CALCICUM-41 REVISITED: DEVELOPMENT OF POTASSIUM ISOTOPE MASS SPECTROMETRY ON CAMECA 1280HR2.
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Introduction: Amongst the short-lived radionuclides whose prior existence has been inferred in meteoritic components, ^{41}Ca plays a crucial role in understanding the timescale between its nucleosynthesis and incorporation into the oldest Solar System solids because of its extremely short half-life (~ 0.1 Myr). The initial abundance of ^{41}Ca relative to ^{40}Ca in the solar nebula was found to be ~1.4×10^{-8}, as first demonstrated by [1-2] through the detection of large excesses of radiogenic ^{41}K in Efremovka CAIs. Combined with nucleosynthesis models, such a low abundance implies that the timescale for the transit from the nucleosynthetic site of ^{41}Ca to the solar nebula should be less than 2 Myr. Soon after the initial discovery, ^{41}Ca was also found to be correlated with the presence or absence of another short-lived radionuclide ^{26}Al in CM hibonite grains, implying that ^{41}Ca and ^{26}Al could have a common stellar origin [3-5]. However, neither the initial ^{41}Ca/^{40}Ca ratio nor the correlation between ^{41}Ca and ^{26}Al has been independently confirmed by other laboratories. Several attempts made by [6-8] failed to provide a conclusive answer for the level of ^{41}Ca/^{40}Ca, primarily due to large systematic uncertainties in the mass spectrometry (corrections for doubly ionized species and for peak tailing). In this study, we propose to use the latest generation of large geometry ion microprobe CAMECA 1280HR2, newly installed at CRPG, Nancy, to reinvestigate the initial abundance and distribution of ^{41}Ca in meteoritic refractory inclusions.

Mass Spectrometry and results: The mass spectrometry for potassium isotope measurements on the CRPG ims-1280HR2 is still under development. The major advantage of 1280HR2 over previous generations of large geometry ion microprobes (e.g., ims-1270) is that 1280HR2 has better corrections for aberrations. This allows users to obtain a similar sharpness of the slit image with a slightly larger entrance slit width, which improves transmission. Several important factors of the instrument that have crucial impacts on the accuracy of ^{41}Ca/^{40}Ca determination have been carefully characterized. The tailing effect of ^{40}Ca at mass 41 (scattered ^{40}Ca ions on ^{41}K) was measured by setting a series of analyses between mass 40 and 41, and was found to be about a few tenth of ppb under the mass resolution (M/ΔM) of 7500. The contribution of the ^{40}CaH^{+} tail at mass 41 was estimated to be around $2\times10^{-5}\times{}^{40}$CaH^{+} by obtaining the count rate at mass 41.95 and assuming the following relationship:

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

The dynamic background of the counting system was also measured overnight when analyses were not performed, and is within the range of 0.003 to 0.009 counts per second. One parameter, which requires special attentions in every measurement, is the $({}^{40}\mathrm{Ca}{}^{43}\mathrm{Ca})^{++}/{}^{43}\mathrm{Ca}^{+}$ ratio. It is used to assess the magnitude of the unresolvable interference $({}^{40}\mathrm{Ca}{}^{42}\mathrm{Ca})^{++}$ at mass 41 by assuming the validity of the following relationship:

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

In the phases where ^{41}Ca/^{40}Ca could be inferred (i.e., fassaite), the high ^{40}Ca/^{39}K ratio (> 1×10^{6}) would result in that >80% of the signal measured at mass 41 is derived from $({}^{40}\mathrm{Ca}{}^{42}\mathrm{Ca})^{++}$. Therefore, having an accurate assessment of $({}^{40}\mathrm{Ca}{}^{42}\mathrm{Ca})^{++}$, i.e., a good measurement of $({}^{40}\mathrm{Ca}{}^{43}\mathrm{Ca})^{++}$, is critical for accurate determinations of ^{41}Ca/^{40}Ca. Unfortunately, this is the most challenging part as the intensity of $({}^{40}\mathrm{Ca}{}^{43}\mathrm{Ca})^{++}$ is always less than 1 count per second. This challenge could be slightly eased by the higher transmission of 1280HR2 achieved by slightly opening the entrance slit. After stripping off the aforementioned interferences, we could deduce the true ^{41}K ($\left[{}^{41}\mathrm{K}\right]_{t}^{+}$) signal of a sample:

$$\left[{}^{41}\mathrm{K}\right]_{\mathrm{t}}^{+} = [41]_{\mathrm{m}}^{+} - \left[{}^{40}\mathrm{Ca}{}^{42}\mathrm{Ca}\right]^{2+} - \left[{}^{40}\mathrm{CaH}\right]_{\mathrm{tail}} - \mathrm{bkgd}$$

We analyzed three terrestrial calcite standards to test if the correct ^{41}K/^{39}K ratio could be obtained in high Ca/K phases with our mass spectrometry. The polished samples were sputtered with a 10 nA ^{16}O^{-} primary beam, and the secondary ions were collected with the axial electron multiplier. Before analysis, 15-min presputtering was applied to the sample surface to remove contaminations. The level of ^{40}CaH was significantly suppressed by using liquid nitrogen. Charging compensation was monitored every 10 cycles. Each spot required ~4-5 hours of analysis time.

The results are summarized in Figure 1. The terrestrial ^{41}K/^{39}K ratio (0.072) was reproduced within errors in all three calcite standards, whose ^{40}Ca/^{39}K spans from 10^{5} to 10^{7}. That spots with the highest ^{40}Ca/^{39}K show slightly elevated ^{41}K/^{39}K ratios probably implies incomplete stripping of $({}^{40}\mathrm{Ca}{}^{42}\mathrm{Ca})^{++}$. Nevertheless, the mass spectrometry developed on the CRPG 1280HR2 appears to be able to correct for interferences effectively. We will perform K isotope analysis in standards with even higher Ca/K (>10^8) first, then in real meteoritic CAIs. Some preliminary results hopefully can be reported in the conference.

References: [1] Srinivasan et al. (1994) *ApJL*, **431**, 67−70 [2] Srinivasasn et al. (1996) *GCA*, **60**, 1823−1835 [3] Sahijpal et al. (1998) *Nature*, **391**, 559−562 [4] Sahijpal et al. (1998) *ApJL*, **509** 137−140 [5] Sahijpal et al. (2000) *GCA*, **64**, 1989−2005 [6] Ireland et al. (1999) *MAPS*, **34**, A57 [7] Ito et al. (2006) *MAPS*, 1871-1882 [8] Liu et al. (2008) *LPS*, 39, #1895 (abstract)

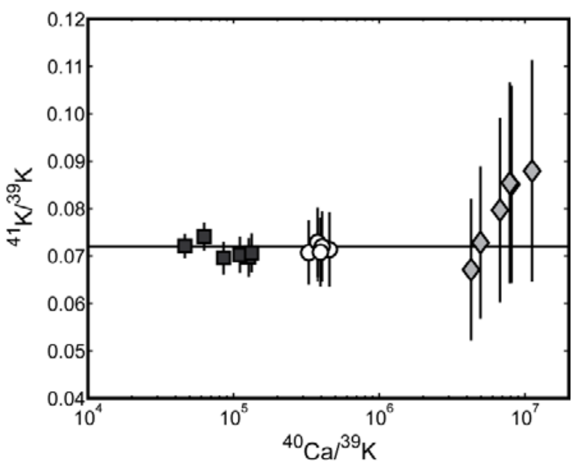

Figure 1. Results of K isotopic compositions in terrestrial calcite standards.