Reliability of detrital marine sediments as proxy for continental crust composition: the effects of hydrodynamic sorting on Ti and Zr isotope systematics

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SUPPLEMENTARY MATERIAL

1. Robustness of δ⁴⁹/⁴⁷Ti results

Figure S1. A) δ⁴⁹/⁴⁷Ti of the OL-Ti reference material at variable proportion p of double spike in the sample–spike mixture (see Rudge et al., 2009). The grey band shows the range in p for the samples measured in this study and the lack of bias due to variable sample–spike mixing proportions. The filled symbol shows the composition of OL-Ti solutions spiked at the optimal proportion that were measured as unknowns alongside the samples (n = 9); B) δ⁴⁹/⁴⁷Ti versus measured ⁴⁴Ca/⁴⁷Ti for Ca-doped OL-Ti solutions, which illustrate that the correction for isobaric interference of Ca is accurate. The grey band shows the range in ⁴⁴Ca/⁴⁷Ti of samples measured in this study, with a single exception at ⁴⁴Ca/⁴⁷Ti = 0.0061. The filled symbol shows the composition of undoped OL-Ti solutions that were measured as unknowns alongside the samples (n = 9).
2. Results for reference materials

Figure S2. The $\delta^{49/47}$Ti composition of geostandards and Ti reference materials measured in this study; literature data (open symbols) are shown for reference (Millet and Dauphas, 2014; Millet et al., 2016; Greber et al., 2017a, 2017b; Deng et al., 2018, 2019; Johnson et al., 2019; Aarons et al., 2020; Kommescher et al., 2020; Williams et al., 2020). The pooled 2s intermediate precision for the five reference materials is 0.022 ‰.

Figure S3. The $\delta^{94/90}$Zr composition of geostandards and synthetic Zr reference material (SPEX) measured over the course of this study. The pooled 2s intermediate precision of the four geostandards is 0.014 ‰ (0.018 ‰ including SPEX).
### Table S1. Zr isotope results for the EMS sediment samples.

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<td>0.010%</td>
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</table>

Reported δ\(^{87/86}\)Zr values are means of all measured replicates for each fraction, expressed relative to the Zr-NIST reference material according to: δ\(^{87/86}\)Zr = ([\(^{87}\)Zr/\(^{86}\)Zr]sample/[\(^{87}\)Zr/\(^{86}\)Zr]Zr NIST) – 1.

Uncertainties reported for each sample are 2 standard error of the mean (2se), calculated using the daily external reproducibility of the Zr NIST reference material (2s) divided by the square root of the number (n) of replicates measured (i.e., 2se = 2s/\(s\sqrt{n}\)).

- **Fraction of Zr (by mass)** from double spike in the spike-sample mixture, calculated by isotope dilution
- **Ratio of measured ion beam intensities**
- **Percent Mo/Zr (atomic)**
3. Regressions of the EMS sediment samples

The average composition of the four EMS sediment groups is given in Table 2 in the main text. We regressed these data to obtain Ti/Nd, δ⁴⁹/⁴⁷Ti, Zr/Nd and δ⁹⁴/⁹⁰Zr of the Nile and Sahara source components, for which we assumed a fixed εNd composition (+2.6 ± 1.2 and -13.8 ± 0.8, respectively). We employed a standard York regression for εNd versus Ti/Nd and Zr/Nd (Figure 5a and c in the main text).

To derive the Ti and Zr isotope composition of Nile sediment and Saharan dust, we employ the general equation for a binary mixing hyperbole in ratio-ratio space (see e.g. (Vollmer, 1976). We outline our approach below. Due to the very limited variation in Nd-Ti-Zr isotope compositions, we use the approximation that the concentration [in square brackets] of the denominator isotope is that of the element, e.g. [¹⁴⁴Nd] = [Nd]. We define:

\[ x = \frac{¹⁴³Nd}{¹⁴⁴Nd} \]
\[ y = \frac{⁴⁹Ti}{⁴⁷Ti} \text{ or } \frac{⁹⁴Zr}{⁹⁰Zr} \]
\[ R = \frac{[Ti]}{[Nd]} \text{ or } \frac{[Zr]}{[Nd]} \]

Subscript “m” for a sample on the mixing hyperbole
Subscript “N” for the composition of the Nile sediment component
Subscript “S” for the composition of the Saharan dust component

The equation for any point \((x_m, y_m)\) that falls on a mixing hyperbole between components N and S is

\[ Ax_m + Bx_my_m + Cy_m + D = 0 \]

Where

\[ A = R_Sy_S - R_Ny_N \]
\[ B = R_N - R_S \]
\[ C = R_Sx_N - R_Nx_S \]
\[ D = R_Nx_Ny_N - R_Sx_Ny_S \]

Rearranging gives

\[ y_m = \frac{Ax_m + D}{-(Bx_m + C)} \]

If \(x_N, x_S, R_N\) and \(R_S\) are known, it is possible to express \(y_m\) as a function of the unknowns \(y_N\) and \(y_S\)

\[ y_m = y_N \frac{R_N(x_S - x_m)}{-(Bx_m + C)} + y_S \frac{R_S(x_m - x_N)}{-(Bx_m + C)} \]

Next, as

\[ \frac{R_N(x_S - x_m)}{-(Bx_m + C)} + \frac{R_S(x_m - x_N)}{-(Bx_m + C)} = 1 \]

It follows that
\[ y_m = (y_N - y_S) \frac{R_N(x_S - x_m)}{-(Bx_m + C)} + y_S \]

Which is in the form of a straight line

\[ y = ax + b \]

Where

\[ a = (y_N - y_S) \]
\[ b = y_S \]
\[ x = \frac{R_N(x_S - x_m)}{R_Nx_S - R_Sx_N - x_m(R_N - R_S)} \]

Which can be solved through ordinary least squares regression of the EMS sediment samples to yield the Ti or Zr isotope composition of the Nile sediment and Sahara dust components \((y_N\) and \(y_S\), respectively). In order to estimate the uncertainty on the isotopic composition of the mixing components, we employed a Monte Carlo approach with 10,000 simulations in the following way. For each simulation, we used:

1. A normally distributed random value for input parameters
   \( x_N \) \( \epsilon \)Nd of Nile sediment
   \( x_S \) \( \epsilon \)Nd of Saharan dust
   \( x_m \) \( \epsilon \)Nd of the four EMS sediment groups
   \( y_m \) \( ^{49}\)Ti/\(^{47}\)Ti or \( ^{94}\)Zr/\(^{90}\)Zr of the four EMS sediment groups
   (See Table 2 in the main text for values and uncertainties used)
2. Normally distributed, correlated random value for the slope and intercept of \( \epsilon \)Nd versus Ti/Nd or Zr/Nd, from the York regressions described above.
3. The composition of \( R_N \) and \( R_S \) (Ti/Nd or Zr/Nd of Saharan dust and Nile sediment), at the given \( x_N \) and \( x_S \) (step 1), was calculated from random values for the slope and intercept from step 2.
4. Ordinary least squares regression of the four EMS sediment groups as described in the equations above to yield \( y_N \) and \( y_S \) (Ti or Zr isotope composition of Nile sediment and Saharan dust, respectively).

This yielded a set of 10,000 mixing hyperboles in \( \epsilon \)Nd versus \( \delta^{49/47}\)Ti or \( \delta^{94/90}\)Zr space from which a 95 % confidence envelope could be distilled (see Figure 5b and d in the main text). The Monte Carlo simulation yields Ti and Zr isotope composition of the provenance components that are distinctly not normally distributed due to the curvature of the mixing hyperboles (Figure S4).
Figure S4. Results of the Monte Carlo simulations; the δ⁴⁹/⁴⁷Ti and δ⁹⁴/⁹⁰Zr composition of the Nile- and Sahara-derived components in the EMS sediments.
References


