

# Determination of Rare Earth Element Isotopic Compositions Using Sample-Standard Bracketing and Double-Spike Approaches

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## Formula for correcting isotope fractionation induced by isobaric interferences

Below we build on Hu and Dauphas<sup>1</sup> to derive a more comprehensive formula to consider the influence of both isotope anomalies and isobaric interferences on the DS approach.

Take differentials on both sides of Eq. 5,

$$\left[ R_{sp}^{i/k} - R_{std}^{i/k} \left( \frac{m_i}{m_k} \right)^\alpha \right] df + (1-f) R_{std}^{i/k} \left( \frac{m_i}{m_k} \right)^\alpha \ln \left( \frac{m_i}{m_k} \right) d\alpha + \left[ (1-f) R_{std}^{i/k} \left( \frac{m_i}{m_k} \right)^\alpha + f R_{sp}^{i/k} \right] \ln \left( \frac{m_i}{m_k} \right) d\beta = \left( \frac{m_i}{m_k} \right)^{-\beta} dR_m^{i/k} - (1-f) \left( \frac{m_i}{m_k} \right)^\alpha dR_{std}^{i/k}. \quad (S1)$$

Define reduced mass  $\mu_{i/j} = \ln \left( \frac{m_i}{m_j} \right)$  and simplify Eq. S1,

$$\left[ \frac{R_{sp}^{i/k}}{R_{std}^{i/k}} \left( \frac{m_i}{m_k} \right)^{-\alpha} - 1 \right] df + (1-f) \mu_{i/k} d\alpha + \left\{ 1 + f \left[ \frac{R_{sp}^{i/k}}{R_{std}^{i/k}} \left( \frac{m_i}{m_k} \right)^{-\alpha} - 1 \right] \right\} \mu_{i/k} d\beta = \left( \frac{m_i}{m_k} \right)^{-\alpha-\beta} \frac{dR_m^{i/k}}{R_{std}^{i/k}} - (1-f) \frac{dR_{std}^{i/k}}{R_{std}^{i/k}}. \quad (S2)$$

For isotope anomalies, we adopted the definition in Hu and Dauphas<sup>1</sup>,

$$\varepsilon_{i/j} = 10^4 dR_m^{i/j} / R_{std}^{i/j}. \quad (S3)$$

We define the isobaric interference on isotope <sup>i</sup>E as,

$$\varphi_i = 10^4 dI_i / I_i, \quad (S4)$$

where  $I_i$  is the intensity of isotope <sup>i</sup>E. The variation of measured isotope ratio <sup>i</sup>E/<sup>j</sup>E can be written as,

$$dR_m^{i/j} = \frac{I_i + dI_i}{I_j + dI_j} - \frac{I_i}{I_j} = \frac{I_i + 10^{-4} \varphi_i I_i}{I_j + 10^{-4} \varphi_j I_j} - \frac{I_i}{I_j}. \quad (S5)$$

Equation S5 can be further simplified,

$$dR_m^{i/j} = 10^{-4} \frac{\varphi_i - \varphi_j}{1 + 10^{-4} \varphi_j} R_m^{i/j} \approx 10^{-4} (\varphi_i - \varphi_j) R_m^{i/j}. \quad (S6)$$

Substituting Eq. S3 and S6 into Eq. S2 gives,

$$\left[ \frac{R_{sp}^{i/k}}{R_{std}^{i/k}} \left( \frac{m_i}{m_k} \right)^{-\alpha} - 1 \right] df + (1-f) \mu_{i/k} d\alpha + \left\{ 1 + f \left[ \frac{R_{sp}^{i/k}}{R_{std}^{i/k}} \left( \frac{m_i}{m_k} \right)^{-\alpha} - 1 \right] \right\} \mu_{i/k} d\beta = 10^{-4} (\varphi_i - \varphi_k) \left( \frac{m_i}{m_k} \right)^{-\alpha-\beta} \frac{R_m^{i/k}}{R_{std}^{i/k}} - 10^{-4} (1-f) \varepsilon_{i/k}. \quad (S7)$$

Substituting Eq. 5 into Eq. S7, one has,

$$\left[ \frac{R_{sp}^{i/k}}{R_{std}^{i/k}} \left( \frac{m_i}{m_k} \right)^{-\alpha} - 1 \right] df + (1-f) \mu_{i/k} d\alpha + \left\{ 1 + f \left[ \frac{R_{sp}^{i/k}}{R_{std}^{i/k}} \left( \frac{m_i}{m_k} \right)^{-\alpha} - 1 \right] \right\} \mu_{i/k} d\beta = 10^{-4} \left\{ 1 + f \left[ \frac{R_{sp}^{i/k}}{R_{std}^{i/k}} \left( \frac{m_i}{m_k} \right)^{-\alpha} - 1 \right] \right\} (\varphi_i - \varphi_k) - 10^{-4} (1-f) \varepsilon_{i/k}. \quad (S8)$$

Since  $\left(\frac{m_i}{m_j}\right)^\alpha \approx 1$ , Eq. S8 can be further approximated to,

$$\left(\frac{R_{\text{sp}}^{i/k}}{R_{\text{std}}^{i/k}} - 1\right) df + (1-f)\mu_{i/k}d\alpha + \left[1 + f\left(\frac{R_{\text{sp}}^{i/k}}{R_{\text{std}}^{i/k}} - 1\right)\right]\mu_{i/k}d\beta \approx 10^{-4} \left[1 + f\left(\frac{R_{\text{sp}}^{i/k}}{R_{\text{std}}^{i/k}} - 1\right)\right](\varphi_i - \varphi_k) - 10^{-4}(1-f)\varepsilon_{i/k}. \quad (\text{S9})$$

Define  $t_{i/j} = \frac{R_{\text{sp}}^{i/j}}{R_{\text{std}}^{i/j}} - 1$  and Eq. S9 can be simplified,

$$t_{i/k}df + (1-f)\mu_{i/k}d\alpha + (1+ft_{i/k})\mu_{i/k}d\beta = 10^{-4}[(1+ft_{i/k})(\varphi_i - \varphi_k) - (1-f)\varepsilon_{i/k}]. \quad (\text{S10})$$

Applying Eq. S10 to three different isotope ratios  $^2\text{E}/^1\text{E}$ ,  $^3\text{E}/^1\text{E}$ , and  $^4\text{E}/^1\text{E}$  gives a set of three linear equations of unknowns  $df$ ,  $d\alpha$ , and  $d\beta$ , which can be solved for  $d\alpha$  using Cramer's rule,

$$d\alpha = \frac{\begin{vmatrix} t_{2/1} & 10^{-4}[(1+ft_{2/1})(\varphi_2 - \varphi_1) - (1-f)\varepsilon_{2/1}] & (1+ft_{2/1})\mu_{2/1} \\ t_{3/1} & 10^{-4}[(1+ft_{3/1})(\varphi_3 - \varphi_1) - (1-f)\varepsilon_{3/1}] & (1+ft_{3/1})\mu_{3/1} \\ t_{4/1} & 10^{-4}[(1+ft_{4/1})(\varphi_4 - \varphi_1) - (1-f)\varepsilon_{4/1}] & (1+ft_{4/1})\mu_{4/1} \end{vmatrix}}{\begin{vmatrix} t_{2/1} & (1-f)\mu_{2/1} & (1+ft_{2/1})\mu_{2/1} \\ t_{3/1} & (1-f)\mu_{3/1} & (1+ft_{3/1})\mu_{3/1} \\ t_{4/1} & (1-f)\mu_{4/1} & (1+ft_{4/1})\mu_{4/1} \end{vmatrix}}. \quad (\text{S11})$$

Equation S11 can be split to give,

$$d\alpha = 10^{-4} \frac{\begin{vmatrix} t_{2/1} & (1+ft_{2/1})(\varphi_2 - \varphi_1) & (1+ft_{2/1})\mu_{2/1} \\ t_{3/1} & (1+ft_{3/1})(\varphi_3 - \varphi_1) & (1+ft_{3/1})\mu_{3/1} \\ t_{4/1} & (1+ft_{4/1})(\varphi_4 - \varphi_1) & (1+ft_{4/1})\mu_{4/1} \end{vmatrix}}{\begin{vmatrix} t_{2/1} & (1-f)\mu_{2/1} & (1+ft_{2/1})\mu_{2/1} \\ t_{3/1} & (1-f)\mu_{3/1} & (1+ft_{3/1})\mu_{3/1} \\ t_{4/1} & (1-f)\mu_{4/1} & (1+ft_{4/1})\mu_{4/1} \end{vmatrix}} + 10^{-4} \frac{\begin{vmatrix} t_{2/1} & -(1-f)\varepsilon_{2/1} & (1+ft_{2/1})\mu_{2/1} \\ t_{3/1} & -(1-f)\varepsilon_{3/1} & (1+ft_{3/1})\mu_{3/1} \\ t_{4/1} & -(1-f)\varepsilon_{4/1} & (1+ft_{4/1})\mu_{4/1} \end{vmatrix}}{\begin{vmatrix} t_{2/1} & (1-f)\mu_{2/1} & (1+ft_{2/1})\mu_{2/1} \\ t_{3/1} & (1-f)\mu_{3/1} & (1+ft_{3/1})\mu_{3/1} \\ t_{4/1} & (1-f)\mu_{4/1} & (1+ft_{4/1})\mu_{4/1} \end{vmatrix}}. \quad (\text{S12})$$

The second term on the right hand side of Eq. S12 has been derived in Eq. 13-24 in Hu and Dauphas<sup>1</sup>, denoted  $d\alpha_{\text{anom}}$  here as isotope fractionation induced by isotope anomalies. We hereby define the first term as  $d\alpha_{\text{intf}}$  for isotope fractionation induced by isobaric interferences.

Therefore, we have,

$$d\alpha = d\alpha_{\text{anom}} + d\alpha_{\text{intf}}. \quad (\text{S13})$$

Let's define,

$$s_{i/j} = \frac{fR_{\text{sp}}^{i/j} - (1-f)R_{\text{std}}^{i/j}}{R_{\text{std}}^{i/j}} - 1 \approx \frac{R_{\text{m}}^{i/j}}{R_{\text{std}}^{i/j}} - 1. \quad (\text{S14})$$

The spike proportion  $f$  can be written as,

$$f = \frac{R_m^{i/j} - R_{std}^{i/j}}{R_{sp}^{i/j} - R_{std}^{i/j}} \approx \frac{s_{i/j}}{t_{i/j}}. \quad (\text{S15})$$

Substituting Eq. S14 and Eq. S15 into the first moment of Eq. S12,  $d\alpha_{\text{intf}}$  can be simplified,

$$d\alpha_{\text{intf}} = 10^{-4} \frac{\begin{vmatrix} (1+s_{2/1})(\varphi_2-\varphi_1) & (1+s_{3/1})(\varphi_3-\varphi_1) & (1+s_{4/1})(\varphi_4-\varphi_1) \\ s_{2/1} & s_{3/1} & s_{4/1} \\ (1+s_{2/1})\mu_{2/1} & (1+s_{3/1})\mu_{3/1} & (1+s_{4/1})\mu_{4/1} \end{vmatrix}}{(1-f) \begin{vmatrix} \mu_{2/1} & \mu_{3/1} & \mu_{4/1} \\ s_{2/1} & s_{3/1} & s_{4/1} \\ s_{2/1}\mu_{2/1} & s_{3/1}\mu_{3/1} & s_{4/1}\mu_{4/1} \end{vmatrix}}, \quad (\text{S16})$$

The variation in isotope fractionation  $d\delta_{i/j}^{\text{intf}} = 10^3 \mu_{i/j} d\alpha_{\text{intf}}$  can therefore be written as,

$$d\delta_{i/j}^{\text{intf}} = \frac{\mu_{i/j} \begin{vmatrix} (1+s_{2/1})(\varphi_2-\varphi_1) & (1+s_{3/1})(\varphi_3-\varphi_1) & (1+s_{4/1})(\varphi_4-\varphi_1) \\ s_{2/1} & s_{3/1} & s_{4/1} \\ (1+s_{2/1})\mu_{2/1} & (1+s_{3/1})\mu_{3/1} & (1+s_{4/1})\mu_{4/1} \end{vmatrix}}{10(1-f) \begin{vmatrix} \mu_{2/1} & \mu_{3/1} & \mu_{4/1} \\ s_{2/1} & s_{3/1} & s_{4/1} \\ s_{2/1}\mu_{2/1} & s_{3/1}\mu_{3/1} & s_{4/1}\mu_{4/1} \end{vmatrix}}. \quad (\text{S17})$$

Expanding Eq. S17,

$$d\delta_{i/j}^{\text{intf}} = \frac{\mu_{i/j}}{10(1-f)O_1^{1,2,3,4}} \left[ N_{2/1}^{1,2,3,4}(\varphi_2 - \varphi_1) + N_{3/1}^{1,2,3,4}(\varphi_3 - \varphi_1) + N_{4/1}^{1,2,3,4}(\varphi_4 - \varphi_1) \right], \quad (\text{S18})$$

where,

$$O_1^{1,2,3,4} = s_{3/1}s_{4/1}\mu_{4/3}\mu_{2/1} + s_{2/1}s_{4/1}\mu_{2/4}\mu_{3/1} + s_{2/1}s_{3/1}\mu_{3/2}\mu_{4/1}, \quad (\text{S19})$$

$$N_{2/1}^{1,2,3,4} = (1 + s_{2/1})(s_{3/1}\mu_{4/1} - s_{4/1}\mu_{3/1} + s_{4/1}s_{3/1}\mu_{4/3}), \quad (\text{S20})$$

$$N_{3/1}^{1,2,3,4} = (1 + s_{3/1})(s_{4/1}\mu_{2/1} - s_{2/1}\mu_{4/1} + s_{2/1}s_{4/1}\mu_{2/4}), \quad (\text{S21})$$

$$N_{4/1}^{1,2,3,4} = (1 + s_{4/1})(s_{2/1}\mu_{3/1} - s_{3/1}\mu_{2/1} + s_{2/1}s_{3/1}\mu_{2/3}). \quad (\text{S22})$$

## REFERENCES

(1) Hu, J. Y.; Dauphas, N. Double-spike data reduction in the presence of isotopic anomalies. *Journal of Analytical Atomic Spectrometry* **2017**, 32 (10), 2024-2033.