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Precise and Accurate Neodymium Isotopic Analysis of Sub-5ng Samples by MC-ICPMS

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Neodymium (Nd) isotope geochemistry has a large number of applications in the Earth Sciences. The optimal exploitation of this powerful tool, however, requires measurement of isotope ratios to 20 ppm (2 std. dev.) or better. A level of precision approaching this is often required on small (* 5 ng) samples. The best TIMS (thermal ionisation mass spectrometry) studies have achieved this but the chemical and mass spectrometric procedures involved are rather more time-consuming, and more dependent on operator's skill, than is desirable. The advent of magnetic sector multiple collector inductively-coupled plasma mass spectrometry (MC-ICPMS) promises improvements in this situation via simpler chemical separation procedures and shorter mass spectrometric analysis times. A previous study (Luais et al. 1997), however, has suggested that static analysis procedures yield a reproducibility that is substantially worse than TIMS (56-72 versus 16 ppm), and only achievable using daily adjustments to cup efficiencies. In addition, the latter study required amounts of material (70 ng) an order of magnitude greater than the best TIMS studies to achieve comparable internal precisions. Here, using a Micromass Isoprobe instrument, we demonstrate that a long-term external reproducibility of 14-22 ppm can be achieved on 30 ng samples, and internal errors of around 30 ppm on samples as small as 3-4 ng. In addition, the well-known Nd isotopic system allows a detailed examination of the mass bias behaviour of these instruments. Our results can be achieved using exactly the same data reduction procedures as have been used previously for TIMS (Thirlwall, 1991).

Data were obtained on pure Nd standards as well as standards and samples with Ce/Nd ratios as high as 0.6 and Sm/Nd ratios up to 0.25. All standards and samples were introduced into the mass spectrometer in 2% HNO3 using an Aridus desolvating nebuliser. The basic design of the mass spectrometer has been described elsewhere (Halliday et al. 1999). A ^{144}Nd ion beam of 0.5-4 x10^{-11}A was obtained on solutions containing 6-70 ppb Nd. Total sample usage varied between 2 and 35 ng. No adjustments have been made to collector efficiencies at any stage.

The main results are summarized below (all precisions are given as 2 sigma and refer to the last significant digits).

1) Internal precisions on samples 2-5 ng in size are 25-35 ppm.

2) For normalisation to ^{146}Nd/^{144}Nd using an exponential law the long-term value for the ^{143}Nd/^{144}Nd ratio of our in-house (Aldrich AA) standard is 0.511376±22 (Figure 1). This compares with a TIMS value of 0.511422±9 over one year after collector renewal or 0.511421±19 over longer periods (4 years). In other words, the new MC-ICPMS data are both inaccurate and less precise than the TIMS data.

3) Thirlwall (1991) noted that TIMS Nd isotope ratios, when normalised to ^{146}Nd/^{144}Nd, displayed residual correlations, with a gradient of 0.176 for the correlation between ^{143}Nd/^{144}Nd and ^{142}Nd/^{144}Nd. The new MC-ICPMS data show the same correlations with a slope of 0.174. However, the spread in the MC-ICPMS data along this line is much greater. When re-normalised to a value of 1.141876 for the ^{142}Nd/^{144}Nd ratio, the TIMS ^{143}Nd/^{144}Nd ratio of our in-house standard is 0.511421±7 over long time periods. When corrected in exactly the same way as the TIMS values the ^{143}Nd/^{144}Nd ratio for the MC-ICPMS data becomes 0.511427±7 (Fig. 1) for pure Nd standards and 0.511429±11 for Ce-bearing standards corrected for ^{142}Ce interference on ^{142}Nd. The same procedure gives 0.511855±11 for La Jolla Nd.

4) The physical cause of these post-normalisation correlations is not clear. Neither is it apparent at this stage whether they are restricted to the Isoprobe or are found on other plasma-source instruments. Detailed examination of our Isoprobe data reveals that they are due to imperfect adherence to an exponential mass bias law. Indeed over the range of the MC-ICPMS data the most appropriate law appears to be the power law. However, when mass bias correction is performed using such a law the result is even more inaccurate - at 0.511287±22. What this essentially means is that neither fractionation exactly describes Nd isotope mass bias on the Isoprobe, though fits to the data in the mass bias region of the instrument are more or less adequate.