

Supplementary Material

Differentiating lithogenic supplies, water mass transport and biological processes on and off the Kerguelen Plateau using rare earth element concentrations and neodymium isotopic compositions

M. Grenier*, E. Garcia-Solsona, N. Lemaitre, T. W. Trull, V. Bouvier, P. Nonnotte, P. van Beek, M. Souhaut, F. Lacan, C. Jeandel

* **Correspondence:** Melanie Grenier: melanie.grenier@legos.obs-mip.fr, melaniegrenier14@yahoo.fr

1 Description of the calculation method of the anomaly uncertainties

We characterized the uncertainties on our REE anomalies as the standard deviations based on the general equation for error propagation, following Kragten (1995).

As detailed by the 4 equations in section 4, we express the anomaly of an element X as

$$\frac{X}{X^*} = \frac{[X]_n}{\alpha[Y]_n + \beta[Z]_n}$$

where $[X]_n$, $[Y]_n$ and $[Z]_n$ refer to the concentration of the elements X, Y and Z normalized to the concentration of these same elements X, Y and Z in the PAAS standard, and $X^* = \alpha[Y]_n + \beta[Z]_n$ refers to the “virtual” PAAS-normalized concentration of the element X calculated from the extrapolation or interpolation of the PAAS-normalized concentrations of the elements Y and Z. Replacing X with A and X^* with B, the standard deviation of the function $f = \frac{A}{B}$ is approximated via the first order linear expansion as:

$$\sigma_f \approx |f| \sqrt{\left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2 - 2 \frac{\sigma_{AB}}{AB}}$$

In this equation, the first two terms are the standard sum of the individual error contributions, and the last term accounts for correlation between these errors¹. Thus, we derive the uncertainty of an anomaly, which is expressed from 3 different REEs, from the individual uncertainty of these 3 REEs, corrected from their “common uncertainty” related to their degree of correlation. The degree of correlation depends on the covariance of these REEs and of their standard deviations and is estimated from repeated measurements of a geostandard (SLRS-5, Supp. Tables 1 and 2).

¹ Internal (e.g. magnet, plasma) or external (e.g. flow rate) variations can influence the internal reproducibility of several isotopes dependently.

Taking the La anomaly definition as an example,

$$\mathbf{f} = \frac{\mathbf{La}}{\mathbf{La}^*} = \frac{\mathbf{La}_n}{3 \cdot \mathbf{Pr}_n - 2 \cdot \mathbf{Nd}_n},$$

the uncertainty of $\mathbf{A} = \mathbf{La}_n$ can be taken as:

$$\sigma_A = 2\sigma_{\mathbf{La}_n}$$

and more generally $2\sigma_{X_n}$ is the 2σ uncertainty on the concentration of the element X reported in Table 1 normalized to the concentration of this same element X in the PAAS standard.

From the general formulation:

$$\mathbf{B} = \gamma\mathbf{C} - \delta\mathbf{D} \rightarrow \sigma_B = \sqrt{\gamma^2\sigma_C^2 + \delta^2\sigma_D^2 - 2\gamma\delta\sigma_{CD}}$$

in which the correlation term σ_{CD} can be calculated from $\sigma_{CD} = r_{C,D}\sigma_C\sigma_D$, where $r_{C,D}$ is the Pearson correlation coefficient, a measure of the linear correlation between the two variables C and D; calculated in the present work from repeated measurements of a geostandard (SLRS-5; Supp. Table 2),

thus for our specific example, the standard deviation of $\mathbf{B} = 3 \cdot \mathbf{Pr}_n - 2 \cdot \mathbf{Nd}_n$ is:

$$\sigma_B = \sqrt{3^2 \cdot 2\sigma_{\mathbf{Pr}_n}^2 + 2^2 \cdot 2\sigma_{\mathbf{Nd}_n}^2 - 2 \cdot 3 \cdot 2 \cdot r_{\mathbf{Pr}_n, \mathbf{Nd}_n} \cdot 2\sigma_{\mathbf{Pr}_n} \cdot 2\sigma_{\mathbf{Nd}_n}}$$

with $\gamma = 3$, $\delta = 2$, $\mathbf{C} = \mathbf{Pr}_n$ and $\mathbf{D} = \mathbf{Nd}_n$

$$\text{For } \mathbf{f} = \frac{\mathbf{La}}{\mathbf{La}^*} = \frac{\mathbf{La}_n}{3 \cdot \mathbf{Pr}_n - 2 \cdot \mathbf{Nd}_n}$$

$$\sigma_f \approx \left| \frac{\mathbf{La}_n}{3 \cdot \mathbf{Pr}_n - 2 \cdot \mathbf{Nd}_n} \right| \sqrt{\left(\frac{2\sigma_{\mathbf{La}_n}}{\mathbf{La}_n} \right)^2 + \left(\frac{\sqrt{3^2 \cdot 2\sigma_{\mathbf{Pr}_n}^2 + 2^2 \cdot 2\sigma_{\mathbf{Nd}_n}^2 - 2 \cdot 3 \cdot 2 \cdot r_{\mathbf{Pr}_n, \mathbf{Nd}_n} \cdot 2\sigma_{\mathbf{Pr}_n} \cdot 2\sigma_{\mathbf{Nd}_n}}}{3 \cdot \mathbf{Pr}_n - 2 \cdot \mathbf{Nd}_n} \right)^2 - 2 \cdot \frac{r_{\mathbf{La}_n, \mathbf{La}^*} \cdot 2\sigma_{\mathbf{La}_n} \cdot \sqrt{3^2 \cdot 2\sigma_{\mathbf{Pr}_n}^2 + 2^2 \cdot 2\sigma_{\mathbf{Nd}_n}^2 - 2 \cdot 3 \cdot 2 \cdot r_{\mathbf{Pr}_n, \mathbf{Nd}_n} \cdot 2\sigma_{\mathbf{Pr}_n} \cdot 2\sigma_{\mathbf{Nd}_n}}}{\mathbf{La}_n (3 \cdot \mathbf{Pr}_n - 2 \cdot \mathbf{Nd}_n)}}}$$

We proceeded similarly for the characterization of the uncertainties on the Ce, Eu and Yb anomalies.

| | SLRS-5, this study | | SLRS-5 (Heimburger et al., 2012) | |
|---------------|--------------------|------|----------------------------------|-----|
| | ppt (n=16) | 2SD | ppt | 2SD |
| La | 208 | 22 | 196 | 44 |
| Ce | 257 | 51 | 236 | 32 |
| Pr | 51.4 | 6.2 | 46.9 | 5.0 |
| Nd | 199 | 16 | 185 | 40 |
| Sm | 34.5 | 2.4 | 32.4 | 6.6 |
| Eu | 5.8 | 0.6 | 5.6 | 2.8 |
| Gd | 28.2 | 5.8 | 24.9 | 6 |
| Tb | 3.4 | 0.5 | 3.2 | 1.2 |
| Dy | 19.1 | 1.6 | 18.2 | 5 |
| Ho | 3.8 | 0.2 | 3.6 | 1 |
| Er | 11.0 | 1.4 | 10.5 | 2 |
| Tm | 1.5 | 0.3 | 1.3 | 0.6 |
| Yb | 9.8 | 1.1 | 9.3 | 1.4 |
| Lu | 1.7 | 0.3 | 1.5 | 0.4 |
| La/La* | 1.01 | 0.08 | 1.06 | - |
| Ce/Ce* | 0.56 | 0.03 | 0.59 | - |
| Eu/Eu* | 0.96 | 0.03 | 0.97 | - |
| Yb/Yb* | 0.96 | 0.06 | 0.95 | - |

Supplementary Table 1. SLRS-5 analyses of this study compared to published concentrations of SMLS-5 (Heimburger et al., 2012). The concentration accuracy of the elements used for the anomaly calculations of our study (shown in bold) varies between 4% (for Eu) and 9% (for Ce). The associated anomalies determined from Heimburger's et al. (2012) results, calculated from the equations used in our study, are within the 2SD confidence interval of our anomaly determinations.

| $\frac{La}{La^*} = \frac{[La]_n}{3[Pr]_n - 2[Nd]_n}$ | $\frac{Ce}{Ce^*} = \frac{[Ce]_n}{2[Pr]_n - [Nd]_n}$ | $\frac{Eu}{Eu^*} = \frac{4[Eu]_n}{3[Sm]_n + [Dy]_n}$ | $\frac{Yb}{Yb^*} = \frac{[Yb]_n}{2[Er]_n - [Dy]_n}$ | $\frac{Nd_n}{Yb_n}$ |
|---|---|---|---|---|
| $r_{Pr_n, Nd_n} = r_{La^*} = 0.88$ $r_{La, La^*} = 0.34$ | $r_{Pr_n, Nd_n} = r_{Ce^*} = 0.88$ $r_{Ce, Ce^*} = 0.83$ | $r_{Sm_n, Dy_n} = r_{Eu^*} = 0.85$ $r_{Eu, Eu^*} = 0.41$ | $r_{Er_n, Dy_n} = r_{Yb^*} = 0.44$ $r_{Yb, Yb^*} = 0.15$ | $r_{Nd_n, Yb_n} = 0.21$ |

Supplementary Table 2. Pearson correlation coefficients used in this study for the anomaly uncertainty calculations, determined from 16 repeated measurements of a geostandard (SLRS-5, Supp. Table 1).

References

- Heimburger, A., M. Tharaud, F. Monna, R. Losno, K. Desboeufs and E. B. Nguyen, Geostand. Geoanal. Res., 2012, DOI: 10.1111/j.1751-908X.2012.00185.x.
- Kragten J., 1995. A standard scheme for calculating numerically standard deviations and confidence intervals. Chemometrics and Intelligent Laboratory Systems 28, 89-97. doi: 10.1016/0169-7439(95)80042-8.