Isotope tracing of atmospheric metals (Pb, Zn, Cd, Hg)

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Among other heavy metals, Cu, Zn, Cd and Pb concentrations are often well correlated in aerosols, precipitation or lichen samples, suggesting common sources of atmospheric emissions. However, quantifying the relative proportions of anthropogenic and natural metals and identifying different pollution sources is not straightforward unless sampling is done in the area of a known specific emitter (smelters, waste incinerators, ...). On the other hand, the isotopic composition of atmospheric Pb was revealed to be a powerful tool to discriminate anthropogenic from natural sources and between pollution sources having different isotopic compositions.

Relationships between Pb isotopes and metal concentrations (Pb, Zn, Cd, …) may be looked at in order to document any coherence between sources and metal compositions in both space and time. Concentration relationships sometimes suggest that metal sources are decoupled and/or that metals have different reactivity during transport, leading to different atmospheric residence time. Zn concentrations in aerosols and precipitation samples are often found in excess relative the other metal concentrations, suggesting a significant source for Zn in atmospheric fallout that is not well constrain, either natural or anthropogenic. For example, a systematic difference in chemical and isotopic compositions (Pb-Zn) is observed between wet and wet+dry atmospheric depositions in NE North America. The data suggests that dissolved and particulate matter are not in isotopic equilibrium and that the different phases do not originate from the same sources. As an other example, Hg concentrations are also often decoupled from those of other heavy metals. In some coastal areas, Hg concentration is rather related to that of halogen elements, suggesting either a source relationship or atmospheric chemical reactions. Isotope fractionation of the $^{202/198}$Hg may be expected between gaseous metal Hg and an oxidised form such as $HgCl_2$ or $HgBr_2$ so that Hg oxidation by halogen elements should be isotopically traceable. In addition, volatil metals like Cd and Hg might be isotopically fractionated by industrial processes (volatilisation and condensation) and be traced in the environment. Combined to Pb isotopes, new isotopic systems such as Zn, Cd, Hg should provide further useful information about surface cycles of heavy metals.

Delta zero reference materials for stable isotope analysis and applications to *in situ* measurements

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For the last 3 to 5 years, measurement of the isotopic composition of various elements, which were classified as "non-traditional", exploded with the development of multi-collector ICP-MS. The data production was faster than consensual agreements on the expression and the notation of all these isotopic systems. In the mean time, simple conventions, such as primary and secondary reference materials (RM) and isotopes of normalisation, were adopted by many laboratories worldwide. Most primary "delta zero" RM were selected out of existing materials, namely from NIST or IRMM. According to the available certificate of analysis, some RM would not be sufficiently homogeneous in isotopic composition to fit the high measurement precision and accuracy now achieved in various laboratories. Except for the NIST SRM 981 Mg, which was effectively inhomogeneous at ±1‰ for the $^{25/24}$Mg ratio, Ca, Li, and Fe selected primary RMs (respectively NIST SRM 915a, CAL-S, IRMM-14) revealed isotopic composition that was much more homogeneous than the reported uncertainties. This made the materials suitable for being delta zero RM. However, these are delivered as a powder or a liquid form, not suitable for *in situ* analysis techniques such as LA-MC-ICP-MS and SIMS.

Moreover, as bulk material is introduced in the mass spectrometer for *in situ* measurements, the instrumental mass bias is very dependent on the sample matrix analysed and a similar matrix is needed for reference materials. Thus, SIMS laboratories usually develop their own internal reference materials (IRM). These IRM are tested for their chemical and isotopic homogeneity at the micrometer scale and are analysed by bulk methods relative to the appropriate delta zero RM. For each isotope system and sample matrix, two IRM are needed, one for normalisation and the other for checking on the signal linearity and accuracy. In order to distinguish true isotopic variations from "cryptic" matrix effects, we measured $^{44/40}$Ca in synthetic samples having different Mg/(Mg+Ca) ratios.

The measurement of O isotopes in garnet required 3 garnet IRM being Ca, Fe and Mg rich respectively. An integrated correction of mass bias using these IRM was used for samples of known chemical compositions (Vielzeuf *et al*., 2005).

References

Vielzeuf D. *et al*., (2005) *Chem. Geol.* **223**, 208-226.