Is Ozone Trapped in the Solid Carbon Dioxide Polar Cap of Mars?

Abstract. *Laboratory experiments show that solid carbon dioxide is an effective trap for ozone at temperatures as high as 156°K. Ultraviolet reflection-absorption spectra of ozone in solid carbon dioxide at 127°K indicate that the ozone observed over the polar cap of Mars may be trapped in solid carbon dioxide.*

The presence of ozone on Mars has been inferred (*1*) from the ultraviolet solar radiation scattered from the southern polar cap and measured with a scanning monochromator on the Mariner 7 spacecraft as it passed near the planet in August 1969. However, no ozone was detected over the desert regions. The amount of ozone observed was considerably greater than the steady-state, gas-phase concentration estimated from the abundance of major chemical species, temperature, pressure, and solar flux in the martian atmosphere (*2*). However, if ozone is "trapped" in the solid carbon dioxide cap, the "reflection-absorption" spectra would be expected to show the absorption feature of ozone.

In order to check this hypothesis, we have studied the trapping of O_3 in solid CO_2 at temperatures approximating the martian pole temperatures. The experimental system consisted of a Pyrex trap, in which solid CO_2 and ozone could be condensed, connected to an absorption cell in which ozone above the solid could be measured. The presence of ozone was measured by means of the absorption of the 2537-Å resonance line of a low-pressure Hg discharge (*3*). The trap was immersed in a slush of 2-methylbutane or 1-propanol, and O_3 was then either deposited simultaneously with CO_2 or deposited on CO_2 that had been previously condensed. With the trap in 1-propanol, the sublimation pressure of CO_2 was ~ 13 torr, corresponding to a surface temperature of about 156°K; the pressure of CO_2 with 2-methylbutane slush was ~ 0.10 torr, corresponding to a temperature of 127°K. However, during the experiments the temperatures may have dropped as much as 5°K when the pressure on the solid CO_2 was reduced.

In a typical experiment at 127°K, O_3 (at 0.1 torr) and CO_2 were passed through the trap until significant condensation had occurred. The trap and cell were then isolated from the supply, and the system was evacuated, the total pressure dropping to ~ 0.08 torr as the CO_2 cooled. Next the trap was isolated from the cell and pump while the absorption cell was pumped out. The cell in turn isolated from the pump and the trap opened to the cell. At this stage, the total pressure was ~ 0.16 torr, and the partial pressure of O_3 was 0.05 torr. This procedure was repeated until, after several cycles, the ozone began to be depleted.

These experiments indicate that O_3 was readily trapped when a mixture of O_3 and CO_2 was condensed in the trap, and it was also found that O_3 was trapped when it was passed over solid CO_2. At the higher temperature, 156°K, ozone was trapped but the partial pressures of ozone over the solid were substantially lower. No ozone was retained in the trap at these temperatures if O_3 alone was passed through the trap.

Absorption-reflection spectra of O_3 in solid CO_2 also have been obtained. Spectra of continuum light (2200 to 3200 Å) from a high pressure xenon arc scattered from mixtures of O_3 in solid CO_2 at temperatures between 127° and 156°K, as compared to that scattered from solid CO_2, show the broad Hartley band absorption of O_3 peaking near 2600 Å (*4*).

These laboratory measurements suggest that the ozone detected over the polar cap of Mars is not in the atmosphere but is trapped in solid CO_2. Moreover, other trapped molecules may possibly be observed. Oxygen might be detected by means of the Schumann-Runge absorption below 2000 Å or by means of the Herzberg absorption bands between 2400 and 2800 Å (*5*). In the infrared region water, methane, and ammonia might be detected (*6*).

H. P. Broida*
Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder 80302

O. R. Lundell, H. I. Schiff
R. D. Ketcheson
Department of Chemistry, York University, Toronto, Ontario, Canada

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* Visiting fellow at the Laboratory for Atmospheric and Space Physics, and the Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder (1969–70), on leave from the Physics Department, University of California, Santa Barbara.

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Jurassic Sandstone from the Tropical Atlantic

Abstract. *The oldest sediment yet sampled from the abyssal margins of South America, late Jurassic (or possibly very early Cretaceous) shallow-water, coarse-grained, calcareous sandstone containing palynomorphs and mollusk prisms, was recovered from a depth of 4400 meters on the seaward scarp of the Demerara Plateau. The sandstone was deposited in a shallow, late Jurassic epicontinental sea after the initial stages of rifting when the newly created Atlantic began to founder.*

In October of 1968 (*1*) the steep eastern escarpment of the Demerara Plateau was investigated (Fig. 1A). Seismic reflection profiles (Fig. 1B) indicate that the plateau is capped by approximately 1500 m (1.5 seconds) of stratified, undeformed strata which appear to outcrop on the eastern escarpment. Fifteen bottom photographs obtained at the base of the escarpment at 4500 m reveal a bottom free of recent sediment, strewn with angular rocks and locally precipitous (Fig. 1, C and D).

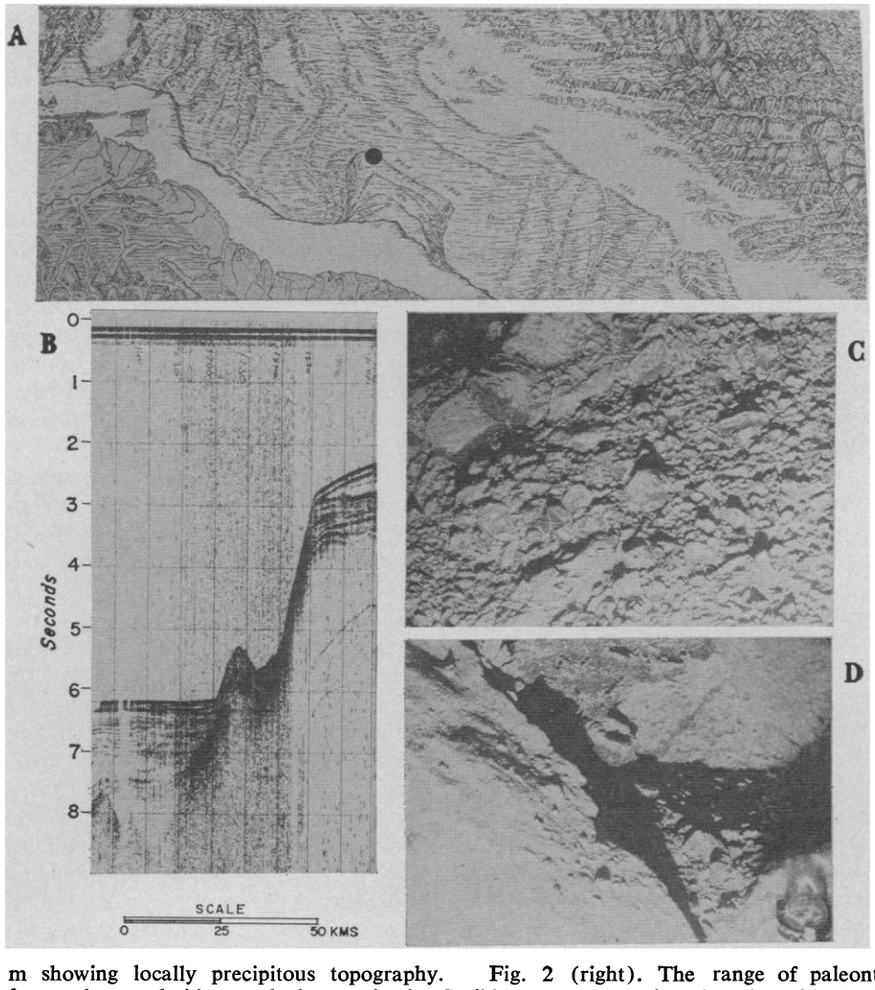
We dredged near the base of the scarp at 4400 m at a point of over 2000 m below the outcrop of the deepest reflector recorded on the seismic reflection profile. The dredge became secured on the bottom and anchored the ship for 3 hours before the dredge broke loose.

The samples recovered are angular pebble-sized fragments of light-green, consolidated, sorted, medium- to coarse-grained calcarenaceous orthoquartzite which is composed of rounded quartz grains, shell debris, nonskeletal granules with minor amounts of glauconite. The binding material is secondary calcite and the percentage of fine-grained interstitial detritus (clay, silt) is very low. These samples are not similar to the modern subgraywacke and graywacke sands which characterize the abyssal plains and continental rises of the ocean basins today (*2*), nor are they similar to the ancient graywackes associated with the fold belts (*3*). Rather, this material is analogous to the recent sediments and ancient sedimentary rocks which characterize shallow depositional environments associated with epicontinental seas (*3*, *4*).

Microscopic examination revealed that the sandstone contained mollusk shell fragments (prisms) and a distinctive, moderately to well preserved palynomorph association composed of Mesozoic spores and pollen. The Mesozoic assemblage was dominated by specimens of *Classpollis* of the *C. classoides* type which accounted for approximately 60 percent of the palynomorph specimens in the sample. In addition, the following Mesozoic forms were identified: *Applanopsis* sp. cf. *A. trilobatus; Cycadopites* sp.; *Exesipollenites tumulus; Equisetosporites* sp. (narrow parallel ribs); *Equisetosporites* sp. (narrow helical ribs); *Equisetosporites* sp. (wide helical ribs). The above species association can be found in strata not older than late Jurassic nor younger than early Cretaceous. A late Jurassic age is preferred because of the absence in the assemblage of *Cicatricosisporites, Appendicisporites,* and other spores of ubiquitous early Cretaceous genera. The occurrence of mollusk prisms mixed with the consolidated calcareous sandstone suggests that the sample was deposited in a shallow-water environment.

The sandstone is from the oldest outcrop yet sampled from the abyssal margins of the South Atlantic. If the samples are representative of an outcropping reflector near the base of the Demerara escarpment, then the Plateau has subsided 4400 m in the last 140 million years (0.03 mm/year). A subsidence history of this kind (Fig. 2) is remarkably similar to that documented for other plateaus and ridges in the Caribbean area (*5*).

The crustal breakup which led to the separation of the fragments of Pangaea, Wegener's (*6*) early Mesozoic supercontinent, has been estimated to have occurred in Jurassic or early Cretaceous time (*7*). In continental reconstructions (*8*), the Demerara Plateau does not fit against the margin of Africa but lies in the confused Caribbean-Bahama region where fits have been unsuccessful or at least inconclusive. The presence of late Jurassic shallow-water sediments establishes that the crust beneath the



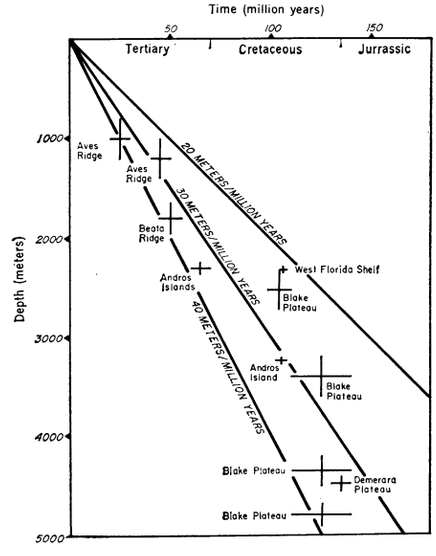


Fig. 1 (left). (A) Physiographic diagram showing the Demerara Plateau and the continental margin of South America. Black dot locates the survey area. (B) Seismic reflection profile showing the escarpment and outcropping horizons. The camera station (4500 m; 09°24.8′N, 54°12.0′W) and dredge station (4400 m; 09°25.7′N, 54°05.9′W) were located on an escarpment close to this profile but the escarpment in the area of the stations lacked the secondary peak located at the escarpment base. (C) Photograph of bottom at 4500 m showing a sediment-free pavement composed of boulders, cobbles, and pebbles. (D) Photograph of bottom at 4500 m showing locally precipitous topography. Fig. 2 (right). The range of paleontologic ages of carbonate samples obtained from submerged ridges and plateaus in the Caribbean area are plotted against the depths at which they were recovered (*5*). From these data, rates of subsidence in millions of years has been calculated.

Demerara Plateau, like that beneath the Blake Plateau and Bahamas, had already been created by the late Jurassic, and that this crust provided a subsiding shallow-water platform upon which sediments were deposited.

PAUL J. FOX
BRUCE C. HEEZEN
Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York 10964
G. LEONARD JOHNSON
U.S. Naval Oceanographic Office, Suitland, Maryland

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Specificity of Antigen Recognition by Human Lymphocytes in vitro

Abstract. *Delayed hypersensitivity reactions in vivo are exquisitely specific, in terms of both a lack of response after induction of tolerance and a response after sensitization. These studies in vitro demonstrate that this specificity, at least at the level of antigen recognition, is probably derived from different populations of cells, each responding to different antigens.*

Lymphocytes from animals primed with certain antigens undergo blast transformation and mitosis in vitro when cultured with the priming antigen. An important question concerning this proliferation is whether the responding cells are part of a totipotent population in which any cell can respond to any antigen to which the animal is primed or whether the responding cells belong to distinct or partially distinct populations of antigen-specific cells.

Using their in vitro antibody plaque-forming-cell system, Dutton and Mishell have shown that different populations of antigen-specific precursor cells exist in the spleens of immunized mice (*1*). Addition of lethal amounts of tritiated thymidine to cultured cells dividing in response to sheep erythrocytes reduced the population to one which could no longer produce plaque-forming cells to the homologous antigen, but would produce plaque-forming cells in response to a heterologous antigen which does not cross-react with homologous antigen (burro erythrocytes). The production of plaque-forming cells to sheep erythrocytes in the suspension of mouse spleen cells in vitro probably involves the interaction of three distinct cell types. These include, in addition to adherent cells, nonadherent cells of two types, probably a "thymic" cell population and a "bone marrow" cell population, both of which may undergo proliferation in response to antigens (*2*). Which cell types show specificity in the Dutton-Mishell experiment is not clear.

One method of ascertaining whether the thymic cells show specificity is to use in vitro lymphocyte cultures of peripheral blood. This in vitro response appears to correlate with in vivo delayed hypersensitivity (cellular immunity) and thymic function rather than with humoral immunity (*3*). To determine whether specificity exists (that is, whether different cell populations respond to different soluble antigens) in this system similarly requires that one eliminate or inactivate all cells in culture that are responding to one antigen. If the hypothesis of separate cell populations is valid, then, while these cell cultures should no longer respond to the homologous antigen, one would expect a normal response to a heterologous antigen.

Inactivation of cells which are synthesizing DNA in response to a soluble antigen with the use of lethal amounts of tritiated thymidine is not accomplished in the leukocyte culture system where response is measured by tritiated thymidine incorporation. The incorporation of 5-bromodeoxyuridine (a thymidine analog) into DNA of dividing mammalian cells in culture provides an alternative means of inactivating specifically responding cells. Such cells become light-sensitive and are readily killed if exposed to light in the visible or near-visible region (*4*). We have adapted this approach to leukocyte cultures and present evidence suggesting that, in part, different cell populations respond to different soluble antigens.

Peripheral blood from healthy donors was drawn into heparinized syringes and allowed to settle for 2 to 3 hours. The leukocyte-rich plasma was removed, and leukocytes were obtained by centrifugation at 150*g* for 10 minutes. Cell-free plasma was prepared by two consecutive centrifugations of the supernatant plasma at 1650*g* for 10 minutes. Leukocytes were suspended and cultured in tissue culture medium 199, Earle's base (Gibco, Grand Island, New York) supplemented to contain approximate final concentrations of penicillin (100 unit/ml), streptomycin (100 μg/ml); and fresh or once-frozen cell-free plasma (20 ml/100 ml). Responding cells were suspended in a final concentration of 0.2×10^6 to 0.4×10^6 mononuclear cells per milliliter. Replicate 2-ml cultures were maintained for 7 days in a humidified atmosphere containing 5 percent CO_2. Cultures were labeled with 2 μc of tritiated thymidine (specific activity 1.9 c/mmole; Schwarz BioResearch) for 16 hours after 6 days of incubation and then harvested on day 7 with the addition of approximately 50 μg of nonradioactive thymidine, chilled on ice, and centrifuged at 1000*g* for 10 minutes. Incorporation of radioactive thymidine was assayed (*5*), and the average standard deviation of replicate cultures for these experiments was 20.9 percent.

Conditions for effective killing of cells synthesizing DNA with 5-bromo-