96	0.98	4.94	0.61	0.19	0.20	2.46
Mekong	3.48	0.39	1.37	5.24	0.66	0.07	0.26	1.95
Colorado	1.10	1.33	0.55	2.98	0.37	0.45	0.19	2.05
Nile	2.40	2.71	4.09	9.20	0.26	0.30	0.45	0.72
Danube	2.03	1.17	1.69	4.89	0.42	0.24	0.35	15.75
Yukon[2]	2.57			6.32	0.41			
Rhone	1.61	0.89	0.83	3.33	0.48	0.27	0.25	8.36
Rio Grande[1]	0.68			2.69	0.25			1.24
Brazos[1]	0.72			3.61	0.20			1.10
Han	0.17	0.11	0.09	0.37	0.46	0.30	0.24	47.90
Burdekin	3.25	0.44	2.33	6.02	0.54	0.07	0.39	1.49
Garonne	2.08	0.99	2.07	5.14	0.41	0.19	0.40	5.54
Tombigbee[1]	2.06			5.09	0.41			2.51
Yodogawa	1.43	1.17	0.88	3.48	0.41	0.34	0.25	7.87
Loire	1.85	0.68	2.75	5.28	0.35	0.13	0.52	6.94
Seine	1.02	0.47	1.34	2.83	0.36	0.17	0.47	9.25
Rhine	1.42	0.09	2.61	4.12	0.35	0.02	0.63	15.84
Connecticut[1]	1.99			5.17	0.39			3.86
Severn	1.74	1.71	1.48	4.93	0.35	0.35	0.30	
Colorado (TX)[1]	0.75			3.74	0.20			1.35
Wye	0.63	1.33	1.31	3.27	0.19	0.41	0.40	6.00
Tyne	2.21	1.14	2.12	5.47	0.40	0.21	0.39	7.93
Clyde	1.07	0.49	1.99	3.55	0.30	0.14	0.56	9.96
Neuse[1]	4.16			7.29	0.57			6.62
Ouse	1.46	0.40	2.64	4.50	0.32	0.09	0.59	8.88
Avon	1.44	0.94	1.46	3.84	0.38	0.25	0.38	12.69
James[1]	3.02			5.95	0.51			5.35
Aire	3.19	0.47	1.32	4.98	0.64	0.09	0.27	9.83
Tees	4.93	0.85	1.58	7.36	0.67	0.12	0.22	11.35

Superscripts denote data from [1]Canfield (1997) and [2]Gibbs (1977).

silicate iron (Berner, 1970; Raiswell and others, 1994). This method also removes approximately 40 percent of the organic C from stream sediment standard STSD-4 and 10 to 55 percent of the organic C found in suspended sediment from the Brahmaputra, Magdalena, Nile and Burdekin rivers (Poulton and Raiswell, 2000). However the concentrations of iron associated with readily degradable organic matter are small (see above). Total iron was liberated with an $HF-HClO_4-HNO_3$ extraction (Walsh, 1980), and any additional iron extracted by this method relative to the HCl extraction can be considered to be present mainly as silicates. All iron analyses were measured by flame AAS. Replicate extractions (n = 8) of stream sediment standard STSD-1 indicate a precision of <4 percent for all methods, and total iron measurements were within 2 percent of the certified value.

    The iron extracted by dithionite (FeD) from oxides is considered to be highly reactive towards dissolved sulfide (Canfield and others, 1992) and is termed Fe_{HR}. The boiling HCl technique additionally removes iron (FeH) which is sulfidized only on a

Comparison of major element literature analyses of suspended river particulate compositions with analyses from the present study (in wt%). Standard deviations based on replicate measurements of stream sediment standard STSD-4 (from Poulton and Raiswell, 2000)

River	FeT This study	FeT Literature	Source
Amazon	5.59±0.11	5.55	Martin and Meybeck, 1979
Huanghe	3.59±0.07	3.72	Huang and others, 1992
Changjiang	4.92±0.10	5.20	Huang and Zhang, 1990
Magdalena	4.94±0.10	5.20	Martin and Meybeck, 1979
Mekong	5.35±0.10	5.60	Martin and Meybeck, 1979
Colorado	2.98±0.06	3.66	Martin and Meybeck, 1979
Danube	5.86±0.12	5.50	Martin and Meybeck, 1979
Garonne	5.42±0.11	5.80	Martin and Meybeck, 1979

time scale of 10^5 to 10^6 years (Canfield and others, 1992; Raiswell and Canfield, 1996). Hence FeH-FeD represents an iron fraction that reacts only slowly with dissolved sulfide and is here termed poorly reactive (Fe_{PR}). Finally, the total iron content (FeT) can be used to define the remaining fraction of iron, which is essentially un-reactive ($Fe_U = FeT-FeH$).

Note that the iron minerals originally present in riverine particulates as dithionite-soluble oxides (FeD) may be converted to sulfides following deposition in the marine environment. Here the oxides react with reduced sulfide produced by microbial sulfate reduction during the early stages of diagenesis (Canfield, 1989; Canfield and others, 1992). Thus the Fe_{HR} pool in the marine sediments of Raiswell and Canfield (1998) includes iron present as oxides (FeD) plus that present as pyrite and acid volatile sulfides (FeP). Hence Fe_{HR} is equal to FeD in riverine particulates and equal to FeD + FeP in marine sediments.

Riverine and glacial samples were also analysed for organic C, which was determined as the difference between total C and inorganic C after ashing at 450°C. Carbon was measured by gas chromatography using a Carlo Erba 1106 Elemental Analyzer, as also was total sulfur.

RESULTS

Mean Compositions of Riverine and Glacial Particulates

Prior to estimating the mean composition of riverine particulates we have compared our total iron data (table 5) with literature analyses of river particulates from the Amazon, Huanghe, Changjiang, Magdalena, Mekong, Colorado, Danube and Garonne. Our total Fe data are within 8 percent of literature data, except for Fe in the Colorado, where the difference is closer to 20 percent. We have also found a close correspondence between our total Al data and literature data for suspended sediments from a selection of these rivers (Poulton and Raiswell, 2000). These comparisons demonstrate that our sampling and analytical approaches provide data which are consistent with literature values.

The iron speciation data for the river suspended sediments sampled during this study are reported in table 4, together with some partial speciation data for 9 additional rivers from Canfield (1997) and Gibbs (1977). Figure 1 shows the relative variations in solid phase iron speciation for the 25 rivers, plotted in order of decreasing sediment discharge. The total iron content consists of rather variable proportions of Fe_{HR} (20-67 percent), Fe_{PR} (7-71 percent) and Fe_U (9-63 percent), but the order of abundance is most commonly Fe_{HR} (40+/−13 percent) > Fe_U (36+/−14 percent) > Fe_{PR} (24+/−16 percent). The riverine data in table 4 can be averaged with each river given equal weight, or averaged following discharge or areal-weighting. All these techniques give essentially similar results in the present case, so our approach has followed that of Milliman and Meade (1983). Thus each of the rivers in table 4 have been allocated to one of the drainage basins identified by Milliman and Meade (1983), and the compositions discharge-weighted to estimate the mean composition of the riverine flux from that basin (table 6). The basinal data are then discharge-weighted again to produce the mean composition of the riverine flux from each continent. The global mean composition of the riverine particulate flux can be estimated by again discharge-weighting the compositions from each continent (table 6). The overall composition of the global riverine particulate flux is FeT 4.49+/−0.18 percent, Fe_{HR} 1.94+/−0.08 percent, Fe_{PR} 1.12+/−0.04 and Fe_U 1.37+/0.05 percent. Our global FeT value of 4.49+/−0.18 percent compares closely with the value of 4.8 percent estimated by Martin and Meybeck (1979), even though they included some river data reported on an organic C-free basis.

The analyses of the 36 suspended sediments collected from glacial meltwaters are reported in table 3, and their relative variations in iron speciation are plotted in figure 1. Total S was below the detection limit (0.01 percent) in 29 samples and < 0.07 percent in the remaining 9 samples, so that Fe_{HR} mainly consists of dithionite-soluble Fe with no significant sulfide Fe. The mean composition is FeT 4.2+/−2.8 percent, Fe_{HR} 0.47+/−0.37 percent, Fe_{PR} 1.6+/−1.3 percent and Fe_U 2.1+/−2.0 percent. The proportions of Fe_{HR} are generally lower than those of Fe_{PR} and Fe_U but the ranges of variation (Fe_{HR} 1-60 percent, Fe_{PR} 6-75 percent and Fe_U 2-92 percent) are wider than those in riverine particulates. The mean total iron content on an organic C-free basis (4.3 percent) is close to the average for sedimentary rock (4.5 percent also organic C-free; Garrels and Mackenzie, 1971). The glacial sediments have a mean Fe_{HR} /FeT = 0.11+/−0.11.

Our approach requires a comparison between riverine and marine sediment, thus corrections must be made for the dilution effects of biogeneous sediment. Table 6 shows the mean and standard deviations for iron speciation in the sampled rivers, with the data discharge-weighted and derived from table 5 by correcting for the dilution effects of organic C (assuming a CH_2O composition). The inorganic C contents of these river particulates are small enough (0.99+/−1.1 percent) to be ignored. Table 7 also shows the continental margin and deep-sea data of Raiswell and Canfield (1998), which are corrected to a carbonate-free basis only. Corrections for organic C contents are small enough to ignore, as both the continental margin and deep-sea sediments have mean organic C contents, which are < 1 percent (continental margin 0.98+/ −0.61 percent, deep-sea 0.92+/−0.86 percent) with no values exceeding 3 percent. A students 't' test shows that there are no significant differences between the continental margin and deep-sea sediments for any of the iron species, and these data have therefore been combined to produce a mean marine sediment composition (table 7). This mean iron content (4.0+/−1.0 percent) is comparable to the estimate of 4.9 percent (on a carbonate-free basis) by Garrels and Mackenzie (1971), and to two estimates of 5.3 percent and 4.5 percent by Wollast and Mackenzie (1983). The mean of all three literature estimates (4.9+/−0.4 percent) is rather higher than our own

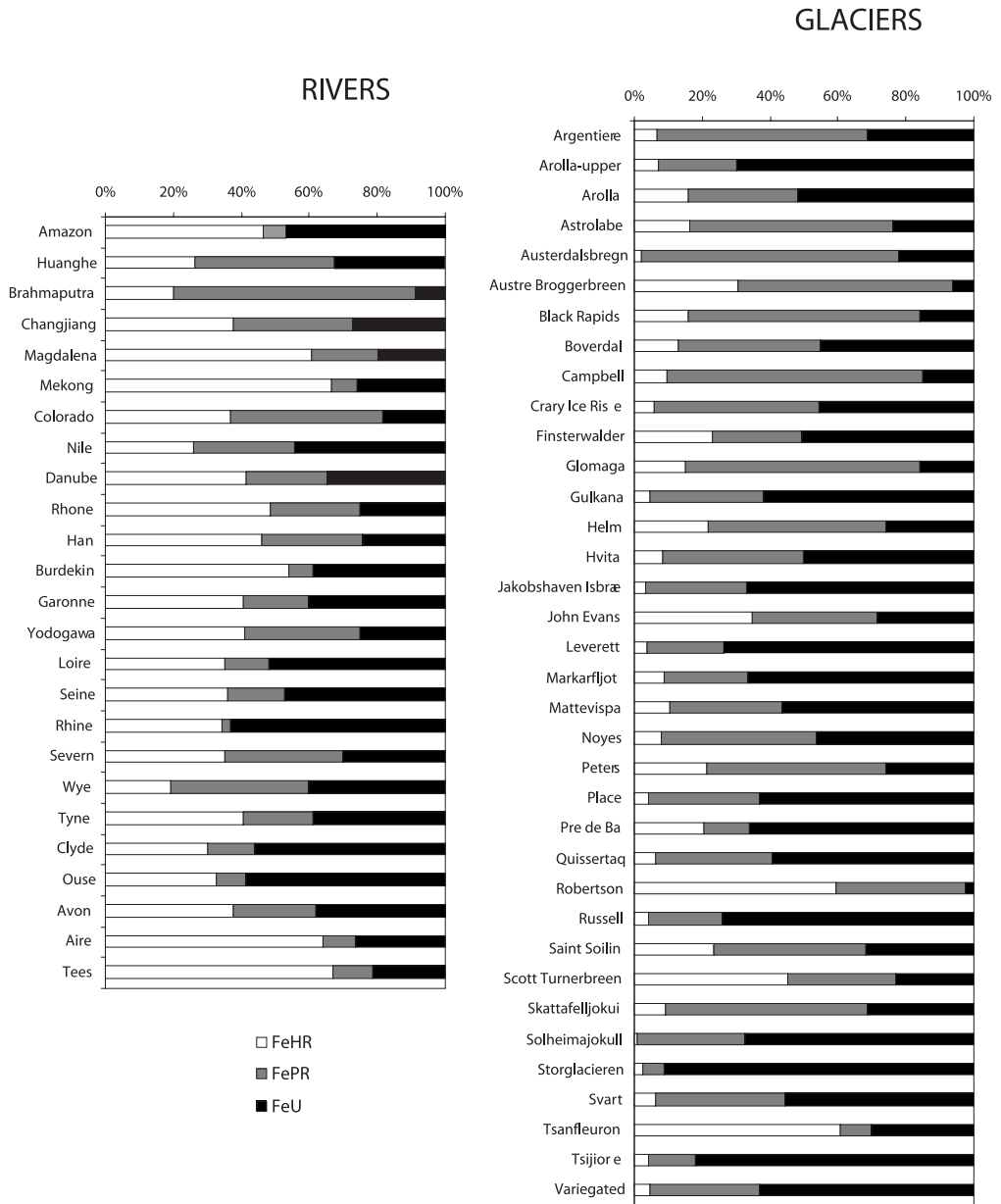GLACIERS

RIVERS

Fig. 1. Relative proportions of Fe_{HR}, Fe_{PR} and Fe_U in riverine and glacial particulates. Riverine discharges decrease downwards.

TABLE 6

Sediment discharge (Milliman and Meade, 1983) and particulate iron riverine fluxes. a. pre-dam discharge b. Milliman and Syvitski (1992) c. Canfield (1997) d. Gibbs (1977). Concentrations in wt%. Column 2 shows the sediment discharge of the rivers sampled in this study

	Sediment Discharge (Tg/yr)	Sampled Sediment Discharge (Tg/yr)	Fe$_{HR}$	Fe$_{PR}$	Fe$_U$	FeT
N. America:						
St. Lawrence	4					
U.S. Atlantic	13	0.7	2.28[c]			5.46[c]
Gulf Coast	466[a]	438.2	1.23[c]			4.11[c]
Colorado	120[a]	120	1.10	1.33	0.55	2.98
Columbia	8					
Rest of W. U.S.	62					
Canada W. Coast	61					
S. Alaska (glacial)	340					
S. Alaska (non-glacial)	104	60	2.57[d]			6.32[d]
N. Alaska	42					
Mackenzie	100					
N. NE Canada	30					
SUBTOTALS	1350	618.9	1.18	1.33	0.55	3.62
Central America:						
Mexico	210					
Remainder	323					
SUBTOTALS	442					
South America:						
Northwest	150					
Magdalena	220	220	3.00	0.96	0.98	4.94
Northern	1218	1200	2.60	0.38	2.61	5.59
Eastern	28					
Southern	154					
Western & South	18					
SUBTOTALS	1788	1420	2.66	0.47	2.36	5.49
Europe:						
Western	31	6.5	1.69	0.78	2.10	4.57
Alpine	66	31	1.61	0.89	0.83	3.33
Black Sea	133	67	2.03	1.17	1.69	4.89
SUBTOTALS	230	104.5	1.86	1.04	1.50	4.40
Eurasian Arctic:	84					
Asia:						
Northeast	100	1.9	1.43	1.17	0.88	3.48
NE China/Korea	658	10	0.17	0.11	0.09	0.37
Huanghe	1100[b]	1100	0.96	1.51	1.20	3.59
Rest of China	930	480	1.86	1.72	1.34	4.92
Ganges/Brahmaputra	1060	540	0.62	2.17	0.27	3.06
SE Asia & Himalayas	2068	160	3.48	0.39	1.37	5.24
India	286					
Indus	100					
Asia Minor	67					
SUBTOTALS	6349	2291.9	1.85	1.11	0.99	3.92
Africa:						
Northwest	110					
West	113					
Southwest	17					
East	240					
Zambesi	20					
Nile	120[a]	120	2.40	2.71	4.09	9.20
SUBTOTALS	620	120	2.40	2.71	4.09	9.20
Australia:						
East, North	62	3	3.25	0.44	2.33	6.02
Oceanic Islands:	9000[b]					
TOTAL AND MEANS	~20,000	4558.3	1.94	1.12	1.37	4.49

TABLE 7

Comparison of the mean corrected compositions of riverine particulates and marine sediments (concentrations in wt. %)

Species	Rivers	Cont. Margin	Deep Sea	Combined Sed.
FeT	4.81±0.19	3.69±0.91	4.29±0.98	3.99±0.98
Fe$_{HR}$	2.09±0.08	1.03±0.40	1.06±0.47	1.04±0.44
Fe$_{PR}$	1.21±0.05	0.84±0.26	1.00±0.58	0.92±0.46
Fe$_U$	1.49±0.06	1.83±0.53	2.25±0.67	2.03±0.63
Fe$_{HR}$/FeT	0.43±0.03	0.28±0.06	0.25±0.10	0.26±0.08
Fe$_{PR}$/FeT	0.25±0.01	0.23±0.07	0.26±0.15	0.25±0.13
Fe$_U$/FeT	0.31±0.02	0.50±0.06	0.49±0.15	0.49±0.09

River data are discharge weighted. Sediment data from Raiswell and Canfield (1998).

estimate (4.0+/−1.0 percent) but the difference is only significant at the 10 percent level. Nevertheless, the following discussion pays the greatest attention to ratios of the Fe species, rather than concentrations, as the former should be unaffected by dilution from Fe-poor phases. On this basis table 7 shows that the riverine particulates have higher Fe$_{HR}$ /FeT ratios than marine sediments (0.43+/−0.03 compared to 0.26+/ −0.08), and lower Fe$_U$ /FeT ratios (0.31+/−0.02 compared to 0.49+/−0.09). Mean and standard deviations of Fe$_{PR}$ /FeT ratios overlap in the two data sets.

Data Representivity

The differences between the composition of riverine particulates and marine sediment might arise if our river samples were not truly representative of the global riverine flux, such that the measured mean riverine Fe$_{HR}$/FeT ratio is too high. The present riverine data set has no samples from Central America and the Oceanic Islands and few from Africa and Australia. However Central America, Africa and Australia together supply less than 6 percent of the global riverine particulate flux (table 6), and even exceedingly low Fe$_{HR}$/FeT ratios (not observed for Australia; table 6) would not produce a significant change in the global mean riverine Fe$_{HR}$/FeT ratio. By contrast the riverine flux from the Oceanic Islands represents approximately 45 percent of the global flux (see table 6), however this region is characterised by high rainfall and rapid runoff that should produce high runoff ratios (which are in turn likely to be associated with high Fe$_{HR}$/FeT ratios; see fig. 2). We cannot discount the possibility that improved sample coverage of the above areas (and especially the Oceanic Islands) might change our global mean Fe$_{HR}$/FeT ratio, but our riverine particulates represent approximately 23 percent of the global riverine flux and it seems unlikely that the poorly-sampled areas would have Fe$_{HR}$/FeT ratios low enough to depress our global riverine mean significantly towards the marine sediment value.

It could be argued that significant compositional differences might occur during major flood conditions, when the daily load of some rivers may reach up to 70 percent of their normal annual load (Milliman, 1991). However there is apparently little seasonal variation in Fe/Al in riverine particulates (see earlier), which were sampled through variations of more than one order of magnitude in water discharge and/or
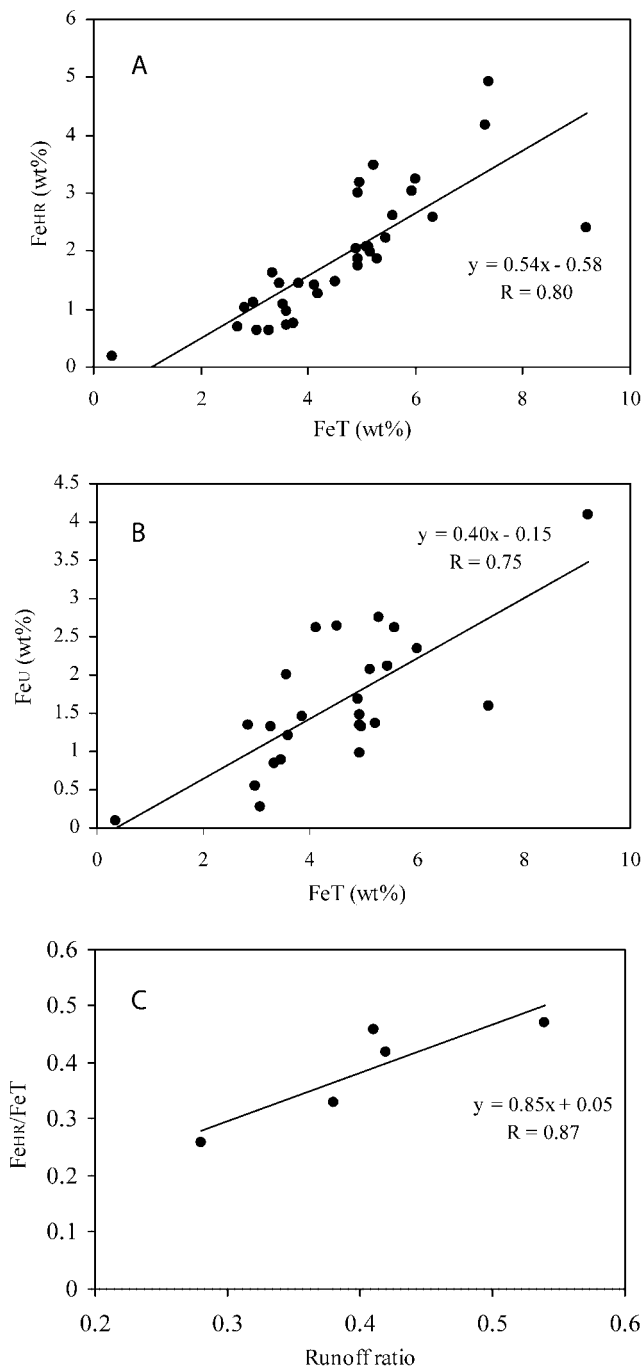
Fig. 2. Riverine particulate variations in Fe_{HR} with FeT (A), Fe_U with FeT (B) for individual rivers, and weighted continental scale variations in Fe_{HR}/FeT with runoff ratio (C).

suspended sediment concentrations. Bedload is estimated to be less than 10 percent of the global riverine flux (Milliman and Syvitski, 1992), which is too small a proportion to significantly modify our observed global mean riverine Fe_{HR}/FeT ratio. Finally we note that the close similarity between our global riverine FeT of $4.5+/-0.2$ percent and that of 4.8 percent by Martin and Meybeck (1979) also supports the representivity of the present riverine data set.

The observed differences between the Fe_{HR}/FeT ratios of riverine particulates and marine sediment might also result from non-representative sampling of marine sediments. Our global FeT for marine sediments ($4.0+/-1.0$ percent) was not significantly different to that found by other workers ($4.9+/-0.4$ percent; see earlier) but might suggest that the data of Raiswell and Canfield (1998) did not fully account for a sediment type high in FeT (which might also have a high Fe_{HR}/FeT ratio). Deep sea red clays represent the only common sediment type which might have these characteristics, and table 1 shows data from a suite of Atlantic and Pacific red clays. FeT values for this limited data set are indeed high (mean $5.0+/-1.2$ percent; comparable to the range given by Chester, 1990) but the Fe_{HR}/FeT ratios are not exceptionally high ($0.33+/-0.16$). Red clays occupy a significant fraction of the ocean floor (38 percent of 360 x 10^6 km^2; Libes, 1992) but receive only low sediment fluxes. For example Thomson and others (1984) estimate that the accumulation rates of authigenic plus detrital FeT are 0.018-0.035 g cm^{-2} in 10^3 years, which produces a FeT flux of 24-48 Tg/yr (1 Tg = 10^{12} g), which is less than 10 percent of the riverine flux (see later). Clearly much higher values of Fe_{HR}/FeT would be needed for red clays to account for the observed compositional discrepancies between the global riverine flux and marine sediments.

The discrepancy between the riverine particulate concentrations of Fe_{HR} and the concentrations in marine sediments could also be resolved if post-depositional changes in iron speciation occurred within the modern marine sediments analysed by Raiswell and Canfield (1998). Total iron is likely to have been conserved because our mean sediment composition is close to that of average sedimentary rock (see earlier). However the iron oxides measured as Fe_{HR} are dissolved when anoxic conditions develop during early diagenesis. This dissolved iron mainly either diffuses to the sediment surface and is re-precipitated under oxic conditions as iron oxides (see for example Van Cappellen and Wang, 1996), or is precipitated anoxically as sulfides (see for example Canfield and Raiswell, 1991) or incorporated into Fe-rich clay minerals (see for example Aplin, 2000). The measurements of Fe_{HR} in the modern sediments of Raiswell and Canfield (1998) include iron from oxides and sulfides (see earlier); thus post-depositional processes affecting these phases will not change our measured speciation. Iron re-mobilised during anoxic diagenesis and incorporated into iron-rich clays such as smectites, glauconite et cetera is also substantially extracted by dithionite (Raiswell and others, 1994). Other clay minerals (chlorite and biotite) contain much less dithionite-soluble iron but are likely to be mainly detrital, rather than authigenic, in origin. We conclude that post-depositional changes in iron mineralogy cannot explain the scale of the observed and required differences in iron speciation, although they may be contributory. Overall we can find no reasonable basis for attributing the observed differences between riverine particulates and marine sediments to sampling artefacts.

INTERPRETATION

Relationships between Iron Species in Riverine and Glacial Particulates

There are no significant correlations between the concentrations of any of the iron species in the riverine particulates and their organic C contents, but correlations between Fe_{HR} and FeT (0.80), and Fe_U and FeT (0.75) are both significant at the less

than 0.1 percent level (fig. 2A and B). The plot of Fe_{HR} against FeT (fig. 2A) shows some scatter but approximates to linearity with the regression equation

$$Fe_{HR} = 0.54 \, FeT - 0.58 \quad r = 0.8$$

The errors on the intercept are sufficiently large $(0.58 +/- 0.35)$ as to suggest that the regression line passes very near (or through) the origin. The larger data set of Poulton (ms, 1998) contains 73 rivers (those described here plus an additional 39 rivers that do not discharge directly into the ocean), which demonstrate a similar relationship of Fe_{HR} with FeT;

$$Fe_{HR} = 0.59 \, FeT - 0.70 \quad r = 0.85$$

These relationships clearly suggest that iron oxides are largely derived from, and retained in association with, the total iron fraction. This close link between Fe_{HR} and FeT arises from the increased removal of the more soluble components of rocks and soils (Na, K, Ca, Mg) at high rates of chemical weathering (which concentrates less-soluble elements like Fe), coupled with the release of iron from parent rock minerals and the subsequent formation of iron oxides (see Canfield, 1997). This influence of chemical weathering on the speciation of iron in world river particulates apparently persists over a wide range of geological, geographical and climatological variability in the sampled river basins. By contrast, the glacial speciation data (table 3) show only a weak correlation between Fe_{HR} and Fe_T (r = 0.22), but strong correlations between Fe_{PR} and FeT (r = 0.78), and Fe_U and FeT (r = 0.88). Both the latter correlations are significant at the $<<0.1$ percent level. These findings are entirely to be expected given the dominance of physical weathering over chemical weathering in glacial environments. Weak chemical weathering results in most iron being retained in pristine phases which are soluble in HCl and/or HF. Thus Fe_{PR} and Fe_U predominate and are well correlated with FeT.

Our riverine data are consistent with Canfield (1997), who has comparable data for Fe_{HR} and FeT for 23 rivers from the United States, which demonstrate the influence of runoff (an indicator of the intensity of chemical weathering) on the Fe_{HR} and FeT contents. These rivers have Fe_{HR}/FeT ratios which increase from values of 0.15 to 0.20 at low runoff to 0.4 to 0.75 at high runoff, and the positive correlation between runoff and Fe_{HR}/FeT was attributed to increased weathering which produced proportionately more Fe_{HR} from the parent rock (see above). Our data in table 4 have a comparable range in Fe_{HR}/FeT (0.19-0.67) but fail to show any significant relationships between Fe_{HR}/FeT and either runoff or precipitation, probably because our rivers are more geographically diverse and include those originating from mountainous and lowland catchments, where the relative influences of chemical versus physical weathering may be vastly different (see Stallard, 1995). There are however weak correlations (significant at around the 5 percent level) between Fe_{HR} and both runoff and precipitation.

Our Fe_{HR}/FeT data do however show a significant dependence on runoff ratio (average river runoff per unit area/average rainfall per unit area) on a continental scale. The discharge-weighted Fe_{HR}/FeT ratios for each continent increase in the order Africa (0.26), North America (0.33), Europe (0.42), South America (0.46) and Asia (0.47), ignoring the Australian continental average, (our data is based only on one sample). These mean continental Fe_{HR}/FeT ratios are closely related to their runoff ratios (fig. 2C), as given by Berner and Berner (1996). Thus our continental-scale data show highest Fe_{HR}/FeT ratios in regions where losses of precipitation by runoff are maximized relative to evaporation. This produces increased chemical weathering which enriches Fe and Al, and depletes Na, Ca, K and Mg (see earlier).

Comparisons between Riverine Particulates and Marine Sediments

A comparison of the corrected riverine and marine sediment compositions in table 7 shows that sediment transport from rivers into the marine environment apparently produces a decrease in the FeT, Fe_{HR} and Fe_{PR} contents, whereas Fe_U appears to increase. The errors on the discharge-weighted riverine data in table 7 are derived from the analytical precision, and may therefore underestimate the effects of temporal and spatial variability. Hence the differences between the riverine and marine sediment data are tested statistically with a 'z' test (rather than with the students 't' test which requires standard deviations for both sets of samples). The z test shows that all these differences are highly significant at the $<< 0.1$ percent level. Comparable results are found if the riverine particulate data are tested separately against the continental margin and deep-sea data. These differences are also reflected in a comparison of the Fe_{HR}/FeT ratios. A z test shows that the Fe_{HR}/FeT ratio of riverine particulates $(0.43+/-0.03)$ is significantly different from marine sediments $(0.26+/-0.08)$ at the $<< 0.1$ percent level.

Note that the decrease in FeT ($\sim$0.8 wt percent) is approximately equivalent to that found for Fe_{HR} ($\sim$1.0 wt percent). However simple removal of Fe_{HR} from the riverine particulates does not appear to be sufficient to produce a marine sediment composition. Thus the removal of 0.8 wt percent Fe_{HR} from the riverine particulates would produce material with the composition; Fe_{HR} = 1.29 percent, Fe_{PR} = 1.21 percent, Fe_U = 1.49 percent and FeT = 3.99 percent. This composition has $Fe_{HR}/FeT = 0.32+/-0.03$, $Fe_{PR}/FeT = 0.30+/-0.02$ and $Fe_U/FeT = 0.37+/-0.02$, which only just overlaps the mean and standard deviation of these ratios in the marine sediments. However simple removal of riverine Fe_{HR} takes no account of other sediment additions to the ocean basins. Thus the following sections evaluate two possible explanations for the differences between the riverine and marine sediment compositions, specifically that;

  (i) There may be net additions of Fe_{HR}-depleted sediment which mix with riverine particulates in the ocean basins,

 (ii) There may be significant removal of Fe_{HR}-enriched material from riverine particulates prior to entry into the ocean basins.

SEDIMENT AND DISSOLVED IRON ADDITIONS TO THE OCEAN BASINS

This section examines whether the addition of other iron sources to the ocean basins could modify the riverine Fe_{HR}/FeT ratio $(0.43+/-0.03)$ towards the observed marine sediment composition $(0.26+/-0.08)$. Modern marine sediments are considered to contain material derived from detrital and non-detrital sources. The main detrital sources, apart from riverine suspended sediment, are from atmospheric particulates, coastal erosion and glacial sources. Non-detrital material is derived from solution in the first instance and can be sub-divided into biogenous, authigenic, hydrothermal and diagenetic sources (Chester, 1990). Clearly the riverine particulate flux can only be modified to approach the marine sediment composition if diluted by mixing with material of low Fe_{HR}/FeT ratios. Biogenous sediments have low Fe contents (and are thus a possible diluent), but their sediment fluxes are too small to produce a significant dilution of the riverine Fe_{HR}/FeT flux ($CaCO_3$ 1500 Tg/yr, organic C 200 Tg/yr and SiO_2 800 Tg/yr; Wollast and Mackenzie, 1983). Our data are anyway compared on a carbonate and organic C-free basis (see earlier). Some of the remaining detrital and non-detrital sediment sources will have low Fe_{HR}/FeT ratios relative to the riverine flux, and are thus possible diluents, whilst others may supply material with high Fe_{HR}/FeT ratios. A rigorous approach requires that we account for all such sources, and weight their contributions relative to riverine particulate supply. Clearly we initially require an estimate of the global riverine particulate flux.

The Global Riverine Discharge Flux

Unfortunately quantifying the global flux of riverine sediment is not a simple matter. Sediment discharge data are significantly affected by both temporal and spatial variability. Substantial temporal variability can occur on hourly, daily, weekly, monthly, seasonal and annual timescales (Horowitz and others, 2001), and regular sampling for long periods of time is thus necessary to produce reliable average values. However river sediment discharges in different regions may have been measured infrequently and/or over very different periods of time (Milliman and Meade, 1983). Furthermore the measurement of sediment discharge during flood conditions may be difficult or even impossible, even though such events may sweep substantial proportions of sediment from temporary storage areas (floodplains, estuaries and salt marshes) into the oceans (Ludwig and Probst, 1998). The paucity of measurements for many rivers during large floods means that the problems of accounting for sediment delivery on the decadal to centennial scale have not been addressed globally (Hay, 1998).

Site-specific spatial variability can occur in two dimensions (river width and depth), thus depth- and width-integrated samples ideally should be collected (Horowitz and others, 2001). Variable data quality also results from the need to produce a geographically widespread database, which integrates sediment discharge measurements from many different rivers. Most global estimates are based on sediment discharge data from the largest rivers (as defined by water discharge), although Milliman and Syvitski (1992) have shown that small mountainous rivers, discharging directly onto active margins, may have relatively low water discharges but relatively high sediment fluxes. Furthermore, small basins tend to have limited floodplain development (and most suspended sediment is thus readily flushed from the basin), in contrast to larger basins where storage effects may be more significant (Ludwig and Probst, 1998).

Difficulties also arise from the influence of natural and anthropogenic activities on sediment production and trapping. It is generally agreed that burning, deforestation and agriculture have increased rates of soil erosion by a factor of 2 to 10 (Milliman and Syvitski, 1992; Hay, 1998). However, increased erosion rates may not have produced equivalent increases in the riverine flux, as many streams may be unable to transport their increased loads, resulting in greater deposition in floodplain areas (Berner and Berner, 1996). However sediment loads 2000 to 2500 years ago (prior to human influences) may have been as low as 10000 Tg/yr (Milliman and Meade, 1983; Berner and Berner, 1996). More recently, the effects of river management practices have largely reduced river sediment fluxes. For example damming has severely reduced the sediment fluxes from the Nile, Colorado, Mississippi, Zambezi and Indus rivers (Milliman and Syvitski, 1992). Our marine sediment data span periods of time which typically range up to several thousand years (as estimated from the sedimentation rate data of Raiswell and Canfield, 1998), which best corresponds to discharge over the pre-dam but human-influenced period.

The most recent estimate of pre-dam discharge (20000 Tg/yr by Milliman and Syvitski, 1992), based on river measurements, is revised upwards from earlier estimates by increased fluxes from the Pacific Islands, the small mountainous rivers of southern Asia and North and South America, and undocumented rivers with basins larger than 10000 km^2. A further 1000 to 2000 Tg/yr of sediment are believed to be transported annually by rivers as bed load and flood discharge. It is, however, uncertain how much of this sediment actually reaches the ocean (Milliman and Meade, 1983). Gauging stations may be located considerable distances upstream from the estuarine/marine boundary, and there may be considerable sediment deposition between the gauging station and the estuarine/marine boundary in environments such as estuaries, tidal flats, salt marshes and floodplains, which range from sub-aerial to sub-aqueous (but

with salinities less than fully marine). For example the gauging station on the Amazon is located approximately 1000 km upstream of the mouth and there is a 30 to 40 percent loss in suspended sediment between the gauging station and the river mouth (Kuehl and others, 1986). Allison and others (1998) measured floodplain sediment accumulation rates in the Brahmaputra basin. Extrapolated over the whole basin, as much as 39 to 71 percent of the river flux appears to be trapped prior to entry into the marine environment. A similar proportion (39 to 40 percent) of the suspended sediment delivered to the main channels of the Rivers Ouse and Tweed (United Kingdom) is also stored on floodplains (Walling and others, 1999). Milliman and Syvitski (1991) also note that a significant proportion of the riverine particulate load of high-yield rivers in tectonically active settings is trapped landward of the ocean.

Storage in these environments may be permanent or transient (because major floods may remove substantial proportions of sediment from downstream storage areas; Hay 1998). Our marine sediment data integrates compositional variations over periods of time, which range up to several thousand years (see earlier). These sediments thus include any compositional effects arising from flood transport of sediment from transient storage areas, and approximate to the steady state condition (although excluding the effects of sediment storage on timescales in excess of several thousand years).

Estimates of river sediment discharge to the oceans have also been based on modeling empirical relationships between river sediment yields and hydrodynamic, biological and geomorphological parameters. Ludwig and Probst (1992) used this approach to produce an estimate of 16000 Tg/yr, which they believed might over-estimate sediment storage effects. Bearing in mind the difficulties in obtaining representative data and the poorly quantified effects of sediment storage, we will initially use the Milliman and Syvitski (1992) riverine sediment flux estimate of 20000 Tg/yr as an upper estimate of pre-dam riverine sediment delivery to the oceans. The effects of storage and/ or lower riverine flux estimates will be arbitrarily examined by also considering the delivery of a smaller riverine load of 13000 Tg/yr (equivalent to a 35 percent storage prior to entry into the ocean basins). These two particulate mass fluxes are both assumed to have the compositions given in table 7, and thus supply sediment with $Fe_{HR}/FeT = 0.43+/-0.03$ which gives fluxes of $625+/-25$ to $962+/-38$ Tg/yr of FeT, and $272+/-11$ to $418+/-16$ Tg/yr of Fe_{HR} (table 8).

The Atmospheric Iron Flux

Preliminary attempts to estimate the global atmospheric flux of dissolved and particulate trace elements, including iron, into the oceans have been reported by GESAMP (1990) and Duce and others (1991). Iron is present mainly in particles derived from natural mineral aerosol sourced from arid and semi-arid regions and can be an important source of non-biogenic material to deep sea sediments (Duce and others, 1980). Atmospheric fluxes of iron have been estimated from measurements of the flux of mineral aerosol material (910 Tg/yr) to the oceans, which is assumed to have an iron content of 3.5 percent, based on upper continental crust abundance (Taylor and McLennan, 1985). This produces a global atmospheric iron flux of 32 Tg/yr, which includes both wet and dry deposition. More recent estimates by Jickells and Spokes (2001) suggest that the use of a scavenging ratio (which relates the concentration in precipitation to that in the aerosol phases) of 200 is more appropriate than the value of 1000 used by Duce and others (1991). Depending on which scavenging ratio is used, Jickells and Spokes (in press) estimate the FeT flux to be 14-35 Tg/yr ($25+/-10$ Tg/yr). We have extracted four samples of Saharan dust (table 1) with dithionite and these give a mean Fe_{HR}/FeT ratio of $0.33+/-0.01$, less than the Fe_{HR}/FeT ratio of riverine particulates. Based on these analyses, atmospheric dust supplies a mass flux of 910 Tg/yr which produces a small dilution of riverine material

TABLE 8

Composition of sediment sources into the ocean basins and estimated compositions obtained on mixing these sources, and on losing iron before entry to the ocean basins (Tg/yr)

INPUT FLUXES (Tg/yr)	Fe_{HR}	Fe_{PR}	Fe_U	FeT	Mass	Fe_{HR}/FeT	Fe_{PR}/FeT	Fe_U/FeT
Rivers (M_R)								
Minimum	272±11	157±6	194±8	625±25	13000	0.43±0.03	0.25±0.01	0.31±0.02
Maximum	418±16	243±10	300±11	962±38	20000	As above	As above	As above
Glaciers (M_G)								
Minimum	4±3	13±10	17±16	34±22	800	0.11±0.11	0.39±0.40	0.50±0.57
Maximum	24±19	82±64	106±95	211±139	5000	As above	As above	As above
Atmosphere	10±1.4	4.6±0.8	16±3	30±3.5	910	0.33±0.01	0.15±0.03	0.52±0.10
Hydrothermal	14±5	0	0	14±5	27	1.0	0	0
Coast Erosion	2±1	2±1	4±1	8±2	200	0.26±0.08	0.25±0.13	0.49±0.09
Authigenic	5	0	0	5	10	1.0	0	0
TOTALS BY MIXING (Tg/yr)								
$M_{R(min)} + M_{G(min)}$	307±13	177±12	231±18	715±34	14950	0.43±0.03	0.25±0.20	0.33±0.03
$M_{R(max)} + M_{G(max)}$	473±25	332±65	426±96	1230±144	26150	0.38±0.05	0.27±0.06	0.35±0.09
$M_{R(min)} + M_{G(max)}$	327±23	246±54	320±95	893±141	19150	0.37±0.06	0.28±0.08	0.36±0.12
$M_{R(max)} + M_{G(min)}$	453±17	263±14	337±20	1053±44	21950	0.43±0.02	0.25±0.02	0.32±0.02
TOTALS BY MIXING WITH 40% Fe_{HR} LOSS (Tg/yr)								
$M_{R(min)} + M_{G(min)}$	198±13	177±12	231±18	606±34	14950	0.32±0.03	0.29±0.03	0.38±0.04
$M_{R(max)} + M_{G(max)}$	306±25	332±65	426±96	1063±144	26150	0.29±0.05	0.31±0.07	0.40±0.10
$M_{R(min)} + M_{G(max)}$	218±23	246±54	320±95	784±141	19150	0.28±0.06	0.31±0.09	0.40±0.14
$M_{R(max)} + M_{G(min)}$	286±17	263±14	337±20	886±44	21950	0.32±0.02	0.30±0.02	0.38±0.03

towards the marine sediment Fe_{HR}/FeT ratio and also supplies fluxes of $Fe_{HR} = 10+/-1.4$, $Fe_{PR} = 4.6+/-0.8$, $Fe_U = 16+/-3$, and $FeT = 30+/-3.5$ Tg/yr (table 8).

Iron Fluxes from Glacial and Coastal Erosion

Material derived from coastal erosion and glacial activities constitute further additions of sediment to the oceans. Garrels and Mackenzie (1971) estimate that coastal erosion by wave activity supplies a sediment flux in the range 200 to 900 Tg/yr, with a preferred value of 250 Tg/yr. Based on earlier work, Lisitzin (1972) used an estimate of 150 Tg/yr. The material eroded is likely to have speciation characteristics similar to our continental margin sediments (table 7). Thus a coastal erosion mass flux of 200 Tg/yr with $Fe_{HR}/FeT = 0.26+/-0.08$ would produce $8+/-2$ Tg/yr FeT, and $2+/-1$ Tg/yr Fe_{HR}, $2+/-1$ Tg/yr Fe_{PR} and $4+/-1$ Tg/yr Fe_U (table 8). This coastal erosion flux is small but is nevertheless capable of diluting the riverine Fe_{HR}/FeT towards the marine sediment value.

The input of glacial sediment to the ocean basins is poorly quantified, principally because the erosive behavior of ice-sheets has not been clarified (Hay, 1998). Mountain glaciers are known to be effective erosion agents but it is unclear whether ice-sheets have a powerful abrasive effect or are relatively ineffective. Hay (1998) reviewed previous glacial mass flux estimates to conclude that the present flux lay in the range 800 to 5000 Tg/yr, most probably at the lower end. Values at the bottom of this range may also be most appropriate since a significant proportion of glacial debris may be trapped in fjords (Andrews and others, 1994).

Table 3 shows the mean and standard deviation of the sampled glacial sediments. We have three samples from Antarctica (currently the largest glaciated region and estimated to supply 90 percent of the global glacial flux; Garrels and Mackenzie, 1971) with a mean Fe_{HR}/FeT of $0.11+/-0.05$, which is the same as the overall glacial mean ($0.11+/-0.11$). Clearly the glacial flux has a relatively low Fe_{HR}/FeT ratio which would drive the riverine flux composition towards that of marine sediments. A glacial mass flux of 800-5000 Tg/yr with the mean composition shown in table 3 suggests that glaciers supply $34+/-22$ to $211+/-139$ Tg/yr FeT, $4+/-3$ to $24+/-19$ Tg/yr of Fe_{HR}, $13+/-10$ to $82+/-64$ Tg/yr Fe_{PR}, and $17+/-16$ to $106+/-95$ Tg/yr Fe_U (table 8).

Authigenic Iron Fluxes

Chester (1990) defines authigenic iron as that which originates from widespread inorganic processes that remove dissolved iron from seawater, excluding hydrothermal activity (which is localised rather than widespread) and iron recycled from porewaters during suboxic diagenesis. Authigenic iron is removed to sediments on an ocean-wide basis but the flux is small and only becomes significant in deep-sea sediments where detrital fluxes are low.

The main sources of authigenic iron are derived from the dissolved input of rivers (plus groundwaters) together with the iron liberated from sediments during oxic diagenesis. These sources will be added to sediments as iron oxides (and thus add material with $Fe_{HR}/FeT \sim 1$), but are small compared to the riverine particulate Fe_{HR} flux of 272-418 Tg/yr. Thus dissolved riverine fluxes of Fe (1.5 Tg/yr; Martin and Windom, 1991) constitute less than 0.5 percent of the total iron particulate flux. Groundwater fluxes of dissolved iron are also likely to provide only small fluxes of total iron, but at present no reliable data are available. Garrels and Mackenzie (1971) estimate groundwater discharge as 4×10^{15} litres/yr but this may be two orders of magnitude too high (Maynard, 1976). Compilations of groundwater analyses (Langmuir, 1997) show that only around 2 percent of these waters contain more than 0.2 ppm dissolved Fe. Using this threshold value, together with the discharge flux of 4×10^{15} litres/yr, produces a dissolved Fe flux of less than 1 Tg/yr into the ocean basins.

Given that the discharge flux may be excessive (see above), groundwaters are unlikely to be an important source of FeT or Fe$_{HR}$.

Estimates of the authigenic flux of iron to deep-sea sediments (which includes dissolved iron from continental sources plus oxic diagenesis) range up to 3 μg cm^{-2} yr^{-1} (Krishnaswami, 1976; Thomson and others, 1984). Such fluxes, sustained on an ocean-wide basis over an area of 360 x 10^6 km^2, give a maximum FeT flux of 10 Tg/yr which will be solely present as iron oxides (Fe$_{HR}$/FeT $\sim$ 1). However the dissolved sources of Fe$_{HR}$ only total about 2 Tg/yr (see above), and we thus prefer a mean authigenic flux of 5 Tg/yr (table 8). However the authigenic flux is clearly Fe$_{HR}$-enriched (and thus unable to reconcile the difference between the riverine and marine sediment compositions) whilst also being too small (table 8) to contribute significantly to the overall Fe$_{HR}$ budget.

The Hydrothermal Iron Flux

Iron can also be delivered to the ocean basins from interactions between basaltic lavas and seawater, which can occur in a range of different geological environments and over a range of temperatures. Typically recognised are axial high temperature and diffuse low temperature hydrothermal activity (the fluxes from which are reasonably well-quantified), together with off-axis low temperature activity and the weathering of hot and cold basalt on the seafloor.

High temperature fluids emerge from chimneys on hydrothermal mounds and can range over compositional extremes from metal-rich and high salinity to metal-free and vapour-rich. The metal-rich fluids can be black smokers (rich in Fe and H$_2$S) or white smokers (less rich in Fe and depleted in H$_2$S) and their Fe contents range from 750 to 6470 μM/kg (Elderfield and Schlutz, 1996). On cooling, metal sulfides are precipitated from the fluids in the vicinity of the vents (where H$_2$S is available), whilst iron oxides are formed further away (by oxidation of sulfides or from solutions with an excess of metals over sulfide).

Diffuse low temperature fluids emerge from the hydrothermal mound surface or from cracks in the seafloor at temperatures of 3° to 40°C, and are believed to be derived from hot hydrothermal fluid which has cooled conductively or mixed with cold seawater below the seafloor (James and Elderfield, 1996). Diffuse flow is difficult to quantify because of the wide range of exit temperatures, and the largely unknown fluid compositions (Kadco and others, 1995). These fluids are generally low in Fe compared to high temperature flows, but the water flux may be substantially higher (2-3 orders of magnitude; Elderfield and Schlutz, 1996).

Estimates of the combined effects of high temperature axial and diffuse flow are usually made by assuming that diffuse flow is derived from black smoker fluids which have been conservatively diluted with seawater (but see above). Elderfield and Schlutz (1996) use this approach and combine the above Fe compositional range (750-6470 μM/kg) with a water flux of $3+/-1.5$ x 10^{13} kg/yr to produce an Fe flux of 1-10 Tg/yr. Wollast and Mackenzie (1983) estimate 15 Tg/yr based on a water flux which is approximately an order of magnitude larger. This hydrothermal iron flux represents iron vented into plumes, which we assume can potentially enter the modern sediment reservoir. We exclude the iron precipitated in massive sulfide deposits in volcanogenic rocks, which are not part of our sediment reservoirs.

Off-axis low temperature activity is poorly quantified but possibly more than 70 percent of the total heat flux occurs on the ridge flanks (Mottl and Wheat, 1994). This suggests that there is an extremely high advective flux of seawater at low to moderate temperatures (estimated to be about 2.5 x 10^{15} kg/yr for a temperature of 20°C). Unfortunately there are few Fe analyses of off-axis fluids. Mottl and others (1998) found 0.34 ppm Fe in the warm springs emitted from basaltic outcrops on the flank of

the Juan de Fuca Ridge and, if typical, the above water flux would then give an Fe flux of 0.85×10^{12} g/yr or approximately 1 Tg/yr.

The low temperature weathering reactions of basalt can take place both on the seafloor (in contact with large volumes of water and under oxidising conditions) or down to 2 to 3 km depth (and involving smaller volumes of water and more reducing conditions). Weathering occurs to a greater extent in the surface basalts but is otherwise similar at surface and at depth. Alt and others (1986) found that goethite was abundant in the uppermost few hundred metres of pillow lavas, and occurred as alteration halos around cracks and veins. Adjacent host rock had lost iron from sulfides and olivine. The implication was that iron was lost from rock-dominated, reducing parts of the system but was retained as oxides on contact with oxygenated seawater. Here we will adopt the simple approach that Fe localised and trapped within the basalt as oxides does not enter the sediment reservoir. Thus transfer of Fe from weathering will occur only where dissolved Fe or particulate oxides are transported to seawater or adjacent sediments. These potential Fe additions from weathering are difficult to quantify but Maynard (1976) and Wolery and Sleep (1976) have estimated an FeT flux of 7 Tg/yr, which is based on estimates of weathering rates to depths of several hundred metres. Edwards and others (in press) have produced a larger estimate of 40 Tg/yr based on the consumption of oxygen by the microbial oxidation of iron in basalt but a proportion of this iron is likely to be trapped within the basalt (see above).

Overall the iron flux from all hydrothermal sources appears to range from 9 to 18 $(14+/-5)$ Tg/yr. The composition of all the hydrothermal products will approximate to $Fe(OH)_3$, and thus $Fe_{HR}/FeT \sim 1.0$. The mass of iron oxides added to marine sediments is about double the FeT flux, or 18 to 36 $(27+/-9)$ Tg/yr of material approximately. Adding this iron source to the riverine Fe_{HR}/FeT would in fact produce a mixture with a higher Fe_{HR}/FeT and thus move the overall composition further away from that of marine sediments (table 8).

Combined Effect of Sediment Additions

Table 8 summarises the data from the sediment additions by hydrothermal activity, authigenic sources, atmospheric deposition, coastal erosion and glacial activity. Their combined influence can be assessed by weighting the Fe flux values or Fe_{HR}/FeT ratios by the appropriate mass flux. Only hydrothermal activity and authigenic sources can produce material which is Fe_{HR}-enriched relative to riverine particulates, whereas all the other sediment sources mix with riverine particulates to produce a combined sediment with a lower Fe_{HR}/FeT ratio than the riverine particulates. Table 8 shows the compositions of the mixtures obtained by combining each maximum and minimum value of the riverine flux (M_R) with the maximum and minimum value of the glacial particulate flux (M_G). Each combination weights the composition of M_R and M_G together with the specified values (table 8) of the other sources. No possible combination of M_R and M_G can produce the observed marine sediment Fe_{HR}/FeT $(0.26+/-0.08)$; this value is most closely approached only by mixing minimum M_R with maximum M_G $(0.35+/-0.06$, see table 8). For completion, table 8 also shows the values of Fe_{PR}/FeT and FeU/FeT of the different mixtures, but these fail to provide any useful constraints. All the mixing models are capable of producing compositions which overlap the mean and standard deviation Fe_{PR}/FeT of marine sediments $(0.25+/-0.13)$, although only the combinations with maximum M_G $(0.35+/-0.09$ and $0.36+/-0.12$, see table 8) overlap the marine sediment FeU/FeT $(0.49+/-0.09)$. The remaining discussion thus concentrates on the Fe_{HR} component.

The possible mixing combinations of the two largest sediment sources (riverine and glacial particulates) which could produce the observed marine sediment $Fe_{HR}/$ FeT can be further explored by a simple two-component mixing model using the data from table 8 (and ignoring the minor contributions from all the other sources). Figure
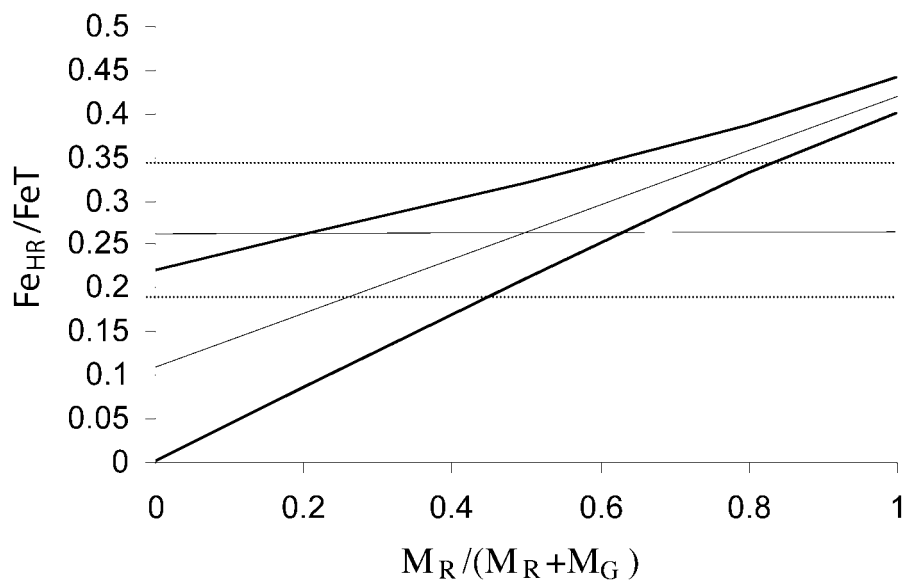
Fig. 3. Variations in Fe_{HR}/FeT with different mixtures of riverine and glacial mass fluxes. Sloping lines show the mean and standard deviation of the Fe_{HR}/FeT values achieved by mixing different mixtures of riverine (M_R) and glacial (M_G) mass fluxes, expressed as (M_R)/($M_R + M_G$). Horizontal lines show the mean and standard deviation of Fe_{HR}/FeT in modern marine sediments.

3 plots the variations in Fe_{HR}/FeT for different mixtures of the riverine (M_R) and glacial (M_G) mass fluxes, expressed as the ratio of the riverine mass flux to the total mass flux or $M_R/(M_R + M_G)$. The errors on the Fe_{HR}/FeT ratios of the mixtures are large, such that any values of $M_R/(M_R + M_G) < 0.83$ are able to produce sediment mixtures with Fe_{HR}/FeT ratios which match (within errors) those found in marine sediments (shown by horizontal lines). For example the highest value of $M_R/(M_R + M_G)$ that can produce a marine sediment composition is 0.83, which requires a combination of either a very high M_G (3400 Tg/yr) with the present day M_R (20000 Tg/yr), or a somewhat lower M_G (1700 Tg/yr) with a low present day M_R (10000 Tg/yr). These combinations require that either the present-day riverine flux delivered to the ocean basins lies at the lower end of the estimated range, or that the present-day glacial flux lies at the upper end of the estimated range. Neither possibility can be completely discounted but it seems probable the discrepancy between the compositions of riverine and marine sediments cannot be completely resolved solely by mixing different sediment sources.

REMOVAL OF Fe_{HR}-ENRICHED MATERIAL PRIOR TO ENTRY INTO THE OCEAN BASINS

The discrepancy between riverine and marine Fe_{HR}/FeT values might also be resolved if the riverine particulate mass flux (and particularly the Fe_{HR} pool) is substantially modified during transport through estuaries, such that riverine particulates enriched in Fe_{HR}/FeT are trapped within a variety of non- to periodically-marine environments (for example in estuaries, floodplains, salt marshes and tidal flats) before reaching the marine environment. Such fractionation would be consistent with the documented behavior of particulate iron in individual estuaries. Figueres and others (1978) analysed the total iron contents of suspended sediments during estuarine mixing and demonstrated extensive losses of iron, which increased with increasing grain size (85 percent loss from the 1.2-5 μm fraction, 75 percent loss from
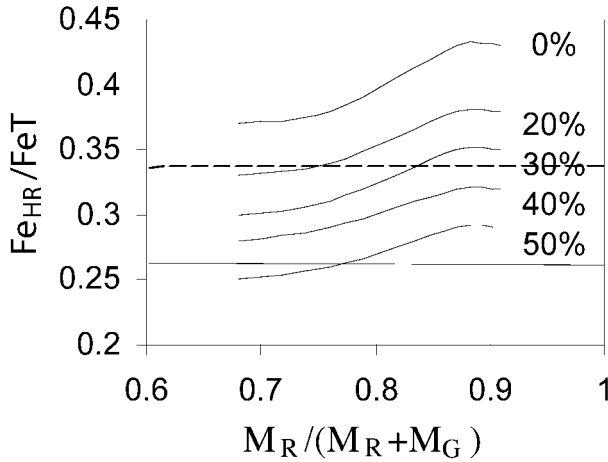
Fig. 4. Fe_{HR}/FeT content achieved by mixing different proportions of the riverine (M_R) and glacial (M_G) particulate fluxes, after removal of 0 to 50 percent Fe_{HR} from the riverine flux prior to entry into the ocean basins. Horizontal lines show mean (solid) and upper standard deviation (dashed) of modern marine sediments.

0.45-1.2μm, 65 percent loss from 0.22-0.45μm, 55 percent loss from 0.05-0.22μm and 50 percent loss from 0.025-0.05μm). Moore and others (1979) examined the total iron and hydroxylamine hydrochloride-soluble iron contents of suspended sediments through a salinity gradient in the Beaulieu Estuary (United Kingdom). Hydroxylamine hydrochloride extracts iron present as ferrihydrite and lepidocrocite, but not haematite and goethite (Canfield, 1988), whereas all four phases are soluble in dithionite (Raiswell and others, 1994). Moore and others (1979) found that the hydroxylamine hydrochloride extractable iron in river particulates decreased through the salinity gradient from approximately 8 to 16 weight percent in the river end-member to approximately 1 weight percent in seawater. By contrast, that fraction of the total iron that was insoluble in hydroxylamine hydrochloride remained essentially uniform through the estuary. There is as yet insufficient data to assess whether such Fe oxide losses are reproduced in most rivers, or whether there are local and regional controls.

These studies do however clearly suggest that a significant fraction of Fe_{HR}-enriched material can be removed from riverine particulates through the salinity gradient, prior to entry into the ocean basins. Table 8 shows the effects of removing 40 percent of Fe_{HR} from riverine particulates before mixing with combinations of minimum and maximum M_R and M_G. All these mixing combinations give mean and standard deviations for Fe_{HR}/FeT, Fe_{PR}/FeT and Fe_U/FeT, which reasonably overlap the values for marine sediment. The combination of mixing plus iron removal thus avoids achieving a marine sediment composition only with combinations of high M_G and low M_R (see earlier). Figure 4 expands on the budget approach of table 8 by plotting the Fe_{HR}/FeT ratio reached for different mixing ratios $M_R/(M_R + M_G)$, assuming Fe_{HR} removal in the range of 0-50 percent. The marine sediment Fe_{HR}/FeT of 0.26+/−0.08 can be achieved at ratios of $M_R/(M_R + M_G) > 0.8$ (consistent with estimated present-day values of $M_R = 16000$-2000 Tg/yr, and M_G 1000-2000 Tg/yr; see earlier). These mixing ratios do however require that approximately 30 to 50 percent of Fe_{HR} is removed prior to entry into the ocean basins.

Removal of Fe_{HR} appears to occur through the salinity gradient through which a proportion of the riverine sediment flux may be deposited (on very variable time-scales) in a range of different environments (estuaries, tidal flats and salt marshes), in

TABLE 9

Fe$_{HR}$/FeT Values for Floodplain, Estuary and Salt Marsh Sediments

Environment	Fe$_{HR}$/FeT (no. samples)	Reference
Loch Etive, Scotland Bottom sediments	0.63+/-0.05 (17)	Strohle (ms)
Saguenay Fjord, Canada	0.34+/-0.7 (10)	This study and see Gagnon and others (1995)
Great Marsh, Delaware, USA	0.62+/-0.24 (4)	Kostka and Luther (1994)
Cocodrie Salt Marsh, Louisiana, USA	0.54+/-0.05	Jackson and others (1995)
Dee Salt Marsh, Cheshire, UK	0.36+/-0.27 (8)	This study
Mersey Salt Marsh, Lancs, UK	0.26+/-0.04 (4)	This study
Humber Salt Marsh, UK	0.36+/-0.06 (8)	This study

conditions, which range from sub-aerial to sub-aqueous (but with salinities less than fully marine). For convenience these depositional regions are hereon collectively referred to as the inner shore. The mass of sediment in the inner shore reservoir may be augmented by the addition of sediment on floodplains (where the river gauging station is located above the riverine boundary) and may be diminished by large floods (which episodically transport particulates into the marine environment). Once beyond the estuarine/marine boundary, deposition occurs as marine sediment.

Table 9 shows literature values for Fe$_{HR}$/FeT for some inner shore environments plus a few values determined as part of this study. Depth profiles have been used where possible to integrate the effects of any surface iron enrichments. Most samples have higher Fe$_{HR}$/FeT ratios than marine sediments, and approximately half are also higher than the mean Fe$_{HR}$/FeT ratio of riverine particulates. Dilution effects from the deposition of bedload and returning marine particulates (especially derived from coastal erosion) may make it difficult to identify preferential deposition of Fe$_{HR}$. The data are sparse and geographically limited in distribution, but their average of 0.44 suggests that some fractionation of Fe$_{HR}$-enriched material appears to occur in the inner shore. This fractionation, combined with dilution effects from sediment additions, provides the most reasonable explanation for the discrepancy in the Fe$_{HR}$/FeT ratio in riverine particulates and marine sediments.

PHANEROZOIC TRENDS IN IRON SPECIATION

The combined modern sediment data in table 7 have ratios of Fe$_{HR}$/FeT = 0.26+/−0.08, Fe$_{PR}$/FeT = 0.25+/−0.09 and Fe$_U$/FeT = 0.49+/−0.09 which provide a baseline for examining trends in iron speciation through the Phanerozoic record. Table 10 shows a Phanerozoic compilation of iron speciation data, which includes most of the normal marine shales, described by Raiswell and Berner (1986) and Raiswell and Al-Biatty (1989). The database is neither large (170 samples) nor geographically widespread (predominantly United Kingdom), and coverage of the Phanerozoic record is uneven. However, with these provisos in mind, the data permit some tentative conclusions to be drawn. Thus the ratio Fe$_{HR}$/FeT seems to have remained roughly constant through the Phanerozoic, but there is some suggestion that the ratio is lower

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TABLE 10

Variations in iron speciation for normal marine sediments through the Phanerozoic record

</div>

	Fe_{HR}/FeT	Fe_{PR}/FeT	Fe_U/FeT
Modern (46)	0.26+/-0.08	0.25+/-0.13	0.49+/-0.09
Lower Cretaceous (13)	0.15+/-0.04	0.49+/-0.08	0.35+/-0.08
Upper Jurassic (27)	0.14+/-0.04	0.30+/-0.04	0.52+/-0.07
Silurian (6)	0.17+/-0.11	0.30+/-0.16	0.53+/-0.07
Middle & Upper Ordovician (46)	0.13+/-0.06	0.35+/-0.10	0.51+/-0.09
Lower Cambrian (60)	0.14+/-0.11	0.41+/-0.11	0.45+/-0.10

Sediments described in Raiswell and Berner (1986), Raiswell and Al-Biatty (1989) and Poulton and others (1998).

in ancient normal marine shales compared to modern normal marine sediments (table 10). Furthermore this change appears to be accompanied by a commensurate increase in Fe_{PR}/FeT. These changes, if real, probably reflect loss of any iron oxides remaining after pyrite formation, during the reducing conditions of deep burial diagenesis. Some of this iron may be incorporated into clay minerals (as non-dithionite soluble Fe). However the observed changes in Fe_{HR}/FeT (and Fe_{PR}/FeT) are not large and there is otherwise no evidence for a significant change in the operation of the iron cycle (in terms of speciation) over the Phanerozoic.

This result is not unexpected, as the geochemical cycle of iron is dominated by oxidative chemical weathering, and oxygen levels have remained high enough through the Phanerozoic to convert Fe(II) to Fe(III) oxides. Greenhouse phases in the Ordovician-Devonian and Jurassic-Cretaceous might have been expected to accelerate weathering rates sufficiently to increase the ratio of Fe_{HR}/FeT, since there is some evidence that this ratio is higher in riverine particulates from modern tropical regions and increases with increased weathering (see earlier and Canfield, 1997). However the effects on speciation may not be detectable globally, or our data may be inadequate to detect such variations. Variations in the elemental composition of the riverine load are usually assumed to be small through the Phanerozoic (Garrels and Mackenzie, 1971). Thus there are close similarities in the elemental composition of modern and ancient muddy sediments (Garrels and Mackenzie, 1971; Wollast and Mackenzie, 1983), with large differences occurring only for CaO, CO_2 and H_2O. More specifically the FeT content of shales appears to show little variation through the Phanerozoic (Ronov and Migdisov, 1971), although there is an increase in the ratio of Fe(II) to Fe(III) with time (see above).

The uniform iron speciation characteristics of normal marine sediments through the Phanerozoic record suggests the existence of robust and persistent sedimentological or geochemical processes which maintain a constant composition for normal marine sediments over geologic time. We suggest that the main controls on the Fe_{HR}/FeT ratio are exerted by variations in the relative proportions of the riverine particulate flux (M_R) and the glacial particulate flux (M_G) which enter the ocean basins, together with Fe_{HR} trapping in inner shore environments. Thus M_G increases

Fe_{HR}/FeT and FeP/FeT ratios in ancient euxinic sediments

	No of Samples	Fe_{HR}/FeT	FeP/FeT
Middle Cambrian Alum Shale, Sweden (Armands,1972)	53	-	0.67+/-0.13
Upper Cambrian Alum Shale, Sweden (Armands, 1972)	39	-	0.85+/-0.04
Devonian-Mississippian, New Albany Group, USA (Frost, 1996)	54	-	0.55+/-0.17
Middle Devonian Oatka Creek Formation, New York State, USA (Werne and others, 2002)	33	-	0.71+/-0.2
Lower Jurassic Birchii Bed, Dorset, UK	8	0.39+/-0.07	0.36+/-0.06
Lower Jurassic Posidoniaschiefer, Germany	18	-	0.47+/-0.07
Lower Jurassic Jet Rock, Yorks, UK	6	0.66+/-0.05	0.57+/-0.17
Upper Jurassic Kimmeridge Clay, Dorset, UK (Raiswell and others, 2001) Oxygen Restricted Biofacies 1 Oxygen Restircted Biofacies 2	59 3	- -	0.90+/-0.10 0.67+/-0.14

during periods of enhanced glacial erosion, but greater volumes of ice also decrease the volume of the oceans, causing a fall in sealevel. Lower sealevel tends also to diminish the mass (and the proportion of Fe_{HR}-enriched) riverine particulates which are stored in inner shore areas. Conversely, as M_G decreases during periods of diminished ice masses and glacial erosion, so the higher sealevels produce more storage of riverine particulates (M_R decreases and is accompanied by more trapping of Fe_{HR}).

The sealevel changes which constrain $M_R / (M_R + M_G)$ also affect the proportions of Fe_{HR}-enriched sediments which may provide long term storage capacity; namely ironstones and euxinic sediments. We have found no relevant speciation data for Phanerozoic ironstones although it has commonly been observed that these contain 30 to 45 weight percent Fe as oxides, silicates (glauconite, chamosite, bertherine) and/or carbonates (Harder, 1989). The extraction data of Raiswell and others (1994) suggest that substantial proportions (at least) of these minerals will be soluble in dithionite and will therefore comprise a significant sink for Fe_{HR}. There is however limited iron speciation data on ancient euxinic sediments (table 11). These data can be supplemented from the literature by using the ratio FeP/FeT, which approximates to Fe_{HR}/FeT because all iron oxides are usually pyritised in euxinic depositional environments (Raiswell and Berner, 1985; Canfield and Raiswell, 1991; Raiswell and Canfield, 1998). Table 11 shows that Fe_{HR}/FeT is consistently higher in euxinic sediments compared to modern and ancient normal marine sediments. The reasons for the high Fe_{HR}/FeT ratios in euxinic sediments are not yet known, although Wijsman and others (2001) have been able to show that enrichment in the Black Sea arises from the preferential transportation of Fe_{HR} from the basin margin sediments together with

conversion of Fe_{PR} and FeU into Fe_{HR} (see also Anderson and Raiswell, unpublished data).

There are thus three sealevel-dependent, potential sinks, which could collectively operate to store Fe_{HR}-enriched sediment, and assist mixing with glacial particulates in maintaining a roughly constant Fe_{HR}/FeT ratio in normal marine shales through the Phanerozoic. Firstly, Fe_{HR}-enriched sediments deposit in the inner shore. During marine transgressions rising sealevel drowns river valleys and coastal embayments, increasing inner shore areas which trap Fe_{HR}-enriched sediment. Secondly, high Fe_{HR}/FeT ratios can clearly occur in sediments deposited beneath euxinic water columns, which allow the formation of water column pyrite (Raiswell and Canfield, 1998; Wijsman and others, 2001; Raiswell and others, 2001; Werne and others, 2002). Many black shales form at the peak of marine transgressions or, to a lesser extent, at the initial stages of transgression (Wignall, 1994). Thirdly, the formation of ironstones (which are ferric oxide enriched) is also favored by high sea-level, which produces extensive flooding of the continental margin and inland seas (Van Houten and Arthur, 1989). A warm global climate with increased precipitation and chemical weathering also favor ironstone formation (note that relatively high Fe_{HR}/FeT ratios are found in tropical basins, and where there is high runoff; see earlier). These observations suggest that there are reasonable mechanisms by which the global cycle of iron could operate to maintain a roughly constant ratio of Fe_{HR}/FeT in normal marine shales deposited through the Phanerozoic record. These mechanisms need more detailed investigation.

CONCLUSIONS

1. Riverine particulates sampled from basins which are geologically, geographically and climatologically diverse show a close correlation between Fe_{HR} and FeT. The iron oxides, which mainly comprise Fe_{HR}, are derived by chemical weathering from the total iron fraction (FeT) and remain closely associated with this fraction.

2. Glacial particulates have relatively low proportions of Fe_{HR} ($0.47+/-0.37$) and show little association with FeT (Fe_{HR}/FeT $=0.11+/-0.11$). These observations are consistent with an origin where the role of chemical weathering has been suppressed (relative to the riverine environment) and the role of physical weathering is enhanced.

3. Riverine particulate Fe_{HR}/FeT ratios averaged on a continental-scale are closely correlated with continental runoff ratios, consistent with the weathering controls in 1) above.

4. The globally averaged, discharge-weighted composition of riverine particulates is enriched in Fe_{HR}/FeT ($0.43+/-0.03$) relative to average marine sediment ($0.26+/-0.08$). This difference can be explained by a combination of; (a) Mixing with Fe_{HR}-depleted glacial particulates, and (b) Loss of Fe_{HR} from riverine particulates to inner shore (floodplain, estuarine and salt marsh) deposits, prior to entry into the oceans. This behavior, which has been well documented in a number of rivers, is apparently reproduced on a global basis.

5. Preliminary measurements of Fe_{HR}/FeT in inner shore sediments suggest that these sediments are enriched relative to marine sediments. Further studies of iron speciation in such sediments, relative to their riverine supply, are required.

6. The speciation of iron in modern normal marine sediments is, to a first approximation, similar to that in comparable sediments through the Phanerozoic record. A long-term steady state may be maintained through glacioeustatic controls. Periods of diminished ice mass volume and glacial erosion produce a high sealevel and lead to effective trapping of Fe_{HR}-enriched sediment in the inner shore deposits, but the remaining riverine material is mixed with lower proportions of Fe_{HR}-depleted glacial particulates. Conversely, increased ice volumes and enhanced glacial erosion are associated with low sealevel, and less Fe_{HR} is trapped before entry into the ocean

basins. Moreover this riverine material is then mixed with higher proportions of glacial particulates.

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