



Iron isotope composition of the suspended matter along depth and lateral profiles in the Amazon River and its tributaries

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ABSTRACT

Samples of suspended matter were collected at different locations, seasons, depths and lateral profiles in the Amazon River and three of its main tributaries, the Madeira, the Solimões and the Negro rivers. Their iron isotope compositions were studied in order to understand the iron cycle and investigate the level of isotopic homogeneity at the river cross-section scale. Samples from four depth profiles and three lateral profiles analyzed show suspended matter $\delta^{57}\text{Fe}$ values (relative to IRMM-14) between $-0.501 \pm 0.075\text{‰}$ and $0.196 \pm 0.083\text{‰}$ (2SE). Samples from the Negro River, a blackwater river, yield the negative values. Samples from other stations (whitewater rivers, the Madeira, the Solimões and the Amazon) show positive values, which are indistinguishable from the average composition of the continental crust ($\delta^{57}\text{Fe}_{\text{IRMM-14}} \sim 0.1\text{‰}$). Individual analyses of the depth and lateral profiles show no significant variation in iron isotope signatures, indicating that, in contrast to certain chemical or other isotopic tracers, one individual subsurface sample is representative of river deeper waters. This also suggests that, instead of providing detailed information on the riverine iron cycling, iron isotopes of particulate matter in rivers will rather yield a general picture of the iron sources.

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1. Introduction

Iron is the fourth most abundant element in the Earth's crust (4.3 wt% as Fe – e.g., Wedepohl, 1995). It is found in practically all rocks and soils and is present in a variety of minerals. Rivers are one of the major providers of iron – along with other elements – to oceans (Zhu et al., 2000; Beard et al., 2003a). Other dissolved and particulate iron sources to oceans and rivers are atmospheric deposition, continental run-off, re-suspended sediments, diagenetic pore fluids, underground waters, vegetation, soils, weathering material and hydrothermal vents (Wells et al., 1995; Elderfield and Schultz, 1996; Johnson et al., 1999; Beard et al., 2003a; Elrod et al., 2004; Jickells et al., 2005; Severmann et al., 2006; Bennett et al., 2008; Rouxel et al., 2008a, 2008b; Escoube et al., 2009).

The suspended matter composition of rivers is controlled by several factors, including climate, weathering, erosion and the

nature of the geological basement (Bouchez et al., 2010). Its abundances may be directly correlated with water discharge increase (Bouchez et al., 2010), although this was shown not to be the case in larger rivers, like the Amazon at the Óbidos Station (Martinez et al., 2009).

Many trace elements of the Amazon River, including iron, are mobilized between dissolved and particulate forms due to abiotic and biological processes (e.g., redox, adsorption, mineral dissolution, organic complexation, precipitation, erosion and continental run-off – see Beard et al., 1999; Bullen et al., 2001; Skulan et al., 2002; Roe et al., 2003; Fantle and DePaolo, 2004; Rodushkin et al., 2004; Johnson and Beard, 2005; Teutsch et al., 2005; Dauphas and Rouxel, 2006) and they may all have an effect on iron isotope signatures of river born matter.

A number of studies have been carried out on compositional variations and fractionation of iron isotopes in rivers, oceans, lakes and soils (Zhu et al., 2000; Rouxel et al., 2004; Emmanuel et al., 2005; Bergquist and Boyle, 2006; Ingri et al., 2006; Severmann et al., 2006; Staubwasser et al., 2006; Fehr et al., 2008; Poitrasson et al., 2008; Severmann et al., 2008, 2010; Zhao et al., 2009; Song et al., 2011), but a great deal of work is still needed to

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successfully use iron isotopes as a tool to understand the biogeochemical cycle of iron (Song et al., 2011).

Riverine inputs to the ocean are described to display $\delta^{57}\text{Fe}$ values from -1.5 to 0.9‰ (Fantle and DePaolo, 2004; Bergquist and Boyle, 2006; Escoube et al., 2009), while atmospheric input yield $\delta^{57}\text{Fe}$ data similar to crustal values (Beard et al., 2003b). Although the particulate load of rivers seemed at first relatively unfractionated with respect to crustal values (Beard et al., 2003b), dissolved Fe in river waters has been reported to exhibit isotopic variability related to the weathering process (Fantle and DePaolo, 2004; Bergquist and Boyle, 2006; Poitrasson et al., 2008). Furthermore, recent reports have shown that Fe isotope compositions of organic and inorganic, dissolved, colloidal and particulate iron forms in rivers may vary (e.g., Bergquist and Boyle, 2006; Escoube et al., 2009). Hence, more detailed studies are required to quantify the various possible sources of iron in rivers, especially during organic and inorganic processes in such environments.

The present study focuses on the iron isotopic composition of suspended matter collected along depth and lateral profiles from the Amazon River and three of its main tributaries: the Solimões River, the Negro River and the Madeira River (Fig. 1). The main objective of this work is to investigate the variability of iron isotope signatures as a function of depth, lateral profiles, seasons and geographic location, to provide a scale of its potential variability and have a better insight into the biogeochemical cycling of iron in the Amazon River and its tributaries.

2. Study area, sampling and methods

2.1. Study area

The Amazon River represents approximately 20% of the world riverine fresh waters and, as such, it is an obvious case study of iron transfer from continent to ocean in inter-tropical zones, where chemical weathering is high. It drains more than 6.4 million km^2 and has an average water discharge of $209,000 \text{ m}^3 \text{ s}^{-1}$. The flux of solids discharged to the ocean by the Amazon River is estimated between 500 and 1200 million tons yr^{-1} (Meade et al., 1979; Dunne

et al., 1998; Maurice-Bourgoin et al., 2007; Filizola and Guyot, 2009).

The five main inflowing tributaries to the Amazon River in Brazil are the Negro, Solimões, Madeira, Tapajós and Xingu rivers. They display a variety of physical and chemical characteristics that have long been recognized for the rivers of the Amazon basin. Its waters have been classified as white, clear, and black (Fittkau, 1971; Gibbs, 1972; Sioli, 1984; Lewis et al., 1995).

Whitewater rivers generally flow from the Andes whereas blackwater rivers drain the central part of the basin, typically covered by the evergreen rainforest (Seyler and Boaventura, 2003). The first type, which presents a yellow color due to high sediment content, has a $\text{pH} > 6.25$ and alkalinity $> 0.2 \text{ meq l}^{-1}$ (e.g., Solimões and Madeira rivers). The latter is tea colored due to high contents of dissolved organic compounds, has very low concentration of suspended solids, a pH lower than 5.5 and alkalinities lower than 0.25 meq l^{-1} (e.g., Negro River, Seyler and Boaventura, 2003). Clearwater rivers, such as the Tapajós and the Trombetas rivers, have high transparencies due to low concentrations of suspended sediments and usually drain the highly weathered shield areas (Seyler and Boaventura, 2003). Due to local conditions and seasonal fluctuations, clearwater rivers may assume black or whitewater characteristics, including pH and alkalinities (Sioli, 1967).

The Andes is the dominant source area for most metals transported by the Amazon River. Trace metals (including Fe) are transported primarily in particulate form, except for the Negro River, where metals are frequently complexed with organic matter, and the iron transport in the dissolved phase is predominant (McClain, 2001).

Large rivers can be vertically and horizontally heterogeneous in terms of suspended particulate matter concentration, due to processes that are responsible for local transport of material, both in the particulate and dissolved phases. These processes include differential sorting of solids and turbulent mixing (Bouchez et al., 2010, 2011a). Therefore, sampling suspended sediments as a function of these parameters can help to understand the controls on the distribution of chemical elements throughout a river profile (Bouchez et al., 2011a, 2011b).

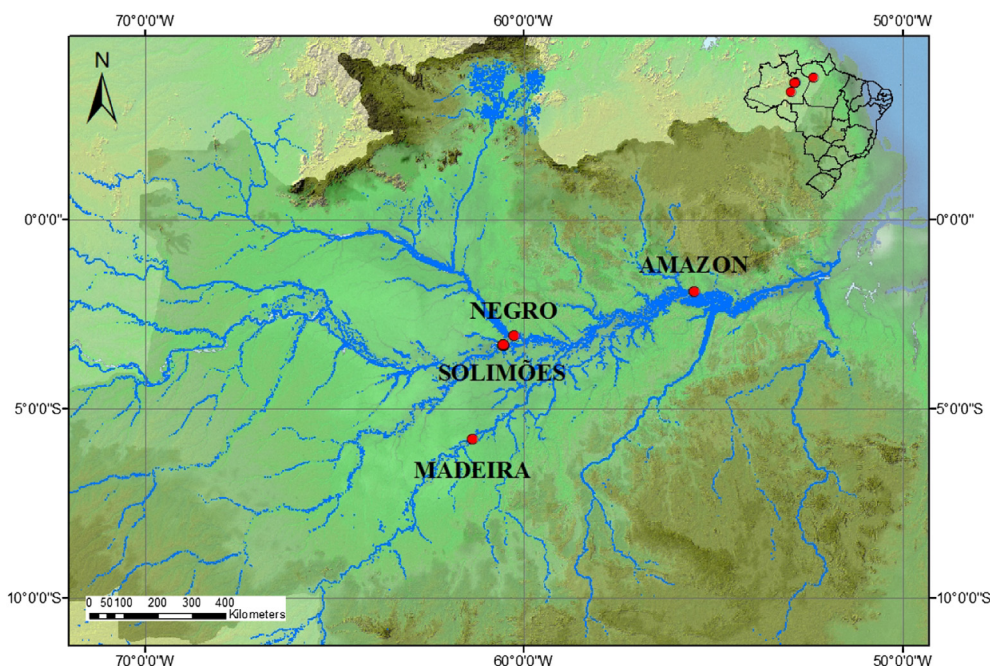


Fig. 1. Map of sample locations.

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