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

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## Abstract

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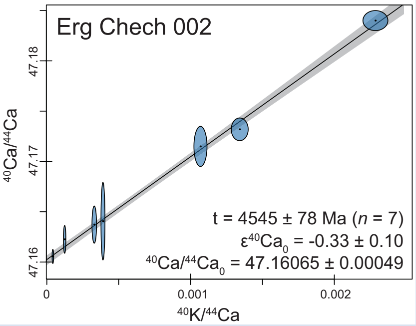

Erg Chech 002 (EC 002) is an andesitic meteorite, which is the oldest lava in the Solar System as determined by the $^{26}$Al-$^{26}$Mg relative chronometer. Here, we present high precision Ca isotope data for the bulk rock and mineral separates of EC 002, and for the first time, obtain a $^{40}$K-$^{40}$Ca isochron by using the Nu Sapphire, a collision cell equipped MC-ICP-MS instrument. The mineral separates yield a $^{40}$K-$^{40}$Ca age of 4545 ± 78 Ma with an initial $^{40}$Ca/$^{44}$Ca = 47.16065 ± 0.00049 ($\varepsilon^{40}\text{Ca}_{\text{SRM 915a}} = -0.33 \pm 0.10$). The age is identical with those obtained from other long lived isotopic systematics but more precise, and it is consistent with the short lived $^{26}$Al-$^{26}$Mg age. The $\delta^{44/40}$Ca 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 $\varepsilon^{40}$Ca values among most meteorites, suggests that the $^{40}$Ca was homogeneously distributed within early formed planetesimals and the $\varepsilon^{40}$Ca value of EC 002 could represent the average of initial $\varepsilon^{40}$Ca of the Solar System.

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## 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 andesitic achondrites but closely matches the experimental melts obtained from non-carbonaceous chondritic composition (Collinet and Grove, 2020; Barrat *et al.*, 2021). The short-lived radioactive system $^{26}$Al-$^{26}$Mg ($t_{1/2} = 0.705$ Ma) yields a precise relative age (1.80 ± 0.01 Ma after CAI formation), which suggests that EC 002 is the oldest magmatic rock and represents the primordial crusts from a protoplanet in the early Solar System (Fang *et al.*, 2022). $^{53}$Mn-$^{53}$Cr dating returned consistently old ages comprising 0.7 ± 0.6 Ma (Zhu *et al.*, 2022) and 1.73 ± 0.96 Ma (Anand *et al.*, 2022) after CAI formation. Compared to the age of EC 002 from the $^{26}$Al-$^{26}$Mg and $^{53}$Mn-$^{53}$Cr systems relative to the initial Solary System, long lived isotopic systems, including $^{40}$K-$^{40}$Ar ($4534^{+117}_{-125}$ Ma, 1σ) and $^{147}$Sm-$^{143}$Nd (4521 ± 152 Ma, 2σ), returned large errors on absolute ages (Barrat *et al.*, 2021; Fang *et al.*, 2022). Furthermore, the negative anomalies on thulium and nucleosynthetic anomalies on Nd isotopes hint that the parent body of EC 002 originated from a non-carbonaceous reservoir (Barrat *et al.*, 2021; Fang *et al.*, 2022 and references therein). To further constrain the accretion history and relationship between the parent body of EC 002 and other planetary embryos, improved geochronology and isotopic tracers are sought for more evidence.

Calcium (Ca) isotopes provide powerful tools for tracing planetary formation and evolution by studying the stable isotopic variations, radiogenic enrichment, and nucleosynthetic anomalies (Russell *et al.*, 1978). Given that Ca is a major element, $^{40}$K-$^{40}$Ca dating could be well suited to date precious samples using the most limited mass of minerals (Shih *et al.*, 1993). The novel collision cell (CC)-MC-ICP-MS, Nu Sapphire, is promising for Ca isotope measurements, including the abundance of $^{40}$Ca, which is impossible to measure by normal MC-ICP-MS due to the interference of $^{40}$K. 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). EC 002, being the oldest achondrite, is an ideal sample to test the application of CC-MC-ICP-MS for future $^{40}$K-$^{40}$Ca dating.

## 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 $^{26}$Al-$^{26}$Mg and $^{147}$Sm-$^{143}$Nd 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 $\delta^{44/40}$Ca and $\varepsilon^{40}$Ca 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 $\delta^{44/40}$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 $\delta^{44/40}$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 planetary materials (Valdes *et al.*, 2021). Meanwhile, limited Ca isotope difference is observed between separated pyroxenes and plagioclases. Two pyroxene fractions show a slightly higher $\delta^{44/40}$Ca values (0.84 ± 0.05 ‰, 2 s.e., $n = 2$) than that of plagioclase fractions (0.75 ± 0.10 ‰, 2 s.e., $n = 3$). Therefore, the Ca isotope difference between pyroxene and plagioclase is around 0.09 ± 0.11 ‰ (2 s.e.), indistinguishable within uncertainty. Such limited variation in $\delta^{44/40}$Ca typically reflects the equilibrium fractionation between minerals, while kinetic isotopic fractionation caused by chemical diffusion would be of much larger magnitude (Antonelli *et al.*, 2019). Different from capture phenocrysts, the mineral fractions we selected are from the matrix. These fractions have no significant chemical zoning which supports the fact that chemical and isotopic equilibrium should have been achieved during the cooling of the lava (Barrat *et al.*, 2021). Based on theoretical calculations, the Ca isotope fractionation between pyroxenes and plagioclases should record an equilibrium temperature higher than 1000 °C (Fig. 1). The liquidus temperature of EC 002 could be roughly estimated by its bulk MgO content and mineral compositions. Two mineral-liquid thermometers provide the equilibrium temperature of 1071 °C and 1114 °C, meanwhile, the melting temperature calculated from its MgO content is ~1224 °C (Putirka, 2008; Barrat *et al.*, 2021). The highly consistent estimated temperature between Ca isotopes and petrology evidence suggests that pyroxenes and plagioclases are at isotopic equilibrium in EC 002 since its formation.

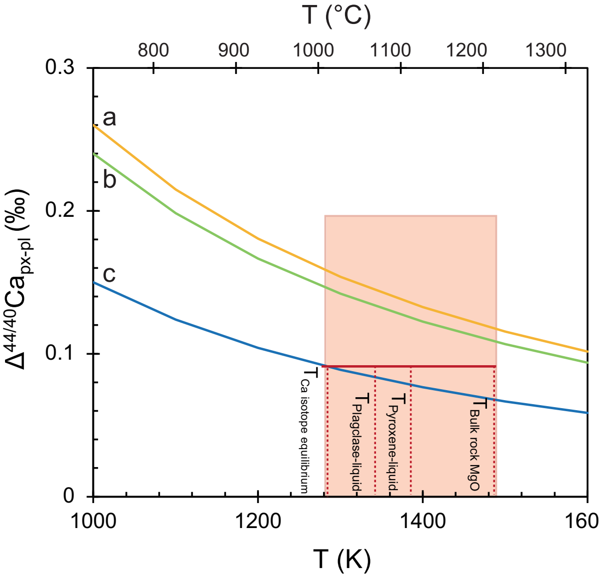

**Figure 1** Plot of $\Delta^{44/40}Ca_{px\text{-}pl}$ *versus* equilibrium temperature of minerals. The red square represents the range of fractionation between pyroxenes and plagioclases and the relative temperature of mineral differentiation. Three solid lines are theoretical equations of equilibrium 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.

## 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 $\delta^{44/40}$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 $^{40}$Ca/$^{44}$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 ($4534^{+117}_{-125}$ 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).

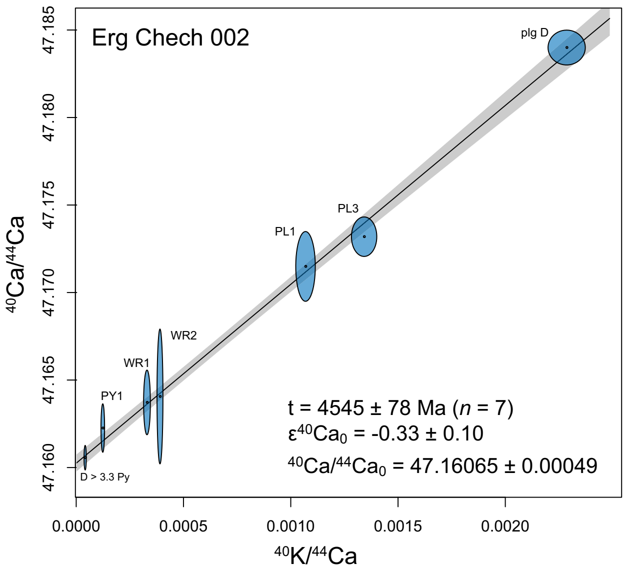

**Figure 2** K-Ca isochron defined by pyroxenes, plagioclases, and bulk rock fractions of EC 002 using IsoplotR (Vermeesch, 2018). The error bars correspond to the 2 s.e. on the ratios. Seven data points define a linear array corresponding to a K-Ca age of 4545 ± 78 Ma for λ($^{40}$K) = 0.5543 Ga$^{-1}$ (Steiger and Jäger, 1977).

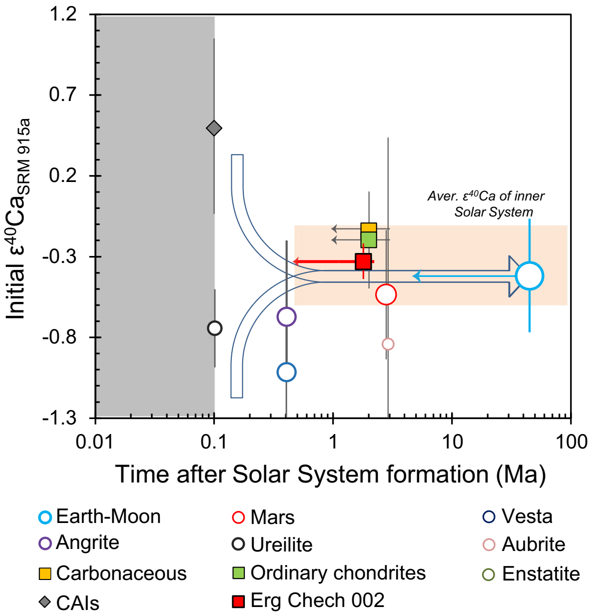

**Figure 3** Time scale for homogenisation of $\varepsilon^{40}$Ca values in the protoplanetary disk, after Simon *et al.* (2009). The $\varepsilon^{40}$Ca of chondrites and planets are homogeneous since the formation of early planetesimals (~1 Ma). The formation of CAIs is considered to represent the time of formation of formation of the Solar System or a maximum of ~0.1 Ma after the formation of the Solar System (Montmerle *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 $\varepsilon^{40}$Ca values of different planets and chondrites are taken from literature, and detailed information is reported in Table S-3.

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.*, 1994). The cooling rate of EC 002 is estimated by diffusion of Fe-Mg in orthopyroxene xenocrysts (~5–10 °C/yr), indicating that the closure temperature from pyroxenes and plagioclases should be around 1000 °C and that it only took decades for EC 002 to close the K-Ca system (Reynard *et al.*, 2006; Barrat *et al.*, 2021). The preservation of the magmatic equilibrium is supported by the consistent equilibrium temperature calculated by mineral compositions and the stable Ca isotope data. It further suggests the K-Ca dating age reflects its formation event.

The reported $^{40}$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 ε-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 corresponds 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.

## Initial $\varepsilon^{40}$Ca Value of EC 002 and Implications for the Ca Isotope Distribution in the Early Solar System

The K-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 $\varepsilon^{40}$Ca value of EC 002 ($-0.33 \pm 0.10$) and reflects its parent body's value at the time of its accretion. Previous studies show variable $\varepsilon^{40}$Ca among different carbonaceous and ordinary chondrites which range from $-0.74$ to $+1.01$ and $-1.43$ to $+0.83$, respectively (Simon *et al.*, 2009; Huang and Jacobsen, 2017; Yokoyama *et al.*, 2017; Moynier *et al.*, 2022). However, the average $\varepsilon^{40}$Ca of these chondrites mostly cluster and return a $\varepsilon^{40}$Ca value of $-0.23 \pm 0.36$ (2 s.e., $n = 15$) for ordinary chondrites and $-0.12 \pm 0.27$ (2 s.e., $n = 15$) for carbonaceous chondrites including the asteroid Ryugu (Table S-4, Fig. 3). The $\varepsilon^{40}$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 $1.80 \pm 0.01$ Ma (the age of EC 002). Given that $\varepsilon^{40}$Ca is variable between refractory inclusions (mostly between $-4$ to $+4$ ε-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 $\delta^{44/40}$Ca values, while carbonaceous chondrites including the primitive asteroid Ryugu have variable $\delta^{44/40}$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 $\varepsilon^{40}$Ca and $\delta^{44/40}$Ca among different meteorites. The positive Tm anomalies found in carbonaceous chondrites and their correlation with

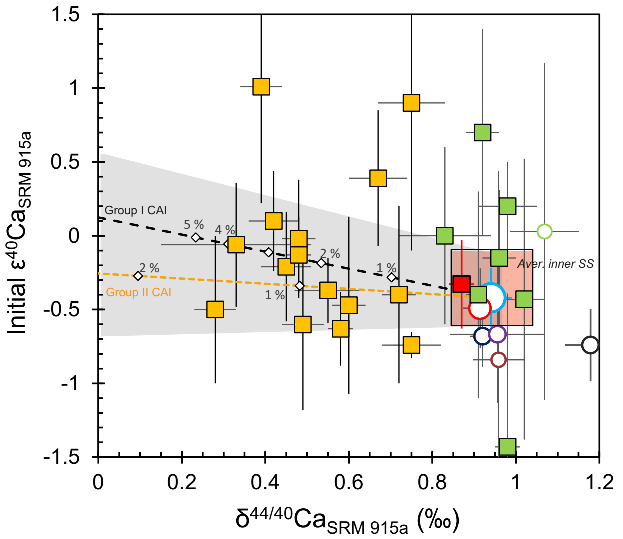

**Figure 4** Plot of $\varepsilon^{40}$Ca values *versus* $\delta^{44/40}$Ca values of different chondrites and planetary bodies; symbols as in Figure 3. The two dashed lines represent the mixing curves between bulk Earth and group I and II refractory inclusions. Detailed information is reported in Table S-3.

$\delta^{44/40}$Ca 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 $\delta^{44/40}$Ca values (as previously suggested by, *e.g.*, Dauphas and Pourmand, 2015), while the effect on $\varepsilon^{40}$Ca 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.*, $^{48}$Ca 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/article2302.

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