Development of highly precise molybdenum isotop analysis by negative thermal ionization mass spectrometry (N-TIMS) for the study of isotope anomalies in bulk meteorites

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Molybdenum is one of promising elements to investigate physical or chemical processes in various fields, including cosmochemistry. Improvements of techniques utilizing state-of-the-art mass spectrometry instruments over the last 15 years made it possible for detecting marginal mass-independent Mo isotopic fractionations (isotope anomalies) observed in extraterrestrial samples. The Mo isotope anomalies for various meteorites provide strong constrains on studies concerning environmental sciences, stellar nucleosynthesis, and the origin and evolution of the Solar System. For example, Mo isotope anomalies in bulk aliquot of meteorites indicated that the anomalies were originated from the heterogeneous distribution of presolar materials in the early Solar System [1]. However, previous studies predominantly focused on carbonaceous chondrites and iron meteorites; otherwise data for the other non-carbonaceous meteorites are limited because the degree of Mo isotope anomalies for these meteorites are only marginal and nearly equal to the analytical uncertainties of standard materials. Here we developed a new, highly precise, and accurate Mo isotope analysis by thermal ionization mass spectrometry in negative ionization mode (N-TIMS) for the study of Mo isotope anomalies in non-carbonaceous meteorites.
A Mo standard solution for atomic absorption spectrometry (Kanto Chem.) was used as an in-house standard. Iron meteorites (Tambo Quemado (IIIAB), Henbury (IIIAB), and Alibion (IVA)) were leached in 6 M HCl and digested with 16 M HNO_3–12 M HCl. After recovering solutions including Mo, the samples were dissolved in 0.4M HCl–0.5M HF to separate Mo by employing the anion exchange resin (Eichrom AG1-X8) through HCl–HF and HF–HNO_3 media [2]. Molybdenum isotopes (MoO^-) were measured by negative-TIMS using TRITON *plus* (Thermo-Fisher Scientific) installed at Tokyo Tech. The instrument was equipped with 9 Faraday cups with 10^{11} Ωamplifiers. Approximately 3 μg of Mo was loaded on a zone-refined Re filament together with $La(NO_3)_3$ as an activator (La/Mo ~5). The results were obtained by averaging 360 ratios collected in the static multicollection mode.
For achieving highly precise Mo isotope analysis, it is important to determe the oxygen isotopic composition of MoO_3 ions in each measurement by monitoring masses 149 ($^{100}Mo^{16}O_2{}^{17}O$) and 150 ($^{100}Mo^{16}O_2{}^{18}O$) ions and to use the data for correcting for the O isotope interferences. After correcting the O isotopic interference and performing mass-dependent fractionation during the TIMS measurement, the acquired Mo isotopic ratios yielded the following reproducibilities (2SD; n = 21): 47, 16, 10, 13, and 33 ppm for $^{92}Mo/^{96}Mo$, $^{94}Mo/^{96}Mo$, $^{95}Mo/^{96}Mo$, $^{97}Mo/^{96}Mo$,and $^{100}Mo/^{96}Mo$, respectively. The reproducibilities have been improved by 1.3–2.7 times compared tothose obtained in previous studies using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS).The accuracy of our technique was confirmed by measuring Mo isotopic compositions for two iron meteorites, i.e., Henbury (IIIAB) and Albion (IVA). Molybdenum isotope anoamlies for these meteorites are consistent with those obtained in the previous study [1]. Moreover, we determined positive Mo isotope anomalies for a new iron meteorite, Tambo Quemado (IIIAB). Our N-TIMS technique can be applied to the studies of nucleosynthetic isotope anomalies in extraterrestrial materials as well as mass-dependent Mo isotopic shift in environmental samples.
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[2] Nagai Y. and Yokoyama T. (2014) *Anal. Chem.*, *86*, 4856.

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