SYSTEMATIC ISOTOPIC VARIATIONS OF BARIUM, LANTHANUM, AND SAMARIUM DUE TO COSMIC-RAY IRRADIATION IN LUNAR SURFACE MATERIALS.

H. Hidaka[1] and S. Yoneda[2], [1]Department of Earth and Planetary Sciences, Nagoya University, Nagoya 464-8601, Japan (hidaka@eps.nagoya-u.ac.jp); [2]Department of Science and Engineering, National Museum of Nature and Science, Tsukuba 305-0005, Japan (s-yoneda@kahaku.go.jp).

Introduction: The model for early solar irradiation from young Sun has long been suggested, but is somehow model-depending and still plausible. Isotopic evidence of excess [10]B decayed from [10]Be in CAIs [1,2] and astronomical observations of intensive X-ray emissions from stellar analogues of the young Sun [3,4] suggest that a fraction of the early solar materials were intensively irradiated by the young Sun. For further quantitative discussion about the early solar irradiation models, the possible occurrence of chemical fractionation of volatile elements including spallogenic B and Li during or after irradiation has been pointed out [5]. In order to dissolve this problem, [138]La has been chosen to be an adequate isotopic tracer as one of refractory and spallogenic products caused by solar irradiation [6]. Spallogenic [138]La may provide isotopic constraints on the early solar irradiation models.

La has two isotopes with mass number 138 and 139. One of two isotopes, [138]La has a very rare odd-odd nuclide consisting of fifty-seven protons and eighty-one neutrons, and its isotopic abundance is very low ([138]La/[139]La=0.00091). There are only three nuclides, [50]V, [138]La and [180]Ta as odd-odd nuclides in nature. Furthermore, [138]La with a half-life of 1.05×10^{11} years decays by electron capture to [138]Ba and by beta decay to [138]Ce. These decay schemes have been applied for geochronometers [7,8]. [138]La is considered to be produced mainly by a neutrino process (ν,n) reactions in SN II layers [9]. Previous studies on La isotopic analyses in CAIs show the correlation of isotopic excesses between [138]La and several neutron-rich iron group nuclides such as [48]Ca, [50]Ti, and [54]Cr in CAIs suggesting the mixing products from ejecta of SNe Ia and SNe II [10,11]. On the other hand, Burnett et al. [5] examined to detect the correlation of isotopic excesses between [10]Be and [138]La in CAIs to clarify isotopic evidence for spallation products in early solar proton irradiation.

In this study, La isotopic analyses were newly performed on a series of lunar surface soils to detect the accumulation of spallogenic [138]La products by solar proton irradiation. The materials on the lunar surface are exposed to cosmic rays. In particular, the study of lunar grain surface is important to recognize the characteristics of the space weathering processes resulted from the interaction of solar cosmic rays. The interaction of cosmic-ray with the planetary surface materials cause nuclear reactions. It is considered that the spallogenic [138]La is produced mainly from [138]Ba(p,n). In addition, Ba isotopes are adequate proxy to learn nuclear reaction mechanism induced by cosmic-ray irradiation in the similar elemental mass region of La. Ba has seven stable isotopes including two p-process isotopes [130]Ba and [132]Ba, and the heaviest Ba isotope, [138]Ba is a target to produce spallogenic [138]La. In addition, one of seven Sm isotopes, [149]Sm is very sensitive to thermal neutrons and the isotopic shift from [149]Sm to [150]Sm is effectively used to estimate neutron fluence induced by cosmic-ray irradiation. We already collected Ba and Sm isotopic data in the same samples prior to this study. Since several types of spallation and neutron capture reactions are also considered to contribute isotopic variations of many elements during irradiation, Ba and Sm isotopic data are informative to interpret the reaction mechanism of spallogenic [138]La from La isotopic data.

Samples and Experiments: Five kinds of the Apollo soils, 78481, 10084, 12001, 14259, and 15011, were used in this study. These five samples were collected within a few mm depth from lunar surface. In particular, [10]Be in excess of that expected from in-situ cosmic-ray spallation reactions is detected in the soil 78481 [12]. Sequential acid-leaching treatments were carried out to obtain chemically different phases from the single sample. About 50 mg of each sample was leached using 5 mL of 0.5 mM HNO_3 + 0.002 mM HF, 2 M HCl, and aqua regia, successively. Finally, the residue was decomposed by treatment with $HF-HClO_4$ with heating. This procedure was modified from the previous methods [12]. In particular, the first leaching step of the procedures is effective to dissolve very surficial material of the fine grains in the depth within 1.5 μm [12]. The four leaching fractions are designated L1, L2, L3, and L4, respectively.

The four leachates (L1 to L4) were taken to dryness and redissolved in 1 mL of 2M HCl. The solutions were divided into two portions: the main portion for isotopic measurements by thermal ionization mass spectrometry (TIMS) and the rest for the determination of elemental abundances by inductively coupled plasma mass spectrometry (ICP-MS). For the isotopic

study, each solution was treated with conventional resin chemistry to get Ba, La and Sm fractions. For future isotopic work, Sr, Ce, Nd, and Gd of individual leachates were also separated in the same sequence of this resin chemistry.

A Triton TIMS equipped with nine Faraday cup collectors was used in this study. La was measured as LaO^+ on double Re filaments. $^{138}La/^{139}La$ isotopic ratios were obtained from $^{138}La^{16}O^+/^{139}La^{16}O^+$ after correction for instrumental mass fractionation by $^{18}O/^{16}O$ ($^{139}La^{18}O/^{139}La^{16}O$) normalization [6,10,11]. Ba and Sm isotopic analyses were carried out by previously reported methods [13].

Results and Discussion: La isotopic variations between $\varepsilon^{138}La$= -27.8 ± 6.3 and +16.5 ± 7.7 were obtained from the chemical leachates of the lunar surficial soils. Although we expected to detect ^{138}La enrichments as spallogenic products, most samples showed negative $^{138}La/^{139}La$ anomalies ($\varepsilon^{138}La<0$). ^{138}La depletion and ^{139}La excess are expected from neutron capture reactions $^{138}La(n,\gamma)^{139}La$ and $^{138}Ba(n,\gamma\beta^-)^{139}La$, respectively.

As the results of Ba isotopic measurements, L1 fractions from all of five lunar soils show significant enrichments of lighter isotopes ^{130}Ba (ε=+11.4 to +21.4) and ^{132}Ba (ε=+13.4 to +28.3) and heavier isotopes ^{137}Ba (ε=+0.16 to +4.9) and ^{138}Ba (ε=+1.5 to +6.0). These isotopic excesses decrease with increase of acid strength in the leaching procedure, and are not observed in final fractions L4. Excesses of neutron-rich isotopes such as ^{48}Ca, ^{54}Cr, ^{58}Fe and ^{66}Zn are considered to be the main products of the nuclear statistical equilibrium process during the last stage of stellar evolution [14]. Considering the existence of ^{137}Ba and ^{138}Ba isotopic excesses in the fractions, ^{139}La might have been also produced together with major nuclides in the mass region around 140 by the same processes. ^{139}La excess by neutron capture $^{138}Ba(n,\gamma\beta^-)^{139}La$ may be favored to explain the negative $^{138}La/^{139}La$ anomalies ($\varepsilon^{138}La<0$).

Our estimates from the Sm isotopic shifts due to neutron capture reaction in the samples provide neutron fluences of (3.8 to 8.1)x10^{16} ncm^{-2} for individual samples. The slight correlation between neutron fluences and degree of ^{137}Ba and ^{138}Ba isotopic excesses suggests the production of ^{137}Ba and ^{138}Ba isotopes by neutron capture reactions. However, the correlation of neutron fluences with $^{138}La/^{139}La$ isotopic variations is unclear. The isotopic excesses of ^{130}Ba and ^{132}Ba possibly from spallation reactions suggest the existence of spallogenic ^{138}La products in the same samples. The systematic isotopic data sets of Ba, La and Sm in this study suggest that spallation and neutron capture reactions to produce ^{138}La and ^{139}La had occurred simultaneously, and that less correlation of $^{138}La/^{139}La$ with the neutron fluences was resulted from the mixture of two products.

References: [1] McKeegan K.D., Chaussidon M. and Robert F. (2000) *Science*, 289, 1334-1337. [2] Liu M.-C. et al. (2010) *Astrophys. J. Lett.*, 719, L99-L103. [4] Güdel M. et al. (2004) *Astron. Astrophys. Review*, 12, 71-237. [3] Feigelson E.D., Garmire G.P. and Pravdo S.H. (2002) *Astrophys. J.*, 572, 335-349. [5] Burnett D. et al. (2015) *LPSC*, 1394. [6] Shen J.J.-S., Lee T., and Chang C.-T. (1994) *Geochim. Cosmochim. Acta*, 58, 1499-1506. [7] Tanaka T. and Masuda A. (1982) *Nature* 300, 515-518. [8] Nakai S., Shimizu H. and Masuda A. (1986) *Nature* 320, 433-435. [9] Woosely S.E. (1997) *Astrophys. J.*, 476, 801-810. [10] Shen J.J.S. and Lee T. (2003) *Astrophys. J.*, 596, L109-L112. [11] Chen H.-W., Lee T., Lee D.-C., and Chen J.-C. (2015) *Astrophys. J. Lett.*, 806, L21(4pp). [12] Nishiizumi K. and Caffee M.W. (2001) *Science* 294, 352-354. [13] Hidaka H. and Yoneda S. (2014) *Astrophys. J.*, 786, 138. [14] Hartman D., Woosley S.E. and El Eid M.F. (1985) *Astrophys. J.*, 297, 837-845.