**AMANDES METADATAFILE**

**Rare Earth Elements and Nd Isotopic Composition**

**Parameters**

Rosette - Rare Earth Elements (REE) concentrations analysed by ICPMS – Nd Isotopic Composition analysed by TIMS

**1.** **Project title:**

AMANDES' (AMAzone-ANDES) project has the objective to improve our knowledge of the fluxes of matter, chemical elements and tracers transported from the continent to the ocean together with their impact on the chemistry of the oceans. More specifically, AMANDES is focused on the Amazon estuarine/shelf system and its impact on the water masses of the neighbour Atlantic. In the Framework of this project, 3 campaigns on the RV/ANTEA were made on the Guyanese shelf and offshore of the margin in October 2007 (AMANDES 1) and February 2008 (AMANDES 2) and in the Amazon estuary in April 2008 (AMANDES 3).

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**3. Overview of the project**

The Amazon basin could act as one of the biggest REE sources to the ocean by bringing the products of the weathering of the Andeans mountains and the Amazonian plain. Complex reactions occurs when fresh water encounters sea water and especially at the colloidal scale where organic and inorganic complexation and coagulation processes take place.

REE are a good tool to explore transition metals behavior in interfaces zones. Indeed REE are an extremely coherent group in terms of chemical behavior but despite this coherence, several processes cause slight fractionations within the group. These are displayed by shale-normalized REE patterns. REE are thus tracers or source and processes. On the contrary to lithogenic patterns (generally flat) fresh water and open ocean water REE concentrations and distribution display differential patterns.

-Sea Water endmembers have: 1) a heavy REE (HREE) enrichment relative to the light ones (LREE) and 2) a depletion of Ce relative to its REE neighbors [[*H. Elderfield and Greaves*, 1982](#_ENREF_3)] [[*Bertram and Elderfield*, 1993](#_ENREF_2); [*H. Elderfield and Greaves*, 1982](#_ENREF_3); [*German et al.*, 1995](#_ENREF_5); [*Sholkovitz et al.*, 1994](#_ENREF_13); [*Tachikawa et al.*, 1999a](#_ENREF_14)].

-Amazon endmember have: 1) a middle REE (MREE) enrichment relative to HREE and LREE [[*Barroux et al.*, 2006](#_ENREF_1); [*H Elderfield et al.*, 1990](#_ENREF_4); [*Sholkovitz*, 1993](#_ENREF_12)] and 2) concentrations ten to hundred times higher than those from the oceanic endmember.

The ƐNd signature in of water is function of its source and behave conservatively in the Ocean allowing its use as a water mass tracer and land to ocean transfer.

We proposed:

-to investigate the fluxes of REE from the Amazon river to the Atlantic ocean with a special interest on their speciation and behaviour within the mixing zone.

-to study ƐNd dynamics at the river seawater interface and characterise the equatorial Atlantic water masses signatures.

**4. Title of publications**

Rousseau, T.C.C., Sonke, J.E., Chmeleff, J., Candaudap, F., Lacan, F., Boaventura, G., Seyler, P., Jeandel, C., 2013. Rare earth element analysis in natural waters by multiple isotope dilution - sector field ICP-MS. Journal of Analytical Atomic Spectrometry 28, 573-584.

Rousseau, T. C. C., J. E. Sonke, J. Chmeleff, P. van Beek, M. Souhaut, G. Boaventura, P. Seyler, and C. Jeandel (2015), Rapid neodymium release to marine waters from lithogenic sediments in the Amazon estuary, Nat Commun, 6.

Rousseau T.C.C., et al (in Preparation), REE concentrations Nd isotopes on guyanese margin and nearby Equatorial Atlantic watermasses.

**5 Data description**

**5.1. Parameters and methodology**

The samples were collected using the Niskin bottles, filtered on board using 140mm diameter and 0.45µm porosity PES filters, and acidified to pH = 2 with twice-distilled HCl. For REE analyses 500ml aliquots were stored in HDPE bottles and sent to the land based laboratory (LEGOS, Toulouse, France). For ƐNd 7.5 l was preconcentrated using two C18 SepPak cartridges loaded with a strong REE complexant (HDEHP/H2MEHP) [[*Shabani et al.*, 1992](#_ENREF_11)].

Rare earth elements

-For AMANDES 1 and 2 samples the purification and preconcentration of REE were performed following the published methods by [[*Lacan and Jeandel*, 2001](#_ENREF_6); [*Tachikawa et al.*, 1999b](#_ENREF_15)]. Briefly, the acidified seawater samples were spiked with 150Nd and 172Yb. Then 2.5 mg Fe (dissolved FeCl3) was added. After isotopic equilibration for at least 24 hours, the pH was increased to 7–8 by addition of NH4OH, yielding REE-Fe(OH)3 co-precipitation. The precipitate was then extracted by centrifugation and rinsed 3 times with deionized water. An anion exchange column was used to purify the REE from the remaining matrix. Rare Earth Element concentrations have then been measured on an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Agilent 4500) This method was validated on the GEOTRACES intercalibration exercise [[*van de Flierdt et al.*, 2012](#_ENREF_16)].

-For AMANDES 3 estuarine samples (River water to Sea water continuum), a new method was developed, using 10 spikes and improving the separation protocols by adding an AG50 X8 chromatographic step in order to fully remove Ba interferent. Samples were measured on a sector field ICPMS (Thermo Scientific Element-XR) with a desolvator (Cetac Aridus 2) for sample introduction. Details of this method can be found in [[*Rousseau et al.*, 2013](#_ENREF_10)] it was validated by replicate analyses and comparison of CRM SLRS 4 and 5 river waters and GS (surface) and GD (2000m) seawater samples collected at Bats Station.

Nd Isotopic composition

Cartridges were eluted using 6M HCl Nd separation was achieved by a two-step chromatography protocol using cationic AG50 X8 and Ln-SPEC resins Details of the procedures used on the cationic and anionic columns are described in [[*Tachikawa et al.*, 1999b](#_ENREF_15)] and [[*Pin and Zalduegui*, 1997](#_ENREF_8)] , respectively.

Nd isotope measurements were made on a Thermo Finnigan MAT 261 at the Observatoire Midi-Pyrenees in static (10 samples) and dynamic mode (23 samples). For the static mode, 36 analyses of La Jolla standard were performed with 0.511882 ± 0.000030 (2SD). The generally accepted value being 0.511850 ± 0.000020 [[*Lugmair et al.*, 1983](#_ENREF_7)] we corrected all these measurements from a machine bias of 0.000022. Dynamic mode of 49 analyses of the same standard displayed 0.511842 ± 0.000020 (2SD). Blank contribution on the Nd isotopic measurement was in average less than 3% of the total signal. Our Lab recently participated to the Geotraces intercalibration exercise [[*van de Flierdt et al.*, 2012](#_ENREF_16)]. Four suspended particles (>0.45) samples were analyzed by in Brest following the method described in [[*Révillon et al.*, 2011](#_ENREF_9)].

**5.2. Sampling strategy**

Water samples were taken on the continental shelf and offshore of french Guyana during AMANDES I, II and and in the Amazon estuary during AMANDES III (Figure 1, Table 1).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Cruise Id | Station | Date | Longitude | Latitude |
| AMANDES 1 | AM1-01 | 25/10/2007 | -51.630 | 4.836 |
|  | AM1-02 | 25/10/2007 | -51.678 | 4.383 |
|  | AM1-03 | 26/10/2007 | -51.236 | 5.337 |
|  | AM1-04 | 27/10/2007 | -50.998 | 5.633 |
|  | AM1-05 | 28/10/2007 | -49.829 | 7.001 |
|  | AM1-06 | 28/10/2007 | -47.956 | 5.717 |
|  | AM1-07 | 30/10/2007 | -48.910 | 7.477 |
| AMANDES 2 | AM2-01 | 17/01/2008 | -52.017 | 5.500 |
|  | AM2-04 | 19/01/2008 | -51.535 | 4.720 |
|  | AM2-05 | 19/01/2008 | -51.507 | 4.667 |
|  | AM2-07 | 20/01/2008 | -51.280 | 5.746 |
|  | AM2-08 | 20/01/2008 | -51.251 | 5.769 |
|  | AM2-09 | 22/01/2008 | -51.471 | 6.571 |
| AMANDES 3 | AM3-01 | 10/04/2008 | -49.762 | 0.961 |
|  | AM3-03 | 10/04/2008 | -49.363 | 1.211 |
|  | AM3-04 | 10/04/2008 | -49.265 | 1.260 |
|  | AM3-05 | 10/04/2008 | -49.159 | 1.338 |
|  | AM3-06 | 10/04/2008 | -49.023 | 1.452 |
|  | AM3-07 | 11/04/2008 | -46.975 | 1.170 |
|  | AM3-08 | 11/04/2008 | -46.733 | 1.488 |
|  | AM3-09 | 12/04/2008 | -47.509 | 2.259 |
|  | AM3-14 | 12/04/2008 | -48.004 | 1.906 |

**5.3. Planning of data availability**

Public access will be open after acceptance of the submitted paper.

**5.4 Datafile description**

**5.5 References**

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