POTASSIUM AND CALCIUM IN LUNAR IMPACT SPHERULES. J. Levine[1,2], R. A. Muller[1,3], P. R. Renne[4,5], and R. A. Rohde[1], [1]Department of Physics, University of California, Berkeley, California 94720, USA, [2]Presently at Chicago Center for Cosmochemistry and Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, USA (jlevine@geosci.uchicago.edu), [3]Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA, [4]Berkeley Geochronology Center, 2455 Ridge Road, Berkeley, California 94709, USA, [5]Department of Earth and Planetary Science, University of California, Berkeley 94720, USA.

Introduction: We have used the $^{40}Ar/^{39}Ar$ isochron method to determine the formation ages of 81 impact spherules from Apollo 12 soil 12023 [1] and 109 spherules from Apollo 14 soil 14163 [2,3]. In addition to their geochronological significance, measurements of argon isotopes released by stepwise laser heating permit the identification and examination of cosmogenic and implanted ^{38}Ar and ^{36}Ar, which we report in a companion abstract [4]. Moreover, we are able to probe the abundance and distribution of potassium and calcium in lunar spherules, using the unstable isotopes ^{39}Ar and ^{37}Ar. Here we report inferred Ca/K ratios for individual spherules as a function of their formation ages, and we show that nearly all spherules are chemically zoned. The latter observation is especially important for constraining models of spherule formation, not only for the fact that spherules are chemically heterogeneous, but also for the sense of the zoning: spherules routinely show relatively potassic rims surrounding more calcic cores.

Method: $^{40}Ar/^{39}Ar$ dating [5] demands that specimens be irradiated by fast neutrons to transmute a fraction of the ^{39}K in the sample to ^{39}Ar. Samples are co-irradiated with a standard of known age to monitor the neutron fluence, allowing one to calculate the fraction of ^{39}K targets which are transmuted by the $^{39}K(n,p)^{39}Ar$ reaction. Fast neutrons also initiate the reaction $^{40}Ca(n,\alpha)^{37}Ar$, and the cross sections for these two reactions are of similar magnitude. Because both ^{37}Ar (35 days) and ^{39}Ar (269 years) are radioactive with short half lives, it is usually acceptable to neglect any pre-irradiation endowment of these isotopes. Once small corrections are made for interferences from the reactions $^{42}Ca(n,\alpha)^{39}Ar$ and $^{39}K(n,nd)^{37}Ar$, the quantities of ^{37}Ar and ^{39}Ar released by laser heating are directly related to the abundances of their respective parent nuclides ^{40}Ca and ^{39}K.

Integrated Ca/K Ratios: In Fig. 1, we show the Ca/K ratios that we infer for the spherules of [1] and [2]. The Ca/K ratios of Apollo 12 spherules are distributed toward larger values than those of Apollo 14 spherules, in keeping with the generally lower potassium content observed among rocks and soils at the Apollo 12 landing site [6]. The fact that spherules are chemically similar to local source materials was used by [2] to argue that spherules are typically formed by nearby impacts. As in [7], we find that glass is compositionally more akin to local rocks than to local bulk soils.

Ca/K ratios of spherules with ages <500 Ma reach much higher values than those of older spherules. The reason for this remains unclear, as most events in lunar history which might have affected the Ca/K ratios of spherule source materials (such as mare volcanism, exhumation of KREEP material, etc.) occurred long before 500 Ma. However, chemical fractionation of Ca from K, which accompanies soil formation [7], may be ongoing. The last 500 Ma may also be different from earlier periods because of the recent increase in meteoroid bombardment inferred by [2,8,9,10]. Apart from seeking the explanation for higher Ca/K ratios in Moon-wide events and processes, we must also consider possible local effects at the Apollo 12 and, to a lesser extent, the Apollo 14 landing sites [11].

Ca and K Distributions Within Spherules: Nearly all spherules released argon with lower $^{37}Ar/^{39}Ar$ early in the heating program and higher $^{37}Ar/^{39}Ar$ later. Figs. 2 and 3 illustrate this behavior for Apollo 12 and Apollo 14 spherules, respectively.

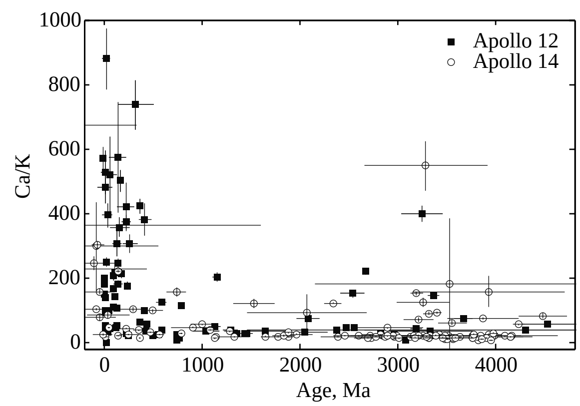

Fig. 1. Ca/K ratios inferred for Apollo 12 (filled squares) and Apollo 14 (open circles) spherules, calculated from total releases of ^{37}Ar and ^{39}Ar. Data are shown as a function of formation age [1,2,3]. Error bars represent 1σ.

This behavior cannot be explained by mass-dependent fractionation of argon isotopes during step heating of the specimens, because we observe the heavier isotope released earlier than the lighter one. Instead, it must be that regions within the spherules that are degassed first are richer in K, while regions richer in Ca are degassed later. The simplest explanation for this behavior is that spherules are chemically zoned, with relatively calcic interiors mantled by relatively potassic rims.

If spherules quenched from melt droplets that were chemically uniform, then we would expect the outer surface to become depleted in K by preferential evaporation of volatile elements from the melt [12]. The fact that the spherules appear to be zoned in the opposite sense may suggest that, rather than freezing from melt, most spherules condense from impact vapor, with refractory elements condensing first. Alternatively, spherules may grow around unmelted Ca-rich clasts (which, for the spherules dated in [1,2] must have been degassed of their argon, even though they are not chemically assimilated). In this scenario, spherules could not have been above their melting temperatures for more than ~1 minute, or they would become chemically well mixed by diffusion. It is also possible that the relatively abundant K arises from tiny grains welded to spherule surfaces, rather than from the spherules themselves.

It would be interesting to obtain in situ Ca/K ratios, along with the distribution of other elements, in sectioned spherules. Scanning electron microscopy and/or microprobe analyses from core to rim would distinguish among the above hypotheses of spherule formation, by identifying chemically distinct clasts, for example.

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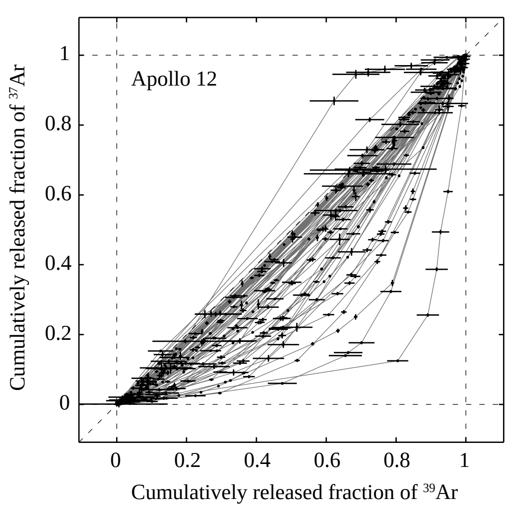

Fig. 2. Cumulative fractional releases of ^{37}Ar and ^{39}Ar from Apollo 12 spherules. The "tracks" of most spherules lie below the diagonal dashed line, indicating earlier release of K-derived ^{39}Ar followed by later release of Ca-derived ^{37}Ar. Error bars denote 1σ.

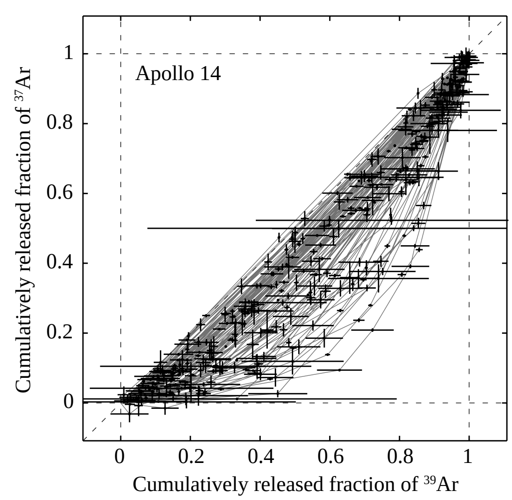

Fig. 3. As in Fig. 2, but for Apollo 14 spherules.