Chemical Geology 377 (2014) 1–11

Contents lists available at ScienceDirect

Chemical Geology

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

# Iron isotope composition of the bulk waters and sediments from the Amazon River Basin

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ARTICLE INFO

*Article history:*
Received 25 July 2013
Received in revised form 28 March 2014
Accepted 29 March 2014
Available online 12 April 2014

Editor: Michael E. Böttcher

*Keywords:*
Amazon River
Fe biogeochemical cycling
Iron isotopes
Freshwater and continental sediments

ABSTRACT

The present study provides iron concentrations and isotopic compositions determined by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), along with key chemical, mineralogical and physical properties of 35 representative bulk (unfiltered) waters and bulk sediments from the Amazon River Basin. These samples from the Amazon River, five of its main tributaries (the Solimões, Negro, Madeira, Tapajós and Trombetas rivers) and four sub-tributaries (the Purus, Jaú, Ucayali and Napo rivers) were essentially collected during seven field missions conducted for over two years. These encompassed the centennial flood of May 2009 and the exceptional low water stage of September–October 2010, thereby providing the most extreme hydrological situations that have been recorded over the last hundred years. While the data confirmed massive losses of iron (up to ~19000 tons/day, *ca.* 50% of the Amazon River bulk water budget) in the Solimões and Negro rivers mixing zone, the Fe isotope signatures of these bulk waters behaved conservatively. This property allows the use of bulk water Fe isotope signature to track iron sources and explain such isotopic signature in terms of simple mixing. Unfiltered samples from the organic-rich black water rivers present light $\delta^{57}$Fe relative to the average continental crust composition. This contrasts with the composition of the bulk white waters carrying a high mineral suspended load that have $\delta^{57}$Fe values undistinguishable from the crustal isotopic signature (~0.1‰ relative to IRMM-14). This observation indicates that the Fe isotopic composition represents a reliable direct tracer of the iron speciation and, therefore, of the host phases of iron in its sources. Specifically, the white water $\delta^{57}$Fe most likely trace the signatures of igneous and sedimentary sources, as well as of their lateritic soil minerals, while the bulk black water $\delta^{57}$Fe track a preferential release of Fe that has gone through a reduction step in the organic-rich horizons of tropical podzols as a result of the biological activity. This study shows that the total iron transferred by the Amazon River represents between 5 and 30% of the world's ocean Fe input by rivers, and this Amazon bulk water iron displays an isotopic composition indistinguishable from that of the average continental crust.



## 1. Introduction

Iron is the fourth most abundant element in the Earth's crust and as such, it plays a key role in many biogeochemical processes at the Earth's surface, notably through its changes in redox states. Iron oxyhydroxide particles are an important carrier for other metals in aquatic systems, and Fe is key for plant and animal metabolism (Langmuir, 1996; Crichton, 2001). Its oxyhydroxide minerals also constitute hill-forming lateritic ferruginous crusts that affect continental water flows in intertropical zones.

Despite extensive studies for over half a century, some important questions pertaining to the iron cycling on continental surfaces remain unanswered. For instance, the role of the vegetation in iron transfer from soils to rivers is still poorly quantified (Pokrovsky et al., 2006). The Amazon River Basin, which is the largest watershed in the world, delivers ~17% of riverine freshwater to the oceans (Callède et al., 2010) and therefore a large fraction of the metals coming from rivers. Despite the significance of the Amazon River Basin, the iron cycling remains little known in this watershed. This is partly because the sources

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http://dx.doi.org/10.1016/j.chemgeo.2014.03.019
0009-2541/

and fluxes of this element still have to be properly determined and quantified (see e.g., Benedetti et al., 2003). Furthermore, an improved knowledge of the amount of iron transferred by rivers to the oceans is essential to understand continental erosional/weathering mechanisms given its redox chemistry combined with the abundance of this element in rocks, soils and in the river loads. Such an improved understanding applied to the sedimentary record may in turn provide keys in the characterization of ancient climates. Similarly, this element is an essential, yet sometimes limiting nutrient for the oceanic phytoplankton that plays a key role in the atmospheric carbon pump (Martin, 1990). The forms and fluxes of the Fe delivered to the ocean by major tropical rivers such as the Amazon are among the clues for a better understanding of this biogeochemical process.

For such source and mass balance questions, the isotopic approach brings a new dimension relative to the study of iron concentrations only. Furthermore, stable isotopes may also provide information on the nature of the chemical reactions involved in the cycling of this element (e.g., Hoefs, 2004). Hence, the last decade has seen a growing number of studies aiming at the understanding of the mechanisms that fractionate iron isotopes on the Earth's surface. Such studies were made possible by analytical developments using plasma source mass spectrometry (Belshaw et al., 2000). They have shown the importance of redox reactions on the Fe isotope fractionation (e.g., Johnson et al., 2002; Wiederhold et al., 2006), making this isotopic approach well suited to study processes like reductive iron dissolution or the interaction with ligands from the organic matter in soils (e.g., Brantley et al., 2001; Fantle and DePaolo, 2004; Emmanuel et al., 2005; Wiederhold et al., 2007). Additionally, these soil processes may, in turn, be traced using the Fe isotope composition of the suspended and dissolved loads of rivers (Ingri et al., 2006; Ilina et al., 2013). Promising first results also suggest that the role of plants in the iron transfer from soil to surface water is likely to leave an imprint on the isotope composition of river-born Fe, since different types of iron metabolism in plants result in contrasting iron isotope signatures (Guelke and von Blanckenburg, 2007; Kiczka et al., 2010).

Besides its global importance, the Amazon River Basin is an interesting target to study the iron cycling because a pioneering study on the suspended and dissolved load of the Amazon River and its two major tributaries (the Solimões and the Negro rivers) has uncovered a large Fe isotope fractionation (~1.8‰ in $\delta^{57}$Fe; Bergquist and Boyle, 2006). However, this study was based on only three sampling stations, making it difficult to have a comprehensive overview on the possible range of Fe isotope signatures and on their likely causes. Bergquist and Boyle (2006) concluded that the iron isotope signature delivered by the Amazon to the Atlantic Ocean was lighter than that of the average continental crust, which seems to be in contradiction with previous work on other rivers rich in clastic sediments (Beard et al., 2003) or inferences based on lateritic soils (Poitrasson et al., 2008) that dominate tropical regions. From these two latter studies, it can be argued that a river such as the Amazon, with a high mineral suspended load, and that drains ferralitic soils, should rather deliver to the Atlantic Ocean an iron with $\delta^{57}$Fe values close to that of the continental crust overall (~0.1‰ relative to IRMM-14; Poitrasson, 2006).

Given the importance of this question towards a better definition of the isotopic composition of Fe sources feeding the oceans (Lacan et al., 2008; John and Adkins, 2010) as well as the remaining unknowns on the Fe cycling in a major intertropical watershed, we have conducted an iron isotopic study of bulk waters and sediment samples taken in various representative locations of the Amazon River Basin in order to provide a comprehensive picture of this continental-scale watershed. To avoid potential biases on the Fe stable isotope composition induced by water filtrations, we worked with bulk samples instead of filtered waters, although our recently published study on this topic suggests that filtration processes do not appear to produce a significant isotopic shift (Ilina et al., 2013). This work is part of an integrated research program that also focuses on the spatial and temporal variation of the suspended matter (dos Santos Pinheiro et al., 2013), the importance of speciation of Fe in waters (Mulholland et al., 2014) and the role of the vegetation and soil transformation on the iron cycling in the Amazon Basin using the isotopic approach.

## 2. Study site and samples

The Amazon River Basin is a continental scale watershed (Fig. 1) that covers more than $6 \times 10^6$ km$^2$ (Molinier et al., 1996), i.e., comprising approximately one third of South America. The intertropical Amazon River is the largest in the world in terms of drained surface area and mean annual water discharge (206 000 ± 6% m$^3$/s) to the ocean (Callède et al., 2010). The water discharge varies by at least a factor of two as a function of the hydrological cycle (Martinez et al., 2009) with the low water level period in October–November and the high water level in May–June. The Peruvian Amazon River is renamed Solimões River at the border between Peru and Brazil, where its water discharge already equates that of the second largest river in the world, the Congo (Molinier et al., 1996), even though it is still ca. 3000 km upstream the Atlantic Ocean. The river is named Amazon in Brazil only from the confluence between the Negro River and the Solimões River (Fig. 1). The latter represents already up to half of the total discharge of the Amazon River at its mouth during the flood season. Besides the Negro River, which represents up to one third of the Amazon water discharge at low waters, other important tributaries include the Madeira, Tapajós, Xingu and Trombetas rivers (Fig. 1).

In order to obtain a complete picture of the rivers variability in terms of chemistry and sources, we investigated bulk water samples from the Amazon River and some of its main tributaries, including the Solimões, Negro, Madeira, Trombetas and Tapajós (Fig. 1). The Solimões and Madeira are classified as white water rivers because of their abundant sedimentary suspended load that results from high erosional rates in the Andes (e.g., Stallard and Edmond, 1983; Seyler and Boaventura, 2003). The Napo and Ucayali rivers, which are tributaries of the Solimões River, drain the Ecuadorian and Peruvian part of the Andes, while the Madeira River drains the Bolivian Andes (e.g., Molinier et al., 1996). These two latter rivers carry 93% of the suspended load found in the Amazon mainstream (Filizola and Guyot, 2009). The Negro is a black water river, rich in both dissolved and suspended organic matter. Although it notably drains giant tropical podzols (Fritsch et al., 2009), its mineralogical and chemical sources are varied (Molinier et al., 1996) since, for example, some of its tributaries come from the Guyana Shield (e.g., the Branco River). More representative rivers that flow over the rainforest soils are the Jaú River (Allard et al., 2011), a tributary of the Negro River, and the Purus River, a tributary of the Solimões River, which has a "blackish" water (Bouchez et al., 2010) with small amounts of suspended matter and low organic content. Lastly, we sampled the Tapajós and the Trombetas rivers that are both clear waters, with low amounts of suspended matter and low organic content, representative of the highly weathered Brazilian and Guyana shields, respectively (e.g., Stallard and Edmond, 1983; Gaillardet et al., 1997).

In order to characterize the rivers suspended load that is lost during its transport to the ocean, we also took sediment samples along the banks of the Solimões, Negro, Madeira and Amazon rivers.

## 3. Methods

Unfiltered, bulk water and bulk sediment samples were collected during seven multidisciplinary cruises along the Amazon River and its tributaries, from May 2009 to September 2010. Additional sediment samples were collected during previous field missions (Guyot et al., 2007). The types of measurements and sampling varied according to the main objective of the cruises, but they typically involved water discharge rates, measured by Acoustic Doppler Current Profiler (ADCP) with a 2SD uncertainty better than 4%, following the methods reported by Filizola and Guyot (2004). Water temperature, conductivity and