Characterizing the Oxidizing Properties of Mars’ Polar Regions. A. R. Hendrix, K. E. Simmons, and K. D. Mankoff.

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Introduction: We investigate the oxidizing properties of Mars’ polar regions using disk-resolved ultraviolet spectra from the Ultraviolet Spectrometer (UVS) on Mariner 9. We detect the spectral characteristic of hydrogen peroxide (H$_2$O$_2$), which has already been found to exist on the icy Galilean satellites. The Mariner 9 UVS data have been archived at NASA’s Planetary Data System (PDS) Atmospheric Node and are also available at http://lasp.colorado.edu/Mariner_9_data/. A software visualization tool, Albatross, provides database access (http://lasp.colorado.edu/albatross/) and enables the user to view reflectance spectra for desired latitude/longitude regions and mission phases. It displays the UVS field-of-view (FOV) tracks along with the corresponding reflectance spectrum for a chosen FOV against a background showing the Mars surface image, or a user specified alternate dataset, such as a thermal, geologic or topographic map.

The UV H$_2$O$_2$ signature: Hydrogen peroxide has been detected on the icy Galilean satellites. A 3.5 µm feature was discovered [1] in a Galileo Near-Infrared Mapping Spectrometer (NIMS) spectrum of Europa, which was found to agree with a laboratory-measured mixture of 0.13±0.07% H$_2$O$_2$ in water ice. A simultaneous measurement of Europa by the Galileo UVS revealed a distinctive spectrum, which agreed with the same H$_2$O$_2$ laboratory mixture that fit the NIMS spectrum [1]. The same distinctive feature was also detected by the UVS on Ganymede and Callisto [2]. The abundance of peroxide was modeled at all observed locations on Ganymede [2] and found a strong correlation with solar angle, where peroxide abundance increases with decreasing solar angle. On Ganymede, hydrogen peroxide abundance is thus generally anti-correlated with ozone abundance. Sample Galileo UVS spectra of Ganymede are shown in Fig. 1. The ozone associated with the polar hood had much higher abundances than the polar cap ozone [4]; both types of ozone displayed a seasonal variation, where more ozone was measured during the winter than in summer (Fig. 2). It was suggested [5] that the lack of equatorial ozone was due to the fact that the infrared instrument on Mariner 9 detected 10 µm of precipitable water vapor in equatorial regions; this water vapor was suggested to constrain the amount of ozone allowed to form at low latitudes.

The Mariner 9 observations led to the following scenario of seasonal variations in Mars’ ozone. During early summer, no ozone is present above the detectable level of 3 µm-atm (where 1 µm-atm = 2.69x10$^{-15}$ mole-
Ozone appears in late summer over the polar cap and associated with the polar hood. Throughout autumn and early winter, ozone amounts increase to maximum values at midwinter, and the spatial distribution increases so that ozone is detected between the poles and 45° latitude. The maximum detected value of ozone in the northern hemisphere was 60 µm-atm, while for the southern hemisphere the maximum amount was 30 µm-atm. Between midwinter and early summer, ozone amounts decrease. It was found that atmospheric ozone abundances vary on a daily time scale as well, where amounts increase as the atmospheric temperature decreases and water vapor amounts decrease. Temporal variations in ozone abundance driven by water vapor changes associated with orbital position have also been displayed with more recent data from HST (e.g. [7]).

Figure 2. Seasonal variation in ozone abundance associated with polar hood (observations from between 50° and 75° latitude). Left panel is for southern hemisphere, right panel is for northern hemisphere [4].

Most early Mariner 9 investigations (e.g. [8]) focused on ozone associated with the polar hood, which is atmospheric ozone, as shown in Fig. 3. Ozone associated with the polar caps has been less thoroughly studied. It is as yet unclear whether the ozone exists in the ice of the winter polar cap, having been snowed out along with CO₂, as suggested by [3], or whether the ozone exists in a thin layer overlying the bright polar cap. Certainly there are differences between the atmospheric ozone and the polar ozone. They both show similar seasonal variations, but overall, much less ozone is present at the polar caps than in the polar hood. The polar cap ozone band is also much shallower than the polar hood ozone, indicating that the ozone might be in a different form. A sample spectrum of the polar cap ozone is shown in Fig. 4 (lower panel).

Figure 3. Sample spectrum of polar hood O₃. From [8].

Figure 4. Mariner 9 data of the south polar cap (Barth, unpublished data). Shown are measured reflectances; the y-scale is from 0.0 to 0.05 on both plots. The bottom panel displays the ozone absorption band while that feature is absent from the top spectrum. Both spectra were taken of the southern polar cap (85° S); the top panel was taken in mid-summer (orbit 124) and the bottom spectrum was taken in late summer (orbit 184).

Figure 5 (from [4]) displays the variation in polar cap ozone abundance with season during the Mariner 9 mission. The left panel shows the southern cap data, while the right panel is for the northern cap. During the summer, no ozone was measured at the southern polar cap. (The spectrum shown in the top portion of Fig. 4 is from southern summer.) Ozone began to be detected in the late summer at that cap. (The spectrum in the lower panel of Fig. 4 is from this time frame.) During the same period of time, the northern polar cap was experiencing winter, and large amounts of ozone were measured at that cap. Northern polar cap amounts decreased as that hemisphere transitioned into...
spring and then summer. As with the polar hood ozone, polar cap ozone amounts were postulated to decrease as odd hydrogen (especially H₂O) amounts increased (during summer).

Figure 5. Variation in ozone abundance on polar caps versus season. The left panel shows Mariner 9-measured ozone abundances for the south polar cap, while the right panel is for the north polar cap. Ozone abundances are greatest during winter and are lowest during summer. From [4].

We note that the spectrum shown in the upper panel of Fig. 4 displays the characteristic spectral shape of H₂O₂, recognized from UV data of the icy satellites. In this study, we model UV spectra of Mars’ polar regions from Mariner 9 UVS in terms of O₃ and H₂O₂ to investigate the spatial and temporal distributions of each, and the relationship to each other. Results indicate that relatively high amounts of H₂O₂ exist at the summer cap, along with relatively low amounts of O₃. The opposite is true for the winter cap. This suggests a relationship between H₂O₂ and O₃ whereby the dissociation of H₂O₂ produces OH which contributes to the destruction of O₃, where odd hydrogen (OH) destroys the odd oxygen that would otherwise go to form ozone:

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\begin{align*}
\text{H + O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \\
\text{HO}_2 + \text{O} & \rightarrow \text{OH} + \text{O}_2 \\
\text{OH} + \text{CO} & \rightarrow \text{H} + \text{CO}_2
\end{align*}
\]

Thus, when more water vapor is present, more odd hydrogen is present, inhibiting the formation of ozone.