

IRON ISOTOPIC SIGNATURE FOR Fe-Ni METAL OF ORDINARY CHONDRITE USING NEWLY DEVELOPED TECHNIQUE; LAL-MC-ICPMS. S. Okabayashi¹, T. Yokoyama², T. Hirata¹, ¹Laboratory for Planetary Sciences, Kyoto University, Sakyo-ku, Kyoto, Japan (okabayashi-s-aa@kueps.kyoto-u.ac.jp), ²Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan.

Introduction: The ordinary chondrite is the most abundant meteorite group, and is also one of the most primitive meteorite groups. This suggests that the ordinary chondrite can be a major source of the primitive materials in the early solar system. Based on this viewpoint, chemical compositions of not only the bulk but also the individual mineral component, including Fe-Ni metals, of the ordinary chondrites has been studied for long time. Though the abundant Fe-Ni metal is one of the characteristic components of the ordinary chondrite, the formation processes of them have been still veiled. The Fe isotopic signature is one of the key information to unveil the formation processes of Fe-Ni metals in the ordinary chondrites because (1) Fe is ubiquitously distributed in various minerals or phases in the meteorites, and (2) Fe isotope composition can vary through the formation processes. However, precise isotope ratio analysis of Fe has been retarded by the analytical difficulty mainly due to very low ionization efficiency of Fe. In this study, Fe isotope ratio analysis was carried out using the multiple collector-inductively coupled plasma mass spectrometry (MC-ICPMS) technique coupled with a desolvating nebulizer system. In order to improve the precision and accuracy of the Fe isotopic data, we applied a newly developed sampling technique described below.

Experimental procedure: In the previous studies, the ordinary chondrites were crushed in the mortar and Fe-Ni metals were sampled through handpicking or micro-mill technique to collect Fe-Ni metals [1, 2]. It should be noted that these techniques have the risk of the contamination from the equipments or apparatus used for the sample handling. The laser ablation (LA) is one of the most sensitive sampling techniques for in-situ elemental and isotopic analysis of solid samples. The LA technique has been widely applied for the sampling technique for the ICP-MS technique to determine the isotopic compositions of the trace-elements. Using the LA-ICP-MS technique, rapid and precise isotopic analyses can be made under the spatial resolution of better than 30 μm . Nevertheless, it should be noted that the resultant precision in the isotopic ratio measurements is significantly poorer than those achieved by the conventional solution introduction technique. Moreover, preparation of matrix matched standard is highly desired to achieve the accurate isotopic ratio measurements for complex minerals or phases. This indicates that the isotopic data obtained

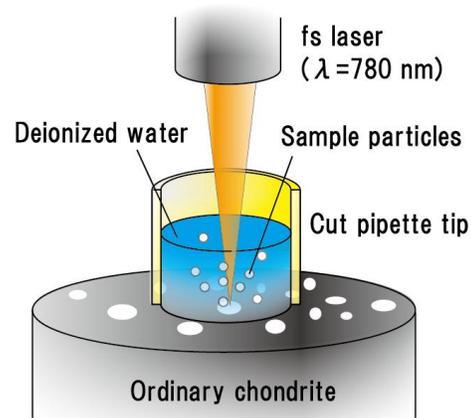


Fig 1. Sample setting for the LAL procedure. The NIR femtosecond laser was applied in this experiment.

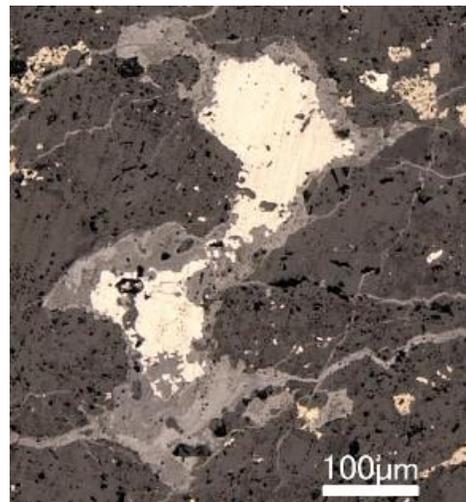


Fig 2. The optical micrograph of the ordinary chondrite surface. The white region is the Fe-Ni metal and the gray thin zone around the Fe-Ni metal is the weathering product.

by the LA-ICP-MS could be erroneous when no proper isotopic standards were available. To overcome this, we have developed new sampling technique using a laser ablation in liquid (LAL) [3, 4]. In this study, a cut pipette tip filled with 50-100 μL deionized water was put on the polished meteorite surface directly, and the laser ablation sampling was carried out directly within high-purity water (Fig. 1). A femtosecond laser (780 nm wave length) was used for the LAL sampling. During the LAL procedure, the fluence was set to 20

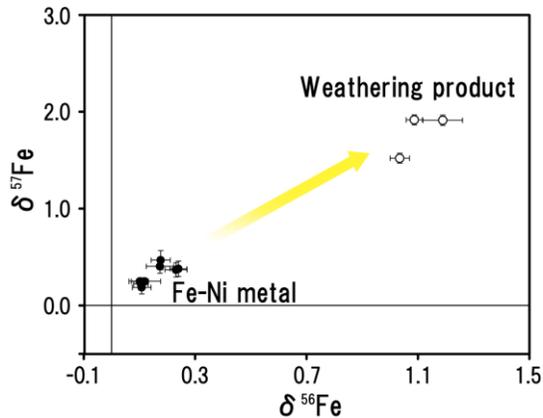


Fig 3. Results of the Fe isotopic compositions obtained from Fe-Ni metals and weathering products. X axis and Y axis represent $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$, respectively.

Jcm^{-2} and the various repetition rates (10-250 Hz) were applied. The suspension of nano-sized particles produced by the LAL procedure was collected using the micro pipette, and the sample particles were subsitized to chemical decomposition procedure using mixture of conc. HCl and conc. H_2O_2 . The sample solution was heated to dryness at 80°C , and the resulting sample cake was re-dissolved in 0.1% HCl, and then used for the isotopic analysis of Fe using MC-ICPMS. In this study, both the fresh Fe-Ni metals and the weathering products were collected using the present LAL technique (Fig. 2). The Fe isotope ratio data for weathering products were very important to evaluate the level of weathering from the inherent Fe-Ni metals.

Results and Discussion: The results of the Fe isotopic ratios obtained from both the Fe-Ni metals and weathering products were summarized in Fig 3. This figure showed that the weathering products had significantly higher Fe isotopic compositions than the fresh Fe-Ni metals. However, it should be noted that there were no significant difference in the resulting $^{56}\text{Fe}/^{54}\text{Fe}$ ratio between the Fe-Ni metals collected from highly weathered and unweathered chondrites/areas. This indicates that the contribution of the weathering processes were too small to change the $^{56}\text{Fe}/^{54}\text{Fe}$ ratios for the Fe-Ni metals.

The $\delta^{56}\text{Fe}$ values for the Fe-Ni metals obtained from 6 H-chondrites, 1 L-chondrites, and 1 LL-chondrites were plotted in Fig. 4. The previously reported $\delta^{56}\text{Fe}$ values by Theis et al. (2008) [1] for the Fe-Ni metals were also plotted in Fig. 4. This figure demonstrated that the Fe-Ni metals in H group chondrites have slightly lighter Fe isotopic compositions ($\sim 0.15\%$) than L or LL group chondrites. Theis et al. (2008) claimed that the difference in the Fe isotopic ratio among the chondrite groups would be a result of

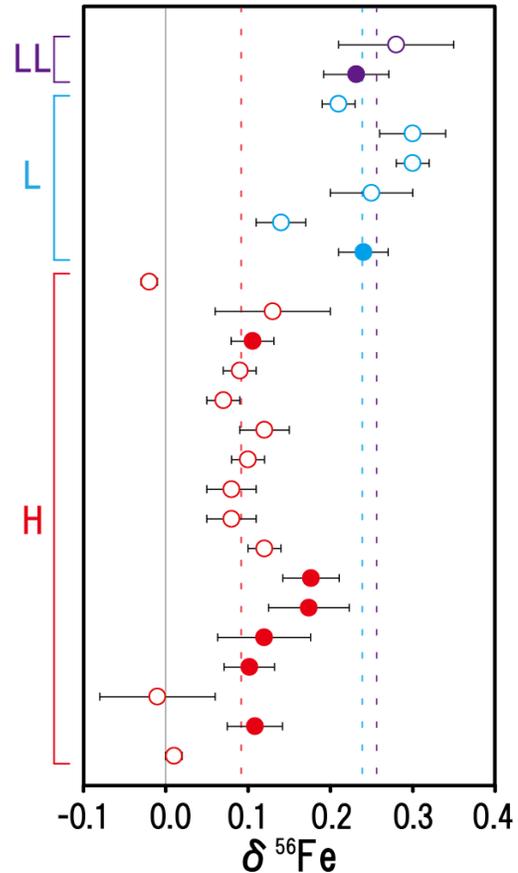


Fig 4. The $\delta^{56}\text{Fe}$ values of Fe-Ni metals. The closed symbols and open symbols represent the data obtained in this study and Theis et al. (2008) [1], respectively.

the differences of the oxidation states for the H, L and LL group chondrites [1]. However, there were no significant differences in the resulting Fe isotope signature between the L and LL chondrites. This suggests that the Fe isotope signature found on the H, L and LL chondrites could not be explained by the simple oxidation-reduction process of the metallic phases. Moreover, there is a possibility that the precursors of Fe-Ni metals in H, L and LL chondrites are different. In this case, it is required the re-evaluation of the formation sequence of the Fe-Ni metals for the ordinary chondrites.

References: [1] Theis, K.J., Burgess, R., Lyon, I.C. and Sears, D.W., (2008), *Geochim. Cosmochim. Acta*, 72, 4440-4456. [2] Needham, A.W., Porcelli, D. and Russell, S.S., (2009), *Geochim. Cosmochim. Acta*, 73, 7399-7413. [3] Okabayashi, S., Yokoyama, T.D., Kon, Y., Yamamoto, S., Yokoyama, T. and Hirata, T., (2011), *J. Anal. At. Spectrom.*, 26, 1393-1400. [4] Douglas, D.N., Crisp, J.L., Reid, H.J. and Sharp, B.L., (2011), *J. Anal. At. Spectrom.*, 26, 1294-1301.