In earlier papers, we have considered the occurrence of water and permafrost on Mars (1, 2, 3, 4), some important questions relating to the phases and physical states of water and ice on Mars (5, 6), and their terrestrial analogues (7, 8), and some of their possible consequences in forming Martian landscapes (9, 10, 11). This paper focuses on the water-ice phase composition, adsorption-desorption and evaporation phenomena, and brine compositions of six antarctic soils that are considered to be good terrestrial analogues of the Martian surface materials.

The water-ice phase composition diagram is shown in schematic form in Figure 1. Water-ice phase composition data for a very large number of frozen terrestrial soils can be adequately represented in this manner, although important, second order, deviations have been recognized in certain special cases (6). The diagram in Figure 1 represents the general equilibrium that is established between ice formed within a particulate matrix and the water remaining unfrozen when temperature, solute concentration, etc. are fixed. All evidence available to date indicates that the ice formed is normal, hexagonal ice I, although differential scanning calorimetry has revealed certain complexities in the release of latent heat on freezing that have been ascribed to the presence of complex phases in the unfrozen, interfacial water. Similarly, anomalous melting behavior also has been observed (11).

Figures 2 and 3 show the water-ice phase composition for one of the six Antarctic soils from the lower Wright Valley (Site 1, Figure 4) Antarctica studied in this investigation. Values of the quantity of water remaining in the unfrozen state as a function of temperature are given when this equilibrium is approached in both cooling and warming cycles. As is evident from these data, the agreement is extremely good, indicating that the transfer of water from one phase to another is nearly reversible. Small discrepancies, when they occur, are attributed to capillary and interfacial effects that cannot be easily controlled.

That equilibrium exists between the vapor phase, also, can be demonstrated. Figure 5 shows the desorption isotherm of water in montmorillonite clay at -5 degrees C. The isotherm cuts the ordinate sharply at a relative humidity of 100% precisely at the value of the unfrozen water content of an ice containing frozen sample of the same montmorillonite clay at -5 degrees C. The results of many experiments have
verified that as water vapor is pumped away from the frozen ice containing clay, the unfrozen water content remains constant until the solid phase is removed. Only after all the ice is gone, does subsequent removal of water vapor deplete the unfrozen interfacial water phase.

Figure 6 shows the evolution of adsorbed water vapor (mass 18) on heating one of the six Antarctic soils in this investigation. Similar curves were obtained for each of the six samples investigated. The detector in this case was a scanning mass spectrometer functioning as an effluent gas analyzer. In addition to measuring the water vapor release, it also measured the release of other volatiles. Release curves were obtained for NO, SO, O, N and CO₂, the most abundant volatile component species of the natural brines present in these soils. The curves for NO (mass 30) and CO₂ with N₂O (mass 44) are included in Figure 6.

The water-ice phase composition curves in Figures 2 and 3 reflect the presence of the natural brines that decompose on heating to yield the mass 30 and mass 44 curves in Figure 5. The values of the water remaining unfrozen at a given temperature are larger in the case of the natural soils than those observed when they are washed free of the brines and again subjected to a determination of the water-ice phase composition curve. The effect of the presence of these brines can be predicted from theory as was done in an earlier paper by Banin and Anderson (12). The difference between the two curves shown in Figures 2 and 3 are consistent with the prediction of their equation 9.

Atmospheric exchange of water vapor with the Martian regolith involves a number of dynamic processes. Some of these involve changes of phase as illustrated in the data shown above. Whenever a change of phase occurs, there is an accompanying latent heat effect. As these data show, latent heat effects in terrestrial soils are not isothermal; they are involved at nearly all stages when ground temperatures fluctuate. This has been graphically shown in diagrams such as those in Figures 7 and 8. Calculations done for temperature fluctuations in Arctic permafrost have shown that these effects are not negligible, but they are relatively easy to include in theoretical calculations (13).

In addition to correlating a number of experimental measurements, all relating to the composition and behavior of permafrost and frozen ground, this discussion illustrates the general utility of a Differential Scanning Calorimetry / Effluent Gas Analysis (DSC/EGA) instrument such as was proposed earlier for the Viking Lander Mission and more recently, for the Comet Rendez-vous and Asteroid Flyby (CRAF) mission (14). Data obtainable from a properly designed and operated DSC/EGA instrument can provide the
means of deducing the answers to many of the questions that have been posed in the papers presented in this workshop.

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Figure 1. The generalized water-ice phase diagram for frozen soil and permafrost. Note that the total sample water content is the sum of the ice content and the unfrozen water content at any given temperature.

Figure 2. Water-ice phase composition data for Antarctic soil No. 1 obtained during a cooling cycle.

Figure 3. Water-ice phase composition data for Antarctic soil No. 1 obtained during a warming cycle.

Figure 4. Location map: sample No. 1 was obtained at site 1.
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Figure 5. Water vapor desorption isotherm for sodium saturated montmorillonite illustrating the maximum amount of unfrozen water that can exist at -5°C.

Figure 6. The evolution of H₂O, CO₂, N₂O and NO on heating Antarctic soil No. 1 from 100°C to 550°C.

Figure 7. Scanning calorimeter traces for montmorillonite No. 26 containing no salt (warming curves).

Figure 8. Scanning calorimeter traces for montmorillonite No. 26 containing salt (warming curves).