REEVALUATION OF CALCIUM-41 IN CM AND CV REFRACTORY INCLUSIONS Ming-Chang Liu[1], Kevin D. McKeegan[1], Andrew M. Davis[2] and Trevor R. Ireland[3] [1]Department of Earth and Space Sciences, UCLA, Los Angeles, CA 90095 (mcliu@ess.ucla.edu), [2]Department of the Geophysical Sciences, Enrico Fermi Institute, and Chicago Center for Cosmochemistry, University of Chicago, Chicago, IL 60637, [3]Research School of Earth Sciences, ANU, Canberra, ACT, Australia.

Introduction: ^{41}Ca is of importance in early solar system chronology as it provides a strict constraint regarding the time span between nucleosynthesis and preservation in refractory solids due to its extremely short half-life (~0.1 My). Its presence is detected through excesses of radiogenic ^{41}K as first demonstrated by Srinivasan and colleagues [1,2] in Efremovka CAIs. Using a small geometry CAMECA 4f ion microprobe, these workers found that the degree of ^{41}K excess correlated with the ^{40}Ca/^{39}K ratio, yielding an initial ^{41}Ca/^{40}Ca~1.4×10^{-8}. The existence of ^{41}Ca in the solar system, if it came from a stellar source, implies a very short timescale for transit and incorporation. On the other hand, ^{41}Ca can also be made locally by irradiation, although the physical conditions that produce ^{41}Ca~$1.4\times10^{-8}\times{}^{40}$Ca would lead to underproduction of ^{26}Al by a factor of 10 compared to the canonical level [3]. Interestingly, ^{41}Ca was soon discovered to be correlated with the presence or absence of ^{26}Al in CM hibonite grains [4], implying ^{26}Al and ^{41}Ca were derived from a common stellar origin. The absence of short-lived ^{41}Ca and ^{26}Al in some platy hibonite crystals has been interpreted as due to a late injection of these isotopes into the solar nebula, after formation of the hibonite [4−7].

Based on the existing correlation of ^{41}Ca with ^{26}Al found by [4,6], McKeegan et al. [8] suggested that the initial ^{41}Ca abundance in the early solar system could have been significantly higher (potentially up to ~$4\times10^{-7}\times{}^{40}$Ca) if the true initial ^{26}Al abundance of the solar nebula was "supracanonical" [9].

Despite its importance for understanding early solar system chronology, the ^{41}Ca abundance in CAIs has never been quantitatively confirmed at other laboratories. Promising results were obtained with the SHRIMP-RG ion microprobe at Stanford University [10], however systematic uncertainties in the mass spectrometry (corrections for doubly ionized species and for peak-tailing) precluded a definitive answer regarding the level of ^{41}Ca in E44. Here we report results of potassium isotope measurements in CM hibonite and the E44 CAI using the UCLA CAMECA IMS 1270 ion probe and we confirm the presence of ^{41}Ca in early solar system materials.

Experimental: The isotopic compositions of potassium in both CM hibonite (6 PLAty hibonite Crystals "PLACs", 2 Spinel-HIBonite spherules "SHIBs" and one Blue AGgregate "BAG") and a piece of E44 CAI were determined by adopting the procedure of [2] with some modifications. Polished, epoxy-mounted samples were sputtered with a 22.5 KeV $^{16}O^{-}$ primary beam with an intensity of ~4 nA to generate sufficient count rates on Ca and K isotopes. Secondary ions were collected in a peak-jumping mode under the mass resolution (M/ΔM) of ~7000, which enables us to well separate ^{40}CaH from ^{41}K as well as some minor interferences from the peaks of interest. However, another major interference at mass 41, $(^{40}Ca^{42}Ca)^{++}$, was still unresolvable from ^{41}K so that its magnitude had to be assessed indirectly. For this, we followed the approach from [11] and [2], assuming the equality holds:

$$\frac{\left({}^{40}Ca\,{}^{42}Ca\right)^{++}}{{}^{42}Ca^{+}} = \frac{\left({}^{40}Ca\,{}^{43}Ca\right)^{++}}{{}^{43}Ca^{+}},$$

where the $(^{40}Ca^{43}Ca)^{++}$ signal can found at m/e=41.5. In most cases, this peak was hard to locate due to its extremely low intensity (<1 cps); therefore, its position was determined by setting a reference peak of $(^{40}Ca^{27}Al^{16}O)^{++}$, which is 9 mamu heavier than $(^{40}Ca^{43}Ca)^{++}$. It is extremely important that this correction be made accurately since the contribution of $(^{40}Ca^{42}Ca)^{++}$ comprises 1−80% of total ^{41}K signal depending on K abundance. In addition to $(^{40}Ca^{42}Ca)^{++}$, special efforts were also made to evaluate the contribution of scattered ions from $^{40}Ca^{+}$ and $^{40}CaH^{+}$ tails at mass 41. The former was monitored by setting a series of analyses at the masses between ^{40}Ca and ^{41}K. Scattered ^{40}Ca ions on ^{41}K were then estimated at the level of ~$1\times10^{-10}\times{}^{40}$Ca by extrapolating signals to mass 41. The latter was assessed by obtaining the count rate at mass 41.95 and applying the following relationship:

$$\left[{}^{40}CaH\right]_{tail} = \frac{[41.95]}{\left[{}^{42}Ca^{+}\right]} \times \left[\left({}^{40}CaH\right)^{+}\right]$$

This contribution of $(^{40}CaH)_{tail}$ to ^{41}K was found to be on the order of ~ $2.3\times10^{-5}\times{}^{40}$CaH and corrected for. In general, this correction is relatively minor (<1%) compared to that of $(^{40}Ca^{42}Ca)^{++}$ as ^{40}CaH signal was suppressed by the use of liquid nitrogen. The dynamic background of the counting system was also measured overnight when analyses were not performed. It was found within the range of 0.003 and 0.007 counts per second. The true ^{41}K/^{39}K in a sample can be calculated after stripping off these interferences:

$$\left[\frac{{}^{41}K}{{}^{39}K}\right]_{true} = \left[\frac{{}^{41}K}{{}^{39}K}\right]_{measured} - \left[\frac{\left({}^{40}Ca\,{}^{43}Ca\right)^{++}}{{}^{43}Ca} \times \frac{{}^{42}Ca}{{}^{39}K}\right] - \frac{\left[{}^{40}CaH\right]_{tail}}{{}^{39}K}$$

Secondary ions were counted by the axial ion counter with the mass sequence of 38.8, ^{39}K, ^{41}K,

$^{40}CaH^+$, $^{40}Ca^{43}Ca^{++}$, $^{40}Ca^{27}Al^{16}O^{++}$, ^{42}Ca and ^{43}Ca. In addition to 10−15 minute presputtering to minimize surface K contaminations, a field aperture was also introduced to filter out scattered K ions from the vicinity. Counting times on ^{39}K, ^{41}K and $^{40}Ca^{43}Ca^{++}$ were adjusted on the basis of their intensities for achieving enough counting statistics. ^{40}CaH, $^{40}Ca^{27}Al^{16}O^{++}$, ^{42}Ca and ^{43}Ca were typically counted for 10 seconds or less. Each measurement consists of 60−100 cycles; the total duration ranges from 1.5 to 3.5 hours. Charging corrections and mass calibration were performed every 5 cycles automatically to compensate the drifts during a long analysis. A series of terrestrial standards with a wide range of Ca/K ratios were analyzed to ensure the K mass spectrometry was properly functional. All measured $^{41}K/^{39}K$ ratios were normalized to the terrestrial reference ($^{41}K/^{39}K$=0.072). Even though ^{40}K was not measured, the finding of "normal" $^{41}K/^{39}K$ within errors throughout all the terrestrial standards was indicative of a small instrumental mass fractionation, which is negligible for the determination of ^{41}K excesses in extraterrestrial samples. In addition, the measured ratios of $^{42}Ca/^{43}Ca$ in standards were very close to the terrestrial value ($^{40}Ca/^{44}Ca$=47.153, $^{42}Ca/^{44}Ca$=0.31221, $^{43}Ca/^{44}Ca$=0.06486 [12]), implying a minor instrumental fractionation of Ca (~1−2 ‰/amu) and insignificant Sr interferences at masses 42 and 43. Therefore, the true $^{40}Ca/^{39}K$ ratio of the measured phase is calculated with $^{40}Ca/^{39}K=^{42}Ca/^{39}K\times^{40}Ca/^{42}Ca$. A relative sensitivity factor of 2.28–2.31 between Ca and K in an ion microprobe was determined by comparison to the NBS 614 glass with known Ca and K concentrations (CaO=12 wt% and K=30 ppm).

Result and Dicusssion: All measured K isotopic ratios in the samples were subject to variable amount of corrections for $(^{40}Ca^{42}Ca)^{++}$, ranging from 1 to 80%. Corrections for $^{40}CaH_{tail}$ were insignificant (<0.1%) due to high mass resolution and the use of liquid nitrogen. CM hibonite, regardless of their morphological type, did not exhibit any resolvable ^{41}K excesses. In three PLAC samples (Mur-P2, Mur-P7 and Mur-P9), wherein K was extremely depleted ($^{40}Ca/^{39}K$ up to 1.2×10^7, 4.8×10^7 and 1.7×10^7, respectively), only an upper limit of $^{41}K/^{39}K$ ratios could be obtained. This indicated that the measured signal at mass 41 was all coming from $(^{40}Ca^{42}Ca)^{++}$ and a fraction of $^{40}CaH_{tail}$. Our result in PLAC samples agrees with the study of [4]; whereas large analytical uncertainties in our measurements and the lack of sufficient fractionation of Ca from K in SHIBs prevented us from revealing any radiogenic potassium. On the other hand, large radiogenic $^{41}K^*$ excesses were found in two of the nine measurements in pyroxene of the E44 CAI; one of which showed a $\delta^{41}K$ enrichment of 8400‰ relative to the terrestrial reference and $^{40}Ca/^{39}K$ of 3.8×10^7, yielding an inferred initial $^{41}Ca/^{40}Ca$~1.5×10^{-8}, which is in perfect agreement with the result from [2], and the other point indicated a model $^{41}Ca/^{40}Ca$ ratio of 7×10^{-9} (Fig 1). The remainders broadly overlapped the terrestrial value within errors, regardless of $^{40}Ca/^{39}K$ ratios, except for two points which could have possibly been due to overcorrection of $(^{40}Ca^{42}Ca)^{++}$.

Our results show that PLACs and one BAG are devoid of both ^{41}Ca and ^{26}Al, indicating that these two isotopes were both lacking in the early solar system for a period of time, most likely prior to the formation of CAIs because of the presence of $\Delta^{26}Mg^*$ deficits in some of the PLACs [13]. This fits into the late injection model [5,7] well; however, the absence of ^{41}Ca in spinel-hibonite spherules, in which ^{26}Al is present at the canonical level, still prevents us from testing the relationship quantitatively.

On the contrary, $^{41}Ca/^{40}Ca$ ratio of 1.5×10^{-8} in the E44 CAI was confirmed in one pyroxene spot. We still have no evidence of a higher initial ^{41}Ca and more K-isotope studies in CAIs that reveal "supracanonical" ^{26}Al abundances are certainly needed. Nevertheless, if 1.5×10^{-8} is truly the solar system initial, the other well-resolved point, which yields a lower apparent $^{41}Ca/^{40}Ca$ of ~0.7×10^{-8}, could have been due to isotopic resetting ~0.1 My after the CAI formed.

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