DATING LUNAR GRANITES BY THE K-Ca CHRONOMETER; C.-Y. Shih and H. Wiesmann, Lockheed Engineering and Science Co., 2400 NASA Road 1, Houston, TX 77258; L. E. Nyquist, NASA Johnson Space Center, Houston, TX 77058.

High-precision measurements have allowed us to identify radiogenic enrichments of  $^{40}$ Ca as low as  $\sim 1$   $\epsilon$ -unit in geological samples. Marshall and DePaolo (1,2) demonstrated that the long-known  $^{40}$ K- $^{40}$ Ca decay system could be an important chronometer as well as a useful radiogenic tracer for studies of terrestrial granitic rocks. We present preliminary results of K-Ca isotopic studies of a suite of lunar igneous rocks including (a) three low K rocks (norite 15445,17, low-Ti mare basalt 15555 and high-Ti,K mare basalt 10017), and (b) four high K rocks (granitic clasts 14321,1062, 14303,206, 12033,576 and 12013,141).

 $^{40}$ Ca/ $^{44}$ Ca and  $^{40}$ K/ $^{44}$ Ca measurements: The Ca and K isotopic data were obtained on the JSC Finnigan-MAT 261 multi-collector mass spectrometer. The  $^{40}$ Ca/ $^{44}$ Ca analyses were made by measuring the  $^{40}$ Ca ion beam with the amplifier equipped with a  $10^{10}$  Ω resistor and the values were normalized to  $^{42}$ Ca/ $^{44}$ Ca=0.31221 of (3). The empirical "modified power law" described in (4) was used for mass fractionation corrections of Ca and K isotopic measurements. The  $^{40}$ Ca/ $^{44}$ Ca values would be  $^{-1}$  ε-unit higher for the exponential mass fractionation correction used by (3). The internal precisions for  $^{40}$ Ca/ $^{44}$ Ca were normally better than  $^{+0.5}$ ε-unit ( $^{20}$ m). The external precision for  $^{40}$ Ca/ $^{44}$ Ca is  $^{-1}$ 1 ε-unit ( $^{20}$ p) for a set of 22 measurements of the Ca standard (JSC) made during the course of this study, as shown in Fig. 1.

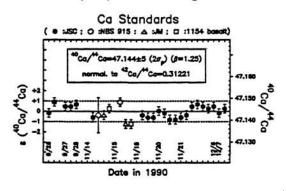


Figure 1. 40Ca/44Ca in standards.

The Ca and K abundances were obtained using a mixed  $^{40}$ K- $^{48}$ Ca spike. High precision K abundances were achieved from the  $^{40}$ K/ $^{41}$ K ratios normalized to  $^{39}$ K/ $^{41}$ K=13.8566 (5). The accuracies for K/Ca ratios reported in this study are  $^{+}$ 0.1%, much better than the accuracies of Rb/Sr ratios in the commonly used Rb-Sr chronometer.

Lunar initial <sup>40</sup>Ca/<sup>44</sup>Ca (LICa): Three pristine lunar igneous rocks, *i.e.* a 4.46 Ga norite (15445,17), a 3.59 Ga high-Ti,K mare basalt (10017) and a 3.32 Ga low-Ti mare basalt (15555), that have been dated previously (e.g. 6-8) were used to establish their source initial <sup>40</sup>Ca/<sup>44</sup>Ca ratios. All these rocks have such low

K/Ca ratios (<0.04) that the corrections for radiogenic growth are insignificant (<0.2  $\epsilon$ -unit). The calculated initial  $^{40}$ Ca/ $^{44}$ Ca ratios for these rocks are essentially identical. The averaged value is  $47.147\pm0.002$ , which is also within error limits of the primordial terrestrial mantle value of 47.149 published by (1). These results suggest that regions of the lunar mantle probably have initial Ca ratios that can not be clearly resolved from each other within present analytical uncertainties. This ratio could be considered to represent a great part of the lunar mantle because these rocks were derived from different parts of the mantle.

K-Ca mineral isochron: Granite 14321,1062 is the largest pristine granitic clast so far identified in lunar samples (9). We have dated this clast by the Rb-Sr, Sm-Nd and  $^{39}$ Ar- $^{40}$ Ar methods (10). Our previous results indicate that Rb-Sr and Sm-Nd internal isochrons for the clast give concordant ages of 4.1 Ga. The current K-Ca isotopic study was undertaken using the non-magnetic fraction of the sample originally allocated to us. This fraction was the remainder from the previous age study (10). After the bulk sample (WR) was taken from the fraction, the clear feldspar (CF) was separated by handpicking. The WR and the CF yield a tie-line age of  $4.10\pm0.04$  Ga( $2\sigma$ ) for  $\lambda(^{40}$ K)=0.5543 Ga<sup>-1</sup> and decay parameters recommended in (11), and initial  $^{40}$ Ca/ $^{44}$ Ca of  $47.144\pm0.007$  (Fig. 2.). The uncertainties of the age and the initial ratio were calculated from the  $2\sigma$  errors in the  $^{40}$ Ca/ $^{44}$ Ca and  $^{40}$ K/ $^{44}$ Ca measurements. When these two data and the LICa value are regressed using the York (12) program, an age of  $4.08\pm0.08$  Ga( $2\sigma$ ) is obtained. The K-Ca isotopic age is in excellent agreement with the Rb-Sr

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age of  $4.09\pm0.03$  Ga for  $\lambda(^{87}\text{Rb})=0.01402$  Ga<sup>-1</sup>, or  $4.13\pm0.03$  Ga for  $\lambda(^{87}\text{Rb})=0.0139$  Ga<sup>-1</sup>, and the Sm-Nd age of  $4.11\pm0.20$  Ga for  $\lambda(^{147}\text{Sm})=0.00654$  Ga<sup>-1</sup> obtained previously for this granite (10). These age results indicate that the granite crystallized from a melt 4.10 Ga ago.

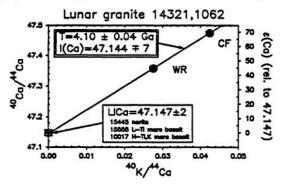


Figure 2. K-Ca isochron for granite 14321.

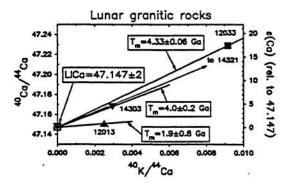


Figure 3. K-Ca model ages for lunar granites.

The λ(87Rb) value: Comparisons of Rb-Sr and U-Th-Pb ages of chondrites (13), Rb-Sr and 39Ar-40Ar ages of Apollo 14 KREEP basalts (e.g. 10) and Rb-Sr and Sm-Nd ages of a pristine eucrite clast Y75011,84B all show that Rb-Sr ages calculated using  $\lambda(^{87}\text{Rb})=0.01402\text{Ga}^{-1}$ are in better agreement with ages obtained by other techniques than those calculated using  $\lambda(^{87}\text{Rb})=0.0142$  Ga<sup>-1</sup> as recommended by (11). The concordancy of K-Ca, Rb-Sr and Sm-Nd age for lunar granite 14321 also seem to require the  $\lambda(^{87}\text{Rb})$  value to be revised to 0.01402 Ga<sup>-1</sup>. K-Ca model ages: Three additional lunar granitic clasts were also dated by the K-Ca method. Two whole rock samples (WR) were taken from the  $<149\mu$  size fractions of granite clasts 12033,576 (15) and 12013,141 (e.g. 16) allocated to us for age studies. One WR sample was taken from the coarsely crushed granite clast 14303,206 which was transferred to us after being irradiated by thermal neutrons for an earlier INAA study by (15). So far only the WR samples have been analysed. All these granites were much less radiogenic than the 14321 granite. The model ages, T<sub>m</sub>, relative to the LICa value are presented in Fig. 3. Since the LICa defined by three low K igneous rocks is within uncertainties of the initial 40Ca/44Ca of

granite 14321, the K-Ca T<sub>m</sub> calculated for the lunar granitic clasts should almost represent their crystallization ages. The T<sub>m</sub> for granite 12033 is 4.33±0.06 Ga. This age is considerably older than the U-Pb age of 3.90 Ga for zircons from two thin sections of 12033,507 (17), but is comparable to old U-Pb ages for zircons in granites 14303,209 and breccias 73217, 73235 and 67975 (17-19). Granitic clasts 14303 and 12013 contain less K and thus are significantly less radiogenic than the two other granites studied here. Their calculated T<sub>m</sub> are 4.0±0.2 Ga and 1.9±0.8 Ga, respectively, which are subject to large uncertainties. The K-Ca T<sub>m</sub> age for 14303 granite is within uncertainties of the K-Ca age of the 14321 granite, but is slightly younger than the 4.33 Ga U-Pb age for zircons in 14303,209 (18). However, the T<sub>m</sub> for our granite chip of 12013,141 is considerably younger than the 4.00 Ga Rb-Sr and <sup>89</sup>Ar-<sup>40</sup>Ar ages obtained from different chips of the granite (16,20). It is hoped that further analyses will clarify this issue.

Implications: The K-Ca ages reported here suggest that both old (~4.3 Ga) and young (~4.0 Ga) granites exist on the Moon, in agreement with U-Pb ages of zircons from lunar granitic rocks as previously established by (17-19). Serial magmatism (17,21) probably played a significant role in generation of the lunar crust.

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