# Natural copper and zinc isotopic compositions measured by Plasma-Source Mass Spectrometry

C. N. Maréchal
F. Albarède
P. Télouk

Laboratoire des Sciences de la Terre, Ecole Normale Supérieure
de Lyon, 69364 Lyon Cédex 07, France

The stable isotope geochemistry of Cu and Zn is poorly known because of the lack of a precise analytical technique. We present a procedure for the analysis of Cu and Zn isotope compositions by plasma-source mass spectrometry (Plasma 54) together with a method to purify Cu and Zn from natural samples of silicates, ores, and biological material. Some preliminary results show the existence of isotopic variations of up to several permil amongst natural samples of silicates, ores, sediments, and biological material, which paves the way for the use of Cu and Zn isotopes as geochemical and biochemical tracers.

## Mass spectrometry

The plasma-source mass spectrometer, or Plasma 54, developped by VG elemental is equipped with a magnetic filter and multiple collection (Walder and Freedman , 1992; Walder *et al.*, 1993; Halliday *et al.*, 1995; Blichert-Toft *et al.*, 1997). The instrumental mass fractionation is corrected with respect to the isotopic composition of a standard of a different element added to the sample (Zn for a Cu sample, Cu for a Zn sample) which therefore has to be strictly purified before analysis. We have adopted the NIST Cu standard (SRM 976) and a Johnson-Matthey Zn solution as references. We demonstrate that the exponential law of mass fractionation must be used for the correction of the instrumental mass bias and not a linear or a power law. It is shown that, in the mass spectrometer, Cu and Zn isotopes do not fractionate to the same extent. The assumption that the same fractionation factor can be used for inter-elemental correction is therefore inaccurate. It is observed however that the ratio of Cu and Zn instrumental mass biases remains constant over one measurement session. This ratio is determined from the analysis of mixed standard solutions, and is then used to correct the isotopic composition measured for Cu or Zn samples. This external normalization method leads to an external reproducibility of 0.04 permil in delta units (95 percent confidence level). The isotopic compositions can be obtained on as little as 200 ng of element. Isobaric interferences are small enough to be neglected or, as for Ni, can be precisely corrected.

## Chemistry

Cu and Zn from various samples are separated and purified by macroporous anion-exchange chemistry using hydrochloric acid mixed with a small quantity of peroxide and a weak nitric solution. As isotopic fractionation is observed for Cu on the anion-exchange resin, a full yield upon purification is required to be achieved.

## Results and discussion

We use the delta permil notation for $\delta^{65}$Cu and $\delta^{66}$Zn. The Cu and Zn isotopic composition of five black smoker replicates which have undergone a separated chemical extraction was measured. The reproducibility of the results is very good: $\delta^{65}\mathrm{Cu} = +0.32 \pm 0.04$‰ and $\delta^{66}\mathrm{Zn} = -0.19 \pm 0.05$‰ at the 95 percent confidence level. The results from different type of samples reported below show that the isotopic compositions vary beyond the precision of the measurements.

The samples, collected in the Central Atlantic Ocean, west of the Mauritanian coast, under mesotrophic and oligotrophic conditions, shows isotopic variations of about 0.4‰ for $\delta^{65}$Cu and 0.2‰ for $\delta^{66}$Zn. The variability increases to the sub-surface samples. We suggest that the isotopic variations is controlled by the preferential uptake of the light isotope by biological activity. The isotopic patterns reflect changes in either the local productivity or in the vertical advection of water masses with different preformed isotopic values.

The $\delta^{65}$Cu values of ores spread over 8‰, but does not seem clearly associated with the nature of the mineral (native copper, sulphide, carbonate). In general, the isotopic variability of Zn seems to be smaller than that of Cu, probably because the latter element has two oxidation states.

We ran the Cu and Zn isotopic composition of fractions of standard solution at different stages of the elution. Whereas a very small isotopic fractionation apparently occurs for Zn, in contrast, a fairly substantial isotopic fractionation is observed for Cu. The lighter isotope is preferentially retained by the resin for Cu. From an analysis of the elution curve of each isotope, a resin/liquid partition coefficient being *c.* 0.05 percent larger for $^{63}$Cu than for $^{65}$Cu is obtained. It is not known at this stage whether the differential behaviour of the two Cu isotopes on the resin is purely kinetic or enhanced by the particular redox conditions imposed by hydrogen peroxide.

## References

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