in the region 1800 to 1000 cm^{-1} (5.5 to 10 μ). Acetaldehyde absorbs at 1752 cm^{-1} (5.71 μ) much more strongly than near 2710 cm^{-1} (3.69 μ). The deuterated forms of water also have their distinctive bending modes in this region; HDO near 1402 cm^{-1} and D_2O near 1179 cm^{-1} (band centers). Unfortunately, much of this region of the spectrum is obscured by terrestrial absorption; Sinton and Strong (*5*) presented a spectral survey of the region 1200 to 800 cm^{-1}. Though subtraction of the background is very difficult, their spectrum could indicate absorption near 1110 cm^{-1}, as would be required by the low-frequency wing of the 1179 cm^{-1} band of D_2O.

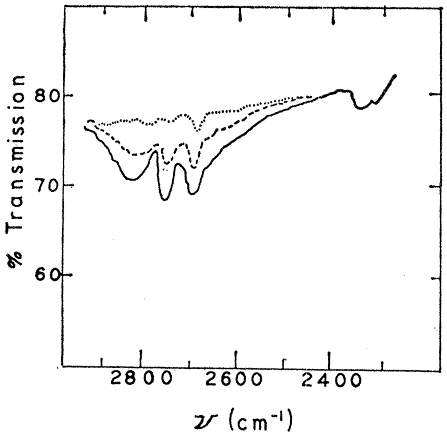

Fig. 1. Infrared spectrum of gaseous D_2O–H_2O mixtures. Path length, 10 cm; pressure, 20 mm; ——, D : H = 4; ------, D : H = 1; •••••, D : H = 1/4.

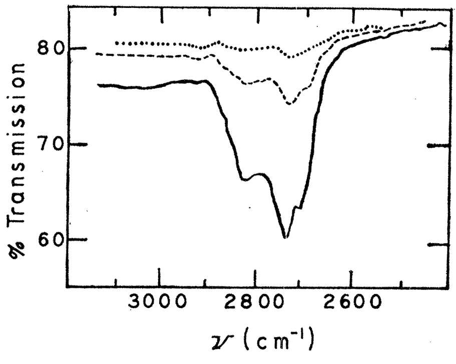

Fig. 2. Infrared spectrum of gaseous acetaldehyde. Path length, 10 cm; ——, p = 9.5 mm; ------, p = 2.7 mm; •••••, p = 0.8 mm.

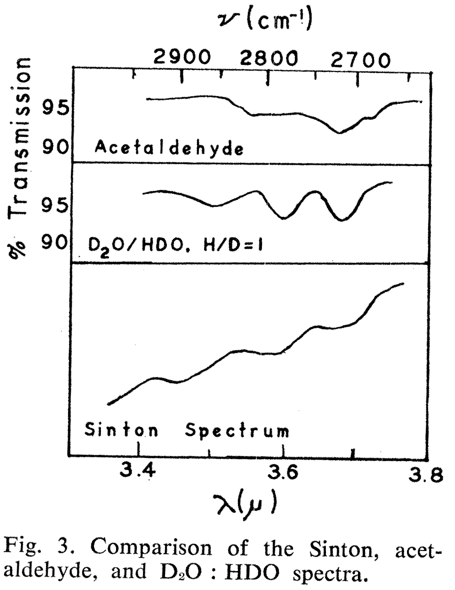

Fig. 3. Comparison of the Sinton, acetaldehyde, and D_2O : HDO spectra.

We then estimated the total water content of the Martian atmosphere, assuming the Sinton bands to be due to deuterated water. Assuming that D : H = 1, the total amount of water above the area (*6*) viewed by Sinton would be only a few mm-atm, perhaps as much as 10 mm-atm; these estimates are about doubled if the D : H ratio is taken to be 1 : 2. Other current estimates of the water vapor content of the Martian atmosphere are somewhat higher (*7, 8*). C. Sagan (*7*), for example, estimates 1.10^{-3} to 2.10^{-2} g/cm^2 (12.5 to 250 mm-atm) to explain surface temperatures on the basis of a greenhouse effect. Kaplan *et al.* (*8*) estimate H_2O content to be 14 ± 7 μ of precipitable water (17 ± 9 mm-atm) on the basis of marginal intensity measurements of Doppler-shifted spectral lines. The discrepancies, we feel, are not large enough to discredit our interpretation of the Sinton bands.

The question of the plausibility of the D : H ratio remains. An explanation may lie in the gravitational fractionation that has occurred on the planets of lowest mass. The mass of Mars is only one-tenth that of Earth, implying more rapid escape of the lighter gases. Photolysis of water by far-ultraviolet light could produce H (and D) atoms. The large mass difference implies that gravitational fractionation of the atoms could be significant, and would favor loss of hydrogen and retention of deuterium.

Regardless of the ease with which the D : H ratio can be explained, the D_2O-HDO spectrum seems to account for the Sinton bands better than does the only alternative, acetaldehyde. If this new interpretation proves to be correct, it dispels what is probably the most direct evidence we now have of organic molecules on Mars, thus deleting an important piece of circumstantial evidence of Martian biota. On the other hand, association of the Sinton bands with only dark areas carries the important implication that the atmosphere above Martian dark spots has higher water-vapor content than does that above light areas. This conclusion would have considerable bearing on the Martian climate and on the design of exobiological experiments for this planet.

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6. In each reference to estimates of atmospheric water content we have quoted the units cited by the original authors, together with our conversion into "mm-atm." In our usage, all units refer to the total amount of gaseous water in a vertical column of atmosphere 1 centimeter square and extending through the entire atmosphere. The units "g/cm^2" express this amount in weight (grams), whereas "μ of precipitable water" expresses it as the height (microns) of the column of liquid water obtained if all of the *gaseous* water is condensed. The units mm-atm designate the product ($h \times p$) if all the vapor is brought to a uniform partial pressure p (in atmospheres) in a gas column of height h (millimeters). The last units, being independent of molecular weight and liquid density, are most useful for comparing concentrations of different molecules, especially different isotopically substituted molecules. For H_2O, 1 mm-atm = 8.04×10^{-5} g/cm^2 = 0.804 μ of precipitable water. For D_2O, 1 mm-atm = 8.94×10^{-5} g/cm^2 = 0.809 μ of precipitable water.
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9. We thank NSF and NASA for support.

18 August 1964

Boron: Another Form

Abstract. *A hitherto undescribed form of boron can be prepared by subjecting ordinary forms of boron to pressures exceeding about 100 kilobars and temperatures between about 1500° to 2000°C. The new form has a density of about 2.52 g/cm^3 and yields a characteristic DeBye-Scherrer pattern. No large crystals have been prepared.*

Elemental boron can be prepared at low pressures in something like four different crystalline modifications (*1–3*). The densest of these is the red form described by Decker and Kasper (*2*) which has a density of 2.46 g/cm^3.

A new form of boron has been prepared in this laboratory by exposing low pressure modifications (β-rhombohedral and "amorphous") of purified boron to high pressures (100 to 150 kilobars)

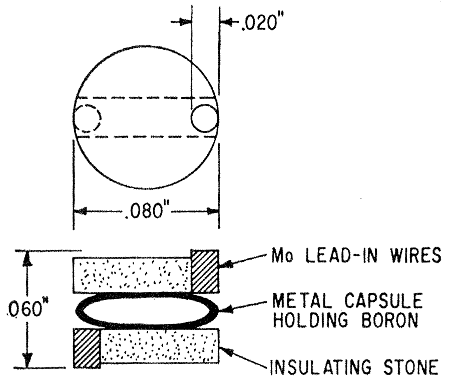

Fig. 1. High pressure, high temperature reaction cell.

and moderate temperatures (1500° to 2000°C) for intervals of a few minutes, cooling the specimen to 25°C, and then reducing the pressure to 1 atm.

This new form of boron was prepared in an apparatus similar to that described by Bundy (*4*). The boron was confined in a tube (Fig. 1) and heated by passing a current through the tube (made of Ti or Ta) by way of molybdenum wires at each end. Usually the boron was placed against the tube wall; in a few experiments the boron particles were insulated from the tube by a liner made of MgO or they were mixed with MgO or silicon powder. Pressures were estimated by reference to transitions in bismuth at 88 kb, barium at 59 and 140 kb, iron at 131 kb, and lead at 160 kb. The temperatures were estimated from the electric power dissipated in the sample; the error may be as much as 10 percent owing to uncertainties in calibration and gradients in temperature.

Table 1. DeBye-Scherrer d-values for the boron prepared as described in this paper.

Å	Relative intensity*
4.4	m
4.1	m
3.75	ms
3.50	m
2.51–2.54	s
2.30–2.32	s
2.15	w
2.10	w
2.00	w
1.98	w
1.68	w
1.60	w
1.50	mw
1.48	mw
1.45	m
1.41	ms
1.39	m
1.38	m
1.35	m
1.30	m
1.27	w

* m, medium; s, strong; w, weak.

The product was a dark, pitchlike solid which was deep red in thin sections; its density ranged between 2.46 and 2.52 g/cm^3 as measured by the sink-float technique. Its electrical resistivity was estimated to be about 10^6 ohm-cm at 25°C, and its resistance fell by about a factor of 3 on heating to about 100°C. Both n- and p-type semiconducting specimens were obtained as determined by measurements of thermoelectric power. (The zone-refined, β-rhombohedral boron starting material had a slightly higher resistivity but about the same relative change of resistance with temperature.)

DeBye-Scherrer x-ray diffraction patterns of various preparations showed some weak lines corresponding to some of the known forms of boron, together with a strong pattern which could not be attributed to any combination of the known forms of boron. The d-spacing values of the main lines in typical patterns of the new form are given in Table 1. When coarsely crystalline rhombohedral boron was used as starting material, the diffraction spots of these crystals could be distinguished from the smooth lines of the new form.

It is not known whether the product is a single crystalline phase or a mixture of new and previously known forms of boron. Increasing the time of heating at high pressure from 6 to 60 minutes did not produce any markedly different product; neither did pressures higher than about 100 kb. Temperatures higher than about 2000°C caused the boron to react with its Ti or Ta container. It is possible that the boron exists in one crystalline phase at high pressures but then reverts to the observed form as the pressure is reduced. However, during pressure release the sample did not show any marked resistance changes that would indicate a change in atomic arrangement of the boron.

What is taken to be a new phase of pure boron might possibly be a boron compound with titanium, tantalum, or silicon, for boron can incorporate small amounts of other elements in its lattice (*5*). However, this possibility does not seem likely in view of the following observations:

1) The same new features of the DeBye-Scherrer pattern are obtained whether the boron is confined in Ta, Ti, or MgO during preparation.

2) The new form is not observed at conditions of about 1800°C and about 80 kb; the product instead has a density less than 2.39 and shows only the rhombohedral β pattern reported by Amendola (*3*).

3) If a fragment of the dense form is buried in hexagonal boron nitride and heated to about 1500°C for about a minute at a pressure of 30 kb, the product has a density between 2.25 and 2.36 g/cm^3 and its DeBye-Scherrer pattern agrees well with that of the well-known rhombohedral form of boron (*3*).

4) The electrical resistivity of the dense form is almost as high as that of the purified boron starting material.

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6. I thank Mrs. D. K. DeCarlo for preparing many DeBye-Scherrer x-ray patterns.

4 October 1964

Ontogeny of a Salt Marsh Estuary

Abstract. *The development of a typical New England salt marsh, and the growth of the sand spit which shelters it, during the past 4000 years has been reconstructed from soundings and borings of the peat. The results have been interpreted with the aid of observations on the structure of the marsh and estimates of the rate of its vertical accretion based on carbon-14 determinations.*

"There is no other case in nature, save in the coral reefs, where the adjustment of organic relations to physical conditions is seen in such a beautiful way as the balance between the growing marshes and the tidal streams by which they are at once nourished and worn away" (*1*).

The existing peat of tidal marshes preserves a record of the conditions which existed when the peat was deposited. In this report I have attempted to reconstruct from this record the history of the development of a typical New England salt marsh and of the estuary which it occupies. The principal factors which interact to determine the development of the marsh