

K-Ca AND Rb-Sr DATING OF LUNAR GRANITE 14321 REVISITED. J. I. Simon¹, C.-Y. Shih², and L. E. Nyquist¹, ¹NASA Johnson Space Center, Houston, TX 77058 (Justin.I.Simon@NASA.gov), ²JE-23 Jacobs Technology/ESCG, P.O. Box 58477, Houston, TX 77058.

Introduction: K-Ca and Rb-Sr age determinations were made for a bulk feldspar-rich portion of an Apollo rock fragment of the pristine lunar granite clast (14321,1062), an acid-leached split of the sample, and the leachate. K-Ca and Rb-Sr data were also obtained for a whole rock sample of Apollo ferroan anorthosite (FAN, 15415). The recent detection [1] of widespread intermediate composition plagioclase indicates that the generation of a diversity of evolved lunar magmas maybe more common and therefore more important to our understanding of crust formation than previously believed. Our new data strengthen the K-Ca and Rb-Sr internal isochrons of the well-studied Apollo sample 14321 [2], which along with a renewed effort to study evolved lunar magmas will provide an improved understanding of the petrogenetic history of evolved rocks on the Moon.

Methods: The lunar samples were spiked with ⁴⁰K-⁴⁸Ca and ⁸⁷Rb-⁸⁴Sr mixed spikes prior to acid digestion. K+Rb, Sr and Ca were separated from each other using cation exchange columns (AG 50Wx8, 200-400 mesh). The K+Rb fractions were purified further using a second clean-up column to remove coelutants Mg and Fe. The Sr fractions were passed through a Sr-spec clean-up column. The chemical procedures for Ca collection reflect a combination of those described by [2] and [3]. Ion inhibition is a problem for the high K/Ca samples and the remaining Ca cuts will benefit from further purification and re-analyses.

The new K, Ca, Rb, and Sr data were obtained on a Thermo Finnigan Triton TIMS instrument. Standard mass spectrometry procedures for Sr were used. Rb and K measurements were run sequentially on the same filament and Ca analyses follow methods developed by [3]. The K abundances in samples were calculated from their ⁴⁰K/⁴¹K ratios, normalized to ³⁹K/⁴¹K = 13.9448. A mean ⁴⁰K/⁴¹K value of 0.001739±7 (2 sd, n=8) was obtained for the NBS985 K standard mixed with the Rb standard NBS984. The Ca abundances in samples were calculated from their ⁴⁸Ca/⁴⁴Ca ratios, normalized to ⁴²Ca/⁴⁴Ca = 0.31221 [4]. An average value of ⁴⁰Ca/⁴⁴Ca = 47.160±5 (2 sd, n=8) was obtained for SRM915a and used to correct the sample ⁴⁰Ca/⁴⁴Ca values accordingly based on the UC Berkeley value of 47.153 [3], cf. [5]. The Rb abundances in samples were calculated from the ⁸⁷Rb/⁸⁵Rb ratios, normalized to the average ⁸⁵Rb/⁸⁷Rb value of 2.6036±77 (2 sd, n=9) for NBS984 mixed with the K standard. The Sr abundances in samples were calculated from their ⁸⁴Sr/⁸⁶Sr ratios, normalized to ⁸⁸Sr/⁸⁶Sr

= 8.37521 and corrected to ⁸⁷Sr/⁸⁶Sr = 0.710250, accordingly based on the measured average ⁸⁷Sr/⁸⁶Sr value = 0.710238±10 (2 sd, n=10). Uncertainties of elemental concentrations largely reflect weighing errors for individual samples and uncertainty in spiking.

Results: Granitic material processed in this study was derived from several small chips originally characterized by [6]. The initial sample handling was done and described by [2]. In order to increase the spread in the K-Ca and Rb-Sr isochrons reported by [2], we processed an additional 2.9 mg aliquant of the feldspar-rich bulk rock (14321 FR), 4.15 mg of acid-washed residues of the sample (14321 FR.r), and a 0.7 mg leachate derived from the washing (14321 FR.l). A split of 15415 was also characterized to allow direct comparison to the initial Ca and Sr compositions of pristine lunar highland rocks.

New K-Ca data for a rock fragment and leachate along with previously reported data [2] for mineral separates and several fragments of the granite clast 14321 are shown in Fig. 1. These data correspond to an isochron age of 4031±74 Ma (2 se, MSWD=0.24, n=7, for $\lambda(^{40}\text{K})=0.5543 \text{ Ga}^{-1}$) with an initial ⁴⁰Ca/⁴⁴Ca = 47.163±12 (2 se). This age is within error of the previously reported K-Ca age of 4059±120 Ma (2 se, MSWD=0.07, n=5). Fig. 2 contains new Rb-Sr data that along with previously reported Rb-Sr data [7] collectively correspond to an isochron age of 4052±81 Ma (2 se, MSWD=1.3, n=8, for $\lambda(^{87}\text{Rb}) = 0.01402 \text{ Ga}^{-1}$) with a relatively imprecise initial ⁸⁷Sr/⁸⁶Sr = 0.7021±65 (2 se). This age is within error of the previously reported Rb-Sr age of 4055±110 Ma (2 se, MSWD=1.8, n=6). The primitive FAN 15415 yields a ⁴⁰Ca/⁴⁴Ca value of 47.145±6 (2 se) that is within error of the initial value accepted for Earth and other differentiated planetary objects [3, 4], but slightly lower than the mean lunar value of 47.155±2 (2 se, n=7) reported by [2]. An estimate for the initial ⁸⁷Sr/⁸⁶Sr value of the ancient lunar highlands based on Apollo FAN sample 15415 yields a value of 0.699251±10 that is consistent with the previously reported value of 0.69925 by (8).

Discussion: Granite 14321 is one of the youngest and most evolved silicic rocks collected from the Moon (6). It has been dated previously by Sm-Nd, Ar/Ar (7), and U-Pb (zircon) methods (9). As expected the precision of the K-Ca and Rb-Sr ages has been improved. Both new ages are slightly younger than previously reported. These ages are now within error of the existing mean U-Pb zircon age (3965±50 Ma).

The total release Ar/Ar age of a feldspar-enriched split of 14321 yields a slightly younger age of 3.88 ± 0.03 Ga (2 se). The concordancy of K-Ca, Rb-Sr, Sm-Nd internal isochrons and (now) the U-Pb model age strongly indicate that the granite formed ~ 4000 Ma ago. The apparent Ar/Ar age suggests that it was brecciated and excavated from near the surface about 100 Ma later.

The initial Ca isotopic ratio provides a constraint on the K/Ca ratio of the source of 14321 (Fig. 3). Using the measured composition of 15415 (this study) or a combination of this and previous estimates for the initial $^{40}\text{Ca}/^{44}\text{Ca}$ of the Moon (2), a more precise estimate for K/Ca of ~ 0.7 is determined. This value is significantly higher than previous estimates and largely due to the new low K/Ca 14321 FR.1 datum near the origin in the K-Ca isochron (Fig. 1). This calculated mean K/Ca value is well above the upper range for the values (0.2-0.3) found in known lunar quartz monzoniorites, e.g., (10) and suggests that 14321 (that has an K/Ca value of ~ 5) was probably generated from an earlier episode of intermediate magmatism.

References: [1] Greenhagen, B.T. *et al.*, *Science* **329**, 1507 (2010). [2] Shih, C.-Y. *et al.*, *GCA* **57**, 4827 (1993). [3] Simon, J. I. *et al.*, *ApJ* **702**, 707 (2009). [4] Russell, W. A. *et al.*, *GCA* **42**, 1075 (1978). [5] Caro, G., *et al.*, *EPSL* **296**, 124 (2010). [6] Warren, P. H., *et al.*, *EPSL* **64**, 175 (1983). [7] Shih, C.-Y. *et al.*, *GCA* **49**, 411 (1985). [8] Tatsumoto, M. *et al.*, *The Apollo 15 lunar samples*, 391 (1972). [9] Meyer, C. *et al.*, *MPS* **31**, 370 (1996). [10] Ryder, G. *EPSL* **29**, 255 (1976). [11] Ludwig, K.R. *Isoplot A Geochronological Toolkit for Microsoft Excel* (2003).

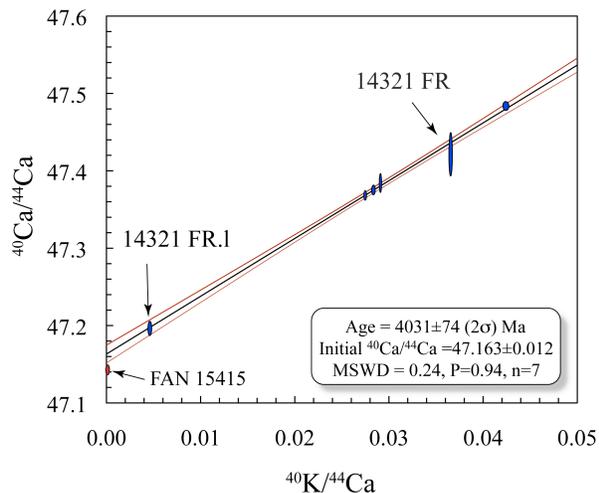


Figure 1. K-Ca internal isochron for lunar granitic clast 14321,1062. New feldspar-rich bulk and sample-leachate data (this study) are combined with two bulk samples and 3 color-sorted mineral separates (2). The isochron age and initial $^{40}\text{Ca}/^{44}\text{Ca}$ ratio are calculated using Isoplot (11). The error envelope represents the 95% confidence interval of the regression. The bulk

measurement of FAN 15415 is representative of primitive lunar highland rocks.

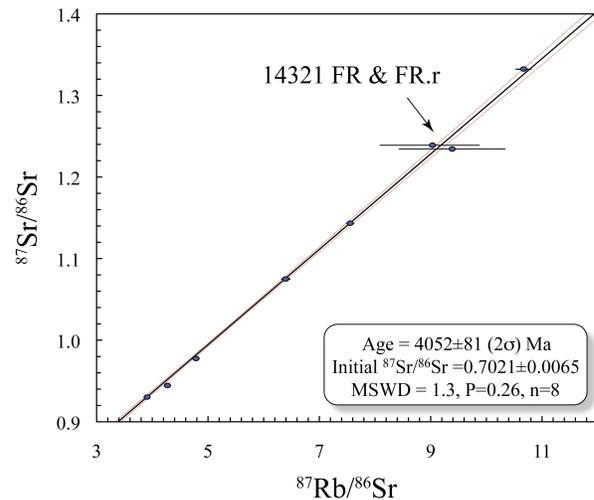


Figure 2. Rb-Sr internal isochron for lunar granitic clast 14321,1062. Two new bulk samples (one that is acid-washed, 14321 FR.r) are combined with data from a bulk sample, 3 feldspar mineral separates and 2 magnetic fractions (7). The isochron age and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio are calculated using Isoplot (11). The error envelope represents the 95% confidence interval of the regression. FAN 15415 plots off scale.

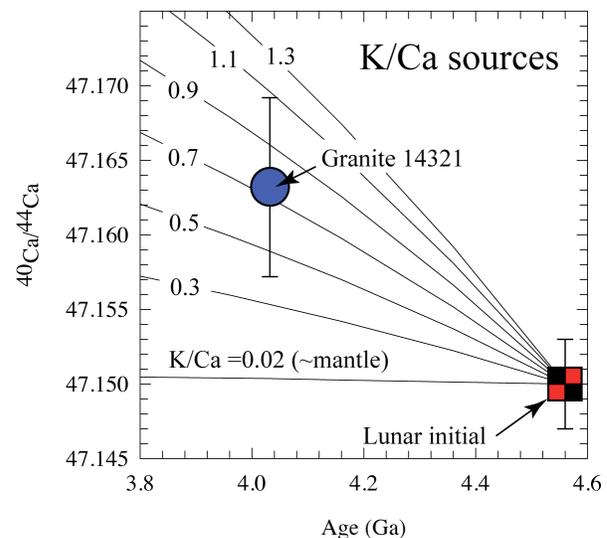


Figure 3. Plot of $^{40}\text{Ca}/^{44}\text{Ca}$ evolution against time. Growth curves are shown for basaltic ($\text{K}/\text{Ca}=0.02$), intermediate, and evolved ($\text{K}/\text{Ca} \geq 1$) crustal sources. The initial $^{40}\text{Ca}/^{44}\text{Ca}$ composition of Apollo granite 14321 when compared to primitive lunar crust (e.g., FAN 15415) indicates that it was derived from a relatively enriched source that has a K/Ca ratio (~ 0.7) that is equivalent to terrestrial andesite.