Potassium stable isotopic compositions measured by high-resolution MC-ICP-MS

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Potassium stable isotopic ($^{41}K/^{39}K$) compositions are notoriously difficult to measure. TIMS measurements are hindered by variable fractionation patterns and too few isotopes to apply an internal spike method for instrumental mass fractionation corrections. Internal corrections via the $^{40}K/^{39}K$ ratio can provide precise values and are appropriate in some cases (e.g. identifying excess ^{41}K [1]) but not others (e.g., determining fractionation effects and metrologically-traceable isotopic abundances). SIMS analyses have yielded results with 0.25‰ precisions [2]. Previous studies have not resolved isotopic variation in terrestrial materials.

We measured $^{41}K/^{39}K$ ratios on NIST K standards with < 0.07‰ precisions (1σ) on the Thermo Scientific NEPTUNE *Plus* MC-ICP-MS. ^{39}K and ^{41}K were sufficiently resolved from the interfering $^{38}ArH^+$ and $^{40}ArH^+$ peaks in wet cold plasma and high-resolution mode. Measurements were made on narrow but flat, interference-free, plateaus (ca. 50 ppm by mass width for ^{41}K). Although ICP-MS does not yield accurate $^{41}K/^{39}K$ values due to significant instrumental mass fractionation (ca. 6%), this bias is sufficiently stable that relative $^{41}K/^{39}K$ values can be precisely determined via sample-standard bracketing. Measurement tolerances on matrix effects that are amplified by the cold plasma were tested; the use of clean samples and standards is critical.

On the Thermo Scientific TRITON TIMS, using a co-loaded Rb standard to normalize for fractionation, accurate but less precise $^{41}K/^{39}K$ ratios have been measured. Differences in $^{41}K/^{39}K$ between NIST K standards identified via MC-ICP-MS are also apparent in the TIMS data. Combined, these approaches yield more reliable K isotopic measurements than were previously possible and may allow for the identification for the first time of sub-permil terrestrial variations in $^{41}K/^{39}K$.

[1] Wielandt and Bizzarro, 2011. [2] Humayun and Clayton, 1995.

Diffusion of Helium in the mantle: an explanation for MORB-OIB patterns of 3He/4He ratios

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OIBs have a wide range of 3He/4He ratios, MORBs have a much narrower range peaked at 3He/4He ≈ 8 Ra. In addition, the ratio of 3He/20Ne (both stable isotopes) is significantly higher in MORB than in OIB, likewise the ratio of 4He/21Ne (both daughter isotopes produced by U and Th decay) are similarly higher in MORB than OIB. (Stable 3He/36Ar and radiogenic 4He/40Ar have the same pattern as the He/Ne plots, only with more scatter.) [See Honda and Patterson, GCA 63, 1999.] To explain this, we assume that rising mantle plumes are ‘lumpy’; a mixture that includes lumps of primordial mantle (which will be rich in 3He, 20Ne, 22Ne, 36Ar, etc.) as well as lumps containing the EM1, EM2, HIMU components, all in a general matrix of relatively-barren, previously-melted 'harzburgite'. When the rising lumps (plums) melt, the He, Ne, Ar, and most of the other incompatible elements will go into the melts that are known as OIB. But not all of the lumps melt (near the cooler edge, some don't rise shallow enough to pressure-release melt); those that don’t melt go into the asthenosphere, flowing horizontally away from the rising column. At a spreading center, this asthenosphere contributes the ‘plums’ left over from OIB partial melt-extraction but also some of the more barren matrix that the plums are embedded in becomes part of the melt because of the higher extents of partial melting that occur when making MORB. What is the effect of diffusion? If the helium, because of its small size, can diffuse a distance of 100 m or 1000 m in a billion-plus years (the ‘age’ of a lump) whereas neon or argon diffuse only decimeters or centimeters in this time because of their larger radii (i.e., not much more than non-noble incompatible elements like K, Rb, or U can diffuse), then the 3He and 4He (and H) can diffuse far out into the 'barren harzburgite' matrix. Thus when the lumps in a plume melt there will be a shortage of 3He and 4He relative to the 20Ne, 21Ne, or argon. With the extensive melting that occurs to make MORB, fluxing causes some of the barren matrix to contribute its 3He and 4He to the MORB melt which results in an excess of helium relative to neon and argon. This extraction of helium from the longtime-diffused-into barren matrix also can explain the uniformity of the 3/4 ratio in MORB as opposed to the variability of 3/4 in OIB.

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DOI:10.1180/minmag.2013.077.5.13