TRACE ELEMENT ANALYSIS AND IRON ISOTOPIC SIGNATURE OF LUNAR REGOLITH. S. Okabayashi¹, T. Yokoyama¹, K. Terakado², E.M. Galimov³. ¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo, Japan (okabayashi.s.aa@m.titech.ac.jp). ²Japan Space Forum, Tokyo, Japan. ³Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow, Russia.

Introduction: The formation process and relationship of Earth and Moon have been debated for over recent decades. Nowadays, a catastrophic giant impact event has been widely accepted as the Earth-Moon forming process. The canonical giant impact model requires that more than 80% of the Moon was derived from an impactor while contribution from the proto-Earth was minor (e.g., [1]). Most of recent isotopic studies including measurement of mass dependent isotopic fractionation and mass independent isotopic fractionation revealed that isotopic compositions of Earth and Moon are significantly similar. For instance, ⁵⁰Ti/⁴⁷Ti ratios of lunar materials were identical to those of terrestrial materials, although the ⁵⁰Ti/⁴⁷Ti ratios of chondrites and achondrites exhibit a significantly large variation [2]. Such isotopic similarity between Earth and Moon indicates that the proto-Earth and the impactor had identical isotopic composition before the catastrophic impact event.

However, many previous studies reported that Fe isotopic composition of Earth and Moon are slightly different from each other. Most of the published Fe isotopic composition ($\delta^{56/64}$ Fe) of lunar meteorites and returned Apollo samples are slightly heavier (~0.1-0.4‰) than that of the bulk silicate Earth (e.g., [3][4]). Poitrasson et al. [3] argued that the difference of Fe isotopic composition between Earth and Moon was caused by the evaporation of Fe during the giant impact event. However, the lack of mass dependent isotopic fractionation of Si between Earth and Moon is inconsistent with this model, because Fe and Si have similar volatility, with 50% condensation temperatures of 1334 K and 1310 K, respectively [5]. On the other hand, Wang et al. [6] found that a lunar dunite sample showed lighter Fe isotopic composition than the bulk silicate Earth. Based on this observation, Wang et al. suggested that the deep Moon was enriched in light Fe isotope while the shallow Moon was enriched in heavy Fe isotope, and hence, Fe isotopic composition of the bulk silicate Moon may be identical to that of the bulk silicate Earth.

In order to estimate the Fe isotopic composition of the bulk silicate Moon, reliable Fe isotopic data of deep Moon and shallow Moon are highly required. However, the lunar surface has been experienced space weathering including micrometeorite impact that induces the formation of nanophase metallic Fe (npFe⁰) on the surface of lunar materials. Some previous works revealed that the Fe isotopic composition of lunar soils were fractionated during the space weathering process (e.g., [7]). Thus, lunar samples that avoided the space weathering process should be measured to determine the reliable Fe isotopic composition of Moon.

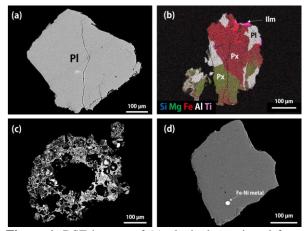


Figure 1. BSE images of (a) plagioclase-mineral fragment, (c) agglutinate, and (d) impact glass with a small Fe-Ni metal grain (~10 μ m). (b) Elemental mapping of a lithic fragment composed of Mg-rich pyroxene (green), Fe-rich pyroxene (red), plagioclase (white), and ilmenite (pink). Scale bars represent 100 μ m.

Experimental: We used lunar regolith samples of Soviet Luna robotic missions (Luna 16, 20, 24). These samples were obtained from a wide range of depth (~0-200 cm). The regolith samples collected from deep region expected to be less affected by the space weathering process. For the microscopic observation and the trace element analysis, relatively large size (>200 µm) of 12 grains from the Luna 20 sample (L2001-4) and 11 grains from the Luna 24 sample (L24130.3-4) were picked up using a vacuum manipulator under a binocular microscope. The grains were mounted in epoxy resin, and the sample surface was polished with diamond paste. Then, the grains were mapped by a SEM-EDS (S-3400N, Hitachi High-Technologies, Japan) to identify the constituent minerals. Subsequently, the mounted regolith samples were measured by a LA-ICP-MS to determine the trace element composition. We utilized a Ti:sapphire UV-fs laser (IFRIT, Cyberlaser, Japan) with a quadrupole ICP-MS (XSERIES 2, Thermo Scientific, USA) for LA-ICP-MS analysis. Trace element compositions of

each grain were measured by spot analysis (~30 μ m). A silicate glass material, NIST SRM 612, was used as a standard. The data acquisition was made in the time-resolved analysis (TRA) mode. The concentrations of trace elements were calculated by using the signal of ⁴³Ca or ²⁹Si as for the internal standard.

We analyzed Fe isotopic composition of lunar regolith samples from Luna 16, Luna 20, and Luna 24. The sample fractions which are different from the mounted grains were digested in acid. The sample digestion technique for the Fe isotopic measurement were adapted from those described by [8]. In order to measure Fe isotopic ratios of the samples, two different chromatographic separation techniques of Fe, using 1.8 mL of AG MP-1 [9] or 1.0 mL of AG1-X8 [10] anion exchange resins, were tested. The recovery yields of Fe were $98.7 \pm 1.4\%$ (2 SD, n = 3) and $98.1 \pm 1.5\%$ (2 SD, n = 3) for the AG MP-1 procedure and the AG1-X8 procedure, respectively. Although both techniques can achieve ~100% recovery of Fe, the AG1-X8 procedure was much faster than the AG MP-1 procedure because of the lower amount of resin and acid reagent. Thus, the procedure using AG1-X8 was applied for the regolith samples. The Fe isotopic ratios of the regolith samples were measured by a MC-ICP-MS (Nu Plasma II, Nu Instruments, UK).

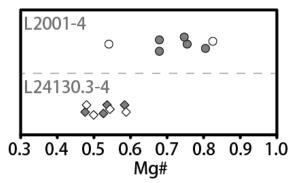


Figure 2. Mg# of L2001-4 and L24130.3-4. Open symbols and closed symbols represent mineral fragments and lithic fragments, respectively.

Results and Discussion: Among the 23 mounted regolith grains, 9 of them were mineral fragments (3 plagioclase, 5 pyroxene, and 1 olivine grains) (Fig. 1a), 9 of them were lithic fragments such as breccia and basalt rock (Fig. 1b), 4 of them were agglutinates (Fig. 1c), and 1 of them were an impact glass (Fig. 1d). The lithic fragments were mainly composed of plagioclase, pyroxene, and olivine, and some of them included small volume of ilmenite. A small apatite grain (~10 μ m) was also found from 1 lithic fragment in L24130.3-4. The impact glass found from L2001-4 included a spherical small (~10 μ m) Fe-Ni metal grain.

Figure 2 shows measured Mg# (=Mg/(Mg+Fe)) for the pyroxene- and olivine-mineral fragments and the lithic fragments. Our data revealed that the Mg# of L2001-4 (0.54-0.82) was clearly higher than that of L24130.3-4 (0.48-0.59). The present Mg# for L2001-4 and L24130.3-4 are consistent with the Mg# of Apollo Mg-suite (~0.65-0.90) and Apollo ferroan anorthosites (~0.40-0.70), respectively.

Figure 3 shows averaged CI-normalized REE pattern of pyroxene- and plagioclase-mineral fragments and lithic fragments in L2001-4. The compositional complementarity for REEs between pyroxene and plagioclase can be observed. The lithic fragment exhibits flat REE pattern and does not show neither positive nor negative anomaly of Eu, reflecting the mixing of pyroxene and plagioclase. The REE concentrations in the olivine-mineral fragment could not be measured because of its significantly low concentrations. The REE element pattern of L24130.3-4 was also similar to that of L2001-4.

In addition to the trace element composition, the Fe isotopic signature of lunar regolith samples will be also discussed in this presentation.

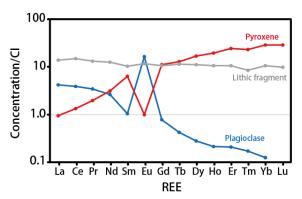


Figure 3. Averaged CI-normalized concentration of REEs in pyroxene- and plagioclase-mineral fragments and lithic fragments in L2001-4.

References: [1] Canup R.M. and Asphaug E. (2001) *Nature*, *412*, 708–712. [2] Zhang J. et al. (2012) *Nature Geosci.*, *5*, 251-255. [3] Poitrasson F. et al. (2004) *Earth Planet. Sci. Lett.*, *223*, 253–266. [4] Moynier F. et al. (2006) *Geochim. Cosmochim. Acta.*, *70*, 6103–6117. [5] Armytage R.M.G. et al. (2012) *Geochim. Cosmochim. Acta.*, *77*, 504–514. [6] Wang K. et al. (2015) *Earth Planet. Sci. Lett.*, *430*, 202–208. [7] Wiesli R.A. et al. (2003) *Earth Planet. Sci. Lett.*, *216*, 457–465. [8] Yokoyama T. et al. (1999) *Chem. Geol.*, *157*, 175–187. [9] Zhu X.K. et al. (2002) *Earth Planet. Sci. Lett.*, *200*, 47–62. [10] Craddock P.R. and Dauphas N. (2011) *Geostand. Geoanal. Res.*, *35*, 101–123.