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Key Points:
- First positive ID of absorption features suggesting mineralogy in MESSENGER surface reflectance photometry
- First ID of absorption features in Mercury's hollows
- Variation in absorption features potential key to alteration (space weathering) with age

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Mineralogical indicators of Mercury's hollows composition in MESSENGER color observations

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Abstract Early during MErcury Surface Space ENvironment GEochemistry, and Ranging (MESSENGER)'s orbital mission, the Mercury Dual-Imaging System imaged the landform called hollows on the two craters Dominici and Hopper, using its Wide-Angle Camera with eight narrowband color filters ranging from 433 to 996 nm. An absorption feature centered in the MDIS 629 nm filter is evident in reflectance spectra for Dominici's south wall/rim hollows. A different absorption feature found in photometry of Dominici's center hollows extends through the MDIS 828 nm filter. Hollows in Hopper exhibit a weaker spectral absorption feature than that observed in Dominici's center. At Dominici, we postulate that fresher hollows-hosting material in the wall/rim was exposed to the space environment through a process of slumping of the overlying material. With time, local and global processes darken the hollows and change or mix the surface mineralogy, so that the spectral signature evolves. The hollows could contain low-density MgS and an opaque component, potentially derived from background material.

1. Introduction

Earth-based spectroscopy of reflected sunlight from Mercury's surface has consistently found a lack of absorption features that would identify specific minerals within the surface material [e.g., *Vilas*, 1985; *Sprague et al.*, 2002; *Warrell and Blewett*, 2004]. One of the primary scientific objectives of the MErcury Surface Space ENvironment GEochemistry, and Ranging (MESSENGER) mission was to characterize the surface mineralogical composition of Mercury in order to explore the geological history of the planet. Mercury's high uncompressed density of 5.4 g/cm^3 indicates the presence of a large metallic iron core and could imply that iron-bearing minerals are abundant in the crust. The 1 μm spectral absorption feature, indicative of Fe^{2+} oxidized iron in mafic silicates, has not, however, been unambiguously detected in Earth-based observations [*Vilas*, 1988]. Spectroscopic and color observations of the planet's surface obtained by MESSENGER's Mercury Atmospheric and Surface Composition Spectrometer (MASCS) and Mercury Dual-Imaging System (MDIS) have not revealed diagnostic mineralogical information [e.g., *Izenberg et al.*, 2014; *Murchie et al.*, 2015]. The mineralogical content of the surface has been inferred based on MESSENGER measurements of the surface's elemental chemistry [e.g., *Stockstill-Cahill et al.*, 2012; *Weider et al.*, 2015]. The elemental abundance of iron within the top tens of centimeters of regolith is placed at ~1.5 wt % as determined by MESSENGER X-ray spectroscopy [*Weider et al.*, 2015].

We report here the first identifications of spectral absorption features in MESSENGER data suggesting a positive mineralogical identification, acquired by the MDIS Wide-Angle Camera (WAC) [*Hawkins et al.*, 2007, 2009]. Early during MESSENGER's orbital operations at Mercury, MDIS imaged the impact craters Dominici (center latitude = 1.38°N, center longitude = 323.5°E, ~20 km diameter) and Hopper (12.4°S, 304.1°E, ~35 km) using eight of the WAC's narrowband color filters having central wavelengths ranging from 433 nm to 996 nm (one color image set comprises one suite of eight sequential images). Examination of high spatial-resolution MDIS Narrow Angle Camera (NAC) images of these two craters (Figure 1) provides geologic context. The center of Dominici crater and the bright south crater wall/rim contain the landform known as hollows. Mercury's hollows are shallow, irregular, rimless, flat-floored depressions with bright interiors and haloes, often found on crater walls, rims, floors, and central peaks [*Blewett et al.*, 2011, 2013]. Hollows are fresh in appearance, increasing less in reflectance with increasing wavelength compared to Mercury's general spectral reflectance. Widely distributed in longitude [*Blewett et al.*, 2011, 2013; *Thomas et al.*, 2014], hollows

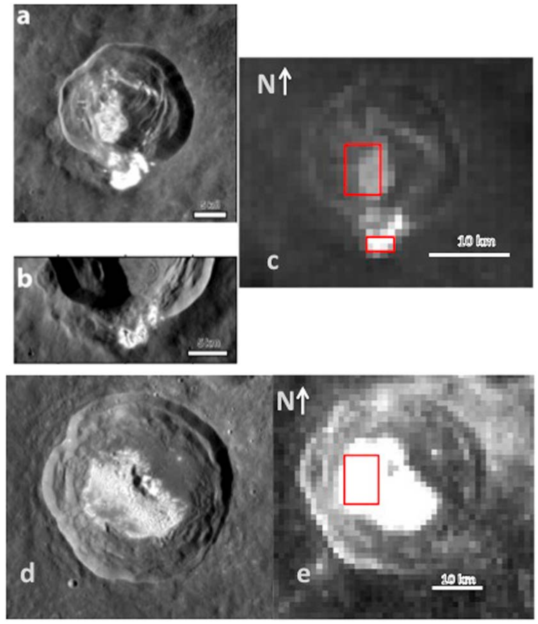

Figure 1. (a) NAC (high-resolution) image (CN0253965560M) of Dominici crater (1.4°N, 323.5°E; ~20 km diameter), a very young crater showing hollows in the center of the crater. (b) Hollows are also apparent in the south crater wall/rim of the NAC image (CN0253965560M). (c) WAC (low-resolution color, 935 m/pixel) image (CW0210848973D) of Dominici crater with the red rectangles marking the areas sampled photometrically. Illumination when the image was acquired diminishes some of the center hollows; this is corrected during the photometric processing. (d) NAC image (CN0223616383M) of Hopper crater (12.4°S, 304.1°E, ~35 km diameter) showing hollows in the center. (e) WAC image (CW0211022288D, 1027 m/pixel) of Hopper crater with the red rectangle marking the area sampled photometrically.

have a slight preference to be located on equator facing slopes. Hollows are concentrated in the widespread surface terrane called Low Reflectance Material (LRM), suggesting a connection with the phase responsible for darkening the LRM [*Blewett et al.*, 2011; *Vaughan et al.*, 2012]. Both the morphological similarity of hollows to pits in the Martian polar cap formed by sublimation of CO_2 ice and MESSENGER's discovery that Mercury is rich in volatile elements such as sulfur, potassium, and sodium [*Nittler et al.*, 2011; *Peplowski et al.*, 2011] suggest that hollows form by loss of a volatile-bearing phase that is unstable when exposed to the planet's surface conditions [*Blewett et al.*, 2011, 2013; *Helbert et al.*, 2013]. The volatiles could exist as buried concentrated volcanic outgassing [*Blewett et al.*, 2013] or distributed throughout the host material and then concentrated by impact melting and differentiation [*Vaughan et al.*, 2012] or incorporated as slag deposits [*Helbert et al.*, 2013]. The hollows located on the south crater wall and rim of Dominici have brighter haloes and better-defined edges than the hollows in the center of Dominici, suggesting that these sets of hollows have undergone different histories of environmental processing.

2. Selection and Processing of MESSENGER MDIS Images to Derive Absolute Reflectance

Near 24 May 2011, as the MESSENGER spacecraft approached one of Mercury's "hot poles" during its first months in orbit around the planet, the MDIS WAC underwent a change in responsivity attributed to the deposition and subsequent removal of a contaminant on its optical surfaces [*Keller et al.*, 2013; *Domingue et al.*, 2015]. For this study, we only used images obtained prior to the contamination event (24 May 2011). We selected WAC images with pixels having surface resolution near or less than 1000 m to ensure sufficient spatial resolution in the color images. For each crater, we required more than one photometrically corrected color image set to be available for comparison and confirmation purposes. We examined three regions within six color image sets containing Dominici and two regions within three color image sets containing Hopper, comparing the spectral properties of hollows material with the surrounding LRM.

MDIS NAC images of each crater and environs were used to identify the latitudes and longitudes bounding bright regions of hollows in each crater center and on the Dominici south wall/rim and regions of LRM. The pixels included in each MDIS WAC image were defined as closely as possible using the latitudes and longitudes identified in the NAC images. Figure 1 compares an MDIS NAC image with one corresponding MDIS WAC 559 nm (D) filter image of the hollows for each of the two craters, demonstrating visually the variation in spatial resolution in images from both cameras and the surface spectral variability in each scene.

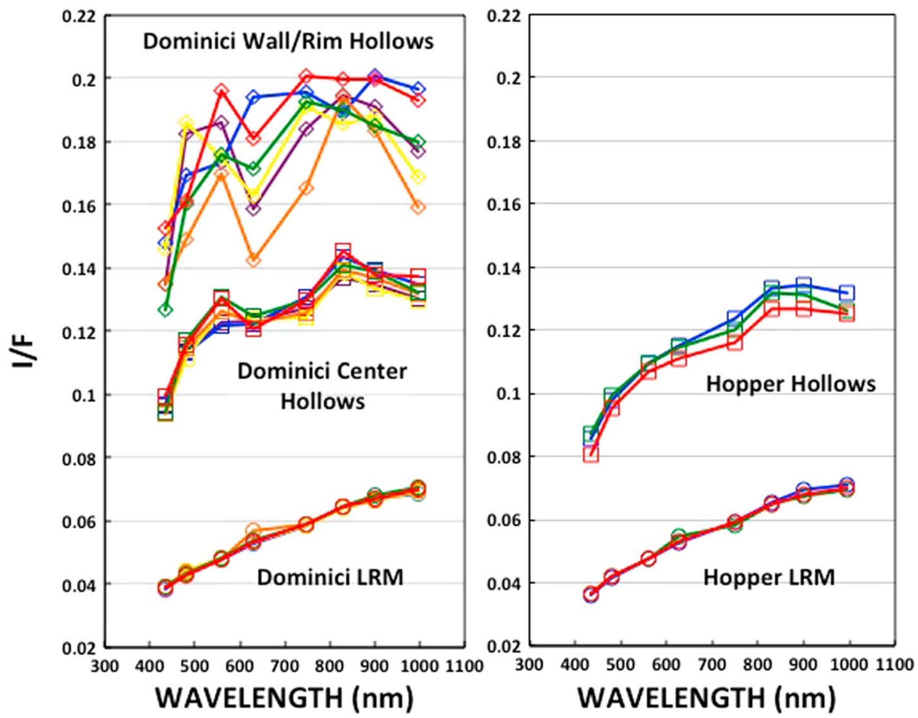

Figure 2. (left) *I/F* for the Dominici crater center hollows, south wall/rim hollows, and LRM. (right) *I/F* for the Hopper crater hollows and LRM.

The MDIS WAC images were radiometrically calibrated and converted to camera standards previously defined [*Hawkins et al.*, 2009], making readout smear, dark subtraction, flat field nonuniformity, and temperature corrections. The reflectance data (expressed as I/F, where I is light reflected from Mercury's surface and F is incident sunlight) have been corrected for global geometric effects following the techniques outlined in *Domingue et al.* [2015]. Figures 2 and 3 show individual and average color image sets for individual craters and LRM.

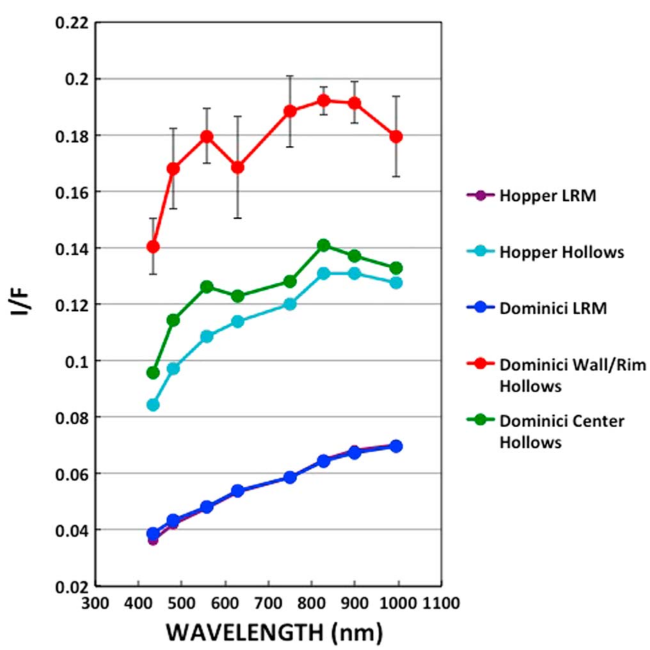

Figure 3. Average *I/F* of hollows areas and LRM areas for both craters. Errors calculated as standard deviation of the mean of the six color sets for the Dominici south wall/rim hollows are shown. Errors for all other averages are contained within the plot symbols.

We identify an absorption feature in the photometry of the hollows in the center of Dominici crater, extending from the 559 nm (D) filter to the 828 nm (L) filter. A different absorption feature is also identified in the photometry of the Dominici crater south wall/rim, strongest—if not uniquely centered—in the 629 nm (E) filter. We attribute the overall range in I/F for the south wall/rim to the small available number of pixels exposed in the lower resolution WAC images (pixel total ranging from 4 to 12 within a single filter for one image) combined with the more extreme underlying topography projected for these small areas within the individual images.

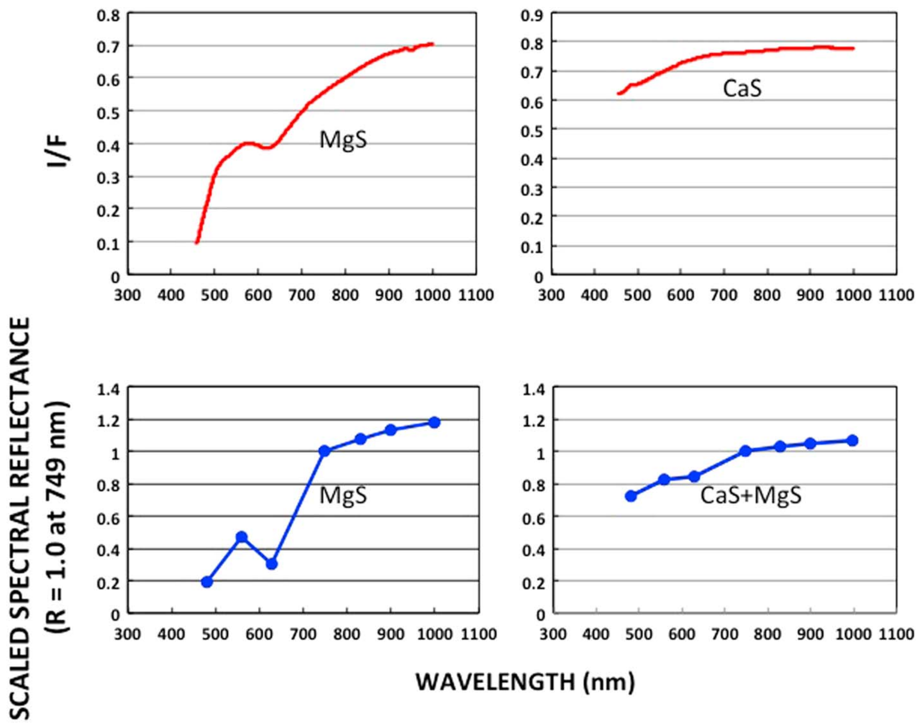

Figure 4. (top row) Laboratory *I/F* spectra of unheated MgS and CaS at phase angle of 13^{o} [*Helbert et al.*, 2013]. (bottom row, left) Laboratory spectrum of MgS convolved with the MDIS WAC filter responses. (bottom row, right) Simple combination of 20% MgS and 80% CaS, demonstrating similarity to the spectrum of the Dominici hollows (Figures 2 and 3) [*Vilas et al.*, 2014].

Three color sets of Hopper hollows show a spectral absorption feature similar in width but of lesser depth compared to that for the Dominici center hollows. These spectral features cannot be observed in MASCS spectra of the hollows due to the larger spatial footprints of these spectra including both bright hollows material and adjacent, different material. Spectra for the LRM extracted from the same WAC frames are featureless and nearly identical in reflectance and spectral slope (Figures 2 and 3).

3. Compositional Analysis of Spectra for the Hollows Materials

We next sought spectrally similar candidate minerals consistent with the elemental composition of Mercury's surface as measured by MESSENGER [e.g., *Weider et al.*, 2015]. The low abundance of Fe, the overabundance of S compared to the other terrestrial planets [*Evans et al.*, 2012], and the presence of Mg throughout the surface material suggest that minerals likely to be present on Mercury include magnesian silicates and sulfides such as magnesium sulfide (MgS) and calcium sulfide (CaS) [e.g., *Burbine et al.*, 2002; *Stockstill-Cahill et al.*, 2012; *Weider et al.*, 2015]. While magnesian silicates are spectrally featureless, these sulfides are not: laboratory reflectance spectra of MgS and CaS show absorption in the vicinity of the WAC E filter (629 nm) similar to the absorption observed in the MDIS photometry (Figure 4) [*Helbert et al.*, 2013; *Vilas et al.*, 2014].

Laboratory experiments demonstrate that MgS and CaS permanently lose spectral contrast upon a single heating to temperatures similar to those that Mercury experiences during one orbit [*Helbert et al.*, 2013]. Surface material on Mercury is churned by micrometeorite impacts. Hollows material, however, must contain MgS or CaS or both in a form that will remain spectrally detectable through many temperature cycles. Alternatively, the MgS and CaS could rejuvenate on Mercurian (~88 day) annual time scales [*Blewett et al.*, 2011, 2013]. For example, fresh material could be exposed as the loss of volatile sulfides creates void spaces and the remaining rock crumbles. Another possibility is that small grains resulting from the process of hollows formation could produce high-porosity deposits that would have high reflectance and retain spectral absorption features. Fine-grained, cohesive materials can exhibit intricate, open, porous microscale "fairy castle structures" [*Hapke and Van Horn*, 1963; *Hapke*, 2012]. The accumulation of fine-grained materials, or the redeposition of "frost-like" grains condensing from sublimated materials, could produce such fairy castle structures within the hollows. Phase ratio analysis of Eminescu crater suggests that hollows have finer particle sizes than ordinary impact-generated regolith [*Blewett et al*., 2014].

We examined laboratory spectra of fresh and thermally cycled synthetic CaS and MgS, measured at five different geometries spanning 13° to 40° phase angle [*Helbert et al*., 2013]. These higher-resolution spectra were convolved with the transmission function of each of seven MDIS WAC filters and plotted in Figure 4 to illustrate the similarity to the observed spectra of the Dominici south wall/rim hollows.

4. Mercurian Hollows Evolution: Dominici Crater Center and South Crater/Rim

The crater Dominici contains hollows that vary in reflectance and spectral properties across the visible/near-infrared spectral region. Physically, the hollows evident on the south crater wall/rim of Dominici span both the interior and exterior sides of the wall/rim. The hollows located on the south crater wall/rim of Dominici have brighter haloes and depressions that are better defined than the hollows in the center of Dominici. This difference suggests that these sets of hollows are of different ages or states of evolution. We propose that the hollows in the center of Dominici crater are material that has been exposed for a longer period of time than material on the south wall/rim and have undergone more space weathering or progressed to a later stage in hollows formation, or both. Mass wasting, in the form of the wall slumping on the south rim of Dominici, has exposed fresher hollows material, less affected by the environment than the hollows in the center of Dominici have been. Both the color and albedo differences (Figures 2 and 3) suggest that these two areas provide clues to the processing of the material in the hollows, as well as the composition. It is not known when the most recent slumping on the south wall/rim took place, so we cannot state that the material exposed there represents raw hollows material. The phenomenon of mass wasting associated with hollows is apparent within Raditlati basin, where a talus apron has accumulated downslope of bright hollows on the peak ring [*Blewett et al*., 2013].

The 629 nm absorption feature indicated in the reflectance spectrum of the Dominci wall/rim hollows strongly suggests the presence of MgS or a combination of MgS and CaS. The material present must be able to withstand multiple heating cycles and retain the absorption feature. Limited laboratory thermal cycling of these candidate minerals suggests that the extreme heating during a Mercury day would generally weaken spectral absorption features over extended time periods [e.g., *Helbert et al*., 2013]. We propose that the mechanism that forms the hollows creates porosity in the material and continues to expose unheated sulfides from the subsurface. Sublimation-like loss of volatiles in the material that hosts the hollows could involve such a process [e.g., *Blewett et al*., 2011, 2013].

The material in the center of Dominici crater has different spectral characteristics than the Dominici south wall/rim. The absorption feature found in the photometry of Dominici's center extends to the MDIS 828 nm (L) filter, showing the presence of an additional component with the sulfides observed in the photometry of the south wall/rim, or a change in these components. The repeatability of the feature in several image sets confirms its presence.

The overall I/F of the south wall/rim hollows is roughly 1.4 times higher across the MDIS WAC spectral range than the I/F of the central crater hollows (Figure 3). Both areas are darker than the I/F of the laboratory MgS and CaS samples [*Helbert et al*., 2013]. This suggests that both the wall/rim hollows and the central crater hollows contain an opaque component, potentially derived from the background LRM. The crater center surface material likely contains more of the dark component. A number of phases have been discussed as possible darkening agents in the LRM. Exploring the creation and composition of the LRM, *Murchie et al*. [2015] propose graphite, in amounts consistent with results from MESSENGER's elemental experiments for the presence of carbon, as the most likely darkening component. Additionally, the 600 nm absorption feature present in laboratory spectra of graphite and observed in spectra of the LRM [*Murchie et al*., 2015] suggests that graphite provides a possible source to extend the hollows absorption feature. *Vander Kaaden and McCubbin* [2015] report that graphite would be the only buoyant phase in an early magma ocean, and any primary flotation crust would have retained carbon in the form of graphite. *Lucey and Riner* [2011] ascribed Mercury's low reflectance to nanophase and microphase iron produced by space weathering, and *Gillis-Davis et al*. [2013] suggest that nanophase and microphase iron could have been created by impacts before and during the late heavy bombardment. Either or both graphite or nanophase and microphase iron could be the darkening agents that uniformly reduce reflectance across the MDIS spectral range. *Blewett et al*. [2013] also discuss the possibility that nanophase or microphase sulfides could be the darkening agent responsible for the low reflectance of the LRM.

Mercury is subject to harsh space weathering conditions that vitrify surface materials and rapidly produce submicroscopic or nanophase material [*Domingue et al*., 2014]. One result of this space weathering could be the creation of nanophase MgS (npMgS) coatings on the surface of the hollows. Particles returned from the near-Earth asteroid 25143 Itokawa contain npMgS weathering by products [*Noguchi et al*., 2011, 2014]. Given the elemental chemistry of Mercury's surface, *Domingue et al*. [2014] suggest that these same nanophase materials, especially npMgS, are present on Mercury.

One or more of these processes would decrease the overall brightness of the hollows material, as well as vertical and lateral impact mixing. Neither CaS nor MgS, however, appears to reproduce the extended absorption feature found in the Dominici crater center hollows photometry. We propose that we are seeing the evolution of the relatively short-term exposure of the hollows material within one crater, resulting in the darkening of the same hollows material through the addition of a darkening agent or creation of darkening coatings. This short-term exposure has changed the existing material or added an additional component responsible for the wider absorption feature.

5. Mercurian Hollows Evolution: The Range of Hollows Bright Materials Composition From Dominici to Hopper

Dominici is the younger crater, with extensive bright ejecta and rays and well-defined features. Hopper is somewhat older, having no rays but retaining sharp features.

Based on strong agreement among the LRM photometry for both crater regions, we assume that the background LRM composition is the same in these regions and that all corrected photometry is intercomparable. The spectral feature present in the hollows in Dominici's center is also present in the hollows in Hopper's center but diminished in strength. We assume that environmental exposure has caused the absorption feature to weaken with time.

The reflectance (I/F values) of the hollows decreases with increasing crater age, coinciding with the diminution of the absorption feature. If we assume that competing processes are operating in the hollows over time (e.g., space weathering, infall of additional darkening material versus exposure of fresh MgS or CaS due to enlargement of the hollows), the sulfides (and other spectrally detectable mineralogies) eventually are masked by the domination of one or more of these processes. Dominici and Hopper are adjacent to the high-Mg area of Mercury's surface [*Weider et al*., 2015]. The lower Mg abundance in the surface at other locations could contribute to the lack of the spectral absorption features we observe in photometry of other hollows. The absence of hollows at higher latitudes is likely related to solar insolation but could also indicate general compositional changes [*Blewett et al*., 2013; *Thomas et al*., 2014]. Larger-scale global changes in Mercury's reflectance properties are the subject of additional studies [e.g., *Murchie et al*., 2015; *Izenberg et al*., 2014].

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