K–Ca DATING OF ALKALI-RICH FRAGMENTS IN THE Y–74442 AND BHOLA LL–CHONDRITIC BRECCIAS. T. Yokoyama[1], K. Misawa[1,2], O. Okano[3], C.-Y. Shih[4], L. E. Nyquist[5], J. I. Simon[5], M. J. Tappa[4], S. Yoneda[6]. [1]SOKENDAI, Tachikawa, Tokyo 190–8518, Japan. (E-mail: yokoyama.tatsunori@nipr.ac.jp). [2]Natl Inst. Polar Res., Tokyo, Japan, [3]Okayama Univ., Okayama, Japan, [4]ESCG/Jacobs., [5]NASA-JSC, [6]Natl Museum Natural & Sci., Tukuba, Japan.

Introduction: Alkali-rich igneous fragments in the brecciated LL-chondrites, Krähenberg (LL5) [1], Bhola (LL3–6) [2], Siena (LL5) [3] and Yamato (Y)–74442 (LL4) [4-6], show characteristic fractionation patterns of alkali and alkaline elements [7]. The alkali-rich fragments in Krähenberg, Bhola and Y–74442 are very similar in mineralogy and petrography, suggesting that they could have come from related precursor materials [6].

Recently we reported Rb–Sr isotopic systematics of alkali-rich igneous rock fragments in Y–74442: nine fragments from Y–74442 yield the Rb–Sr age of 4429 ± 54 Ma (2σ) for $\lambda(^{87}Rb) = 0.01402\ Ga^{-1}$ [8] with the initial ratio of $^{87}Sr/^{86}Sr = 0.7144 \pm 0.0094$ (2σ) [9]. The Rb–Sr age of the alkali-rich fragments of Y–74442 is younger than the primary Rb–Sr age of 4541 ± 14 Ma for LL-chondrite whole-rock samples [10], implying that they formed after accumulation of LL-chondrite parental bodies, although enrichment may have happened earlier.

Marshall and DePaolo [11,12] demonstrated that the ^{40}K–^{40}Ca decay system could be an important chronometer as well as a useful radiogenic tracer for studies of terrestrial rocks. Shih et al. [13,14] and more recently Simon et al. [15] determined K–Ca ages of lunar granitic rocks, and showed the application of the K–Ca chronometer for K-rich planetary materials. Since alkali-rich fragments in the LL-chondritic breccias are highly enriched in K, we can expect enhancements of radiogenic ^{40}Ca. Here, we report preliminary results of K–Ca isotopic systematics of alkali-rich fragments in the LL-chondritic breccias, Y–74442 and Bhola.

Methods: Alkali-rich fragments in Y–74442 and Bhola were separated from the host chondrites, decomposed in a mixture of HF and $HClO_4$ acids and then combined with mixed ^{40}K–^{48}Ca and ^{87}Rb–^{84}Sr spikes. The (K + Rb), Ca and Sr fractions were separated and collected individually using standard cation exchange column chemistry (AG 50W X8, 200–400 mesh). The (K + Rb) fractions were purified further using a second clean-up column to remove coeluants Mg and Fe. The Ca fractions were also purified further using a cation exchange column (AG 50W X8, 200–400 mesh) with 0.5 N HF to remove Ti.

The K and Ca isotopic data were obtained on Thermo Finnigan Triton (NASA-JSC) and Triton-plus (NMNS) mass spectrometers. The Ca abundances in samples were calculated from their $^{48}Ca/^{44}Ca$ ratios, normalized to $^{42}Ca/^{44}Ca = 0.31221$ [16]. An average value of $^{40}Ca/^{44}Ca = 47.164 \pm 0.004$ ($2\sigma_p$, N = 6) was obtained for the well-known standard NBS 915a, where $\sigma_p = [\,\Sigma\,(m_i-\mu)^2/(N-1)]^{1/2}$ for N measurements m_i with mean value $\mu = 47.164$. Shown in Fig. 1 are the variations in ^{40}Ca of the alkali-rich fragments and other planetary materials reported by [17,18] on a scale where Earth's mantle is $\varepsilon^{40}Ca$=0, where $\varepsilon^{40}Ca = (^{40}Ca/^{44}Ca_{\text{sample-normzlied to 915a}}/^{40}Ca/^{44}Ca_{\text{maltle}} - 1) \times 10^4$.

Results and Discussion: While the Ca and Sr abundances in alkali-rich fragments of Y–74442 are almost constant and chondritic (Fig. 2), the fragments show enrichments of K (2700 to 8400 ppm, 5–15 x CI) and Rb (30 to 260 ppm, 14–70 x CI) [9]. This suggests that the fragments of Y–74442 were enriched in alkali elements by solid/vapor or liquid/vapor processes in which moderately volatile alkalis are distributed into vapor phase. Over time, the enrichment of K in alkali-rich fragments of Y-74442 and Bhola result in large $\varepsilon^{40}Ca$ values ($\varepsilon^{40}Ca$ = 2–8) relative to other planetary materials [17,18] (Fig. 1).

K–Ca data for seven alkali-rich fragments of Y–74442 and one alkali-rich fragment of Bhola were obtained. The data of Y–74442 fragments yield a K–Ca age of 4513 ± 230 Ma (2σ, MSWD = 3.5, n = 6) for $\lambda(^{40}K) = 0.5543\ Ga^{-1}$ [11,19] with an initial $^{40}Ca/^{44}Ca = 47.1587 \pm 0.0032$ (2σ) using the Isoplot/Ex program [20] (Fig. 3). Since K–Ca data for one fragment of Y–74442 deviates from the isochron, we exclude the data from the calculation. This age is within error of the previously reported Rb–Sr age of 4429 ± 54 Ma (2σ) [9]. We could obtain a mean initial $^{40}Ca/^{44}Ca$ ratio of 47.1597 at 4.429 Ga (the more reliable Rb-Sr age). Then, using the initial $^{40}Ca/^{44}Ca$ value of bulk silicate earth at 4.568 Ga, the source $^{40}K/^{44}Ca$ ratio of 0.00162 for the fragments is obtained. This alkali-rich fragment source is about 4.5 times higher than that of the LL-chondrite parent bodies ($^{40}K/^{44}Ca = 0.00035$) [21]. It is consistent with the Rb–Sr systematics of Y–74442 fragments [9] and suggesting that the K enrichment may have also occurred in the early solar system. Unfortunately, the large error of K–Ca age (~230 Ma) precludes further discussion. A data point of the Bhola fragment does not plot on the 4513 Ma isochron and deviates downward by –1.5 ε-units from the isochron. The K–Ca systematics of the Bhola fragment seems to be somewhat different from the Y–74442 fragments, suggesting that formation of alkali-rich fragments in the two chondrites might represent different events. Compared with high-K planetary materials such as lunar granitic rocks [13,14], the K/Ca ratios of these fragments are small. As a result, the uncertainty associated with the K–Ca age is large. Mineral separates of alkali-rich fragments and/or further measurements of alkali-rich fragments in these meteorites should make it possible to reduce the uncertainties of the K–Ca age and initial $^{40}Ca/^{44}Ca$ ratio.

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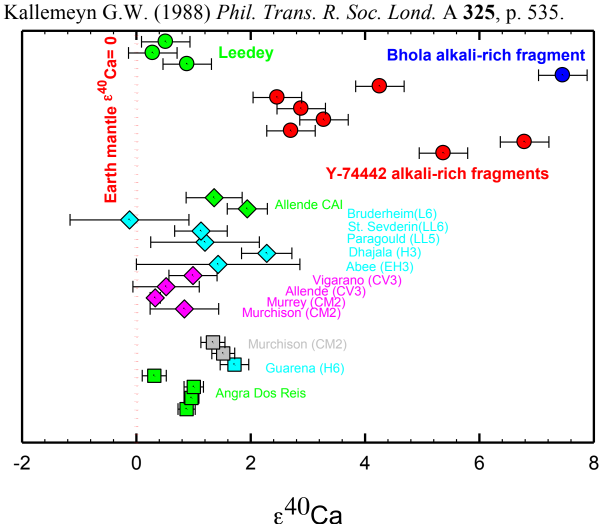

Fig. 1. Variation in ^{40}Ca for a range of planetary materials and alkali-rich fragments in Y–74442 and Bhola. The data are from [17] (squares) and [18] (diamonds). $\varepsilon^{40}Ca$ shows the deviation from the Earth's initial composition $[(^{40}Ca/^{44}Ca_{sample}\ /^{40}Ca/^{44}Ca_{mantle} - 1) \times 10^4]$, where the $^{40}Ca/^{44}Ca_{mantle}$ value from [12] was normalized to NBS 915a of [18], and then all data were normalized to NBS 915a of [17].

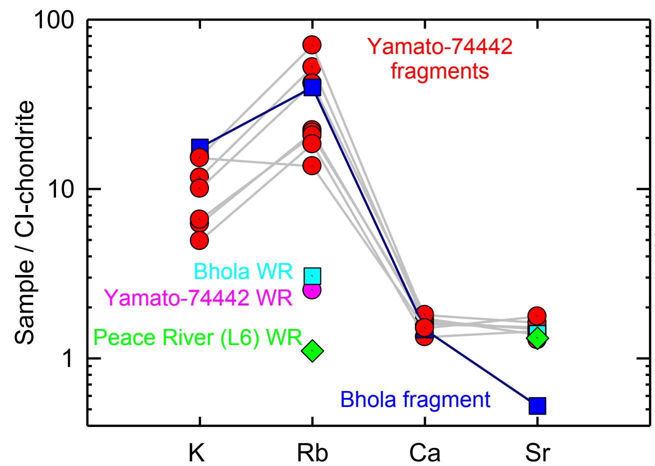

Fig. 2. K–Rb–Ca–Sr abundances of the alkali-rich fragments in Y–74442 and Bhola normalized to CI-chondrites. The data are from [9] and the present study.

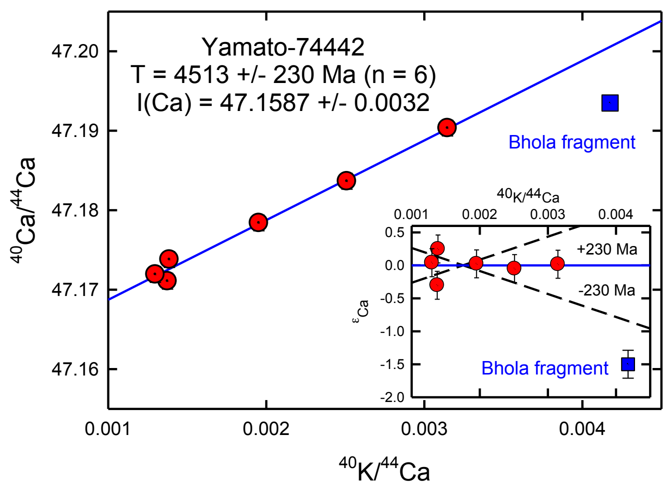

Fig. 3. K–Ca isochron diagram for alkali-rich fragments in Y–74442. Six data points define a linear array corresponding to a K–Ca age of 4513 ± 230 Ma (2σ). The inset shows deviation of $^{40}Ca/^{44}Ca$ in parts in 10^4 (ε-units) relative to the 4513 Ma isochron. The Bhola fragment (blue square) does not plot on the line. The $^{40}Ca/^{44}Ca$ value of Earth's mantle [12] is ~0.9 ε-units lower than that of NBS 915a [17,18 and this study]. When the data were normalized to the $^{40}Ca/^{44}Ca$ value of Earth's mantle, we obtain an initial $^{40}Ca/^{44}Ca$ ratio of 47.1545 ± 0.0032 for alkali-rich fragments in Y–74442.