thermal conductivity of the lunar rock is the implication it has for interpretations of the thermal regime of the moon's interior. If the Apollo 11 specimens are in any way representative of specimens at deeper levels or even if they contributed a significant fraction of the moon's original composition, it is clear that the thermal gradient resulting from a given rate of heat production on the moon could be substantially steeper than that on the earth. It seems improbable that the interior of the moon could be composed entirely of material as rich in iron and as opaque as the Apollo 11 samples (*6*), and the actual composition and thermal conductivity were probably intermediate between those of the lunar surface rocks and terrestrial ultramafic rocks, such as the dunite and lherzolite studied by Kawada (*7*). From the relations shown in Fig. 2 one can estimate the thermal conductivity of such an intermediate composition if the proportions of the component compositions are known. Extraction of the material with an iron-rich composition through partial melting and eruption at the surface must have produced a marked increase in the thermal conductivity in the levels from which the lunar lavas were derived.

TSUTOMU MURASE
ALEXANDER R. MCBIRNEY
Center for Volcanology, University of Oregon, Eugene 97403

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Mars: Is Nitrogen Present?

Abstract. *If the atmosphere is uniformly mixed, a mixing ratio of nitrogen to carbon dioxide of 5 percent is consistent with the observational data on the ultraviolet dayglow of Mars. If the magnitude of the eddy coefficient in the atmosphere is similar to that for the earth, this limit is reduced to less than 0.5 percent.*

The fractional abundance of nitrogen relative to carbon in the martian atmosphere is an important parameter in studies of the evolution of the planet. An extension of Rubey's (*1*) classic discussion of volatile gases in the atmosphere-ocean system of the earth suggests a mixing ratio of N_2 to CO_2 of a few percent if the atmospheres of Mars and the earth have a common origin and the amount of CO_2 in the martian polar cap is not large relative to that in the atmosphere. The difference in composition of the planetary atmospheres is due largely to the presence of oceans on the earth in which carbon is effectively precipitated as $CaCO_3$. If the N_2 mixing ratio in the martian atmosphere were much less than a few percent, a serious revision of current thinking on atmospheric evolution would be necessary.

The failure of the ultraviolet experiment on Mariners 6 and 7 (*2*) to detect emissions associated with nitrogen has already provoked such speculation. We discuss here the implications of the Mariner results by examining the detailed physical and chemical processes that lead to nitrogen emission in the martian airglow.

The strongest emissions from N_2 below 4000 Å are excited primarily by electron impact and have been extensively studied in the earth's atmosphere (*3, 4*). Electrons are produced by photo-ionization of atmospheric gases at high altitudes in the atmosphere. Their mean energy upon production is approximately 10 ev (*5*) and they are degraded in energy by collision processes, both elastic and inelastic. Some of these collision processes correspond to excitation of optical emissions from nitrogen, which is our primary concern. To compute the resulting emission spectrum one must first determine the energy distribution function for photoelectrons. The convolution of this quantity with an appropriate electron excitation cross section gives the excitation rate of optical emission per molecule.

We adopt models for the neutral atmosphere composed of CO_2 (*6*) with a small uniform admixture, x percent, of N_2 and a solar radiative flux appropriate to the Mariner 6 flyby. The rate of energy degradation for electrons in CO_2 has been estimated by Henry and McElroy (*7*) and by Strickland and Green (*8*); similar data for N_2 are given by Green and Barth (*9*) and by Dalgarno *et al.* (*5*). The distribution function derived for electrons with energy greater than 5 ev is shown in Fig. 1 for a height of 187 km in the martian atmosphere. For comparison we include a similarly computed distribution function for electrons at a height of 200 km in the earth's atmosphere. The interesting feature of these results is the sharp break in the martian distribution function near 7 ev, the threshold for excitation of electronic transitions in CO_2.

The threshold energy for excitation of the lowest electronically excited level of N_2, $A^3\Sigma_u{}^+$, is 6.5 ev. The $A^3\Sigma_u{}^+$ level is the upper level of the Vegard-Kaplan band system which appears as a weak emission feature in the dayglow of the earth. This feature is weak for the earth partly because the metastable $A^3\Sigma_u{}^+$ level is efficiently quenched by collisions with atomic (*10*) and molecular oxygen (*11*), constituents that are abundant in the earth's atmosphere but relatively rare in the martian upper atmosphere (*12*). Quenching by CO_2 is relatively inefficient (*11*), and most of the molecules in the $A^3\Sigma_u{}^+$ level produced above an altitude of about 100 km on Mars will radiate. If contributions due to cascade from higher levels are included, we predict an overhead intensity of $800x$ rayleighs for Vegard-Kaplan band emission in the martian atmosphere.

Unfortunately from the point of view of detection, this emission is distributed over many bands. The intensity in any given band is not expected to exceed $10x$ rayleighs. The stronger emissions, such as the (7-0) and (6-0) bands, occur near 1700 Å in a spectral region containing strong bands of CO produced by dissociation of CO_2 and by dissociative recombination of $CO_2{}^+$. We suggest that an intensity of 50 rayleighs, corresponding to an assumed N_2 mixing ratio of 5 percent at the emitting altitude, might have escaped detection in the preliminary study of Barth *et al.* (*2*) despite the high quality of their spectra.

The second most intense emission band of N_2, according to our calculations, is the first positive system associated with the transition $B^3\Pi_g \rightarrow A^3\Sigma_u{}^+$. We estimate that the overhead intensity due to electron impact would be

250x rayleighs. Additional emission is expected as a result of fluorescent scattering from the $A^3\Sigma_u{}^+$ level. However, the first positive system would not have been detected by Mariners 6 or 7. The emission is widely distributed over many bands in the red and infrared regions of the spectrum, whereas the long-wavelength cutoff in the Mariner experiment was at 4300 Å (*2*). The (1-0) band of the first positive system may, however, have been detected in the earth's dayglow by Wallace and Broadfoot (*13*).

The second positive system of N_2 has definitely been observed in the dayglow of the earth (*4*). The (0-0) band at 3371 Å has an overhead intensity above 165 km of 400 rayleighs, and is perhaps the obvious feature to seek in the Mariner spectra. However, our calculations indicated that the intensity of the entire band system on Mars is less than 10x rayleighs. The (0-0) bond has an intensity of less than 3x rayleighs. The difficulties in the detection of such a weak emission in the martian dayglow are enhanced since the (0-0) band of the second positive system of N_2 overlaps the strong (0-1) band of the $A^2\Pi_u$-$X^2\Pi_g$ system of $CO_2{}^+$.

The Lyman-Birge-Hopfield system provides no more encouragement. From electron impact we predict an intensity of 50x rayleighs for the entire band system. The strongest band, (3-0) at 1354 Å, has a predicted intensity of 2x rayleighs but is blended with a strong oxygen emission already reported at 1356 Å (*2*).

Other band systems of N_2 are also produced by photoelectron impact. Their intensities, however, are less than the values discussed above. Of particular interest is the first negative system of $N_2{}^+$ whose (0-0) band at 3914 Å is a prominent feature of the earth's dayglow (*14*). Several mechanisms contribute to excitation of emission at 3914 Å and we estimate a total intensity for Mars of about 7x rayleighs, in harmony with an earlier discussion by Dalgarno and Degges (*15*). The predicted intensity for emission from the first negative system is therefore comparable to that discussed earlier for the Vegard-Kaplan bands. The emission occurs, however, in the same spectral region as the (4-2) and (5-3) bands of the $\tilde{A}^2\Pi_u \rightarrow \tilde{X}^2\Pi_g$ system of $CO_2{}^+$, the predicted intensities for which are about 1 kilorayleigh. Again we conclude that the N_2 mixing ratio at high altitudes could be as large as 5 percent.

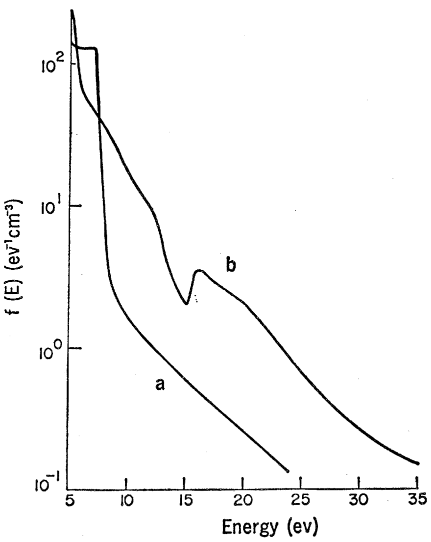

Fig. 1. Equilibrium electron energy distributions (curve a) on Mars at 187 km and (curve b) on the earth at 200 km (× 10).

For all calculations reported here we adopted a uniformly mixed atmosphere. The intensities of photoelectron-excited emissions would be increased by a factor of 2 if diffusive separation occurred above 125 km, but the accuracy of our predictions is not better than a factor of 2 in any case. Of greater significance is the effect of the height of the turbopause on the altitude dependence of the mixing ratio of N_2 to CO_2. If the turbopause occurs at 125 km, the surface mixing ratio is 0.35; if the turbopause occurs at 100 km, the surface mixing ratio is 0.15 times, and if at 80 km, 0.07 times the value of the mixing ratio at 200 km. The extent of mixing on Mars is uncertain. The atmosphere may be uniformly mixed up to the emission altitudes. If so, the presently available observational and laboratory data do not exclude the possibility that the N_2 mixing ratio in the martian atmosphere is consistent with a model for atmospheric evolution in which N_2 and CO_2 are added to the atmosphere by outgassing from the solid body. The volatile gases, with the exception of H_2O, may be present in the martian atmosphere in the same proportions as in the earth's atmosphere-ocean system. If, however, the eddy mixing coefficient in the martian upper atmosphere is similar to that observed for the earth, namely, 5×10^6 cm^2 sec^{-1}, then the turbopause should be at 90 km and, according to the analysis presented here, this would place a limit of about 5×10^{-3} on the mixing ratio of N_2 to CO_2.

In summary, we argue that the ultraviolet spectrometer data from Mariners 6 and 7 are consistent with a mixing ratio of N_2 in the martian atmosphere as large as 5 percent, if eddy mixing is extremely efficient. If the eddy mixing coefficient is similar to that for the earth, the limit is reduced by a factor of about 10. The most sensitive emissions for the detection of N_2 appear to be the Vegard-Kaplan band system of N_2 and the first negative system of $N_2{}^+$. The emission associated with the Vegard-Kaplan band system is relatively brighter in the martian dayglow than in the earth's dayglow since the metastable $A^3\Sigma_u{}^+$ state is not strongly quenched by CO_2 and since competing energy-loss processes for photoelectrons below 7 ev are slow in a predominantly CO_2 environment.

A. DALGARNO
Harvard College Observatory and
Smithsonian Astrophysical Observatory,
Cambridge, Massachusetts 02138
M. B. MCELROY
Kitt Peak National Observatory,
Tucson, Arizona 85717

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