ULTRAVIOLET, VISIBLE AND NEAR-INFRARED REFLECTANCE SPECTROSCOPY OF HIGHLY-REDUCED PHASES UNDER OXYGEN- AND WATER-FREE CONDITIONS

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Introduction: Some common extraterrestrial minerals are extremely rare or absent in Earth materials. Important planetary materials including oldhamite and nanophase iron oxidize and hydrolyse rapidly in contact with Earth's atmosphere and hydrosphere. Other highly-reduced phases are less reactive, but may still be affected by adsorbed atmospheric water or gases. We have conducted a spectroscopic study of CaS (oldhamite), TiN (osbornite), CrN (carlsbergite), nanophase graphite and nanophase iron (10 μm and 50 nm nominal particle sizes) under an oxygen-free anhydrous atmosphere. Both oldhamite and osbornite have absorption features in the 350-2500 nm range that could be spectrally detectable. Both nitrides and oldhamite are typically only trace or minor components in meteorites; however, this may reflect sampling bias. Oldhamite is very susceptible to terrestrial weathering and is rapidly altered to sulphate (e.g., gypsum, basanite). Clasts of oldhamite-rich lithologies are known from several enstatite meteorites including the Abee EH4 impact melt breccia [1] and the Norton County aubrite [2] and Bustee aubrite [3]. Oldhamite may be more abundant on some E-type asteroids, for instance, an oldhamite abundance of up to 42% has been suggested by Nedelcu et al., [4] for asteroid 2867 Steins. Clark et al., [5] concluded from spectroscopic observations and compositional modelling that several E-type asteroids contain abundant sulphides, possibly including oldhamite, and that several E-types may not correspond with known enstatite meteorites (E chondrites or aubrites). Osbornite is a trace constituent of many enstatite chondrites [e.g., 6], and has been reported in an oldhamite-rich lithology from the Bustee aubrite [3]. Osbornite, likely formed as an early solar system condensate, has also been reported from comet Wild-2 [7]. Carlsbergite is a fine-grained trace constituent of many iron meteorites [e.g., 8, 9]. Given the considerable uncertainty concerning the extent to which known meteorites are representative of the asteroids, spectral studies of diverse highly-reduced materials are useful for understanding the properties of planetary surfaces using telescopic, orbiter and lander data sets.

Methods: Spectra were collected in a Plas-Labs 818 GBB glovebox with interior dimensions of 152.4W × 96.5D × 79H cm (Plas-labs Inc., Lansing, MI) under a dry N_2 atmosphere. Samples were only opened within the glovebox and were exposed to the environment within the glovebox for a few minutes at most. The 350 to 2500 nm reflectance spectra were measured with an ASD FieldSpec Pro HR spectrometer, with a spectral resolution of between 2 and 7 nm, and a viewing geometry of i=30º and e=0º. Incident light was provided by an in-house 100 W quartz-tungsten-halogen collimated light source. Sample spectra were measured relative to a Spectralon® 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.

The 250-400 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 a 30 W deuterium lamp through a bifurcated fibre optic bundle consisting of six illumination fibres surrounding a central pick-up fibre feeding into the detector array. This assembly consisted of 400-μm diameter solarization-resistant (XSR) fibers, with a 25.4º field of view and transmission efficiencies between 23 and 40% across the 200–400 nm range. The fiber optic bundle was used in normal incidence (i=30º and e=0º). 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, and 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 sample. 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 fibres bundle (~5 mm) [10]. The 250-400 nm spectra were corrected for irregularities in $BaSO_4$ reflectance using a calibrated Edmund Optics 25mm Diameter Deep UV Enhanced Mirror.

Results: *350-2500 nm region (near ultraviolet, visible, and near infrared)*: Oldhamite has a strong feature with a minimum at 399 nm and shoulders near 550 nm and 750 nm. Reflectance spectra of osbornite and carlsbergite have not previously been measured over the wavelengths studied here. Osbornite has an absorption feature with a minimum at 440 nm (Fig.

1A, B). Carlsbergite is dark and spectrally featureless with a blue slope (Fig. 1A, B). Nanophase iron at both 10 μm and 50 nm nominal particle sizes have dark and featureless spectra with nearly flat to slightly red spectral slopes (Fig. 1A, B). Nanophase graphite has extremely low reflectance, is spectrally featureless, and has a slight red slope. For nanophase graphite and iron, the spectral slopes may be artefacts due to noise and thermal excess (Fig. 1A, B).

Ultraviolet region (250-400 nm): All materials studied here have monotonically decreasing reflectance with decreasing wavelength in the ultraviolet, with the exceptions of oldhamite and carlsbergite (Fig 1C). Oldhamite has a distinctive spectrum with a local maximum near 338 nm (Fig. 1C). Osbornite does not have a monotonically decreasing reflectivity in the ultraviolet, but shows a decrease towards longer wavelengths (Fig. 1C).

Discussion and Conclusions: Ultraviolet spectra of many materials show monotonically decreasing reflectance with decreasing wavelength from 400 to 200 nm [10]. Oldhamite is distinctive and has a high reflectance in the ultraviolet with a local maximum near 338 nm, which could facilitate remote detection. Osbornite shows an absorption feature centered near 450 nm, and has a broad local maximum in ultraviolet reflectance. Comparison of our measurements with RELAB and previous HOSERLab data for oldhamite in the 350-2500 nm range show similar spectral characteristics including the absorption at ~399 nm [11]. The spectral characteristics of oldhamite and osbornite may allow for their detection on asteroidal and other planetary surfaces.

Observable spectral changes other than the appearance of absorption features can be caused by the presence of materials like those studied here. For instance, finely-dispersed opaque phases can greatly darken a material and reduce the contrast of spectra features and can induce large changes in spectral slope.

The dusty envelopes of some stars (carbon stars) contain high abundances of C and N. In these settings, significant abundances of refractory nitrides and carbides can be formed. Carbides and nitrides formed in astrophysical settings including supernovae outflows and the early solar nebula have been observed in primitive meteorites [e.g., 12, 13] and from comets [7]. While the spectra here are not directly comparable to those of dust in stellar envelopes, they may still provide some constraints on the presence of highly-reduced phases in astrophysical settings, particularly oldhamite.

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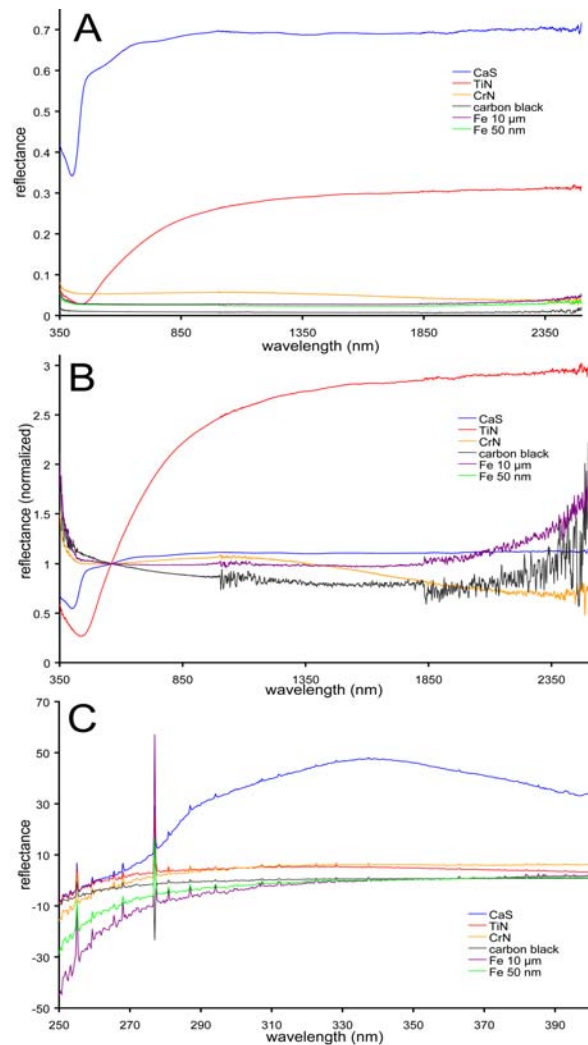
Figure 1: Spectra of CaS (oldhamite), TiN (osbornite), CrN (carlsbergite), nanophase graphite (carbon black) and nanophase iron (10 μm and 50 nm nominal particle sizes). A) Near-UV, visible and near IR spectra collected with i = 30° and e=0°, absolute reflectance. B) Near-UV, visible and near infrared spectra, absolute reflectance normalized to reflectance at 560 nm. C) UV spectra i=0° and e=0°.