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Contrasting iron isotopic compositions in river suspended particulate matter: the Negro and the Amazon annual river cycles

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ABSTRACT

Iron isotopic compositions ($\delta^{56}Fe_{IRMM\text{-}14}$) of suspended particulate matter (SPM) from two major rivers in the Amazon Basin, the Amazon River itself (at the Óbidos Station) and the Negro River (at the Serrinha Station), were investigated in the present study. The main objective was to search for temporal variations during their annual river cycles. $\delta^{56}Fe_{IRMM\text{-}14}$ values for the Amazon River at Óbidos range between 0.00 and +0.15‰, indistinguishable from the average continental crust value. In contrast, the iron isotopic compositions of the Negro River (Serrinha Station) SPM vary between −0.34 and −0.82‰, whereas the dissolved matter is isotopically heavier in this river. The lack of significant isotopic variations in the Amazon River indicates that one individual SPM subsurface sample is representative of the river during the whole annual river cycle, in opposition to results obtained for the Negro River. The data suggest that in organic-poor white water rivers, such as the Amazon, iron isotopic signatures of the suspended fraction reflect a detrital crustal component with little isotopic fractionation. On the other hand, in the organic-rich Negro River, which has tropical podzols as the main iron source, the iron redox cycling at the water–soil interface influences the iron isotopic composition.

1. Introduction

On a global scale, the Amazon River Basin supplies the greatest amount of suspended particulate matter (SPM) to oceans (Gaillardet et al., 1997), figuring as a very important carrier of iron (in dissolved, colloidal and particulate phases – see definitions in Methods section). It is, therefore, an interesting area to study variations on the iron isotopic signature in the different river fractions.

A variety of physical and chemical characteristics recognized in the Amazon Basin rivers lead to the classification of the waters in three different types (Fittkau, 1971; Gibbs, 1972; Sioli, 1984; Lewis et al., 1995): clear and black water rivers (e.g., the Tapajós and the Negro, respectively) are mostly related to chemical erosion, whereas white water rivers (e.g., Amazon and Solimões) are associated with mechanical erosion and, consequently, contain much more important sediment loads (Allard et al., 2004).

Iron (Fe) concentration in river SPM is normally at the percent level in Amazonian rivers (Allard et al., 2004) and organic complexation of Fe^{2+} is minor when compared to that of Fe^{3+} (e.g., Weber et al., 2006; Allard et al., 2011). Iron is transported primarily in the particulate form in the Amazon mainstream, whereas in the Negro River half of the iron is carried in the dissolved and colloidal load (Bergquist and Boyle, 2006).

A reconnaissance study made in the Amazon region reported distinct $\delta^{56}Fe_{IRMM\text{-}14}$ values for the Negro River dissolved and particulate phases (Bergquist and Boyle, 2006). The study demonstrated that the dissolved load is isotopically heavy ($\delta^{56}Fe_{IRMM\text{-}14} =$ +0.3‰), whereas the suspended load is light (−0.9‰). The light iron isotopic composition for the Negro River SPM was recently confirmed (at the Paricatuba Station), however, to a lesser extent ($\delta^{56}Fe_{IRMM\text{-}14} \sim -0.3$‰, dos Santos Pinheiro et al., 2013). A similar relationship between river dissolved and particulate fractions was reported by Escoube et al. (2009) for the North River, Massachusetts, though in a smaller magnitude. Nonetheless, $\delta^{56}Fe_{IRMM\text{-}14}$ variations exist among suspended phases from different types of tributaries of the Amazon River (Bergquist and Boyle, 2006; dos Santos Pinheiro et al., 2013).

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Strong seasonal variations in the iron speciation in the Negro River have been documented (Allard et al., 2011), with the amount of iron bound to organic matter (FeOM) varying from 10 to 50% for samples taken at the Moura Station, depending on the season (July 1996 and October 1998). Seasonal variations also occur in the SPM iron isotopic composition of rivers around the world, as observed by Ingri et al. (2006) and Song et al. (2011).

According to Fantle and DePaolo (2004), reactions within soils produce both isotopically light and heavy iron: biological processes, such as the growth of surface vegetation and synthesis of organic ligands, produce a source of isotopically light and relatively mobile iron that can be more easily transported. Other important processes may also produce iron chemical fractionation in rivers and, consequently, modify the iron isotopic composition of riverine materials. They include equilibrium speciation, formation of colloidal Fe^{3+} and sorption of dissolved iron onto particle surfaces (de Baar and de Jong, 2001).

The main objectives of this work were to (i) evaluate if processes (such as water mixing and soil leaching) and specific parameters (such as organic matter content and seasons) could affect the SPM iron isotopic composition in Amazonian rivers through the annual river cycles; (ii) characterize, during the annual river cycles, the behavior of SPM iron isotopic signatures in waters with different chemical natures (black *versus* white water rivers); and (iii) verify if there is a fractionation between the dissolved and the particulate loads in organic-rich, acidic waters (i.e., Negro River).

In order to answer these questions, SPM samples from two extreme types of water in the Amazon region (the organic-rich Negro River at Serrinha, and the suspended mineral-rich Amazon River at Óbidos) were analyzed for iron isotopes during at least one complete year. A set of five samples available from the Negro River dissolved fraction (Paricatuba Station) was also investigated.

2. Study area

The Amazon River is formed after the mixing of the Negro (black water river) and the Solimões (white water river), near Manaus (Amazonas, Brazil). The contrasted water characteristics generate a front where many reactions occur, such as possible losses of elements and total organic carbon (TOC), coagulation and dissolution of minerals (Aucour et al., 2003; Benedetti et al., 2003a).

The Solimões River water has a temperature of approximately 29 °C and a neutral pH (>6.8). The suspended load of this river consists mainly of materials that occur in the floodplain sediments (Irion, 1983; Martinelli et al., 1993; Guyot et al., 2007). Its light brown waters drain the Peruvian Andes and contain a high suspended sediment load (inherited from physical denudation in the Andes and erosion of alluvial terraces), with iron mostly exported as Fe-oxides and clay minerals (Gibbs, 1977; Irion, 1991). This river has low bulk organic carbon (OC) concentration (Benedetti et al., 2003a) and carries more than half of both the major ion dissolved load and the water budget of the Amazon River (Bergquist and Boyle, 2006).

In contrast, the black waters of the Negro River drain lowlands that include the most weathered terrains in the Amazon (Stallard, 1980). These waters are characterized by low sediment loads, high concentration of organic matter (dissolved and particulate) and very high levels of iron complexed to organic matter (Allard et al., 2004, 2011). This element is mainly present as Fe^{3+} bound to organic colloids (Senesi, 1992; Allard et al., 2002; Benedetti et al., 2003b; Nascimento et al., 2008). The Negro is warmer than the Solimões by 1–2 °C and has a low pH of ~4.8 (Furch et al., 1982; Kuchler et al., 2000; Bergquist and Boyle, 2006).

The Negro River drainage area is about 600 000 km^2 and covers parts of Colombia, Venezuela and Brazil. Tropical podzols occur in 33% of the Negro River watershed (Radambrasil, 1972–1978). Significant iron chemical and isotopic fractionation is reported in podzolic environments (Fantle and DePaolo, 2004; Ingri et al., 2006; Wiederhold et al., 2007a, 2007b; dos Santos Pinheiro et al., 2013; Ilina et al., 2013; Fekiacova et al., 2013). This fractionation contrasts with the one that takes place in soils from oxic environments, which is characterized by limited iron isotope variations (Emmanuel et al., 2005; Wiederhold et al., 2007b; Poitrasson et al., 2008; Fekiacova et al., 2013).

This study focuses mainly on time series of SPM samples that represent at least one annual river cycle from two very different rivers in the Amazon Basin: the Negro (Serrinha Station) and the Amazon (Óbidos Station, Fig. 1). The first one was sampled for one year, while the second one for almost two years.

3. Methods

Supplementary Online Material (**SOM**) for a full description of Methods and summary of results (Table S1) related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2014.03.008.

4. Results

4.1. Environmental parameters

Precipitation data from the Negro River area (Barcelos Station, approximately 250 km downstream from the Serrinha Station, Fig. 1) and the Amazon River area (Óbidos Station, Fig. 1) are shown in Fig. 2. For the Amazon River (Óbidos Station), the water discharge response was approximately 1–3 months after the precipitation peaks or troughs (Fig. 3). In the Negro River case (Serrinha Station), the water discharge response was more immediate, since it happened only one month after the precipitation minimum (February 2007, Fig. 4). On the other hand, after the precipitation maximum, in March–April 2007, the water discharge in the Negro River took approximately 4 months to reach its highest peak, in July 2007, month when the water level finally started to decrease (Fig. 4).

These observations indicate that the dynamics of both the Amazon and Negro rivers are complex, especially because the relationship between precipitation and river discharge rate is not well understood and often discussed in literature (e.g., Getirana et al., 2011 and references therein). Also, floodplains (called *Várzeas* or *Igapós*, related to white and black waters respectively, Junk and Piedade, 2010) are very common in the Amazon region and should be evaluated. There is an intense exchange of matter and energy between rivers and their floodplains and, therefore, complex interactions between the two (Junk et al., 2010). In any case, the rivers hydrological regimes have to be considered in order to understand the elements transfers and the variations on chemical parameters in these rivers.

The Amazon River samples (Óbidos Station) show relatively uniform water pH values, within analytical uncertainties, along the year studied. They varied from 6.4 (September 2010) to 7.6 (May 2009, Table S1). In the Negro River (Serrinha Station), water pH values varied from 5.0 in July 2007 to 6.5 in October 2006 (Fig. 5, Table S1 – pH values shifted compared to *in situ* pH values, see Methods section). A response of this parameter to the monthly water discharge can be seen, especially during the first months studied (October 2006 to May 2007). Water pH seems to respond *ca*. two months in advance relative to the water discharge (Fig. 5). When the water level is the lowest (March 2007), pH values started to increase, reaching a peak in May 2007, a couple months ahead the water discharge peak (July 2007). In the following months, the pH started to decrease, reaching its lowest value