Chemical Geology 253 (2008) 162–171

Contents lists available at ScienceDirect

Chemical Geology

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

Iron isotopes in acid mine waters and iron-rich solids from the Tinto–Odiel Basin (Iberian Pyrite Belt, Southwest Spain)

M. Egal [a], F. Elbaz-Poulichet [a,*], C. Casiot [a], M. Motelica-Heino [b], P. Négrel [b], O. Bruneel [a],
A.M. Sarmiento [c], J.M. Nieto [c]

[a] *Laboratoire Hydrosciences, UMR 5569, Université Montpellier 1 & 2, CNRS-IRD, Place E. Bataillon, 34095 Montpellier cedex 05, France*
[b] *BRGM, Orléans, France*
[c] *Departamento de Geología, Universidad de Huelva. Av. Fuerzas Armadas s/n 21071 Huelva, Spain*

ARTICLE INFO

Article history:
Received 27 February 2008
Received in revised form 29 April 2008
Accepted 13 May 2008

Editor: D. Rickard

Keywords:
Fe isotopes
Acid mine drainage
Iberian Pyrite Belt

ABSTRACT

The isotopic composition of Fe was determined in water, Fe-oxides and sulfides from the Tinto and Odiel Basins (South West Spain). As a consequence of sulfide oxidation in mine tailings both rivers are acidic ($1.45 < pH < 3.85$) and display high concentrations of dissolved Fe (up to 420 mmol l^{-1}) and sulphates (up to 1190 mmol l^{-1}).

The δ^{56}Fe of pyrite-rich samples from the Rio Tinto and from the Tharsis mine ranged from −0.56±0.08‰ to +0.25±0.1‰. δ^{56}Fe values for Fe-oxides precipitates that currently form in the riverbed varied from −1.98±0.10‰ to 1.57±0.08‰. Comparatively narrower ranges of values (−0.18±0.08‰ and +0.21±0.14‰) were observed in their fossil analogues from the Pliocene–Pleistocene and in samples from the Gossan (the oxidized layer that formed through exposure to oxygen of the massive sulfide deposits) (−0.36±0.12‰ to 0.82±0.07‰). In water, δ^{56}Fe values ranged from −1.76±0.10‰ to +0.43±0.05‰.

At the source of the Tinto River, fractionation between aqueous Fe(III) and pyrite from the tailings was less than would be expected from a simple pyrite oxidation process. Similarly, the isotopic composition of Gossan oxides and that of pyrite was different from what would be expected from pyrite oxidation. In rivers, the precipitation of Fe-oxides (mainly jarosite and schwertmannite and lesser amounts of goethite) from water containing mainly (more than 99%) Fe(III) with concentrations up to 372 mmol l^{-1} causes variable fractionation between the solid and the aqueous phase ($-0.98‰ < \Delta^{56}Fe_{solid-water} < 2.25‰$). The significant magnitude of the positive fractionation factor observed in several Fe(III) dominated water may be related to the precipitation of Fe(III) sulphates containing phases.

1. Introduction

Fe is the fourth most abundant element on Earth. It is an essential element for most living organisms. It is used as an electron donor or acceptor in numerous microbiological metabolisms especially those involving acidophilic organisms (Ehrlich, 1996; Amils et al., 2007). Fe is also a key micronutrient in the limitation of oceanic production and thus plays a direct role in the control of CO_2 assimilation by phytoplankton (Martin and Fitzwater, 1988; Martin, 1990; Coale et al., 1996).

Fe isotopes are a good tool to improve our understanding of Fe-cycling and have been used in many scientific fields as reported in the review of Dauphas and Rouxel (2006). Non redox reactions can fractionate Fe isotopes (Anbar et al., 2000), but major effects are due to redox processes (Johnson et al., 2002; Schauble et al., 2001). Fractionation can be predicted theoretically (Polyakov and Mineev, 2000; Schauble et al., 2001; Anbar et al., 2005; Polyakov et al., 2007). The theoretical approach of Anbar et al. (2005), based on the density functional theory, predicts a fractionation of 3‰ at 25 °C for the equilibrium fractionation between $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$, Fe(III) being isotopically heavier than Fe(II), which is in good agreement with the experimental data of Johnson et al. (2002) and Welch et al. (2003).

The possible fractionation of Fe isotopes during biologically mediated reactions and the observation of rather homogeneous isotopic composition in low C and S clastic rocks compared to that of chemically precipitated sediments (Beard and Johnson, 1999; Beard and Johnson, 2004) paved the way for Fe biosignatures, though the picture was shown to be more complex that originally thought (Anbar et al., 2000; Anbar, 2004). With the exception of magnetotatic bacterial oxidation (Mandernack et al., 1999), Fe isotope fractionation has been experimentally demonstrated for all biologically mediated Fe reactions including extracellular reductive dissolution of hematite (Beard et al., 2003), extracellular dissolution of ferrihydrite (Beard and Johnson, 1999; Beard et al., 2003), anoxygenic photosynthesis of

---

[*] Corresponding author. Tel.: +33 467143931; fax: +33 467144774.
E-mail address: felbaz@univ-montp2.fr (F. Elbaz-Poulichet).

0009-2541/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2008.05.006

ferrihydrite by photoautotrophic bacteria (Croal et al., 2004), dissolution of hornblende in presence of bacteria (Brantley et al., 2004). However, Fe isotope fractionation has also been observed during abiotic processes such as abiotic Fe(II) oxidation (Bullen et al., 2001), isotopic exchange between Fe(II) and Fe(III) (Skulan et al., 2002; Welch et al., 2003), Fe(III) precipitation (Bullen et al., 2001; Skulan et al., 2002; Beard and Johnson, 2004; Balci et al., 2006), Fe(III) dissolution (Brantley et al., 2004).

Most Fe isotope data for natural environments concern solid samples including meteorites and lunar samples (Beard and Johnson, 1999; Poitrasson et al., 2004, Poitrasson and Freydier, 2005). Particular attention has been paid to the Fe isotope composition of Banded Iron Formations (BIFs) (Johsnson et al., 2003; Dauphas et al., 2004, 2007; Yamaguchi et al., 2005), black shales (Rouxel et al., 2005), oceanic crust (Rouxel et al., 2003), ferromanganese crust and nodules (Levasseur et al., 2004; Chu et al., 2006), hydrothermal deposits (Markl et al., 2006; Dideriksen et al., 2006).

An increasing number of studies are now considering the fractionation between water and solids in natural environments such as oceanic hydrothermal systems (Sharma et al., 2001; Severmann et al., 2004; Dauphas and Rouxel, 2006), shelf sediments and porewaters (Severmann et al., 2006), rivers and sediments (Fantle and DePaolo, 2004; Berquist and Boyle, 2006). However the number of data on the Fe isotope composition of natural waters remains limited. Yet this knowledge is important to better understand the biogeochemical processes that fractionate Fe isotopes in nature.

Fe-rich acidic water also called acid mine drainage (AMD) is produced upon oxidation of pyrite in mining residues. The formation of iron stromatolite-like structures is common in AMD (Brake et al., 2002, 2004; Morin et al., 2003) and is linked to microbial activity, which plays a major role in the oxidation of Fe and in the precipitation of the Fe-rich solids (Ferris et al., 2004). These modern stromatolites are very similar to those of Late Archean–Early Proterozoic BIFs. AMD may thus be studied as a model for early Earth and extraterrestrial environments (Fang et al., 2007). With the exception of the study of Herbert and Schippers (2008), few data on the isotopic composition of Fe in acid mine environments have been reported to date.

The Tinto and Odiel Rivers drain the central and eastern part of the Iberian Pyrite Belt, which has the largest known concentration of massive sulfide deposits in the world. Pyrite oxidation is still taking place in the huge mining spoil heaps that resulted from a long history (5000 years) of mining (Leblanc et al., 2000). As a consequence, the waters of both rivers are strongly affected by AMD and display extremely high Fe concentrations (up to a few hundreds of mmol l^{-1}) and low pH values (2.5 to 3.5) from the mining area to the estuary (ca. 50 km) (Braungardt et al., 2003). The system is currently being studied as a terrestrial analogue for the planet Mars because of the abundance of Fe and the occurrence of jarosite which resembles that at the Martian Meridiani Planum site (Fairen et al., 2004; Fernandez-Remollar et al., 2005; Amils et al., 2007).

The objective of this study was to assess the variability of Fe isotope composition in relation to the main processes affecting Fe cycling in this Fe(II)–Fe(III)–pyrite–sulphates-rich system.

Iron isotope composition was determined in the water of the Tinto and Odiel Rivers, in the Fe sulfides of the mining wastes, in the Fe-rich solids that are currently being precipitated from the water, and in similar Fe-oxide precipitates that have been preserved in the Pliocene–Pleistocene river terraces. In parallel, dissolved Fe concentrations (including total, Fe(II) and Fe(III)) were determined. The mineralogical composition of the Fe-rich solids in this system was also analysed.

2. Site description

The Iberian Pyrite Belt (IPB) forms part of the South Portuguese Zone, which comprises the southernmost zone of the Iberian Variscan Belt. The IPB has been reported as one of the largest massive sulfide provinces in the world (Leistel et al., 1998; Sáez et al., 1999; Tornos, 2006), containing more than one hundred individual massive sulfide deposits with original reserves being estimated to exceed 1700 million tons scattered over an area about 250 km in length and 40 km in width extending from Seville (Spain) to south of Lisbon (Portugal) (Fig. 1). Two contrasting styles of mineralization can be recognized in the IPB suggesting two different geological settings: shale-hosted exhalative deposits in the southern part of the area, and volcanic-hosted deposits in the northern part formed by stratabound replacement of felsic volcanic rocks. Most of the deposits formed over a short time span, from the Late Devonian to the Early Carboniferous. Some of the sulfide deposits have been exposed at the surface at least since the Miocene, and have consequently undergone extensive oxidation processes, developing a thick cover of iron oxides and hydroxides known as "Gossan", (Pomiès et al., 1998; Nieto et al., 2003).

The metallic ore, which consists of massive bodies of iron and copper sulphides, has been mined since the Third Millennium BC (Leblanc et al., 2000; Nocete et al., 2005), leaving numerous abandoned mining wastes that contain mainly pyrite.

The area is drained by the Tinto and Odiel Rivers. The Odiel River (length: 140 km, surface of the basin: 2300 km^2) has an average annual flow of about 460 Mm^3 yr^{-1}. The Tinto River (length: 100 km, surface of the basin: 720 km^2) has an average annual flow of 90 Mm^3. yr^{-1}. Except for the upper Odiel River, which is located upstream from the mines, all the water bodies in the area are acidic ($pH = 1.45–3.85$) and contain extremely high concentrations of Fe and associated heavy metals and sulphate (Olias et al., 2004; Ferris et al., 2004; Sanchez-Espana et al., 2005).

Despite such extreme conditions, the Tinto and Odiel waters are host to a diverse biota of eukaryotes and prokaryotes (Lopez-Archilla et al., 2001; Zettler et al., 2002; Sabater et al., 2003; Gonzalez-Toril et al., 2003; Aguilera et al., 2006). These organisms probably promote the precipitation of the Fe-rich solids that are ubiquitously encountered in the riverbeds around biological remains (Fernandez-Remolar et al., 2005). In the Pliocene (>500,000 years) terraces of the Tinto River, similar structures are observed that can be considered as fossil analogues of modern stromatolites (Amils et al., 2007).

3. Materials and methods

3.1. Sample collection

Four surveys were carried out from 2003 to 2006. Samples for Fe isotope analysis were taken in July 2003 and July 2006. The locations of the sampling stations are shown in Fig. 1. Water samples were taken in several acid streams rising in the vicinity of former mining areas and in the mainstream of the Tinto and Odiel Rivers. Three samples (TP-1, TP-2, TP-3) were taken in what is generally considered as the source region of the Tinto River. TP-2 was taken immediately (less than 1 m) below the outlet of the pyrite tailings stock. TP-1 was taken in another branch of the river at a few hundred meters approximately from the source and has already undergone geochemical modification relative to the source water. TP-3 was sampled downstream from the junction of the TP-1 and TP-2 streams.

Solid samples representing the major types of iron-rich material found in the Tinto and Odiel basins were also collected. Ferruginous solids from old river terraces were taken near Nerva, and at stations ISL and PC (Fig. 1); samples of pyrite were collected in the Tharsis mining district, and from Peña del Hierro mine (Rio Tinto mining district), and Gossan samples were collected in the Tharsis mining district. Different facies of recent sediments – laminated concretions, ferruginous crust and gel-like precipitates – were sampled in the effluents flowing from mine galleries or spoil heaps, and in the mainstream of the Tinto and Odiel Rivers.