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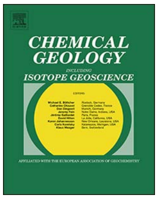

Factors influencing the precision and accuracy of Nd isotope measurements by thermal ionization mass spectrometry

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ABSTRACT

Taking the example of Nd, we present a method based on a 4-mass-step acquisition scheme to measure all isotope ratios dynamically by thermal ionization mass spectrometry (TIMS); the aim being to minimize the dependency of all mass fractionation-corrected ratios on collector efficiencies and amplifier gains. The performance of the method was evaluated from unprocessed JNdi-1 Nd standards analyzed in multiple sessions on three different instruments over a period of ~1.5 years (n = 61), as well as from standards (18 JNdi-1 and 19 BHVO-2) processed through different chemical purification procedures. The Nd isotopic compositions of standards processed through fine-grained (25–50 μm) Ln-spec resin show a subtle but clear fractionation caused by the nuclear field shift effect. This effect contributes to the inaccuracy of Nd isotope measurements at the ppm level of precision.

Following a comprehensive evaluation of the mass spectrometer runs, we suggest several criteria to assess the quality of data acquired by TIMS, in particular to see whether the measurements were affected by domain mixing effects on the filaments. We define maximum tolerable Ce and Sm interference corrections and the minimum number of ratios to acquire to ensure the best possible accuracy and precision for all Nd isotope ratios. Changes in fractionation of Nd isotope ratios in between acquisition steps can result in significant inaccuracy and bias dynamic μ_{142} values by > 15 ppm. To correct for these effects, we developed a systematic drift-correction based on the monitoring of Nd isotope ratios through time. The residual components of scatter in the JNdi-1 and BHVO-2 datasets were further investigated in binary isotopic plots in which we modeled the theoretical effects of domain mixing on filaments, nuclear field shift and correlated errors from counting statistics using Monte-Carlo simulations. These plots indicate that the 4-step method returns precisions limited by counting errors only for drift-corrected dynamic Nd isotope ratios. Data acquired on three different TIMS instruments suggest the following composition for the JNdi-1 reference standard: ^{142}Nd/^{144}Nd = 1.141832 ± 0.000006 (2s), ^{143}Nd/^{144}Nd = 0.512099 ± 0.000005 (2s), ^{145}Nd/^{144}Nd = 0.348403 ± 0.000003 (2s), ^{148}Nd/^{144}Nd = 0.241581 ± 0.000003 (2s), and ^{150}Nd/^{144}Nd = 0.236452 ± 0.000006 (2s) when normalized to ^{146}Nd/^{144}Nd = 0.7219. Measurements performed on different instruments (Triton™ vs. Triton Plus™) show resolvable differences of about 10 ppm for absolute ^{143}Nd/^{144}Nd, ^{145}Nd/^{144}Nd and ^{148}Nd/^{144}Nd ratios. The different criteria and corrections developed in this study could be applied to other isotopic systematics to improve and better evaluate the quality of high-precision data acquired by TIMS.

1. Introduction

Thermal ionization mass spectrometry (TIMS) is the state-of-the-art technique to measure isotope ratios at the ppm precision level provided that the element of interest has the right properties to ionize efficiently (see Carlson, 2014 for a review). The advent of multicollector TIMS allowed isotope ratios to be calculated by simultaneous collection of the ion beams of different masses, reducing the consequences of temporal variations in ion intensity and increasing the amount of signal integration per measurement interval, both of which foster higher precision isotope ratio determinations. The simplest of these methods is so-called static multicollection where all the ion beams are measured

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simultaneously. To calculate accurate isotope ratios from simultaneously detected ion beams requires knowledge of the amplifier gains and collection efficiencies of each faraday detector used in the measurement. The amplifier gains and faraday efficiencies theoretically can be eliminated through the technique of dynamic multicollection. In this approach, at least two magnet steps are made that move both the target and a standardizing isotope into the same faraday cup. The unknown isotope ratio is then calculated by combining the equations for the unknown ratio and the standardizing ratio in a way where the cup gains and efficiencies divide out. The relative deterioration of faraday collectors and their change of efficiency through time has been pinpointed as an important source of imprecision and inaccuracy for the determination of isotope ratios using static multicollection since the 1990s (Makishima and Nakamura, 1991; Thirlwall, 1991). Similarly, changes in amplifier gain during measurement can affect isotope ratio determinations. The role of amplifier drift has been addressed by electronically rotating amplifiers between faraday cups so that any inaccuracy in the amplifier gains will be averaged over the entire measurement. By minimizing the consequences of relative cup inefficiencies and amplifier gain variability, the dynamic acquisition of isotope ratios avoids the consequences of cup deterioration and amplifier gain changes and yields better long-term precision and accuracy than static multicollection (Carlson, 2014; Fukai et al., 2017; Thirlwall, 1991).

Many studies have used the dynamic technique to investigate the small ^{142}Nd anomalies created by the decay of 103 million year half-life ^{146}Sm in both terrestrial and extra-terrestrial materials. Recent studies typically yield external isotope ratio precisions ranging from 3 to 8 ppm (2s) on the ^{142}Nd/^{144}Nd ratios of reference standards repeatedly measured through different analytical sequences (cf. Bouvier and Boyet, 2016; Burkhardt et al., 2016; Carlson et al., 2007; O'Neil et al., 2008; Rizo et al., 2012; Roth et al., 2013). More recently, Burkhardt et al. (2016) and Fukai et al. (2017) used a two mass-step acquisition method to calculate dynamic ^{148}Nd/^{144}Nd and ^{150}Nd/^{144}Nd ratios, in addition to ^{142}Nd/^{144}Nd ratios. Here, we propose a new method based on a 4 mass-step acquisition routine able to return all Nd isotope ratios dynamically, including the radiogenic ^{143}Nd/^{144}Nd ratio. We investigate the potential sources of imprecision and inaccuracy in the measurement of Nd isotope ratios by TIMS, and additionally suggest corrections to improve the quality of the data as well as criteria to recognize poor-quality runs after acquisition. While the study focuses on Nd, the processes, corrections and recommendations discussed here could potentially be applied to the measurement of other isotopic systems and provide keys to improve both the acquisition and the reduction of high-precision isotopic data in general.

2. The 4 mass-step method: principles and equations

The dynamic measurement of all Nd isotope ratios involves the use of 4 different magnet settings per cycle. Two different mass-step sequences were tested to investigate how the mass fractionation rate affected the measurement of dynamic Nd isotope ratios (cf. Roth et al., 2014). They are shown in Table 1 together with run parameters such as voltages employed in the zoom optics, integration times, and the idle time spent before initiating signal integration after mass steps. The two tested configurations have the same collector positions, with the axial faraday cup successively centered on ^{143}Nd, ^{144}Nd, ^{145}Nd, and ^{146}Nd, and only differ by the order in which the acquisition lines are measured. Each 4-step cycle returns four static ratios for ^{142}Nd/^{144}Nd, ^{143}Nd/^{144}Nd, and ^{145}Nd/^{144}Nd, three static ratios for ^{148}Nd/^{144}Nd, one static ratio for ^{150}Nd/^{144}Nd, two dynamic ratios for ^{142}Nd/^{144}Nd, ^{143}Nd/^{144}Nd, and ^{148}Nd/^{144}Nd, three dynamic ratios for ^{145}Nd/^{144}Nd, and one dynamic ^{150}Nd/^{144}Nd ratio, all normalized to ^{146}Nd/^{144}Nd = 0.7219.

2.1. Equations for dynamic ^{142}Nd/^{144}Nd ratios

Dynamic ratios are calculated assuming that Nd mass fractionation follows an exponential law during the run (Andreasen and Sharma, 2009; Upadhyay et al., 2008). The veracity of this assumption for our measurements is re-examined below when evaluating the results in Section 4.1.1.1. The first dynamic ^{142}Nd/^{144}Nd ratio, $\left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Dyn\ 1}}$, is obtained by combining the ^{142}Nd/^{144}Nd ratio measured on line 1, $\left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Meas\ 1}}$, together with the ^{146}Nd/^{144}Nd ratio measured on line 3, $\left(\frac{^{146}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Meas\ 3}}$, to minimize the difference of efficiencies and amplifier gains between faraday collectors L1 and H1. This gives:

$$\left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Dyn\ 1}} = \left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Meas\ 1}} \times \left(\frac{m_{142}}{m_{144}}\right)^{F_3} \text{ with } F_3 = \frac{\ln\left(\frac{\left(\frac{^{146}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{True}}}{\left(\frac{^{146}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Meas\ 3}}}\right)}{\ln\left(\frac{m_{146}}{m_{144}}\right)} \tag{1}$$

where m_{142}, m_{144}, and m_{146} are the atomic masses of isotopes ^{142}Nd, ^{144}Nd and ^{146}Nd, respectively; $\left(\frac{^{146}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{True}} = 0.7219$ is the normalizing ratio used for mass fractionation correction. Given that the measured ion-beam intensities depend on the collector efficiencies and amplifier gains, we can write:

$$\left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Meas\ 1}} = \frac{I^{142}\mathrm{Nd}_{\mathrm{Meas\ 1}}}{I^{144}\mathrm{Nd}_{\mathrm{Meas\ 1}}} = \frac{I^{142}\mathrm{Nd}_1 \times C_{L1} \times G_{L1}}{I^{144}\mathrm{Nd}_1 \times C_{H1} \times G_{H1}}$$

and

$$\left(\frac{^{146}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Meas\ 3}} = \frac{I^{146}\mathrm{Nd}_{\mathrm{Meas\ 3}}}{I^{144}\mathrm{Nd}_{\mathrm{Meas\ 3}}} = \frac{I^{146}\mathrm{Nd}_3 \times C_{H1} \times G_{H1}}{I^{144}\mathrm{Nd}_3 \times C_{L1} \times G_{L1}}$$

where $I^{142}\mathrm{Nd}_1$, $I^{144}\mathrm{Nd}_1$, $I^{146}\mathrm{Nd}_3$, and $I^{144}\mathrm{Nd}_3$ are the “true” intensities of the different Nd isotope beams on acquisition lines 1 and 3; C_{L1} and C_{H1} are the efficiencies of the faraday collectors L1 and H1 that change with time depending on instrument use; G_{L1} and G_{H1} are the gains of the amplifiers to which the faraday collectors L1 and H1 are attached. Using this notation, (Eq. (1)) can be re-written as follows:

$$\begin{aligned}
\left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Dyn\ 1}} &= \frac{I^{142}\mathrm{Nd}_1 \times C_{L1} \times G_{L1}}{I^{144}\mathrm{Nd}_1 \times C_{H1} \times G_{H1}} \\
&\quad \times \exp\left(\frac{\ln\left(\frac{\left(\frac{^{146}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{True}}}{\frac{I^{146}\mathrm{Nd}_3 \times C_{H1} \times G_{H1}}{I^{144}\mathrm{Nd}_3 \times C_{L1} \times G_{L1}}}\right)}{\ln\left(\frac{m_{146}}{m_{144}}\right)} \times \ln\left(\frac{m_{142}}{m_{144}}\right)\right) \\
\Longleftrightarrow \left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Dyn\ 1}} &= \frac{I^{142}\mathrm{Nd}_1 \times C_{L1} \times G_{L1}}{I^{144}\mathrm{Nd}_1 \times C_{H1} \times G_{H1}} \times \left(\frac{\left(\frac{^{146}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{True}}}{\frac{I^{146}\mathrm{Nd}_3 \times C_{H1} \times G_{H1}}{I^{144}\mathrm{Nd}_3 \times C_{L1} \times G_{L1}}}\right)^{\varphi} \text{ with } \varphi \\
&= \frac{\ln\left(\frac{m_{142}}{m_{144}}\right)}{\ln\left(\frac{m_{146}}{m_{144}}\right)} \\
\Longleftrightarrow \left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{Dyn\ 1}} &= \frac{I^{142}\mathrm{Nd}_1}{I^{144}\mathrm{Nd}_1} \times \left(\frac{^{146}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{True}}^{\varphi} \times \left(\frac{I^{146}\mathrm{Nd}_3}{I^{144}\mathrm{Nd}_3}\right)^{-\varphi} \\
&\quad \times \left(\frac{C_{L1} \times G_{L1}}{C_{H1} \times G_{H1}}\right)^{1+\varphi}
\end{aligned} \tag{2}$$