Laboratory simulation of space weathering: ESR measurements of nanophase metallic iron in laser-irradiated materials

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(Received July 19, 2002; Revised November 8, 2002; Accepted November 14, 2002)

S-type asteroids are believed to be parent bodies of ordinary chondrites. However, the reflectance spectra of S-type asteroids are different from those of ordinary chondrites. This spectral mismatch is strongly considered as a result of space weathering, where high-velocity dust particle impacts should change the optical properties of the uppermost regolith surface of asteroids. To simulate space weathering by impact heating of dust particles, we irradiated nanosecond pulse laser beam onto planetary surface materials, whose pulse duration and energy rate are comparable with those of real dust impacts. The laser-irradiated samples show optical changes similar to that by space weathering, and contain nanophase metallic iron particles considered as the essential cause of space weathering. After laser-irradiations, we observed the samples by an Electron Spin Resonance (ESR) to perform quantitative analysis of nanophase metallic iron particles. We report the first description that the quantities of nanophase metallic iron particles in olivine samples increase at higher space weathering degree.

Key words: Space weathering, electron spin resonance, nanophase metallic iron, laser irradiation, reflectance change.

1. Introduction

S-type asteroids, majority in asteroids, are believed to be parent bodies of ordinary chondrites, which are a large majority in meteorites (Chapman, 1996). Although both S-type asteroids and ordinary chondrite contain the same mineral assemblage, mainly olivine and pyroxene, the reflectance spectra of the asteroids are different from those of ordinary chondrites. Asteroids exhibit more overall depletion (darkening) and reddening of spectra, and more weakening of absorption bands relative to the meteorites. This spectral mismatch is explained by space weathering process, where high-velocity dust particle impacts should change the optical properties of the uppermost regolith surface of asteroids.

Recently, nanophase metallic iron particles, which were first suggested theoretically by Hapke *et al.* (1975), were discovered in lunar materials (e.g., Keller and McKay, 1993, 1997; Pieters *et al.*, 2000) and were suggested theoretically that they cause the optical changes similar to that by space weathering (Hapke, 2001), so that nanophase metallic iron particles are considered as the most essential cause of space weathering.

In order to simulate the space weathering in a laboratory, we irradiated nanosecond pulse laser beam onto planetary surface materials (e.g. olivine). We got spectral changes in our samples similar to that by space weathering on asteroids (Yamada *et al.*, 1999; Hiroi *et al.*, 2001; Sasaki *et al.*, 2001) and observed nanophase α-metallic iron particles in irradiated olivine samples by Transmission Electron Microscopy (TEM) (Sasaki *et al.*, 2001). In this paper, we report the first confirmation of the quantities of nanophase metallic iron particles in olivine samples by Electron Spin Resonance (ESR) observations.

2. Experimental Procedure

To simulate space weathering, we use a solid-state Nd-YAG pulse laser beam (1064 nm, 20 Hz, 30 mJ) with pulse duration of 6–8 nanoseconds, which is comparable with real dust impacts (Yamada *et al.*, 1999). The focused beam was 500 μm in diameter. We irradiated pellet samples (2 cm in diameter) of olivine powders ($<$75 μm) under a vacuum at 2–3 $\times$ 10^{-5} torr. The total irradiated energy in a unit area was 240 mJ/mm^2 at 30 mJ pulse energy. After laser irradiation, bi-directional reflectance spectra of the samples were measured (Kurahashi and Sasaki, 2002) and we observed the samples by TEM. Finally, ESR signals of the surface of the laser-irradiated samples were measured using an ESR imaging device nondestructively (Ikeya *et al.*, 1994). ESR spectra were obtained on an ESR spectrometer JEOL-RE2X at Osaka University. Measurements were performed using a cylindrical TE_{111} mode cavity with an aperture diameter of 3 mm. A laser-irradiated sample was placed on a cavity, and then ESR only on the aperture area (3 mm in diameter $\times$ 100 micron in depth) was obtained. The intensities were measured at room temperature with a microwave power of $P = 3$ mW, microwave frequency $f = 9.294$ GHz. Field modulation at 100 kHz was about 0.1 mT on the aperture area.

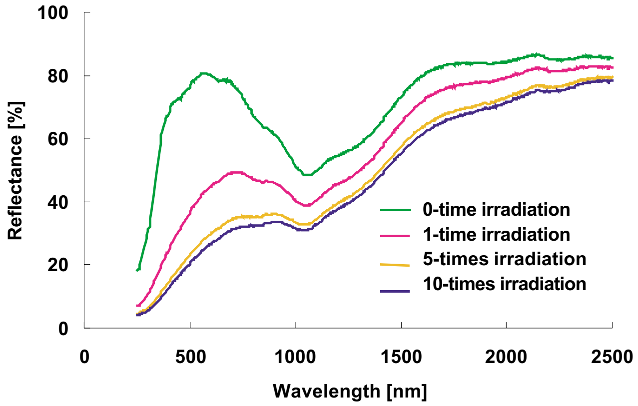

Fig. 1. Bi-directional reflectance spectra (UV-VIS-NIR) of olivine samples with 0, 1, 5 and 10-times pulse laser irradiation.

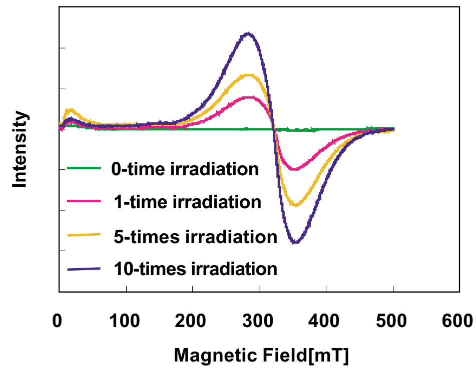

Fig. 3. ESR spectra of olivine samples, which were irradiated by 30 mJ pulse laser for 1, 5 and 10-times. Non-irradiated sample shows no ESR signal.

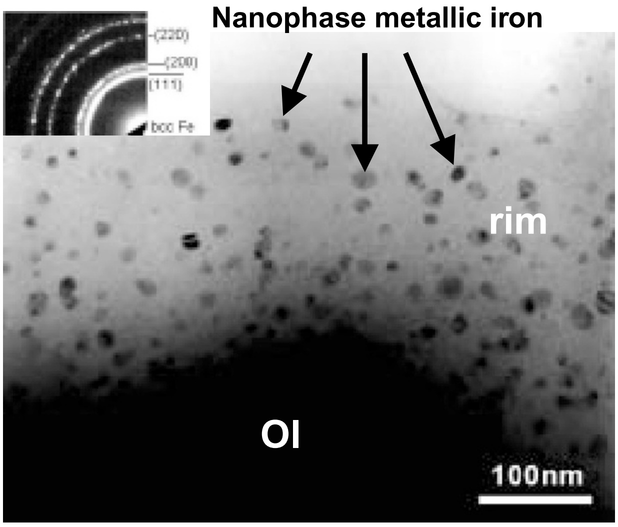

Fig. 2. TEM image of nanophase iron particles with the electron diffraction patterns. Nanophase metallic iron particles are shown in amorphous rims of 5-times laser irradiated olivine grains.

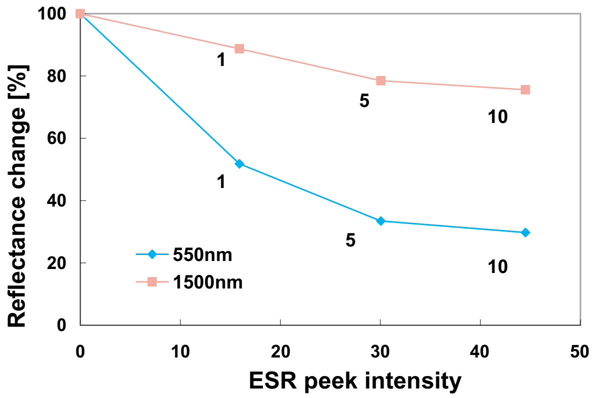

Fig. 4. Relation between the reflectance changes and the ESR peak intensities of each sample. The vertical axis shows reflectance scaled to that of the non-irradiated sample. Each number beside a plot is irradiation time.

3. Spectral Changes and Occurrence of Nanophase Metallic Iron Particles in Irradiated Materials

The laser-irradiated olivine samples show clearly darkening and reddening of the spectra, and more weakening of the absorption bands (Fig. 1) (Yamada *et al.*, 1999; Sasaki *et al.*, 2001, 2002). Figure 2 is a TEM image of nanophase metallic iron particles found in the olivine samples (Nakamura *et al.*, 2001) with the electron diffraction patterns. Nanophase metallic iron particles (several up to 30 nm in diameter) were widely scattered throughout the amorphous rims (∼200 nm in thickness) developed along the olivine grains. We also confirmed the measured interlayer spacing of nanophase metallic iron is 0.204 nm in average, which is consistent with the spacing of a crystal lattice plane (110) of α-Fe ($d_{110} = 0.203$ nm). Average atomic percents of the amorphous materials of the rims are O 59.05 (57.07), Si 18.10 (14.08), Mg 20.60 (25.05), Fe 2.25 (3.80), where values in brackets are composition data of the host olivine (Nakamura *et al.*, 2001). The amorphous rims with iron nano-particles were produced through the vapor-deposition process by laser-irradiation (Sasaki *et al.*, 2001). These nanophase metallic iron particles are clearly similar to those found in the rim of lunar soil grains in occurrence and size (Keller and McKay, 1993).

4. ESR Confirmation of Nanophase Metallic Iron Particles

To perform quantitative analysis of nanophase metallic iron particles, we used ESR measurements. This paper is the primary ESR demonstration for a pulse-laser irradiated materials containing nanophase iron particles. Figure 3 shows ESR spectra of olivine samples for 1, 5 and 10-times irradiation at 30 mJ with non-irradiated one. Though the non-irradiated sample shows no ESR signals, uniquely intense ESR signals are observed in all irradiated samples. In an ESR experiment, resonance is observed at value of the applied magnetic field, H, given by $H = h\nu/g\beta$, where h is Planck's constant, ν is the spectrometer frequency, β is the Bohr magneton and g is a parameter (spectroscopic splitting factor). All samples have the characteristic g-value $= 2.10 \pm 0.03$ resonance, which are very close to the g-value in lunar materials arising from metallic iron (g-value $= 2.12 \pm 0.05$) (Manatt *et al.*, 1970; Tsay and Chan, 1971). The mean peak-to-peak linewidth is 70 mT. Considering our observation by TEM, the ESR signals should derive from nanophase metallic iron particles and do not derive from Fe^{3+} ion in olivine because of the no signal from the non-irradiated sample with the same measuring condition. Although we have not yet performed the mossbauer investigation on Fe^{3+} components with the irradiated samples, ESR spectral shapes, g-value and strong signal intensities also suggest the origin of this signal is nanophase metallic iron particles which were confirmed by TEM.

The ESR intensities of the olivine samples strengthen clearly with increasing irradiation times. These results suggest that the amount of nanophase metallic iron particles in olivine samples increases at higher space weathering degree. Because nanophase metallic iron should be evaporated and condensed on the samples over and again with repetitive laser irradiations, the ESR intensities are not in proportion to the irradiation times. Figure 4 shows the relation between reflectance changes and ESR peak intensities of each sample. Although the ESR intensities clearly increase with irradiation times, the reflectance changes for the 5-times and 10-times irradiated samples are small. This suggests darkening trends of the reflectance spectra relative to the quantities of nanophase metallic iron particles become moderate at higher space weathering degree. The optical effects of nanophase metallic iron particles might become weaker at higher space weathering degree because of the growth of nano-iron particles. Instead of the crater density, we can estimate relative ages of asteroids using the relation between optical effects and quantities of produced nanophase metallic iron particles except for higher space weathering degree, as we will quantitatively examine this relation in the laboratory.

5. Conclusions

This is the first ESR demonstration for a pulse-laser irradiated olivine samples containing nanophase metallic iron particles. Amounts of nanophase metallic iron particles in olivine samples increase at higher space weathering degree. Darkening trends of the reflectance spectra relative to the quantities of nanophase metallic iron particles become moderate at higher space weathering degree.

Acknowledgments. We are most grateful to Mr. T. Ueno of Osaka University for a lot of supports with ESR observations. We thank Dr. T. Hiroi of Brown University for helpful discussions and a lot of advice. We also thank referees for their valuable comments.

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