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

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ABSTRACT BODY: Potassium isotopic ($^{41}K/^{39}K$) compositions are notoriously difficult to measure. TIMS measurements are hindered by variable fractionation patterns throughout individual runs and too few isotopes to apply an internal spike method for instrumental mass fractionation corrections. Internal fractionation corrections via the $^{40}K/^{39}K$ ratio can provide precise values but assume identical $^{40}K/^{39}K$ ratios (e.g. 0.05‰ (1σ) in [1]); this is appropriate in some cases (e.g. identifying excess ^{41}K) but not others (e.g., determining mass fractionation effects and metrologically traceable isotopic abundances). SIMS analyses have yielded measurements with 0.25‰ precisions (1σ) [2]. ICP-MS analyses are significantly affected by interferences from molecular species such as $^{38}ArH^+$ and $^{40}ArH^+$ and instrument mass bias. Single collector ICP-MS instruments in “cold plasma” mode have yielded uncertainties as low as 2‰ (1σ, e.g. [3]). Although these precisions may be acceptable for some concentration determinations, they do not resolve isotopic variation in terrestrial materials.

Here we present data from a series of measurements made on the Thermo Scientific NEPTUNE *Plus* multi-collector ICP-MS that demonstrate the ability to make $^{41}K/^{39}K$ ratio measurements with 0.07‰ precisions (1σ). These data, collected on NIST K standards, indicate the potential for MC-ICP-MS measurements to look for K isotopic variations at the sub-permil level. The NEPTUNE *Plus* can sufficiently resolve ^{39}K and ^{41}K from the interfering $^{38}ArH^+$ and $^{40}ArH^+$ peaks in wet cold plasma and high-resolution mode. Measurements were made on small 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 can be sufficiently stable over the time required for several measurements so that relative $^{41}K/^{39}K$ values can be precisely determined via sample-standard bracketing. As cold plasma conditions can amplify matrix effects, experiments were conducted to test the matrix tolerance of measurements; the use of clean, matrix-matched samples and standards is critical. Limitations of the cold-plasma high-resolution MC-ICP-MS methodology with respect to matrix tolerance are discussed and compared with the limitations of TIMS methodologies.

References:
[1] Wielandt and Bizzarro, 2011. [2] Humayun and Clayton, 1995. [3] Murphy et al., 2002.

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