

## Double spikes: the gourmets' choice

TH. F. NÄGLER

Institute of Geological Sciences, University of Bern,  
Switzerland (naegler@geo.unibe.ch)

Recent advances in isotope ratio mass spectrometry, namely multiple collector ICP-MS and refined TIMS techniques, will significantly enhance the ability to measure heavy stable isotope fractionation, which will lead to the development of a wide array of process-identifying (bio)-geochemical tools. MC-ICP-MS is the most versatile technique in this respect. The major problems are the analytical mass bias produced, which largely exceeds natural fractionation, and the problem of elemental and molecular isobaric interferences. Different methods to account for the analytical mass bias are in use.

Particular features of the double spike technique are: A) As with element doping (using isotopes of another element), variations of the analytical mass bias are accounted for within analyses. Thus unsystematic variations on different time scales are resolved, as well as matrix effects that change the instrumental fractionation between sample and standard. B) As with bracketing standards (standards measured before and after each sample), the mass range is restricted to the isotopes of the target element. This is favourable for static measurements, in particular when mass dispersion is large. Also, problems effecting the isotope ratio of a doping element (e.g. isobaric interferences, matrix dependent influence on the effective fractionation behaviour) are avoided.

Thus the double spike technique combines the advantages of bracketing standards and element doping and demagnifies worries about matrix effects. In addition, it provides precise concentrations from the very same aliquot. Correction for analytical mass fractionation is extended to chemical separation, provided the spike is added beforehand. Thus purification can be optimised, further reducing matrix and interference problems.

The main limitation of the double spike technique is the requirement of four or more stable isotopes. This condition however is given for ca 2/3 of elements suitable for heavy stable isotope studies (polyisotopic elements with masses >39). Notwithstanding a persistent myth, a simple double spike calibration procedure for MC-ICP-MS was given by Siebert et al. (2001). The consistency of TIMS results between different laboratories could recently be shown (Hippler et al. 2002). On line-three dimensional data reduction is straightforward and enables error assessment without propagation procedures. The choice of method and the set up of procedures will be exemplified on Ca (TIMS) and Mo (MC-ICP-MS) isotope analytics.

### References

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## Mass fractionation of tin in ancient bronze

SHUN'ICHI NAKAI<sup>1</sup> AND TSUTOMU SAITO<sup>2</sup>

<sup>1</sup>Earthquake Research Institute, University of Tokyo, Tokyo  
113-0032, Japan, snakai@eri.u-tokyo.ac.jp  
<sup>2</sup>National Museum of Japanese History, Sakura 285-8502,  
Chiba, Japan, saito@rekihaku.ac.jp

We report isotopic fractionation of tin in bronze probably caused by evaporation. Provenance studies of bronze have been conducted by using lead isotopic tracers. Budd et al. (1995) suggested the possibility that tin isotopic ratios in bronze may have been fractionated by evaporation and they suggested that the isotopic ratio of tin may become a good tracer for recycling and mixing processes of ancient metal. Precise isotopic analyses of tin of cassiterite by McNaughton and Rosman (1991) reported that the mineral showed little fractionation irrespective of their ages. Gale (1997) analysed isotopic compositions of tin in the ancient metal and bronze and reported that the mass fractionation was less than 0.1% for the ratio of <sup>122</sup>Sn/<sup>116</sup>Sn. The reported data, however, were mass fractionation corrected, which may have erased mass fractionation by evaporation.

We used a MC-ICP-MS (IsoProbe, Micromass) for isotopic measurements of tin. Sample analyses were bracketed by the analyses of a in-house standard solution in order to normalize isotopic composition of a sample. Measurements of standard solutions of tin from four chemical companies showed isotopic fractionations, as large as 1.0 ‰ in <sup>116</sup>Sn/<sup>120</sup>Sn, probably introduced during purification. External precision of <sup>116</sup>Sn/<sup>120</sup>Sn measurements was about 0.1‰ (2σ). Six samples of bronze and a slag unearthed from China were analysed. Tin was purified using the method described by Yi et al. (1995). Isotopic fractionation during the purification was about 1 ‰. The extent of mass fractionation in <sup>116</sup>Sn/<sup>120</sup>Sn was about 4 ‰. If we follow the model of Mulliken and Harkins (1922) that described mass fractionation by evaporation, 20% loss of tin is required to explain the observed mass fractionation.

We also conducted an evaporation experiment using synthesized bronze in inductive heater under argon flow. About one percent of bronze was lost by evaporation. We found that the condensate was enriched in light isotopes, 2 ‰ in <sup>116</sup>Sn/<sup>120</sup>Sn, compared with the starting material. In summary, the results of this study have revealed isotopic fractionation of tin in bronze. In addition, we reproduced mass fractionation, although the extent seemed to be too large for the extent of evaporation loss.