EARLY SOLAR SYSTEM ALKALI FRACTIONATION EVENTS RECORDED BY K-Ca ISOTOPES IN THE Yamato-74442 LL-CHONDRITIC BRECCIA. Tatsunori Yokoyama[1] K. Misawa[2,3], O. Okano[4], C.-Y. Shih[5], L.E. Nyquist[6], J.I. Simon[6], M.J. Tappa[5,6,7], S. Yoneda[1]. [1]Natl Museum Nature & Sci., 4-1-1 Amakubo, Tsukuba, 305-0005, Japan, [2]Natl Inst. Polar Res., [3]SOKENDAI, 10-3 Midoricho, Tachikawa, Tokyo, 190-8518, Japan (misawa@nipr.ac.jp), [4]Graduate School of Natural Sci. & Tech., Okayama Univ., 3-1-1 Tsushimanaka, Okayama, 700-8530, Japan, [5]Jacobs, NASA Johnson Space Center, Mail Code XI3, Houston, TX 77058, U.S.A., [6]Astromaterials Res. & Exploration Sci., NASA-JSC, 2101 NASA Parkway, Houston, TX 77058-3696, U.S.A., [7]Aerodyne Industries – Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, U.S.A.

Introduction: Radiogenic ingrowth of ^{40}Ca due to decay of ^{40}K occurred early in the solar system history causing the ^{40}Ca abundance to vary within different early-former reservoirs. Marshall and DePaolo [1,2] demonstrated that the ^{40}K-^{40}Ca decay system could be a useful radiogenic tracer for studies of terrestrial rocks. Shih et al. [3,4] determined ^{40}K-^{40}Ca ages of lunar granitic rock fragments and discussed the chemical characteristics of their source materials. Recently, Yokoyama et al. [5] showed the application of the ^{40}K-^{40}Ca chronometer for high K/Ca materials in ordinary chondrites (OCs).

High-precision calcium isotopic data are needed to constrain mixing processes among early solar system materials and the time of planetesimal formation. To better constrain the solar system calcium isotopic compositions among astromaterials, we have determined the calcium isotopic compositions of OCs and an angrite. We further estimated a source K/Ca ratio for alkali-rich fragments in a chondritic breccia using the estimated solar system initial ^{40}Ca/^{44}Ca.

Experimental: Whole-rock samples of Yamato-(Y-) 74442 (LL4), Bhola (LL3–6), Peace River (L6), Leedey (L6), Shaw (L6/7), Zhaodong (L4), Guangrao (L6) and D'Orbigny (angrite) were analyzed for calcium isotopes. Calcium was separated from other major elements using a polyethylene column filled with 1 mL cation exchange resin (BioRad AG50W-X8, 200–400 mesh) and was further purified using a quartz column filled with 200 µL Eichrom DGA resin (particle size: 50–100 µm) to remove titanium and aluminum.

The calcium isotopic data were obtained on a multi-collector thermal ionization mass spectrometer, Thermo Scientific Triton *Plus* at the National Museum of Nature and Science. Instrumental mass fractionation was corrected using the exponential law with ^{42}Ca/^{44}Ca = 0.31221 as the normalizing ratio [6].

Results and Discussion: After internal normalization, 26 measurements of calcium standard, NIST SRM915a yield ^{40}Ca/^{44}Ca = 47.1646 ± 0.0044 ($2\sigma_p$). Here, we report ^{40}Ca/^{44}Ca measurements for other samples normalized to the NIST SRM 915a, i.e.,
$\varepsilon^{40}Ca = [(^{40}Ca/^{44}Ca)_{sample}/(^{40}Ca/^{44}Ca)_{SRM915a} - 1] \times 10^4$. We plot ε^{40}Ca for seven OCs and D'Orbigny with the internal uncertainties as $2\sigma_m$ (Fig. 1). The K/Ca ratios of OCs vary from 0.053 to 0.071. D'Orbigny is depleted in volatile elements (K/Ca = 0.00064 [7]). Hans et al. [8] reported strontium isotopic compositions of angrites, and suggested that volatile loss from the angrite parent body (APB) occurred within <1 Ma after formation of Ca, Al-rich inclusions. If this is the case, calcium isotopic compositions of the APB (i.e. quenched angrite, D'Orbigny) could be primordial, and represent isotopic compositions of early accreted materials.

The OCs analyzed here (except Y-74442 and Bhola breccias) have ε^{40}Ca values (–0.5 ± 0.2 ε-units; 4.563 Ga age corrected) that are slightly larger than the ε^{40}Ca value of D'Orbigny (–1.0 ± 0.2 ε; age-corrected), implying that the initial ^{40}Ca/^{44}Ca ratio of APB is lower than those of OC parent bodies. Mixing of a chondritic component with an alkali-rich component formed in the early solar nebula [9] would have modified the age corrected ε^{40}Ca values for Y-74442 and Bhola. Alternatively, some early solar system material remained heterogeneous in ε^{40}Ca such that observed in Dhajala (H3.8) (+ 1.7 ε) [10,11].

The K/Ca ratio of the source of alkali-rich fragments can be estimated using the more precise Rb-Sr age of 4.420 Ga [5]. We obtain an age-corrected initial ^{40}Ca/^{44}Ca ratio of 47.1621 ± 0.0009 using the present-day ^{40}Ca/^{44}Ca values of the fragments, which is within uncertainty of the initial ^{40}Ca/^{44}Ca ratio obtained from the *y*-intercept (Fig. 2). Using the initial ^{40}Ca/^{44}Ca value of the D'Orbigny angrite at 4.563 Ga, a source K/Ca value of 0.44 for the Y-74442 fragments is obtained (Fig. 3), although the associated error (± 0.18 ε) is slightly large due to the narrow range of ^{40}K/^{44}Ca ratios. If we adopt this value as the source K/Ca value for the Y-74442 alkali-rich fragments, it is seven times larger than that of the LL-chondrite parent body (K/Ca = 0.061 [12]). The results are generally consistent with the Rb-Sr systematics of the fragments [9], and suggest that the potassium enrichment may have also occurred in the early solar system.

If calcium and strontium contents in the parental melt at 4.420 Ga are chondritic, a K/Rb ratio of the precursor material is calculated to be ~170, which is approximately thirty percent less than that of the LL-chondrite ($(K/Rb)_{LL}$ = 255 [12]) or CI ($(K/Rb)_{CI}$ = 235

[13]) values. This indicates that mutual fractionations (i.e. an enrichment of heavier alkalis) could have occurred during the formation of the alkali-rich component (via alkali enrichment on a planetesimal or by early nebular condensates [9]). Abundance ratios of potassium and rubidium for the Y-74442 fragments are fairly constant [$(K/Rb)_{fragments}$ = 41–79], suggesting that further enrichments of rubidium (and possibly cesium) over potassium may have occurred just after a mixing event [9].

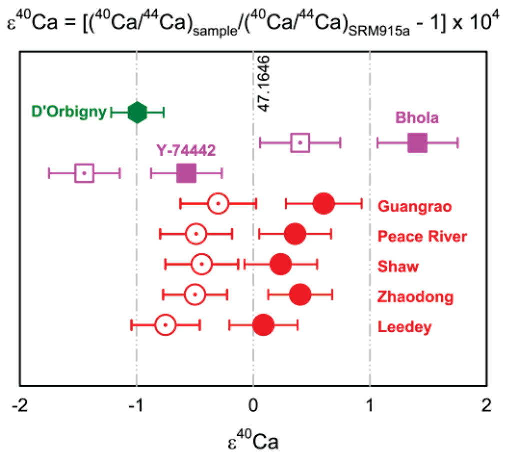

Figure 1. $^{40}Ca/^{44}Ca$ results, normalized to $^{42}Ca/^{44}Ca$ = 0.31221 [6], for seven OCs and D'Orbigny (solid symbols, errors are $2\sigma_m$). Assuming OC parent bodies formed contemporaneously with the APB at 4.563 Ga [16], age corrected $\varepsilon^{40}Ca$ values are calculated from the present-day $^{40}Ca/^{44}Ca$ and K/Ca values of the whole-rock samples (open symbols). The correction for *in situ* ^{40}K decay for D'Orbigny is insensitive to the age assumed.

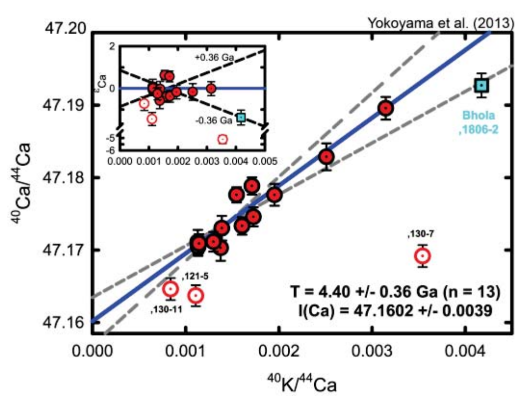

Figure 2. Potassium-calcium isochron diagram for alkali-rich igneous rock fragments in Y-74442 [5]. Thirteen data points define a linear array corresponding to a K-Ca age of 4.42 ± 0.28 Ga (95% C.L., MSWD = 9.5) for $\lambda(^{40}K)$ = 0.5543 Ga^{-1} [14] using the Isoplot/Ex program [15]. Bhola (LL3–6) fragment ,1806-2 (solid square, blue) is plotted for comparison.

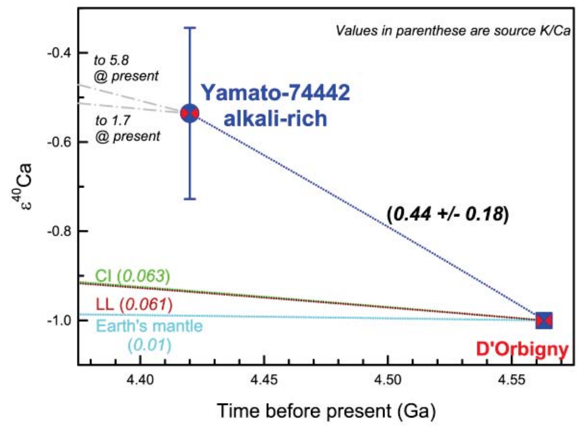

Figure 3. Initial $^{40}Ca/^{44}Ca$ (I_{Ca}) *versus* age (T) for alkali-rich fragments in Y-74442. We used the more reliable Rb-Sr age of 4.420 Ga [5] as a crystallization age of the fragments, and obtained an initial $^{40}Ca/^{44}Ca$ ratio of 47.1597 ± 0.0009 by back calculations from the present-day $^{40}Ca/^{44}Ca$ and K/Ca values of the fragments. Lines represent the K/Ca growth curves. A time-averaged K/Ca value for the source of the Y-74442 fragments is calculated to be 0.44 ± 0.18 for the D'Orbigny initial $^{40}Ca/^{44}Ca$ ratio of 47.1599 (K = 69 ppm and Ca = 10.72% [7]) and the crystallization age of 4.563 Ga [16]. A large enrichment of the K/Ca ratio is required during the formation of the fragments. Radiogenic ingrowths of $^{40}Ca/^{44}Ca$ in CI- and LL-chondrites and Earth's mantle are shown.

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