

REDISTRIBUTION OF ALKALINE ELEMENTS IN CHONDRULES OF THE SAYAMA (CM2) METEORITE: POSSIBLE ALTERATION EFFECT IN ASSOCIATION WITH AQUEOUS ACTIVITY IN THE EARLY SOLAR SYSTEM.

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Introduction: Early alteration processes that probably occurred on the primitive asteroids are important activities for understanding the evolution of the solar system and the differentiation of solar planetary materials. Aqueous alteration in the early solar system is one of the primitive activities in the asteroidal bodies. The presence of hydrous minerals observed in the CI and CM2 chondrites provides evidence that aqueous alteration occurred on the meteorite parent body.

Isotopic studies using the decay of short-lived radionuclides put temporal constraints on the occurrence of early activities in the CI and CM chondrites. The ⁵³Mn-⁵³Cr isotopic system has been usefully applied to determine the formation ages of carbonates in carbonaceous chondrites, suggesting the timing of occurrence of aqueous alteration on the meteorite parent bodies. The ¹³⁵Cs-¹³⁵Ba isotopic system in chondritic materials is expected to work as a sensitive chronometer for aqueous processes on the parent bodies, because Cs is one of the elements that react strongly with water. To develop the ¹³⁵Cs-¹³⁵Ba chronometry, precise determination of the Ba isotopic compositions in the early solar system materials is required. Ba has seven stable isotopes consisting of p-, s-, and r-process nucleosynthetic origin. Most previous Ba isotopic studies of meteorites focused on the variation of r- and s-process nucleosynthetic components due to additional inputs in the early solar system. ¹³⁵Ba and ¹³⁷Ba isotopes are sensitive to s- and r-process variations, and often have deficits and/or excesses in chemical separates and whole rocks in carbonaceous chondrites due to the existence of presolar grains [1,2]. Furthermore, the isotopic variation due to the existence of presolar grains gives disadvantages to find the contribution of the isotopic excess of ¹³⁵Ba decayed from the presently extinct radioisotope ¹³⁵Cs ($t_{1/2}=2.3$ Ma).

It is known that the Sayama meteorite (CM2) shows an extensive signature for aqueous alteration on the meteorite parent body, and that most of the primary minerals in the chondrules are replaced to phyllosilicates as the result of the aqueous alteration. In our previous study, Ba isotopic composition of the chemical separates from chondrules in the Sayama CM2 chondrite shows the excess of ¹³⁵Ba isotopic abundance

up to (0.33 ± 0.06) %, which is independent of the isotopic components from s- and r-process nucleosyntheses [3]. In this paper, SHRIMP analyses were performed for the determination of elemental abundances of alkaline elements (Rb, Sr, Cs, and Ba) and of the isotopic abundances of Ba in the chondrules collected from the Sayama meteorite.

Samples and Experiments: The Sayama meteorite fell in 1986, and was recognized as a meteorite of CM2 in 2000. The mineralogy of the Sayama meteorite is similar to those of highly altered CM meteorites such as EET83334 and ALH88045, which are characterized as the most phyllosilicate-rich members [4], showing an extensive signature for aqueous alteration on the meteorite parent body. In our previous study, 35 chondrules with diameters from 100 to 600 μ m were handpicked from the matrix portion of the Sayama meteorite [3]. Although most of them were consumed in the previous isotopic study with complete decomposition and chemical treatments, two remained, and were used in this study. The polished section was prepared from these two chondrules. Prior to the identification of serpentine phases by Raman spectrometry, elemental mapping of Mg, Fe, Si, O, Al, Ca, and K of the samples were performed with a SEM-EDX (JEOL JSM-6390A). The beam size was 1 μ m and the current was 1 nA at 15 kV of acceleration voltage. The data were treated with a standardless ZAF correction method for semi-quantitative electron probe micro-analyses of microscopical particles.

Raman spectroscopy was completed on a Renishaw inVia Raman Reflex microscope equipped with a Leica DMLM microscope. The spectra were excited with a 532 nm LD laser and the Raman spectra were obtained on the thin section. The instrument had Streamline capabilities for rapid mapping 200 times faster than the traditional point-by-point mapping. It was used to collect spatially resolved chemical images of serpentinized phases transformed from olivine in chondrules on the thin section.

Determination of the elemental concentrations of Rb, Sr, Cs and Ba was performed with a SHRIMP at Hiroshima University. The samples were sputtered with a 5 nA O₂⁻ primary ion beam. The mass resolution

(M/ΔM at 1% of peak height) was set at 9000 to resolve the oxide ion species (MO^+) from the mass region in this study. The masses of ^{86}Rb , $^{87}\text{Rb}+^{87}\text{Sr}$, ^{88}Sr , $^{120}(\text{Si}_2^{16}\text{O}_4)$, ^{133}Cs , ^{135}Ba , ^{137}Ba , ^{138}Ba , ^{139}La , and ^{140}Ce and backgrounds (at masses of 85.5 and 140.5) were monitored. Standard glass SRM 612 obtained commercially from NIST was used for the calibration of secondary ion ratios to the elemental concentrations.

Results and Discussion: The existence of serpentine replaced from olivine in the Sayama chondrules is considered to be clear evidence for the occurrence of an early aqueous alteration on the parent body. Our major concern is the redistribution of alkaline elements in association with the aqueous alteration, and the search for radiogenic ^{135}Ba decayed from the presently extinct ^{135}Cs . Because selective adsorption of alkaline elements into serpentine is expected [3], finding serpentine phases in the samples is required to look for the isotopic excess of radiogenic ^{135}Ba .

The abundances of Rb, Sr, Cs and Ba vary widely in individual chondrule grains, and in particular those in serpentine phases are relatively higher than in other parts. This suggests selective adsorption of alkali elements into the serpentine phases in association with aqueous alteration. Comparing the data obtained in this study with the CI reference data, there is a significant chemical fractionation between Cs and Ba by the redistribution in the chondrules, but little fractionation between Rb and Sr. The Rb/Sr ratios collected from the chondrules range from 0.045 to 0.69, and most of the data points show a similar trend with the CI value (Rb/Sr=0.295). On the other hand, the Cs/Ba ratios varied widely between 0.047 and 1.11, and most are higher than the CI value (Cs/Ba=0.0799). The result shows the heterogeneous distributions of the alkaline elements in the chondrules. Interestingly, four analytical points from serpentine phases show higher contents of Rb, Sr, Cs, and Ba than other points. The higher Rb/Sr and Cs/Ba ratios at these four points suggest the selective adsorption of Rb and Cs in the serpentines in association with the early aqueous alteration on the parent body.

Three Ba isotopes ^{135}Ba , ^{137}Ba and ^{138}Ba were selected for the in-situ isotopic analysis in this study, because they have less isobaric interferences than the other Ba isotopes. ^{135}Ba and ^{137}Ba have no isobaric isotopes of other elements. Although ^{138}Ce and ^{138}La are isobaric interferences of ^{138}Ba , their isotopic abundances are very minor (0.25% and 0.09%, respectively). One of major concerns in this study is isotopic search for radiogenic ^{135}Ba decayed from ^{135}Cs . Although most of the Ba 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 the decay of radioactive ^{135}Cs , those of the chemical separates from chondrules in the Sayama meteorite shows an excess of ^{135}Ba isotopic abundance up to $(0.33 \pm 0.06)\%$, which is not derived from the isotopic components from s- and r-process nucleosyntheses but possibly from the decay of ^{135}Cs [3].

Because some of the Ba isotopic data set obtained from the Sayama chondrules are affected by additional s-process isotopic component, the existence of radiogenic ^{135}Ba is hidden at the present state. However, because the isotopic ratio of the s-process component is given as $^{135}\text{Ba}/^{137}\text{Ba}=2.145$ by the stellar model [5], the radiogenic ^{135}Ba component can be estimated from subtracting the s-process component by conventional method [3,6]. Furthermore our previous study on the bulk analyses of the Sayama chondrules suggests the possibly large redistribution of Cs in the chondrules during the aqueous alteration in the early solar system. Although we carefully selected the analytical points for micro-region isotopic measurements of Ba to find isotopic evidence of radiogenic ^{135}Ba , the existence of initial ^{135}Cs in the solar system is still unclear from this study. Interference from additional nucleosynthetic components in the solar primitive materials is one of the major problems in this study. Based on the stellar model, a correction was made in this study to detect radiogenic ^{135}Ba by subtraction of the s-process component. The isotopic excess from radiogenic ^{135}Ba is considered to be too small to be detected by in-situ analysis in the current situation, finding specific phases having a much higher Cs/Ba elemental abundance ratio (>10) is required.

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