K ISOTOPE SYSTEMATICS OF INDIVIDUAL CHONDRULES FROM THE UNEQUILIBRATED ORDINARY CHONDRITES QUE 97008, GRO 95658, GRO 95539 AND MET 00452 P. Koefoed[1,2] and K.Wang (王昆)[1,2] [1]McDonnell Center for the Space Sciences, [2]Department of Earth and Planetary Sciences, Washington University in St. Louis, One Brookings Drive, St. Louis, MO 63130 USA (piers.koefoed@wustl.edu).

Introduction: Chondrites and their namesake component chondrules are some of the oldest and most primitive solids from within our solar system. As such, chondrules are fundamental to understanding how our solar system formed. Nevertheless, the process of chondrule formation is still debated. Key to resolving this long-standing question is understanding the distribution and behavior of volatile elements in the early solar system. 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. Yet until recently the significant MVE potassium, with a 50% Tc of 1006 K [1], was unable to be isotopically explored at high-precision 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].

In respect to 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 K isotopic analysis of individual chondrules from type 3 chondrules (Semarkona and Bishunpur) have been conducted by SIMS [6,7], Nevertheless due to precision constraints and possible analytical artifacts the results were somewhat inconclusive. More recently bulk chondrite and individual chondrule analysis have been conducted using a technique similar to that used in this study [8,9]. These studies found a δ^{41}K range significantly more constrained than that found in the SIMS studies. Additionally, the chondrules from the LL4 chondrite Hamlet showed a correlation between δ^{41}K and chondrule weight, with the larger chondrules showing heavier K isotopic compositions [9].

In order to further investigate the formation of chondrules using K isotopes, the K isotopic systematics of chondrules from the Antarctic ordinary chondrites QUE 97008 (L3.05), GRO 95658 (LL3.2/3.4), GRO 95539 (LL3.1), and MET 00452 (L(LL)3.05) are investigated here.

Methods: Analysis was conducted on a total of thirty-five fractions, consisting of twenty-eight chondrule fractions (between ~1 to ~24 mg) and seven bulk fractions (~60 to ~100 mg each). Of the thirty-five fractions analyzed, sixteen were on QUE 97008 (fourteen chondrule and two bulk), ten on GRO 95658 (eight chondrule and two bulk), five on GRO 95539 (three chondrule and two bulk) and four on MET 00452 (three chondrule and one bulk). Each fraction was subjected to dissolution in concentrated HF and HNO_3 at a 3:1 ratio. Once complete dissolution was achieved, 10% of each chondrule fraction and 5% of each bulk fraction was taken for elemental analysis using a Thermo Fisher iCAP Q ICP-MS at Washington University in St. Louis. The remaining material 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 15 ng.

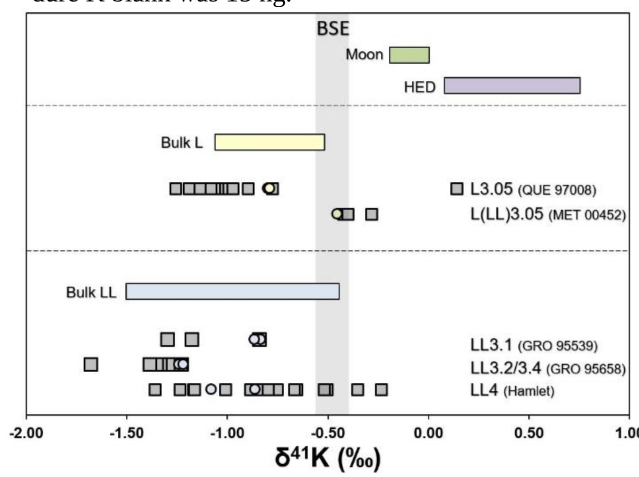

Figure 1. *K isotopic compositions of L and LL chondrules and bulk compared to bulk analysis of relevant materials. Grey squares represent chondrules while colored circles represent bulks for each individual chondrite. For clarity errors are not shown. Bulk L = bulk LL ordinary chondrite range, Bulk LL = 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 [2,8,9]*

Results: As shown in Fig. 1 the δ^{41}K for all chondrule samples measured here lie between −1.68 to 0.14 ‰. This range is significantly less than the δ^{41}K seen in chondrules measured *in situ* by SIMS (−15.5 to 17.8 ‰) [6, 7], but similar to the range seen in the Hamlet chondrules measured by MC-ICP-MS (−1.36 to −0.24 ‰) [9]. The K concentrations of all chondrules from all four ordinary chondrites measured here range from 60 ppm to 2378 ppm. For comparison, all the bulk fractions analyzed here have K concentrations ranging from 674 ppm to 1127 ppm.

The four chondrites show overall similar δ^{41}K values amongst their chondrules, however they are not identical. QUE 97008 shows a δ^{41}K range from −1.26 to 0.14 ‰ (excluding the one outlier the range is from −1.26 to −0.78 ‰), GRO 95658 has a δ^{41}K range from −1.68 to −1.22 ‰, GRO 95539 shows a δ^{41}K range from −1.30 to −0.84 ‰, while MET 00452 chondrules range from −0.42 to −0.28 δ^{41}K.

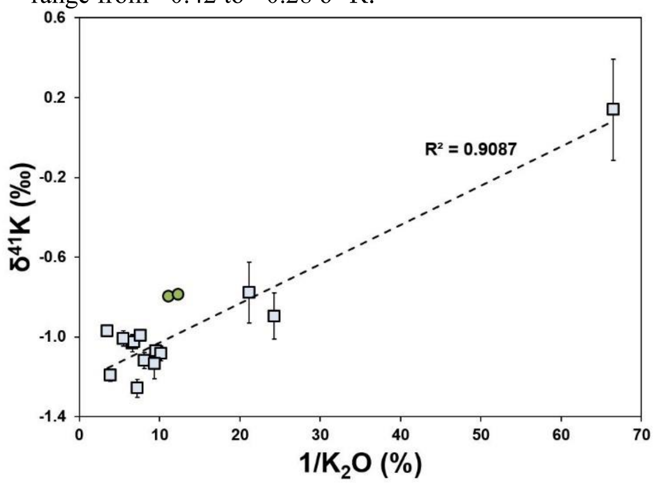

Figure 2. *δ^{41}K vs 1/K_2O (representing K depletion) for all QUE 97008 chondrules and bulk fractions. errors shown are 95% C.I.*

A plot of δ^{41}K vs K_2O depletion (Fig.2) for QUE 97008 shows a significant correlation between K concentration and K isotopes. Nevertheless, this correlation is anchored by only three chondrules, with the other eleven chondrules clustered together. Although not shown here, there is no strong correlation observed between the chondrule K isotopic compositions and K_2O depletion for the other three chondrites. Nevertheless, for GRO 95539 and MET 00452 this could be due to the small sample size (n=3), while for GRO 95658, there is almost no δ^{41}K variation observed at all between the chondrules. Interestingly QUE 97008 also shows limited variation among chondrule δ^{41}K values and K concentrations with the exception of three chondrules. So, it may be the case that chondrules such as these have just not yet been analyzed for GRO 95658.

Discussion: A comparison of the K isotope data from this study with the previous chondrule data show that these MC-ICP-MS analyses agree much closer with the previous MC-ICP-MS on chondrules and chondrites than with the *in situ* SIMS data. Nevertheless, as seen in Fig. 1 the chondrules measured here show a general lower overall spread than the LL4 Hamlet chondrule data from [9]. QUE 97008 does show an overall greater range than Hamlet, however the total δ^{41}K range of the QUE 97008 chondrules is largely dictated by a single point.

Another significant difference between QUE 97008 and Hamlet is that QUE 97008 shows no correlation between δ^{41}K and chondrule weight (Fig. 3). In contrast, Hamlet showed a striking correlation between these two parameters, with larger chondrules showing heavier K isotopic values. This may signify that the cause of this correlation in Hamlet is due to secondary effects rather than chondrule formation processes.

Mostly intriguingly, QUE 97008 does show a trend between δ^{41}K and K_2O depletion suggesting that chondrules did experience K isotopic fractionation during K loss, likely during evaporation processes. This systematic K isotopic fractionation is consistent with evaporation experiments [10], however under non-Rayleigh conditions.

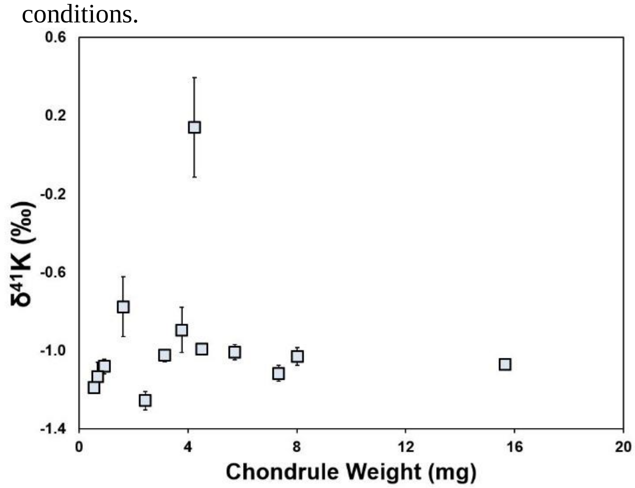

Figure 3. *δ^{41}K vs chondrule weight for QUE 97008 chondrules. errors shown are 95% C.I.*

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