Chemical Geology 257 (2008) 65–75

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Accuracy of stable Mg and Ca isotope data obtained by MC-ICP-MS using the standard addition method

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ARTICLE INFO

Article history:
Received 19 May 2008
Received in revised form 19 August 2008
Accepted 19 August 2008

Editor: R.L. Rudnick

Keywords:
Multi collector inductively coupled mass spectrometry
Standard addition
Magnesium
Mg isotopes
Mg
Ca
Calcium
Ca isotopes

ABSTRACT

The standard addition method is evaluated to verify the accuracy and precision of Mg and Ca isotope data with complex matrices, using the standard-sample bracketing technique and analysis by MC-ICP-MS. The ^{44}Ca/^{42}Ca ratio of seawater (expressed as δ^{44}_{42}Ca relative to SRM915a) was determined as 0.93±0.03‰ (95% confidence), in agreement with estimates obtained by the double spike method. Using standard addition, the seawater ^{26}Mg/^{24}Mg ratio (expressed as δ^{26}Mg relative to the DSM3 standard) was determined as −0.80±0.06‰ (95% confidence) in agreement with previous estimates. Four terrestrial silicate rocks (MORB, flood basalt, glacial flour, and granodiorite) and olivine mineral separates from an island basalt are shown to exhibit no scatter within the error of the method, averaging a δ^{26}Mg of −0.20±0.05‰ (95% confidence). Although a number of silicate rock data for Mg isotope ratios have already been reported, this is the first detailed effort to validate the accuracy of such data and test for residual analytical artifact after chemical purification of samples. Data regressions were evaluated statistically using the mean square weighted deviate (MSWD), demonstrating that the uncertainty on individual data points are generally over estimated. The external two standard deviation uncertainty on individual data points is estimated by Monte Carlo simulation as <0.075‰ (about a factor of two improvement on early publications of Mg isotope data). The consistency of the standard addition estimates of δ^{26}Mg in silicate rocks imply that if any residual matrix effects are present, then they must be less than the spread of the data (0.11‰) given the diverse range of matrices in each of the samples. The δ^{26}Mg values of the silicate rocks suggest that Mg isotope ratios in silicate material may only have a very restricted range. The δ^{26}Mg values of silicate material in the present study falls between the average values reported by Teng et al. [Teng, F.Z., Wadhwa, M., Helz, R.T., 2007. Investigation of magnesium isotope fractionation during basalt differentiation: implications for a chondritic composition of the terrestrial mantle. Earth and Planetary Science Letters 261, 84–92. doi:10.1016/j.epsl.2007.06.004] and Wiechert and Halliday [Wiechert, U., Halliday, A.N., 2006. Non-chondritic magnesium and the origins of the inner terrestrial planets. Earth and Planetary Science Letters 256, 360–371. doi:10.1016/j.epsl.2007.01.007] and given the spread of published δ^{26}Mg values for chondritic material, a chondritic composition for terrestrial Mg cannot be ruled out. We suggest that some of the small discrepancies between our data and analysis of the same samples in earlier studies, may have arisen because the chemical purification of Mg prior to analysis can easily induce analytical artifact. This method could be expanded to the isotope ratios of other elements, which also rely on correcting for mass bias using the standard-sample bracketing method, where similar analytical discrepancies may also exist.

1. Introduction

Multi collector inductively coupled mass spectrometry (MC-ICP-MS) has become the method of choice for many isotopic analyses over recent years. In particular, the analysis of "non traditional" stable isotope ratios by MC-ICP-MS is now becoming routine and data are reported with very high precision. For example, Mg isotope ratios are typically reported with a two standard deviation external precision of better than 0.14‰ (e.g., Galy et al., 2001, 2002; Chang et al., 2003; Black et al., 2006; Tipper et al., 2006a,b; Wiechert and Halliday, 2006; Teng et al., 2007), and in some cases as good as 0.03‰ (e.g., Buhl et al., 2007). Whilst such a high degree of precision permits a diverse new range of geological and environmental questions to be addressed using novel isotopic systems, there remains a challenge in ascertaining the accuracy of the data, which is easily biased during chemical

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doi:10.1016/j.chemgeo.2008.08.016

preparation and analysis (e.g., Russell and Papanastassiou, 1978; Galy et al., 2001; Vance and Thirlwall, 2002; Albarède and Beard, 2004; Wieser et al., 2004), particularly when the standard-sample bracketing technique is used.

The issue of accuracy is well illustrated by the current debate in the literature concerning the Mg isotope composition of the Earth and chondrites. Wiechert and Halliday (2006) reported $^{26}Mg/^{24}Mg$ ratios in chondrites that were, on average, offset to lighter isotopic ratios by 0.15‰ compared to terrestrial samples, for an overall reported analytical precision of 0.1‰. In contrast, Teng et al. (2007) have reported $^{26}Mg/^{24}Mg$ ratios in basalts which have the same average value as chondrites, for an overall analytical precision of better than 0.1‰. Potentially both sets of data are correct, and the differences could be reconciled by real heterogeneities in natural samples. However, both groups analysed one common homogenous basaltic rock standard, BCR1 and San-Carlos olivine. The measurements of $^{26}Mg/^{24}Mg$ ratios are discordant by 0.24 and 0.62‰ for BCR1 (a fine powder standard) and the olivine respectively, which is significantly larger than the precision quoted by both studies. Such discrepancies make the interpretation of the chondrite and bulk Earth data rather difficult. This stumbling block may reflect the fact that it is possible to measure isotope ratios to a greater precision than they are accurate because of subtle differences in mass bias between sample and standard, using the bracketing method due to residual matrix after chemical purification of Mg. It also reflects the fact that there are currently no natural rock standards which have calibrated Mg isotope compositions, partly because no method existed to verify the data.

In this contribution, we evaluate the method of standard addition, as a potential method for determining both accurate and precise isotope data. Ca isotope ratios are frequently measured by double spike on TIMS instruments. Here we demonstrate the utility of the standard addition approach by comparing double spike measurements of seawater Ca isotope ratios to those obtained by standard addition by MC-ICP-MS. We then demonstrate that seawater Mg isotope ratios determined by the standard addition method are consistent with measurements using independent techniques in other laboratories. Finally, we extend the evaluation of the method to silicate rock material for Mg isotope ratios, and to river waters for Ca isotope ratios. This time-consuming technique cannot provide a definitive proof of the accuracy of the isotope data, but the consistency of the data for a range of terrestrial samples would be very difficult to generate as the result of an analytical artifact, particularly given the range of sample matrices considered. Our Mg isotope data on the basaltic rock standard BCR2 is in agreement with some previous studies, but in disagreement with other studies. Modeling of the standard addition method using an inverse Monte Carlo method, also provides an alternative method to robustly assess the full external precision.

2. Methods of testing accuracy

Previous work (Galy et al., 2001, 2002; Chang et al., 2003, 2004; Tipper et al., 2006a,b, 2008) has attempted to verify the accuracy of Mg and Ca data by processing "home made" synthetic standards (made using mono-elemental Mg and Ca of known isotopic composition, and

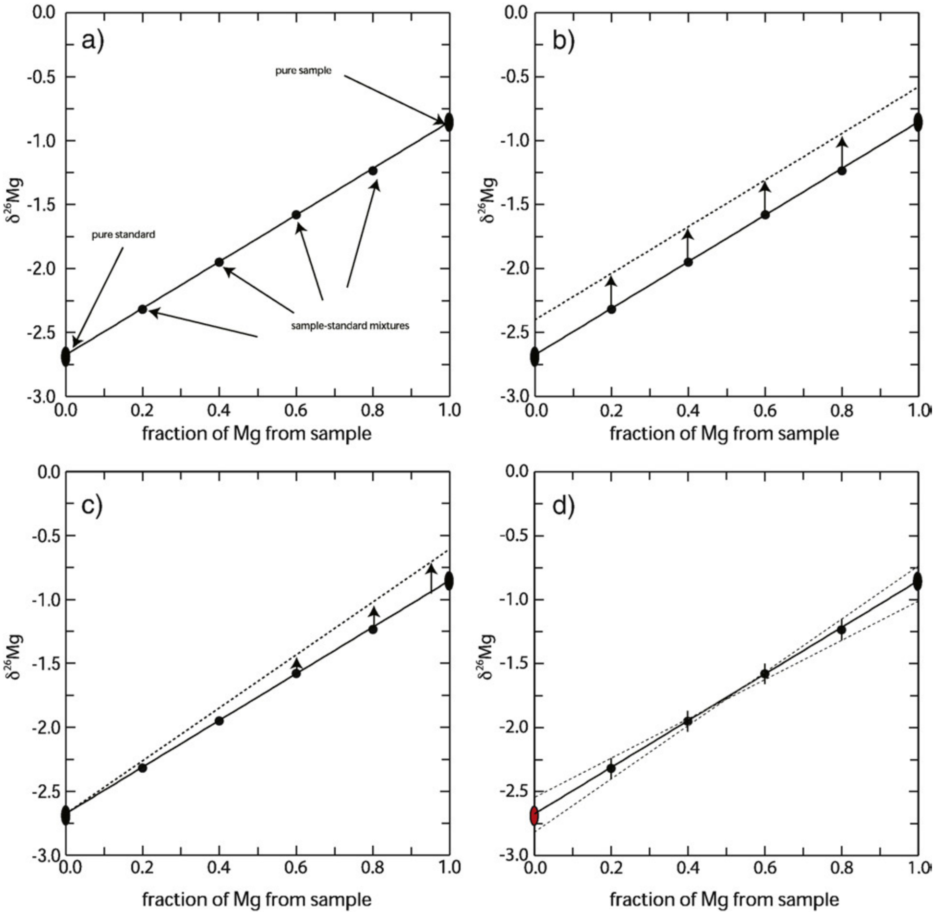

Fig. 1. Schematic example of how the standard addition method can be applied to isotope work, using Mg. a) The simple case where the method successfully works with four sample-standard mixtures defining a line which extrapolates through both the sample and the standard. b) Example of the predicted effect of a constant matrix effect of 0.5‰. c) Example of the anticipated effect of the diluted matrix effect, with the intercept for the standard having the correct isotopic composition, but the intercept for the sample having an incorrect value. d) Schematic geometrical construction of the uncertainty envelope, leading to an uncertainty on the extrapolated sample and standard values which is necessarily greater than the uncertainty on an individual data point.