A DEVIL IN THE DETAILS: MATRIX-DEPENDENT $^{40}Ca^{42}Ca^{++}/^{42}Ca^{+}$ AND ITS EFFECTS ON ESTIMATES OF THE INITIAL $^{41}Ca/^{40}Ca$ IN THE SOLAR SYSTEM.

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The first hints of the former presence of the short-lived radionuclide ^{41}Ca ($t_{½}$ = 0.1 Ma) in CAIs were found by Huneke et al. at Caltech in 1981 [1]. Soon after, Ian Hutcheon piloted the PANURGE ion probe (ims-3f) and careful analyses confirmed that excesses of ^{41}K (= $^{41}K^{*}$) were spatially correlated with the Ca/K ratio in pyroxene and plagioclase from two Allende CAIs that implied an initial $^{41}Ca/^{40}Ca \sim 5\times10^{-8}$ at isotopic closure [2]. Possibilities for the development of dual Ca-K and Al-Mg chronologies and attendant constraints on the timescales of injection of fresh nucleosynthetic matter into the early solar system were immediately recognized [2, hereafter HAW84].

Although still in the very early days of SIMS, HAW were fully cognizant of the difficulties of recognizing and correcting for molecular ion interferences in the mass spectrum, a problem which can be severe when count rates of the isotope of interest are exceedingly low as they are for K^{+} in CAIs where typically [K] < 200 ppb. Although singly charged molecular ions comprised of abundant lighter elements are easily separated at moderately high mass resolution, the doubly charged dimer $^{40}Ca^{42}Ca^{++}$ is unresolvable from $^{41}K^{+}$ at any available mass resolution (then or now). This interference is particularly pernicious because its magnitude relative to ^{41}K correlates with the Ca/K ratio, thus failure to accurately correct for it will appear as $^{41}K^{*}$ attributable to the extinct parent isotope, ^{41}Ca.

The first quantitative evaluation of the fraction of $^{40}Ca^{42}Ca^{++}$ in the total signal at mass 41 was performed on a terrestrial calcite ([K] < 50 ppb) by HAW84. By assuming the yield of $^{40}Ca^{42}Ca^{++}/^{42}Ca^{+}$ from calcite is the same as that from fassaite, the data seemed to confirm the previous hint of live ^{41}Ca. However, Hutcheon was not satisfied and further investigation soon revealed that the yield of doubly-charged species is strongly matrix dependent: the ratio of $^{40}Ca^{43}Ca^{++}$ to $^{43}Ca^{+}$ (approximately equal to $^{40}Ca^{42}Ca^{++}$ to $^{42}Ca^{+}$) in fassaite is 10 times that in calcite [3]. Applying the yield from calcite to fassaite led to an undercorrection for the magnitude of $^{40}Ca^{42}Ca^{++}$ at mass 41 and thus an overestimation of initial $^{41}Ca/^{40}Ca$. With proper corrections for $^{40}Ca^{42}Ca^{++}$, HAW84b [3] revised the initial $^{41}Ca/^{40}Ca$ value down to $(8\pm3)\times10^{-9}$ with Hutcheon's admonition to SIMS practitioners to "beware of the double-cross".

That $^{40}Ca^{42}Ca^{++}/^{42}Ca^{+}$ strongly depends on the matrix has been confirmed by later studies [4] including those with large-radius SIMS instruments [5,6]. The higher throughput of ims 1270/1280 SIMS enables the measurement of $^{40}Ca^{43}Ca^{++}/^{43}Ca^{+}$ for every spot analyzed in meteoritic samples [5,6], as opposed to stand-alone characterizations of this ratio on terrestrial standards [3,4]. The more robust determination of the $^{40}Ca^{42}Ca^{++}$ interference has helped improve the accuracy of $^{41}K^{*}$ estimates, as matrix effects between terrestrial standards and phases in CAIs have been quantified [5,6]. Data on various refractory phases yield inferred $^{41}Ca/^{40}Ca = 4\times10^{-9}$ which is the best representative of the initial $^{41}Ca/^{40}Ca$ value in the Solar System [5,6] and is within error of that found by Hutcheon and colleagues 31 years ago.

Ref: [1] Huneke et al. 1981, LPSC XXII, 381. [2] Hutcheon et al. 1984, LPSC XXIV, 387. [3] Hutcheon et al. 1984, MAPS, 19, 243. [4] Srinivasan et al. 1996, GCA, 60, 1823. [5] Ito et al. 2006, MAPS, 41, 1871. [6] Liu et al. 2012, ApJ, 761, 137.