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Radioactive Cs capture in the early solar system

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Barium isotopic compositions of primitive materials in the solar system are generally affected by s- and r-process nucleosynthetic components that hide the contribution of the isotopic excess of ^{135}Ba formed by decay of radioactive ^{135}Cs. However, the Ba isotopic composition of the chemical separates from chondrules in the Sayama CM2 chondrite shows an excess of ^{135}Ba isotopic abundance up to (0.33 ± 0.06)%, which is independent of the isotopic components from s- and r-process nucleosyntheses. The isotopic excesses of ^{135}Ba correlate with the elemental abundance of Ba relative to Cs, providing chemical and isotopic evidence for the existence of the presently extinct radionuclide ^{135}Cs ($t_{1/2} = 2.3$ million years) in the early solar system. The estimated abundance of $^{135}\mathrm{Cs}/^{133}\mathrm{Cs} = (6.8 \pm 1.9) \times 10^{-4}$ is more than double that expected from the uniform production model of the short-lived radioisotopes, suggesting remobilization of Cs including ^{135}Cs in the chondrules of the meteorite parent body.

The short-lived isotopes with half-lives less than 10^8 years that were present in the early solar system have completely decayed away. Their decay products can be effectively used as chronometers to study early differentiation processes on the planets such as core formation and mantle-crust differentiation, if the decay system between the parent and daughter elements has been fairly closed. Mass spectrometry is the only way to verify the presence of the extinct radioisotopes as isotopic excesses of their daughter elements. Because detection of these excesses is difficult as a result of their rapid decay and originally low abundances in the early solar system, high precision and sensitivity are required for the isotopic analyses by mass spectrometry.

^{129}I was the first extinct radioisotope detected based on the isotopic excess of ^{129}Xe in a meteorite[1], and the ^{129}I-^{129}Xe system has been widely applied to determine the formation order of early planetary materials. Since then, other decay systems including extinct isotopes such as ^{26}Al-^{26}Mg, ^{53}Mn-^{53}Cr, ^{107}Pd-^{107}Ag, ^{146}Sm-^{142}Nd, ^{182}Hf-^{182}W and ^{244}Pu-Xe have also been developed as useful chronometers to examine early planetary differentiation[2–8].

^{135}Cs is also an extinct radioisotope with a half-life of 2.3×10^6 years, finally decaying to ^{135}Ba. The ^{135}Cs-^{135}Ba decay system is expected to be a useful chronometer to examine aqueous activities on the early planets, considering the high solubility and reactivity of Cs relative to Ba. Isotopic analyses of carbonaceous chondrites provide hints concerning the early evolution of planetary materials, because carbonaceous chondrites consist of materials that have not differentiated since the formation of the solar system. However, the isotopic analyses of bulk carbonaceous chondrites and early condensation materials are not suitable to search for ^{135}Cs because of the large difference in volatility between Cs and Ba. In general, the Cs/Ba elemental ratios of bulk carbonaceous chondrites are very low (e.g., 0.086 for CI chondrite, and 0.0406–0.0421 for CM2 chondrites[9]). Furthermore, the elemental ratio of Cs/Ba in the early condensation materials such as calcium-aluminum-rich inclusions (CAIs) is extremely low (<0.00888 for the Allende CAIs[10]). In addition, the isotopic excess of ^{135}Ba formed by decay of ^{135}Cs may be hidden by additional nucleosynthetic components of s- and r-isotopes. Our early work showed that the larger isotopic anomalies of ^{135}Ba correlated with ^{137}Ba in two CM2 chondrites, Murchison and Sayama, rather than in other carbonaceous chondrites[11]. In particular, the Ba isotopic patterns of acid residue fractions in CM2 show largely negative ε^{135}Ba and ε^{137}Ba, which are strongly subjected to an additional isotopic component of the s-process because of presolar materials[9,11–14]. As well as the s-process nucleosynthetic components due to migration of presolar materials, there are some other contributors providing Ba isotopic anomalies in the early solar system[15–18].

The main purpose of this study is to search for isotopic evidence of ^{135}Cs in the early solar system based on ^{135}Ba isotopic excess and possibly also to develop ^{135}Cs-^{135}Ba chronometry. In this study, we focus on the Ba isotopic compositions of chemical leachates from the chondrules of the Sayama meteorite, which show strong evidence of aqueous alteration. The Sayama meteorite fell in 1986, and it was recognized as a CM2 meteorite after a 14-year

Table 1 | Isotopic variations of Ba from chemical leachates of the Sayama chondrules

sample	$\varepsilon_{135\mathrm{Ba}}$	$\varepsilon_{137\mathrm{Ba}}$	$\varepsilon_{138\mathrm{Ba}}$	Cs (ppb)	Ba (ppm)	^{133}Cs/^{136}Ba
#1-1	+5.6 ± 3.0	+7.3 ± 2.9	+3.3 ± 5.1	14.7 ± 3.9	1.70 ± 0.03	0.11 ± 0.03
#1-2	−1.7 ± 3.8	+1.2 ± 3.6	+1.2 ± 6.6	129 ± 4	2.30 ± 0.03	0.74 ± 0.03
#1-3	+24.1 ± 3.6	+4.0 ± 4.2	−2.8 ± 6.9	113 ± 4	1.36 ± 0.03	1.09 ± 0.05
#1-4	+15.3 ± 4.2	+1.0 ± 3.4	0 ± 6.2	19.0 ± 5.6	0.55 ± 0.04	0.46 ± 0.14
#1-5	+13.1 ± 3.3	−2.4 ± 3.6	+0.4 ± 5.6	6.2 ± 3.3	0.26 ± 0.03	0.31 ± 0.23
#2-1	+14.7 ± 4.3	−3.2 ± 5.0	−0.4 ± 8.4	63.4 ± 14.0	0.34 ± 0.05	1.73 ± 0.34
#2-2	−0.3 ± 6.8	−0.7 ± 6.9	+0.3 ± 4.9	71.6 ± 15.0	0.68 ± 0.04	1.08 ± 0.19
#2-3	−1.6 ± 2.5	−3.4 ± 3.2	−0.6 ± 4.6	105 ± 9	1.28 ± 0.20	1.38 ± 0.30
#2-4	+33.4 ± 6.1	−3.5 ± 6.8	−1.0 ± 13.5	54.5 ± 9.7	0.31 ± 0.01	2.34 ± 0.43
#2-5	+2.9 ± 3.5	+0.7 ± 3.4	+0.5 ± 5.5	49.4 ± 9.3	0.38 ± 0.02	2.45 ± 0.63
#3-1	−0.6 ± 4.7	−4.0 ± 4.6	−0.7 ± 7.5	51.0 ± 24.7	1.05 ± 0.13	0.64 ± 0.32
#3-2	−1.6 ± 1.7	0 ± 1.9	−1.9 ± 3.2	17.1 ± 1.8	0.45 ± 0.24	0.50 ± 0.27
#3-3	+13.5 ± 5.0	−5.2 ± 5.0	−0.5 ± 8.0	7.0 ± 1.4	0.11 ± 0.01	0.85 ± 0.18
#3-4	+4.6 ± 5.0	−1.7 ± 3.7	−0.1 ± 3.2	82.6 ± 16.6	1.31 ± 0.14	0.83 ± 0.19
#3-5	+0.3 ± 0.9	+0.6 ± 1.0	−0.3 ± 1.5	10.5 ± 3.9	10.6 ± 1.1	0.013 ± 0.005

The diameter and the total weight of the chondrule grains in each sample are as follows: Sample 1 (200 to 400 μm, 470 μg), 2 (<200 μm, 210 μg), and 3 (>400 μm, 590 μg) $\varepsilon_{i\mathrm{Ba}} = \{(^{i}\mathrm{Ba}/^{136}\mathrm{Ba})_{\mathrm{sample}}/(^{i}\mathrm{Ba}/^{136}\mathrm{Ba})_{\mathrm{standard}} - 1\} \times 10^4$. Uncertainties are 2σ of the mean.

interval, in 2000. The mineralogy of the Sayama meteorite is similar to those of highly altered CM meteorites such as EET83334 and ALH88045, characterized as the most phyllosilicate-rich members[19], showing an extensive signature for aqueous alteration on the meteorite parent body. There are many reports of selective adsorption behavior of Cs on some types of phyllosilicates[20–23]. It is known that most of the primary minerals in the chondrules of Sayama are replaced by phyllosilicates[19]. Therefore, we expected to find isotopic evidence for the adsorption of presently extinct ^{135}Cs in the Sayama chondrules including phyllosilicates before the complete decay of ^{135}Cs.

Results

Isotopic results of individual samples are shown in Table 1. The data are expressed in ε units defined as follows:

$$\varepsilon_{i\mathrm{Ba}} = \left\{ \frac{(^{i}\mathrm{Ba}/^{136}\mathrm{Ba})_{\mathrm{sample}}}{(^{i}\mathrm{Ba}/^{136}\mathrm{Ba})_{\mathrm{standard}}} - 1 \right\} \times 10^4$$

Large analytical uncertainties in individual fractions are caused by low ion beam intensities resulting from the limited sample weights, but the isotopic deviations obtained in this study are sufficiently large to distinguish the deviation and permit further discussion of the existence of ^{135}Cs. Our major concern is only the isotopic excess of ^{135}Ba derived from ^{135}Cs decay used to develop the Cs-Ba chronometry, but in most cases it is anticipated that the isotopic contribution of ^{135}Cs decay may be hidden by s-process isotopic anomalies because of presolar material. Interestingly, the chemical leachates from the Sayama chondrules show three different types of Ba isotopic patterns.

The Ba isotopic deviation patterns obtained from the chemical leachates of the Sayama chondrules in this study are classified into three cases, as shown in Figs. 1 (1) to 1(3). The first case, type 1, found only in fraction 1-1 in Fig. 1(1) shows positive ^{135}Ba and ^{137}Ba isotopic anomalies, possibly because of depletion of s-process isotopes, that is often observed in the bulk of CM2 meteorites[9–11,17]. For reference, an s-process depletion pattern based on the stellar model[24] is also shown in Fig. 1(1). In the second case, type 2, which appears in fractions 1-2, 2-2, 2-3, 2-5, 3-1, 3-2, 3-4 and 3-5 in Fig. 1(2), no significant deviations were observed in any Ba isotopic abundances, considering the analytical uncertainties. Although fractions 2-3 and 3-1 may include minor isotopic deviations of ^{135}Ba and ^{137}Ba, as shown in type 1, these are unclear because the deviations are smaller than the analytical uncertainties. On the other hand, in the third case, type 3, only significant isotopic excesses of ^{135}Ba greater than the analytical uncertainties were observed in fractions 1-3, 1-4, 1-5, 2-1, 2-4, and 3-3. In most Ba isotopic patterns related to CM2 samples, the isotopic anomalies of ^{135}Ba correlate significantly with those of ^{137}Ba. In the case of large deviations of ^{135}Ba in the samples, small deviations of ^{138}Ba are also often observed. However, in type 3 cases, the Ba isotopic patterns in fractions 1-3, 1-4, 1-5, 2-1, 2-4, and 3-3 are different from those of SiC-enriched or -depleted materials. The data reveal that the

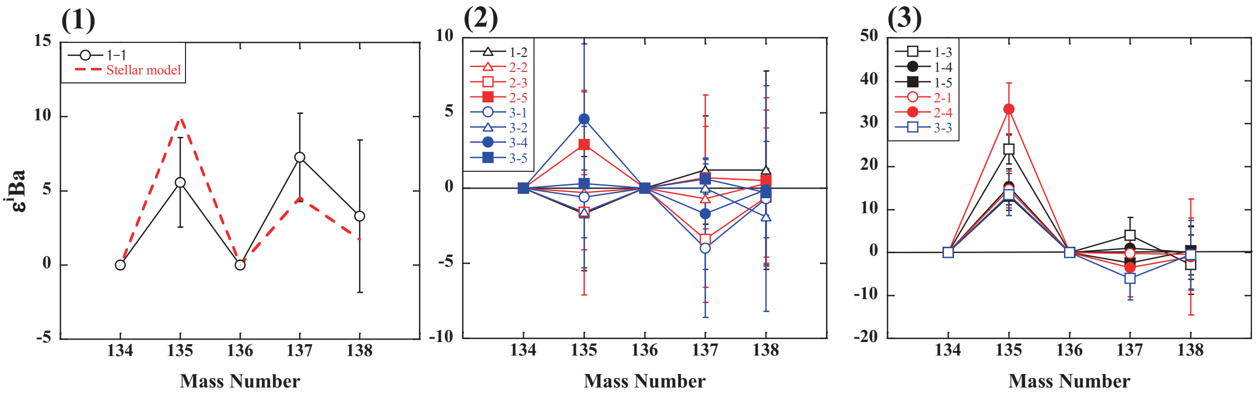

Figure 1 | Isotopic deviation patterns of Ba found in the chemical leachates of the Sayama chondrules. (1) type 1 with positive ^{135}Ba and ^{137}Ba isotopic anomalies due to depletion of s-process isotopic components; (2) type 2 having no significant isotopic anomalies; (3) type 3 with isotopic excess of ^{135}Ba only. For reference, the pattern calculated from the stellar model[24] is also given in (1).

contribution of s-process isotopic component from presolar materials is negligibly small at the present analytical quality. Type 3 isotopic patterns are not observed in the chemical leachates from the bulk sample[11], and have never been reported in any other samples[15–18]. The presence of three different types of isotopic patterns in a single meteorite sample suggests the heterogeneous redistribution of ^{135}Cs by intensive aqueous alteration of the meteorite parent body.

The elemental abundances of Cs relative to Ba, shown as ^{133}Cs/^{136}Ba in Table 1, for individual leaching fractions of the chondrules from the Sayama meteorite are in a wide range from 0.01 to 2.45, and all of them are significantly higher than those of whole rocks and leachate fractions of other carbonaceous chondrites (CI, CM, CV, CO and CK) reported previously[9,11]. Interestingly, the extent of isotopic excesses of ^{135}Ba ($\varepsilon_{135Ba} = +13.1 \sim +33.4$) in fractions 1-3, 1-4, 1-5 and 2-4 correlates well with the ^{133}Cs/^{136}Ba ratios, anticipating the decay from presently extinct ^{135}Cs.

The isotopic excess of ^{135}Ba from the decay product of ^{135}Cs is expressed by the following equation:

$$\left(\frac{^{135}\mathrm{Ba}}{^{136}\mathrm{Ba}}\right)_{\mathrm{present}} = \left(\frac{^{135}\mathrm{Ba}}{^{136}\mathrm{Ba}}\right)_{\mathrm{initial}} + \left(\frac{^{135}\mathrm{Cs}}{^{133}\mathrm{Cs}}\right)_{\mathrm{initial}} \cdot \left(\frac{^{133}\mathrm{Cs}}{^{136}\mathrm{Ba}}\right)_{\mathrm{present}}$$

$(^{135}\mathrm{Ba}/^{136}\mathrm{Ba})_{\mathrm{present}}$ and $(^{133}\mathrm{Cs}/^{136}\mathrm{Ba})_{\mathrm{present}}$ can be experimentally determined by isotopic and elemental analyses. Although $(^{135}\mathrm{Ba}/^{136}\mathrm{Ba})_{\mathrm{initial}}$ and $(^{135}\mathrm{Cs}/^{133}\mathrm{Cs})_{\mathrm{initial}}$ cannot be directly determined from the analytical data, they can be estimated from the correlation between $(^{135}\mathrm{Ba}/^{136}\mathrm{Ba})_{\mathrm{present}}$ and $(^{133}\mathrm{Cs}/^{136}\mathrm{Ba})_{\mathrm{present}}$. Assuming that the ^{135}Ba isotopic excesses in the fractions 1-3, 1-4, 1-5 and 2-4 are products of ^{135}Cs decay, the correlation line between $(^{135}\mathrm{Ba}/^{136}\mathrm{Ba})_{\mathrm{present}}$ and $(^{133}\mathrm{Cs}/^{136}\mathrm{Ba})_{\mathrm{present}}$ provides information about the isotopic abundance of ^{135}Cs. The slope of the correlation line, (^{135}Cs/^{133}Cs), corresponds to the isotopic abundance of ^{135}Cs relative to ^{133}Cs at the time of formation of the chondrules.

Figure 2 shows a correlation between ^{133}Cs/^{136}Ba and ε^{135}Ba for the individual fractions resulting from chemical leaching of the Sayama chondrules. The data from fractions 1-3, 1-4, 1-5 and 2-4 give a straight line (black dotted) with a correlation coefficient of $r = 0.99996$ and a slope of $(9.9 \pm 1.2) \times 10^{-4}$. Although the two data points from fractions 2-1 and 3-3 deviate significantly from the correlation line in Fig. 2, their ε_{135Ba} values may require correction to subtract the s-process isotopic component from their ε_{135Ba} values. Judging from their ε_{137Ba} values, they may be partly influenced by s-process isotopic component. Assuming that the two data points 2-1 and 3-3 include s-process isotopic component, a correction was made to the data by subtracting the s-process contribution from the ^{135}Ba isotopic abundance using the following equation:

$$(\varepsilon_{135Ba})_{\mathrm{corrected}} = (\varepsilon_{135Ba})_{\mathrm{measured}} - (\varepsilon_{137Ba}) \times 2.145$$

The isotopic ratio of $\varepsilon_{135Ba}/\varepsilon_{137Ba} = 2.145$ given by the stellar model[24] is used in the equation. For further discussion, we would like to use the regression line of six points including the two corrected data, because the Ba isotopic deviation patterns of all of six data belonging to type 3 are clearly different from those of other two types (see Fig. 1). Given the correlation line (red solid line in Fig. 2) between ^{133}Cs/^{136}Ba and ε^{135}Ba consisting of the data from the six fractions reveals an isochron of ^{135}Cs-^{135}Ba, the slope of $(8.1 \pm 2.3) \times 10^{-4}$ corresponds to the ^{135}Cs/^{133}Cs isotopic abundance of $(6.8 \pm 1.9) \times 10^{-4}$. On the other hand, the ^{135}Cs/^{133}Cs isotopic abundances estimated in previous studies[9–11] are 1.5-4 times lower than in this study: 1.6×10^{-4} for FUN inclusion C1 of Allende (CV3 chondrite)[25], 4.8×10^{-4} for the Allende CAIs[10] and 2.7×10^{-4} for chemical leachates of Murchison (CM2)[9]. Considering the large difference in the estimated ^{135}Cs/^{133}Cs abundance between the Sayama chondrules (this study) and others, it may be reasonable to consider that the correlation line of the Sayama chondrules is not an isochron directly showing a relative formation interval between this sample and others, but rather a modified isochron probably reformed after enrichment of live ^{135}Cs into the chondrules during aqueous alteration.

Discussion

The average abundances of presently extinct radioisotopes in various stellar sources have been estimated from a uniform galactic production (UP) model[26–29]. The average ratio of an extinct radioisotope to a stable reference isotope in the early solar system, $(N_R/N_S)_{ESS}$, normalized to their nucleosynthetic production ratio, (P_R/P_S), can be expressed according to the following equation as a function of the mean life τ_R of the extinct radioisotope to determine the environment of the early solar system:

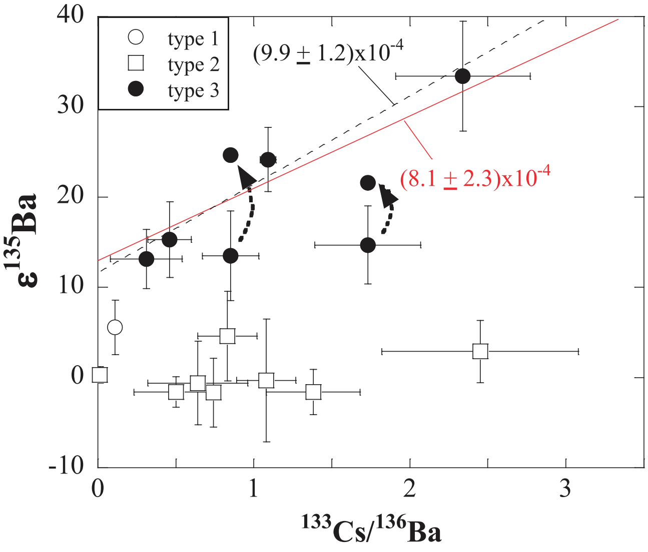

Figure 2 | A correlation diagram between ^{133}Cs/^{136}Ba and ε^{135}Ba of the individual fractions resulted from chemical leaching of the Sayama chondrules. The black dotted line regressed for 4 data (leachate 1-3, 1-4, 1-5 and 2-4) gives a slope of $(9.9 \pm 1.2) \times 10^{-4}$, while the red solid line for 6 data including 2 corrected data (leachates 2-1 and 3-3) gives a slope of $(8.9 \pm 2.3) \times 10^{-4}$.

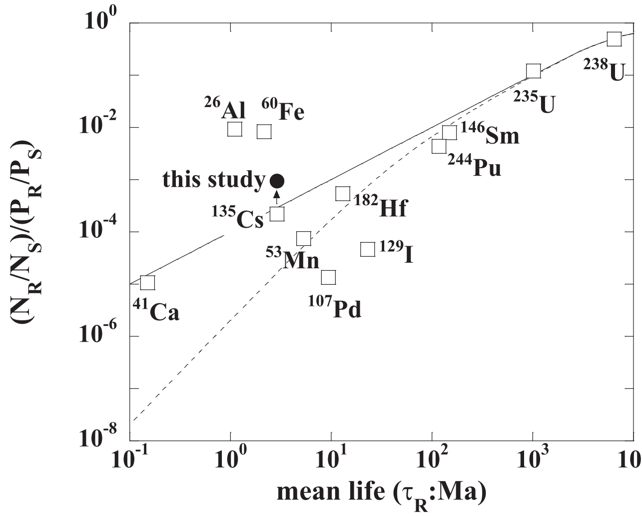

Figure 3 | A correlation diagram between the abundances of short-lived radioisotopes and their mean life. The abundance data are shown as the isotopic ratio of a short-lived isotope (N_R) to a stable reference isotope (N_S) normalized to the ratio of the nucleosynthetic production rates (P_R/P_S). The data point shown in the open symbols in the figure are after previous studies. The closed symbol of ^{135}Cs is obtained in this study.

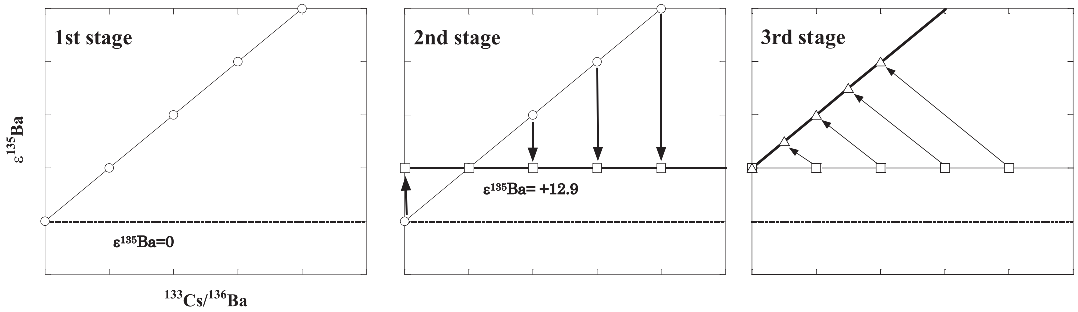

Figure 4 | Possible scenario for the evolution of the Ba isotopes in the Sayama chondrules. (1) Before disturbance of ^{135}Cs-^{135}Ba by aqueous alteration, ε^{135}Ba values of individual samples increased with the ^{133}Cs/^{136}Ba ratios, and the correlation line had a slope. (2) The ^{135}Cs-^{135}Ba chronometer once (or several times) reset, and individual ε^{135}Ba values were homogenized by intense aqueous event(s) on the early planet surfaces. At this stage, the slope of the correlation line was equal to zero, and the ε^{135}Ba values in the Sayama chondrules were homogenized to be +12.9. (3) After the alteration event, individual samples had evolved again their ε^{135}Ba with the ^{133}Cs/^{136}Ba ratios and formed a new isochron with an apparent initial value of ε^{135}Ba = +12.9.

$$(N_R/N_S)_{ESS}/(P_R/P_S) = \tau_R/T\bullet\left(1-e^{-T/\tau_R}\right) \approx \tau_R/T$$

where T is the duration of nucleosynthesis. The time interval (ΔT) is required in case of the isolation of the stellar sources from the formation of the solar system because of further decay of the radioisotope up to the injection into the solar system.

Figure 3 shows a relationship between $(N_R/N_S)/(P_R/P_S)$ and τ_R in logarithm scale. The data points other than ^{135}Cs were from previous studies[27,28]. The extinct radioisotopes can be classified into three groups from the trends of the data points[29] shown in Fig. 3. It is interpreted that ^{53}Mn, ^{182}Hf, ^{244}Pu and ^{146}Sm with a slope of about 2 were produced by a similar source and injected into the interstellar medium. The r-process is considered to be not a single process but two or more processes, one of which produces low mass r-nuclei with $A < 140$, while the other produces heavy r-nuclei with $A > 140$[27]. A type II supernova (SN II) is a possible source of the r-nuclei with $A > 140$ including ^{182}Hf and actinides like ^{238}U, ^{235}U and ^{244}Pu, which differ from the production of ^{129}I and ^{107}Pd. Because the mass of ^{135}Cs is at the boundary between heavy and light mass r-process nucleosyntheses, ^{135}Cs may have two or more sources of production by r-process. Furthermore, asymptotic giant branch (AGB) sources may also contribute production of ^{135}Cs, because ^{135}Cs is also produced by the s-process. Considering several possible contributors for ^{135}Cs production, the production rate from the SN II model may provide an underestimate for the total production of ^{135}Cs. On the other hand, the data point for ^{135}Cs estimated from the Allende C1 FUN inclusion, ^{135}Cs/^{133}Cs = 1.6×10^{-4}, almost lies on the UP model line with a slope of 1. The abundance of ^{135}Cs in the Sayama chondrules in this study, ^{135}Cs/^{133}Cs = $(6.8 \pm 1.9) \times 10^{-4}$, is 2.3 times higher than that expected from the UP model. There is a possibility that remobilization of Cs including ^{135}Cs occurred in the chondrules of the meteorite parent body as a result of intensive aqueous alteration.

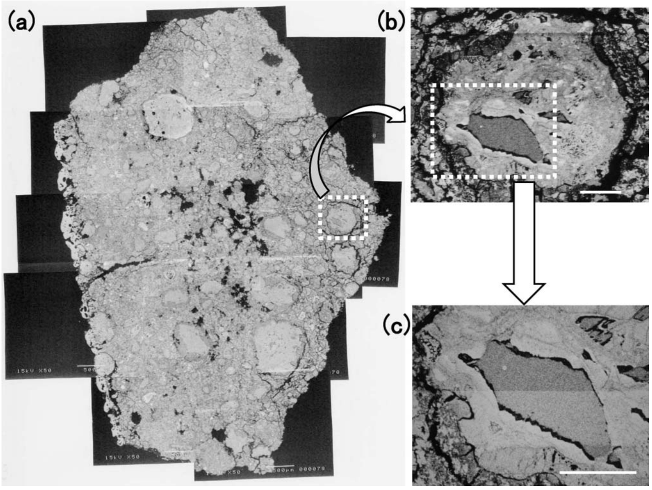

Figure 5 | Back-scattered electron images of (a) a thin section of the Sayama meteorite, (b) enlargement of one of condrules in the thin section, and (c) irregular-shaped relict olivine crystals found in the chondrule. The scale bars in (b) and (c) correspond to 100 μm.

The y-intercept of the correlation line shown in Fig. 2 provides ε^{135}Ba = $+12.9 \pm 3.1$, suggesting that the Ba isotopes of the Sayama chondrules were initially affected by a ^{135}Ba-rich component before the occurrence of aqueous activity. To explain the evolution of Ba isotopes in the Sayama chondrules, the following scenario is proposed. (1) At the first stage, ε^{135}Ba values of individual samples increased with the ^{133}Cs/^{136}Ba ratios, and the correlation line had a nonzero slope. (2) The ^{135}Cs-^{135}Ba chronometer was reset once (or several times) because of one or more intense aqueous event(s) on the early planet surfaces, and individual ε^{135}Ba values were homogenized. At this stage, the slope of the correlation line was equal to zero, and the ε^{135}Ba values in the Sayama chondrules were homogenized to +12.9. (3) Since then, individual samples had evolved their ε^{135}Ba with the ^{133}Cs/^{136}Ba ratios and formed a new isochron with an apparent initial value of ε^{135}Ba = +12.9. This scenario is illustrated in Fig. 4.

As another interpretation, the correlation line can be explained by a two-component mixing model between high- and low-Cs/Ba material in the meteorite parent body. However, in this case, the existence of high-Cs/Ba matters is required in the sample. We searched for high-Cs/Ba matter using an electron probe microanalyzer and for highly enriched ^{135}Ba material using a secondary ion mass spectrometer to identify the specific phase for the ^{135}Cs carrier, but had no success. The original high-Cs/Ba material might have disappeared or been reformed by intense aqueous alteration in the Sayama parent body. As a result of major and minor element analyses in the whole rock of the Sayama meteorite, significant deviations of alkaline elements Na and Rb relative to the CM average composition were found in the Sayama meteorite[19]. These results suggest mobilization of alkaline elements by aqueous alteration of the meteorite parent body.

Ba isotopic studies of the natural fission reactor, Oklo, in the east of Gabon in central Africa, may provide a hint to consider the situation of Cs/Ba differentiation under aqueous activity[30,31]. In the Oklo natural reactor, various types of radioisotopes were produced by fission 2.0 billion years ago, and the remnants of the fissiogenic isotopes can still be detected as isotopic anomalies associated with enrichment or depletion of the decay products. In the case of the Oklo natural reactor, the short-lived radioisotope ^{137}Cs ($t_{1/2}$ = 30 years) as well as ^{135}Cs can be used to consider the Cs/Ba differentiation timing in spite of the large difference in half-lives between ^{135}Cs and ^{137}Cs. The data suggest the occurrence of early differentiation between Cs and Ba within 20 years after the production of fissiogenic Cs (^{135}Cs and ^{137}Cs) in the reactors[31].

It is reasonable to consider that the Cs/Ba differentiation in the Sayama meteorite parent body occurred in the early stage of the aqueous alteration while ^{135}Cs was still alive. As a result, Cs might have been enriched in the aqueously altered chondrules, because of the selective uptake of Cs (including live ^{135}Cs) into phyllosilicates in the chondrules. The experimental data for ^{133}Cs/^{136}Ba support the selective uptake of Cs in the chondrules. Among the type 3 leachates having clear isotopic excesses of only ^{135}Ba, fractions 1-3, 2-1 and 2-4 show 2.0 to 4.3 times higher ^{133}Cs/^{136}Ba ratios than those of CM2 whole rocks.

Presently extinct radioisotopes that have a limited time of existence in the solar system put temporal constraints on the early evolution of the solar system. In the case of ^{135}Cs, it is difficult to apply the ^{135}Cs-^{135}Ba decay system for chronometry in the early solar system because of the high reactivity and volatility of Cs. However, our approach provides a hint of how to develop a ^{135}Cs-^{135}Ba chronometer to study the early aqueous activity on the primitive planetary materials. The Ba isotopic composition of the chemical separates from chondrules in the Sayama CM2 chondrite shows a significant excess of ^{135}Ba resulting from the decay of ^{135}Cs, because the excesses are independent of any other nucleosynthetic components and correlate with the Cs/Ba elemental ratios. The results show large excesses of the ^{135}Ba isotope without any other Ba isotopic anomalies and correlation with the elemental Cs/Ba ratios. However, the ^{135}Cs/^{133}Cs ratio estimated in this study is more than double the expected value, suggesting remobilization and enrichment of Cs including ^{135}Cs in the chondrules of the meteorite parent body. This is the first isotopic evidence to show the existence of presently extinct ^{135}Cs and the relationship with an alteration effect in the early solar system.

There are several reports on the high initial abundance of extinct radioisotopes probably caused by late input into the solar system[32]. Adsorption mechanism may also provide one of great contributions to produce the high initial abundances of short-lived radioisotopes, if the extinct radioisotope shows a geochemical signature for strongly selective uptake into the specific minerals.

Methods

The Sayama meteorite consists mainly of black matrix, with no large chondrules and no specific inclusions found inside the meteorite. From observation with optical and scanning microscope, most of the primary minerals in the chondrules are replaced by phyllosilicates. Around half of the olivine crystals in the several chondrules have been replaced by serpentine. This is mineralogical evidence of intensive aqueous interaction. Figure 5 shows back-scattered electron images of (a) a thin section of the Sayama meteorite, (b) one of typical condrules in the thin section, and (c) irregular-shaped relict olivine crystal found in the chondrule.

Thirty five chondrules with diameter from 100 to 600 μm were hand-picked from the matrix portion of the Sayama meteorite. The collected chondrules were classified into three according to their approximate sizes. Each sample weighing 210 to 590 μg was used individually in this study. To obtain chemical separates from each sample, sequential acid leaching technique was carried out. Each sample was leached successively by 0.5 mL of 0.1 M acetic acid-ammonium acetate, 0.1 M HCl, 2 M HCl, and aqua regia. The residue was finally decomposed by HF-HClO$_4$ treatment with heating, and dissolved in 0.5 mL of 2 M HCl. The procedures performed to obtain samples with a wide range of Cs/Ba fractions were based on our previous study[10].

The Ba fraction was chemically separated using a conventional cation exchange method[30]. Each fraction obtained from leaching and acid digestion treatments was evaporated to dryness, and dissolved in 0.5 mL of 2 M HCl. The sample solution was loaded onto a cation-exchange resin packed column (Bio-Rad AG50WX8, 200–400 mesh, H$^+$ form, *l*50 mm × ϕ4.0 mm). The column was washed with 5 mL of 2 M HCl and 0.5 mL of 2 M HNO$_3$, successively, and the Ba fraction was then eluted with 3.0 mL of 2 M HNO$_3$. The Ba fraction was divided into two portions: one for thermal ionization mass spectrometry (TIMS) analysis to determine the isotopic composition, and the other for inductively coupled plasma mass spectrometry (ICP-MS) analysis to determine the Cs and Ba elemental abundances.

A thermal ionization mass spectrometer (Micromass VG54-30) equipped with seven Faraday cups was used in this study. Data collection was performed in the static multimode. The seven Faraday cup collectors were configured to monitor ^{134}Ba, ^{135}Ba, ^{136}Ba, ^{137}Ba, ^{138}Ba, ^{139}La and ^{140}Ce. Monitoring of ^{139}La and ^{140}Ce during the Ba isotopic analyses is required to check the isobaric interferences of ^{136}Ce, ^{138}Ce, and ^{138}La on ^{136}Ba and ^{138}Ba mass spectra. Two minor Ba isotopes, ^{130}Ba and ^{132}Ba, were not monitored in this study. A Ba standard solution produced by SPEX Certi Prep, Inc. was used as a standard material in this study.

The Ba sample was loaded onto a Re outer filament of Re-triple filament assembly. A ^{138}Ba$^+$ ion beam of $(0.3–1.5) \times 10^{-12}$ A was obtained for more than 1 h from individual fractions.

All isotopic data are referenced to ^{136}Ba, and the isotopic ratios are normalized to ^{134}Ba/^{136}Ba = 0.307776 to correct for instrumental mass fractionation[3]. Because both ^{134}Ba and ^{136}Ba are s-only isotopes as a result of shielding by ^{134}Xe and ^{136}Xe, respectively, the normalization by ^{134}Ba/^{136}Ba is useful to find isotopic anomalies from processes other than the contribution of s-isotopes. However, most of the bulk CM2 meteorites are known to suffer mainly from s-process isotopic anomalies because of depletion or enrichment of presolar grains[11]. Besides the use of ^{134}Ba/^{136}Ba, two other normalization factors, ^{134}Ba/^{138}Ba = 0.033715[33] and ^{135}Ba/^{138}Ba = 0.09140[11] have previously been used. The use of ^{135}Ba/^{138}Ba for normalization is not suitable for detection of isotopic variation of ^{135}Ba, which is one of the major purposes in this study. In previous studies of the Ba isotopic compositions in carbonaceous chondrites[11], the ^{134}Ba/^{136}Ba-normalized data provided a typical isotopic pattern in the presence or absence of the s-process isotopic component because of presolar materials[12]. Therefore, in this study, we used ^{134}Ba/^{136}Ba = 0.307776 as a normalization factor.

Determination of the elemental abundances of Ba and Cs in individual chemical leachates was performed using ICP-MS. The solution was evaporated to dryness, and redissolved with 5 mL of 0.5 M HNO$_3$. 0.5 g of 10 ppb-indium solution was added precisely to the individual sample solutions as an internal standard element to optimize the analytical conditions for Cs and Ba measurements. An Agilent 7500 ICP-MS was used in this study. The detailed analytical procedures were based on a previous method[34].

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Author contributions

All authors contributed equally to the paper.

Additional information

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