Meteoritics & Planetary Science 37, 1233–1244 (2002)
Available online at http://www.uark.edu/meteor

Spectra of extremely reduced assemblages: Implications for Mercury

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(Received 2002 January 25; accepted in revised form 2002 June 7)
(Presented at the Workshop on Mercury, The Field Museum, Chicago, Illinois, 2001 October 4–5)

Abstract–We investigate the possibility that Mercury's crust is very reduced with FeO concentrations of less than ~0.1 wt%. We believe that such a surface could have a composition of enstatite, plagioclase, diopside, and sulfide, similar to the mineral assemblages found in aubritic meteorites. To test this hypothesis, we investigated the spectra of aubrites and their constituent minerals as analogs for the surface of Mercury. We found that some sulfides have distinctive absorption features in their spectra shortwards of ~0.6 μm that may be apparent in the spectrum of such an object. Determination of the surface composition of Mercury using orbital x-ray spectroscopy should easily distinguish between a lunar highlands and enstatite basalt composition since these materials have significant differences in concentrations of Al, Mg, S, and Fe. The strongest argument against Mercury having an enstatite basalt composition is its extreme spectral redness. Significant reddening of the surface of an object (such as Mercury) is believed to require reduction of FeO to nanophase iron, thus requiring a few percent FeO in the material prior to alteration.

INTRODUCTION

Determining the surface composition of Mercury is one of the science objectives of a number of upcoming missions: MESSENGER (MErcury, Surface, Space ENvironment, GEochemistry, Ranging) and BepiColombo (*e.g.*, Ksanfomaliti, 2001; Solomon *et al.*, 2001; Anselmi and Scoon, 2001). Each spacecraft will observe Mercury over a variety of different wavelength regions (*e.g.*, visible, near-infrared, x-ray, gamma-ray). Only one previous mission (Mariner 10) (*e.g.*, Murray *et al.*, 1974) has visited Mercury, but it imaged less than half of the surface.

Telescopic observations of Mercury (*e.g.*, McCord and Adams, 1972; Vilas *et al.*, 1984; Vilas, 1985, 1988) from Earth are extremely difficult due to Mercury's proximity to the Sun. Previous spectral reflectance measurements (such as the spectrum plotted in Fig. 1) show a weak feature centered at ~0.9 μm; however, it has been debated if this feature is due to low Fe^{2+} contents in the silicates or due to the incomplete removal of an atmospheric water feature.

More recent observations of Mercury at thermal infrared wavelengths suggest that some portions of the surface may be composed of a powdered glassy material (Cooper *et al.*, 1998). Other observations suggest heterogeneity across the surface with iron-depleted basaltic, mafic, and ultramafic regions (Sprague *et al.*, 1994, 2000; Sprague and Roush, 1998; Cooper *et al.*, 2001).

Current models for Mercury's surface composition usually use the lunar analogy since so much is known compositionally about the Moon and so little is known about Mercury. Both the Moon and Mercury are heavily cratered bodies (*e.g.*, Murray *et al.*, 1974; Neukum *et al.*, 2001) and appear similar in appearance in many images. Many researchers (*e.g.*, McCord and Adams, 1972; McCord and Clark, 1979; Vilas, 1988; Blewett *et al.*, 1997) have noted the spectral similarity (Fig. 1) in shape and slope of ground-based mercurian spectra to those of the lunar highlands. However, analyses (*e.g.*, Rava and Hapke, 1987) of the relationships between color (ratio of reflectances at different wavelengths) and different types of terrain on Mercury show them to be distinctly different from those on the Moon.

The lunar highlands are dominated by ferroan anorthosites, which are characterized (*e.g.*, Papike *et al.*, 1998) by high modal abundances (~90 vol%) of calcic plagioclase with accessory Fe-rich pyroxenes and olivines. Ferroan anorthosites are widely believed to have originated by flotation of plagioclase from a global magma ocean (*e.g.*, Wood *et al.*, 1970; Warren, 1985). Ferroan anorthosites have FeO contents ranging from trace to ~7 wt%. Analyses (*e.g.*, Blewett *et al.*, 1997) of the "best" telescopic spectra of Mercury have led to estimates of FeO contents of its surface of between 3 and 6 wt%.

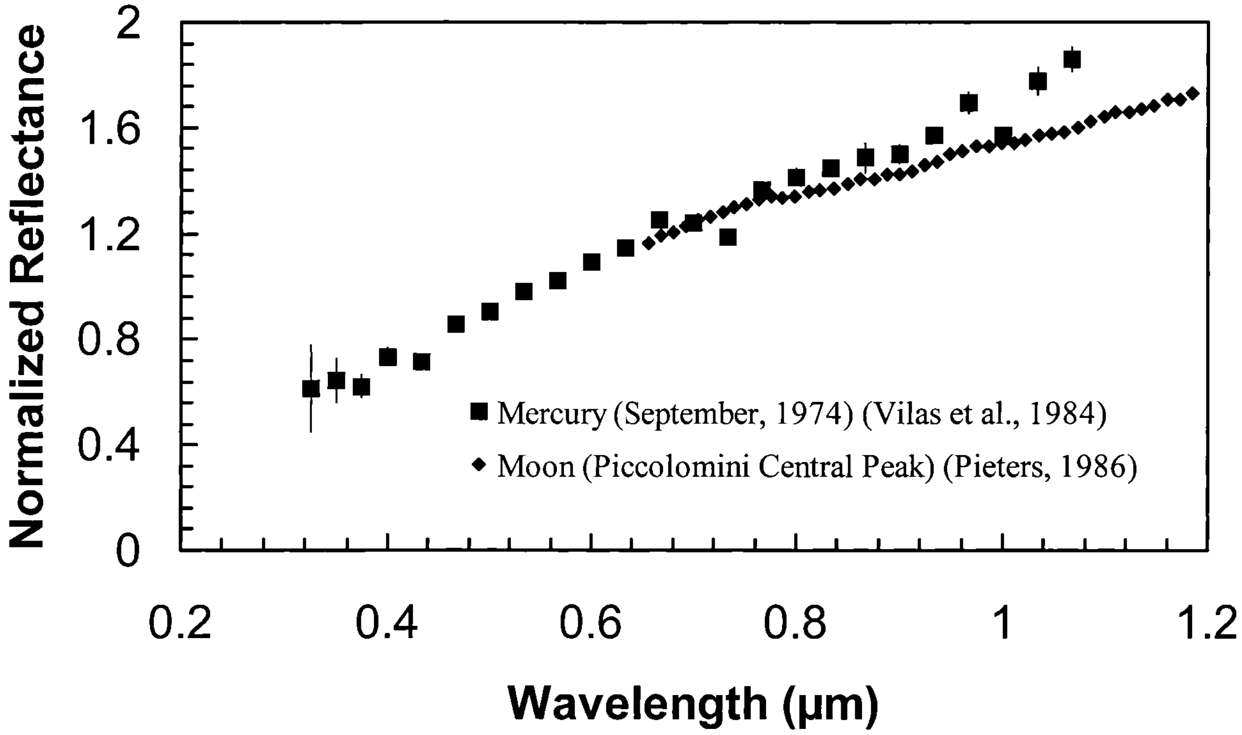

FIG. 1. Normalized reflectance *vs.* wavelength for Mercury and the central peak of the Piccolomini crater on the Moon. The Mercury spectrum is from Vilas *et al.* (1984) and is normalized to unity at 0.55 μm. The spectrum of the Piccolomini central peak is from Pieters (1986) and is normalized to overlap the Mercury spectrum at 0.7 μm. The spectrum of the Piccolomini central peak is interpreted to be of anorthosite due to the absence of mafic mineral bands (Pieters, 1986).

Dynamical models by Wetherill (1988) argue that while growing, Mercury-sized bodies experience a wide migration of their semi-major axes, possibly moving as far out as the orbit of Mars. These theoretical Mercury-like planets would have experienced a number of catastrophic impact events that would perturb their semi-major axes. Wetherill (1988) also argues that Mercury would have formed out of material that condensed over a wide variety of heliocentric distances.

However, some geochemists (*e.g.*, Lewis, 1972; Wasson, 1988) believe that Mercury's location at 0.4 AU may be consistent with its formation from highly reduced material that condensed at relatively high temperatures (about 1300–1400 K), possibly similar to the enstatite chondrites. Enstatite chondrites are composed (*e.g.*, Keil, 1968) primarily of enstatite, metal, sulfides, and plagioclase. This precursor material would then have experienced significant degrees of melting and formed a basaltic crust. Mercury's mean density (~5.4 g/cm^3) (*e.g.*, Cameron *et al.*, 1988) is consistent with a large core that formed out of reduced (Fe^o) metallic iron that sank to the center of the planet during differentiation.

However, Mercury's density is much higher than that of enstatite chondrites (about 3.4–3.7 g/cm^3) (Consolmagno and Britt, 1998), implying a much higher metallic iron content. One possibility for solving this density disagreement is to form Mercury out of material enriched in metallic iron relative to enstatite chondrites. Another possibility is to strip away Mercury's basaltic crust and much of its mantle through impacts (*e.g.*, Benz *et al.*, 1988; Cameron *et al.*, 1988; Wetherill, 1988). Fegley and Cameron (1987) propose that Mercury may have been subjected to a very high-temperature phase (2500–3000 K) of the primitive solar nebula, which volatilized the silicate crust and much of the mantle. The absence and/or presence of a basaltic crust on Mercury would provide important constraints on why Mercury has such a high density.

If Mercury formed out of highly reduced material, our closest meteoritic analog to Mercury's surface composition would be the aubrites (enstatite achondrites). Aubrites (*e.g.*, Watters and Prinz, 1979) are composed of essentially iron-free enstatite plus minor accessory phases such as diopside, metallic iron, and sulfides. Enstatite has a relatively featureless spectrum (*e.g.*, Lucey and Bell, 1989) and a high visual albedo due to the almost complete absence of iron (<0.1 wt%) in the silicates.

Using the aubrite analogy, the crust of Mercury would be relatively FeO-free and derived from the partial melting and recrystallization of material from the mantle. Mercury would then have formed a basaltic surface composed predominantly of FeO-poor pyroxenes (such as enstatite and diopside) and plagioclase. The removal of this crust would expose an enstatite-dominated mantle.

Determining Mercury's surface composition is important scientifically because the FeO concentration of the surface reflects that of the mantle and bulk planet (*e.g.*, Robinson and Taylor, 2001). This in turn constrains models for planetary accretion for Mercury and other terrestrial planets (*e.g.*, Wasson, 1988; Taylor and Scott, 2001; Grard and Balogh, 2001). In addition, better constraints on Mercury's surface composition might allow for the identification of mercurian meteorites in our meteorite collection, which have presently not been identified but appear theoretically possible (Love and Keil, 1995; Gladman *et al.*, 1996). Palme (2002) proposes that the eucrite Northwest Africa (NWA) 011 (Yamaguchi *et al.*, 2002), which has oxygen isotope values significantly different from other basaltic meteorites, may be a fragment of Mercury. NWA 011 is relatively FeO-rich (ferrosilite contents of the pyroxenes ranging from 43 to 64 mol%) (Afanasiev *et al.*, 2000). However, the high FeO content in this basaltic meteorite would indicate it came from a body with a small metallic iron core (Palme, 2002), which is inconsistent with the large iron core that is believed to exist in Mercury.

This paper explores the "theoretical" chemical and spectral properties of a very reduced "basaltic" crust in order to aid analyses of data from the upcoming Mercury missions. To investigate the possible spectral properties of such a surface, we have conducted a spectral survey of several aubritic meteorites and their constituent minerals in the visible and near-infrared. We have constrained the chemistry and mineralogy of basaltic surface material for a very reduced planetary body using melting experiments of enstatite chondrites as a guide. We have also examined theoretical x-ray spectra of a very reduced "basaltic" assemblage.

SAMPLES AND ANALYTICAL METHODS

Three aubrites were chosen from the Smithsonian Institution collection for petrologic and spectral studies. We selected bulk samples of Khor Temiki (USNM 1551) and Mayo Belwa (USNM 5873) and a coarse-grained, igneous clast from Peña Blanca Spring (USNM 5441). Prior to spectral analyses, polished thin sections of each meteorite were studied optically to examine textural features. We also studied samples from the Norton County aubrite, which were not obtained from the Smithsonian's collection.

We report here analyses of the Peña Blanca Spring clast. Silicate analyses were determined using a JEOL JXA-8900R electron microprobe operated at a 15 kV accelerating voltage and a 20 nA beam current. Standards with well-known compositions were used for calibrating the data and analyses were corrected using a company-supplied ZAF (atomic number (Z), absorption (A) and fluorescence (F)) routine to compensate for matrix effects.

Watters and Prinz (1979) reported modal mineralogies and mineral chemistries for Khor Temiki, Mayo Belwa, and Norton County. We expect no significant compositional differences between the aubrite samples measured by Watters and Prinz (1979) and the samples measured spectrally here. All measurements of these aubrites (*e.g.*, Hey and Easton, 1967; Graham *et al.*, 1977; Watters and Prinz, 1979; Okada *et al.*, 1988) indicate assemblages dominated by FeO-poor enstatite.

We measured spectra of oldhamite from the Norton County aubrite, a mixture of enstatite from Peña Blanca Spring with oldhamite from Norton County; and a mixture of Norton County silicates and synthetic troilite. The Norton County oldhamite is from a large oldhamite clast (clast L-50 that is 3.5 cm in length in the longest dimension) (Wheelock *et al.*, 1994) found in a sample located at the Institute of Meteoritics at the University of New Mexico. Troilite (FeS) extracted from the LL5 chondrite Paragould (USNM 921) (due to the difficulty in extracting significant amounts of troilite from aubrites) was also measured spectrally.

Reflectance spectra at room temperature were obtained on the powders using the bidirectional spectrometer at Brown University's Keck/NASA Reflectance Experiment Laboratory (RELAB). The incident angle was 30° and the emission angle was 0°. The spectral coverage was 0.32–2.55 μm with a sampling interval of 0.01 μm for all samples, except the mixture of Norton County silicates and synthetic troilite, where the sampling interval was 0.005 μm. All samples measured for this study were sieved to particle sizes <125 μm, except for the Norton County oldhamite (where the grain size was not measured) and the mixtures of Norton County (<45 and 45–90 μm, respectively) and synthetic troilite (<45 μm). The sulfur spectrum discussed here is from Clark *et al.* (1993).

Mixing experiments to look for albedo changes were done using opaque-free samples of the Norton County aubrite and samples of a synthetic troilite (iron sulfide reagent). These samples were also spectrally measured at RELAB. The Norton County sample was obtained from a solid piece that was crushed in an alumina mortar and then dry-sieved to obtain two size fractions. A few very minor rust spots were removed using a binocular microscope. The sample seemed very fresh and clean and there are no noticeable absorption bands at ~1.4 or ~1.9 μm in the spectra as would be expected if the silicates had weathered to any appreciable extent. Features at ~1.4 and ~1.9 μm are due to combination and overtone features of water and OH–fundamental absorptions (*e.g.*, Gaffey *et al.*, 1993), which are characteristic of terrestrial alteration products such as clays and iron oxides. Aubrites formed in very reducing (and water-poor) environments so pre-terrestrial water- or OH-bearing minerals are extremely rare.

The Norton County fractions included both enstatite and olivine on the basis of visual examination of the sample prior to crushing. Measurements of Norton County by Watters and Prinz (1979) indicate 85 vol% enstatite ($Fs_{0.1}$) and 10% olivine ($Fa_{0.01}$).

PETROLOGY AND SPECTRA OF AUBRITES

The aubrites measured spectrally represent a wide variety of lithologies. Khor Temiki and Mayo Belwa (Fig. 2a) exhibit the fine-grained brecciated texture typical of aubrites. They are both enstatite-dominated (89–98 vol%) with minor amounts of plagioclase (0.3–6.6%), diopside (0.6–1.5%), and forsterite (1.6–3.6%) with trace amounts of FeNi metal (kamacite) and troilite (Watters and Prinz, 1979). Khor Temiki contains slightly higher abundances of plagioclase and forsterite. These two meteorites have similar mineral chemistries with enstatite of $Fs_{0.1}$, diopside of $Fs_{0.1}$ and Wo_{42-45}, forsterite of $Fa_{0.2}$ and

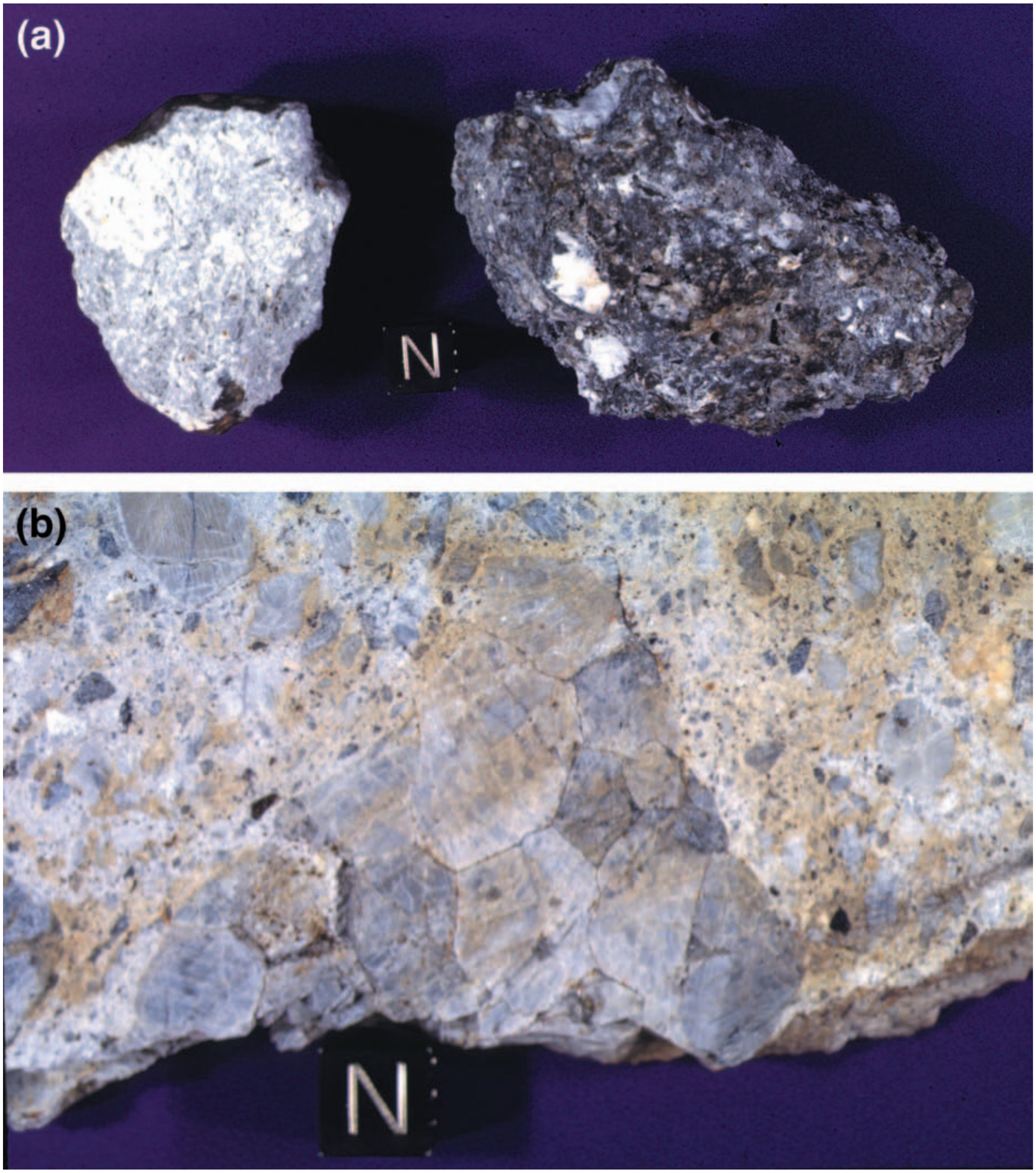

FIG. 2. (a) Photograph of Khor Temiki (USNM 1551) (left) and Mayo Belwa (USNM 5873) (right). Khor Temiki exhibits the whitish color typically associated with aubrites, while Mayo Belwa, which is chemically and mineralogically very similar, exhibits prominent shock-blackening. Cube is 1 cm on a side. (b) Photograph of Peña Blanca Spring (USNM 5441). A finely brecciated host dominates the meteorite. This specimen contains an ~10 cm clast composed of centimeter-sized, equant enstatite crystals. This lithology may represent the pre-brecciated texture of the enstatite-rich lithology, which dominated the aubrite parent body. Cube is 1 cm on a side.

plagioclase of $An_{2.0-3.3}$ (Watters and Prinz, 1979). The main difference between them is that Mayo Belwa appears extensively shock darkened, while Khor Temiki retains the whitish appearance typically associated with aubrites. Shock-darkening in aubrites (*e.g.*, Graham *et al.*, 1977; Okada *et al.*, 1988; Newsom *et al.*, 1996) is due to a combination of structural alteration of enstatite (*e.g.*, parting, cleavage, voids) and limited infilling of these openings in the enstatite grains by opaque phases. We selected these two meteorites on the premise that shock-darkening might affect their spectral properties.

Like Mayo Belwa and Khor Temiki, Peña Blanca Spring is dominated by a fine-grained groundmass interspersed with coarse crystals and rock fragments throughout. We identified and studied a clast (Fig. 2b) composed of centimeter-sized, equant enstatite grains that could represent the pre-brecciated texture of the enstatite lithology, which must have been widespread on the aubrite parent body. In addition, these large enstatite crystals provide an ideal sample of natural, pure end-member enstatite. This clast contains >99 vol% of nearly FeO-free enstatite ($Fs_{0.1-0.2}$) with rare inclusions of forsterite ($Fa_{0.1-0.2}$), metal and sulfides that reach up to 200 μm in diameter.

For our spectral studies, bulk samples were taken of Khor Temiki and Mayo Belwa while the sample of Peña Blanca Spring was a single enstatite crystal from the coarse-grained clast. Spectra (Fig. 3) of Khor Temiki, Mayo Belwa, and Peña Blanca Spring are all relatively featureless with slight ultraviolet (UV) features. Both Khor Temiki and Peña Blanca Spring have slight features at ~1.9 μm indicative of terrestrial weathering. If the surface of Mercury is composed predominately of enstatite, we would expect to see a relatively featureless spectrum.

The visual albedos (reflectances at 0.55 μm) of these samples vary from 0.41 to 0.53. Mercury's average visual albedo is ~0.14 (Veverka *et al.*, 1988) with some areas as high as ~0.29 (Robinson and Lucey, 1997).

"MERCURIAN (PARTIAL MELT) BASALTS"

The enstatite-rich aubrites may provide some insights into the possible nature of the mercurian crust. Aubrites are thought to represent residual silicates after partial melting and melt removal of the metal, sulfide, and pyroxene-plagioclase components. In aubrites, clasts of this basaltic material are extremely rare, although Fogel (1994, 1997) has documented a few basaltic vitrophyres. In the case of the aubrites, the lack of basaltic material may reflect removal of the basalts by eruption at velocities exceeding the escape velocity of their small, asteroidal parent body or bodies (Wilson and Keil, 1991). Wilson and Keil (1991) pointed out that such a mechanism would not operate on a body as large as Mercury and, thus, we should expect these partial melts to be present on the surface. Here we speculate on the nature of these basaltic rocks.

To determine what the mineralogy of Mercury's crust might be, we calculated (Table 1) normative (CIPW Norm) mineralogies of melts produced during experiments on powdered samples of the EH4 chondrite Indarch. These experiments were an initial attempt to understand the differentiation of highly reduced chondritic rocks and understand the link between enstatite chondrites and aubrites (McCoy *et al.*, 1999; Benedix *et al.*, 2001). Powdered samples of Indarch were heated from 1000 to 1500 °C with intermediate temperature steps at 1100, 1200, 1300, 1400, 1425, and 1450 °C (McCoy *et al.*, 1999). The samples were placed in evacuated, sealed silica tubes, which were heated in gas-mixing furnaces with $CO-CO_2$ gas maintained near the iron-wüstite buffer to increase the stability of the silica tubes. Partial melting of the silicates begins between 1000 and 1100 °C and is complete by 1500 °C. We calculated normative mineralogies (excluding sulfides) for the silicate melts in the 1400 and 1425°C experiments, which represent 20% and 29% partial melting, respectively. Sulfides are not included in the calculations since it is unclear what the

TABLE 1. Normative mineralogies (vol%) calculated from bulk compositions of silicate glass formed in melt experiments on EH4 chondrite Indarch at two temperatures (1400 and 1425 °C).*

	Indarch melt (powder) (1400 °C)	Indarch melt (chip) (1425 °C)	Indarch melt (powder) (1425 °C)
Hypersthene†	43.56	47.47	41.22
Plagioclase	38.31	33.15	37.74
Diopside	14.92	14.95	16.94
Quartz	2.91	3.45	3.69
Ilmenite	0.3	0.55	0.42
Orthoclase	0	0.41	0
Apatite	0	0.02	0

*Sulfides are not included in the calculations since it is unclear what the sulfur would be bonded with (most likely Ca and Mg). The Indarch melt powders contain ~4 wt% sulfur so the melts would be assumed to contain ~6 vol% sulfides.

†The hypersthene is >99% enstatite.

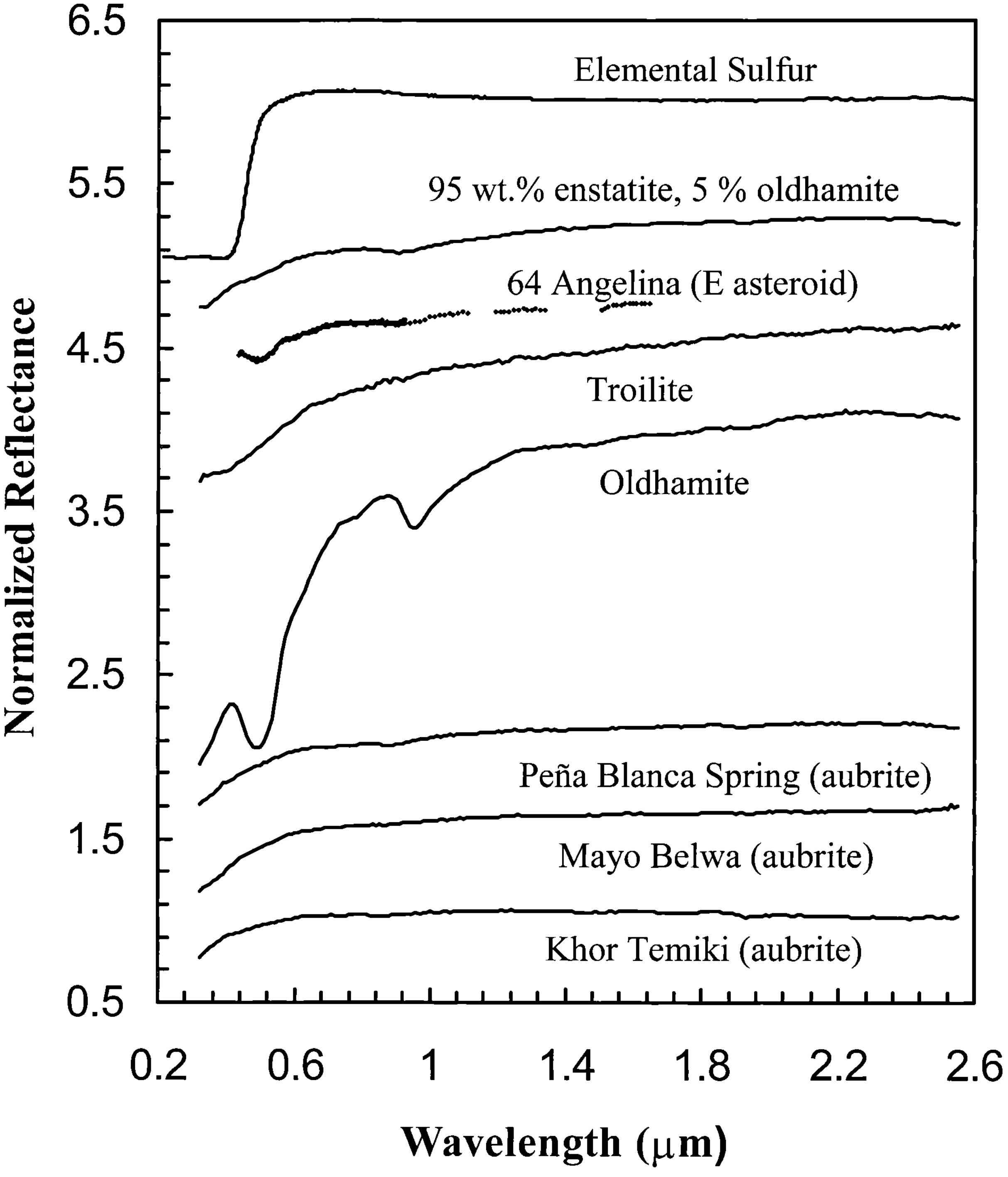

FIG. 3. Normalized reflectance spectra of Khor Temiki (aubrite), Mayo Belwa (aubrite), Peña Blanca Spring (aubrite), oldhamite (extracted from the Norton County aubrite), troilite (extracted from the LL6 chondrite Paragould), 64 Angelina (E asteroid), mixture of 95 wt% enstatite (from Peña Blanca Spring) and 5% oldhamite (from Norton County), and elemental sulfur. All samples measured for this study were sieved to particle sizes <125 μm, except for the Norton County oldhamite and the elemental sulfur, which have unknown particle sizes. The absorption feature shortwards of ~0.6 μm that is found in the oldhamite spectrum matches the position of the feature in the Angelina spectrum. The plotted asteroid spectrum for 64 Angelina is a combination of SMASS II (second phase of the small main-belt asteroid spectral survey) (0.44 to 0.92 μm) (Bus, 1999) and SMASSIR (SMASS in the near-infrared) (~0.90 to ~1.65 μm) (Burbine, 2000) data. The sulfur spectrum is from Clark *et al.* (1993). All spectra are normalized to unity at ~0.55 μm. All spectra offset in reflectance from each other by 0.5, except for the oldhamite and sulfur spectra, which are offset by 1.0 from the spectra underneath them.

sulfur would be bonded with (most likely Ca and Mg). The Indarch melt powders contain ~4 wt% sulfur so the melts would be assumed to contain ~6 vol% sulfides. Chips of Indarch melted at 1425 °C may contain slightly greater percentages of melt (about 30–40%) relative to powder melted at ~1425 °C.

Using the melting experiments as a guide, the mineralogies (including sulfides) for Mercury's basaltic crust would be expected to be ~34 vol% plagioclase, ~42% enstatite, ~15% diopside, and ~6% sulfides. These calculated mineralogies provide reasonable estimates for the surface of Mercury, if Mercury is analogous to the aubrite parent body. Next we discuss the spectral features expected for a lithology of this approximate mineralogy using aubrites as our guide.

Aubrites tend to contain (Watters and Prinz, 1979) minor amounts of plagioclase (<8 vol% except for Bishopville, which contains 16%) and diopside (<9%). The addition of significant amounts of diopside ($CaMgSi_2O_6$) with aubritic iron contents (usually between 0.09 and 0.12 wt%; Watters and Prinz, 1979) to an aubritic assemblage would not be expected to significantly change the spectral properties since the relative absence of iron should make the diopside featureless. Plagioclase has a feature at ~1.25 μm that is due to trace amounts of Fe^{2+}, which has been found in the spectra of lunar samples. However, this feature would be expected to be weak to absent on Mercury's surface, if Mercury has mineralogies analogous to the aubrite parent body. This feature is usually not present in plagioclase with FeO contents of <0.1 wt% (Adams and Goulland, 1978) and most aubrites contain plagioclase with <0.04 wt% FeO (Watters and Prinz, 1979). A mixture of aubritic enstatite, diopside, and plagioclase, which we believe may be compositionally similar to Mercury's "hypothetical" basaltic crust, would be expected to have a relatively flat and featureless spectrum similar to aubrites.

SPECTRA OF SULFIDES AND SULFUR

The minerals in aubrites that do have distinctive absorption features are the sulfides. The reduced nature of aubrites (and also enstatite chondrites) results in normally lithophile elements (*e.g.*, Ca, Mg, Mn) forming a wide variety of sulfides (*e.g.*, Whitby *et al.*, 2002). These sulfides include troilite (FeS), oldhamite (CaS), ferromagnesian alabandite ((Mn,Fe,Mg)S), and daubréelite ($FeCr_2S_4$). Troilite is the most abundant sulfide in aubrites, but is usually found in abundances of 1 vol% or less, although the Shallowater aubrite, which is anomalous in many respects from other aubrites, contains 7.1 vol% troilite (Watters and Prinz, 1979). In lunar ferroan anorthosites, sulfides are only found in trace amounts (Papike *et al.*, 1998).

Sulfides tend to be characterized by a very sharp absorption feature in the visible wavelength region band (*e.g.*, Vaughan and Craig, 1978; Fritsch and Rossman, 1988; Clark, 1999). This feature is due to transitions between a high-energy conduction band, where electrons can move freely throughout the lattice and a low-energy valence band, where electrons are attached to individual atoms. The difference between the energy levels is called the band gap and corresponds to the energy of visible photons in sulfides. Different sulfides have absorption edges at different wavelengths.

However, many sulfide minerals, including troilite, normally exhibit varying degrees of short- and long-range structural order between samples (Vaughan and Craig, 1978). These structural variations can manifest themselves through changes in the wavelength position and slope of the absorption edge, and possibly the presence of additional absorption bands (Cloutis and Gaffey, 1994). Samples of a synthetic troilite (65.5 wt% Fe) (Cloutis and Gaffey, 1993) have been found to have a feature centered at ~0.5 μm. However, meteoritic troilite (*e.g.*, Canyon Diablo (IAB iron) troilite, which has an iron content of 61.5 wt% Fe) does not have a well-defined feature (Britt *et al.*, 1992; Cloutis and Gaffey, 1994). The lack of a well-defined feature could be due to the meteoritic troilite containing a variety of Fe/S ratios at very small scales, leading to a variety of absorption energies, which average out into a gradual reflectance rise rather than a sharp well-defined absorption edge (Vaughan and Craig, 1978).

We have measured (Fig. 3) the spectra of Norton County oldhamite (CaS) and Paragould troilite (FeS). Norton County oldhamite has a deep absorption band centered at ~0.49 μm plus a weaker feature centered at ~0.95 μm. The band depth of this feature is ~40%. In the visible, the oldhamite spectrum (normalized to unity at 0.55 μm) is extremely red and reaches a value of ~2 at ~0.9 μm. This sample has a visual albedo of 0.17. Troilite extracted from Paragould has an absorption feature shortwards of ~0.6 μm that is much weaker in strength than the oldhamite feature. This troilite sample has a visual albedo of 0.05. As with previous meteoritic troilite spectra, the troilite from Paragould does not have a well-defined absorption feature.

Even though the abundances of these sulfides are small in aubrites, an absorption feature centered at ~0.5 μm and similar to that found in sulfides has been found in the spectra of a number of E-class asteroids (such as 64 Angelina in Fig. 3). E-class asteroids have relatively featureless reflectance spectra and high visual albedos (>30%) and these spectral characteristics have been interpreted (*e.g.*, Zellner *et al.*, 1977) as indicating surfaces dominated by an essentially iron-free silicate such as the enstatite in aubrites. This feature has been identified in high-resolution charge-coupled device (CCD) spectra of a number of E-class asteroids (*e.g.*, Bus, 1999; Fornasier and Lazzarin, 2001). One suggestion for the origin of this feature is a sulfide (*e.g.*, Burbine *et al.*, 1998). Oldhamite's absorption feature matches the position of the feature in the spectra of E-class asteroids.

A physical mixture of enstatite and oldhamite was made in an attempt to duplicate the strength of this absorption feature for a body with an aubritic surface composition. However, a mixture (particle sizes <125 μm) of 95 wt% enstatite from Peña Blanca Spring and 5% oldhamite only produced a ~0.5 μm feature (Fig. 3) with a strength of ~1%. The ~0.5 μm feature

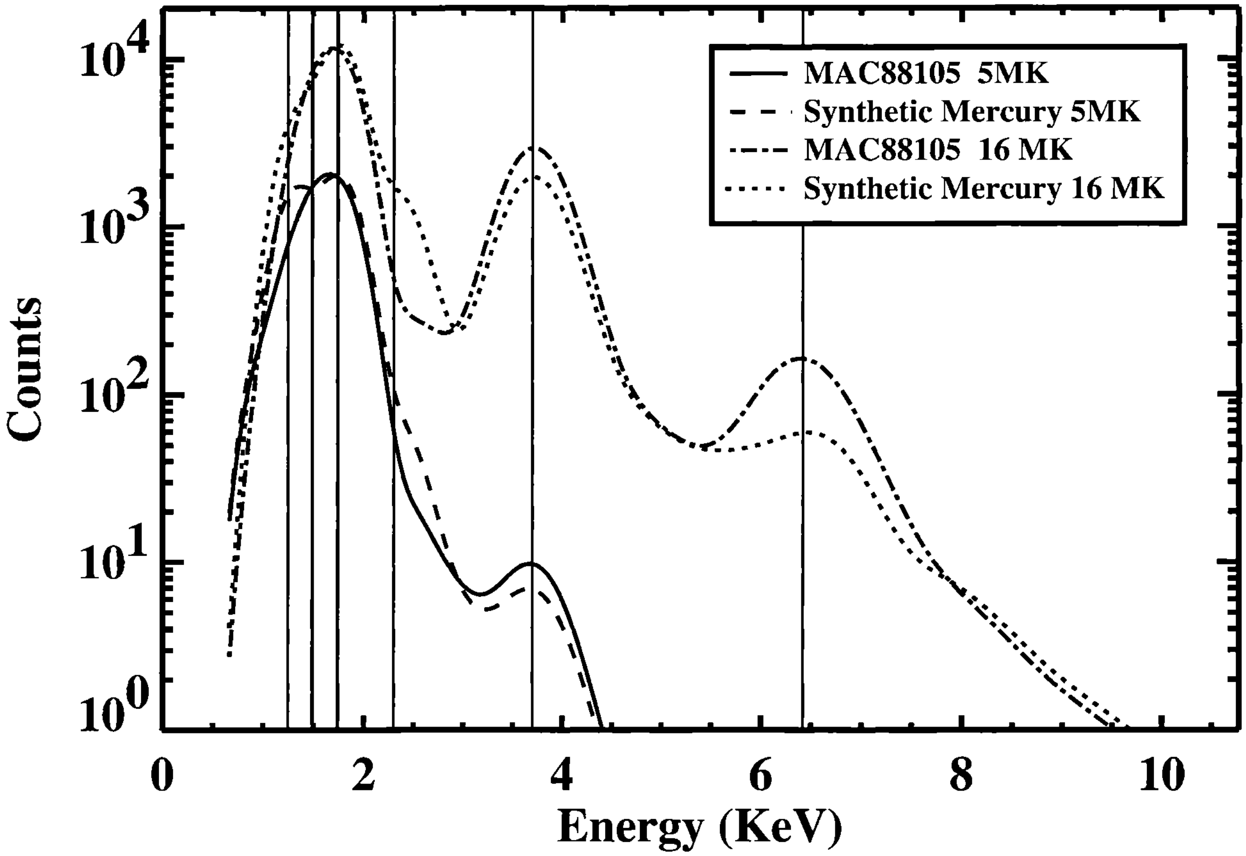

FIG. 4. Theoretical x-ray spectra (fluorescence and scatter) for MAC 88105 (lunar anorthositic breccia) and synthetic Mercury (Indarch melt powder at 1425 °C) compositions for temperatures of 5×10^6 K (lower curves) and 16×10^6 K(upper curves). Figure plots counts (logarithmic scale) *vs.* energy (KeV). Vertical lines indicate positions of Kα lines of Mg (1.254 keV), Al (1.487 keV), Si (1.740 keV), S (2.308 keV), Ca (3.691 keV), and Fe (6.403 keV). The 5×10^6 K temperature represents "quiet" Sun and the 16×10^6 K temperature represents a typical solar flare. The counts in the spectra correspond roughly to a 2000 s integration for "quiet" Sun and a 200 s integration for the flare.

appears consistent with a sulfide; however, the required abundances needed to produce this feature are much higher than those found in aubrites. Further work needs to be done to understand the abundances needed to produce this feature in the regolith of a planetary body.

Sulfur, volatilized from sulfides in Mercury's crust, has been proposed (*e.g.*, Sprague *et al.*, 1995) as a possible alternative to water ice as the cause of Mercury's bright radar spots (Butler *et al.*, 1993) at its poles. Elemental sulfur (*e.g.*, Clark *et al.*, 1993) has a strong absorption edge shortwards of ~0.6 μm (Fig. 3). The visual albedo of this sulfur spectrum is ~0.8. This absorption feature would make sulfur deposits on Mercury very spectrally distinctive.

In terms of the mismatch between the absolute albedo of aubrites (>30%) and the Mercury surface (as low as ~14%), we have investigated the possibility of whether small amounts of troilite can reduce the reflectance of aubritic silicate spectra sufficiently to match these low albedos. Intimate mixtures of 10 wt% synthetic troilite with the opaque-free fractions of an aubrite (Norton County) were made.

There was a reduction in albedo (at 0.55 μm) from 55 to 39% in the case of 100% 45–90 μm size aubrite *vs.* 90% 45–90 μm grain size aubrite plus 10% (<45 μm) troilite. There was a reduction in albedo of 52 to 42% in the case of 100% (<45 μm) aubrite *vs.* 90% (<45 μm) aubrite plus 10% (<45 μm) troilite. In addition, heating of troilite can also lead to reductions in absolute reflectance. Meteoritic troilite heated at 200 °C in air for 1 h shows a reduction in reflectance at 0.55 μm from 5.5 to 2.3%, while synthetic troilite exhibits a reduction from 6.3 to 2.9%. Simple mixtures of aubritic silicates and opaques can not reduce albedos sufficiently to match the low albedos (~14%) seen in some mercurian spectra.

X-RAY SPECTRA

To see if remotely sensed x-ray spectra can distinguish between a low-FeO anorthositic composition and an enstatite basalt composition, synthetic x-ray spectra (Fig. 4) for these two postulated compositions were generated using the models of Nittler *et al.* (2001) for homogeneous compositions. The excitation source for x-ray emission from planetary surfaces is the Sun, where x-rays are produced in high-temperature plasma in the corona. As solar activity increases, the x-ray spectra are said to "harden" where there is an increased output at higher energies, reduced steepness in the spectral slope, and increased overall x-ray flux (Trombka *et al.*, 2000). During solar flares, the spectral hardening allows higher energy lines of calcium and iron to be excited. The figure plots synthetic x-ray spectra (including both fluorescent x-rays and coherently scattered solar photons) predicted for an unfiltered gas proportional counter, as will be part of the x-ray detector system on *MESSENGER*. The lower curves correspond to incident spectra for a "quiet" Sun (5×10^6 K) and the upper curves indicate a solar flare (16×10^6 K). Counts are those expected for an integration of ~200 s for the flare spectra and ~2000 s for the "quiet" Sun spectra. The overall normalization for these spectra was determined by scaling the x-ray fluxes observed by *NEAR (Near-Earth Asteroid Rendezvous)–Shoemaker* from Eros to account both for detector design differences between *NEAR–Shoemaker* and *MESSENGER* and the much closer proximity of Mercury to the Sun, compared to Eros.

For the low-FeO anorthositic composition, we use the bulk chemical of MacAlpine Hills (MAC) 88105 (Table 2). MAC 88105 is a lunar anorthositic breccia (*e.g.*, Takeda *et al.*, 1991; Taylor, 1991) with an FeO concentration of 4 wt% (Jarosewich, 1990; Joliff *et al.*, 1991), similar to the FeO concentration suggested by many researchers (*e.g.*, Blewett *et al.*, 1997) for Mercury. For the enstatite basalt composition (called synthetic Mercury in Fig. 4), we use the bulk chemical composition of the silicate melt produced at 1425 °C of the Indarch bulk powder (Table 2) (McCoy *et al.*, 1999) since we believe it has the composition most similar to an enstatite basalt.

As can be seen in the figure, significant spectral differences can be seen for these two compositions. A peak at 2.308 keV (sulfur Kα line) apparent in the flare spectrum of synthetic Mercury is not found in the MAC 88105 spectrum due to the absence of sulfur in MAC 88105. For the "quiet" Sun spectra, the sulfur peak is also apparent in the synthetic Mercury spectrum, but not as strong. The spectrum of MAC 88105 has a much higher peak at 6.403 keV (iron Kα line) than synthetic Mercury for the solar flare due to the higher iron concentration in MAC 88105. Even for the MAC 88105 composition, the iron content is an order of magnitude lower than that inferred for Eros by *NEAR–Shoemaker* (Nittler *et al.*, 2001). However, for the same level of solar activity, the MESSENGER x-ray detector is expected to have a ~50-fold increase in sensitivity over *NEAR–Shoemaker* (Richard Starr, pers. comm.), so detection limits should not be a problem.

The magnesium, aluminum, and silicon lines all overlap (Fig. 4), but will be discriminated on *MESSENGER* by a filter system similar to that on *NEAR–Shoemaker* (Trombka *et al.*, 2000). Figure 5 plots Mg/Si and Al/Si weight ratios for a number of differentiated meteorites and enstatite chondrites. (Ratios are usually determined more accurately than elemental abundances by x-ray remote-sensing missions since ratioing eliminates geometrical effects.) MAC 88105 can be seen to plot far away from the other meteorites due to its higher Al/Si content. Aubrites, which may be compositionally similar to Mercury's mantle, plot away from most of the meteorite groups due to their high Mg/Si and low Al/Si.

TABLE 2. Average bulk compositions (wt%) of MacAlpine Hills 88105 (Jarosewich, 1990) and synthetic Mercury (Indarch melt at 1425 °C) (McCoy *et al.*, 1999).

	MAC 88105	Synthetic Mercury
SiO_2	44.58	52.7
Na_2O	0.33	b.d.
FeO	4.31	0.25
CaO	16.86	11.7
TiO_2	0.25	0.21
MgO	3.89	19.1
K_2O	0.03	b.d.
Al_2O_3	29.32	13.5
Cr_2O_3	<0.1	b.d.
MnO	0.07	0.12
H_2O^+	<0.1	–
H_2O^-	0.32	–
Fe(metal)	n.d.	–
Ni	0.03	–
Co	0.00	–
FeS	0.00	–
S	–	4.36
C	0.03	–
Total	100.03	101.95

Abbreviations: b.d. = below detection limit; n.d. = not detected. H_2O^+ is chemically bound water and H_2O^- is adsorbed water.

We have also plotted the Indarch melt powder composition (1425 °C) (Al/Si = 0.29, Mg/Si = 0.47) and it can be seen to have a significantly lower Al/Si (by a factor of ~2.5) ratio and higher Mg/Si (by a factor of ~5) ratio than MAC 88105. The Indarch melt powder (1425 °C) has an Al/Si ratio similar to that found in most eucrites, but is enriched in Mg relative to most eucrites by a factor of ~2.

"SPACE WEATHERING"

Mercurian spectra are extremely red (reflectances tending to increase with increasing wavelength) (Fig. 1). For the lunar regolith and S-asteroids, this reddening is believed (*e.g.*, Hapke *et al.*, 1975a; Pieters *et al.*, 2000; Sasaki *et al.*, 2001; Hapke, 2001a) to be due to surface alteration processes (*e.g.*, micrometeorite impacts, solar wind sputtering) that produce vapor-deposited coatings of nanophase iron.

One argument against Mercury having a very-reduced surface composition with virtually no FeO is that there would not be enough iron present in the regolith to produce appreciable amounts of nanophase iron as the surface is being "space weathered". Hapke *et al.* (1975b) and Hapke (1977, 2001a,b) argue that the surface of Mercury must contain a few weight percent of FeO to produce enough nanophase iron to

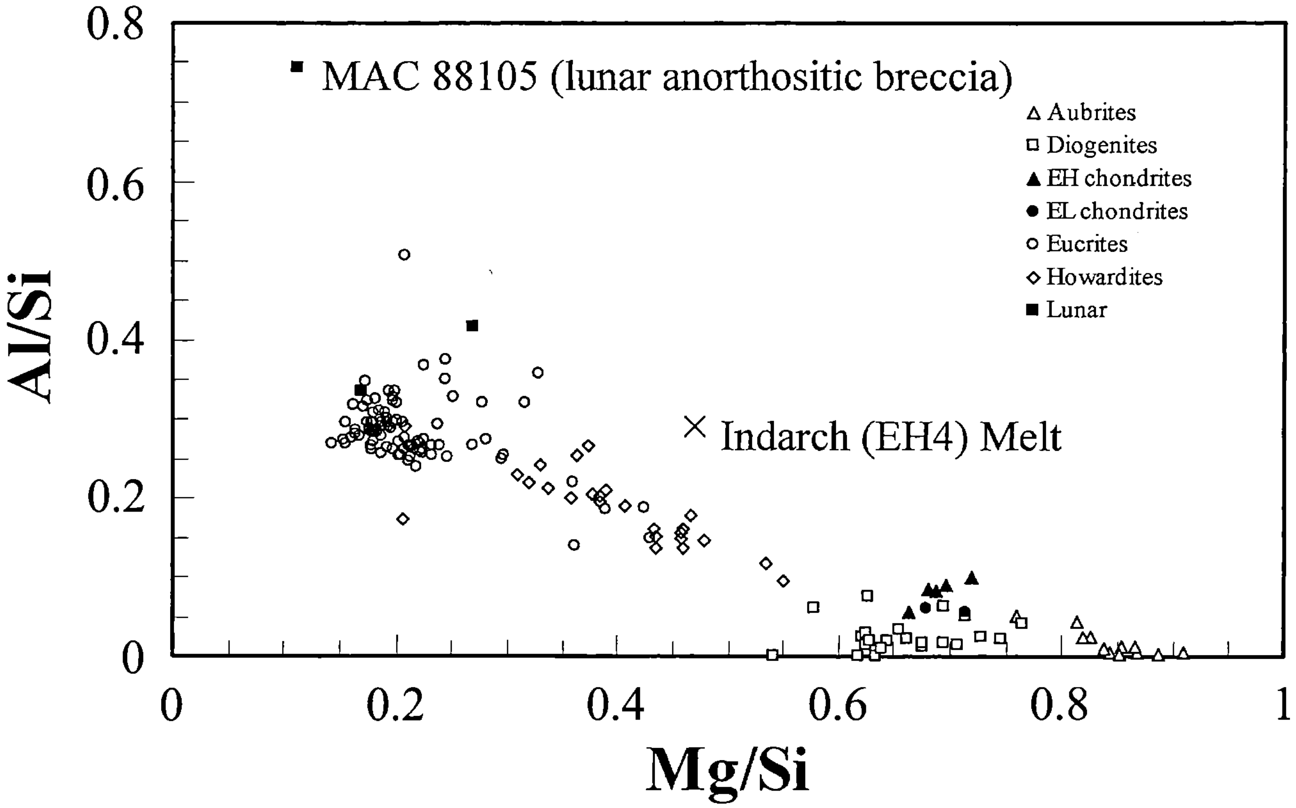

FIG. 5. Mg/Si *vs.* Al/Si weight ratios for whole-rock samples of aubrites, EH chondrites, EL chondrites, eucrites, howardites, and lunar meteorites from the Nittler *et al.* (2000) database. The Indarch (EH4) melt (1425 °C) powder composition (cross) is also plotted and can be seen to plot significantly away from MAC 88105 (lunar anorthositic breccia).

redden its spectrum. These arguments for FeO concentration of a few weight percent on Mercury's surface may be supported by the relatively flat spectra of E-class asteroids (such as 64 Angelina) in the visible and near-infrared. If E-class asteroids are the parent bodies of the aubrites, their regoliths would contain a few tenths of a percent concentrations of FeO, which would not be high enough to produce significant amounts of nanophase iron during "space weathering" to redden their spectra.

OTHER POSSIBLE BUILDING BLOCKS OF MERCURY

If Mercury's surface contains a few weight percent FeO, Mercury may have formed out of material similar to bencubbinites, as suggested by Taylor and Scott (2001). Bencubbinites contain ~60 vol% metal and silicates with ~1.5 to ~5 wt% FeO (Weisberg *et al.*, 2001). The formation of Mercury out of Bencubbin-like material is consistent with a surface containing a few weight percent FeO and Mercury's high density.

CONCLUSIONS

Spectral studies in the visible and near-infrared and the x-ray wavelength regions by the MESSENGER and BepiColombo missions should give considerable insight on Mercury's surface composition. If Mercury has a surface composition similar to an enstatite basalt, we would expect the reflectance spectrum to be relatively featureless, except for a the possible presence of a feature shortwards of ~0.6 μm due to sulfides and/or sulfur. X-ray measurements should easily distinguish between a ferroan anorthosite and an enstatite basalt composition for Mercury. The most important elements for discriminating between these two compositions are Mg, Al, S, and Fe. The biggest argument against Mercury having an enstatite basalt composition may be its extreme spectral redness. It is generally believed that to significantly redden the surface of an object (such as Mercury) by surface alteration processes, the material must contain a few weight percent FeO, exceeding the FeO abundances present in aubrites but similar to that found in bencubbinites.

Acknowledgments–This work was supported by a Smithsonian Institution Fellowship to T. H. B., NASA grant NAG5-4490 to T. J. M., and a NSERC research grant and Canadian Space Agency research contract to E. A. C. Brown University's Keck/NASA Reflectance Experiment Laboratory (RELAB) is a multi-user facility supported by NASA grant NAG5-3871. The authors would like to thank Takahiro Hiroi for running the spectra of the aubrites and sulfides at RELAB and Jeff Taylor for his encouragement. The authors would like to thank Bruce Hapke and Faith Vilas for their reviews and associate editor Mike Gaffey for his helpful comments.

Editorial handling: M. J. Gaffey

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