

OPTIMAL DOUBLE SPIKE FOR HIGH-PRECISION MEASUREMENTS OF STABLE ISOTOPES IN EARLY SOLAR SYSTEM MATERIALS. R.T.C. Marquez¹ and F.L.H. Tissot¹, ¹The Isotoparium, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA (marquez@caltech.edu).

Introduction: The past few decades have seen dramatic improvements in the analytical precision of isotope measurements of natural samples. This is mostly due to developments in instrumentation, namely in mass spectrometry (MC-ICPMS) and in situ techniques (ion microprobe, laser ablation, RIMS) [1, 2]. The improved precision has greatly benefited cosmochemistry, as it allowed for the discovery of nucleosynthetic anomalies that demonstrate resolvable heterogeneity in the early solar system [3, 4]. The availability of computational tools for optimizing isotope dilution techniques also plays an important yet underexplored role in these developments. For example, the double spike toolbox [5] has opened access to a computational means for determining optimal spike combinations with minimal error propagation. Formulas for correlating nucleosynthetic anomalies, as well as correcting for associated systematic offsets (Δ) from isotopic excesses, have also been made available [6, 7].

We have integrated these computational tools, and prescribe optimal double spike combinations for elements that exhibit large nucleosynthetic anomalies in Ca-Al-rich inclusions (CAIs) such as Ti, Sr, Cr, Ba, and Mo. This work selects spike combinations based on considerations that are specific to meteoritics, and aims to maximize the analytical precision of the double spike technique for cosmochemical applications.

Methods: A *cocktail list* was generated for each element using the double spike toolbox [5]. Several spike combinations were selected based on:

- (1) Minimal error in the δ value of interest (typically less than 100 ppm/amu)
- (2) Isotopes with isobaric interferences were deprioritized for spike and data reduction.
- (3) Isotopes with high isotopic anomalies were considered but generally disfavored for data reduction (i.e. ^{50}Ti).

A key difference in our calculations of double spike errors compared to the default double spike toolbox implementation is that we consider a fixed amount of natural sample. We do this by assigning a voltage of 10V for the sample, instead of a fixed voltage for the spike-sample mixture. As noted by [8], this model is more representative of actual measurements where one adjusts the amount of spike added instead of diluting the sample to reach an optimal spike-sample ratio.

The correction in the reported delta values (Δ), along with the error in correction ($\sigma \Delta$), were calculated using formulas from [7]. The study considers an optimal

spike to yield the lowest combined error from both the double spike and correction of systematic offsets.

Results: The plots (Fig.1) show the relationship between the anomalies tied to certain nucleosynthetic processes (calculated using formula from [6]) and the necessary correction for delta values (in ‰). The separate contributions of the double spike and offset correction to the combined error are also shown.

Titanium: All selected spike combinations exclude ^{50}Ti since it exhibits the largest nucleosynthetic anomalies [4, 9]. $\epsilon^{46}\text{Ti}$ has been shown to correlate well with $\epsilon^{50}\text{Ti}$ [4], and thus used for the plot axis. All values were normalized to the $^{49}\text{Ti}/^{47}\text{Ti}$ value of a reference material (OL-Ti; [10]). Previous literature have used a ^{46}Ti - ^{50}Ti [11] and ^{47}Ti - ^{49}Ti [10] spike. While the ^{46}Ti - ^{48}Ti spike has the lowest correction per $\epsilon^{46}\text{Ti}$, it has a relatively large combined error ($\sigma \delta^{48/47}\text{Ti} = \sim 0.06\text{‰}$), which makes it a poor choice. The ^{47}Ti - ^{49}Ti (0.50:0.50; 42.97% spk) spike remains as the best combination for CAIs with nucleosynthetic anomalies.

Strontium: As Sr has only four isotopes, all are included in the data reduction. Sr measurements are internally normalized to a reference $^{86}\text{Sr}/^{88}\text{Sr}$, avoiding ^{87}Sr due to possible radiogenic contributions from ^{87}Rb [12]. Previous studies have used a ^{84}Sr - ^{87}Sr double spike [13, 14], which is predicted to have a combined error of $\sigma^{84/86}\text{Sr} = \sim 0.07\text{‰}$. Our results show that the ^{84}Sr - ^{87}Sr spike (0.58:0.42; 29.85% spk) also requires the least amount of correction and is indeed the ideal spike combination.

Chromium: Cr has four isotopes similar to Sr. Isotope measurements are normalized to a reference $^{52}\text{Cr}/^{50}\text{Cr}$ ratio [15, 16]. A ^{50}Cr - ^{54}Cr double spike has been used previously due to the lower abundance of both isotopes [17]. While this spike combination has a small error from the double spike ($\sigma \delta^{53/52}\text{Cr} = \sim 0.062\text{‰}$), there is a 100-fold larger error added when correcting the offsets from isotope anomalies ($\sigma \delta^{53/52}\text{Cr} = \sim 6.11\text{‰}$). We thus recommend a ^{52}Cr - ^{54}Cr spike (0.76:0.24; 54.63% spk), which has the smallest error from the double spike ($\sigma \delta^{53/52}\text{Cr} = \sim 0.042\text{‰}$), and minimal added error from offset correction.

Barium: Ba has seven isotopes that originate from multiple nucleosynthetic process. Measurements are normalized to a common $^{134}\text{Ba}/^{136}\text{Ba}$ ratio, as both isotopes are purely from the s-process [19]. Multiple spikes have been used in the literature, mostly for terrestrial/seawater samples (^{130}Ba - ^{135}Ba [20]; ^{135}Ba - ^{136}Ba [21]; ^{135}Ba - ^{137}Ba [22]; ^{132}Ba - ^{136}Ba [23]). It must be noted that both ^{134}Ba and ^{136}Ba have significant isobaric

interference from Xe, and are thus not ideal for measurement with MC-ICPMS. While the ^{130}Ba - ^{137}Ba and ^{130}Ba - ^{135}Ba spike have similar combined errors, the latter tends to be more sensitive to excessive spike addition. The precision of the ^{130}Ba - ^{135}Ba spike dramatically decreases beyond a 40% spiking ratio and as inaccurate spiking is difficult to avoid with small samples and low concentrations such as in meteorites and their components, we thus recommend the ^{130}Ba - ^{137}Ba spike (0.57:0.43; 22.03% spk) as a more general optimal spike for cosmochemical analysis. In theory, when spiking above ~75%, the ^{135}Ba - ^{137}Ba spikes have the lowest error, but such high spiking ratios might be impractical as they result in large dynamic ranges during analysis.

Molybdenum: Similar to Ba, Mo has seven isotopes that originate from the p-, r-, and s-processes [25]. Values are typically normalized to a common ^{96}Mo / ^{98}Mo ratio [6], but some works have normalized to ^{97}Mo / ^{95}Mo [26]. Here we used the former, and calculated the combined errors in the presence of expected anomalies from the three nucleosynthetic processes [19, 24, 25]. Previous works have used a ^{97}Mo - ^{100}Mo spike [25], which is shown here to have a large error from correction. Our results demonstrate that a ^{95}Mo - ^{100}Mo spike (0.48:0.52;

52.17% spk) performs better based on having the lowest double spike error while simultaneously having minimal added error from correcting $\Delta^{98/95}\text{Mo}$.

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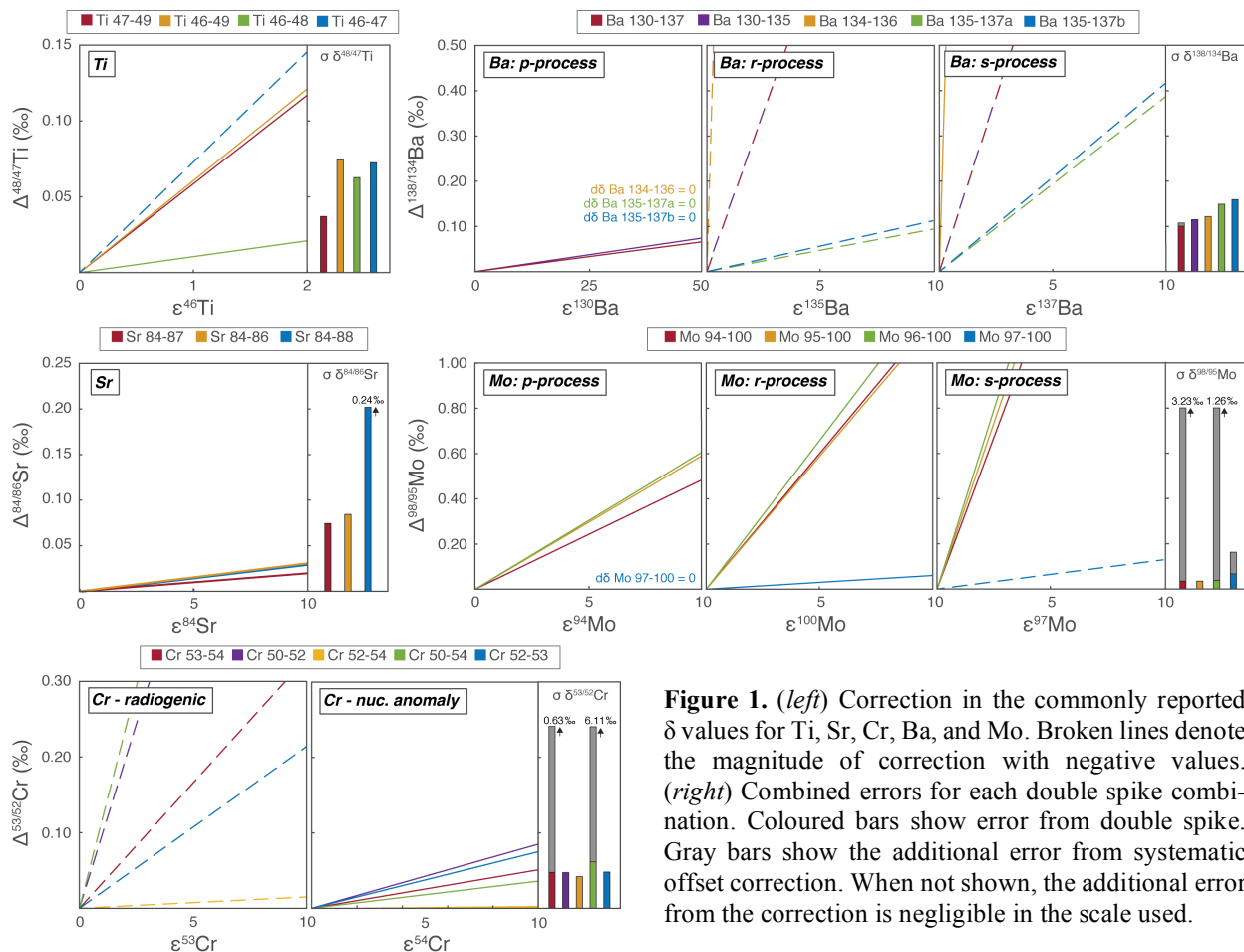


Figure 1. (left) Correction in the commonly reported δ values for Ti, Sr, Cr, Ba, and Mo. Broken lines denote the magnitude of correction with negative values. (right) Combined errors for each double spike combination. Coloured bars show error from double spike. Gray bars show the additional error from systematic offset correction. When not shown, the additional error from the correction is negligible in the scale used.