sphere is 100°K higher than that predicted from radiative transfer alone. The observations also indicate a sudden decrease of temperature at 0.2 mb, with the temperature gradient becoming superadiabatic. However, this is the least certain feature of the temperature profile.

2) The temperature distributions in midafternoon near the southern polar cap (Fig. 6) and in the subtropics in the early morning hours (Fig. 7) appear to be quite close to the profiles predicted when atmospheric dynamics were taken into account.

3) At 79°N, where the polar night is just beginning, the observed temperature profile, if interpreted with the assumption of saturation and condensation of CO_2 in the atmosphere, suggests that condensation of CO_2 is occurring at practically all heights in the atmosphere.

The case of the tropical atmosphere in daytime (Fig. 5) is the most interesting. At the equator, the atmosphere is much warmer than expected. For the 100 percent CO_2 case, the atmospheric temperature near the surface is about 283°K. However, the actual surface temperature measured by the infrared radiometer near the point of occultation is about 275°K (*10*), indicating an inconsistent negative temperature discontinuity of 8°K. For the case with 10 percent Ne, the atmospheric temperature near the ground is 268°K and the temperature discontinuity is only 7°K, differing markedly from the predicted value of Gierasch and Goody. In addition, the problem still remaining is that the atmosphere is substantially warmer than that suggested from the theoretical calculations. Either the opacity of the atmosphere is much higher than that estimated from the various CO_2 band models, or a significant amount of solar radiation is deposited in the middle atmosphere by absorption in the near-infrared bands of CO_2, or a combination of both.

The Mariner 1969 refractivity measurements in the upper atmosphere of Mars yielded results similar to those obtained with the Mariner 4 in 1965 (*1*). On the dayside, the main layer was now located near 135 km altitude, and it had a peak density of approximately 1.7×10^5 electron/cm^3. The minor layer was observed near an altitude of 110 km. The topside plasma temperature was 400° to 500°K on the assumption that CO_2^+ is the principal ion. No ionization was detected on the dark side of the planet (*11*).

Figures 9 and 10 show the density and temperature profiles deduced from the high latitude dayside measurements made with Mariners 4 and 7. The atmospheric models illustrated in these figures are based on the assumption that the main ionization layer is an F_1 region produced by solar extreme ultraviolet. Solid curves represent results derived from the refractivity data. Stippled curves indicate interpolation between the measurements made in the ionosphere and the neutral atmosphere. The figures show both the upper and the lower atmosphere to be warmer now than in 1965. The temperature increases are presumably due to seasonal changes, increased solar activity, and a 10 percent reduction in the distance to the sun.

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Man-Made Carbon-14 in Deep Pacific Waters: Transport by Biological Skeletal Material

Abstract. *Calcareous particles present in Pacific waters at depths of 50 to 3500 meters were collected by filtering seawater through spongin matrix. The specific activity of carbon-14 could be measured in two of these collections from depths of 2300 and 3500 meters. The ratios of carbon-14 to carbon-12 correspond to values observed in surface waters in recent years as a result of the addition of man-made carbon-14, thus indicating that the calcareous particles resulted from recent biological productivity. The results are related to the mean settling rates and the sizes and dissolution rates of biogenic calcareous particles in transit through a seawater column.*

During the Nova Expedition of the Scripps Institution of Oceanography, experiments were carried out between Hawaii and New Zealand in which spongin matrix treated with ferric hydroxide was used for the extraction *in situ* of trace elements from seawater (*1*) with stainless steel samplers (*2*). Seawater was flushed through the matrix at the desired depth by raising and lowering the sampler for 10 to 15 hours at mean speeds of about 10 m/min. The samplers descended to the profile depth in an orientation which did not allow water to flow through the matrix. Corrosion of a magnesium strip at the profile depth swung the samplers into the correct orientation for the free flow of water.

In the expectation that the matrix could also serve as a collector of particulate calcareous matter, we treated portions of the seawater-treated matrix with hydrochloric acid in a vacuum system and measured the amount of carbon dioxide evolved. All samples yielded measurable amounts of CO_2 and two of the deep samples yielded sufficient carbon dioxide to permit measurements of C^{14} activity. The results of these measurements, carried out by the use of procedures discussed by Agrawal *et al.* (*3*), are given in Table 1.

As a check on any contamination of CO_2 introduced by the direct pickup of impurities in the atmosphere by the ferric hydroxide–loaded spongin, we analyzed control samples of spongin matrix; no measurable carbon dioxide was found. Laboratory experiments with aqueous solutions of carbonate, bicarbonate, and CO_2 (gas) showed that

Table 1. Amount of CO_2 evolved from calcareous matter trapped in spongin matrix; δC^{14} values refer to the quantity $[(S_s/0.95\ S_o) - 1] \times 1000$, where S_s and S_o are the net measured counting rates due to C^{14} activity in CO_2 from the sample and from National Bureau of Standards standard-grade oxalic acid, respectively, counted (*3*) under identical conditions; ΔC^{14} values are the corrected values of the isotopic fractionation (per mille) on the Lamont normalization scale, derived on the assumption that $\delta C^{13} = 0$ in CO_2 evolved from the samples.

Sample No.	Location	Depths at which water was flushed (m)	Weight of sponges (kg)	Volume of CO_2 (liters)	δC^{14} (per mille)	ΔC^{14} (per mille)
	Nova III (station No. 10), 25 June 1967					
A	09°53.5′N, 179°00′W	50–150	4	0.015		
	Nova III (station No. 7), 22 June 1967					
B	16°00′N, 179°05.7′W	2200–2300	4	1.20	149 ± 13	92 ± 12
	Nova VI (station No. 4), 27 September 1967					
C	27°20.9′S, 175°25′E	50–150	8	0.05		
D	27°20.9′S, 175°25′E	3400–3500	1.5	0.04		
	Nova VI (station No. 1), 21 September 1967					
E	31°41′S, 177°16.2′W	3400–3500	5	3.00	57 ± 13	4.2 ± 12

the spongin matrix did not pick up any carbon dioxide. Low-magnification microscopy of the seawater-treated matrix revealed the presence of particles resembling biological calcareous skeletons. A few of the particles were larger than 100 μm in diameter, but most seemed to be smaller than 20 μm; some of the large particles were aggregates. No quantitative analysis could, however, be made since these particles were admixed with the dark-brown ferric hydroxide–loaded spongin matrix. Thus (*4*) we infer that the CO_2 evolved by treatment with hydrochloric acid is a result of the decomposition of calcareous particles trapped *in situ* from seawater at the depths where water was flushed.

The measured ΔC^{14} value for sample B (16°N) is inferred (*5*) to correspond to that in surface waters during June through August 1964. Similarly in view of the values reported (*6*) for Makara (41°S) and other southern stations (*5, 6*), we infer that sample E corresponds to the measured ΔC^{14} value in the surface water during mid-1961 through May 1962. The mean dates of formation of the calcareous skeletons trapped in the matrix can be deduced fairly precisely because they correspond to the nuclear-weapons era.

Thus there is a precise man-made C^{14}-labeled "sinking chronology" for the suspended biogenic calcareous material transiting through a seawater column. The mean dates of formation of calcareous skeletons recovered in samples B and E correspond to mean particle settling rates of $(2.5 \pm 0.1) \times 10^{-3}$ cm/sec and $(1.9 \pm 0.2) \times 10^{-3}$ cm/sec for the depth intervals from the surface to 2300 m and from the surface to 3500 m, respectively. These in turn correspond to values of 4.1 and 3.6 μm for the average radii of the particles, respectively, if we assume that the density of calcareous particles is 2 g/cm³. In this calculation, we have neglected the effects of dissolution of $CaCO_3$ particles in transit, which seem to be important on the basis of the smaller deduced mean velocity for the deeper sample (E).

The rates of dissolution have been experimentally determined (*7*) for $CaCO_3$ balls and for foraminifera shells at different depths in an oceanic column. These experiments yield values for the dissolution rates of 4×10^{-5} and 1×10^{-3} g/cm² per year, respectively, for the depth interval from 1500 to 3500 m, over which range the values do not show an appreciable depth dependence. On the basis of these rates, we deduce from a simplified theoretical model (assuming that all particles are of the same size and neglecting any effects due to conglomeration) that the initial mean particle radii are of the order of 7 to 9 μm. The effects due to dissolution for depths of less than 3500 m become important for rates exceeding $\sim 10^{-4}$ g/cm² per year. In fact, the observation of a lower mean settling velocity for the deeper sample (E) would be more consistent with the rates of dissolution measured for foraminifera shells than for $CaCO_3$ balls. However, samples B and E are not from the same location. At depths greater than 3500 m, the dissolution rates, even for $CaCO_3$ balls, are appreciable; thus the bulk of the calcareous particles in the seawater present at depths of less than 3500 m will not escape dissolution in a water column with a depth of 4500 to 5000 m (the depth of the water column at the sites of samples B and E was 5270 and 10,000 m, respectively).

On an average basis, of the total mass of biological carbon leaving the mixed layer by gravitational settling, only about 4 percent reaches the ocean floor (*8*). Part of the 96 percent which dissolves at depths is organic, but an appreciable amount must be attributed to the dissolution of slowly settling calcareous particles. [These deductions are based on simple considerations of material balance, involving data on the concentration of total dissolved carbon (see *9*), oxygen profiles, and the time scales of mixing in oceans based on C^{14} data.] Our data imply that at intermediate depths in the oceans, say, 1500 to 3500 m, the standing crop of calcareous particles is chiefly composed of small particles (5 to 10 μm) which eventually dissolve in transit through the seawater column. Thus the bulk of calcareous particles caught in the sponge matrix are those which result in a production *in situ* of carbon at depths in the ocean. Calcareous particles which escape the water column to reach sediments settle quickly with a Stokes settling velocity of the order of 10^{-2} cm/sec (*10*), and the standing crop of these particles (which escape dissolution) therefore constitutes only 1 percent (by weight) of the small particles which dissolve, if we assume (i) that, on the average, only 4 percent of the biological matter introduced in deep layers escapes to the sediment, and (ii) that the differences in the settling rates for these particles are of the magnitudes discussed above. This applies only for depths of less than 3500 m; at greater depths, the standing crop will increasingly be comprised of particles of larger size.

The volume of evolved CO_2 in the deepwater samples, B and E, is one to two orders of magnitude higher than that for samples A and C (50 to 150 m); this may be a result of a combination of three factors: (i) there are geographical and seasonal variations in biological productivity; (ii) the spongin matrix is more efficient for trapping small particles which remain confined within its narrowly spaced fibrous network; and (iii) the particles in the upper layers exist chiefly as larger aggregates or are attached to organic matter, for example, coccoliths. (In the depth interval above and near the oxygen minimum, the concentration of particles which exist as aggregates or are attached to biological matter would be expected to be lower because of their faster settling rate.) Based on the amount of CO_2 evolved from samples B and E and assuming a 100 percent trapping efficiency for the matrix, we deduce values of 5×10^{-8} and 10^{-7} mole of particulate $CaCO_3$ per liter of seawater at depths of 2300 and 3500 m, respectively. The average value for the ocean based on material balance considerations (*8*) is $\sim 10^{-6}$ mole of total organic and inorganic carbon per liter for depths of less than 3500 m. The agreement is quite satisfactory in view of the fact that we are analyzing only the inorganic biological carbon and the fact that the trapping efficiency of the matrix is not expected to be better than 10 to 20 percent.

Thus the data presented here provide experimental evidence (*8*) that a considerable direct addition of "surface" carbon occurs at depths in the oceans as a result of the dissolution of biological matter. This has to be considered implicitly in any theoretical analysis of C^{14} data for the evaluation of diffusion-advection rates and can be taken into account in measurements of the concentration of total "stable" carbon in seawater (*8*).

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Tuhualite Crystal Structure

Abstract. *As judged by crystal structure analysis, the crystallochemical formula of tuhualite is* $(Na,K)_2^{VI} (Fe^{+3})_2^{VI} (Fe^{+2})_2^{IV} Si_{12}O_{30} \cdot H_2O$*, with four such formulas in the unit cell. The structure is characterized by six-repeat double chains of silicon tetrahedrons and chains of edge-sharing, alternating iron tetrahedrons and octahedrons. Chains of each kind are connected by corner sharing to four chains of the other type. The iron cations appear to be anomalously ordered with* Fe^{+2} *in tetrahedral and* Fe^{+3} *in octahedral sites.*

The mineral tuhualite (*1*) was first found in the comendites of the Mayor Island, New Zealand; no other occurrence has since been recorded. The physical properties, morphology, and x-ray crystallography of tuhualite, including references to its petrogenesis, have been reported by Hutton (*2*), who, on the basis of an analysis of purified material, suggested the following formula as representing the empirical unit-cell contents: $H_9(Na,K,Mn)_{12}Fe_6^{+2}(Fe^{+3},Al,Mg,Ti)_9(Si_3O_{18})_{15}$. However, from three microprobe analyses of tuhualite crystals (*3*) and by assuming the water content and the ratio of Fe^{+3} to Fe^{+2} (*2*), we can infer the ideal formula, $(Na,K)_2Fe_2^{+2}Fe_2^{+3}Si_{12}O_{30} \cdot H_2O$, with four such formulas in the unit cell. The following crystal data are given by Hutton (*2*): a = 14.31, b = 17.28, and c = 10.11 Å; space group *Cmca* or *C2ca*; measured density, D_m = 2.89 g cm^{-3}.

Intensity data were collected from a small single crystal (*4*) by integrated Buerger precession photographs with Zr-filtered MoKα radiation; three layers with a as precessing axis ($h = 0$, 1, and 2) and the zero layer with c as precessing axis were taken. The intensities, measured with a Nonius microdensitometer, were corrected for Lorentz and polarization factors; no transmission factor correction was applied.

If we take into account that in tuhualite $b \simeq 3^{1/2} c$, a close relation can be observed between the cell data of tuhualite and osumilite $(K,Na)(Mg,Fe^{+2})_2(Al,Fe^{+3})_3(Si,Al)_{12}O_{30} \cdot H_2O$, with a = 10.155, c = 14.284 Å, and space group *P6/mcc* (*5*). These relations, together with the examination of the Patterson projection along [100], gave the key for the solution of the structure. This projection showed a very strong peak at coordinated v = 0.090 and w = 1/4; this peak corresponds to an interatomic distance of 2.96 Å, very close to the distance 2.93 Å

Table 1. Atomic coordinates for tuhualite. Figures in parentheses signify standard deviations with reference to the last significant figures given. *B* is the temperature factor.

Atom	*x*	*y*	*z*	*B*(Å²)
Fe(1)	0.2484(9)	0	0	1.1(1)
Fe(2)	1/4	−0.0945(2)	1/4	0.5(1)
Si(1)	0.3906(7)	0.1321(4)	0.0118(7)	0.7(1)
Si(2)	0.3894(6)	0.0704(3)	0.3060(8)	0.6(1)
Si(3)	0.3902(6)	0.1894(3)	0.5434(7)	0.5(1)
O(1)	0.3692(15)	0.2246(8)	−0.0094(18)	1.1(3)
O(2)	0.3298(17)	0.0797(7)	−0.0876(15)	0.4(2)
O(3)	0.3643(20)	0.1105(10)	0.1619(20)	1.5(3)
O(4)	0.3295(11)	−0.0051(8)	0.3370(15)	0.4(2)
O(5)	0.3639(19)	0.1358(9)	0.4107(18)	1.1(3)
O(6)	0.3292(18)	0.1710(7)	0.6674(18)	0.9(3)
O(7)	1/2	0.1130(12)	−0.0090(28)	1.0(3)
O(8)	1/2	0.0532(12)	0.3068(31)	1.3(4)
O(9)	1/2	0.1790(13)	0.5792(31)	1.8(4)
Na	1/4	0.2197(7)	1/4	1.8(2)