OPAQUES IN MERCURY'S CRUST: ADDITIONAL EVIDENCE FOR A LOW-FEO MAGMA OCEAN.

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Introduction: Analysis of Mariner 10 and MESSENGER datasets reveal the importance of opaque components on Mercury's surface. A global darkening agent, suggested to be ilmenite or other Fe-,Ti-bearing opaque mineral, has been invoked to explain the lower albedo of Mercury relative to the lunar highlands. Separately, a low-reflectance material (LRM) has been recognized as one of three dominant color terrains. We present laboratory reflectance spectra of ilmenite size separates and other candidate Fe-Ti-bearing oxide minerals. These oxides cannot sufficiently darken Mercury without violating neutron spectrometer constraints on surface iron content. The spectra of all samples exhibit negative spectral slopes shortward of 500nm, consistent with the LRM. We review crystallization models of FeO-poor magma oceans and show that lack of a plagioclase flotation crust could lead to a thin quench crust with near surface layers of incompatible- and Ti-rich late stage cumulates, consistent with Mercury's albedo and LRM.

Mercury's surface composition is poorly constrained. Energy dependent neutron measurements by the MESSENGER Neutron Spectrometer (NS) and Earth-based microwave emission observations have Fe ≤6wt.% on Mercury's surface [1,2]. Earth-based telescopic and spacecraft spectra of Mercury lack any unambiguous features near 1µm that would indicate the presence of ferrous iron bearing silicates, limiting silicate FeO content to ≤2-3 wt.% [3-5].

Mercury's surface probably contains one or more opaque components, inferred from two lines of evidence. [5-8]. A global darkening agent has been suggested to explain Mercury's low overall albedo relative to the lunar highlands. Immature Mercury surface material is 30% darker than immature lunar highlands at 490nm [8]. Denevi and Robinson [8] suggest a mercurian crust with composition similar to the lunar highlands, but containing a global darkening agent, possibly ilmenite. The other expression of an opaque component is within a low-albedo, relatively blue terrain, termed "low-reflectance material" (LRM) [5]. MESSENGER multispectral images suggest a high-opaque material associated with some craters and ejecta, indicative of a high-opaque layer underlying a moderate-opaque layer [5]. LRM spectra have negative slopes shortward of minima at 400nm (MASCS) or 600nm (MDIS) in ratioed spectra [4, 5].

The identity of the proposed opaque component may provide constraints on the FeO content and surface conditions of Mercury. To aid in the identification of the opaque components on Mercury's surface, we present new spectral reflectance data for plausible candidate opaque minerals. While ilmenite is suggested by analogy with the Moon, many other opaque minerals occur in lunar rocks [9]. We also present spectra of ilmenite size fractions to determine the effect of particle size on its albedo and spectral properties.

Results: The reflectance spectra of powdered, synthetic Fe-Ti-rich members of major oxide solid solution series present on the Moon (Table 1, [9]), all show a negative slope shortward of 500nm (Fig. 1). In ilmenite this has been attributed to the long-wavelength shoulder of a reflectance peak at 330nm due to Fe-Ti charge transfer [10]. The negative slope shortward of 500nm is characteristic, perhaps diagnostic of Fe-,Ti-bearing oxides.

Mineral	TiO_2	FeO	Other
Armalcolite $(Mg,Fe)Ti_2O_5$	74.5	14.0	MgO 7.8 Al_2O_3 1.8 Cr_2O_3 2.0
Armalcolite-Anosovite $0.85(Mg,Fe)Ti_2O_5 0.15Ti_3O_5$	74.4	14.6	MgO 7.6 Ti_2O_5 3.4
Ferropseudobrookite $FeTi_2O_5$	68.8	31.2	
Ilmenite $FeTiO_3$	52.6	45.4	
Ulvospinel $Mg_{1.2}Fe_{0.8}TiO_4$	43.0	30.9	MgO 26.0
Ulvospinel $Mg_{0.4}Fe_{1.6}TiO_4$	37.9	54.5	MgO 7.6

Table 1 – Composition of oxides (wt%), verified by X-ray powder diffraction and electron microprobe analysis.

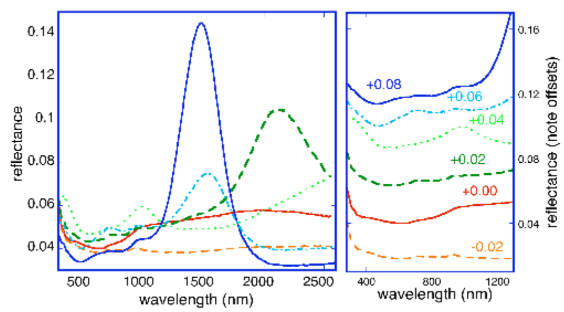

Figure 1 – Spectra of six synthetic opaque oxides (see Table 1 for legend). Inset shows spectra in the MASCS wavelength range and offset for clarity. Minerals are spectrally similar in the UVVIS range (inset).

The synthetic ilmenite was sieved and particle sizes verified via scanning electron microscope images. Ilmenite darkens (~23-29%) with decreasing grain size from 300-700nm (Fig. 2). The two finest size fractions show a dramatic increase in reflectance resulting in a distinct maximum at 1µm.

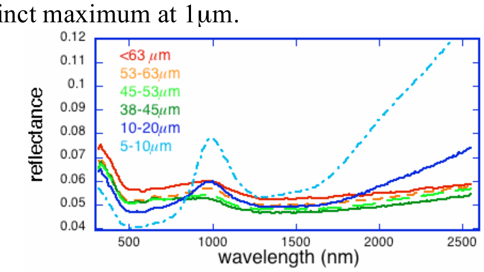

Figure 2 - Spectra of six size fractions of a single synthetic ilmenite sample.

We explore the ability of ilmenite to darken Mercury's surface by modeling mixtures (using the equations of Hapke [12]) of ilmenite (10-20μm) with the 490nm immature lunar highlands reflectance values published by [8]. We use the 10-20μm ilmenite sample since studies of lunar soils show that this size fraction best represents the spectra of the bulk soil [11]. To darken immature lunar highlands (0.2-0.26 reflectance) to match Mercury (30% darker at 490nm) requires 27-38wt.% ilmenite. A mercurian crust 10-20% darker than the Moon's, as estimated by [5], requires 8-20wt.% ilmenite.

High possible abundances of ilmenite suggest the maximum in ilmenite's spectrum near 1μm may be important and may affect silicate FeO abundance estimates. The maximum at 1μm in ilmenite has been noted previously [10], but was weaker, probably due to the larger grain size of that sample (<150μm). We explore the ability of ilmenite to mask the ferrous iron 1μm absorption by modeling mixtures [after 12] of ilmenite (10-20μm) with a laboratory spectrum of a Mercury analog, lunar highland soil (61141, 5.14 wt.% FeO). The 1μm feature is completely masked for ilmenite weight fractions 16-40 wt.% (Fig. 3).

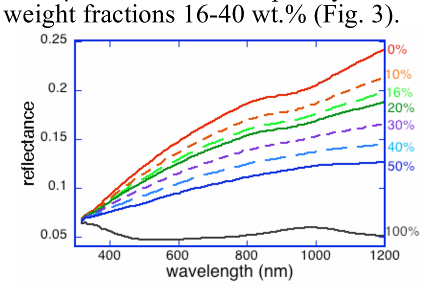

Figure 3 - Modeled mixture spectra of lunar soil 61141 with ilmenite (both 10-20μm). The 1μm ferrous iron absorption feature in the lunar soil is masked by 16-40 wt.% ilmenite.

Discussion: The measurements and model results above constrain the nature of the global darkening agent and LRM, and provide insights into the evolution of Mercury's magma ocean. We can exclude the oxides studied here as the global darkening agent because the oxide abundances required to sufficiently darken lunar highlands material are inconsistent with the limits on Fe and Ti abundance from neutron and microwave observations. Fe- Ti-rich opaque oxides are too iron-rich, particularly since coexisting silicates would also be iron rich. This argues for the presence of a low iron opaque. No spectra of low-Fe members are available but it is plausible that these minerals are sufficiently dark while also sufficiently low in Fe to explain the Mercury observations.

In contrast, Fe-,Ti-bearing oxides measured here are consistent with a possible LRM opaque component. The observed minima at 400nm or 600nm, the shallow spectral slope and low albedo of the LRM can be explained by the presence of Fe-,Ti-bearing oxides. While the LRM is widespread, it does not cover sufficient surface area to be subject, individually, to the constraints provided by microwave and neutron observations.

The identities of opaques have implications for the chemistry of co-existing silicates. The liquid from which the Fe-bearing opaque oxides formed would necessarily be enriched in iron, implying the silicates crystallizing, in equilibrium, are similarly Fe-rich. However, absorption by ferrous iron at 1μm is not observed anywhere on Mercury. This apparent contradiction could be resolved by the presence of more magnesian oxides, the ability of fine-grained ilmenite to mask the ferrous iron absorption, or some combination of these two.

The high oxide abundances required to explain Mercury's albedo are inconsistent with a lunar-like plagioclase flotation crust but may be consistent with a low FeO magma ocean. The details of magma ocean crystallization and evolution depend critically on Mercury's composition [13,14]. The flotation of plagioclase is sensitive to the Mg number (Mg/Mg+Fe) of the residual liquid [13]; if Mercury's magma ocean contained <2-3 wt.% FeO, then plagioclase would have been denser than the residual liquid, and would not have formed a plagioclase-rich flotation crust [14]. Instead, the upper crust may consist of clinopyroxene and plagioclase mixed with late-stage oxides [14].

If Mercury had a low FeO magma ocean, its crust is not the lunar highlands, modified, but is a unique array of lithologies. The stratigraphy observed by MESSENGER is consistent with the products of a low FeO magma ocean. Mercury's crust may consist of a thin quench crust mixed (perhaps by impact gardening) with underlying incompatible-rich cumulates, including oxides. The LRM terrain may be a crustal component of high-Ti cumulates, exposed by impact craters.

Our measured spectra provide constraints on the opaque minerals in Mercury's surface and LRM. However, spectra of more magnesian members of the solid solution series studied here must also be measured before the opaque components can be identified. The existing data are compatible with a low FeO mercurian magma ocean. Quantitative tests require detailed modeling, but qualitatively, Mercury's crust should be more magnesian and less aluminous than the lunar highlands. Elemental maps expected from MESSENGER X-ray, gamma-ray and neutron spectrometers can test this hypothesis.

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