in the Plains and Great Lakes regions 7000 to 9000 years ago, are found on sites exposed after the draining of the proglacial lakes in the Dubawnt and Kazan river systems. These sites were forested until 3500 years ago. The first arrival of Arctic culture in the region (pre-Dorset stage of the Arctic small-tool tradition) probably took place 3000 to 4000 years ago, with the onset of more severe climate and the retreat of the forest border. The recent Caribou Eskimo came after the forest retreat of 900 years ago.

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5. Numbers preceded by WIS- are the serial numbers of the samples at the University of Wisconsin Radiocarbon Laboratory.
6. Charcoal-over-podzol has also been dated from Black Fly Cove, Ennadai Lake (260± 160 B.C., WIS-29) and Sterns Lake (A.D. 515±90, WIS-15). These dates have not been used in this report because the charcoal was buried by solifluction; the samples probably represent mixtures of material from the two forest epochs. Only sites with unequivocal stratigraphy have been used.
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Sinton Bands: Evidence for Deuterated Water on Mars

Abstract. *The infrared absorption bands observed by Sinton at 2710, 2793, and 2898 cm^{-1}, in the spectrum of Mars, may be due to gaseous D_2O and HDO in the Martian atmosphere. The implication would be that the deuterium : hydrogen ratio exceeds that on Earth, presumably because of escape of the lighter gases from Mars, with accompanying gravitational fractionation of the hydrogen isotopes.*

In 1959, Sinton (*1, 2*) reported infrared spectra of the atmosphere of Mars in the region 10,000 to 2400 cm^{-1} (1 to 4.2 μ). Although terrestrial atmospheric absorptions of CH_4, H_2O, and CO_2 obscured part of the region, Sinton could detect definite absorptions at 3.69 μ (2710 cm^{-1}), 3.58 μ (2793 cm^{-1}), and (a less well-defined band) at 3.45 μ (2898 cm^{-1}). These absorptions were recorded when viewing a darkened area of Mars, including Syrtis Major. Sinton noted that these absorptions fall in the region characteristic of C-H stretching modes of carbohydrates; he speculated that they might be evidence of organic matter on Mars.

Colthup (*3*) later recognized that the two prominent absorptions at 2710 and 2793 cm^{-1} are close to two absorptions of acetaldehyde, CH_3CHO. Since these frequencies are rather distinctive, this molecule is usually mentioned in current speculations on the Martian atmosphere and on the likelihood of Martian biogeny.

Rea, Belsky, and Calvin (*4*) have reexamined the possibility that surface reflection and thermal emission participate in the Sinton spectrum. They conclude that surface carbonates could account for the high frequency band (2793 cm^{-1}), but that "the other two bands remain without a satisfactory explanation."

We concur with Rea *et al.* in their conclusion that neither acetaldehyde nor carbohydrate satisfactorily explains the Sinton bands; we have sought other explanations. Surprisingly, we find that the reported absorptions could be attributed to D_2O and HDO in the Martian atmosphere. Table 1 contrasts the Sinton bands with the frequencies at which D_2O and HDO molecules (and acetaldehyde) absorb when the spectra are recorded under low resolution. Even more convincing, perhaps, are the spectra themselves. Figure 1 shows a tracing of the spectra of 20 mm of water at various D : H ratios; they were recorded on a Beckman IR-7 spectrophotometer in double-beam operation with a 10-cm gas cell and with a spectral slit width of 44 cm^{-1}, the same as that used by Sinton (0.056 μ) (*1*). Absorptions at 2722 cm^{-1} (3.67 μ) and 2785 cm^{-1} (3.59 μ) and a broad feature near 2860 cm^{-1} (3.50 μ) are seen in the spectra.

Figure 2 compares the traced spectra of acetaldehyde at a series of pressures in the 10-cm cell and at the same low resolution used to record Fig. 1. Two absorptions are indeed present but are not distinct, either under such low resolution or when recorded under higher resolution.

Figure 3 reproduces, all on the same scale, the original Sinton spectrum together with the optimum water spectrum (D : H = 1) and an acetaldehyde spectrum (p = 2.7 mm). Clearly the Sinton bands are more readily attributable to HDO and D_2O than to CH_3CHO. Each low-frequency absorption in the water spectrum agrees in frequency with one reported by Sinton within his experimental uncertainty, ± 16 cm^{-1}. The proposal of Rea *et al.* (*4*) that the high-frequency band, 2898 cm^{-1}, may be due to surface carbonates could explain the frequency discrepancy for this band. We conclude that the Sinton spectrum could reflect water in the gas phase at a D : H ratio near unity.

Since the startling contrast of this D : H ratio with the terrestrial value, 0.0002, challenges the credibility of this explanation, we have sought other relevant evidence. The proposal could be critically tested by spectral studies

Table 1. Possible assignments of the Sinton bands. ν, Frequency (cm^{-1}); λ, wavelength (μ).

Observed		CH_3CHO		HDO		D_2O	
ν	λ	ν	λ	ν	λ	ν	λ
2710	3.69	2705	3.70	2722	3.67		
		2735	3.66				
2793	3.58	2820	3.55	~2810	~3.56	2785	3.59
~2898	~3.45					2860	3.50

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.

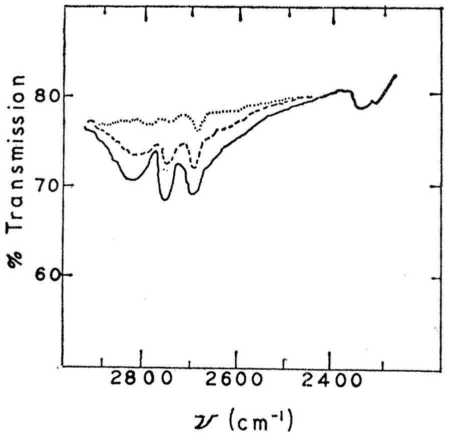

Fig. 1. Infrared spectrum of gaseous D_2O–H_2O mixtures. Path length, 10 cm; pressure, 20 mm; ——, D : H = 4; – – – –, D : H = 1; •••••, D : H = 1/4.

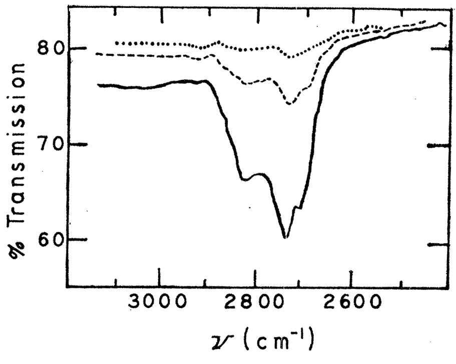

Fig. 2. Infrared spectrum of gaseous acetaldehyde. Path length, 10 cm; ——, p = 9.5 mm; – – – –, p = 2.7 mm; •••••, p = 0.8 mm.

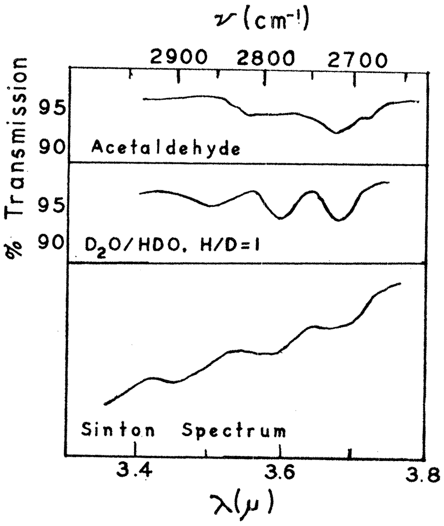

Fig. 3. Comparison of the Sinton, acetaldehyde, and D_2O : HDO spectra.

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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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)