Diffuse reflectance spectra for heated samples of an H5 chondrite: Importance of oxygen fugacity at heating

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Abstract: We obtained (biconical) diffuse reflectance spectra of the Nuevo Mercurio (H5) ordinary chondrite in the 200–2500 nm wavelength region. The samples were heated in the temperature range of 800–1200°C at constant oxygen fugacities at one log unit below the iron-wüstite (IW) buffer (IW-1) and two log units above the IW buffer (IW+2). The spectra of the samples heated to temperatures lower than 1050° C at IW+2 show low spectral contrast and shorter wavelength positions of UV drop-off compared with the unheated < 100 μ m sample. On the basis of our heating experiments, this work suggests that oxygen fugacity affects the spectra of the heated samples especially at IW+2, implying that oxygen-fugacity control is important for heating experiment and that oxygen fugacity may play a role in the surface processes on asteroids.

1. Introduction

Many meteorites, except for the primitive meteorite groups, show evidence of being reheated (e.g., Dodd, 1981). Heating alters the mineral assemblage of planetary materials and affects their reflectance spectra. We have investigated the spectral effects of oxygen fugacity during heating (800–1200°C) of the Nuevo Mercurio (H5) ordinary chondrite in the UV-Visible-Near IR wavelength (UV-VIS-NIR) region (200–2500 nm).

Both Wasson et al. (1997) and Hiroi and Pieters (1998) have discussed the trend of spectral alteration in meteorites on the basis of spectral measurements of laser impulse irradiated HED meteorites. Other studies have examined spectral changes related to heating the Murchison (CM2) meteorite. Miyamoto (1991) discussed infrared diffuse reflectance spectra of Murchison heated in a silica glass tube with hydrogen gas flow at the temperature range of 200–700°C and compared them with other metamorphosed and unmetamorphosed carbonaceous chondrites. Hiroi et al. (1994, 1996) measured the diffuse reflectance spectra of Murchison heated in a low-pressure hydrogen atmosphere at 400–1000°C and compared them with other carbonaceous chondrites and asteroid spectra. Hiroi and Zolensky (1998) obtained diffuse reflectance spectra of some phyllosilicates heated at the temperature range of 200–600°C to study thermal histories of primitive asteroids by remote sensing method.

Few studies have systematically measured diffuse reflectance spectra of meteor-

ite samples heated under different oxygen-fugacity conditions, although oxygen-fugacity is known to alter mineral assemblages in heated samples. Main purpose of this paper is to show spectral changes of heated samples of an H5 chondrite at the oxidizing condition. Our results may provide valuable information on spectral changes due to alteration processes on asteroidal surfaces.

2. Experiments

We used the Nuevo Mercurio H5 ordinary chondrite to study spectral changes at more oxidizing conditions than its intrinsic oxygen fugacity. A chip (a few cm in size) of Nuevo Mercurio was broken in a corundum mortar to make small chips and less weathered chips were selected. The small chips of Nuevo Mercurio were ground in a corundum mortar and sieved to obtain a $< 100 \,\mu\text{m}$ powder sample. Powder sample shows dark gray with a brownish tinge. Some material was ground to obtain a $\ll 37 \,\mu\text{m}$ size fraction. Splits of the sample were made into 100 mg pellets and placed in Pt-foil and heated to temperatures of 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200°C and held for 48 hr in a vertical 1-atm H_2/CO_2 gas-mixing furnace at constant oxygen fugacities at one log unit below the iron-wüstite (IW) buffer (IW-1) and two log units above the IW buffer (IW+2). Intrinsic oxygen fugacity of H chondrite is near IW-1 (Brett and Sato, 1984). Oxygen fugacity was monitored by a zirconia cell (Miyamoto and Mikouchi, 1996). The charge was cooled to room temperature by cutting the electricity to the furnace. To avoid oxidation of the charge during cooling the gas flow to the furnace was retained during cooling.

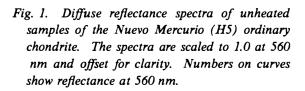
Subsequent to the heating experiment, the pellet was re-ground and passed through a $100 \,\mu\text{m}$ sieve to obtain powders for spectral characterization.

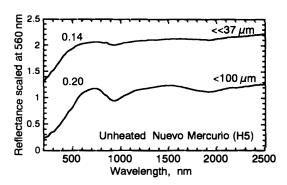
Biconical diffuse reflectance spectra were measured by using a UV-VIS-NIR spectrophotometer with the incident and emission angles of 30 degrees. Two detectors, a photomultiplier in the range of 200–850 nm and a PbS cell cooled at 0°C in the range of 850–2500 nm were used. Illumination is a deuterium lamp in the spectral range of 200–300 nm and a tungsten lamp in the range of 300–2500 nm. The spectra were scanned at a constant rate of 1 nm/s and were recorded every 2 nm using Halon as a reflectance standard. The reflectance spectra (The reflectance ratio of sample/Halon) were not corrected for absolute reflectance of Halon. Samples were placed in a 1.5 mm deep sample holder.

3. Results and discussion

3.1. Spectra of unheated samples of Nuevo Mercurio

Figure 1 shows the diffuse reflectance spectra of the unheated Nuevo Mercurio (H5) samples at grain sizes of $< 100 \,\mu\text{m}$ and $\ll 37 \,\mu\text{m}$. The absorption bands near 1000 nm are due to the presence of Fe²⁺ in pyroxene and olivine. The asymmetry of the 1000 nm band is caused by the absorption bands in olivine. The shoulder absorption-band near 1250 nm is due to Fe²⁺ in feldspar, pyroxene, or olivine. The absorption band near 2000 nm is due to pyroxene. These absorption features are





consistent with the mineral assemblage of the H5 chondrite (e.g., Dodd, 1981). The spectrum of the $\ll 37 \,\mu m$ sample shows (1) a lower spectral contrast (weak absorption bands) (2) a shorter wavelength of UV drop-off compared with the $< 100 \,\mu m$ sample.

3.2. Heating at IW-1

The samples heated to 1100° C and 1200° C show strong absorption bands near 1050 nm due to olivine (Fig. 2a). This is consistent with the result that Jurewicz *et al.* (1995) in an experimental heating study showed that at 1200° C the Lost City (H5) charge was about 80% olivine. In this study the samples heated below 1000° C show the spectra of the mineral assemblage similar to that of the unheated sample, although the wavelengths of UV drop-off for the heated samples are shorter than that of the unheated $< 100 \,\mu\text{m}$ sample.

3.3. Heating at IW+2

The spectra of the samples heated at IW+2 are much different from those heated at IW-1 except for those heated to 1200° C (Fig. 2b). The spectra of the 1200° C samples heated at both IW-1 and IW+2 are similar to that of olivine. The samples heated at temperatures lower than 1050° C show (1) low spectral contrast, (2) short wavelength of UV drop-off and (3) low reflectance (at 560 nm) compared with the unheated $< 100 \,\mu\text{m}$ sample.

3.4. Comparison among the spectra of heated samples

Figure 3 shows the reflectance at 560 nm of the spectra of heated samples. The samples heated below 1100° C at IW+2 show low reflectances compared with those of the unheated $< 100 \,\mu\text{m}$ sample and the samples heated at IW-1 (the IW-1 samples). The IW-1 samples show higher reflectances compared with the unheated sample.

Figure 4 shows the wavelength position of reflectance minimum near 1000 nm versus temperature. The increase in the position for the samples heated over 1000°C suggests an increase in the amount of olivine in the samples.

Hiroi et al. (1995) and Hiroi and Pieters (1998) defined the following spectral parameters:

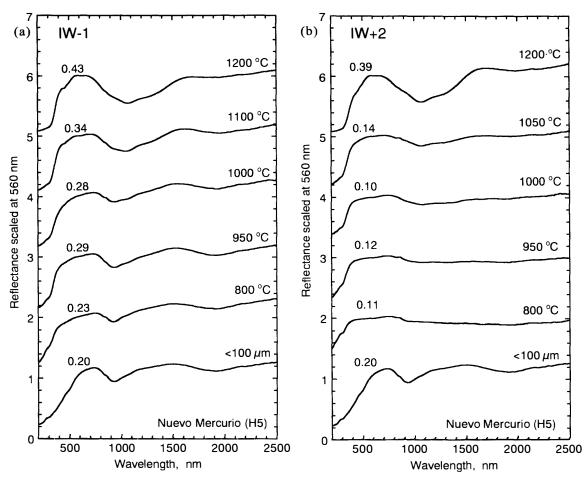
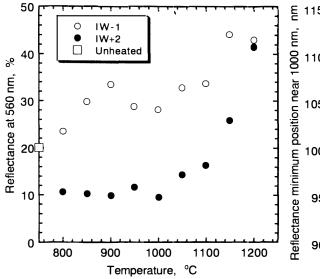


Fig. 2. Diffuse reflectance spectra for samples of the Nuevo Mercurio H5 chondrite heated at one log unit below the IW buffer (a) and two log units above the IW buffer (b). The spectra are scaled to 1.0 at 560 nm and offset for clarity. Numbers on curves show reflectance at 560 nm.

1-
$$\mu$$
m band depth = ln (R_M/R_C) ,
Visible redness = ln (R_M/R_{55}) ,

where $R_{\rm M}$ indicates the reflectance maximum around 740 nm, $R_{\rm C}$ is the reflectance at the 1- μ m band center, and R_{55} is the reflectance at 550 nm. Figure 5 shows the 1- μ m band depth that increases with temperature, suggesting that the increase in the amount of olivine.

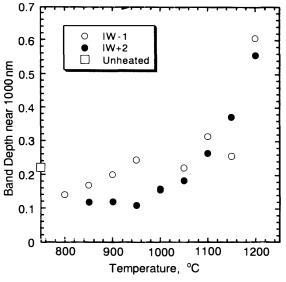
Figure 6 shows the wavelength position at which the reflectance is 70% ($\approx 1/\sqrt{2}$) of $R_{\rm M}$ to study UV drop-off of the spectra. All heated samples have shorter wavelength positions of UV drop-off compared to the unheated $< 100\,\mu{\rm m}$ sample. Although the wavelength positions of UV drop-off of the samples heated at IW-1 are similar, those of the samples heated at IW+2 gradually shift toward shorter wavelengths as temperature decreases. The $\ll 37\,\mu{\rm m}$ sample shows a wavelength of UV drop-off shorter than that of the $< 100\,\mu{\rm m}$ sample. Although UV drop-off is considered to be related to charge-transfer absorption (e.g., Fe²⁺-Fe³⁺, Burns, 1970), our results cannot be readily explained.



1150 1100 1050 IW-1 IW+2 1000 Unheated 950 900 800 900 1000 1100 1200 ٥С Temperature,

Fig. 3. Plot of heating temperature vs. reflectance at 560 nm. Solid circles show the samples heated at two log units above the IW buffer and open circles at one log unit below the IW buffer. Square shows the unheated < 100 μm sample.

Fig. 4. Plot of heating temperature vs. the reflectance-minimum position near 1000 nm. The symbols are the same as Fig. 3.



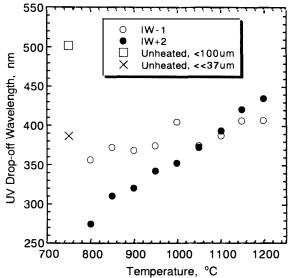


Fig. 5. Plot of heating temperature vs. the band depth near 1000 nm. For the definition of the spectral parameter, see text. The symbols are the same as Fig. 3.

Fig. 6. Plot of heating temperature vs. UV drop-off wavelength. For the definition of the spectral parameter, see text. The symbols are the same as Fig. 3.

3.5. Importance of oxygen fugacity at heating

Our experimental results show importance of oxygen-fugacity control at heating, because spectral features are different among the spectra heated at different oxygen-fugacities. Attention has to be paid to oxygen fugacity for studying spectral

changes of heated samples.

Metamorphic temperatures of 400–900°C and 400–800°C are reported for ordinary chondrites (e.g., Dodd, 1981) and thermally metamorphosed carbonaceous chondrite (e.g., Akai, 1990; Zolensky et al., 1993), respectively. These temperature ranges are high enough to alter the spectra if oxygen fugacity changes on the basis of our heating experiments.

In addition to heating of whole planetary bodies, local heating of their surface region also affects the reflectance spectra because they depend on the mineral assemblage of very thin surface layer (less than about 1 mm). For example, bombardments on asteroidal surfaces by icy meteorites or meteorites that contain a large amount of hydrous minerals may locally increase temperature and change oxygen fugacity in the surface. Oxygen fugacity plays an important role in the mineral assemblage. The results of laboratory experiments performed by Yakshinskiy and Madey (1999) on explaining the surface process which produces the Na atmosphere of the Moon implies that the (micro)meteorite bombardment can plausibly affect oxygen fugacity at asteroidal surfaces.

By heating below 900°C recrystallization due to the presence of melt cannot be expected. To better understand the spectral changes studied in this paper, further studies are needed to investigate (1) what mineral assemblage causes the spectral change of the samples heated at IW+2 by using an electron microscope and (2) spectral changes of different meteorites heated at the oxidizing condition.

4. Conclusions

The conclusions reached in the present study are the followings:

- 1) Oxygen fugacity of our heating experiments affects the spectra of the samples, implying that oxygen-fugacity control is important for heating experiment.
- 2) The samples heated at temperatures lower than 1050° C show (1) low spectral contrast, (2) short wavelength of UV drop-off and (3) low reflectance (at 560 nm) compared with the unheated $< 100 \,\mu\text{m}$ sample, implying that oxygen fugacity may play a role in the surface processes on asteroids.

Acknowledgments

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References

- Akai, J. (1990): Mineralogical evidence of heating events in Antarctic carbonaceous chondrites, Y-86720 and Y-82162. Proc. NIPR Symp. Antarctic Meteorites, 3, 55-68.
- Brett, R. and Sato, M. (1984): Intrinsic oxygen fugacity measurements on seven chondrites, a pallasite, and a tektite and the redox state of meteorite parent bodies. Geochim. Cosmochim. Acta, 48, 111-120.
- Burns, R. G. (1970): Mineralogical Applications of Crystal Field Theory. Cambridge, Cambridge University Press, 224 p.

- Dodd, R. T. (1981): Meteorites: A Petrologic-Chemical Synthesis. New York, Cambridge Univ. Press, 368 p.
- Hiroi, T. and Pieters, C. M. (1998): Origin of Vestoids suggested from the space weathering trend in the visible reflectance spectra of HED meteorites and lunar soils. Antarct. Meteorite Res., 11, 163-170.
- Hiroi, T. and Zolensky, M. E. (1998): UV-VIS-NIR absorption feature of heated phyllosilicates as remote-sensing clues of thermal histories of primitive asteroids. Antarctic Meteorites XXIII. Tokyo, Natl Inst. Polar Res., 30-32.
- Hiroi, T., Pieters, C. M., Zolensky, M. E. and Lipschutz, M. E. (1994): Possible thermal metamorphism on the C, G, B, and F asteroids detected from their reflectance spectra in comparison with carbonaceous chondrites. Proc. NIPR Symp. Antarct. Meteorites, 7, 230-243.
- Hiroi, T., Binzel, R. P., Sunshine, J. M., Pieters, C. M. and Takeda, H. (1995): Grain sizes and mineral compositions of surface regoliths of Vesta-like asteroids. Icarus, 115, 374-386.
- Hiroi, T., Zolensky, M. E., Pieters, C. M. and Lipschutz, M. E. (1996): Thermal metamorphism of the C, G, B, and F asteroids seen from the $0.7 \,\mu\text{m}$, $3 \,\mu\text{m}$, and UV absorption strengths in comparison with carbonaceous chondrites. Meteorit. Planet. Sci., 31, 321-327.
- Jurewicz, A. J. G., Mittlefehldt, D. W. and Jones, J. H. (1995): Experimental partial melting of the St. Severin (LL) and Lost City (H) chondrites. Geochim. Cosmochim. Acta, 59, 391-408.
- Miyamoto, M. (1991): Thermal metamorphism of CI and CM carbonaceous chondrites: An internal heating model. Meteoritics, 26, 111-115.
- Miyamoto, M. and Mikouchi, T. (1996): Platinum catalytic effect on oxygen fugacity of CO₂-H₂ gas mixtures measured with ZrO₂ oxygen sensor at 10⁵ Pa from 1300 to 700°C. Geochim. Cosmochim. Acta. 60, 2917–2920.
- Wasson, J. T., Pieters, C. M., Fisenko, A. V., Semjonoval, L. F., Morozl, L. V. and Warren, P. H. (1997): Simulation of space weathering of HED meteorites by laser impulse irradiation. Lunar and Planetary Science XXVIII. Houston, Lunar Planet Inst., 1505-1506.
- Yakshinskiy B. V. and Madey T. E. (1999) Photon-stimulated desorption as a substantial source of sodium in the lunar atmosphere. Nature, 400, 642-644.
- Zolensky, M. E., Barrett, R. and Browning, L. (1993): Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. Geochim. Cosmochim. Acta, 57, 3123-3148.

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