

DOUBLE-SPIKE DATA REDUCTION IN THE PRESENCE OF ISOTOPIC ANOMALIES. J.Y. Hu¹ and N. Dauphas¹, ¹Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago IL.

Introduction: Isotopic analyses of planetary materials provide insights into the natural processes that govern those variations, such as evaporation/condensation in the nebular, metamorphism, and igneous processes in planets and meteorite parent bodies. Those measurements can be performed by either TIMS or MC-ICPMS. A challenge to isotope analysis is to distinguish per-mil level natural fractionation from even larger instrumental mass bias. This problem can be solved by using the double-spike technique for elements with four or more isotopes [1]. Through double-spike technique, true isotope ratios can be inverted mathematically by analyzing a mixture of sample and spike solution. However, implementation of the double-spike technique is hindered by several difficulties including 1) determination of spike composition and sample/spike proportion, 2) double-spike calibration and, 3) tedious data inversion. On the other hand, the sample-standard bracketing (SSB) method provides comparable precision with a simpler protocol for isotope analysis. In the SSB method, mass bias of samples is assumed to be similar to that of standards. However, the SSB method is not a silver bullet for isotope analysis. Its robustness lies in the stability of plasma source mass spectrometers (*e.g.* MC-ICPMS) and similarity of sample and standard. Therefore, the SSB method is sensitive to the status of mass spectrometers and vulnerable to mismatched concentration and matrix effect. Mass bias correction in the SSB method is limited to instrumental measurement and consequently requires 100% yield in chemical purification.

In contrast, double-spike does not require as high yield and purity as the SSB method and is gaining traction in isotopic analysis by MC-ICPMS [2]. A critical assumption of the double-spike data reduction is the mass-dependent relationship between standards and samples. Uncorrected isotopic anomalies will affect the accuracy of double-spike reduction. The influence of isotopic anomalies can be corrected numerically [3]. Here we present an analytical method to correct isotopic compositions determined by the double-spike technique for the presence of isotopic anomalies. The true isotopic ratio can be obtained through a simple correction of the routine double-spike data reduction algorithm that assumes terrestrial mass dependent fractionation. We focus below on an application to Mo. Details on the formalism will be presented in the conference and will follow in a forthcoming publication.

Double-spike with Mo anomalies: Molybdenum is a refractory and moderately siderophile element. Substantial mass-dependent isotopic fractionation of Mo has been reported in the solar nebular and during planetary differentiation [4, 5]. Mo isotopic composition in bulk meteorites can be interpreted as a mixture of a terrestrial source and an *s*-depleted source [3]. Therefore, Mo nucleosynthetic anomalies are correlated with each other. Burkhardt et al. (2014) modeled the effects of nucleosynthetic anomalies (Table S2 in Burkhardt et al., 2014) and obtained a relationship between the size of the anomaly and the correction in the double-spike data reduction. From the numerical test, Burkhardt et al. (2014) obtained a parameterized relationship:

$$\delta^{98/95}\text{Mo}_{\text{corrected}} = \delta^{98/95}\text{Mo}_{\text{measured}} - \varepsilon^{96/95}\text{Mo}_{\text{nucleosynthetic}} \times 0.066 \quad (1)$$

Where $\varepsilon^{96/95}\text{Mo}_{\text{nucleosynthetic}}$ is the nucleosynthetic anomaly normalized to $^{97/95}\text{Mo}$. We tested our analytical method with the simulated data presented in Table S2 in Burkhardt et al. (2014) and obtained the following relationship

$$\Delta^{98/95}\text{Mo} = 0.0304\varepsilon^{97/95}\text{Mo} + 0.1136\varepsilon^{98/95}\text{Mo} - 0.0206\varepsilon^{100/95}\text{Mo} \quad (2)$$

Where $\Delta^{98/95}\text{Mo}$ is the correction that needs to be applied if one does the data reduction blindly, not accounting for the presence of isotopic anomalies (*i.e.*, $\delta_{\text{true}} - \delta_{\text{calc}}$). The correction given by Eq. 2 is consistent with the simulated data in Burkhardt et al., (2014) (Table 2). Based on correlations of anomalies on different isotopes, a formula similar to Eq. 1 can be derived

$$\delta^{98/95}\text{Mo}_{\text{corrected}} = \delta^{98/95}\text{Mo}_{\text{measured}} - \varepsilon^{96/95}\text{Mo}_{\text{nucleosynthetic}} \times 0.070 \quad (3)$$

As shown in Table 1, the analytical approach accurately corrects the synthetic compositions for the presence of anomalies.

Table 1

$\delta^{98/95}\text{Mo}$	SRM 3134 Mo	-0.005‰ ^a	-0.01‰ ^s	-0.05‰ ^s
δ by anomalies ^b	0	-0.06	-0.12	-0.60
δ to be corrected ^c	0	0.06	0.12	0.60

^a Deficit of *s*-process Mo in synthetic composition

^b Apparent fractionation induced by nucleosynthetic anomalies

^c Applicable correction

Conclusion: We introduce an analytical formula that allows one to apply a uniform double-spike data reduction to all samples regardless of the presence of isotopic anomalies. One can assume mass-dependent relationship with terrestrial composition to calculate the double-spike corrected values. Our formula gives

the correction that one needs to apply to account for the presence of isotopic anomalies. This is useful when investigating stable isotopic fractionation in extraterrestrial samples where isotopic anomalies are ubiquitous.

References: [1] Dodson (1963) *JSI* 40.6, 289. [2] Millet and Dauphas (2014) *JAAS* 29.8, 1444-1458. [3] Burkhardt et al. (2014) *Earth Planet. Sci. Lett.* 391, 201-211. [4] Dauphas et al. *Astrophys. J. Lett.* 569, L139-L142. [5] Hin et al. (2013) *Earth and Planet. Sci. Lett.* 379, 38-48.