phere in contact with it, since the temperatures are the same. In the spring, winds may be more prevalent and stronger than in the winter. If the wind regime is symmetric and the air flow at the surface is from south to north, the cold air at the polar cap displaces the warmer air over the adjacent clear ground. The CO_2 gas produced in the sublimation will reinforce this effect. Thus the temperature of the air moving over the CO_2 deposit will be essentially that of the deposit, so that conductive effects will be absent. If the winds are not symmetric, then some warmer air may flow over the cap. Its effect in conductively heating the CO_2 deposit will be diminished by the boundary layer at the temperature of the surface, which hinders conductive heat transport to the surface (*9*). We realize the qualitative nature of this discussion, but we believe that it is reasonable, particularly in view of the low density of the Martian atmosphere.

Various other temporary bright patches have been observed on Mars. Slipher (*3*) discussed morning frost patches of "islands in the south" over Martian light areas during the summer and early fall between $\phi = 60^\circ$ and 70°S. This is precisely what is expected if these areas were valleys. The minimum nighttime temperature for those latitudes in that season might be just low enough for CO_2 condensation to occur (*8*, fig. 2) in regions of higher $p_s(CO_2)$. The CO_2 frost would then vaporize daily as the surface warms up on exposure to Sun. The same reasoning might apply to the light area Hellas which is "often snow-covered, and in winter forms a vast extension of the polar cap down to latitude 30°" (*13*).

Bright patches have been occasionally observed on the light area Nix Olympica at $\phi = 20^\circ$N in summer (*7, 14*). Although it is clear that CO_2 cannot condense under these conditions, H_2O ice might form either in the atmosphere or on the surface of Nix Olympica. We suggest that this area is also depressed, since the partial pressure of the atmospheric H_2O would be higher in the lower areas. The conditions for condensation of H_2O in the Martian atmosphere will be somewhat different from those in our own atmosphere. For example, the negligible heating effect of the Martian atmosphere on its surface will have the following implications: The severe nightly cooling of the surface will form a pronounced inversion with a very cold boundary layer. This occurrence, together with the higher H_2O partial pressure in the depressions, will form fog or frost. Whether or not this analysis is applicable to all of the observations of bright patches is not clear—it requires a detailed study of the circumstances of each observation.

It has been frequently suggested that the deserts are elevated (*3, 6, 7*). Rea (*15*) favored the idea that the light areas are lower because dust storms, which sometimes obscure even the dark areas but consist of material from the light areas, settle back into the light areas. It would be difficult to imagine dust settling preferentially in areas of higher elevation. Wells (*16*) argued that the dark areas are elevated because of the tendency for white clouds to remain over light areas bordering dark areas, which he interpreted as being a result of lee waves formed by mountainous Martian maria. The results of our study support this thesis that the light areas are depressed.

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25 November 1966

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Frost Phenomena on Mars

Abstract. *The hypothesis that the Martian wave of darkening might be a frost-heaving phenomenon has been examined. Consideration of the water-vapor sorption characteristics of a silicate mineral surface at temperatures below freezing leads to the conclusion that, without strongly deliquescent salts to attract and retain liquid water in the Martian soil, frost-heaving phenomena are not to be expected on Mars. On the other hand frost-heaving phenomena involving the freezing and thawing of ammonia may be common in the soils of Jupiter.*

Otterman and Bronner have suggested (*1*) that the dark regions on Mars may be caused by small-scale surface roughening associated with frost phenomena in the Martian soil. Frost phenomena common on earth are frost heaving (including needle-ice formation as a special case), the formation of hoar frost at or below the surface, the formation of massive ice bodies exemplified by ice wedges, ice lenses, and pingos found in the terrestrial arctic, and finally, the simple freezing *in situ* of soil water. Of these phenomena only frost heaving produces changes in the texture of the soil surface of the type required by the hypothesis of Otterman and Bronner.

The principal requirements for frost heaving in the terrestrial environment are (i) a temperature gradient with temperatures below freezing at the soil surface but above freezing at depth; (ii) soil water in the liquid state available at depth for transfer to the freezing zone; (iii) soil containing a significant proportion (5 to 20 percent or more) of fine particles (50-μ diameter or less). Frost heaving occurs when soil water is drawn upward from unfrozen regions to the freezing zone where it then accumulates as ice. During crystallization the tendency to exclude solutes and particles at the interface between ice and water results in the growth of segregated ice lenses. This disturbance often is expressed in changes in the configuration of the soil surface, and in various ways it can lead to roughening. The rate and extent of frost heaving depend critically on a favorable balance between the movement of soil water to the growing ice lenses and removal of the latent heat of freezing. This balance is governed by the initial water content of the soil, the depth to the water table, the hydraulic and thermal conductivity, the thermal regime during freezing, and the overburden pressure. When conditions are at an optimum (porous, water-saturated soil, with temperatures just below freezing) needle ice of the type shown by Otterman and Bronner to illustrate their hypothesis may grow to a height of several centimeters overnight. Heaving rates invariably diminish rapidly with an increase in distance to the groundwater table. For a water table at 300 cm, heaving rates usually do not exceed 0.1 mm/hr (*2*), and such slow rates of heave are seldom observed to roughen or otherwise greatly disturb the soil surface.

Studies of frozen earth materials in several laboratories, including ours, have established that the contact between ice and soil mineral surfaces consists of an interfacial zone of water that has liquid-like properties above approximately −20°C. It is now generally thought that the existence of an unfrozen, liquid-like interface through which water moves and redistributes itself under a growing ice lens is an essential requirement for frost heaving. The thickness of this zone of unfrozen interfacial water is greatly affected by temperature (*3*). The temperature effect for kaolinite and two homoionic montmorillonites is shown in Fig. 1 (*4*). Above −1°C the unfrozen, interfacial zone may be many molecular layers in thickness, and, as conductance and electroosmotic measurements have shown, the unfrozen water in this zone has a relatively high mobility (*5*). Water molecules in this thick interfacial zone experience only relatively slight restrictions due to adsorptive forces as they move to growing ice lenses; frost heaving is thus facilitated and may proceed rapidly. Below −5°C, the thickness of the interfacial zone is reduced to only one or two molecular diameters, and the ease with which water can be moved is correspondingly less. Consequently, at soil temperatures below −5°C ice-lens growth is greatly inhibited. Although an "unfrozen" interfacial zone appears to exist down to −180°C or lower (*6*), below about −20°C the mobility of water in the interfacial region is exceedingly low so that the time required for ice-lens growth must be measured in years, if such growth occurs at all.

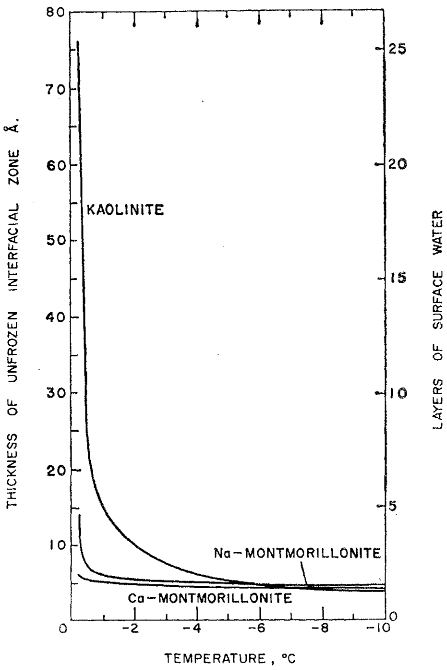

Fig. 1. Unfrozen water content plotted against temperature for three representative clays [after Nersesova and Tsytovich (*3*)].

In relation to freezing and thawing phenomena, conditions on Mars differ from conditions prevailing on Earth in two important ways: the quantities of water in the atmosphere and on the surface of Mars are very small, and the Martian temperature regime is characterized by much lower temperatures. The water vapor content of the atmosphere of Mars is uncertain; estimates range from about 10^{-3} to 10^{-5} g per square centimeter of planetary surface (*7*). The Mariner IV occultation experiment established with little doubt that the pressure of the Martian atmosphere is less than 10 mb and that carbon dioxide is the major constituent (*8*). Leighton and Murray (*9*) have examined this problem and report that the thermal model they consider to represent conditions best on Mars suggests that frozen CO_2 is the dominant substance making up the polar caps on Mars and that the temperature regime is such that frozen CO_2 permafrost exists under the ice cap and elsewhere in the Martian soil. They do not rule out the likelihood of ice being present, however, but conclude that if one accepts an atmospheric water vapor content of 10^{-3} g/cm^2, frozen water permafrost may exist to unknown depths at all latitudes poleward of 40° to 50°. This follows from the fact that soil temperatures at depth in these regions are expected to be perpetually lower than the corresponding 190°K sublimation temperature; therefore these regions may be regarded as serving as a low-temperature trap for water vapor. Since water vapor is a minor constituent in the atmosphere it follows that if the total atmospheric pressure is 10 mb or less, then the partial pressure of water vapor at any place on Mars is almost certainly below the triple-point pressure (6.3 mb). This means that the occurrence of free water in the liquid state is exceedingly improbable. Conceivably, small quantities of liquid water could exist briefly during late stages of sublimation of the polar caps, and strongly deliquescent salts, if present, could lead to liquefaction as suggested by Leighton and Murray; but it is generally conceded that solid-liquid phase changes are rarely if ever possible on Mars. Anticipating objections based on these facts, Otterman and Bronner suggest that freezing might proceed as follows:

$$\text{water vapor} \rightarrow \text{adsorbed soil water} \rightarrow \text{ice} \quad (1)$$

It is of interest to examine this possibility further. Experimental data on adsorption of water vapor and contents of unfrozen water, adequate for a discussion of the possibility of frost heaving on Mars, are available only for the mineral montmorillonite. Fortunately, however, the adsorption characteristics of montmorillonite surfaces are sufficiently representative of silicate surfaces in general to warrant a discussion based on these data and to justify the resulting conclusions.

Mooney, Keenan, and Wood (*10*) have determined water vapor adsorption isotherms at 0° and 20°C for sodium montmorillonite. There are no available data for temperatures below 0°C, but it is possible to compute water-vapor adsorption isotherms at subzero temperatures from the data of Mooney, Keenan, and Wood by means of a thermodynamic equation giving the change in relative vapor pressure with temperature at constant water content (surface coverage). The equation is:

$$\ln\frac{(p/p_0)_2}{(p/p_0)_1} = \frac{(\bar{H}_w - H_i^0)\,(T_1 - T_2)}{RT_1\,T_2} \quad (2)$$

in which p is the vapor pressure of the sorbed water; p_0 is the vapor pressure of ice at the temperature in question; T is the absolute temperature; and $(\bar{H}_w - H_i^0)$ is the difference in the partial molar enthalpy of the sorbed water and that of ice. The only assumption involved in the derivation of Eq. 2 is that $(\bar{H}_w - H_i^0)$ does not change appreciably with temperature. To use Eq. 2, $(\bar{H}_w - H_i^0)$ is identified as equivalent to $(\bar{H}_w - H_l^0) - (H_i^0 - H_l^0)$, where H_l^0 is the enthalpy of pure water at 0°C. The first of these two terms is the differential heat of wetting; the second is simply the heat of freezing pure water (−1435.5 cal/mole at 0°C). The data of Mooney, Keenan, and Wood provide $(\bar{H}_w - H_l^0)$ and $\ln p/p_0$ at 0°C for a number of water contents. Hence it is possible to compute estimates of p/p_0 for these water contents at lower temperatures.

Some results are shown in Fig. 2 in which the relation between the relative vapor pressure and water content is given for six temperatures, from −10°C to −250°C. The ordinate on the right gives the number of adsorbed water layers, if one assumes that the water is distributed evenly over the entire surface area (8×10^6 cm^2/g) of the mineral. To illustrate the meaning and significance of Fig. 2, consider first the −10°C isotherm. At the saturation vapor pressure of ice, the isotherm intersects the right-hand ordinate at a surface coverage only slightly greater than a monolayer. For all relative pressures less than 1.0 this silicate surface adsorbs correspondingly less water. One then notes that the effect of a decrease in temperature is, at all relative pressures, to diminish the amount of water adsorbed.

Adsorption isobars computed from Fig. 2 for possible partial pressures of water vapor in the Martian atmosphere are given in Fig. 3. In addition, this figure displays the phase composition of water in the montmorillonite–water system. The dotted curve gives the maximum adsorbed, unfrozen water content possible at the various temperatures. Above these water contents, an increasing proportion of the water is present in the form of ice, and it is thus segregated from the adsorbed phase. Below the solidus all the water present exists in the more liquid-like, adsorbed state.

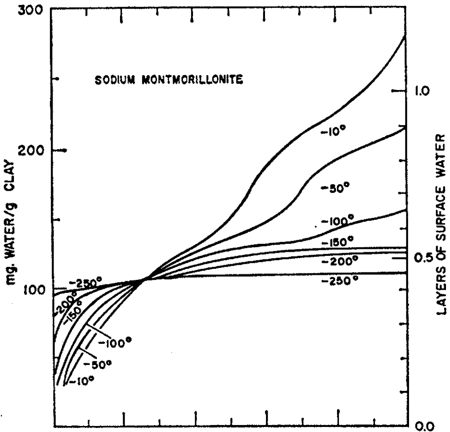

Fig. 2. Calculated water adsorption isotherms for sodium saturated Wyoming bentonite.

Two salient facts emerge from a study of Figs. 2 and 3. First, silicate or silicate-like surfaces exposed to the atmosphere of Mars cannot be expected normally to attract and retain more than a monolayer of adsorbed water. Second, if the water content could somehow be raised to provide thicker adsorbed layers, the result would be the formation of frost or ice. In any case, therefore, the unfrozen, interfacial water could seldom, if ever, exceed a monolayer; moreover, for interfacial films approaching a monolayer in thickness, the temperature almost certainly must be below −20°C. As pointed out earlier, below −20°C the mobility of this surface-held water is exceedingly low; thus it appears that the thinness of the adsorbed water films and the low mobility of these thin films at temperatures encountered on Mars virtually preclude the possibility of soil-water movement to growing ice lenses so that frost heaving on the scale required in the hypothesis of Otterman and Bronner is highly improbable. It may also be said that the amount of water vapor that could be sorbed by silicate particles of colloidal size is too low to expect swelling and shrinking phenomena associated with surface hydration. One concludes, then, that optically significant changes in the surface texture of Mars of the kind that would explain the regime of the dark regions are not caused by phenomena associated with water vapor sorption or freezing.

The foregoing arguments are valid if the water content of Martian atmosphere does not exceed 10^{-3} g/cm^2 greatly, and if the water vapor sorption characteristics of the Martian soil do not greatly exceed the capacity of terrestrial soil materials. If, however, Martian soils contain large quantities of deliquescent salts, for example, frost-heaving phenomena again become a possibility, for it is obvious that the presence of a strongly deliquescent salt could greatly increase the water vapor sorption capacity of any soil material. The presence of the salt would also lower the freezing temperature of the soil water. This, in effect, would shift the curves of Fig. 1 to the right and, conceivably, could result in unfrozen interfacial films with the mobility required for frost heaving. Experimental data bearing on this point are lacking, and hence a definite conclusion is not possible. Consequently, the conclusion mentioned in the preceding paragraph must be limited in order to admit the possibility of frost heaving if strongly deliquescent salts are present in the Martian soil.

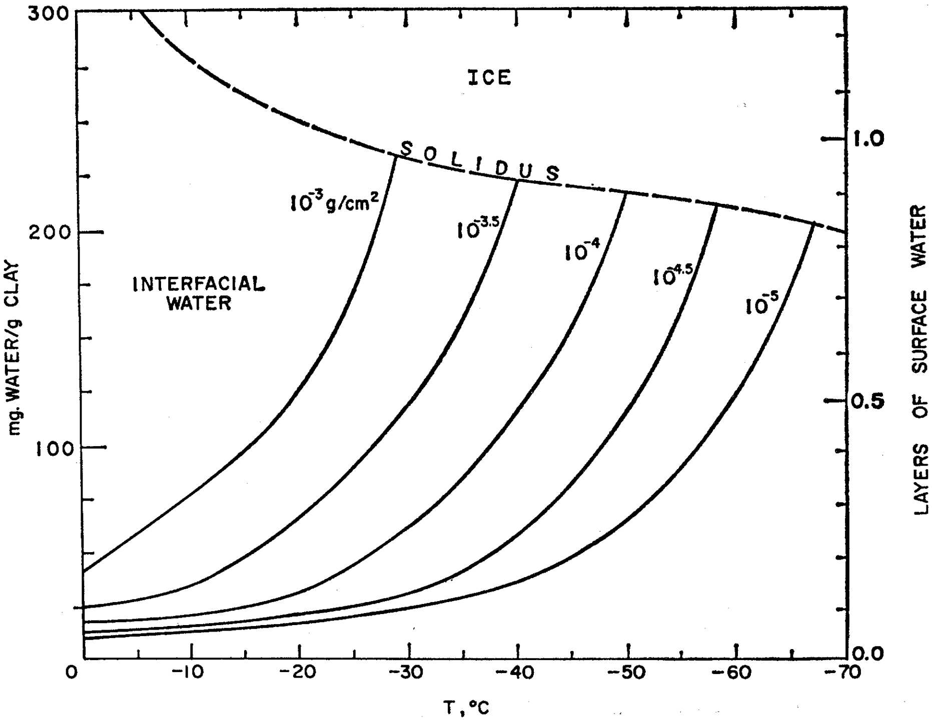

Fig. 3. Calculated water adsorption isobars (solid lines) and maximum adsorbed water content (dashed line) for sodium saturated Wyoming bentonite.

In passing, it may be said that frost heaving involving CO_2, the major constituent of the Martian atmosphere, and probably also of the polar cap, is not a likely possibility, for the temperature and pressure conditions on Mars do not at any point lie within the liquid field of the phase diagram for CO_2; and, as stated above, the existence of a mobile liquid-like layer seems to be a requirement for the separation and growth of an ice lens. However, it is worth mentioning that frost heaving due to the freezing of NH_3 is a very real possibility on Jupiter. Spectral analysis has established that NH_3 is a major constituent of the Jovian atmosphere. In fact, it is thought that the thick cloud blanket of Jupiter is largely due to small crystals of NH_3.

Infrared radiation from the top of the cloud layer has established the temperature there to be about 130°K. Murray, Wildey, and Westphal (*11*) found that during solar eclipses the temperature observed in the 10-μ region is 185° to 196°K. They explain the temperature rise either as a decrease in opacity of the upper Jovian atmosphere due to a photosensitive reaction or a convective overturn of the atmosphere. In any case, the temperature of the lower atmosphere and on the surface must be about 190°K or possibly greater. Thus liquid NH_3 is possible on Jupiter (m.p. 195.4° K at 1 atm), and Glasstone (*12*) has suggested the possibility of NH_3 rainstorms. Given the possibility of large amounts of the liquid, fluctuating temperatures near the freezing point, and a fine-grained, porous soil, ammonia frost heaving is possible—even probable—on Jupiter.

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11 October 1966

Composition Measurements of the Topside Ionosphere

Abstract. *Data from a magnetic mass spectrometer flown on the Explorer 31 satellite show that the ionosphere above 1000 kilometers usually consists of hydrogen ions as the predominant species. Between this altitude and perigee (500 kilometers) the dominant ion species shifts to atomic oxygen, with a significant amount of atomic nitrogen ions also present. Helium ions are present in small quantities at all altitudes. Other minor ions observed are those of 2, 7, 8, 15, 18, and 20 atomic mass units.*

On 29 November 1965 the Explorer 31 satellite (Direct Measurements Explorer) was launched piggyback with the Canadian Alouette II Topside Sounder from the Western Test Range. The satellites were placed in an 80° prograde, 3000-km-apogee, 500-km-perigee orbit. The Explorer 31 satellite contains experiments designed to measure directly various properties of the earth's ionosphere. This report gives some preliminary data from the magnetic mass spectrometer experiment which identifies the various positive ion species in the ionosphere and gives their relative abundances.

The instrumentation flown in this experiment consists of a small magnetic sector-field mass spectrometer. There is no ion source employed in the instrument, since it is designed to measure the relative abundances of the positive ions formed in the upper atmosphere by natural processes. The operating potentials are adjusted to permit thermal energy ambient ions to enter the mass spectrometer through an aperture in the side of the satellite. These ions then pass through the magnetic analyzer having a 1½-inch (3.8-cm) radius (the permanent magnet has a field strength of 2200 gauss) and into an electron multiplier. A 5-decade logarithmic solid-state electrometer amplifier measures the output current from the electron multiplier. The mass spectrum from 1 to 22 amu (atomic mass units) is continually swept by an exponentially decreasing voltage having a 3-second period.

Figure 1 shows a portion of an analog telemetry record taken from the satellite. A monitor of the sweep voltage is shown in the top channel and the mass spectrum appears below. The mass peaks are identified by mass number (amu). The amplitude of the peaks is given in volts, this voltage being proportional to the logarithm of the ion current detected by the electron multiplier for each ion species. This ion current is a function of the number density of that species in the vicinity of the satellite.

The satellite is oriented so that its spin axis is normal to the orbital plane. Thus, the mass spectrometer entrance aperture on the side of the satellite alternately points along the satellite velocity vector and opposite to it. Since the satellite is traveling at a speed equal to or greater than the mean velocity of the ambient ions, there is a ram and wake effect exhibited in the data as a modulation of the ion peak amplitudes. The satellite spin period is approximately 7 sweep periods. Figure 1 shows one roll-modulation cycle of data. The mass 1 peak amplitude is relatively constant while the heavy ion (mass 14, 16, 18) peaks are absent in nearly half of the spectra.

Figure 2 is a plot of the peak amplitudes of successive mass spectra as a function of time. These data were obtained from the Fort Myers, Fla., tracking station on 14 March 1966 between 1331 and 1334 GMT. The satellite altitude was 600 km at the left side and 700 km at the right side of the figure. It should be noted here that the amplitude of the roll modulation is a strong function of ion mass. For hydrogen (H^+), it is about 1 order of magnitude; for helium (He^+), 2½ orders of magnitude; and for oxygen (O^+), more than the 5 orders of magnitude shown in the figure. This results from the satellite velocity being large compared to the thermal velocity of the oxygen ion.