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An estimate of the Bulk Silicate Earth potassium isotopic composition based on MC-ICPMS measurements of basalts

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Abstract

We report a method for high-precision potassium isotope measurements that improves by an order of magnitude the precision compared to previous methods. The purification of K is achieved through ion exchange chromatography on AG50W-X8 cation exchange resins. The $^{41}K/^{39}K$ ratios are analyzed with a GV Instruments IsoProbe P Multiple-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) equipped with a hexapole collision gas cell. With this technique, the argon-hydride interferences as well as the large $^{40}Ar^+$ peak from the Ar-plasma are eliminated. The $^{41}K/^{39}K$ ratios can thus be obtained with a precision of 0.05 per mil. The precision and accuracy of this method is validated with gravimetrically determined ^{41}K or ^{39}K enriched standards. New precise K isotopic compositions of three terrestrial basalts (BCR-2, BHVO-1 and a MORB) are also reported. These basalts have indistinguishable K isotopic compositions and are used to define a reference value of -0.479 ± 0.027 per mil for the $^{41}K/^{39}K$ ratio of the Bulk Silicate Earth (BSE) relative to a Merck Suprapur potassium nitrate standard. Seawater and sylvites from evaporite deposits have similar $^{41}K/^{39}K$ ratios, but higher by up to 0.227 per mil compared to the Merck Suprapur standard. Other commercially available K-salts/solutions also have $^{41}K/^{39}K$ ratios similar to the Merck standard, while a SPEX K-chloride was higher by 0.384 per mil. This shows that K isotope variations will be useful as a tracer in low-temperature geochemistry processes.

1. INTRODUCTION

Terrestrial planets, such as the Earth, Moon, Mars and asteroid 4 Vesta, have long been known as depleted in volatile elements relative to CI meteorites and the bulk solar composition (Wasserburg et al., 1964). The cause of this volatile depletion in the inner Solar System is still not entirely known (*cf.* Humayun and Cassen, 2000; Halliday and Porcelli, 2001); it has been proposed to be related to processes such as the incomplete condensation of solar nebular materials or partial vaporization/condensation via giant impacts during the accretion stages of the Earth and other planetary bodies. Potassium is a moderately volatile element, and the ratio of K to a refractory element such as U has been used as a key index of this volatile depletion. For example, the K/U ratio in the silicate Earth (13,800; Arevalo et al., 2009) is fivefold depleted compared to that in CI chondrites (~70,000; Wasserburg et al., 1964; Anders and Grevesse, 1989); and the K/U ratio in the Moon (2500; Taylor, 1982) is even more than five times depleted relative to that in the silicate Earth. This depletion of K and other volatile elements is one of the fundamental characteristics of the bulk chemistry of the Earth, Moon and other inner solar system bodies (such as Mars, 4 Vesta and Angrite Parent Body); hence it should provide vital information regarding the accretion of the terrestrial planets and the Giant Impact origin of the Moon.

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Previously, Humayun and Clayton (1995a) first proposed to use the isotopes of potassium as a tool to study this volatile element depletion. The important questions such as the site and processes responsible for the loss of K and other volatile elements could potentially be answered by the isotopic fractionation of K isotopes associated with this loss. They predicted that a Rayleigh style partial evaporation would induce a large K isotope fractionation, however, no detectable K isotopic fractionation between terrestrial samples, lunar rocks and meteorites has been observed in their studies. These measurements of K isotopes were conducted on an ion microprobe and their best analytical uncertainty is 0.5 per mil for the $^{41}K/^{39}K$ ratio (Humayun and Clayton, 1995b). Potassium isotope studies with Thermal Ionization Mass Spectrometry (TIMS) instruments prior to Humayun and Clayton, have even larger uncertainties (>1 per mil; *e.g.*, Garner et al., 1975). Hence, it would be timely and necessary to re-examine the K isotopic data acquired with the ion microprobe or TIMS two decades ago, and to re-evaluate these potassium isotope measurements with the new generation of Multiple-Collector Inductively Coupled Plasma Mass Spectrometers (MC-ICP-MS). The measurements of K isotopes with ICP-MS have been challenging due to large argon-based interferences ($^{38}Ar^{1}H^{+}$ and $^{40}Ar^{1}H^{+}$) and the large $^{40}Ar^{+}$ peak of the Ar plasma. Basically two methods can be used to alleviate or eliminate this problem: (1) "cold plasma" method: reducing ArH^{+} ions in the plasmas by lower the RF generator power (Jiang et al., 1988; Morgan et al., 2014); and (2) "collision gas" method: dissociating the molecular ions by introducing a collisional gas (Feldmann et al., 1999a,b; Bourg et al., 2010; Richter et al., 2011, 2014). The "collision gas" method is used in this study.

Recent developments of isotopic studies for other volatile elements also suggest the need to revisit K isotopes. Chlorine and zinc are both moderately volatile elements like potassium; their 50% equilibrium condensation temperatures (T_c) at 10^{-4} bar from a solar composition gas are 948 K, 726 K and 1006 K, respectively (Lodders, 2003). Both Zn and Cl isotopes in lunar samples have been reported to be significantly enriched in heavy Zn and Cl isotopes (Sharp et al., 2010; Paniello et al., 2012), which conflicts with the result from previous K isotopes measurements. In addition, the deviations of Zn and Cl isotopes of lunar rocks from those of terrestrial samples are explained as either through a fractionation during a global vaporization event or during local volcanic degassing events. New and improved K isotope measurements are needed in order to reconcile these different explanations, and to compare to the current high-precision isotopic data of Zn and Cl.

Potassium is a lithophile and moderately volatile element in term of its geochemical and cosmochemical characteristics. Potassium is the eighth most abundant element in the Earth's crust and fifteenth in the bulk Earth. Potassium has only one oxidation state (+1) in silicate rocks. It has two stable isotopes ^{39}K (93.2581%) and ^{41}K (6.7302%), as well as one naturally occurring long half-life ($t_{1/2} = 1.277 \times 10^{9}$ years) radioactive isotope ^{40}K (0.0117%). This radioactive potassium, which generates heat as it decays to ^{40}Ca and ^{40}Ar, has long been recognized as one of the major sources (along with U and Th) of internal heating of the Earth (Urey, 1955). High-precision K–Ar and Ar–Ar dating techniques depend on accurate knowledge of the absolute abundance of ^{40}K (Naumenko et al., 2013). The ^{40}K abundance is potentially subjected to change if there is K isotope fractionation between different samples. Studying K isotopes is thus also very important in avoiding systematic inaccuracies in the determination of high (sub-per mille) precision ^{40}K–^{40}Ar–^{40}Ca ages.

Here we report a procedure for precisely and accurately measuring K isotopes in silicate rocks. We also report data on a few selected terrestrial samples to explore any possible isotopic fractionation of potassium, which has not been reported in the past.

2. ANALYTICAL METHODS

2.1. Sample description

Terrestrial samples studied here include two geostandards, the Columbia River continental flood basalt (BCR-2) and a tholeiitic basalt from the Kilauea crater of Hawaii (BHVO-1). These geostandards are prepared and distributed by the USGS (United States Geological Survey), and their petrography and geochemical compositions have been well studied and documented. We also analyzed a Mid-Ocean Ridge Basalt (MORB) from East Pacific Rise (CHEPR) (Langmuir, 1988). The sylvites used in this study are from Stassfurt, Germany and Carlsbad Potash District, New Mexico, USA. Pacific seawater was collected during the trans-Pacific sections (TPS) cruises (R/V Thomas Thompson) in the summer of 1985 at a depth of 400 m.

In addition to the natural samples, we have also analyzed a series of industrially produced potassium salts or solutions commercially available from companies such as Merck KGaA, Alfa Aesar, High-Purity Standards and SPEX CertiPrep. These potassium samples are widely accessible, and have been used in different laboratories. In order to compare data corrected with different potassium standards in different laboratories, we have thus analyzed these commercially available samples here in this study.

2.2. Sample preparation and chemical purification of potassium

All samples but the sylvites and seawater were digested with a CEM MARS 6 microwave digestion system. They were first dissolved in a concentrated $HF/HNO_3/HCl$ mixture (0.5 mL HF + 2 mL HNO_3 + 1 mL HCl) and then dried with heat lamps in an ultrapure nitrogen environment to remove HF. They were then digested again with diluted aqua regia (0.5 mL HNO_3 + 1.5 mL HCl + 1 mL H_2O). The microwave power was set up to 400 W in order to reach a temperature of 230 °C (20 min ramping time + 60 min holding time + 30 min cooling time). Sylvites (KCl) were directly dissolved in Milli-Q water and were centrifuged first before dried down. They were repeatedly dissolved in concentrated HNO_3 and dried down in order to remove chlorine.