The isotopic composition and atomic weight of lanthanum

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Abstract

The isotopic composition of lanthanum has been measured with high precision using a thermal ionization mass spectrometer, equipped with a Daly collector, whose linearity was verified by measuring an isotopically certified reference material for potassium (NIST 985), whose isotopes span a wide range of isotope ratios. The abundance sensitivity of the mass spectrometer in the vicinity of the measured LaO^+ ion beams was examined to ensure the absence of tailing effects and interfering isotopes. The isotope fractionation of the lanthanum isotopes was estimated by reference to the isotopically certified reference material for lead (NIST 981) and the fractionation of oxygen isotopes determined from LaO^+ measurements. These procedures are essential because of the extremely low isotope abundance of ^{138}La. An accurate determination of the abundance of ^{138}La is required in order to calculate the atomic weight, and because it is the parent nuclide of two geochronometers, ^{138}La–^{138}Ba and ^{138}La–^{138}Ce. The magnitude of the rare odd–odd neutron-deficient isotope ^{138}La is a key nuclide in p-process nucleosynthetic calculations. The measured isotopic composition has been corrected for isotope fractionation to give $^{139}La/^{138}La = 1125 \pm 3$, which gives isotope abundances for ^{138}La of 0.000888 ± 0.000002 and ^{139}La of 0.999112 ± 0.000002. The isotope abundances and relative atomic masses of the two isotopes give an atomic weight of La of 138.905461 ± 0.000003.
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1. Introduction

Lanthanum has the lowest atomic number of all the rare earth elements, and consists of two isotopes ^{138}La and ^{139}La. Its name is derived from the Greek word "lanthanein" which means "to be hidden or to escape notice", because it "hid" in Ce ore and was difficult to separate from that rare earth mineral. In addition to the then known La isotope of mass 139 [1], a new isotope of mass 138 was discovered in 1947 [2]. Thermal ionization mass spectrometry (TIMS) was used to measure the isotopic composition of La by means of LaO^+ ions emitted from a La_2O_3 sample deposited on a W filament. The possibility of isobaric interferences from ^{138}Ba and ^{138}Ce was monitored, but no evidence of these nuclides was observed. Measurements of the linearity of the detector system showed a linear response to within 0.2%, and the authors

estimated that the sum of all the systematic errors were less than 1% [2]. The isotope abundances of La were measured to be $(0.089 \pm 0.001)\%$ for ^{138}La and $(99.911 \pm 0.001)\%$ for ^{139}La, to give a $^{139}La/^{138}La$ ratio of 1123 ± 12 [2]. ^{138}La is a member of three adjacent isobaric elements—^{138}Ba, ^{138}La and ^{138}Ce. According to Mattauch's rule of nuclear stability, which forbids the existence of three stable isobars whose atomic numbers differ by unity [3], it was suspected that ^{138}La was radioactive, though Inghram et al. [2] were unable to confirm this. However, the weak radioactivity of ^{138}La was demonstrated in 1950 [4]. In fact, ^{138}La decays by electron capture to ^{138}Ba and by beta decay to ^{138}Ce with a half-life of 1.1×10^{11} years [5].

In 1956, a two stage mass spectrometer with high abundance sensitivity was used to search for possible naturally occurring isotopes of low abundance in a number of elements, including La [6]. A solution of La_2O_3 in dilute HCl was deposited on a Ta filament in the ion source, and La^+ and LaO^+ peaks were observed. The La isotope ratio had to

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be corrected for an isobaric ^{138}Ba interference. The resulting ^{139}La/^{138}La ratio was 1120 ± 20, but it is neither clear as to the level of uncertainty quoted, nor whether the linearity of the mass spectrometer was evaluated [6]. No evidence of any other naturally occurring isotopes of La was observed.

In the 1980s, two geochronological decay schemes, based on ^{138}La as the parent nuclide, were developed. The first geochronometer involves the decay of ^{138}La to ^{138}Ce. Using this decay scheme, the age of a gabbro from the Bushveld, in South Africa was measured to be 2390 ± 480 Ma using a partial disintegration constant of 2.58×10^{-12} year^{-1} [7]. It was found that Ba was present as an isobaric interference at mass 138, so that the Ce isotope ratios were measured as the oxide to avoid this potential interference. Since La and Ce are both rare earth elements, this geochronometer can be used in combination with the Sm–Nd geochronometer in isotope geochemistry. Constraints on the use of the La–Ce geochronometer include an accurate knowledge of the beta decay disintegration constant, the low abundance of ^{138}La, and its long half-life [7]. The age of two Archaean granites from the Yilgarn craton in Western Australia were determined by the Rb–Sr, Sm–Nd and the U–Pb techniques. The three decay schemes gave ages, which were in good agreement. The beta decay disintegration constant for ^{138}La was calculated by assuming the La–Ce age was identical with the mean age determined by the other three decay schemes to give a value of $(2.33 \pm 0.24) \times 10^{-12}$ year^{-1} [8].

The second geochronometer involves the decay of ^{138}La to ^{138}Ba. Experimental constraints of this decay scheme are imposed by the low elemental abundance of the rare earth element La, the low isotope abundance of ^{138}La, and the relatively high abundance of ^{138}Ba. Despite these difficulties, minerals from the Amitsoq gneiss gave a metamorphic age of 2408 ± 24 Ma determined by the ^{138}La–^{138}Ba isochron technique using a half-life for the electron capture decay constant of 4.4×10^{-12} year^{-1} [9]. This age is in good agreement with that from Sm–Nd systematics on the same gneiss, of 2410 ± 54 Ma [9].

The emergence of these two geochronometers led to the re-measurement of the isotopic composition of La [10]. Johnson–Matthey La$_2$O$_3$ reagent was mounted in a VG-54-38 double focussing TIMS equipped with a Faraday cup. The abundance sensitivity of the instrument was more than adequate for the experiment [10]. The ^{139}LaO$^+$ ion beam was approximately 5×10^{-11} A, and the isotope fractionation was calculated by taking the sample to extinction. Cerium and Ba were monitored for possible isobaric interferences, but there were little interferences from these elements. Oxygen isotope ratios were determined using PrO$^+$ ions and these values were used to correct the measured LaO$^+$ ion beams. The ^{139}La/^{138}La ratio was determined to be 1108 ± 1 at the 2σ level [10]. In 1992, another determination of the isotopic composition of La was made in which the isotope fractionation of the raw LaO$^+$ ratios were estimated by normalising to the O isotopes, in order to detect small isotope shifts in this two isotope element [11]. A ^{139}La/^{138}La ratio of 1101 ± 1 at

the 2σ level was reported. The unusual nucleosynthetic origin of this odd–odd isotope makes it a good candidate to find evidence of early solar irradiation, and meteoritic material has been analysed to search for such proton or photon-induced effects, unfortunately without any positive results [12].

The "best" measurement of La from a single terrestrial source is given as ^{138}La $= 0.0009017 \pm 0.0000005$ and ^{139}La $= 0.9990983 \pm 0.0000005$ to give a ^{139}La/^{138}La ratio of 1108 ± 3 [13]. The "best" measurement for La bears the notation "N" in the Table of the Isotopic Compositions of the Elements, which implies that the selected measurement is neither a calibrated measurement, nor has it been demonstrated that linearity and isotope fractionation effects have been satisfactorily assessed [13]. The dilemma in assessing these mass spectrometric measurements is that the data fall into two distinct sets—an average ^{139}La/^{138}La ratio of 1122 ± 12 for [2,6], and an average of 1105 ± 1 for [10,11], with a "best" selected value of 1108 ± 3 [13].

Various nucleosynthetic scenarios have been proposed to account for the bulk p-process content of stellar nucleosynthesis, which produces the stable neutron-deficient nuclides heavier than Fe, and these mechanisms have recently been reviewed by Arnould and Coriely [14]. The odd–odd neutron-deficient heavy nuclide ^{138}La is among the rarest Solar System species but, in spite of its small abundance, ^{138}La is under-produced in all p-process calculations, so that an accurate knowledge of the isotope abundance of ^{138}La is required [14]. The under-production of ^{138}La in p-process calculations is due to the unfavourable balance between its main production by ^{139}La(γ,n) ^{138}La and its mass destruction by ^{138}La(γ,n) ^{137}La [14]. The present project has measured the isotopic composition of La using a VG 354 TIMS for which the linearity and abundance sensitivity have been confirmed, and the isotope fractionation estimated.

2. Experimental

2.1. Laboratory standard

A laboratory standard solution of La was prepared by dissolving spectroscopically pure La$_2$(CO$_3$)$_3$ (Johnson Matthey Chemicals Ltd., Laboratory Number G 51113) in ultrapure 1 M HCl. This solution had a concentration of 2000 μg La/g of solution, which enabled 10 μg of LaCl$_3$ to be loaded routinely for TIMS analysis on the two side filaments of a triple Re filament assembly. Large La metal and LaO$^+$ ion beams could be obtained using this ion source configuration. Unfortunately, small Ba ion beams were observed when La$^+$ ions were analysed, and despite attempts to remove this isobaric element, small traces were always present. A correction could be made for the ^{138}Ba in the measured mass 138 abundance using the measured ^{136,137}Ba ion beams, but in practice, the uncertainties introduced by this procedure mitigated against its use. Therefore the LaO$^+$ ion beams were used to measure the ^{139}La/^{138}La ratio where isobaric interferences were not detected. An adequate time