Note

Reflectance spectroscopy (200–2500 nm) of highly-reduced phases under oxygen- and water-free conditions

CrossMark

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A B S T R A C T

Spectra of highly-reduced mineral phases from 200 to 2500 nm provide new laboratory constraints on the surfaces of asteroids and other extremely reduced solid assemblages. Synthetic oldhamite (CaS) is distinguished by high ultraviolet reflectance (which decreases toward shorter wavelengths). Oldhamite and osbornite spectra show absorption features at $\sim$401 nm and $\sim$436 nm, respectively. Chemically pure synthetic oldhamite is spectrally distinct from naturally-occurring oldhamite from the Norton County aubrite, possibly due to differences in minor and trace element compositions, presence or absence of inclusions, or differences in oxidation/hydration (terrestrial weathering). Iron powders at 50 nm and 10 μm nominal particle sizes, nanophase graphite, and carlsbergite (CrN) all have very low reflectivity over the 200–2500 nm wavelength range. Carlsbergite has a slight blue spectral slope in the visible and near-infrared (400–2500 nm), while the iron powders and nanophase graphite show slight red slopes over this wavelength range.

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1. Introduction

Some common extraterrestrial minerals are extremely rare or absent in Earth materials. Important planetary materials, including oldhamite and nanophase iron, oxidize and hydrolyze rapidly in contact with Earth's atmosphere and hydrosphere (e.g., Cooper et al., 2012; Haberle et al., 2013; Okada et al., 1981). Oldhamite is particularly susceptible to terrestrial weathering, and is rapidly altered to sulfates (bassanite, gypsum), oxhydroxides (portlandite), and carbonates (vaterite, calcite) as described by Okada et al. (1981). Nitrides and graphite are less reactive, but may still be affected by adsorbed atmospheric water or gases. We have conducted a spectroscopic study of synthetic versions of CaS (oldhamite), TiN (osbornite), CrN (carlsbergite), nanophase graphite, and iron (10 μm and 50 nm nominal particle sizes) under an oxygen-free anhydrous N_2 atmosphere. In the subsequent discussion we use the mineralogic terms for these synthetic equivalents unless otherwise indicated. Given the considerable uncertainty concerning the extent to which known meteorites are representative of the asteroids, and the lack of any known meteorites that sample of the surface of Mercury, spectral studies of diverse highly-reduced materials are useful for understanding the properties of planetary surfaces using telescopic, orbiter and lander data sets. Objects which may contain highly-reduced mineral assemblages include the parent asteroids of enstatite chondrites, aubrites, iron meteorites, pallasites, mesosiderites (or similar materials not present in terrestrial meteorite collections), and the surface of Mercury.

2. Methods

The samples used in this study are described in Table 1. All of the samples are air-sensitive. Special procedures were implemented to preserve their integrity. Spectra were collected in a Plas-Labs 818 GBB glovebox with interior dimensions of $152.4W \times 96.5D \times 79H$ cm (Plas-labs Inc., Lansing, MI) under a dry N_2 atmosphere, where dry nitrogen was passed through a series of Drierite filters. The glovebox also contained Drierite and Chemisorb to remove any remaining water and CO_2. Humidity and CO_2 levels were monitored continuously, and remained $\ll$1% throughout the measurements. Samples were only opened within the glovebox and were exposed to the glove box atmosphere for minutes at most. Possible oxidation and hydration were monitored by periodically measuring spectra of samples of 50 nm nanophase iron and oldhamite that were left exposed within the glovebox. If oxygen or water vapor were present, they would produce Fe-oxyhydroxides from the nanophase iron and Ca-sulfates from the oldhamite, which would be detectable via Fe–O charge-transfer transitions, or overtones of O–H or S–O vibrational features. Because no such spectral features were detected, we are confident that contamination from, or alteration by, Earth's atmosphere did not occur and did not affect our data set.

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Table 1
Sample descriptions.

Mineral name	Ideal chemical formula	HOSERLab sample ID	Notes
Oldhamite	CaS	CAS001	Calcium sulfide, synthetic CaS; 99.9% (metals basis excluding Sr) Sr typically 500 ppm; CAS #20548-54-3. Alfa Aesar stock number 13121, lot #G16U051, −325 mesh powder. 5 g packed under argon
Osbornite	TiN	TIN001	Titanium nitride (TiN), synthetic. 99.5% (metals basis), Alfa Aesar stock number 41556-18, lot #X29S045. CAS #25583-20-4
Carlsbergite	CrN	CAR101	Carlsbergite: synthetic CrN (ESPI Corp., #K1367R)
Graphite, nanophase	C	GRP200	Graphite nanopowder; synthetic (MTI Corporation); <30 nm particle size; 99.5% purity, non-crystalline; >60 m^2/g specific surface area
Iron, Britt-Pieters particles	Fe	IRO103	Iron, synthetic powder, spherical, <10 μm, 99.9%+ (metals basis), 99.5% (Alfa Aesar stock #00170-14, 62-03-02; lot #L05R011)
Iron, nanophase	Fe	IRO102	Iron, synthetic nanophase; average particle size <50 nm. MTI Corporation. PCVD manufacturing method. Packed under vacuum. 40–60 m^2/g surface area

We have consistently used the mineral names of the synthetic compounds (e.g., oldhamite for CaS, osbornite for TiN) because these synthetic compounds are crystallo-graphically and chemically equivalent to idealized (without impurities) versions of the corresponding natural minerals. Chemical substitutions in the natural minerals (e.g., minor substitution of Mg^{2+} or Sr^{2+} for Ca^{2+} in oldhamite) will not significantly change the crystal structures.

2.1. 350–2500 nm measurements (near UV, VIS, and near IR regions)

The 350–2500 nm reflectance spectra were measured with an Analytical Spectral Devices FieldSpec Pro HR spectrometer which acquires data from 350 to 2500 nm in 1.4 nm steps, with a spectral resolution of between 2 and 7 nm. The data are internally resampled by the instrument to output data ultimately at 1 nm intervals. Data below approximately 400 nm may be affected by low signal levels and hence data in the 350–400 nm region, particularly the abrupt changes in slope, are suspect. Unless otherwise indicated, spectra were measured at a viewing geometry of $i = 30°$ and $e = 0°$. Incident light was provided by an in-house 100 W quartz–tungsten–halogen collimated light source. Sample spectra were measured relative to a Spectralon (Labsphere, North Sutton, NH) standard and corrected for minor (less than ∼2%) irregularities in its absolute reflectance. In each case, 200 spectra of the dark current, standard, and sample were acquired and averaged, to provide sufficient signal-to-noise for subsequent interpretation. Locations of reflectance minima in oldhamite and osbornite were determined by fitting a 3rd-order polynomial to the measured spectra.

2.2. 200–400 nm measurements (UV region)

The ultraviolet spectroscopy methods used in this study were initially described by Cloutis et al. (2008) and are briefly summarized here. The 200–400 nm spectra were measured with an Ocean Optics S-2000 spectrometer equipped with a grating that provides coverage from 200 to 859 nm with spectral resolution between 0.36 nm (at 200 nm) and 0.28 nm (at 859 nm). Illumination was provided by an Analytical Instrument Systems Inc. Mini-DTA light source with output from a 30 W deuterium lamp directed through a bifurcated fiber optic bundle consisting of six illumination fibers surrounding a central pick-up fiber feeding into the detector array. This assembly consisted of 400-μm diameter solarization-resistant (XSR) fibers, with transmission efficiencies between 23% and 40% across the 200–400 nm range. The fiber optic bundle was used in normal incidence and we used an integration time of 1000 ms

and averaged 100 individual spectra. Measurements for each sample were made by first acquiring a dark current spectrum (with the input to the spectrometer blocked), a reference spectrum of our $BaSO_4$ standard (Alfa Aesar Puratronic grade: 99.998% metals basis; CAS #7727-43-7), followed by measurement of the samples. All three measurements were made using an identical viewing geometry, integration time, and number of averaged spectra. The reference and target were both placed at the same distance from the end of the fibers bundle (∼5 mm). The fibers have a 25.4° field of view, and this working distance provided the best compromise between measurement time, uniform target illumination, and size of the sample being imaged. The most appropriate definition of the instrument configuration is a biconical arrangement with i and e centered on ∼0° and detector and illumination fields of view of 25.4°. The spectra were corrected for irregularities in the $BaSO_4$ standard using a calibrated deep UV mirror as described in Cloutis et al. (2008).

2.3. Note on terminology for fine iron particles

Various terms have been used in the planetary science literature for very small iron particles thought to influence the spectral properties of airless bodies, including nanophase iron (npFe^0) (Keller and McKay, 1993; Pieters et al., 2000), submicroscopic metallic iron (SMFe) (Hapke, 2001), and Britt-Pieters particles or microphase iron (Lucey and Riner, 2011; Riner and Lucey, 2012). In the present study, we have used commercially available iron powders of 50 nm and 10 μm particle sizes. The 50 nm powder consists of nanophase iron, applying the widely accepted definition adopted by the American Society for Testing and Materials (ASTM) "nanoparticle: sub-classification of ultrafine particle with lengths in two or three dimensions greater than 0.001 μm (1 nm) and smaller than about 0.1 μm (100 nm) and which may or may not exhibit a size-related intensive property" (ASTM, 2012). The 10 μm powder would be classified as a coarse particle according the ASTM definition "a particle smaller than about 10 μm and larger than about 2.5 μm in size" (ASTM, 2012). For the 50 nm powder, we have used

Table 2
Albedo and reflectance ratio measurements.

Sample ID	Albedo (560 nm) (%)	Reflectance ratios (wavelength positions given in nm)				
		2400/560	600/500	1800/800	1800/1250	1250/600
CAS001 (oldhamite)	62.35	1.12	1.07	1.02	1.00	1.08
TIN001 (osbornite)	10.59	2.95	2.17	1.36	1.06	2.18
CAR101 (carlsbergite)	5.33	0.67	1.01	0.80	0.81	1.03
GRP200 (np graphite)	0.97	1.23	0.94	0.89	0.98	0.83
IRO103 (np iron, 10 μm)	2.81	1.48	0.98	1.00	1.00	0.99
IRO102 (np iron, 50 nm)	2.60	1.23	0.97	0.91	0.98	0.92