



Isotopic composition of atmospheric Fe: first measurements in pollution aerosols

J. Rimetz (1), N. Mattielli (2), J. de Jong (2), **P. Flament** (1), K. Deboudt (1), D. Weis (3)

(1) Université du Littoral Côte d'Opale, ELICO, CNRS 8013, Wimereux, France, (2) Université Libre de Bruxelles, DSTE, Brussels, Belgium, (3) University of British Columbia, PCIGR, DEOS, Vancouver, Canada, (pascal@mren2.univ-littoral.fr / Fax: +33 321996401 / Phone : +33 321996429)

Introduction

It is now well recognized that iron is a key micronutrient that controls primary productivity in the HNLC (high-nutrient low-chlorophyll) zones of the global ocean (Boyd et al., 2000). For oligotrophic regions, atmospheric deposition is one of the most important way for Fe dissemination in surface waters (Sarhou and Jeandel, 2001; Sarhou et al., 2003). This deposition occurs both by the wet and dry deposition modes, of comparable magnitude at the global scale (Gao et al., 2003). The major part of aeolian Fe is constituted by mineral dust originating from the main desert areas in the world, but strong atmospheric inputs due to human activities (e.g. steel metallurgy) can occur along populated coastal areas. Source variability of atmospheric Fe can be characterized by a monitoring of Fe concentrations combined with an isotopic approach (e.g. Nd and Pb isotopes). Besides the source heterogeneities, processes involved in atmospheric Fe transport can be also highly variable. Fe isotopic tracing might represent an attractive opportunity to investigate relative contributions of those physical-chemical processes. However, up-to-now, no study has been publishing dealing with this area of interest. Fe isotopic compositions (δ notation) in mineral dusts seem to be comparable to those of igneous rocks (Beard et al., 2003). However, non biological fractionation processes, at ambient temperature and pressure, could happen during the aeolian transport of Fe, through partial dissolution of Fe aerosols and redox reactions in the

aqueous phase of the troposphere (evolution of Fe(II)/Fe(III) ratios during dissolution of Fe aerosols in clouds ; Deguillaume et al., 2004). In addition, Chen and Siffert (2004) have observed fluctuations of Fe(II)/Fe(III) ratios with the solubility of atmospheric Fe in the North Atlantic region and conclude that anthropogenic activities in Europe and North America may influence the mobilization of Fe in aerosols. Our work consists here in a preliminary study on the ability of MC-ICP-MS (Multiple Collector – Inductively Coupled Plasma – Mass Spectrometry) analysis to provide trustworthy measurements of $\delta^{56}\text{Fe}$ in pollution aerosols, with the objective of relating $\delta^{56}\text{Fe}$ with Fe(II)/Fe(III) ratios and solubility of Fe in clouds.

Methods and results

Pollution aerosols consist here in steel metallurgy plant emissions. The plant is located along the coast of the southern bight of the North Sea. Particles were directly sampled on filtration devices mounted on the main exhaust systems of the plant. After microwave assisted acid digestion of the particles, Fe was purified by separation on anionic resin Dowex AG MP1 (100-200 mesh), following a one-step ion-exchange chromatography method slightly different from those of Maréchal et al. (1999) and Zhu et al. (2002). Fe isotopic compositions were analyzed on a Nu Plasma MC-ICP-MS (ULB-Brussels) in dry plasma mode. Instrumental mass bias was controlled by using simultaneous external normalization (Cu-doping method in dynamic mode) and standard-sample bracketing with the IRMM-014 reference material. A Cr correction on mass 54 was systematically applied. Every sample was analyzed at least in duplicate. Also an in-house quality control sample, a basalt, was measured repeatedly, giving a long-term accuracy and reproducibility of $0.15 \pm 0.06 \%$, for $\delta^{56}\text{Fe}$ (1 sigma; $n = 21$) relative to IRMM014, in excellent agreement with global igneous rock values from Beard et al. (2003). The recovery for quantitative Fe determination (99%, by Z-GFAAS analysis) is determined by reference to the NIST SRM 1648 standard (Urban particulate matter) and the NCS DC 14001a reference material (Fe ore). Our detection limit in Z-GFAAS is largely inferior to Fe concentrations measured here. Table 1 summarizes the isotopic fractionation obtained for steelworks emissions, compared with $\delta^{56}\text{Fe}$ measured for some BIF ores exploited by the manufacturer.

Sample	Number of Analyzed samples	$\delta^{56}\text{Fe}$
Carajas and MRB (Brazil) BIF ores	3	-0.46 – 1.27
Robe River (Australia) BIF ore	1	-0.21 – -0.11
Agglomeration Shop emissions	2	0.74 – 0.84
Steelworks emissions	12	-0.23 – 0.47

Table 1 : $\delta^{56}\text{Fe}$ (by normalization to the IRMM-014 standard) for iron ores (BIF) and iron aerosols related to the studied steel metallurgy plant

Conclusion

Beard et al. (2003) reported the first $\delta^{56}\text{Fe}$ for mineral dusts (- 0.091 /IRMM-014) indicating slight isotopic fractionation in Fe aerosols. Conversely, our study of Fe pollution aerosols displays a wide range of isotopic fractionations (- 0.23 < $\delta^{56}\text{Fe}$ < 0.84). These fractionations are consistent with $\delta^{56}\text{Fe}$ values obtained for BIF minerals, used by the manufacturer as ores in the steel production plant (7.10⁶ Tons steel produced per year). In addition, our data set shows a trend of light isotopes enrichment correlated with the progress of manufacturing process. Other studies will be necessary to describe the evolution of $\delta^{56}\text{Fe}$ in the troposphere, but our work will also focus on laboratory experiments to simulate the dissolution of Fe particles in rain waters.

References

Beard, B.L., Johnson, C.M., Von Damm, K.L. and Poulson R.L. (2003): Iron isotope constraints on Fe cycling and mass balance in the oxygenated Earth oceans. *Geology*, 31, 629-632.

Boyd P.W., Watson A.J., et al (2000) : A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature*, 407, 695 – 702.

Chen, Y., and R. L. Siefert (2004): Seasonal and spatial distributions and atmospheric total and labile iron over the tropical and subtropical North Atlantic Ocean, *J. Geophys. Res.*, 109, XXXXXX, doi:10.1029/2003JD003958.

Deguillaume, L., Leriche, M., Monod, A. and Chaumerliac, N. (2004): The role of transition metal ions on HOx radicals in clouds: a numerical evaluation of its impact on multiphase chemistry. *Atmos. Chem. Phys.*, 4(1), 95-110.

Gao, Y., S. Fan, and J. L. Sarmiento (2003): Aeolian iron input to the ocean through precipitation scavenging: A modelling perspective and its implication for natural iron fertilization of the ocean, *J. Geophys. Res.*, 108(D7), 4221, doi:10.1029/2002JD002420.

Maréchal, C.N., Télouk, P. and Albarède, F. (1999): Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology*, 15, 251-273.

Sarthou, G. and C. Jeandel (2001): Seasonal variations of iron concentrations in the Ligurian Sea and iron budget in the Western Mediterranean Sea. *Marine Chemistry* 74: 115-129

Sarthou, G., A. R. Baker, et al. (2003): Atmospheric iron deposition and sea-surface dissolved iron concentrations in the eastern Atlantic Ocean. *Deep Sea Research Part I Oceanographic Research Papers* 50(10-11): 1339-1352.

Zhu, X. K., Y. Guo, et al. (2002): Mass fractionation processes of transition metal isotopes. *Earth and Planetary Science Letters* 200: 47-62.