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Proposal for an International Molybdenum Isotope Measurement Standard and Data Representation

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Abstract

Molybdenum isotopes are increasingly widely applied in Earth Sciences. They are primarily used to investigate the oxygenation of Earth's ocean and atmosphere. However, more and more fields of application are being developed; e.g. magmatic and hydrothermal processes, planetary sciences or the tracking of environmental pollution. Here we present a proposal for a unifying presentation of Mo isotope ratios in studies of mass dependent isotope fractionation. We suggest that the $\delta^{98/95}$Mo of the NIST SRM3134 be defined as +0.25‰. The rationale is that the vast majority of published data are presented relative to reference materials that are similar, but not identical, and that are all slightly lighter than NIST SRM3134. Our proposed data presentation allows a direct first order comparison of almost all old data with future work while referring to an international measurement standard. In particular, canonical $\delta^{98/95}$Mo values like +2.3‰ for seawater or -0.7‰ for marine Fe-Mn precipitates can be kept for discussion. As recent publications show that the mean ocean molybdenum isotope signature is homogeneous, the IAPSO ocean water standard or any other open ocean water sample is suggested as a secondary measurement standard, with a defined $\delta^{98/95}$Mo value of +2.34 ±0.10‰ (2SD).

The purpose of this short note is to propose an international agreement on notation for the reporting of stable Mo isotope data using the delta notation. Modern multiple collector inductively coupled plasma mass spectrometers (MC-ICP-MS) enable the investigation and application of Mo isotopes in geosciences since they are capable of measuring Mo isotope ratios to a precision of ≤ 0.1 ‰ (on the $^{98}Mo/^{95}Mo$ ratio). Basically two different measurement methods have been applied so far, both using MC-ICP-MS; firstly the double spike method and secondly the Zr doping method. Analytical protocols, sample purification methods and the mathematics for the different techniques, and from different laboratories, can be found in Greber et al., (2012) for the University of Bern and the University of Oxford, or in Goldberg et al. (2013) for Imperial College London, Arizona State University, the Open University and the University of Bristol (or citations within these publications). We recommend the reporting only of $\delta^{98/95}Mo$ values in future. Mo isotope ratios have been reported using the delta notation for two ratios, $\delta^{98/95}Mo$ and the $\delta^{97/95}Mo$. The $\delta^{97/95}Mo$ ratio can be transformed to the $\delta^{98/95}Mo$ ratio by multiplying by $^{3}/_{2}$, assuming a linear fractionation law. The bias resulting from the application of other fractionation laws (see Young et al. 2002) is insignificant given the measurement precision achieved to date.

Initiated by pioneering studies such as Barling et al. (2001), Siebert et al. (2003), Arnold et al. (2004), Poulson et al. (2006), Archer and Vance (2008), Neubert et al. (2008) and Pearce et al. (2008), most Mo isotope fractionation studies concern the past and present Mo cycle in surface environments, with the purpose of modelling the spatial extent of past ocean euxinia and the onset of oxidative weathering on Earth. However, the application of Mo isotopes has also been suggested recently in other scientific fields, such as the tracking of metal pollution (Chappaz et al., 2012; Lane et al., 2013), the investigation of core formation and in planetary sciences more generally (Burkhardt et al., 2012) as well as in the study of igneous and hydrothermal processes (Mathur et al., 2010; Greber et al., 2011). Therefore, increasing numbers of laboratories are starting to use Mo isotopes for their research. In the absence of a universally accepted international measurement standard, different groups report their data relative to their adopted in-house reference materials (RMs) with similar but not identical $\delta^{98/95}$Mo ratios (Goldberg et al., 2013).

Recent publications from Wen et al. (2010), Greber et al. (2012) and Goldberg et al. (2013) present $\delta^{98/95}$Mo values for the different RMs that have been used so far. Greber et al. (2012) showed that the NIST SRM 3134 is different from the laboratory RM used at the University of Bern (JMC Bern = -0.25‰; relative to NIST SRM 3134) and Oxford (Alfa Aesar = -0.12‰; relative to NIST SRM 3134). Goldberg et al., (2013) published the Mo isotope ratios of nine RMs currently in use, measured by four different laboratories. All these RMs have lighter $\delta^{98/95}$Mo than the NIST SRM 3134, ranging from -0.16‰ to -0.37‰ (relative to NIST SRM 3134). As a consequence it can be concluded that the vast majority of all data published so far have been normalized to a narrow range of values, all slightly below NIST SRM 3134. Rigorous comparison of results generated in different laboratories is of course only possible if an identical RM is used to present the $\delta^{98/95}$Mo values. However, if NIST SRM 3134 were set to be zero delta, it would require transposing all the already published data in order to make even a first order comparison with values obtained in the future and reported relative to NIST SRM 3134 = 0‰. According to Coplen, (2011) and Vogl et al. (2012) a specific δ value ($\delta \neq 0$) can be assigned to a reference material. Therefore we suggest setting the $\delta^{98/95}$Mo of the NIST SRM 3134 to +0.25‰. This would allow canonical values like +2.3‰ for seawater or -0.7‰ for marine Fe-Mn precipitates to be kept for discussion, and would facilitate the comparison of almost all old data with future work, with a reasonable level of precision.

Calculating $\delta^{98/95}$Mo relative to the NIST SRM 3134 = 0.25 ‰ can be done as follows:

$$\delta^{98/95}\mathrm{Mo} \, / \, ‰ = \left(\frac{(^{98}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{sample}}}{((^{98}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{NIST3134}} * 0.99975)} - 1 \right) * 1000 \quad (1)$$

The results of Greber et al. (2012), Goldberg et al. (2013) and Nakagawa et al. (2012) show that modern open ocean water is homogeneous within ±0.10 ‰ (2SD), irrespective of ocean basin or water depth. If the standardisation as suggested in this short note is applied, the $\delta^{98/95}$Mo of ocean water is therefore +2.34 ± 0.10‰ (2SD). Note that waters from restricted basins, as well as shallow shelf areas, may have different Mo isotope values (Nägler et al., 2011, Kowalski et al., 2013). However, IAPSO standard ocean water, or any sample from the open ocean, would serve as a good secondary measurement standard to check Mo purification and MC-ICP-MS performance.

As a consequence of the above, we propose NIST SRM 3134 to be the basis of a common standardization, with its $\delta^{98/95}$Mo value set at +0.25‰, and to use open ocean seawater (+2.34 ± 0.10‰; 2SD) as a secondary measurement standard, with the advantage of its being inexhaustible.

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