Infrared Absorptions near Three Microns Recorded over the Polar Cap of Mars

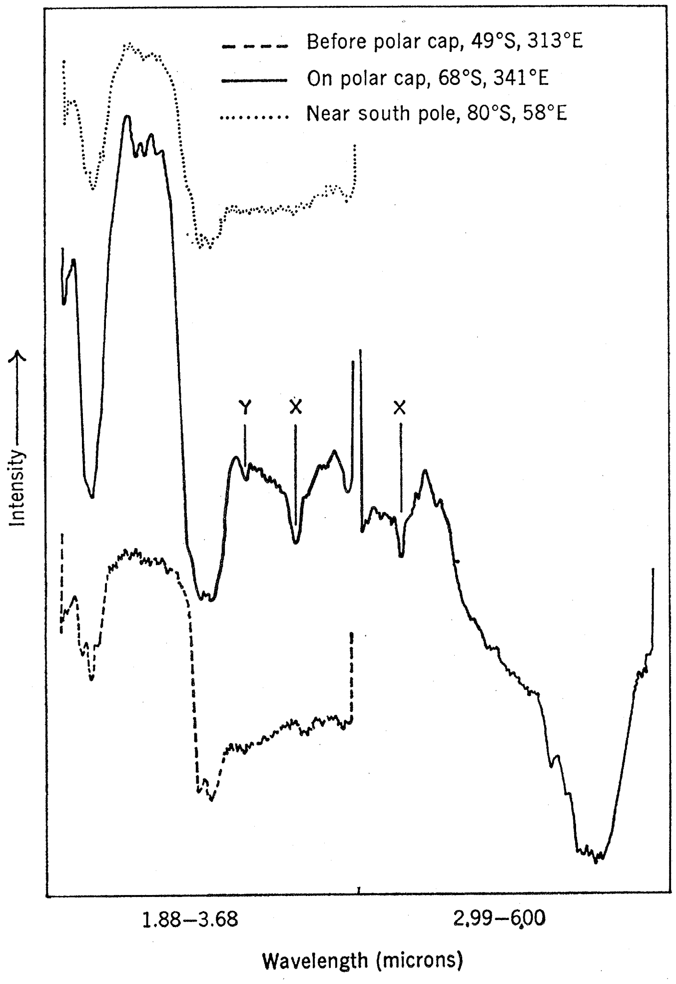
Abstract. *During the Mariner 7 flyby of Mars, the infrared spectrometer recorded distinct, sharp absorptions near 3020 and 3300 reciprocal centimeters between 61°S and 80°S, at the edge of the southern polar cap, with maximum optical density near 68°S and 341°E. These bands, which match in frequency the* ν_3 *bands of methane and ammonia, can be associated with previously unreported spectral features of solid carbon dioxide exceeding 1 millimeter in thickness. Possible reasons for the geographic localization are discussed.*

The Mariner 6 and 7 spacecraft (*1*) each carried an infrared spectrometer (*2*) that scans the spectral region from 1.9 to 14.3 μ every 10 seconds. The instrument telescope has a field of view of 2 degrees; thus at closest approach (~ 3100 km), the geographical area sampled is about 120 km square. A circular variable-transmission interference filter (*3*) provided a spectral resolution of 0.5 to 1 percent. Every 12th spectrum was recorded through a polystyrene film to provide frequency and photometry calibration *in situ*. We present here spectral observations in the spectral region near 3 μ during the Mariner 7 flyby on 4 August 1969.

Figure 1 shows a spectrum typical of those recorded at latitudes near the martian equator. Most of the spectral features are attributable to CO_2, the predominant atmospheric constituent. Also visible are two features near 2150 cm^{-1} attributable to the P and R branches of carbon monoxide and a broad absorption near 3250 cm^{-1} attributable to solid H_2O or, perhaps, to surface hydrates. A portion of the 3-μ region is recorded twice on either side of the radiometer spike, as shown by the instrumental background absorption at 2980 cm^{-1}. Spectral resolution is slightly higher in the low-frequency recording of the 3-μ overlap region.

The infrared spectrometer first viewed the planet on 4 August at 04 hours 48 minutes 54 seconds G.M.T. [all times are G.M.T. data receipt times (*4*), 5 minutes and 32 seconds after the data were recorded at Mars] at 20°N and 345°E. The instrument view swept south to 13°S and 5°E. During this period, 18 spectra were recorded, and none showed any evidence for atmospheric absorptions between 2900 and 3100 cm^{-1}.

At 04 : 51 : 41 G.M.T. the Mariner 7 scan platform was pointed so that the spectrometer viewed an area at 45°S and 315°E, 15 degrees north of the edge of the polar cap. Figure 2 shows a sampling of spectra recorded as the scan track passed onto the polar cap, moving toward the martian south pole. At 62°S and 330°E (04 : 54 : 51 G.M.T.) there were two distinctive spectral changes which indicated that the field of view of the spectrometer was directed toward the polar cap. Near 2.7 μ the brightness increased by 60 percent, and at 2.0 μ the triplet structure of the gaseous CO_2 absorption was lost and the peak intensity of



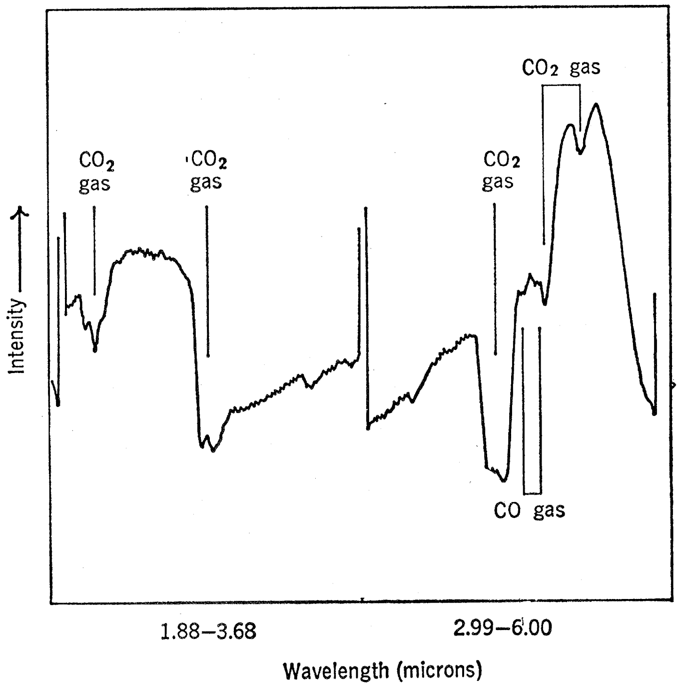


Fig. 1 (left). Near-infrared spectrum recorded at 0°N, 359°E.

Fig. 2 (right). Near-infrared spectrum recorded over the southern polar cap.

the feature more than doubled. In this same spectrum, two new absorptions are clearly recorded, *X* and *Y* (the *X* feature is recorded twice on either side of the radiometer spike). These features are recorded in every one of the subsequent 18 spectra. Both intensities grow, reaching maxima near 68°S and 341°E (4 : 56 : 05 G.M.T.) and then steadily decreasing, becoming almost indiscernible at 78°S, 20°E (4 : 58 : 11 G.M.T.). These two absorptions were detected again as the scan platform slewed back to northerly latitudes at a time approximately corresponding to that at which the spectrometer view would pass over the edge of the polar cap, but in none of the 120 spectra recorded at latitudes more northerly than the edge of the polar cap. Plainly, the *X* and *Y* absorptions are geographically concentrated near 68°S and localized over the edge of the polar cap, 61° to 80°S (*5*). The edge of the martian polar cap at the date of encounter was near 60° to 61°S.

An on-board measurement of the frequency is provided by the polystyrene calibration spectrum. Laboratory spectra measured before the launch of the Mariner 7 spectrometer indicated that this particular polystyrene film has absorption features centered at 2940 and 3050 cm^{-1}. Linear interpolation gives two independent measurements of the *X* frequency, 3020 and 3027 cm^{-1}. A less accurate estimate of the *Y* frequency obtained by extrapolation is 3294 cm^{-1}.

The most accurate determination of *X* and *Y* frequencies is based upon laboratory reference spectra recorded with the Mariner 7 spectrometer before launch. Figure 3 shows the superposition of a laboratory spectrum of a gas sample containing about 0.2 m-atm each of methane and ammonia pressure-broadened by 1 atm of air. The Q-branch frequency of the laboratory methane ν_3 band at 3020.3 cm^{-1} matches the *X* frequency in both left and right spectra within the possible accuracy, which we estimate to be ± 15 cm^{-1}. Similarly, the Q-branch frequency of the laboratory ammonia ν_1 band at 3336.7 cm^{-1} matches the *Y* frequency. The bandwidths at half height are estimated to be about 30 cm^{-1}, to be compared with an expected resolution of 24 cm^{-1}.

The identification of these features is of particular interest because of the close frequency match to bands of methane and ammonia, molecules that might have biological origin. These bands were not initially associated with the spectrum of solid CO_2 for a number of reasons:

1) The intensities of the *X* and *Y* features do not correlate uniformly with each other or with the intensity of the rather intense solid CO_2 absorption near 4900 cm^{-1}. For example, the ratio of optical density at 4900 cm^{-1} to that at 3020 cm^{-1} varies by as much as a factor of 2, sometimes in successive spectra.

2) No features have been attributed to solid CO_2 at these frequencies in the spectra reported in the literature (*6, 7*).

3) No features were detected at these frequencies in our laboratory spectra of solid CO_2 recorded before launch with the Mariner instruments or with conventional infrared spectrometers.

4) These features became quite indistinct during the Mariner 7 scan period while the spectrometer was still viewing the polar cap between 79° and 80°S.

Nevertheless, we felt it necessary to prove that these features could not be due to solid CO_2 since the spectra recorded near 68°S are so heavily dominated by spectral features obviously attributable to solid CO_2. Accordingly, two kinds of experiments were performed to test this possibility.

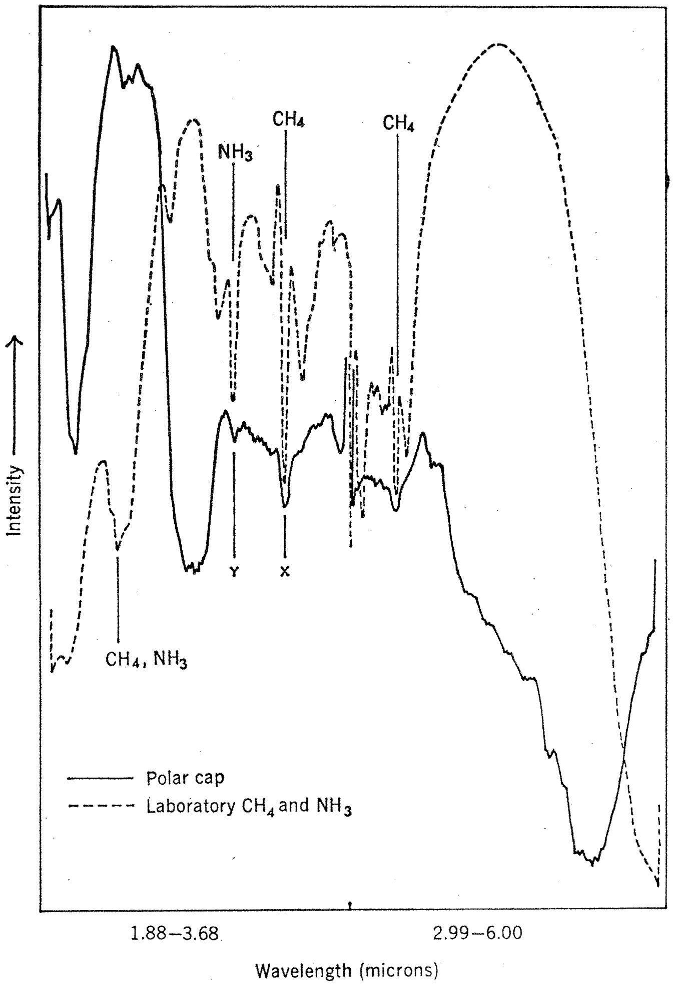
A flight model spectrometer identical to the Mariner instruments was placed in an evacuated environmental chamber with wall temperatures of 77°K. The spectrometer telescope viewed at normal incidence a stainless steel plate that filled the field of view. The steel plate, which has an emissivity of 0.3 at 3 μ, was cooled to 77°K. Gaseous CO_2 (Matheson) was allowed to condense upon this plate at a thickness rate of 0.7 mm per hour. The spectrum of the solid was then periodically recorded in the 2- to 4-μ region under illumination by a concentric ring of tungsten filaments heated to about 2800°K. At the center of the sample, the angle between the optical path and the direction of illumination could be selected to be 73, 55, or 33 degrees. Figure 4 shows a typical "reflection-absorption" spectrum recorded with a sample thickness near 2 to 3 mm. Absorption features corresponding to the *X* and *Y* features are clearly visible in the thickest samples. A mass spectrometric analysis of the carbon dioxide used showed that less than 10 parts per million CH_4 or NH_3 were present as an impurity.

In addition, using a conventional cold cell (*8*) and a Beckman IR-7 spectrophotometer, we recorded transmission spectra of thick solid CO_2 samples. Gaseous CO_2 (Matheson) was deposited at a rate of 0.005 mole per hour onto a CsI salt window held at 77°K [the temperature was measured with a thermocouple (Au-Co versus Cu) embedded in the window]. The transmission spectrum was recorded with a solid sample 1.5 mm thick. A distinct absorption at 3013 cm^{-1} was observed, and absorption near 3350 cm^{-1} was discernible, though not distinct. This same sample displayed no absorption at 1305 cm^{-1} that could be attributed to methane suspended in solid CO_2 (*9*).

At first consideration, it seems surprising that these absorptions have not been reported earlier. Herzberg (*10*), for example, does not list them among the 43 transitions observed in the infrared and Raman spectra of gaseous CO_2. Nevertheless, there are possible transitions that correspond to these frequencies. The transitions $(0,0,0) \rightarrow (0,1,1)$ and $(0,0,0) \rightarrow (1,3,0)$ are calculated to be near 3016 and 3320 cm^{-1}, respectively. The first transition is harmonic oscillator–forbidden (as a binary combination), and it is also selection rule–forbidden $(g \not\leftrightarrow g)$. The second transition is harmonic oscillator–forbidden (as a quaternary combination). Among the 43 transitions listed by Herzberg, none involve odd changes of both quantum numbers ν_2 and ν_3 as required for the transition at 3016 cm^{-1}.

Solid CO_2 has crystal symmetry T_h, and the CO_2 molecules occupy sites of symmetry C_{3i} with four molecules per unit cell (*6*). The combination of ν_2 (symmetry Π_u) and ν_3 (symmetry Σ_u+) gives a state of symmetry Π_g which does not lead to an infrared-active component either in the site group or in the factor group analysis. These facts are sufficient to explain the *absence* of the band—we must explain its appearance.

There is, perhaps, an analog in the spectrum of solid oxygen (*11*). Despite a completely forbidden selection rule for this homonuclear diatomic molecule, the fundamental transition at 1549 cm^{-1} can be observed in very thick samples comparable to those used



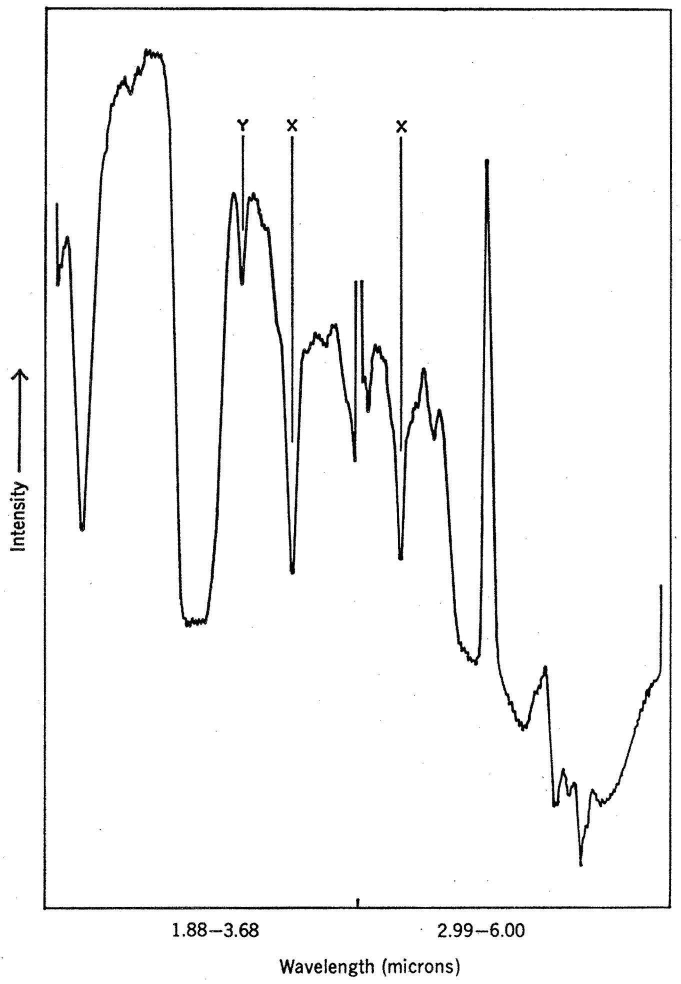


Fig. 3 (left). Calibration with the laboratory spectrum of gaseous methane and ammonia. Fig. 4 (right). Laboratory near-infrared "reflection-absorption" spectrum of solid CO_2 (77°K).

in the present work. In the case of oxygen, the intensity of the forbidden band is sensitively dependent upon deposition conditions; it becomes about four times more intense if the deposition is carried out at 4°K. All of the evidence indicates that the feature appears because of lattice imperfections, a thesis strongly supported by the enhancement of the band after the deliberate addition of inert-gas impurities (*12*). The evidence suggests that the band at 3013 cm^{-1} observed in the laboratory spectra is due to the forbidden (0,0,0) → (0,1,1) transition of solid CO_2, appearing because of lattice imperfections (surface sites, impurity sites, vacancies, stacking faults, or grain boundaries). We believe that the same explanation is probably applicable to the martian spectral feature at 3020 cm^{-1}. The appearance and frequency of the feature are also consistent with the spectrum of gaseous methane, but the more mundane explanation seems more likely (*13*). Though the band near 3300 cm^{-1} was difficult to obtain in transmission spectra, its presence in the "reflection-absorption" spectra suggests that this band, too, should be attributed to solid CO_2.

There remains the need to explain the lack of intensity correlation between the bands at 3020, 3300, and 4900 cm^{-1}, if they are all to be attributed to solid CO_2. Furthermore, we must rationalize the disappearance of these features at the more southerly latitudes if the polar cap near the pole is attributed to solid CO_2. Several possibilities are under investigation. The edge of the polar cap could be shrouded by a solid CO_2 cloud (or fog) which the spectra suggest clears at the more southerly latitudes and more easterly longitudes. This would explain both discrepancies since cloud height, thickness, and coverage could vary during the 10-second period needed to obtain a spectral record. Such a cloud should, however, be detectable through poorer definition in the television pictures near the edge of the polar cap, an observation that has not been reported. If the solid CO_2 we observe is on the ground, then its spectrum at the edge of the polar cap must differ quite significantly from that nearer the pole. The difference may be due to the thickness of the layer, particle size, the inclusion of impurities (such as water), or different growth conditions. It may be significant that the southern polar cap may recede only to latitudes near 80°S.

It is clear that our continuing studies, directed at laboratory reproduction of the spectra of the martian polar cap, will settle more definitely the proper assignment of the two 3-μ features. For the present, the interpretation that they are due to solid CO_2 must be preferred, despite the fact that other questions remain that must be considered further.

KENNETH C. HERR
GEORGE C. PIMENTEL
Chemistry Department and *Space Sciences Laboratory, University of California, Berkeley 94720*

References and Notes

1. Mariner 6 and 7 were NASA missions managed by the Jet Propulsion Laboratory (JPL) and directed by Project Manager H. M. Schurmeier.
2. The spectrometers were designed and constructed by the authors in the Chemistry Department and Space Sciences Laboratory at the University of California at Berkeley. This instrument will be described in detail in a later publication.
3. Provided by Optical Coating Laboratories, Inc., Santa Rosa, California.
4. All times, latitudes, and longitudes are based upon JPL Pegasis calculations made on 8 August 1969 after the encounter. Because the Mariner 7 spacecraft experienced an orbit anomaly before the encounter, these latitudes and longitudes are subject to change as post-encounter tracking refines the actual orbit.
5. There was no trace of either of these absorptions in any of the 150 spectra recorded during the Mariner 6 flyby, which viewed an equatorial region between 13°N and 16°S and between 280°E and 95°E.
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7. D. A. Dows, *Spectrochim. Acta* **13**, 308 (1959).
8. E. D. Becker and G. C. Pimentel, *J. Chem. Phys.* **25**, 224 (1956).
9. In a separate experiment, conducted with Y. M. Huang, CH_4 was trapped in solid CO_2 at 20°K. When the sample was warmed to 77°K, the spectrum of CH_4 became more diffuse and somewhat weaker, but plainly most of the methane remained. After the solid was warmed to 100°K and recooled to 77°K, the amount of methane was reduced by approximately half. The experiment shows that methane can be trapped in solid CO_2 even at temperatures as high as 100°K and that near 3020 cm^{-1} the spectrum of methane suspended in solid CO_2 is not readily distinguishable from the Mars absorption.
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11. B. R. Cairns and G. C. Pimentel, *J. Chem. Phys.* **43**, 3432 (1965).
12. B. R. Cairns, thesis, University of California, Berkeley (1964).
13. No methane absorption was observed at 1305 cm^{-1} in the martian spectra, but this does not constitute sufficient evidence to eliminate the methane interpretation. Spectra recorded in this spectral region depend upon the temperature difference between the planetary surface, which furnishes the spectral source, and the gaseous absorber. This provides a "thermal attenuation factor" that approaches zero as these temperatures approach each other. Thus a gas near the ground could not be observed at all. Furthermore, the feature at 1305 cm^{-1} is weaker than the band at 3020 cm^{-1} (under our resolution) and the path length is less than half as great (because the solar light at 3020 cm^{-1} passes through the atmosphere twice).
14. We acknowledge generous support by NASA for the development of the 1969 Mariner infrared spectrometers, as well as the endurance of the JPL Project staff and their courage as they turned on our instrument when it was thought to be the cause of the flight anomalies of the Mariner 7 spacecraft and a threat to the mission. We thank the personnel of the Chemistry Department Machine Shop and the staff of the Space Sciences Laboratory Electronic Shop for their enormous contribution to the fabrication of this instrument. We express our indebtedness to the Berkeley Group, led by P. B. Forney, J. L. Hughes, D. A. Waston, R. H. Weitzmann, and M. A. Carlson, for their dedicated efforts throughout the project.

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Glacier Oxygen-18 Content and Pleistocene Ocean Temperatures

Abstract. *The mean oxygen-18 content of continental ice sheets during the last glacial maximum is estimated to* $\delta O^{18} = -30$ *per mille or less, and the consequent change in the isotopic composition of the oceans at that time to 1.2 per mille or more. This means that at least 70 percent of the oxygen-18 variations found in shells of planktonic foraminifera from deep-sea cores between times of glacial maximums and minimums are due to isotopic changes in ocean water, and at most 30 percent to changes in ocean surface temperature. Hence, Emiliani's "paleotemperature" curve rather depicts the amount of ice on the continents in excess of that present today. In this sense it may be renamed a "paleoglaciation" curve.*

The O^{18}/O^{16} ratio in shells of pelagic and benthonic foraminifera depends on the temperature of formation and on the isotopic composition of the ambient water (*1*). The empirical relation between these quantities was given by Epstein *et al.* (*2*) as

$$T = 16.5 - 4.3\,(\delta_f - \delta_{oc}) + 0.14\,(\delta_f - \delta_{oc})^2 \quad (1)$$

where δ_f and δ_{oc} are the relative per mille deviations of the O^{18}/O^{16} ratios from the SMOW (standard mean ocean water) standard (*3*) for foraminifera and ocean water, respectively. It is seen that temperatures derived from this equation depend critically on the isotopic composition of ocean water. During the Pleistocene this composition varied in response to the amount and the isotopic composition of excess continental ice.

Emiliani (*4–6*) has measured δ values of planktonic foraminifera from several deep-sea cores raised from the Caribbean and the equatorial Atlantic and has deduced a well-known generalized paleotemperature curve for Atlantic equatorial surface water, covering about 425,000 years. Paleotemperatures were calculated from Eq. 1 by assuming a mean isotopic composition of Pleistocene glaciers $\delta_g = -15$ per mille and a maximum variation in $\delta_{oc} = +0.5$ per mille. In Emiliani's measurements peak-to-valley variations of δ_f between glacial maximums and minimums averaged 1.65 per mille. With the above-mentioned assumptions this corresponds to a temperature variation of 5° to 6°C in Atlantic equatorial surface water.

This temperature variation has been questioned by a number of authors from various points of view (*7*). In the present report the mean isotopic composition δ_g of continental glaciers during the last glacial maximum, and hence the variation in δ_{oc}, is estimated on the basis of recent isotopic measurements on precipitation in presently and previously glaciated areas, on present ice caps, and even on ice actually formed during the last glaciation and still preserved in Greenland. These data have greatly improved the reliability of estimates of the isotopic composition of the large Pleistocene ice sheets at their maximum extension.

The disagreement between previous estimates of the isotopic composition of Pleistocene glaciers apparently is due not only to the scarcity of data, but also to a number of misunderstandings relating to ice-sheet dynamics. It may therefore be mentioned that a glacier is in a state of steady mass exchange, with accumulation of snow above the firn line and melting of snow and ice in the ablation zone. According to generally accepted theories of flow pattern in ice sheets (*8*), ice formed in the accumulation zone follows tracks that go deeper in the ice sheet (that is closer to the bottom) the closer to the ice divide the site of formation is (*8*). Ice formed in the periphery of the accumulation zone follows relatively superficial tracks and is melted in the ablation zone within a comparatively short time. The bulk of ice in an ice sheet, therefore, originates from precipitation far inland on the glacier (*9*). This also applies to an expanding glacier.

In agreement with this flow pattern it has been found that a considerable part of the ice in the ablation zone has a much lower δ value than precipitation in the source area of the upper layers. Isotope measurements on a core drilled to the rock bed in Antarctica, only 700 m from the coast at Adelie Land, and 86 m above sea level, showed this relation (*10*). The mean isotopic composition of the upper 31 m of the core (total length 98 m) corresponded to a $\delta = -20$ per mille, similar to the mean δ of precipitation in the area, whereas that of the lower 45 m corresponded to a $\delta = -44$