K-Ca dating and Ca isotope composition of the oldest Solar System lava, Erg Chech 002

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Abstract

Erg Chech 002 (EC 002) is an andesitic meteorite, which is the oldest lava in the Solar System as determined by the 26Al-26Mg relative chronometer. Here, we present high precision Ca isotope data for the bulk rock and mineral separates of EC 002, and for the first time, obtain a 40K-40Ca isochron by using the Nu Sapphire, a collision cell equipped MC-ICP-MS instrument. The mineral separates yield a 40K-40Ca age of 4545 ± 78 Ma with an initial 40Ca/44Ca = 47.16065 ± 0.00049 (ε40CaSRM 915a = -0.33 ± 0.10). The age is identical with those obtained from other long lived isotopic systematics but more precise, and it is consistent with the short lived 26Al-26Mg age. The δ44/40Ca of EC 002 is 0.87 ± 0.05 % suggesting that EC 002 might represent a differentiated melt from an ordinary chondritic parent body. The extremely old age of EC 002, along with the similar ε40Ca values among most meteorites, suggests that the 40Ca was homogeneously distributed within early formed planetesimals.

Introduction

Some evolved, silica-rich achondrites have been the major source of knowledge on early Solar System crustal magmatism (e.g., Day et al., 2009; Srinivasan et al., 2018). Erg Chech 002 (EC 002) is an andesite achondrite, with high MgO and FeO content and a smooth trace element pattern, which is quite different from other anedicite achondrites but closely matches the experimental melts obtained from non-carbonaceous chondritic parent body. The extremely old age of EC 002, along with the similar ε40Ca values among most meteorites, suggests that the 40Ca was homogeneously distributed within early formed planetesimals.

Calcium (Ca) isotopes provide powerful tools for tracing planetary formation and evolution by studying the stable isotope variations, radiogenic enrichment, and nucleosynthetic anomalies (Russell et al., 1978). Given that Ca is a major element, 40K-40Ca dating could be well suited to date precious samples using the most limited mass of minerals (Shih et al., 1993). The novel collision cell (CO)-MC-ICP-MS, Nu Sapphire, is promising for Ca isotope measurements, including the abundance of 40Ca, which is impossible to measure by normal MC-ICP-MS due to the interference of 40K. Both stable and radiogenic Ca isotopic data can be obtained with high precision and the most limited sample consumption (~100 ng of Ca for each measurement; Dai et al., 2022; Moynier et al., 2022).

Equilibrium Ca Isotope Fractionation between Mineral Separates

We selected two pyroxene fractions and three plagioclase fractions, together with two bulk rock fractions which have been used for 26Al-26Mg and 147Sm-143Nd systematics, for Ca isotope analysis (Fang et al., 2022). Our method has the advantage of providing both stable and radiogenic Ca isotopic composition simultaneously (noted as δ44/40Ca and ε40Ca relative to SRM 915a standard; Table S-1, Supplementary Information). The stable isotopic composition can be used to test whether minerals are within isotopic equilibrium, which

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is a prerequisite for radiometric dating but rarely tested. Considered as a melting product, EC 002 is also a well suited sample for studying stable Ca isotope fractionation during early planetary differentiation.

The $^{44/40}$Ca values of two bulk rock fractions are 0.88 ± 0.07 ‰ (2 s.d.) and 0.85 ± 0.11 ‰ (2 s.d.), which suggests that the $^{44/40}$Ca value of Erg Chech 002 is 0.87 ± 0.05 ‰ (2 s.d.), similar within error to the composition of most inner solar system.

Modelling the Ca Isotope Fractionation during Partial Melting of the EC 002 Parent Body

Partial melting would have affected the bulk Ca isotopic composition of the EC 002 lava. This effect needs to be corrected for estimating the composition of the parent body. The trace and major element compositions of EC 002 correspond to high proportions of melting (around 20–25 %) of an ordinary chondrite-like parent body (Barrat et al., 2021). Considering that the melting temperature for EC 002 is ∼1224 °C, a simple calculation based on the incremental non-modal batch melting model of an ordinary chondrite-like parent body can be used to estimate the effect of partial melting and obtain the original Ca isotope composition (see Supplementary Information for more details). Under this scenario, most of the Ca (85 %) was extracted from plagioclases and augites and caused limited fractionation (<0.1 ‰) between source materials and melts. Therefore, the $^{44/40}$Ca of EC 002 parent body is estimated to be around 0.94 ‰ (Fig. S–4). This result is distinct from carbonaceous meteorites and Ryugu samples (Moynier et al., 2022) and provides further evidence for a non-carbonaceous chondrite parent body (Valdes et al., 2021).

K-Ca Systematics of EC 002

The $^{40}$K–$^{40}$Ca data and $^{44}$Ca/$^{40}$Ca ratio of mineral separates yield an age of 4545 ± 78 Ma (2σ error) with an initial $^{40}$Ca/$^{44}$Ca ratio of 47.16065 ± 0.00049 (2σ) (Fig. 2). The $^{40}$K–$^{40}$Ca age for EC 002 is consistent with the $^{40}$K–$^{40}$Ar (4534 ± 117 Ma) and $^{147}$Sm–$^{143}$Nd ages (4521 ± 152 Ma) obtained from the same mineral fractions, but with an improvement on the error by about a factor 2, and also consistent with the closure age for the $^{26}$Al–$^{26}$Mg system (4565.5–4566.9 Ma) within uncertainties (Barrat et al., 2021; Fang et al., 2022).

![Figure 1](https://example.com/fig1.png)

**Figure 1** Plot of $\Delta^{44/40}$Ca$_{py-xp}$ versus equilibrium temperature of minerals. The red square represents the range of fractionation between pyroxenes and plagioclases and the relative temperature of mineral differentiation. Three solid lines are theoretical equations of equilibrium fractionation between pyroxenes and plagioclase: a, diopside-labradorite (Antonelli et al., 2019); b, diopside-anorthite (Zhang et al., 2018); c, diopside-anorthite (Huang et al., 2019). Four dashed lines represent equilibrium temperatures determined by different methods.

![Figure 2](https://example.com/fig2.png)

**Figure 2** K-Ca isochron defined by pyroxenes, plagioclases, and bulk rock fractions of EC 002 using IsoplotR (Vermeesch, 2018). The error bars correspond to the 2 s.e. on the ratios. Seven data points define a linear array corresponding to a K-Ca age of 4545 ± 78 Ma for $\lambda^{40}$K = 0.5543 Ga$^{-1}$ (Steiger and Jäger, 1977).
The resetting of the isotopic system would occur when elemental and isotopic diffusion happened under secondary events. For the K-Ca system, the relatively slow diffusion coefficients of Ca can make it more resistant to reheating processes than the Rb-Sr or K-Ar systems (Shih et al., 2006). Timing of accretion of different planet bodies is from Schiller et al. (2018). The latest accretion ages of meteorites are set by their formation age: EC 002 (0.43–1.80 Ma), derived from the $^{26}$Al-$^{26}$Mg system with different initial $^{27}$Al/$^{26}$Al ratios; Fang et al., 2022), chondrites (mostly around 1–3 Ma; Krot et al., 2009). The $^{40}$Ca values of different planets and chondrites are taken from literature, and detailed information is reported in Table S-3.

The $^{40}$K-$^{40}$Ca ages of extraterrestrial samples are limited and all cases were obtained using TIMS (Shih et al., 1993; Yokoyama et al., 2017). These ages commonly have less precision than other systems, such as Rb-Sr, due to the limited fractionation of K/Ca ratio in most igneous rocks and the high abundance of $^{40}$Ca compared to $^{40}$K. While the mineral separates of EC 002 comprised a relatively small range of $^{40}$K/$^{40}$Ca ratios, yielding ~5 $\varepsilon$-unit enrichments on $^{40}$Ca/$^{44}$Ca ratios, a precise and accurate age was still obtained by using the CC-MC-ICP-MS, Nu Sapphire. Given the small amount of Ca processed for each phase (~200 ng for each individual measurement) which correspond to less than 0.1 mg of minerals, this method displays great potential for future chronology of precious extraterrestrial materials such as future samples returned by space missions.

The $^{40}$K-$^{40}$Ca isochron is obtained from the variation in the abundance of the radiogenic $^{40}$Ca in minerals with different K/Ca ratios. Meanwhile, the intercept of the K-Ca isochron represents the initial $^{40}$Ca value of EC 002 (~0.33 ± 0.10) and reflects its parent body’s value at the time of its accretion. Previous studies show variable $^{40}$Ca among different carbonaceous and ordinary chondrites which range from ~0.74 to ~1.01 and ~1.43 to ~1.83, respectively (Simon et al., 2009; Huang and Jacobsen, 2017; Yokoyama et al., 2017; Moynier et al., 2022). However, the average $^{40}$Ca of these chondrites mostly cluster and return a $^{40}$Ca value of ~0.23 ± 0.36 (2 s.e., n = 15) for ordinary chondrites and ~0.12 ± 0.27 (2 s.e., n = 15) for carbonaceous chondrites including the asteroid Ryugu (Table S-4, Fig. 3). The $^{40}$Ca value of EC 002 which represents the average of its parent body, is similar to those of chondrites and rocky planets in inner Solar System, such as Mars and Earth, within uncertainty (Fig. S-5). This observation suggests a homogenous $^{40}$Ca/$^{44}$Ca distribution within early planetesimals, as early as 1.80 ± 0.01 Ma (the age of EC 002). Given that $^{40}$Ca is variable between refractory inclusions (mostly between $-4$ to $+4$ $\varepsilon$-units; Simon et al., 2009 and reference therein), this homogenisation must have occurred rapidly at the birth of Solar System (Fig. 3).

Ordinary and enstatite chondrites as well as terrestrial rocks have fairly homogeneous $^{44}$Ca/$^{40}$Ca values, while carbonaceous chondrites including the primitive asteroid Ryugu have variable $^{44}$Ca/$^{40}$Ca ranging from 0.28 % to 1.19 % (Simon and DePaolo, 2010; Valdes et al., 2014; Huang and Jacobsen, 2017; Moynier et al., 2022). Most CAIs are enriched in the lighter Ca isotope due to the large fractionation during condensation (Huang et al., 2012; Amsellem et al., 2017; Simon et al., 2017). Assuming that the homogenisation of Ca isotopes occurred quickly, variable CAI contents in different chondrites could be the main source accounting for the variation on $^{40}$Ca and $^{44}$Ca among different meteorites. The positive Tm anomalies found in carbonaceous chondrites and their correlation with...
δ44/40Ca point to a variable distribution of a refractory component similar to that in group II fine grained CaIs between carbonaceous chondrites (Huang et al., 2012; Dauphas and Pourmand, 2015). For example, the addition of ~4 % group I or ~1.5 % group II CaIs to a non-carbonaceous chondritic Ca isotopic composition could reproduce the range of δ44/40Ca values (as previously suggested by, e.g., Dauphas and Pourmand, 2015), while the effect on δ40Ca is more limited (Fig. 4). This may suggest that the inner Solar System is isotopically different from the outer Solar System due to its depletion in refractory materials (e.g., δ60Ca anomalies; Schiller et al., 2018). As a product of homogenisation during accretion, EC 002 may be taken as a representative sample for the average Ca isotope composition of the inner Solar System.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article/2302.

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