Iron isotopes in acid stream waters and iron-rich solids from abandoned mining areas along Tinto and Odiel watersheds

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ABSTRACT

δ^{56}Fe of acid stream waters ranged from –1.12 to 0.43‰ ; they were generally enriched in the lighter ^{54}Fe isotope compared to pyrite ($-0{,}56<\delta^{56}\mathrm{Fe}<+0{,}25$‰). The sediments had an isotopic signature ($-1{,}30<\delta^{56}\mathrm{Fe}<-0{,}68$‰) closed to that of the corresponding water while most of the stromatolite-like structures were enriched in the heavier isotope compared to acid stream waters ($\Delta\mathrm{Fe}_{\text{strom-water}}$ = +0.8 to 2.2‰).

INTRODUCTION

The metal-rich massive sulfide deposits of the Iberian Pyrite Belt (SW Spain) have been exploited for at least 5000 years (Leblanc et al., 2000). The area is drained by two main rivers, the Tinto and the Odiel, which receive numerous inputs from small creeks rising in the abandoned mines. As a result of pyrite oxidation, the waters of the watershed are acidic (pH 2-4) and contain extremely high iron and sulfate concentrations (Olias et al., 2004 ; Ferris et al., 2004). The oxidation reactions resulting in pyrite dissolution are mainly driven by the metabolic activity of chemolithotrophic bacteria involved in S and Fe cycles (Lopez-Archilla et al., 2001). The reaction produces Fe oxides, which precipitate around bacterial cells or colonies forming laminated sedimentary structures that resemble to the fossilized microbial mats or stromatolites which were produced 3.5 billion years ago by filamentous phototrophic bacteria (Brock et al., 1994). In the Tinto-Odiel watershed, modern and also fossil stromatolites, as suggested by the structure of Fe-rich precipitates recovered in 0,5-1 million years old terraces, are recovered.

At the molecular scale, the role of bacterial activity on Fe isotope fractionation is still controversial but may provide a tool for identifying life signature in Fe-rich fossil minerals even when the laminated structure is not apparent. According to Beard and Johnson. (1999), Croal et al. (2004), and Johnson et al. (2004) the bacterial activity produces significant Fe isotope fractionations.

In Precambrian Banded Iron Formations, Beard et al., (2003) ascribe the relatively important Fe isotope variations compared to the near-uniform isotope composition of Fe (<0.4‰) in terrestrial and lunar igneous rocks to biologically-mediated Fe redox cycling. At the contrary, the study of Bullen et al., (2001) provides evidence of Fe isotope fractionation during the abiotic precipitation of ferrihydrite from dissolved Fe(II). Sharma et al. (2001) attribute the variations of the isotopic composition of Fe in fluids and rocks associated with hydrothermal systems to non-biological fractionation of Fe isotopes.

The present study was designed to assess the variability of Fe isotopic signatures and eventually the processes, which control fractionation in acidic Fe- and sulphate-rich waters. The ultimate objective is to develop tools for recognising the early form of life in Martian like environments. For this the Tinto and Odiel watershed is ideally suited since according to Fairen et al. (2004), the iron minerals from the Tinto and Odiel rivers may constitute terrestrial analogues to those which formed in the primitive Martian ocean which was assumed to be moderately acidic on the basis of mineralogical and geochemical data.

Fe isotope ratios have been determined in the water of various acid streams along the Tinto and Odiel watersheds, in stromatolithes and in other iron-rich solids present on the site.

MATERIALS AND METHODS

Site description

The Iberian Pyrite Belt (IPB) forms part of the South Portuguese Zone which constitutes the southernmost zone of the Iberian Variscan Belt. The IPB includes more than one hundred massive sulfide deposits with original reserves exceeding 1700 million tons, that are found scattered in an arcuate belt of about 250 km in length and 40 km in width extending from Seville (Spain) to south of Lisbon (Portugal) (Figure 1).

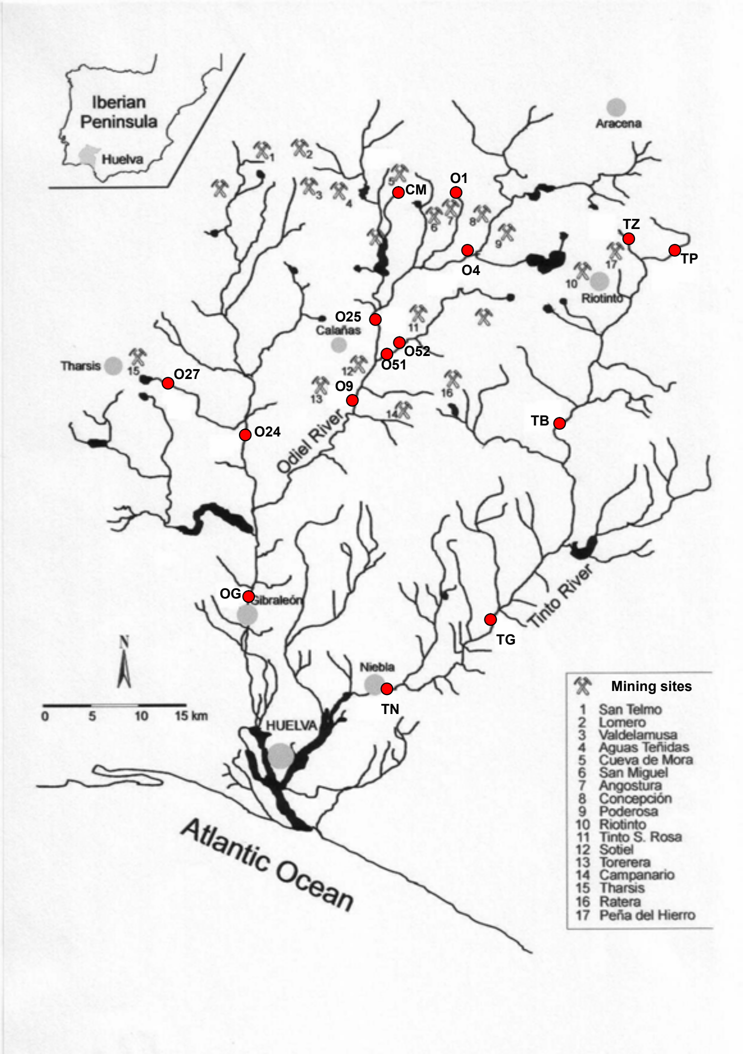

Figure 1 : Map of the Tinto and Odiel rivers with sampling points.

The metallic ores, which consist of massive bodies of iron and copper sulfides, have been mined since the Third Millennium BC, leaving numerous abandoned mining wastes. The area is drained by the Tinto and Odiel rivers. The Tinto river rises in the mining district of Peña del Hierro at the bottom of a pyrite-rich tailing stock; it flows through the abandoned RioTinto mines, discharging 50km downstream in the Atlantic ocean. Before joining the Tinto river to form a common estuary in Huelva, the Odiel river receives several creeks: the Rio Agrio and the Rio Oraque being the most important ones.

Excepted the upper Odiel river upstream from the confluence with the Rio Agrio, all water bodies in the area are acidic (pH=2-3) in relation to the oxidation of the pyrite. In the Odiel, the presence of detrital pyrite in the river sediments is scarce, and is only present close to mining areas. In the Tinto, the situation is different and detrital pyrite is observed throughout the river bed including in 5000 years old sediments (Elbaz-Poulichet et al., 2000). The oxidation of the pyrite results in the precipitation of Fe (III)-containing solids which present often a stromatolite-like structure.

We studied different acid streams rising in the vicinity of former mining areas and on the course of Tinto and Odiel rivers. Sampling stations CM, O1, O51-O52 and O27 were located on drainages closed to the mining sites of Cueva de la Mora, Angostura, Tinto Santa Rosa and Tharsis respectively, all located along the upper drainage basin of the river Odiel. O4, O25, O9 and OG were sampled along the river Odiel itself while O24 was sampled on the river Oraque which is a tributary of the river Odiel. Sampling stations TP, TZ, TB, TG, TN were located along the Tinto river, from the source at Peña del Hierro (TP) to the estuary in Niebla (TN) (Figure 1).

Sample collection

Water and solid samples were collected during two surveys in July 2003 and 2004. Stromatolites and sediment samples were collected in the streams. Fossilized stromatolites and transported Gossan were collected in old terraces in the upper part of the Tinto basin and near the Huelva coast. Pyrite, goethite and hematite samples were collected in gossans deposits from the Tharsis mining area. The pH and conductivity were measured in the field with an Ultrameter^{TM} Model 6P (Myron L Company, Camlab, Cambridge) equipped with a pH sensor. Water samples were filtered immediately through 0.22 µm Millipore membranes fitted on Sartorius polycarbonate filterholders. For Fe(II) determinations, filtered samples were buffered to pH 4.5 with an ammonium acetate/acetic acid buffer in the field, and Fe(II) was complexed by adding 1 ml of a 0.5 % (w/w) 1,10-phenanthrolinium chloride solution to 10 ml of sample (Rodier, 1996). Samples for total Fe determination were acidified to pH=1 with HNO_3 (14.5 M) and stored at 4°C in polyethylene bottles until analysis.

Stromatolite and sediment samples were completely dissolved on a hot plate with HCl/HF (5:1) (80°C, 24h) followed by HNO_3/H_2O_2 (5:1) (80°C, 24h), evaporated to dryness and resuspended in 10 ml of HNO_3 3%.

Analysis

Analysis of Fe(II) were made by colorimetry at 510 nm. The detection limit is 0.2 mM and the precision better than 5 %. Total Fe in water (dissolved + colloidal) and solids was determined by Flame Atomic Absorption Spectrometry (AAS).

Isotope measurements

For Fe isotopes analysis, water and dissolved solid samples were oxidized with a few drops of concentrated H_2O_2. The sample was then purified with a resin (2 ml) (RE Spec resin Eichrom Technologies Inc., IL, USA). 10 ml of the sample (diluted to 5 mg.l^{-1} Fe on average) was loaded on a column with the resin (2 ml). Sample matrix was removed with elution of 10 ml of HNO_3 8N and the Fe was eluted with 10 ml of HNO_3 3 %. Additionally, samples were spiked at 1 mg.l^{-1} with Cu from a 1000 mg.l^{-1}stock solution (CPIInternational, Santa Rosa, CA, USA) for internal normalization. Iron isotope (^{54}Fe, ^{56}Fe) measurements were performed with Neptune double focusing, sector field multiple collector ICP-MS (Thermo-Finnigan, Bremen, Germany). The high resolution allows to measure iron isotopes without isobaric interferences of polyatomic species with the peak-shoulder method developed by Weyer and Schwieters (2003). Precise determination of isotopic ratios of complex samples is possible with external calibration using the reference material IRMM-14 (IRMM, Geel, Belgium), after internal normalisation with Cu isotopes spiked in sample and standard; external reproducibility is 0.06 ‰ δ^{56}Fe (2 standard deviations). All δ^{56}Fe values are expressed relatively to the IRMM-14 isotopic reference material (IRMM, Geel, Belgium).

RESULTS

Aqueous and solid chemistry

All water samples are acidic with pH values comprised between 1.45 and 3.32 in the source region, the lowest pH being observed at the spring of the Tinto river (station TP2) (Table 1). In both rivers the pH increases of about 1 unit from the headwaters to the estuary. In the Tinto river, the maximum pH is 2.74 in Niebla. In the Odiel river a pH value of 3.84 was recorded in Gibraleon during the 2004 survey.

The increase of pH is generally accompanied by a decrease in the Fe content as shown in Figure 2.

Table 1 – Main physico-chemical parameters, total Fe concentrations and speciation in waters

Sampling site	Sampling station	Comments	date	T °C	pH	C µS/cm	O2 ppm	FeII ppm	Fetot ppm	FeIII ppm	FeII %	Fe(III)/Fe(II)
Mine drainages along Odiel watershed												
Cueva de la Mora	CM		juil-03	27.6	3.1	4576	10	27	307	280	91	10
			juil-04	28.6	3.0	4575	10	8	257	250	97	33
Angostura	O1		juil-03	25.6	2.9	4542	_	18	173	155	89	8
Santa Rosa	O52B-1	main stream	juil-03	24.1	3.3	3853	8	32	614	583	95	18
	O52B-2	tailings	juil-03	21.3	3.5	3812	3.5	32	625	593	95	19
	052A	algae stream	juil-04	21.8	3.1	3543	3.5	19	685	666	97	35
	052B	mixing	juil-04	25.9	3.0	3582	7	21	664	643	97	30
	052C	galery	juil-04	22.6	3.0	3594	10	17	716	699	98	42
Tharsis	O27C	springwater	juil-03	33.5	3.1	8077	>12	1	9	8	88	7
	O27-2C	downstream	juil-03	32.1	2.5	16150	_	76	1779	1702	96	22
	O27	springwater	juil-04	32.5	2.3	15490	9	7	1604	1598	100	239
Odiel river												
	O4		juil-03	23.8	2.7	5710	8	16	149	132	89	8
			juil-04	34.2	2.3	8006	12	2	213	211	99	91
	O25		juil-03	29.2	2.8	3956	8	7	17	10	59	1
Sotiel bridge	O9		juil-03	32.1	2.9	3243	8	6	11	5	44	1
			juil-04	25.4	2.1	3049	10	11	11	0.4	3	0
Gibraleon	OG		juil-03	27.8	3.8	733.1	6	1	1	0	0	0
			juil-04	30.1	3.2	1588	6	2	2	0	0	0
Oraque river												
	O24		juil-03	29.6	2.8	2245	_	6	6	0	0	0
Tinto river												
Pena del Hierro	TP1	main creek	juil-04	35.5	2.4	9558	10	27	1148	1121	98	42
	TP2	tributary	juil-04	35	1.4	26980	11	14	2082	2081	100	1535
Zarandas	TZ		juil-04	33.9	2.2	13110	12	41	3366	3325	99	81
Berrocal	TB		juil-03	29.6	2.4	9605	_	58	2056	1998	97	34
			juil-04	27.8	2.0	9508	>12	1	2193	2192	100	2529
Gadea	TG		juil-04	26.9	2.1	3318	>12	19	76	57	75	3
Niebla	TN		juil-03	31.8	2.6	3320	_	7	91	84	92	11
			juil-04	26	2.7	2228	_	8	8	0	0	0

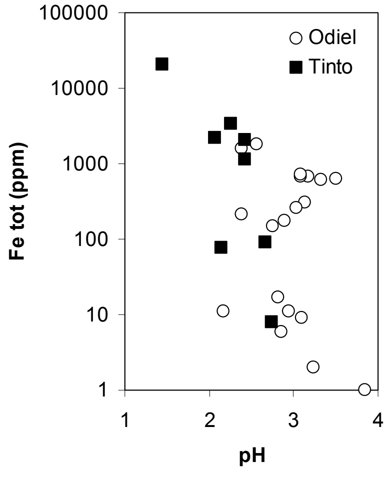

Figure 2 : Variation of total Fe concentrations as a function of pH of the water samples.

Total dissolved concentrations drop to the detection limit of our analytical technique in Gibraleon. In Niebla the maximum value is 91 ppm. Such values contrast with those recorded in the mine region where total dissolved Fe concentration displays a maximum value (20829ppm) at station TP2. The proportion of Fe(III) in solution is almost 100% at sampling stations closed to the mines. It decreases with the concentration of total dissolved Fe (Figure 3). The highest concentration of Fe (III) in solution (20816ppm) is observed at station TP2.

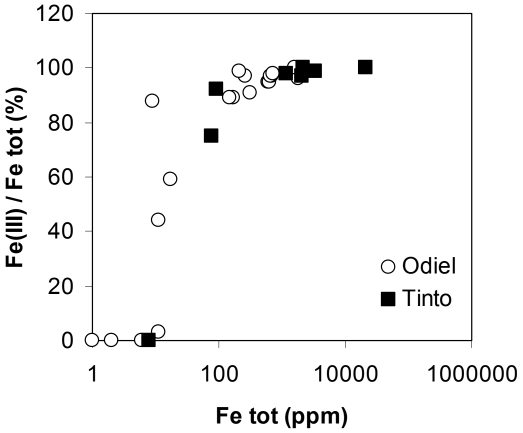

Figure 3 : Proportion of Fe(III) as a function of total Fe concentrations of the water samples

Iron isotope ratios

The δ^{56}Fe is defined by the following equation :

$\delta^{56}Fe = [(^{56}Fe/^{54}Fe_{sample}/^{56}Fe/^{54}Fe_{IRMM})-1] \times 1000$ (1),

Data are reported in Table 2 and 3.

The range of variation of δ^{56}Fe in the local pyrite, in water and in the diverse iron oxides are reported in Figure 4.

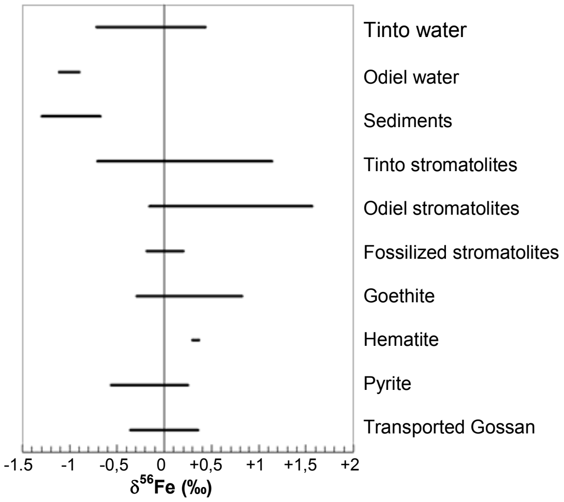

Figure 4 : Range of variations of δ^{56}Fe of water and solid samples from Odiel and Tinto watersheds.

The Fe isotope composition of pyrite is comprised between –0.56 ‰ and 0.25 ‰ (Table 2) in agreement with literature data (Sharma et al., 2001). The isotope composition of the transported Gossan sample is similar to pyrite. This is also the case for goethite from gossan deposits, whereas hematite displays only positive values (δ^{56}Fe=0.29 ± 0.03 ‰).

				Stromatolites			**Sediment**			**Pyrite**		
	Sampling site	**Sampling station**	**date**	**%Fe**	**δ^{56}Fe ($^{0}/_{00}$)**		**%Fe**	**δ^{56}Fe ($^{0}/_{00}$)**		**%Fe**	**δ^{56}Fe ($^{0}/_{00}$)**	
					mean	SD		mean	SD		mean	SD
Mine drainages along Odiel watershed												
	Cueva de la Mora	CM	juil-03	39	1.12	0.05						
		CM	juil-04				50	-0.68	0.13			
	Santa Rosa	O52B-1	juil-03	45	1.10	0.07						
		O52B-2	juil-03	40	1.57	0.08						
		O52B	juil-04	46	1.11	0.11						
	Tharsis	O27C	juil-03	47	0.79	0.08				11	-0.56	0.08
		O27-2C	juil-03	39	-0.16	0.09				10	-0.47	0.10
Oraque river												
		O24	juil-03				45	-1.30	0.02			
Tinto river												
	Pena del Hierro	TP1	juil-04				48	-0.69	0.15	18	0.25	0.10
	Zarandas	TZ	juil-04	46	1.14	0.10						
	Berrocal	TB	juil-04				23	-0.69	0.09	37	-0.41	0.05
	Gadea	TG	juil-04	37	-0.71	0.07	43	-0.97	0.10			
Fossils and Fe minerals from Tharsis mine												
Fossils	Islantilla		juil-04	18	-0,18	0,08						
	Pinares de Cartaya		juil-04	15	0,21	0,14						
	Transported Gossan		juil-04	53	-0,36	0,12						
Fe minerals	Goethite	fs8	juil-03	8	-0,29	0,03						
	Goethite	fn8	juil-03	19	0,83	0,07						
	Goethite	f4e	juil-03	54	-0,08	0,04						
	Hematite	fs11	juil-03	61	0,29	0,03						
	Hematite	fn10	juil-03	53	0,37	0,02						

Table 2 – Fe isotope composition of solid samples

The Odiel water is characterized by δ^{56}Fe < 0 with remarkably homogeneous values (δ^{56}Fe = –1.02 ± 0.09 ‰). The Tinto water displays also generally negative δ^{56}Fe value at the exception of the sample TP2 (δ^{56}Fe =0.43 ± 0.05 ‰) (Table 3).

Sampling site	Sampling station	date	δ^{56}Fe ($^0/_{00}$) mean	SD
Mine drainages along Odiel watershed				
Cueva de la Mora	CM	juil-03	-1.12	0.07
		juil-04	-1.11	0.10
Santa Rosa	O52B-1	juil-03	-1.03	0.09
	052B	juil-04	-0.90	0.12
Tharsis	O27-2C	juil-03	-0.96	0.07
	O24	juil-03	-0.31	0.13
Tinto river				
Pena del Hierro	TP1	juil-04	-0.37	0.12
	TP2	juil-04	0.43	0.05
Zarandas	TZ	juil-04	-0.72	0.06
Berrocal	TB	juil-04	-0.36	0.07
Gadea	TG	juil-04	-0.19	0.12

Table 3 – Fe isotope composition of waters

In water, a decrease of δ^{56}Fe with increasing pH is generally observed (Figure 5) reflecting a depletion of ^{56}Fe in the aqueous phase when pH increases.

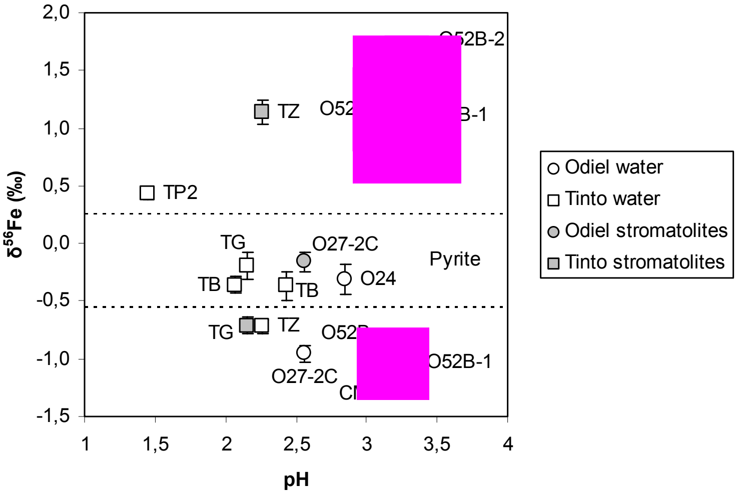

Figure 5 : Isotope composition (δ^{56}Fe) of water and stromatolite samples versus pH.

The isotope composition of stromatolites samples varies within a larger range compared to the water and other Fe-rich solids of the site (Figure 4). The stromatolites from the Odiel basin have generally positive δ^{56}Fe (up to 1.57±0.08 ‰) excepted at station 027-2C where a slightly negative value (δ^{56}Fe=-0.16±0.09 ‰) is recorded. In the Tinto river, the stromatolite sample taken in the source region is characterized by a positive δ^{56}Fe value (1.14±0.10 ‰) whereas the sample taken downstream has a negative value (δ^{56}Fe=-0.71±0.07 ‰).
Sediment samples all display negative (down to –1.30±0.02 ‰) δ^{56}Fe values.

DISCUSSION

The cycle of iron in acid mining environments involves biotic and abiotic processes, both able to change Fe isotope ratios. The first step is the oxidation of pyrite by dissolved oxygen. This step proceeds abiotically and is considered as slow. The oxidation produces Fe (II), which is oxidised into Fe (III). The Fe (II) oxidation reaction is mediated by acidophilic chemolithotrophic bacteria. Fe(III) is a more efficient oxidizing agent than O_2; thus, its formation increases the rate of pyrite oxidation by several orders of magnitude ; in this case, extremely low pH values are reached, which maintain elevated Fe(III) concentrations in solution (Langmuir, 1997). When the water pH becomes higher than that require for maintaining Fe (III) in solution, the later precipitates, forming either stromatolites when the oxidation of Fe(II) and the precipitation occur simultaneously at the surface of Fe-oxidizing bacterial colonies, or sediment when Fe (III) initially stable in solution precipitates.
Among the Odiel river water samples, those characterized by pH>3 display negative δ^{56}Fe. The stromatolites recovered at the same stations display systematically positive δ^{56}Fe value for pH>3 (Figure 5), giving a fractionation ($\Delta^{56}\text{Fe}_{\text{solid-water}}$) of 2,1 ± 0.1 ‰ between stromatolites and the corresponding stream water. As shown

in Figure 5, a negative δ^{56}Fe is observed in one stromatolite sample from the Odiel basin (Station 027-2C). Nevertheless, the data indicate a fractionation of +0.80 ± 0.15 ‰ between the stromatolite and the corresponding water. Thus, in the Odiel river, the data suggest that the formation of stromatolite leads to the relative enrichment of water in ^{54}Fe and to its depletion in stromatolites. In contrast to stromatolites, sediments always display negative δ^{56}Fe values. Hence, the comparison between stromatolites of the Odiel river and sediments would suggest a positive fractionation of Fe in relation to biological oxidation of Fe(II) and precipitation. The fractionation between stromatolite samples and the corresponding water reaches extremely high values ($\Delta^{56}Fe_{solid\text{-}water}$ = +2.24 ‰) in comparison with previous studies related to isotopic fractionation associated with hydrous ferric oxide precipitation. Fractionation of 1.1-1.5 ‰ may be typical of systems in which Fe undergoes oxidative precipitation when equilibrium and kinetic isotope effects are intertwined (Anbar, 2004). However, the net isotope shifts documented for oxidation of Fe(II) and precipitation of HFO are only +0.75 ‰/amu for anoxigenic photosynthetic oxidation (Croal et al., 2004) and +0.45 ‰/amu for O_2-mediated oxidation (Bullen et al., 2001 ; Dauphas et al., 2004). The fractionation measured between ferrihydrite and $Fe(II)_{aq}$ from an Fe-rich groundwater spring averages 1 ‰ according to Bullen et al. (2001). Therefore the high fractionation observed in the Odiel river may result from biological effects.

In the Tinto river, the data obtained at station TZ, showing negative δ^{56}Fe values in water and a positive value in the corresponding stromatolite corroborate the interpretation of Odiel data, at the exception of one water sample (TP2) and one stromatolite sample (TG), which display respectively a positive fractionation and a negative fractionation relative to pyrite. Indeed, the water sample contains extremely high concentrations of Fe(III) which is stable in solution at low pH. This suggests that the biological oxidation of pyrite produces Fe (III) slightly enriched in ^{56}Fe. The precipitation of the Fe(III) which occurs simultaneously when the pH is high enough to promote Fe (III) precipitation depletes relatively the water in ^{56}Fe and enriches the stromatolite in the heavier isotopes. The negative δ^{56}Fe value of TG stromatolite suggests that differences between sediments and stromatolites cannot necessarily be taken as a biosignature, because abiotic oxidation and precipitation processes can give similar fractionation than microbially-mediated reactions.

From these values it appears that water and sediments exhibit an Fe isotopic composition within the range of those of pyrite or slightly lighter while stromatolites are generally heavier than pyrite. Thus, isotopic variations seems to be related to the mechanism involved: oxidation of pyrite or oxidation of Fe(II) in solution and precipitation.

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