K–Ca ISOTOPIC SYSTEMATICS OF ALKALI-RICH FRAGMENTS IN THE YAMATO–74442 LL–CHONDRITIC BRECCIA.


Introduction:

Alkali-rich rock fragments were reported in LL- and H-chondritic breccias, Krähenberg (LL5), Bhola (LL3-6), Yamato (Y)-74442 (LL4), Siena (LL5) and Acfer 111 (H3-6) [1,2,3,4,5]. Previous studies revealed that alkali and alkaline elements in Krähenberg, Bhola, Y-74442 and Acfer 111 rock fragments are fractionated relative to CI-chondrites with heavier alkalis in general being progressively more enriched while their sodium abundances are sub-chondritic (C/Si-norm > Rb/Si-norm > K/Si-norm > Na/Si-norm) [1,2,3,5].

Highly enriched rubidium in Krähenberg and Y-74442 enable Rb-Sr isotope dating and determination of isotopic constraints on the chemical characteristics of their source materials [1]. We recently reported a new Rb-Sr crystallization age of 4.429 ± 0.054 Ga for Y-74442 fragments [5]. The results suggested that the source material of Y-74442 fragments could have formed from mixtures of an alkali-rich component from an alkali-rich planetesimal or early nebular condensates and a chondritic component that was flash heated during an impact on the LL-chondritic parent body ~4.4 Ga ago. Further enrichments of rubidium relative to strontium as well as a progressive enrichment of the heavier alkalis could have occurred during the final melt differentiation event on the parent body [5].

Because the alkali-rich rock fragments in Y-74442 and Bhola also show relatively high potassium abundances, up to 20 x CI-chondrites and highly radiogenic 87Sr/86Sr ratios up to ~5 [5], we have undertaken K–Ca isotopic analyses of the samples previously analyzed for Rb–Sr isotopes. We also report a refinement of our Rb-Sr isochron by including Rb-Sr measurements for an additional nine Y-74442 fragments.


Results:

Over time, the enrichments of potassium in alkali-rich fragments from Y-74442 and Bhola result in comparatively large enrichments in 40Ca relative to other planetary materials. Measured values ε40Ca range from 1.5 to 7, where $\varepsilon^{40}\mathrm{Ca} = (^{40}\mathrm{Ca}^{39}\mathrm{Ca})_{\text{sample}} / (^{40}\mathrm{Ca}^{39}\mathrm{Ca})_{\text{CI}} - 1 \times 10^3$. Here 47.1583 is the mantle 40Ca/44Ca value of Caro et al. (2010) [12] re-normalized on the basis of the measured value from SRM 915a of 47.1487 reported by Marshall and DePaolo (1989). The average of 15 analyses of NIST SRM 915a standard during the course of this study was $^{40}\mathrm{Ca}^{39}\mathrm{Ca}_{\text{915a,NNMS}} = 47.16408 \pm 0.0040 \ (2\sigma \ \text{p. error}).$ Potassium-calcium data for sixteen alkali-rich fragments of Y-74442 and one alkali-rich fragment of Bhola were obtained. The ε40Ca values are shown in Fig.1. Also shown in Fig. 1 are the variations in ε40Ca of other planetary materials reported by [11,12] on a scale where Earth’s mantle is ε40Ca mantle = 0. The ε40Ca values of the Y-74442 fragments yield an age of 4.40 ± 0.36 Ga (2σ error, n = 13) for $\lambda(4^{0}\mathrm{K}) = 0.5543 \ \text{Ga}^{-1}$ [13] with an initial 40Ca/44Ca = 47.1602 ± 0.0039 (2σ) using the Isoplot/Ex program [14] (Fig. 2). We excluded three data points (1215, 1307 and 130-11) from the age calculation of Y-74442 fragments since they appear to contain some amount of host material and showed large scatter. A data point of the Bhola fragment deviates downward by ~1.5 ε-units from the Y-74442 isochron, and apparently reflects a later event on the LL parent body.

A similar but more precise age of 4.420 ± 0.031 Ga for $\lambda(4^{7}\mathrm{Rb}) = 0.01402 \ \text{Ga}^{-1}$ with an initial ratio of $^{87}\mathrm{Sr}^{86}\mathrm{Sr} = 0.7203 ± 0.0044$ was determined after combining the Rb-Sr results from nine additional Y-74442 fragments to the nine previously reported data [5].

Discussion:

A refined value for the 40Ca/44Ca ratio of the alkali-rich source can be obtained using the more precise Rb–Sr age of 4.420 Ga. With this age, a model initial 40Ca/44Ca ratio of 47.1597 is determined from the present-day 40Ca/44Ca values of the fragments. Then, using the initial 40Ca/44Ca value of bulk silicate earth at 4.568 Ga (40Ca/44CaSESB04,558), a source K/Ca value of 0.27 for the Y-74442 fragments can be obtained, although the associated error (± 0.19, 2σ) is large due to the narrow range of 40Ca/44Ca ratios. If we adopt this value as the source K/Ca value for the Y-74442 alkali-rich fragments, it is four
times larger than that of the LL-chondrite parent body (K/Ca = 0.061, [15]). These results are generally consistent with the Rb–Sr systematics of the fragments, and suggest that the potassium enrichment may have also occurred in the early Solar System. If the parent melt had calcium and strontium abundances at 4.420 Ga that were chondritic, a K/Rb ratio of the precursor material is calculated to be ~100, which is less than forty percent of the LL-chondrite [(K/Rb)LL-chondrites = 255, [15]] or CI [(K/Rb)CI = 235] value. This result indicates that mutual fractionations (i.e. an enrichment of heavier alkalalis) could have occurred during the formation of an alkali-rich component from an alkali-rich planetesimal or early nebular condensates, [5]).

Abundance ratios of potassium and rubidium for the Y-74442 fragments are fairly constant (K/Rb = 41–79, except for fragment .130-7), suggesting that further enrichments of rubidium (and possibly cesium) over potassium could have occurred in a completely different way. Potassium and rubidium were selectively added to individual fragments without significant change in the calcium and strontium abundances. This possibility could have happened during a final melting event that produced a vapor cloud enriched in potassium and rubidium (∆NaCl-norm < KCl-norm < RbCl-norm < CsCl-norm), which condensed into a melt (later glass) phase.

The K–Ca systematics of the Bhola fragment seems to be somewhat different from the Y-74442 fragments, suggesting that a formation process of alkali-rich fragments in the two chondrites might be similar but represent different fractionation events. Assuming an Earth’s mantle initial $^{40}$Ca/$^{44}$Ca of 47.1583 [12] and an initial $^{87}$Sr/$^{86}$Sr of 0.69889 (Allende initial, [16]), K–Ca and Rb–Sr model ages for Bhola .1806-2 are calculated to be 4.19 and 4.33 Ga, respectively. Bhola .1806-2 also is different from the Y-74442 fragments in terms of its strontium content (Sr = 4.09 ppm and thus Rb/Sr = 22), implying that the Bohla fragment could have formed at a different time and/or have been derived from a precursor with different proportions of alkali and chondritic components compared to those of Y-74442 fragments. Nevertheless, fractionation processes and precursor components of the Bhola fragment are considered to be almost identical to those of the Y-74442 fragments.

References: