Mars: Is the Surface Colored by Carbon Suboxide?

Abstract. The reflection spectrum of Mars can be well matched from 0.2 through 1.6 microns (and farther) by polymers of carbon suboxide, reflection spectra for which have now been measured. We propose that the reddish color of Mars might be attributed to carbon suboxide, not the commonly considered limonite or other iron-bearing minerals.

The planet Mars is conspicuously red even when seen without a telescope. This redness is accentuated by the predominantly blue color of most bright stars; Mars itself is colored more nearly a dull orange, popularly attributed to an iron-bearing mineral such as limonite (1). Some iron compounds show approximately the same color as Mars, but there are numerous spectral discrepancies, such as a reflectance minimum at 0.87 μ which is weak or absent on Mars (2). A better spectral match is shown by certain polymers of carbon suboxide, an uncommon material which may plausibly form in the atmosphere of Mars.

Carbon suboxide, or C_3O_2, is a noxious, clear liquid which boils at 7°C. Its linear molecules readily (and sometimes explosively) polymerize to form a sequence of heavier molecules, most of them quite hygroscopic. Their colors are graded through pale yellow, orange, reddish-brown, and violet, to nearly black. The first few members of this sequence can be formed from the monomer even at temperatures well below 0°C, under ultraviolet light or with various acidic catalysts.

For this investigation we prepared carbon suboxide by dehydrating finely powdered malonic acid in an excess of phosphorus pentoxide at 145°C (3). The gaseous products, which also included carbon dioxide and acetic acid, were collected in a cold trap. The carbon suboxide was then isolated by fractional distillation, transferred to a quartz-windowed cell, and polymerized either by ultraviolet light from a mercury lamp or thermally by being warmed to room temperature.

The polymers formed a multicolored coating on the quartz window. We illuminated this deposit by a quartz-tungsten lamp and measured reflection spectra with a Perkin-Elmer model 12C spectrometer, equipped with a LiF prism and a PbS detector. Comparison spectra were also recorded with the light reflected from sulfur, powdered silica, and magnesium oxide, the reflective properties of which have been described elsewhere (4). Measurements at wavelengths shorter than 0.8 μ were made with a second instrument—a grating monochromator adapted for this purpose with a 1P28 photomultiplier cell. The region from 0.6 to 0.8 μ was recorded on both instruments to provide unambiguous matching.

Figure 1 presents the spectral reflectivity of the polymer most closely matching the color of Mars. The agreement includes a slight decrease from 0.30 to 0.35 μ, low reflectivity for violet and blue light, the proper curvature from 0.35 to 0.8 μ, a moderate peak at 0.8 μ, a shallow minimum near 1.1 μ, and generally high reflectivity for longer wavelengths. The Mars reflectivity from 0.2 to 1.6 μ is taken from the review article by McCord and Adams (5). Although the Mars spectrum for longer wavelengths is less well established, there is a general rise in reflectivity to about 1.8 μ, followed by a decline of about 50 percent from 1.8 to 3.0 μ (6). The same is true of polymerized carbon suboxide.

Dollfus attempted to evaluate water vapor absorption in the martian atmosphere by measuring the integrated absorption across the water vapor band at 1.38 μ (7). His value of about 0.015 g/cm^2 of H_2O was an order of magnitude higher than has been estimated by other observers using higher spectral resolution (8). Moroz has also shown that the 1.38-μ absorption does not appear in the spectrum of the martian polar caps, so it cannot correspond to
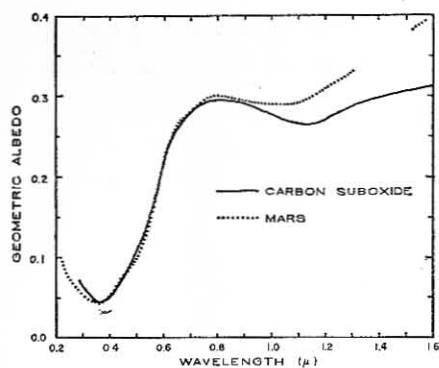
Fig. 1. Spectral reflectivity of the planet Mars compared with that of a dull yellow-orange polymer of carbon suboxide observed in the laboratory. For comparison with data in (5) we have converted our reflectivity measurements into geometric albedo by supposing that the polymer scatters light as an ideal (Lambert) diffuse reflector.

an atmospheric constituent (9). We believe that the absorption Dollfus measured at that wavelength was not from atmospheric water, but rather from water combined with the hygroscopic carbon suboxide polymers coating the martian surface. We find that just such an absorption can be produced in the laboratory by allowing a minute quantity of water vapor to combine with the polymer, possibly forming a polymeric carboxylic acid.

The slight differences between the polymer spectrum and the Mars spectrum may be explained by supposing that Mars is not entirely coated nor densely coated with carbon suboxide. Mars shows a somewhat steeper rise in reflectivity between 0.9 and 1.6 μ, for example; but the carbon suboxide is relatively nonabsorbing in this region, and underlying sand or rock could contribute to the spectrum. Most igneous rocks do, in fact, show an increase in reflectivity here.

A similar argument must be made for limonite, which would also have to be present as a coating or stain on some other material, probably an igneous rock (10). Limonite alone does not exhibit quite the proper infrared reflectivity, shows too steep a rise in reflectivity from 0.5 to 0.65 μ, and does not show the required increase in reflectivity below 0.3 μ. Younkin (2) has discussed the great difficulty of matching the near-infrared spectrum of Mars with limonite and places an upper limit of 2 percent on the limonite content.

Although the reflection properties of carbon suboxide provide an excellent match for Mars, we have yet to consider the source of this material. In the atmosphere of Mars, which is almost pure carbon dioxide (11), the monomer might be formed by a photochemical reaction such as

$$CO_2 + 2CO \rightarrow C_3O_2 + O_2$$
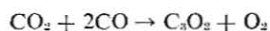
We need only suppose that trace quantities of carbon monoxide are sometimes available in the atmosphere, as from occasional volcanic venting, because the polymers ultimately formed have low vapor pressures at the martian surface temperature (less than 20°C) and can accumulate very slowly. Since the reaction is a sink for carbon dioxide there must be some limit on its rate, such as a usual scarcity of carbon monoxide, or at least some mechanism by which carbon dioxide might be replaced to the atmosphere. We do not suggest a time scale for the carbon suboxide production; if it were fast enough it could account for the occasional presence of the strange yellow clouds of Mars which, unlike the blue and white clouds, are most commonly found in warm areas of the planet (12).

In the reaction flask which we used for desiccating malonic acid, some carbon suboxide was observed to polymerize in a broad range of colors. A temperature gradient existed in the flask wall: hottest near the level of an oil bath used to apply heat, and coolest near a supporting clamp at the top. The polymers which collected on the glass were arranged in bands of well-defined color, the darkest being found on the hottest glass. Spectra measured through the glass wall were in good general agreement with those of the pure polymers, although additional infrared absorptions were seen which corresponded to acetic acid and water. The most prominent difference between successive polymers of deepening color is a uniform shift of the abrupt reflectivity jump (which on Mars is centered at 0.55 μ) by approximately $+0.05$ μ from each polymer to the next higher one. Four members of this progression were observed.

Interestingly, the measured ratio between the spectral reflectivities of each adjacent pair closely resembles the spectral ratio between martian light and dark areas presented by McCord and Adams (5). We suggest, therefore, that the principal difference between martian light and dark zones may be the degree of polymerization,

perhaps a result of local irregularities in temperature. If the time scale for formation and polymerization of new carbon suboxide is sufficiently short, then the further polymerization of a freshly produced deposit might even account for some of the martian color changes, phenomena which appear quite difficult to explain if the surface is colored by the more stable iron oxides.

Carbon suboxide has also been proposed as a constituent of the Venus clouds by Sinton and later by Kuiper (13). Spectroscopic evidence precludes the monomer, and no evidence has been found that the Venus clouds contain the polymers, but very slight traces of the lowest polymers, mixed with ice clouds, might produce a slightly yellow appearance (as Venus is observed to have) without revealing themselves by measurable absorptions in other parts of the spectrum (14).

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