POTASSIUM ISOTOPE HETEROGENEITY WITHIN CHONDRITES.
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Introduction: When compared to the solar photosphere and CI chondrites, moderately volatile elements are fractionated in planetary bodies. Moderately volatile elements include sodium, potassium (K) and rubidium, which have 50% nebular condensation temperatures between 650 K and 1250 K [1]. Different mechanisms have been proposed to account for this fractionation, including nebular and planetary processes as well as initial disk heterogeneity [2],[3]. The isotope composition of moderately volatile elements in chondrites can provide insights into the origin of the fractionation of volatile elements in Solar System solids [3]–[5]. As an abundant and lithophile element with two stable isotopes ($^{39}$K and $^{41}$K), K is potentially an important tracer of moderately volatile element fractionation. However, measuring potassium isotopes has long been hindered by instrumental limitations [6] such as direct isobaric Ar-interference in plasma source mass spectrometers. Recent improvements of MC-ICP-MS and chemistry methods [7] have lowered the sample requirements for precise K isotope analysis, such that variations in K isotope composition under 0.5‰ became resolvable for sample sizes of a few µg K [3]–[5]. As a result, searching for small-scale potassium isotope variations in primitive meteorites has become technically feasible. Here, we report the K isotope composition of multiple individual aliquots of the Orgueil and Murchison chondrites using improved methods that allow for the determination of precise and accurate $^{41}$K/$^{39}$K ratios using only 1 µg of potassium, thus reducing chondritic sample size to only 2.5 mg.

Methods and Samples: We prepared six aliquots of 100 mg of both the CI1 Orgueil and CM2 Murchison meteorites of which ~2.5 mg were processed (~1 µg of K). We also processed variable amounts of pure Alfa Aesar potassium standard through the column chemistry to evaluate potential limitations on our potassium sample size due to blank contributions from the purification process and performed signal mismatch tests. Crushed samples were digested in a 28 M HF/7 M HNO$_3$ mixture (3:1) using Teflon Parr Bomb high-pressure digestion vessels at 210°C for two days. The chemical purification protocol utilized here was adapted from Chen et al.[7]. Total procedural blanks were kept under 20 ng and negligible. Isotope analyses were conducted using a ThermoFischer Neoma MC-ICP-MS equipped with an Apex ICR to reduce isobaric Ar-interference. The instrument was run with 900 W RF power and using the extra-high resolution slit allowing a mass resolving power of ~20,000 (M/ΔM). Samples were dissolved in 2% HNO$_3$ and, to further minimize the formation of ArH$^+$, we used D$_2$O water to make all analyte solutions. The instrument sensitivity using this setup corresponds to ~30 V/ppm at sample uptake rate of ~100 µl/min. Each analysis comprised 25 scans of 8 s integration and each sample was analyzed 3 times. The NIST SRM 3141a was used a bracketing standard.

Results: The six Orgueil digestions returned $\delta^{41}$K values ranging -0.135 ± 0.034‰ and -0.102 ± 0.039‰. At face value, these new data indicate that at the scale of the sampling performed here (~100 mg), no K isotope heterogeneity is present in Orgueil. This observation is inconsistent with a recent report [5] documenting $\delta^{41}$K variability between two Orgueil digestions using similar sample sizes although this apparent variability may reflect the external reproducibility of the technique utilized. Combining the six individual measurements returns a $\delta^{41}$K value of -0.114 ± 0.024‰ (2SD), which we infer represents the most robust estimate of the bulk K isotope composition of the Solar System. We note that this value is heavier than some earlier estimates [3] that range from -0.239 ± 0.030‰ to -0.154 ± 0.038‰. However, given that our results demonstrate the lack of K isotope heterogeneity in Orgueil, we interpret the lighter composition reported earlier as reflecting a terrestrial contamination. In contrast to Orgueil, the six Murchison digestions return distinct compositions with $\delta^{41}$K values ranging from -0.079 ± 0.058‰ to 0.156 ± 0.043‰, establishing the presence of K isotope heterogeneity in Murchison at the scale of our sampling. The lighter estimate of -0.079 ± 0.058‰ is within error of the Orgueil average, indicating that the K isotope composition of this Murchison aliquot is dominated by a CI-like matrix component. In contrast, the heavier composition may be attributed to the incorporation of high temperature refractory components, which have experienced evaporative loss of K and, hence, are enriched in heavy K.