## Comparison of the Fe isotope composition of unfiltered waters, dissolved and particulate fraction of the Amazon River and its tributaries

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Pioneering studies revealed that for some river waters, large  $\delta^{57}$ Fe fractionations are observed between the suspended and dissolved load, and isotopic variations were also recognized on the suspended matter along the hydrological cycle. On land, soil studies in various locations have shown that  $\delta^{57}$ Fe signatures depend mostly on the weathering regime. It thus seems that Fe isotopes could become an interesting new tracer of the local interactions between soils, rivers and the biosphere.

We therefore conducted Fe isotope surveys through multidisciplinary field missions on rivers from the Amazon Basin. It was confirmed that acidic, organic-rich black waters show strong Fe isotope fractionation between particulate and dissolved loads. Furthermore, this isotopic fractionation varies along the hydrological cycle, like previously uncovered in boreal waters suspended matter. In contrast, unfiltered waters show very little variation with time.

It was also found that Fe isotopes remain a conservative tracer even in the case of massive iron loss during the mixing of chemically contrasted waters such as the Negro and Solimões tributaries of the Amazon River. Given that >95% of the Fe from the Amazon River is carried as detrital materials, our results lead to the conclusion that the Fe isotope signature delivered to the Atlantic Ocean is undistinguishable from the continental crust value, in contrast to previous inferences.

The results indicate that Fe isotopes in rivers represent a promising indicator of the interaction between organic matter and iron in rivers, and ultimately the nature of their source in soils. As such, they may become an interesting tracer of changes occurring on the continents in response to both weathering context and human activities.

## Probing gold and sulfur geological fluids at extreme conditions by in-situ spectroscopy

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Although aqueous fluids account for a tiny fraction of our planet, they play a key role in chemical elements transfer on Earth. These fluids dissolve and precipitate minerals, form economic ore deposits, and control geochemical cycles of metals and volatiles. Knowledge of the chemical status of dissolved elements - their speciation, and the solubility of minerals is the key to quantifying the geological impact of such fluids operating at 'extreme' conditions of high pressure and temperature in Earth's interiors. Because these milieus are not accessible to direct observations, their study requires insitu spectroscopic approaches.

In this contribution, we report on our recent findings on the behavior of sulfur and gold in hydrothermal-magmatic fluids, revealed by in-situ Raman and X-ray absorption spectroscopy coupled with thermodynamic and molecular modeling. Results challenge the long-standing paradigm that sulfate (HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and sulfide (H<sub>2</sub>S, HS<sup>-</sup>) are the two major forms of sulfur in terrestrial fluids [1]; they demonstrate that in the liquid and supercritical fluid phase in addition to these two common sulfur redox states, the trisulfur ion,  $S_3^-$ , forms in significant amounts above ~300°C and over a range of depth (to ~100 km) [2]. The  $S_3^-$  ion binds gold in hydrothermal fluids, forming stable [HS-Au<sup>(I)</sup>-S<sub>3</sub>] complexes largely enhancing the metal solubility; thus,  $S_3^-$  is likely to be an important carrier of sulfur and associated metals (Au, Pt, Cu, Mo) for magmatic-hydrothermal deposits in subduction zones [3]. The formation of  $S_3^-$  requires a revision of metal speciation models in S-rich aqueous and carbonic fluids [3, 4, 5] and, potentially, silicate melts, operating in the Earth's crust and upper mantle.

[1] Ohmoto & Lasaga (1982) GCA 46, 1727-1745. [2]
Pokrovski & Dubrovinsky (2011) Science 331, 1052-1054. [3]
Kouzmanov & Pokrovski (2012) SEG Special Publication 16, 573-618. [4] Pokrovski et al (2009) GCA 73, 5406-5427. [5]
Kokh et al (2013) MinMag, this volume.