

Mariner 9 Ultraviolet Spectrometer Experiment: Observations of Ozone on Mars

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The Mariner 9 Ultraviolet Spectrometer has observed the 2550 Å ozone spectral absorption feature on Mars. This absorption was previously detected in the south polar region by Mariner 7 in 1969. Mariner 9 did not observe ozone at any time in the equatorial region, nor at the south polar cap during its summer season. However, ozone was found in the north polar region beginning at a latitude of 45°N and extending northward. Ozone later appeared in the southern hemisphere southward of 50°S as the Mars autumnal equinox approached. The presence of ozone on Mars seems to be coupled to the water vapor content of its atmosphere.

INTRODUCTION

The ultraviolet spectrometer on Mariner 7 in 1969 observed ozone on the Mars south polar cap during its late spring season and not elsewhere (Barth and Hord, 1971). With Mariner 9 arriving at Mars in the early part of the Martian summer in the southern hemisphere, it was hoped that clear observations could be made at the south polar cap and in the vicinity of the south polar area in order that determinations of the presence and the amount of ozone could be repeated. Another objective was to search for the presence of local ozone concentrations elsewhere on the planet.

INSTRUMENT

The ultraviolet spectrometer instrument has been described in detail elsewhere (Hord *et al.*, 1970). The instrument scans from 2100 to 3500 Å in one of its two spectral channels every 3sec with a spectral resolution of 15 Å. At the mean altitude of 2300km, where many of the south polar and northern latitude measure-

ments were made, the effective field of view projection on the planet surface is approximately 20km. Observations of various portions of the planet were performed with differing viewing parameters such as slant range, illumination angle, viewing angle, spacecraft altitude, latitude, and longitude.

PLANETARY OBSERVATIONS

An extensive dust storm, which totally obscured the visible surface of the planet, existed when Mariner 9 arrived at Mars (Masursky *et al.*, 1972). Over most of the planet, the ultraviolet spectrometer was not able to see the ground; however, it was able to observe an increased signal in the 3000-Å region when observing the south polar cap. This was caused by the high reflectivity of the south polar cap as compared to the normal Martian surface.

Figure 1 shows two of the spectra taken by the spectrometer on orbit 26. The middle spectrum is one taken precisely over the bright portion of the south polar cap with no bare surface showing through

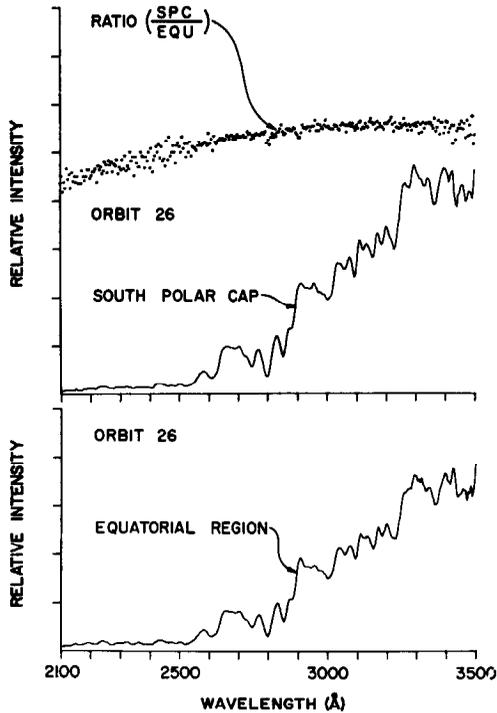


FIG. 1. Ultraviolet spectra of the equatorial region and south polar cap during the dust storm (orbit 26). The south polar cap intensity is almost three times greater than the equatorial intensity which has been multiplied by two. The ratio of the south polar cap intensity (SPC) to the equatorial region intensity (EQU) which is plotted as dots demonstrates the lack of detection of any ozone absorption at 2500–2600 Å.

the white covering layer, as verified by locating the instrument's field of view in a high-resolution television picture. The lower spectrum in this figure is one observed from the equatorial region of the planet also on orbit 26. The reflectivity of the polar cap is larger. In neither spectrum is there any obvious evidence of ozone absorption. Comparisons of equatorial region spectra with the solar spectrum show no evidence of the presence of ozone absorption. In order to see if there were any small spectral differences over the polar cap in the ozone absorption wavelengths, the polar cap spectrum was divided by the equatorial region spectrum. The ratio is the dotted trace in the upper portion of Fig. 1. There is no evidence for

the Hartley ozone absorption feature centered at 2550 Å. This result was typical of all observations of the south polar cap during the dust storm.

During this early part of the mission, no evidence of ozone was found in any location on the planet that was under examination (90°S–30°N). During the dust storm, over the equatorial region, the spectrometer could only probe the atmosphere down to approximately 10 km above the surface because of the dust obscuration. Continued observations of the south polar cap during the time of the clearing of the dust storm did not reveal any ozone absorption, although the measured reflectivity of the south polar cap did increase by about a factor of three as the dust in the atmosphere settled. Figure 2 shows the spectrum of the south polar cap on orbit 124 well after the dust storm had cleared. The arrangement of the data is identical to that found in Fig. 1. Once again, there is no evidence of absorption in the Hartley system of ozone near 2550 Å. Figures 1 and 2 represent typical spectra observed over the south polar cap throughout the period from orbits 1 through about 140 (a period of 70 days), and no spectrum in this time period showed the presence of ozone at the cap, even well after the dust storm had cleared.

The Mariner 9 spacecraft performed a maneuver on orbit 94 that permitted the

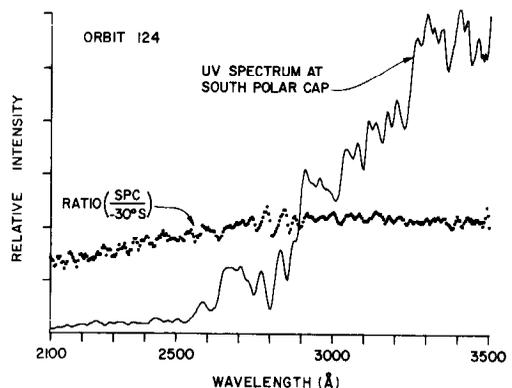


FIG. 2. Ultraviolet spectrum of the south polar cap well after the dust storm had subsided (orbit 124) and the ratio of this spectrum with one recorded at 30°S latitude on the same orbit. Again there is no evidence for ozone absorption.

instruments to look farther into the northern hemisphere. On orbit 102 an enhanced reflectivity at 3050 Å was observed as the spectrometer field of view crossed into the latitudes above 30°N for the first time. Figure 3a shows the behavior observed by the instrument for this orbit. The reflectivity of the planet and the atmosphere in the 3050-Å band is plotted versus the Mars north latitude at the center of the field of view of the

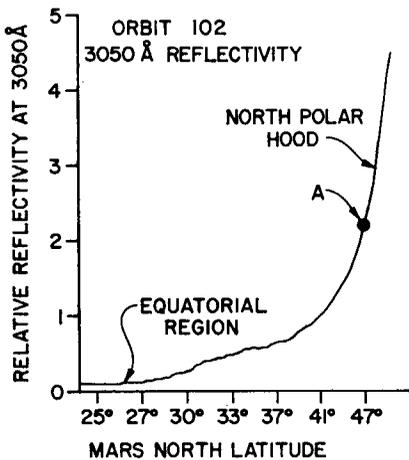


FIG. 3a. The onset of enhanced 3050 Å reflectivity as observed on orbit 102. The north polar hood is the cause of this change. A spectrum corresponding to point A at 47°N is shown in Fig. 3b.

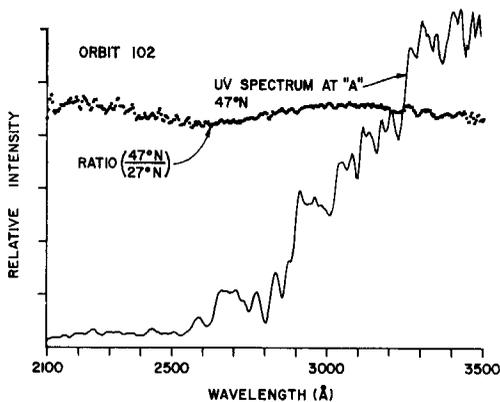


FIG. 3b. Ultraviolet spectrum at 47°N on orbit 102. The ratio of this spectrum to one observed near 27°N shows a small dip near 2550 Å. This was the first discernable evidence of ozone on Mars during the Mariner 9 mission.

spectrometer. At about 30°N the instrument recorded the onset of a 3050-Å brightening similar to that seen over the south polar cap. However, this brightening did not have the extremely rapid increase which was observed at the edge of the south polar cap. As the motion of the spacecraft carried the measurements farther northward, the brightening continued to grow.

TV pictures were examined to try to understand the cause of this increased reflectivity. For those pictures taken in the latitude zone of 30–40°N there was no obvious anomaly in the television images to provide information as to the cause of the enhanced reflectivity. Only in the pictures farther north (45–50°N) where the uv signal was much more intense was a haze observed which is identified with the “north polar hood” (Leovy *et al.*, 1972). A spectrum taken at point A in Fig. 3a (47°N latitude) is shown in Fig. 3b. The actual spectrum shows, to the eye, no distinctive features. Applying the ratio method to accentuate small changes, a small absorption feature is seen in the dotted ratio curve. Ratios of two different equatorial spectra on this same orbit produce nearly flat lines showing no discernable absorption or emission features. However, the ratio of this polar spectrum at 47°N to an equatorial spectrum at 27°N shows a noticeable depression near 2550 Å. This was the first indication of the existence of ozone on Mars during the 1971 mission, and it was found in the atmosphere in a location very different from that observed in 1969.

Continued observations of the northern hemisphere above 35°N showed enhanced reflectivity at 3050 Å and increasing concentrations of ozone as inferred from the depth of the absorption feature as more northerly observations were obtained. By orbit 144, the absorption feature had become quite strong. Figure 4a shows the 3050 Å reflectivity as a function of Mars latitude. At the edge of the visible north polar hood there is again a strong increase in signal intensity. A spectrum at 57°N latitude (point B in Fig. 4a) was examined for ozone absorption (Fig. 4b). Here

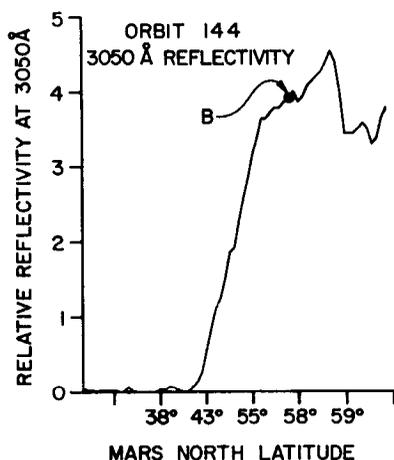


FIG. 4a. The transition from the equatorial region to the north polar hood on orbit 144. A very strong enhancement of 3050 Å reflectivity was observed on this orbit. A spectrum at point B, 57°N latitude, is shown in Fig. 4b.

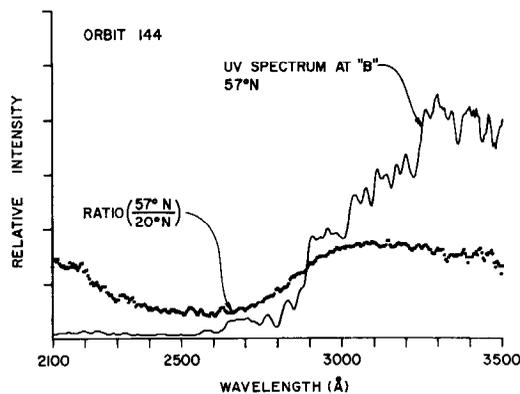


FIG. 4b. Ultraviolet spectrum at 57°N on orbit 144. This spectrum does show distinctive changes from the one shown in Fig. 3b. When the ratio is formed using a spectrum from 20°N latitude on this same orbit, a pronounced ozone absorption is seen at 2550 Å.

changes in the spectral shape are observed near 2400–2700 Å. The ozone absorption feature is very pronounced when the spectral ratio is formed comparing this north polar hood spectrum at 57°N to an equatorial region spectrum at 20°N. Thus, by orbit 144, the presence of ozone in the region above 30°N latitude was repeatedly measured while no ozone south of this latitude had been seen on any portion of the illuminated planet. The areal coverage in

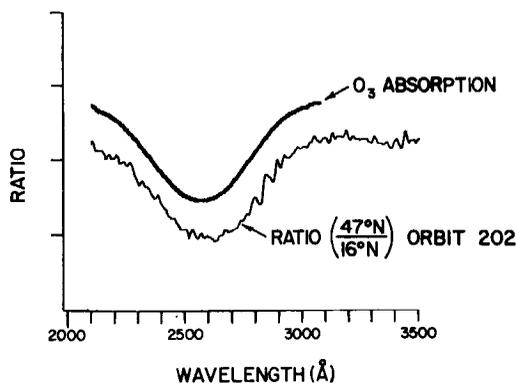


FIG. 5. Laboratory absorption curve for ozone is compared with absorption observed on Mars. The laboratory curve has been offset to facilitate comparison.

the southern latitudes and near the south polar cap had been extensive.

The identification of this absorption feature as ozone is shown in Fig. 5, where the ratio of the north polar hood spectrum to the equatorial spectrum is taken from orbit 202. The ozone absorption curve is from laboratory data of Griggs (1968).

LOCATION AND TIME VARIABILITY OF OZONE

The south polar cap showed no evidence of ozone during the first 70 days of observation. For these early orbits the observation sequences covered Mars local time periods from 09.00 through about 16.00 in the southern hemisphere which was in its summer season. As the season changed and the subsolar point moved northward, the southerly latitudes began to cool, both on the ground and in the lower atmosphere (Hanel *et al.*, 1972b). Ultraviolet observations near the morning terminator showed an anomalous brightening at ~05.30 Mars local time. Within a change of 1 hr in local time, this condition disappeared. Examination of the spectra with enhanced brightening showed some absorption by ozone, which also disappeared when the enhanced reflectivity was no longer present. By orbit 180 there were indications that a more persistent high-reflectivity region existed. With the transit of the subsolar point northward almost to

the Mars equator, this zone of heightened reflectivity persisted beyond the morning terminator and became visible first in the morning and finally, by orbit 190, was noticeable in the Mars early afternoon spectra near 70°S. The television pictures of this area at this time did not show any discernable haze or obscuration. However, the temporal nature of this phenomenon indicated that the uv spectrometer was detecting the onset of the south polar hood.

On orbit 188 the remnant south polar cap was viewed again and this time the spectra showed the ozone absorption feature that was observed in 1969. A ratio formed from the south polar cap spectrum with an equatorial spectrum is shown in Fig. 6, along with the spectrum of the cap. When comparing Fig. 6 to Figs. 1 and 2, a marked change is seen, showing that ozone has a large seasonal variability. Utilizing the same analysis technique, spectra which now showed enhanced reflectivity in the southern hemisphere were examined in detail. Those spectra which had only weakly enhanced 3050 Å reflectivities showed slight dips in the ratio curve (much like Fig. 3b). Spectra which had stronger 3050 Å intensities relative to the mean of the equatorial zone produced deeper absorption minima in the ratio curve. By

orbit 200, ozone was found extensively throughout the area below 60°S latitude.

DISCUSSION

The inability to reproduce the observations of Mariner 7 in 1969 at the south polar cap during the early phase of the Mariner 9 mission was puzzling. One of the hypotheses advanced for the Mariner 7 observations was absorption of gaseous ozone into the freshly deposited CO₂ snow lattice on the surface of Mars. Laboratory experiments conducted by Broida *et al.* (1970) demonstrated that ozone could be incorporated into a fresh CO₂ snow at low temperatures. The 1969 Mariner 7 television pictures in the south polar area were reasonably clear, showing many ground details. Thus, it would seem that the ozone might be in the snow on the ground. Yet the uv observations in 1969 did not provide data by means of which one could separate atmospheric ozone from ozone incorporated in ground snow. Even if the residual 1971 cap remained cold, 150–170°K as measured by the infrared instruments (Hanel *et al.*, 1972a; Chase *et al.*, 1972), there is the possibility that ozone could diffuse out of the lattice.

The observations of ozone in the north polar hood suggested the possibility that there may be atmosphere-borne, fine-particle CO₂ snow which has ozone in it. If so, why was the onset of both enhanced reflectivity and ozone presence so abrupt? Such comparatively sharp discontinuities seemed unusual. An alternate proposal invoking solid state photochemistry is possible. Ultraviolet photons with $\lambda < 2200$ Å would be absorbed by the CO₂ snow and produce O + CO. The relatively large carbon monoxide molecule remains bound to the lattice site of the photo-destroyed CO₂ molecule and the O atom is free to migrate through the lattice. Recombinations of O–O can occur with the lattice acting as a very efficient third body. The resultant O₂ molecule probably resides at an interstitial site and because of size has almost no mobility. Other mobile O atoms could lead to O₃ formation with the lattice again acting as an efficient third body.

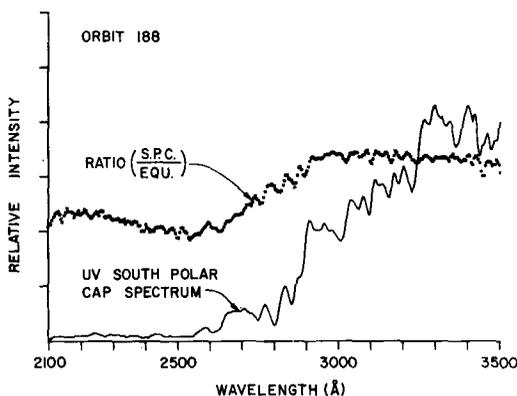


FIG. 6. Ultraviolet spectrum of the south polar cap on orbit 188. The ratio of this spectrum to one from the equatorial region on orbit 188 (dotted curve) shows the presence of ozone at the south polar cap. Compare this figure to Figs. 1 and 2 where no ozone was observed previously at the south polar cap.

This explanation seemed plausible except it could not answer the question, "If this process can occur in atmospheric CO_2 snow, why does it not occur at the south cap?" Of course, the question assumes that the south cap is CO_2 and not water ice. If the above mechanism were viable then the uv data might imply that the south cap is not pure CO_2 but contains some water ice. However, the Mariner 9 Infrared Interferometer Spectrometer experiment (Burke, 1972) indicated that, at the edge of north polar hood where ozone is observed, the ground and atmospheric temperatures for $40\text{--}60^\circ\text{N}$ latitude showed that CO_2 precipitation was not possible. Thus, the most likely candidate for the haze is water clouds.

Theoretical studies of the photochemistry of ozone in the Earth's atmosphere have revealed that less ozone is produced in a "wet" atmosphere as compared to a "dry" one (see Hunt, 1966). Observations by the Mariner 9 Infrared Interferometer Spectrometer show about $10\mu\text{m}$ of precipitable water vapor over the planet, south of 30°N during the early part of the Mariner 9 mission (Hanel *et al.*, 1972b). It is possible that this amount of atmospheric water would permit sufficient photochemical activity to reduce the amount of ozone below the detectable level. Lowering the atmospheric temperature to the water condensation point removes water vapor from the atmosphere. The photochemistry of CO_2 (McElroy and Hunten, 1970) and the observed O_2 concentrations of about one part in 400 (Barker, 1972; Traub and Carleton, 1972) in a "dry" atmosphere will produce ozone. Thus, it appears that it is the presence or absence of water vapor that controls the existence of atmospheric ozone.

Parkinson and Hunten (1972) have reexamined the Mars CO_2 photochemistry problem in connection with observational studies of molecular oxygen on Mars. The earlier model of McElroy and Hunten which was calculated for a "dry" atmosphere had predicted about one part per million ozone which is well above the ultraviolet spectrometer detection limit. In a current calculation, Parkinson and

Hunten have lowered the concentration of ozone in a "wet" model atmosphere to an amount not detectable by the uv spectrometer.

SPECTRAL IDENTIFICATION

It has been suggested that the absorption feature near 2550 \AA in the spectrum of Mars recorded by OAO-II may be the result of the presence of carbon suboxide (C_3O_2) monomer in the atmosphere of Mars (Owen and Sagan, 1972). This conclusion was presumably based upon the fact that C_3O_2 has an absorption minimum near 2650 \AA . Figure 7 shows the relative absorption coefficients for O_3 (Griggs, 1968) and C_3O_2 (Smith *et al.*, 1963); except that the absorption coefficient for C_3O_2 has been increased 600 times to facilitate a comparison with that for O_3 . Two important facts are noted. First, the laboratory maxima for optical absorption are separated by at least 100 \AA , many times greater than the Mariner 9 uv spectrometer resolution element. Second, the absorption coefficient of O_3 decreases towards a minimum near 2100 \AA while that of C_3O_2 begins to rise again. The relative

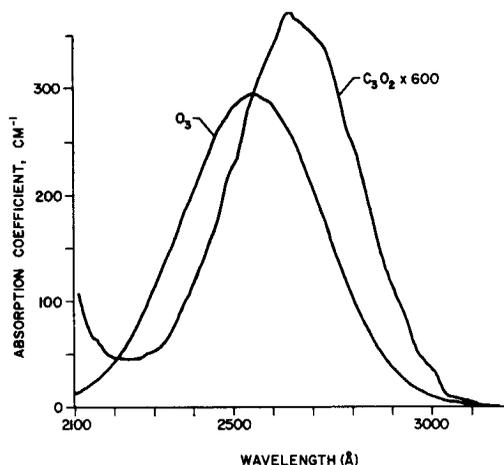


FIG. 7. A comparison of the absorption coefficients of ozone and carbon suboxide monomer from $2100\text{--}3100\text{ \AA}$. The C_3O_2 data have been increased by a factor of 600 to facilitate comparison. Identification of each species as distinct from one another is easily achieved by the Mariner 9 uv spectrometer.

difference of a factor of 2.5 at 2100 Å is easily discernable in the Mariner 9 Mars spectra since the spectrometer is sensitive at this wavelength. The Mars absorption curve shown in Fig. 5 clearly indicates that there is no onset of strong absorption at 2100 Å. Therefore, the instrument is not detecting carbon suboxide, and the accurate fit to the laboratory Hartley band absorption width and the shape of the minimum indicate that the observed species is ozone.

ACKNOWLEDGMENTS

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