K ISOTOPE SYSTEMATICS OF INDIVIDUAL CHONDRULES FROM THE LL4 CHONDRITE HAMLET

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Introduction: Understanding the distribution and behavior of volatile elements in the early solar system has become a fundamental field of study for understanding how our solar system formed. Of the volatile elements, the group classified as the moderately volatile elements (MVEs) based on their 50% Tc (condensation temperatures at 10^{-4} bar pressure) of between 665 K and 1335 K [1], have proven to be significant as they possess the optimal volatility for recording many early solar system processes. Potassium, which is classified as a MVE with a 50% Tc of 1006 K [1], is one such element, yet until recently the isotope systematics of K were unable to be explored with the same precision as the other MVEs due to restrictions imposed by analysis techniques. Within the last few years however, technical advancements have been developed which allow us to now measure K isotopes with a precision greater than 0.5 per mil [2,3,4,5].

One significant area of study which we are now able to explore using K isotopes is the formation of chondrules. The ideal volatility of K could result in K isotopes recording key evaporation or condensation events which occurred in the early solar system. Previous attempts have been made to analyze the K isotopic compositions of individual chondrules using SIMS [6], however due to precision constraints their results were somewhat inconclusive. Nevertheless, it was shown that the chondrules of the LL3.0 chondrite Semarkona showed a wide range of δ^{41}K, ranging from −9.5 ‰ to 17.8 ‰ [6]. More recently bulk chondrite analysis has been conducted using a technique similar to that used in this study [7]. They found a range of δ^{41}K much more constrained than that found in the individual chondrules of Semarkona, with all LL ordinary chondrites showing bulk δ^{41}K range from −1.5 to −0.4 ‰.

In order to further investigate the K isotope systematics of chondrules from ordinary chondrites we have conducted K isotopic analysis on chondrules from the LL4 chondrite Hamlet. This sample is a "fall" that was recovered immediately, thus limiting any terrestrial contamination or alteration.

Methods: Analysis was conducted on a total of nineteen fractions (all between 1-15 mg), consisting of fifteen chondrule fractions (made up of fourteen individual chondrules in total, with the largest chondrule being split into two fractions), two matrix fractions, and two bulk fractions. Each fraction was rinsed in MQ H_2O before being subjected to dissolution in concentrated HF and HNO_3 at a 3:1 ratio. Once complete dissolution was achieved, 5% of each fraction was taken for elemental analysis using a Thermo Fisher iCAP Q ICP-MS at Washington University in St. Louis. The remaining 95% underwent K separation by means of a double pass column chemistry procedure using Bio-Rad AG50W-X8 100-200 mesh cation exchange resin where 0.5 M HNO_3 was used as the elution liquid. Potassium isotopic analyses were conducted using the Neptune *Plus* MC-ICP-MS at Washington University in St. Louis. The standard used in this study was SRM 3141a and the total procedure K blank was 12 ng.

Results: As shown in Fig. 1-3 the δ^{41}K for all Hamlet samples lie between −1.36 to −0.24 ‰. This range is an order of magnitude less than the δ^{41}K measured *in situ* for chondrules in the LL3.0 Semarkona [6] and essentially the same as the overall range seen in all 8 LL bluk ordinary chondrites [7]. The K concentrations of the Hamlet chondrules range from 0.73 wt% to 1.90 wt%. For comparison, the Hamlet matrix fractions both have K concentrations of 1.05 wt%, while the bulk fractions have 1.06 and 1.24 wt% K.

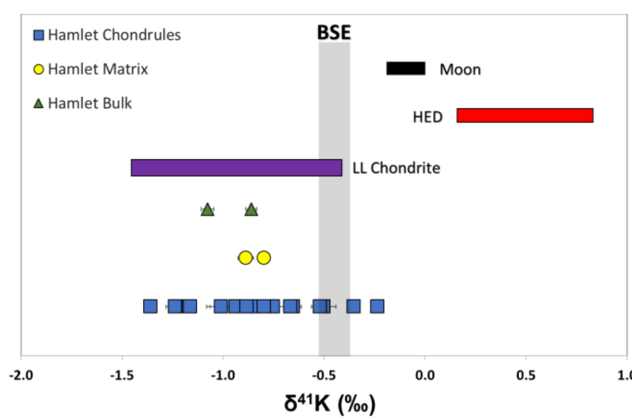

Figure 1. *K isotopic compositions of Hamlet chondrules, matrix and bulk comparted to bulk analysis of relevant materials. LL Chondrite = bulk LL ordinary chondrite range, HED = bulk howardite–eucrite–diogenite group range, BSE = the bulk silicate Earth δ^{41}K value. Comparison data taken from [2,7,8]*

A plot of δ^{41}K vs K_2O depletion (Fig.2) suggests a trend but shows no strong correlation between K concentration and K isotopes. Although not shown here, there is also no strong correlation between the chondrule K isotopic compositions and K/Ca, indicating cosmogenic ^{41}Ca decay is unlikely to be the primary cause of the chondrule δ^{41}K variations. Nevertheless as seen in Fig.3, there is a strong correlation between the mass/size of the chondrule and its δ^{41}K, with the heavier/larger chondrules displaying heavier δ^{41}K.

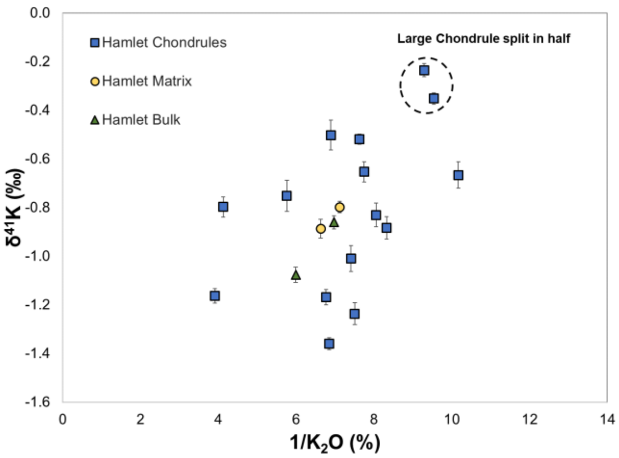

Figure 2. δ^{41}K vs 1/K_2O (representing K depletion) for all Hamlet chondrules, matrix and bulk fractions.

Discussion: A comparison of the K isotope data from this study with the *in situ* chondrule data [6] suggests that while chondrules from LL chondrites may exhibit significant internal variability, their overall isotopic variation is within ~1 ‰. Yet, the largest chondrule analyzed in this study was split into two separate fractions to check for chondrule homogeneity and the difference between the two is only ~0.1‰. The large overall range difference seen between the *in situ* Semarkona chondrule data and the bulk Hamlet chondrule data could be caused by the presence of rims as they would be expected to mask isotopic variations and would be more pronounced in the smaller chondrules (the rims are likely present in many bulk analyses but can be avoided *in situ*). Another possible cause of this discrepancy is the petrologic type of the two meteorites, as Semarkona is a LL3.0 while Hamlet is a LL4 [6]. This could result in some of the initial K isotope variability present in the Hamlet chondrules being subsequently masked by the post formation processing. Nevertheless, the correlation between chondrule mass and δ^{41}K indicates that the initial K isotopic composition in the chondrules was not completely overprinted. A third possible cause of the K isotope discrepancy between the two LL chondrites is that the large δ^{41}K range of Semarkona is simply an analytical artifact as having been proposed by [6]. In order to investigate this further we plan to analyze chondrules from chondrites as close to 3.0 as possible in the future.

A strong correlation between chondrule mass and δ^{41}K shows that the heavier, and thus larger chondrules have isotopically heavier K, suggesting that the larger chondrules experienced a longer period of heating and thus lost more K to evaporation. This explanation is supported by the chondrule shock wave formation model proposed by [9]. According to this model, the larger chondrules experienced more frictional heating after their formation as they took longer to accelerate (due to drag) to the velocity of the shockwave. As a result, the larger chondrules would experience more evaporative loss of K causing them to exhibit heavier δ^{41}K values. Nonetheless, it would be expected that the larger chondrules would also be depleted in K resulting in a correlation between K depletion and δ^{41}K. While it could be argued that there is a slight trend (The largest chondrule is also one of the most depleted in K), it is likely that this trend is being masked by other factors, such as later rim additions (described in [9]) and chemical and mineralogical heterogeneities between chondrules.

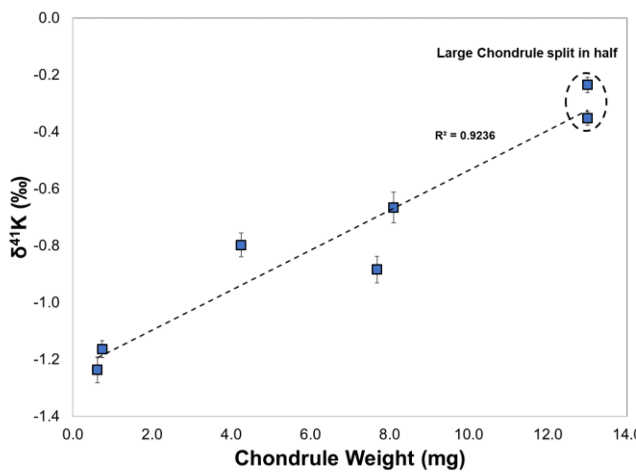

Figure 3. *δ^{41}K vs chondrule weight for selected chondrules. Only chondrules where the full intact chondrule could be weighed were selected. All other chondrules analyzed in this study were chondrule fragments.*

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