NOTE
Sulfur at Mercury, Elemental at the Poles and Sulfides in the Regolith

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We propose that the bright radar spots seen at Mercury's north and south poles are a result of volume scattering from elemental sulfur. Further we suggest that the high average index of refraction for surface materials and notable microwave transparency of the Mercurian regolith can be explained by the presence of iron sulfides (troilite, pyrrhotite) and low-iron sulfides (daubreelite and sphalerite). Sulfides deposited throughout the regolith are a result of fumarolic and magmatic events following initial accretion of meteoroids rich in troilite and pyrrhotite to the planet. Calculations are made illustrating how solar abundances of sulfur volatilized from such a surface can provide an adequate supply over the history of the planet to be cold-trapped at high latitudes, be covered partially with dust, and be seen as bright regions in radar images. To test our hypothesis, we suggest a series of observations in the ultraviolet to search for the SI multiplet centered at 1814 Å, in the midinfrared to search for emissivity features at 7.7 and 11.8 µm, and at millimeter wavelengths to search for sulfurous molecules like H₂S and SO₂.

1. Introduction. This paper integrates a variety of ground-based observations of Mercury into coherent support for the presence of a significant inventory of sulfur in the surface materials and in the atmosphere. These are highly radar-reflective regions at the north and south poles of Mercury (Slade et al. 1992), low microwave opacity of the Mercurian regolith (Mitchell and de Pater 1994), the Na and K atmosphere (Potter and Morgan 1985, 1986), the index of refraction derived from disk-integrated photometry (Hapke 1994), low FeO absorption in near-infrared spectra (Vilas et al. 1984), and the indication in mid-infrared spectra of a plagioclase-rich regolith at Mercury (Tyler Sprague et al. 1988, Sprague et al. 1994). In particular, we suggest that elemental sulfur is cold-trapped at the poles and is the primary substance causing the bright radar backscatter signature tentatively attributed to water ice (Slade et al. 1992, Butler et al. 1993, Harmon et al. 1994). We also suggest that the cause of the high index of refraction of regolith materials is Fe-bearing sulfides such as pyrrhotite (Fe₆S₈), daubreelite (Fe₃S₄), alabandite (Mn₃S₄), sphalerite (ZnS), and oldhamite (CaS) mixed with impact-generated silicate glasses. The first four of these sulfides are common in enstatite chondrites and aubrites (Keil 1968, Watters and Prinz 1979) and have relatively high densities (4.6, 3.8, 4.1, 4.0 g cm⁻³, respectively), and for pyrrhotite, sphalerite, and oldhamite the indices of refraction are near 2 (Berry and Mason 1959), close to the value calculated from polarization measurements by Hapke (1994).

Any Mercury formation model must be able to explain the several recent observations of Mercury's surface and atmosphere mentioned above, and also the exceptionally high density of Mercury. However, the condensation/ accretion model by Lewis (1972, 1988), which invokes condensation of more refractory materials in the inner Solar System leading to preferential accumulation of metal and silicates closer to the Sun, does not result in high abundances of volatiles (only a few tenths of a percent of alkali oxides) and, as Lewis (1988) notes, the high density is also not explained by straightforward condensation and accretion models. Other models involving silicate vaporization (Cameron et al. 1988) or catastrophic fragmentation (Benz et al. 1988) may be capable of explaining Mercury's high density but generally result in a silicate mantle which is extremely poor in alkali elements and other volatiles. One may argue that the alkali elements now observed on the surface are due to deposition by later meteoritic impacts. This may be unlikely because the most likely meteoritic impactors are chondritic with Na/Fe ratios of about 0.02–0.03 (by weight), which would significantly increase the iron abundance of Mercury's regolith.

2. Evidence for a sulfur-rich regolith and possible relation to reduced meteorites. The recent work mentioned above demonstrates the incorrectness of the old notion that the mercurian and lunar surfaces are similar. As summarized by Veverka et al. (1988), the disk-integrated brightnesses of Danjon show a phase function similar to that of the Moon but with a slightly greater back-scatter peak and higher overall albedo, as high as 0.45 at some locations (compared with lunar values of 0.05 to 0.13). Mercurian 10 images show a surface generally more reflective at blue wavelengths than the Moon (Broadfoot et al. 1974, Raya and Hapke 1987). Polarization measurements show variations with longitude that can be attributed to variations in either grain size or composition and have most recently been used to derive an index of refraction of 2.07 ±
0.08 (Hapke 1994) significantly higher than that of the Moon and of silicates with indices of refraction commonly between 1.6 and 1.9.

A case has been made for a basalt-free surface for Mercury (Jeanloz et al. 1995) based upon the notable microwave transparency of Mercury's surface (Mitchell and dePater 1994) which implies a low abundance of FeO and TiO₂, the likely presence of plagioclase (Sprague et al. 1994), and the apparent absence of globally distributed FeO (Villas et al. 1984). This important conclusion has several implications. It is therefore natural to ask what rock types may cover the mercurian surface and remain consistent with the observed properties.

The observation of surface rocks with low FeO (Villas et al. 1984), together with the occurrence of plagioclase (Abb15-40, bytownite or labradorite: Sprague et al. 1994), may support Wassen and Kallemeyn's (1988) suggestion that Mercury formed by accreting enstatite chondritic matter. Some problems involving the condensation scenario of enstatite chondritic matter in the Mercury region are also discussed by Cameron et al. (1988). One major problem is that Mercury's large core size is not sufficiently explained, because differentiation of enstatite chondrites would lead to a metal-sulfide core of about 38 wt% (e.g., Lodders 1995) while Mercury's core is about 60-70 wt% and it is thus clear that an additional process must be involved to increase the core metal (sulfide) size. However, properties of enstatite chondrites are taken as building blocks for Mercury, because enstatite chondrites contain almost Fe-free pyroxene that have high alkali element contents (e.g., Keil 1968, Wassen and Kallemeyn 1988). Enstatite is colorless, sometimes even translucent. The dark color of other pyroxenes is primarily caused by the presence of FeO. Plagioclase, especially in the observed compositional range, has a characteristically high albedo. A surface covered in these two minerals would appear consistent with the Mariner 10 images and the photometric studies.

An important consequence of the enstatite chondrites to Mercury is that Mercury would accrete material which also contained a suite of highly reduced sulfides, such as oldhamite (CaS), caswell silverite (NaCaS₄), djursholmit (K₂(Si₆O₁₈)(Fe, Ni)₆), and other sulfides mentioned above. Upon core-mantle differentiation, some of these sulfides would be removed into Mercury's core, together with metal-rich, and other sulfides such as alabandite and daubreeite. However, the extraction mechanism may not be complete, as these sulfides are still observed in subsites, which are silicate rocks formed by differentiation from enstatite chondrites (for discussion, see Lodders 1995). Sulfur may be an important constituent of Mercury's core and sulfur-bearing compounds may also be present in Mercury's mantle and crust. It is also worth mentioning that the sulfides trapped in the silicates can also react with the silicates during extensive melting and further mantle–crust differentiation processes and that sulfur may dissolve in the magma which are formed. These processes have not been investigated in detail and need further studies but this dissolution of sulfur may be significant because more reduced magmas tend to dissolve higher sulfur concentrations than, e.g., magmas formed under terrestrial mantle redox conditions. The possibility of sulfur transport to the surface on Mercury may also be strengthened by the fact that this process is taking place on the Earth and is also likely to be a source of the sulfur on Io and the sulfur–bearing clouds on Venus.

An outstanding problem is to explain the presence of the magnetic field at Mercury. It is not certainly known if Mercury's substantial magnetic dipole moment is a remanent field, frozen in aeons ago, after Mercury's interior froze, or if there continues to be an active dynamo. For there to be an active dynamo generating the observed field there must be some substance other than iron in the core to decrease the liquidus temperature. Stevenson et al. (1983) pointed out that radial mixing in the solar nebula at the time of accretion would provide some S during the formation of Mercury and lower the temperature at which the inner core freezes. As the solid inner core grows, the concentration of S in the outer liquid core increases, further depressing the solidus temperature and permitting a dynamo-generated magnetic field (e.g., Schubert et al. 1988, Goettel 1998). The solidus temperature could be lowered further by plausible traces of carbon and phosphorus. We suggest that the observational evidence and inferred processes like those described above strongly favor the presence of sulfur in the core as well as on the surface.

3. Sulfur sources, sinks, and recycling on Mercury's surface. Sulfur could be injected into the atmosphere by sputtering, volatilization, or degassing. Morgan et al. (1988) calculate that a large fraction of the Na and K atmosphere can be a result of micrometeorite impact vaporization; the same would be true for sulfur, which is considerably more volatile. Certainly sulfur from volatilized micrometeoritic material will be present in Mercury's atmosphere, and we base our calculations for the migration of S to the poles (next section) on a combined meteoritic and surface source, scaling the observed Na column abundance to account for the higher solar system and meteoritic abundance of sulfur. Table I shows Solar System, average stony and stony-iron meteoritic, and atmospheric abundances for Earth and predicted for Mercury. The Earth's atmospheric S value is calculated by using the sulfur mass in the stratosphere (Hofmann and Rosen 1983) and converting to number density at 90 km. We calculate our predicted S abundance by assuming that the same source and sink processes set for Na and K. An average Na column abundance at Mercury is 1.5 × 10¹⁴ atoms cm⁻² (Potter and Morgan 1987). By averaging the Solar System and meteoritic S abundances shown in Table I and scaling the Na atmospheric value, we get an expected S column in Mercury's atmosphere of ~8 × 10¹³ atoms cm⁻². This number, however, does not reflect the large difference in ionization times between Na and S (~1 hr and 1 Earth day, respectively). It is generally thought that the major sink for both S and Na is photostabilization; half the ions are swept away in the solar wind and the other half are forced back to the surface. Thus, the column abundance calculation above should probably be multiplied by a factor of 24 giving ~2.4 × 10¹⁴ S atoms cm⁻². The number density shown in Table I has been calculated assuming both Na and S are accommodated to a surface temperature of 520 K.

If trapped sulfides do exist in grain boundaries as has been suggested (Sprague 1990), then S diffusing out of grain-boundaries might be measurable (although probably considerably less than the meteoritic/regolith volatilization source). Diffusion coefficients are usually exponentially dependent on temperature, and small differences in temperatures expected at Mercury can make a large difference in flux of Na and K from surface materials. Given an adequate source reservoir, diffusion fluxes become significant at about 400–500 K for Na. The character of the diffusion process from materials at depth critically depends upon the penetration of the diurnal or biannual thermal wave or some other heating mechanism. While current furanore activity is highly unlikely, there could have been, in an earlier period, outgassing from volcanic furanores with subsequent deposition of endogenic sulfides. We highlight the possibility of sphalerite because of its highly translucent optical properties, its high index of refraction, and high density. Butler et al. (1993) also discuss radar-bright basins at midlatitudes that are not associated with possible ice deposits (they correspond to locations of enhanced Na brightness), and we suggest here that they could also correspond to regions of high sulfur and sulfide content.

Loss of elemental sulfur from the atmosphere is by photoionization and adsorption. The ionization time for S at Mercury is ~24 hr, modulated by the changing solar flux as Mercury moves in its highly eccentric (e = 0.21) orbit. Electric fields act on ions created by photoionization of neutrals. A large fraction interacts with Mercury's substantial magnetic field and escapes into the interplanetary medium.

Those that are not swept away further the atmosphere. Some ions are expected to accelerate to high energies and to impact the surface (Potter and Morgan 1990, Sprague 1993). Impact zones are most likely the auroral zones and regions in the midnight sector where the magnetosheath intersects the surface. Here ions, if energetic enough, can be implanted up to a few hundred angstroms into the surface materials. The subsequent
### TABLE I
Comparative Sulfur and Sodium Abundances

<table>
<thead>
<tr>
<th>Solar System $^a$ abundance (per $\times 10^8$ Si)</th>
<th>Meteorite $^b$ stony, stony iron (Wt. %)</th>
<th>Earth atmosphere atoms cm$^{-3}$ at 90 km</th>
<th>Mercury atmosphere atoms cm$^{-3}$ at surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$  $5.5 \times 10^5$</td>
<td>2.0</td>
<td>$\sim 3 \times 10^4$ $^c$</td>
<td>$\sim 8 \times 10^5$ $^e$</td>
</tr>
<tr>
<td>$Na$ $5.7 \times 10^4$</td>
<td>0.6</td>
<td>$\sim 4 \times 10^3$ $^d$</td>
<td>$\sim 2 \times 10^4$</td>
</tr>
</tbody>
</table>

$^c$ See text for calculation.
$^d$ Hunten (1967).
$^e$ Prediction, this paper.
$^f$ Potter and Morgan (1985).

4. Sulfur polar deposits and transport. Mercury’s radar-bright polar caps have been tentatively explained as deposits of water ice (Slade et al. 1992, Harmon and Slade 1992, Paige et al. 1992, Butler et al. 1993, Harmon et al. 1994). Here we suggest that sulfur is another candidate that deserves consideration. The remarkably high radar reflectivity and the reversal of circular polarization both suggest that coherent backscatter is at work (Hapke 1990, 1993; Hapke and Blewett 1991). This mechanism operates “when a collimated source illuminates a weakly absorbing, particulate medium in which wavelength-sized scatterers are separated by distances somewhat larger than the wavelength…” (Hapke 1990). Sulfur is an excellent insulator and therefore highly transparent to microwaves; the requirements are beautifully satisfied by a deposit of this material containing voids or pebbles.

We prefer $S$ over $H_2O$ as the material at the polar regions because it has more suitable thermodynamic properties; there are good reasons why it may be present in sufficient quantities at Mercury, and it is abundant in Venus, Io, and meteorites. The work of Paige et al. (1992) makes a case for the stability of water ice in craters having just the right geometry to keep their interiors in permanent shadow, and the observed bright regions almost certainly occupy such spots (Harmon et al. 1994). However, the parameters must be strained somewhat to keep the ice from evaporating even at these special locations; Paige et al. state that temperatures of less than 112 K would be required to limit the rate to 1 m per billion years. The vapor pressure of sulfur is substantially lower, but still high enough to ensure that it will migrate to the polar regions. A comparison with the volatility of the well-observed sodium is useful. At a typical mercurian temperature of 400 K, S has a vapor pressure $\sim 4 \times 10^8$ times that of Na. Vapor pressures in the region 100–200 K must be extrapolated from measurements at higher temperatures and are therefore significantly uncertain, but there is also a substantial uncertainty in predicted temperatures, so an accurate vapor-pressure curve is not crucial. In any case, the vapor pressure refers to the vapor in equilibrium with a pure surface of the same material and is only a general guide when the surface is the impure one of a planet. We have simply fitted a curve of the form $p = A e^{\beta T}$ to data tabulated in the American Institute of Physics Handbook (Gray 1965). For the number density we use the ideal-gas relation $n = \rho/kT$, where $k$ is Boltzmann’s constant. Table II shows comparative vapor pressures and densities for 180 and 500 K for $S$, Na, and $H_2O$, as well as ionization and photodissociation times and other relevant information.

When a vapor is in equilibrium with a solid surface of the same material, the evaporation and deposition rates are equal and have the value $nc^2/4$, where $c = \sqrt{8kT/m}$ is the mean velocity. If the vapor density is substantially less than the equilibrium value, evaporation (strictly, sublimation) dominates and the rate can be estimated by the same expression. Conversely, a higher vapor density will result in deposition. The last line of Table II shows the temperatures at which the rate would correspond to accretion or disappearance of 10 m per billion years. The entry in the $H_2O$ column illustrates the difficulty with this material: if it is to be stable, the temperature must be extremely low, 120 K by our extrapolation or 112 K according to Paige et al. A deposit of sulfur is stable below 180–190 K, a temperature easily attained in the shadowed craters, but the warmer temperatures in the nearby unshadowed regions assure that the $S$ atoms will migrate into the craters.

The discussion above of probable crustal composition suggests that the vapor density of $S$ at low latitudes is $\sim 10^5$ cm$^{-3}$; at this density, condensation would start at $\sim 190$ K. According to Fig. 1 of Paige et al. (1992) the maximum temperature at the poles for a flat surface is 200 K; thus, sulfur is not stable on such a surface and will migrate to the same cold, shadowed areas as water ice. For all latitudes below 82°, the biennial maximum temperatures are at least 350 K and the saturation vapor densities greater than $10^4$ cm$^{-3}$. On the biennial time scale, condensation to the surface will not be a factor.

The photoionization time of a sulfur atom exposed to sunlight at Mercury is about $10^5$ sec (Kumar 1985). The fate of the average sulfur atom is to be ionized, caught up in the motional electric field of the solar wind, and swept either away from the planet or back into the surface. Photoionization occurs only on the day side, but this is also the side that is warm enough to evaporate the atoms. Sulfur atoms in the atmosphere near the poles can migrate there and be trapped if the migration time is on the same order as the ionization time. For migration we estimate the number of hops in a random walk to move a distance $L$, which is to be determined. We use a temperature of 500 K, for which the scale height of an S atom is 36 km; this is a typical hop distance (cf. Chamberlain and Hunten 1987, p. 362). To migrate a distance $L$, an atom must make a number of hops of order $(L/H)^2$. The time $t_h$ for a hop is twice the free-fall time: $t_h = 2\sqrt{H/g} = 205$ sec, where $g$ is the acceleration of gravity. The migration time is therefore $t_m = (L/H)^2$; if this is equated to $10^5$ sec $L$ turns out to be 795 km, or 19° of latitude. The zone from which
the polar caps collect therefore extends poleward from latitudes of 71°. These estimates do not include the extra time spent sitting on the ground between hops, during which photoionization does not happen. As long as the temperature is high enough to support the expected number density of \( n = 3 \times 10^6 \text{ cm}^{-3} \), the deposition rate is \( 4.3 \times 10^6 \text{ cm}^2 \text{ s}^{-1} \). For solid sulfur with a density of 2.07  g cm\(^{-3}\), the deposition rate converts to 35 m per billion years of daylight, or half as much for the same total elapsed time. To account for other inefficiencies, we adopt a rate of 10 m per billion years elapsed. The total depth of a deposit could therefore be tens of meters. Therefore, S is a highly attractive candidate for the material of the caps.

5. Proposed observations to search for sulfur. Ultraviolet: A measurement of atomic sulfur abundance in Mercury’s atmosphere can be made using the Si multiplet \( \lambda \sim 300 \text{ Å} \) centered at 1813.7 Å. Unfortunately, these observations cannot be made from the ground as the Earth’s atmosphere is highly absorbing in this wavelength region. The observation is feasible from a small telescope above the Earth’s atmosphere. A quick calculation of the expected line intensity relative to Mercury’s continuum demonstrates this. We calculate a scattering probability (g factor) and ratio of line to continuum at 1816 Å using a solar flux value at 1800 Å of \( 4.39 \times 10^{-2} \text{ photons cm}^{-2} \text{ sec}^{-1} \text{ Hz}^{-1} \), from Allen (1972). At Mercury, the solar flux is on average \( \sim 6 \) times greater so \( g = 7.7 \times 10^{-4} \text{ sec}^{-1} \). With the suggested abundance in Table 1, we obtain an expected line intensity of \( 116 \text{ R} \). Mercury’s surface brightness at 1816 Å can be estimated from the Lambert albedo, \( \lambda_S = 0.03 \) (Broadfoot et al. 1974). For observations near the bright limb, we obtain a continuum brightness of 0.1 Å of 480 R. Thus, sulfur emission in the UV multiplet can easily be seen from an instrument of this resolution, as a line 25% the height of the continuum from above the Earth’s atmosphere.

Midinfrared: Particulate, elemental sulfur has well-defined minima in its reflectance spectrum at 7.7 and 11.8 μm. A slightly weaker feature exists at 10.7 μm (Nash 1986). These reflectance minima should show up as emissivity features in midinfrared spectra of Mercury’s surface. Such spectra could be obtained with the medium- and high-resolution spectrographs currently available.

Millimeter: A search for sulfurous molecules emitting at millimeter and longer wavelengths is also recommended. In particular, H₂S is a good candidate. Mercury’s regolith is likely to be saturated with H₂S from constant bombardment of the surface by \( \text{H}^+ \) ions of the solar wind. Hydrogen atoms entering the mercurian regolith will recombine quickly to produce a saturated \( \text{H}_2 \text{S} \) environment that readily forms \( \text{H}_2 \text{S} \) upon entry of an impacting \( \text{S}^+ \) ion. Photolysis of released \( \text{H}_2 \text{S} \) would produce HS.

Another candidate is SO₂. The ultraviolet spectrograph aboard the Mariner 10 spacecraft placed an upper limit on atomic oxygen of \( 1 \times 10^{11} \text{ cm}^{-2} \) (Broadfoot et al. 1974). Still, oxygen is expected to be present, presumably sputtered from the surface materials or liberated during volatilization episodes following meteoric impacts. It will be quick to combine with any suitable atom. If sulfur is present, SO and SO₂ are also expected. These molecules have lines at millimeter wavelengths. At 200 K, lines will be narrow and small abundances may be observable using a medium-sized millimeter observatory.

6. Conclusions. We suggest that Mercury’s surface has a significant inventory of sulfides like sphalerite and its atmosphere has atomic S in comparable amounts to Na. Thus, we propose that the radar bright regions seen at high latitudes, both at the north and south polar regions are a result of elemental sulfur cold-trapped in permanently shadowed regions and mixed with surface dusts. These conclusions are based upon spacecraft and ground-based observations of Mercury, measuring its magnetic field. high density, surface materials that have a relatively high index of refraction and are transparent or translucent to a large portion of the electromagnetic spectrum, and the known presence of semivolatiles like Na and K in its atmosphere.

The presence or absence of S or sulfurous molecules at Mercury is of cosmochemical significance. As described above, a Solar System condensation model is highly dependent upon the distribution of volatiles throughout the solar nebula and their capture during accretion. The abundant Na and K in Mercury’s atmosphere strongly suggests that semivolatile elements are present in greater abundance at Mercury than at the Moon. The other lines of evidence described above argue strongly for the presence of sulfur.

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REFERENCES


MITCHELL, D., AND I. DE PATER 1994. Microwave imaging of Mercury's thermal emission at wavelengths from 0.3 to 20.5 cm. *Icarus* **110**, 2–32.


