was observed. Hydrogen gas was then put back into the tube, and, after another equilibration, a stronger ESR signal was observed.

The data for five runs at room temperature are presented in Table 1 (*4*). The equilibrium quotient tabulated in the fourth column of the table increases with increasing concentration of amide ion. We would not have predicted this trend with amide concentration. Indeed, because we believed that the ratio of the activity coefficients for the amide ion and the electron would be relatively independent of ionic strength, we expected the equilibrium quotient to be independent of the potassium amide concentration. Perhaps the ESR signals (and hence the calculated electron concentrations) were too low by a factor due to dielectric loss that increased with increasing electrolyte concentration. As the electrical conductivity of a solution in an ESR cavity increases, the dielectric loss increases, and consequently both the cavity $Q$ and the instrument sensitivity decrease. Our results would be explicable if, as the potassium amide concentration increased, the instrument sensitivity for the ammoniacal electron decreased more rapidly than that for the reference sample of diphenylpicrylhydrazyl (which was located in a different part of the cavity). If the trend in equilibrium quotient is caused by either an unusual activity coefficient trend or a dielectric loss phenomenon, extrapolation of the quotient to zero concentration should yield an approximation to the equilibrium constant. Our data extrapolate to an equilibrium constant of approximately $10^5$, a value in fair agreement with the previously estimated value.

A rough optical absorption spectrum was obtained for a $0.5M$ potassium amide solution equilibrated for 45 days with hydrogen at approximately 10 atm pressure in a glass tube of 11 mm diameter. In the 6000 to 10,000-Å region, the solution showed the gradually increasing absorption characteristic of the short-wavelength tail of the 15,000-Å absorption band of the ammoniacal electron. Measurements at longer wavelengths were precluded by strong absorption by the ammonia.

ERNEST J. KIRSCHKE
WILLIAM L. JOLLY
*Department of Chemistry,*
*University of California,* and
*Inorganic Materials Research Division,*
*Lawrence Radiation Laboratory,*
*Berkeley, California 94720*

**References and Notes**

1. W. L. Jolly, *J. Chem. Educ.* **33**, 512 (1956).
2. C. A. Hutchison, Jr., and R. C. Pastor, *J. Chem. Phys.* **21**, 1959 (1953).
3. These results are consistent with the known exothermicity of the reaction as written above. Thermochemical data of L. V. Coulter, J. R. Sinclair, A. G. Cole, G. C. Roper, *J. Am. Chem. Soc.* **81**, 2986 (1959), and S. R. Gunn and L. G. Green, *J. Chem. Phys.* **36**, 368 (1962), yield $\Delta H^0 = -12$ kcal/mole.
4. The concentration of amide ion was calculated from the weight of potassium and the volume of the solution. The hydrogen pressure was calculated from the weight of potassium and the volumes of the liquid and gas spaces, the solubility of hydrogen in liquid ammonia (*5*) being taken into account. The electron concentration was determined by indirectly comparing the signal with that of a benzene solution of recrystallized vanadium (IV) oxyacetylacetonate of known concentration. A sample of solid diphenylpicrylhydrazyl fixed in the sample cavity was used as an intermediate standard of comparison.
5. R. Wiebe and T. H. Tremaerne, *J. Am. Chem. Soc.* **56**, 2357 (1934).
6. We thank Prof. R. J. Myers, D. W. Pratt, and J. B. Spencer for assistance in obtaining the ESR spectra. E.J.K. acknowledges support by the U.S. Naval Postgraduate Educational Program. This research was supported in part by AEC.

29 October 1964

## Radiocarbon and Soil Evidence of Former Forest in the Southern Canadian Tundra

Abstract. *Radiocarbon dating of charcoal on podzols along a transect reaching 280 kilometers north of the present tree line from Ennadai Lake indicates that former forests were burnt about 3500 years ago and again about 900 years ago. These forests probably were associated with periods of relatively mild climate.*

The tree line in central Canada marks a major discontinuity in vegetation, physiography, and culture. Northward across this boundary, rather continuous forest gives way to tundra vegetation, and string bogs are replaced by patterned ground. Chipewyan Indians live in the forest, and until recently Caribou Eskimos occupied the tundra close to the forest. From July through October the tree line coincides with the average position of the northern edge of the Arctic frontal zone; from November through February it marks the southern edge of this zone (*1*). It is thus the climatic boundary between Arctic air on the north and airmasses of Pacific or continental origin on the south. Former changes in the position of the tree line therefore can be expected to have had biotic, physiographic, cultural, and climatic consequences. In this report we present evidence of forests at least 280 km north of the present tree line about 3500 years ago and at least 90 km north about 900 years ago; we conclude that those were times of relatively mild climate.

The northern edge of continuous forest, which now crosses Ennadai Lake at about 60°45′N, 101°W, has the same general characteristics as when it was first described in 1896 (*2*)—black and white spruce (*Picea mariana* and *P. glauca*) are the dominant trees, the latter being less abundant and growing chiefly on special habitats (Fig. 1). At the north end of Ennadai Lake, tundra plants of southern Arctic affinities are dominant, although widely scattered clumps of white spruce are found on sheltered or otherwise favorable sites. Black spruce in these clumps reproduces primarily by layering, in contrast with its reproduction by seed in the forest. The transition from forest to tundra is quite sharp in this area, occurring within a distance of about 20 km (*3*). North of Dimma Lake, only black-spruce clumps are found, and north of Dubawnt Lake no trees are found except for outliers in the Thelon Valley near 64°15′N, 103°30′W.

Buried soils and charcoal show that forests extended north of Ennadai Lake as far as Dubawnt Lake in postglacial time. One site with evidence of a former forest is at the lake shore in front of the Ennadai Aeradio Station, about 40 km north of the tree line. Here, at the edge of a large esker, a buried podzol indicative of a former forest is covered by a layer of charcoal under a layer of wind-blown sand derived from the esker (*4*). Tundra vegetation grows on the surface. Podzol and charcoal are similarly associated along an esker about 25 km south of the tree line at Birch Bay at the south end of Ennadai Lake. Charcoals from these sites show carbon-14 dates of A.D. 1070±180 and A.D. 1080±100, respectively (WIS-5 and WIS-6) (*5*). Charcoal in a similar charcoal-podzol profile at Dimma Lake, 100 km north of the tree line, has been dated at A.D. 810±90 (WIS-17).

There is evidence of a still older forest at Caribou Point, near the tree line on Ennadai Lake; in each of two successive layers, charcoal overlies pod-

zol. Charcoal in the lower layer is dated 1604±116 B.C. (WIS-18); in the upper, which seems to correlate with the sites at the Aeradio Station and Birch Bay, the charcoal is dated A.D. 860± 135 (WIS-27). Three layers of charred peat in a wave-cut peat bank about 8 km north of the Ennadai Aeradio Station record three periods during which the forest was destroyed by fire; they lie 47, 77 (the thickest), and 98 cm below the surface. The 77-cm layer is dated 2050±160 B.C. (WIS-7); it is older than the lower charcoal at Caribou Point, associated with the earlier forest epoch, but it is likely that some of the peat was burned off at the time of the fire, leaving the charred remains of older peat. Peat grows only 2 to 3 cm per century; if we assume that 10 to 12 cm of peat was burned, this date is consistent with that for the lower Caribou Point charcoal and also with a date for charcoal at Slow River, 63°01′N, 100°40′W. The Slow River charcoal, 280 km north of the tree line on Dubawnt Lake, is the northernmost site at which the charcoal-podzol combination was found. Here the podzols are weak and patchy, and north of this location only Arctic brown soils characteristic of tundra are found. The date for the Slow River charcoal is 1475± 110 B.C. (WIS-12) (*6*).

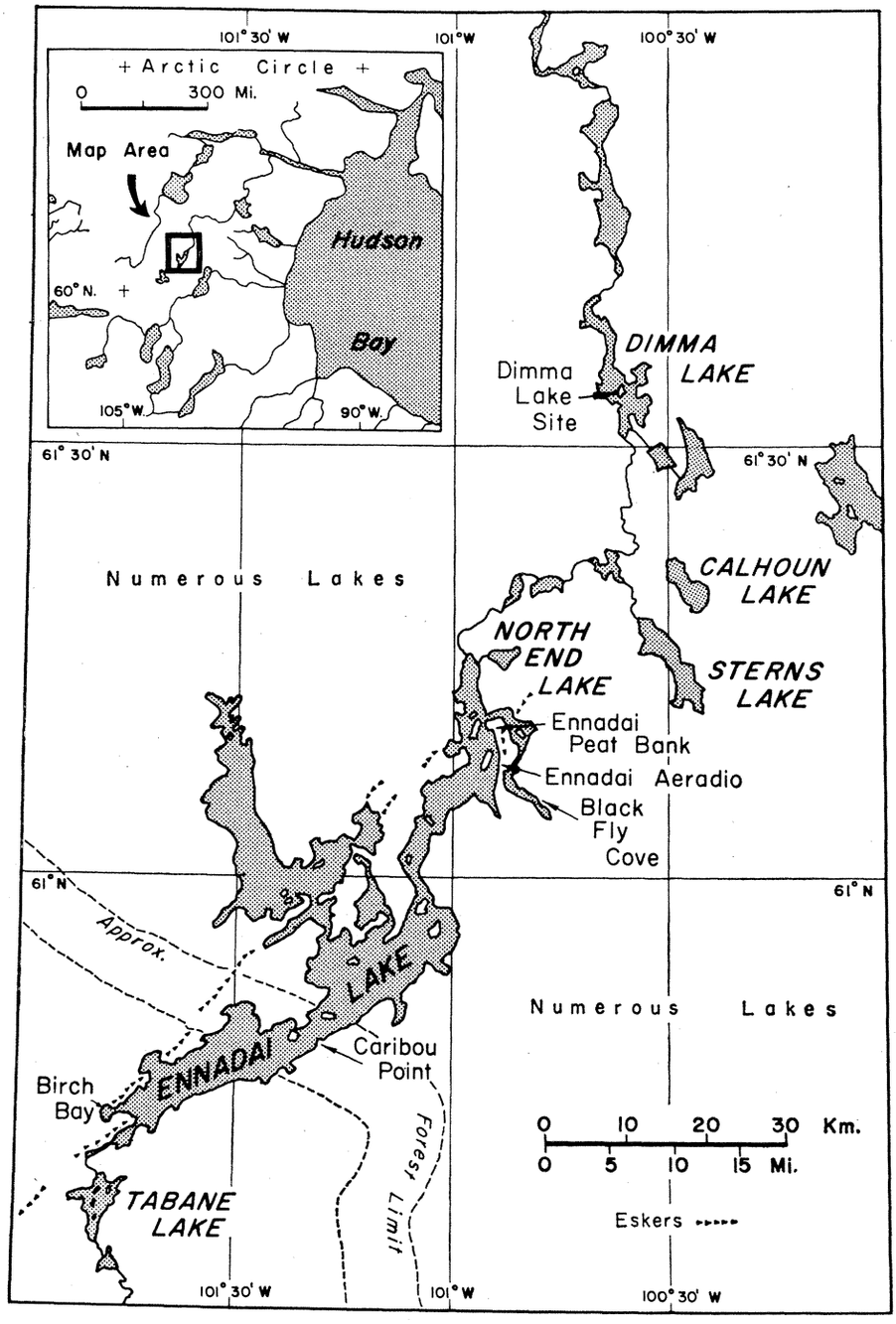


Fig. 1. Guide map of the Ennadai Lake–Dimma Lake area of southwestern Keewatin, Northwest Territories. Dubawnt Lake, the northern end of the study transect, is about 160 km north-northwest of Dimma Lake.

Between Ennadai Lake and Dubawnt Lake, however, podzols are frequent. Trenches dug in the Ennadai area, extending from localities with buried charcoal-over-podzol into areas where the podzol is not buried, show clearly that the podzols exposed over much of the surface are really fossil soils. They therefore do not represent soils developed under tundra (*7*).

The history that emerges from this stratigraphy is as follows. After the draining of great glacier-dammed lakes in southwestern Keewatin not later than 3500 B.C. (*8*), forest encroached northward to at least about 63°N and remained until about 1500 B.C., developing a typical podzol soil. About 1500 B.C. the forest failed to regenerate after fires, and the tree line retreated south of Ennadai Lake. By A.D. 1000 the forest had again advanced to at least 61°30′N or 62°N. Fires of that time were not followed by forest regeneration north of the present tree line (*9*).

Thus, the tree line twice advanced north of its present position and was farther south than at present during an intervening period between 1500 B.C. and A.D. 1000. Because the tree line presently coincides with the position of the Arctic front, we infer that these periods of northward forest extension were periods with a more northerly frontal position. Judging that the advances represent periods of relatively milder climate, we correlate the first advance with the Climatic Optimum and the second with the Little Climatic Optimum (*10*).

The clumps of black spruce presently found in the area north of the present tree line and extending to Dubawnt Lake appear to represent relics that survived the fires and now occupy rare favorable sites. The evidence we present clearly shows that a wide strip at the southern edge of the tundra was once forested long enough to develop podzol soils, and that the tree line has not been moving steadily northward during all of postglacial time.

The known history of human occupancy of this area also reflects this sequence of biotic and climatic change. Late Paleo-Indian [Protoarchaic (*11*)] artifacts, like those of buffalo hunters

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.

REID A. BRYSON
WILLIAM N. IRVING
JAMES A. LARSEN
*Departments of Meteorology, Anthropology,* and *Botany, University of Wisconsin, Madison 53715*

### References and Notes

1. R. J. Reed, "Scientific Rept. No. 2, Contract 19(604)-3063," Occnl. Rept. No. 11, Dept. of Meteorology and Climatology, Univ. of Washington (1959).
2. J. B. Tyrrell, *Geological Survey of Canada Annual Report, 1896* (Ottawa, 1897), vol. 9.
3. J. A. Larsen, *Ecol. Monographs*, in press.
4. Soil samples from various horizons at this locality (archeological site Jg Mf-11) were analyzed by R. C. Morris and F. D. Hole, Soils Survey Branch, U.S. Geological Survey, University of Wisconsin. The U.S. Forest Products Laboratory identified pieces of the charcoal as either *Picea* or *Larix*. Both are found in the black-spruce communities at Ennadai; hence differentiation is relatively insignificant.
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.
7. The distribution of podzol soils mapped north of the tree line in the Canadian National Atlas gives some idea of the former extent of the forest.
8. J. Terasmae and B. G. Craig, *Can. J. Botan.* **36**, 567 (1958). For a more general summary: B. G. Craig and J. G. Fyles, *Can. Dept. Mines Tech. Surv., Geol. Surv. Can. Paper* **60-10**, 1–21 (1960).
9. Field work during the summer of 1964 east and west of the area described in this paper showed a similar general sequence of events in the Henik Lake (61°40′N, 97°30′W) and Artillery Lake (63°20′N, 107°35′W) areas.
10. R. A. Bryson, in *Proc. Conf. on the Climate of the 11th and 16th Centuries, NCAR Technical Notes 63-1*, R. A. Bryson and P. R. Julian, Eds. (National Center for Atmospheric Research, Boulder, Colo., 1963), p. 86.
11. E. J. Harp, Jr., *Arctic Institute of North America, Technical Paper No. 8* (Washington, D.C., 1961).
12. Supported by the Geography Branch, ONR, [Nonr 1202(07)] and Atmospheric Sciences Division, NSF (GP-444).

20 November 1964

## 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 $\mu$). 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 $\mu$ (2710 cm$^{-1}$), 3.58 $\mu$ (2793 cm$^{-1}$), and (a less well-defined band) at 3.45 $\mu$ (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 $\mu$) (*1*). Absorptions at 2722 cm$^{-1}$ (3.67 $\mu$) and 2785 cm$^{-1}$ (3.59 $\mu$) and a broad feature near 2860 cm$^{-1}$ (3.50 $\mu$) 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. $\nu$, Frequency (cm$^{-1}$); $\lambda$, wavelength ($\mu$).

| Observed | | $CH_3CHO$ | | HDO | | $D_2O$ | |
|---|---|---|---|---|---|---|---|
| $\nu$ | $\lambda$ | $\nu$ | $\lambda$ | $\nu$ | $\lambda$ | $\nu$ | $\lambda$ |
| 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 |