stant, (0.033 cal $\mathrm{cm}^{-1}\mathrm{sec}^{-1}$), σ the Stefan-Boltzmann constant, and T the temperature in degrees Kelvin. (One astronomical unit is equal to the mean radius of the earth's orbit.)

The time in seconds for a nonrotating sphere to reach temperature equilibrium is somewhat less than $2.4L^2/Z$, where L is the radius in cm and Z the thermal diffusivity. The exact temperature distribution over the surface is difficult to determine, but the most extreme difference would occur in a nonrotating sphere. In this case, the maximum temperature gradient would fall between the point on the surface of sphere closest to the sun and the point diametrically opposite. The amount of energy emitted from a unit area of the cold side is $\varepsilon\sigma T^4$. If all this energy were conducted from a unit area of the hot side, the difference in temperature between the two points would be $2\,L\varepsilon\sigma T^4/k$ where k is the thermal conductivity. For a sphere 3 m in diameter at perihelion where the temperature is 400°K, if the values of k and Z of Butler and Jenkins (*2*) are used, the maximum possible temperature difference would be 7°C with an equilibrium time of less than 5 days. The values for temperature and time would be smaller for a rotating body.

To demonstrate how the temperature of a small body varies with distance from the sun, we have assumed that the body is following the Pribram orbit (*3*), corresponding to one of the few well-observed falls. The value of H is found by calculating the distance from the sun at various positions and then by applying the inverse-square law to the solar constant. The temperature of the body is a function of H and the ratio α/ε as is shown in Eq. 1. Since the value of α/ϵ is a function of the temperature, it was necessary to use a series of approximations to obtain the desired temperature. At each position, a temperature was arbitrarily assumed, the values of α and ε corresponding to this temperature were taken from Fig. 1, and were entered, with the appropriate value of H, in Eq. 1. The temperature so calculated was usually different from that assumed therefore, new values of α and ε were selected and the process repeated until the calculated temperature agreed with that used to select α and ε. The results of these calculations are plotted in Fig. 2.

The maximum temperature of the meteoroid is 125°C at perihelion; it is 90°C at one astronomical unit and the lowest temperature is −80°C at aphelion.

That meteoroids are quite cold before entering the earth's atmosphere (*3*) is contrary to our measurements and calculations. Had we assumed that the entire surface of the meteoroid exhibited the surface characteristics of the measured sample its temperature would be 137°C, at 1 astronomical unit, and if it were all optically black, it would be 13°C at 1 astronomical unit.

We conclude that the equilibrium temperature of an iron meteoroid just before entering the earth's atmosphere will be close to 90°C.

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14 August 1963

Tellurium Content of Marine Manganese Oxides and Other Manganese Oxides

Abstract. *Tellurium in amounts ranging from 5 to 125 parts per million was present in all of 12 samples of manganese oxide nodules from the floor of the Pacific and Indian oceans. These samples represent the first recognized points of high tellurium concentration in a sedimentary cycle. The analyses may lend support to the theory that the minor-element content of sea-floor manganese nodules is derived from volcanic emanations.*

As a part of a continuing study of the distribution and abundance of tellurium in various materials of the earth's crust, analyses were made of 100 samples of manganese oxide by the analytical method of Lakin and Thompson (*1*) for determining tellurium.

Samples supplied by D. F. Hewett and H. A. Tourtelot of the U.S. Geological Survey consisted of 12 samples of sea-floor nodules and 88 others (22 oxides from hot-spring aprons, 14 supergene oxides, 18 hypogene vein oxides, 9 stratified oxides, and 25 unclassified continental oxides). Of the 88 samples only 9 contained tellurium in concentrations exceeding the sensitivity of the tellurium test (0.1 part per million when a 50-mg sample is used). Seven of the nine, representing all types of continental oxides, contained 0.1 to 0.5 ppm tellurium; the remaining two, both supergene vein oxides, contained 6 and 15 ppm.

All the sea-floor nodules, however, contained appreciable amounts of tellurium. They were collected by the Scripps Institution of Oceanography at widespread localities in the Pacific and Indian Oceans, and contained 5 to 125 ppm tellurium with a median content of 30 ppm and an average content of 40 ppm. Sample locations and analyses are listed in Table 1. Semiquantitative spectrographic analyses of 10 of these samples (280491 to 280500) have been published (*2*).

The last two samples in Table 1 were analyzed at a later date than the other ten samples and there seems to be no chance of anomalously higher tellurium contents resulting from contamination of any kind.

The high tellurium content of the nodules is of particular interest because, so far as the authors are aware, it represents the first place in the sedimentary cycle of tellurium where appreciable concentration of tellurium has been found. Tellurium apparently is concentrated in oxides, and is unlike selenium, which is known to be concentrated in sulfides.

Neither enough information is now available to the authors regarding the samples whose analyses are reported here, nor were a sufficient number of manganese nodules analyzed, to per-

Table 1. Tellurium analyses of samples (*5*) of manganese oxide nodules from the Pacific and Indian Oceans.

Location		Depth	Source	Te (ppm)
Latitude	Longitude			
19°07′N	169°44′W	1750	HoG*	125
17°48′N	174°22′W	1810–2290	HG	125
9°57′N	137°47′W	4930	PO	8
18°55′S	146°32′W	4460	PO	50
11°14′S	88°35′W	4460	PO	5
21°27′N	126°43′W	4300	PO	25
41°59′S	102°01′W	4200	PO	13
29°44′S	37°15′E	4840	IO	40
23°17′N	141°13′W	5400	PO	30
40°23′N	127°59′W	1260	MR, PO	30
16°29′S	145°33′W	1140–1300	PO	10
19°30′N	122°00′W	4400	PO	125

* HoG, Horizon Guyot, Pacific Ocean; HG, Hess Guyot, Pacific Ocean; PO, Pacific Ocean; IO, Indian Ocean; MR, Mendocino Ridge.

mit the drawing of any general conclusions concerning the origin of the tellurium in the nodules. However, Wedepohl (*3*), and Hewett, Fleischer, and Conklin (*2*) have suggested that volcanic emanations may have contributed some of the elements that are concentrated in manganese oxide nodules.

The first two samples in Table 1 were both taken down the prevailing wind and current from Hawaiian volcanos whose sulfur fraction is known to contain tellurium (*4*).

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References and Notes

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2. D. F. Hewett, M. Fleischer, N. Conklin, *Econ. Geol.* **58**, 1 (1963).
3. K. H. Wedepohl, *Geochim. Cosmochim. Acta* **18**, 200 (1960).
4. Publication authorized by the director, U.S. Geological Survey.
5. From H. W. Menard and M. N. Bramlette, Scripps Institute of Oceanography. The samples have been assigned numbers at both the Scripps Institute and the Geological Survey, and these can be obtained on request.

7 October 1963

Tautomerism and Site of Protonation of 1-Methylcytosine: Proof by Nuclear Magnetic Resonance Spin-Spin Coupling

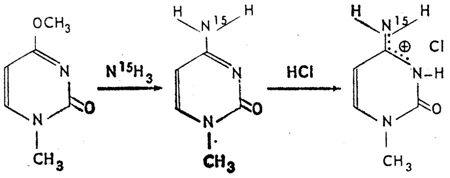
Abstract. *New nuclear magnetic resonance data lead to a completely unambiguous proof that the predominant tautomeric form of 1-methylcytosine is the amino form and that in acid solution the molecule protonates at 3-N. The close similarity of the nuclear magnetic resonance spectra of this compound to the spectra of the cytosine nucleosides indicates that these structures also exist in the nucleosides. These conclusions are reached on the basis of the spectra of analogs labeled with N^{15} and of the proton spin decoupling measurements made at low temperature.*

Cytosine and its nucleosides have been the subject of several recent structural studies (*1–7*), stimulated in part by the relevance of these substances to nucleic acid structure and function. Infrared studies (*1, 2*) have shown that the predominant tautomeric form of cytidine is amino (I) and that in acid solution protonation occurs at 3-N (III). Most nuclear magnetic resonance (NMR) investigations (*2, 5, 7*) support these conclusions, but the interpretation of the NMR results is not completely unequivocal since it rests on arguments of relative chemical shifts expected for different tautomers (*5*) and upon the observation of a single peak with an area corresponding to two protons rather than two single proton peaks that would be expected from the imino structure, II (*2*). The foregoing observation provides strong presumptive evidence for the amino form I, but the remote possibility of accidental coincidence of two imino peaks could vitiate this assignment. In the protonated forms the location of the NMR peak resulting from the additional proton is in doubt.

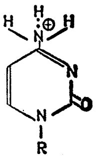
We have made a detailed NMR study of some pertinent cytosine derivatives and wish to report from this work several new experiments and certain conclusions concerning structure which may be unambiguously derived from them. In making peak assignments we have relied primarily upon synthesis of labeled N^{15} analogs, proton-spin decoupling, and temperature variation (*8*).

The spectra were obtained with a Varian A-60 spectrometer and 30-cm-magnet system. The spin decoupling measurements were made with a Varian HR-60 spectrometer and a single side-band proton-proton decoupler (*9*). Chemical shifts are reported in parts per million relative to tetramethylsilane which was used as an internal reference.

1-Methylcytosine (*10*) was prepared by heating 1-methyl-4-methoxypyrimidone-2 (VI) in methanolic ammonia in a sealed tube at 155°C for 10 hours and the product was recrystallized from methanol. The corresponding N^{15} analog (VII) was prepared by distilling 250 mg $N^{15}H_3$ (*11*) into a frozen mixture of 3 ml of methanol and 700 mg of VI in a high vacuum (about 10^{-5} mm-Hg). The chilled tube was sealed at atmospheric pressure and the reaction was heated at 155°C for 10 hours. In a second preparation $N^{15}H_3$ in an amount about 10 percent in excess of VI was used, and the conversion was as good as when the excess of $N^{15}H_3$ was larger. The crude yield of VII was 600 mg. After recrystallization the melting point was 297° to 301°C, and it was not depressed by admixture with an authentic sample of the N^{14} compound.



VI VII VIII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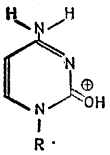
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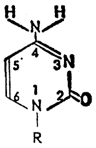

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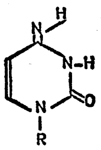
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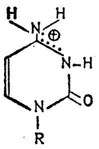
III

Figures 1*C* and *D* show that the hydrochloride of 1-methylcytosine has two broad peaks on the low field side of the 6-H doublet, at 8.85 and 10.00 parts per million (ppm), while its N^{15} analog shows each of these split by N^{15} (peaks at 484, 576, 551, and 643 cy/sec; mean values of the appropriate pairs at 530 and 597 cy/sec, or 8.83 and 9.95 ppm). The only other difference in the spectra of the two molecules is the presence of a small splitting of the 5-H doublet (the spin-spin coupling constant, $J = 0.7$ cy/sec) in the case of the N^{15} compound, presumably as a result of long range coupling with the N^{15}.

When 1-methylcytosine hydrochloride was heated, the two peaks at 8.85 and 10.00 ppm first broadened (~40°C), then disappeared (by 60°C), and finally reemerged as a single peak at 7.13 ppm (~160°C).

Since dimethyl sulfoxide freezes at 18°C, liquid sulfur dioxide was used as a solvent in order to make measurements at low temperatures. At −60°C, 1-methylcytosine hydrochloride has the spectrum shown in Fig. 1*E*. Irradiation with a strong proton-spin decoupling field at 11.43 ppm caused collapse of the 2.5 cy/sec splitting of the 5-H multiplet, leaving a 7 cy/sec doublet. Irradiation at 7.35 ppm had no effect on the 5-H absorption, while irradiation at 7.82 ppm (where the third NH peak virtually coincides with the 6-H peak) caused collapse of the 7 cy/sec splitting, but did not affect the 2.5 cy/sec splitting. On warming, the 11.43 ppm peak broadens, presumably because of proton exchange at an inter-