

STABLE STRONTIUM ISOTOPIC COMPOSITION OF ENRICHED SHERGOTTITE, ZAGAMI. K. Misawa¹, T. Niihara², L. E. Nyquist³, C.-Y. Shih⁴, T. Kani⁵, S. Yoneda⁶. ¹Natl Inst. Polar Res., 10-3 Midoricho, Tachikawa, Tokyo 190-8518, Japan. E-mail: misawa@nipr.ac.jp., ²Dep. of Systems Innovation, School of Engineering, Univ. of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, ³XI/NASA-JSC, Houston TX 77058, U.S.A., ⁴16406 Locke Haven, Houston, TX 77059, U.S.A. ⁵Faculty of Advanced Sci. & Technology, Kumamoto Univ., 2-39-1 Kurokami, Kumamoto 850-8555, Japan, ⁶Natl Museum Nature Sci., 4-1-1 Amakubo, Tsukuba, 305-0005, Japan.

Introduction: Prior Rb-Sr isotopic analyses of Zagami subsamples show that they have nearly identical crystallization ages of ~170 Ma, but different initial $^{87}\text{Sr}/^{86}\text{Sr}$ (I_{Sr}) ratios are clearly resolved [1]. This finding has not received much attention even after confirmation of different I_{Sr} ratios among the fine-grained lithology, the coarse-grained lithology, the dark mottled lithology, and the olivine-rich lithology [1-4]. The observed I_{Sr} heterogeneities were interpreted as a result of assimilation of Martian crustal material by mantle derived magmas [3]. Nevertheless, the Sr isotope variability in Martian meteorites is still poorly understood. To better understand the Sr isotope systematics of the Martian mantle and crust, we started Sr stable isotope analysis of shergottites by double-spike thermal ionization mass-spectrometry (DS-TIMS).

Experimental: Zagami UNM Consortium samples A23.9b (fine-grained) and A23.12b1 (coarse-grained) [1-3] and Kanagawa Zagami samples [4,5] were used for this study. Two spikes enriched in ^{84}Sr (Oak Ridge National Laboratory) and in ^{87}Sr (ISOFLEX) were mixed to reach a double spike (DS) $^{84}\text{Sr}/^{87}\text{Sr}$ ratio of ~1.2 [6]. After digestion of bulk-rock and mineral separate samples using a mixture of HF + HNO₃, small aliquots were analyzed to determine the concentration of Sr in the solution using a single ^{84}Sr -spike. The sample was re-dissolved in 6N HCl from which aliquots were taken for spiked and unspiked runs. The former was mixed with the DS prior to chromatography. The sample solutions were first loaded onto columns filled with AG1-X8 resin (Cl⁻ form) to remove Fe and then passed twice through Sr-resin columns. Total procedural blanks for Sr were ~65 pg. Strontium isotopic measurements were made in a static mode using multicollector TIMSs, *i.e.*, a Thermo-Triton Plus at NMNS and at KU. The instruments are of standard configuration having 9 Faraday collectors connected to 10¹¹ Ω feedback resistors. Approximately 500 ng of Sr were loaded on outgassed W filaments with Ta activator. Runs were carried out using an ^{88}Sr beam intensity of 8 V for 10 cycles of 15 block ratio measurements with a 16.8 sec integration time and a 3 sec idle time. Before each block the baseline (deflected beam) was measured for 80 sec. Unspiked Sr isotopic analyses were normalized to $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$. The final $^{87}\text{Sr}/^{86}\text{Sr}$ results for the samples were adjusted to $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.710250 for the NIST SRM987

standard. Using the algorithm developed by [7], the stable Sr isotope composition $\delta^{88}\text{Sr}$ value in permil (‰) was calculated versus the $(^{88}\text{Sr}/^{86}\text{Sr})_{\text{SRM987}}$ value of 8.375209 via

$$\delta^{88}\text{Sr} = [(^{88}\text{Sr}/^{86}\text{Sr})_{\text{sample}} / (^{88}\text{Sr}/^{86}\text{Sr})_{\text{SRM987}} - 1] \times 10^3.$$

Results and Discussion: A variety of reference materials (terrestrial basalts: BCR-1, BHVO-2, BIR-1a, JB-1, JB-2, JB-3, terrestrial carbonates: EN-1, JCp-1, and modern seawater: NASS-6) were analyzed for Sr isotopes (Fig. 1). A typical run with an optimal sample/DS ratio shows a symmetrical distribution of individual $\delta^{88}\text{Sr}$ values with a standard deviation (SD) of ~0.03‰. Weighted averages for replicate DS spiked runs that used the within-run SD as a weighting factor were calculated with the Isoplot program [8]. External errors (2SD) for averaged $\delta^{88}\text{Sr}$ values are typically 0.03–0.04‰. The results obtained are consistent with previous DS-TIMS measurements [7].

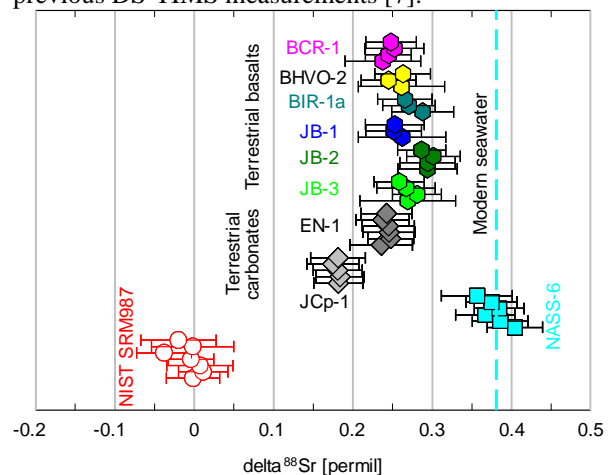


Fig. 1. A comparison of $\delta^{88}\text{Sr}$ values of standard materials obtained by DS-TIMS (this investigation). Error bars are one SD.

Analyses of UNM coarse- and fine-grained allocations were as follows: Approximately half of each allocation was processed for analyses reported in 1995 [1]. Samples remaining for this investigation were two fractions with grain size <45 μm, and residues of pyroxene-enriched (2.85 < p < 3.45, 3.45 < p < 3.55 [g/cm³]) fractions sized to 45–75 μm. The second half of the UNM allocation was processed in 2006 to yield bulk (“whole rock”) samples of both the coarse-grained

(CG) and fine-grained (FG) lithologies sieved to grain sizes $<150 \mu\text{m}$. Plagioclase samples ($\phi < 75 \mu\text{m}$, $\rho < 2.85 \text{ [g/cm}^3\text{]}$) also were available for both the CG and FG lithologies from the earlier study [2]. Results are shown in Fig. 2. Isotopically heavy signatures with $\delta^{88}\text{Sr}$ values up to 0.43‰ were observed for the finer grain sized bulk samples 95FGBK and 95CGBK compared to the more representative bulk-rock samples 06FGBK and 06CGBK with $\delta^{88}\text{Sr}$ values of 0.24–0.28‰.

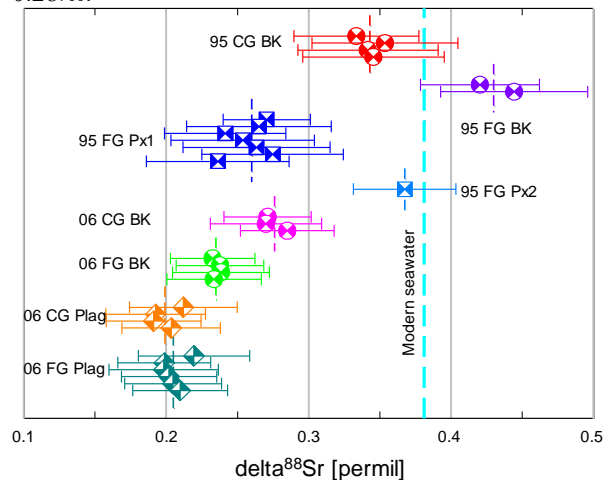


Fig. 2. $\delta^{88}\text{Sr}$ data for UNM Zagami bulk (BK) and mineral separate samples. Error bars are one SD. Weighted averages are used for samples with multiple measurements and are presented by vertical dashed lines.

Figure 3 shows a relationship between Sr concentrations and $\delta^{88}\text{Sr}$ values. Samples with low Sr concentrations tend to have high $\delta^{88}\text{Sr}$ values. The typical Sr concentration of Zagami whole-rock is $45 \pm 2 \text{ ppm}$ [9], thus the 95BK samples ($\text{Sr} = 20\text{--}28 \text{ ppm}$) could be enriched in low-Sr minerals. An Fe-rich pyroxene fraction (95FGPx2: $3.45 < \rho < 3.55 \text{ [g/cm}^3\text{]}$; $\text{Sr} = 4.9 \text{ ppm}$) also shows a high $\delta^{88}\text{Sr}$ value of 0.37‰. On the other hand, the $\delta^{88}\text{Sr}$ value of maskelynitized plagioclase (06GGPlag and 06FGPlag) has a low value of approximately 0.20‰. Most of the samples plot on a two-component mixing curve (end-member-1: low Sr concentration and enriched in heavy Sr; end-member-2: high Sr concentration and enriched in light Sr), except for 95FGPx2, which may be a fractional crystallization product of a highly evolved but clearly different magma composition from that from which early formed pyroxene cores formed [10,11].

The previous data for Zagami whole-rock samples obtained by MC-ICP-MS did not show isotopically heavy Sr signatures ($\delta^{88}\text{Sr} = 0.26 \pm 0.17\text{‰}$ [12]; $0.17 \pm 0.15\text{‰}$ [13], errors are 2SE). The weighted average of the 06CGBK and 06FGBK samples is $0.25 \pm 0.03\text{‰}$ in

good agreement with these earlier results. This is the first time to detect Sr mass fractionation in a single Martian meteorite. Different aliquots of Zagami also revealed varying $\delta^{44}\text{Ca}$ values outside the analytical uncertainty [14–16]. The observed features are not easily explained by a contribution of late-stage trapped liquids to enriched shergottites [17], but could be due to (a) intra-mineral fractionation of stable Sr isotopes during fractional crystallization, (b) highly evolved residual components preserved in the $<45 \mu\text{m}$ “bulk” material, or (c) by interactions with crustal material.

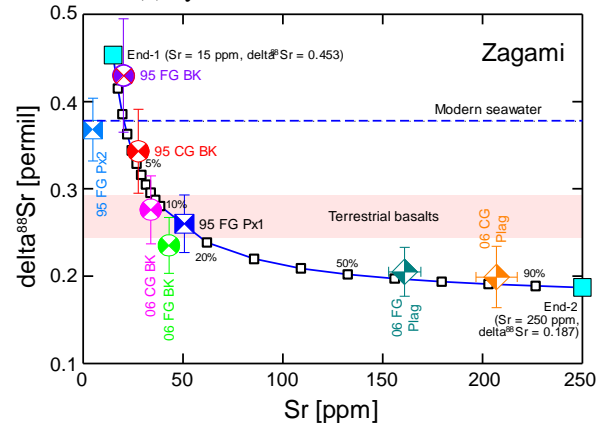


Fig. 3. $\delta^{88}\text{Sr}$ for the UNM Zagami samples are plotted against their Sr concentrations. Weighted averages are used for samples with multiple measurements. Error bars are 2SD. A two-component mixing curve is fitted. Modern seawater ($\delta^{88}\text{Sr} = 0.378\text{‰}$) and terrestrial basalts ($\delta^{88}\text{Sr} = 0.24\text{--}0.29\text{‰}$) are shown for comparison.

References: [1] Nyquist L. E. et al. (1995) *Lunar Planet. Sci. XXVI*, 1065–1066. [2] Nyquist L. E. et al. (2006) *Meteoritics & Planet. Sci.*, 41, A135. [3] Nyquist L. E. et al. (2010) *Meteoritics & Planetary Science* 45, A154. [4] Misawa K. et al. (2012) *Meteoritics & Planet. Sci.*, 47, Abstract #5190. [5] Niihara T. et al. (2012) *Meteoritics & Planet. Sci.*, 47, Abstract #5075. [6] Rudge J. F. et al. (2009) *Chem. Geol.* 265, 420–431. [7] Neymark L. A. et al. (2014) *JAAS* 29, 65–75. [8] Ludwig K. R. (2009) *Spec. Publ.*, vol.2. Berkeley Geochronol. Cent., Berkeley, CA, USA. [9] Lodders K. (1998) *Meteoritics & Planet. Sci.*, 33, A183–A190. [10] McCoy T. J. et al. (1999) *GCA* 63, 1249–1262. [11] Niihara T. and Misawa K. (2018) *Lunar Planet. Sci. XLIX*, Abstract #2652. [12] Moynier F. et al. (2010) *EPSL* 300, 359–366. [13] Charlier B. L. A. et al. *EPSL* 329–330, 31–40. [14] Farkaš, J. et al. (2010) *Lunar Planet. Sci. LXI*, Abstract #2266. [15] Simon J. I. and DePaolo D. J. (2010) *EPSL* 289, 457–466. [16] Magna T. et al. (2015) *EPSL* 430, 86–94. [17] Borg L. E. and Draper D. S. (2008) *Meteoritics & Planet. Sci.*, 38, 1713–1731.

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