

**STRONTIUM STABLE ISOTOPIC ANOMALIES IN PRIMITIVE METEORITES AND CHONDRULES.** Wataru Okui<sup>1</sup> and Tetsuya Yokoyama<sup>1</sup>, <sup>1</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-21-1 Ookayama, Meguro-ku, Tokyo, Japan (okui.w.aa@m.titech.ac.jp)

**Introduction:** Chondrules are one of the main constituents of chondrites (CC: 15-60 vol.%, OC: 60-80 vol.%, EC: 60-80 vol.%). The identification of the mechanisms responsible for chondrule formation must be an important clue to understand the processes of materials evolution in the proto solar system. Numerous astrophysical and physicochemical models have been proposed to account for the chondrule formation, including (1) condensation, (2) nebular lightning, (3) magnetic reconnection flares, (4) gas dynamic shock waves, (5) planetesimal bow shocks, and (6) radiative heating [1-6]. The other chondrule formation mechanisms are summarized elsewhere [7]. Mechanisms for forming chondrules that are consistent with the petrological and geochemical observation prefer various flash heating models: nebular lightning, magnetic reconnection flares, gas dynamic shock waves and radiative heating. However, there still lacks a comprehensive model that ultimately explain the mechanism of chondrule formation.

Almost all of the previous investigations in isotope cosmochemistry regarding chondrules have utilized light elements such as oxygen [8], or radiogenic isotopes [9]. Only a few researches examined to measure stable isotopes of heavy elements. Moynier et al. [10] measured stable Sr isotope variations ( $\delta^{88/86}\text{Sr}$ ) in bulk Allende, Allende chondrule, Allende CAI, Allende matrix, and bulk rock samples of chondrites and achondrites by using MC-ICP-MS. They reported that single chondrules and one CAI from Allende are strongly enriched in light isotopes (up to -1.73‰) and Allende matrix is slightly enriched in heavy isotopes (+0.66). Because they did not measure  $^{84}\text{Sr}/^{86}\text{Sr}$  ratios, it remained unclear whether these chondritic components have nucleosynthetic Sr isotope anomalies.

More recently, our group found the existence of nucleosynthetic Sr isotope anomalies in bulk meteorites and CAIs [11], the anomalies that vary in different meteorite groups and correlates with oxygen isotopes. The correlation between Sr and O isotopes implies that most solar system materials formed by mixing of at least two components: a CV-chondrite-like component (rich in  $^{16}\text{O}$  and in p-process  $^{84}\text{Sr}$  or r-process  $^{88}\text{Sr}$ ) and an ordinary chondrite-like component (poor in  $^{16}\text{O}$  and  $^{84}\text{Sr}$  or  $^{88}\text{Sr}$ ). To further investigate this correlation, it is important to identify Sr isotope compositions in individual chondritic constituents.

In this study, we have developed a Sr double spike technique using TIMS to simultaneously determine the extent of mass dependent fractionation and nucleosynthetic anomalies for Sr in chondrules, aimed to understand the origin and formation process of chondrules.

**Experimental:** Two chondrules ( $\phi = 1\text{-}2\text{ mm}$ , 2-3 mg) were separated from Allende (CV3.6) by a freeze-thaw

method. They were cleaned by acetone and  $\text{H}_2\text{O}$  in an ultrasonic bath and powdered in a quartz mill. For Sahara 97072 (EH3) and Sahara 98175 (LL3.5), individual chondrules were sampled from the sliced specimens by using a micro milling system (Geomill 326, Izumo), in which the drilled chondrule powder was recovered with a micro-powder recovery system [12]. The chondrule powders were dissolved with HF and  $\text{HNO}_3$  and were evaporated at 120 °C, followed by the addition of  $\text{HClO}_4$ . The samples were heated at 165 °C and 195 °C in a stepwise fashion to decompose insoluble fluorides, and were finally dissolved in 0.4 mL of 3M  $\text{HNO}_3$  [13]. For each chondrule, ~10% of the sample solution was removed and used for the determination of major and trace element concentrations, and the rest was used for high precision Sr isotopic measurement. The Sr in each chondrule was purified by passing through 0.3 mL of Sr Spec resin (Eichrom) twice. The Sr solution was passed through 0.1 mL of CG71-C to remove organic matters derived from the Sr Spec resin. About a half of the purified Sr was removed, to which a  $^{84}\text{Sr}$ - $^{86}\text{Sr}$  enriched spike solution was added at an appropriate mixing rate following ref. [14] for the determination of mass dependent fractionation.

Sr isotopic measurements were carried out by using a thermal ionization mass spectrometry (TIMS) in positive ion mode (Triton plus at Tokyo Tech, ThermoFisher Scientific). In addition to Sr isotopic measurements of each chondrule, we also measured NIST 987 as a standard sample, and bulk rocks of Allende and Sahara 97072. Approximately  $\geq 10\text{ ng}$  of Sr was loaded onto single out-gassed W filament (Nilaco, Japan) with Ta solution as a Sr ionization activator. The data were obtained by averaging 100 to 400 ratios with 2 sigma rejection, acquired by 5 to 20 block measurements (20 scans/block) in the static multi-collection using five Faraday cups. In this study, instrumental mass fractionation during TIMS analysis is corrected for by two different approaches. For unspiked Sr runs, the Sr ratios were normalized to correct for mass fractionation by assuming that  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ . For spiked Sr measurements, the Sr ratios were normalized by the double spike inversion. To avoid confusion, we report the  $^{84}\text{Sr}/^{86}\text{Sr}$  ratios in  $\mu$ -unit ( $\mu^{84}\text{Sr}$ ) for non-spiked Sr measurements, whereas  $\delta$ -unit is used to represent the mass dependent stable Sr isotope variations ( $\delta^{88/86}\text{Sr}$ ) that determined from the double spike method. The  $\mu$ -unit and  $\delta$ -unit are  $10^6$  and  $10^3$  relative deviations from the average of NIST 987, respectively.

**Results:** The  $\mu^{84}\text{Sr}$  values of bulk rocks and chondrules for Allende, Sahara 97072, and chondrules for Sahara 98175 are presented in Fig. 1. Those of the bulk rock of RBT 04127 (LL6) and Allende CAIs obtained from Moynier et al. [11] are plotted for comparison. All chondrules have  $\mu^{84}\text{Sr}$  values

greater than the bulk of their host meteorite. Of these chondrules, Allende chondrules have the greatest  $\mu^{84}\text{Sr}$  values that are comparable to the Allende CAIs.

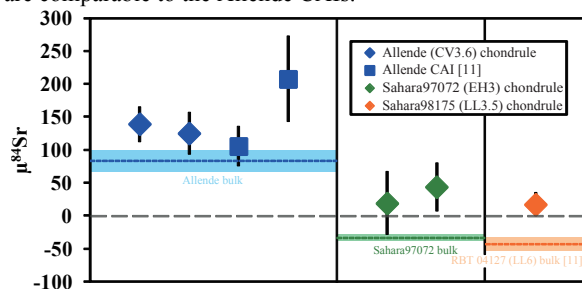


Fig. 1.  $\mu^{84}\text{Sr}$  values of bulk rocks and chondrules for Allende (CV3.6), Sahara 97072 (EH3) and Sahara 98175 (LL3.5). Bulk rock data of RBT 04127 (LL6) and CAIs data of Allende (CV3.6) from [11] are presented for comparison.

The  $\delta^{88/86}\text{Sr}$  values for the bulk meteorites and their chondrules are plotted in Fig. 2. Allende chondrules are extremely enriched in light Sr isotopes. The result is generally consistent with the previous study [10]. In contrast, isotopic fractionation in chondrules from Sahara 97072 and Sahara 98175 are limited, and they have  $\delta^{88/86}\text{Sr}$  values close to that of the bulk chondrite of the same meteorite group.

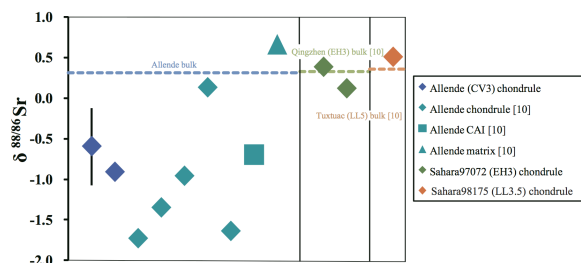


Fig. 2.  $\delta^{88/86}\text{Sr}$  values for bulk rocks and chondrules from Allende (CV3.6), Sahara 97072 (EH3) and chondrules from Sahara98175 (LL3.5). CAI and matrix and chondrules data of Allende (CV3), bulk rock of Tuxtuac RT (LL5) and Qingzhen (EH3) from [10] are shown for comparison.

**Discussion:** It has been suggested that carbonaceous chondrites possess internal nucleosynthetic isotope anomalies for heavy elements including Sr. Stepwise leaching experiments of bulk chondrites revealed that isotopically distinctive carriers for Sr in carbonaceous chondrites are CAIs and presolar grains [15]. Our new data indicate that chondrules are also isotopically distinctive carrier for Sr not only in carbonaceous but also in ordinary and enstatite chondrites. Because all chondrules have  $\mu^{84}\text{Sr}$  values higher than their host bulk meteorites, the matrix components should have relatively low  $\mu^{84}\text{Sr}$  values. This strongly argues against the genetic linkage between chondrules and matrix components in a single meteorite.

As for the mass dependent Sr isotope variations, Moynier et al. [10] concluded that the origin of different  $\delta^{88/86}\text{Sr}$  values between chondrules and matrix from Allende is the fluid-assisted metamorphism on the Allende parent body. The process fractionated Sr during low-T element redistribution due to mobilization of Sr from matrix into chondrules, as chondrules are lighter than matrix. In such a case that Sr was redistributed on the parent body during fluid-assisted metamorphism, our observation regarding the  $\mu^{84}\text{Sr}$  values (Fig.1) suggests that the effect of fluid-assisted metamorphism must be restricted in order not to erase the effect of nucleosynthetic Sr isotope anomalies in chondrules. If fluid-assisted metamorphism occurred extensively, the  $\mu^{84}\text{Sr}$  value in chondrule could shift to the value in the metamorphic fluid. For LL and EH chondrites, there is no sign of significant mass dependent fractionation between chondrule and matrix.

From our observation, it is conceivable that chondrules and matrix in each chondrite type have formed in separated locations in time and space, and the Sr variations are inherited from an initial heterogeneous distribution of Sr isotopes within the solar nebula. If chondrules and matrix of Allende were subject to fluid-assisted metamorphism on the parent body which lessened the extent of nucleosynthetic Sr isotope anomalies in chondrules, the original isotopic anomalies in chondrules must have been much greater than now detected. Additional data is needed to further discuss the origin of Sr isotope anomalies in chondrules.

**References:** [1] Suess, (1949) *Electrochem.* 53, 237..

- [2] Cameron, (1966) *Earth and Planet. Sci. Lett.* 1, 93. [3] Cameron, (1995) *Meteoritics* 30, 133. [4] Connolly and Love, (1998) *Science* 280, 62. [5] Hood, (1998) *Meteorit. Planet. Sci.* 33, 97. [6] Eisenhour and Buseck, (1994) *Science* 265, 1067. [7] Rubin, (2000) *Earth-Science Reviews* 50, 3. [8] Clayton et al., (1991) *Geochem. Cosmochim. Acta* 55, 2317. [9] Shimoda et al., (2005) *Science* 40, 1059. [10] Moynier et al., (2010) *Earth and Planet. Sci. Lett.* 300, 359. [11] Moynier et al., (2012) *ApJ*. 758, 1 [12] Sakai and Kodan, (2011) *Rapid Commun. Mass Spectrom* 25, 1205. [13] Yokoyama et al., (1999) *Chem. Geol.* 157, 175. [14] Rudge et al., (2009) *Chem. Geology* 265, 420. [15] Yokoyama et al., (2012) *Goldschmidt*.