tached to biological matter would be expected to be lower because of their faster settling rate.) Based on the amount of CO₂ 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 CaCO₃ 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: $H_9(Na,K,Mn)_{12}Fe_6^{+2}$ $(Fe^{+3},Al,Mg,Ti)_{9} (Si_{3}O_{18})_{15}$. 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, $(Na,K)_2 Fe_2^{+2} Fe_2^{+3} Si_{12}O_{30}$. H₂O, 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, $D_{\rm m}$ $= 2.89 \text{ g cm}^{-3}$.

small single crystal (4) by integrated Buerger precession photographs with Zr-filtered MoK α radiation; three layers with a as precessing axis (h=0, 1, and2) 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 $b \simeq 3^{\frac{1}{2}}$ 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)₁₂O₃₀ • H₂O, 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

Intensity data were collected from a

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	v V	2	$B(A^2)$
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)

between (Mg,Fe⁺²)^{VI} and (Al,Fe⁺³)^{IV} in osumilite. A strong peak with such coordinates is consistent with the existence of two iron atoms at the center of edge-sharing polyhedrons, in special positions 0.090 and 1/4 part in y and z coordinates, respectively, and with equal or nearly equal x coordinates. Therefore, the space group C2ca is ruled out. In space group Cmca two possibilities arise: (i) Fe(1) in 8c at 1/4, 1/4, 0 on a symmetry center and Fe(2) in 8e at 1/4,0.160,1/4 on a binary axis; (ii) Fe(1) in 8d at \sim 1/4,0,0 and Fe(2) in 8e at 1/4,-0.090, 1/4, both on a binary axis.

In the latter case, Fe(1) and Fe(2)have to be in tetrahedral and octahedral coordination, respectively, with the two polyhedrons sharing an edge. Thus a chain of alternating tetrahedrons and octahedrons develops along the c direction; a similar chain is found along the a axis of osumilite. The three tetrahedrons corresponding to the three silicon atoms of the asymmetric unit were connected to the chain of iron polyhedrons, as suggested by the crystal structure of osumilite. The symmetry operations of the space group give rise, from these three silicon tetrahedrons, to a six-repeat double chain which links together the four chains of alternating iron tetrahedrons and octahedrons running in the unit cell. The sodium cation was placed, on the basis of stereochemi-

Table 2. Metal-oxygen distances (in angstroms \pm 0.02). An asterisk is used to distinguish equivalent atoms.

Bond	Dis- tance	Bond	Dis- tance
Si(1)-O(1)	1.64	Fe(1)-2 0(2)	2.01
Si(1)-O(2)	1.61	Fe(1)-2 O(4)	1.99
Si(1)-O(3)	1.61		
Si(1)-O(7)	1.61		
Si(2)-O(3)	1.65	Fe(2)-2 O(2)*	2.02
Si(2)-O(4)	1.59	Fe(2)-2 O(4)	2.11
Si(2)-O(5)	1.59	Fe(2)-2 O(6)*	1.93
Si(2)-O(8)	1.61		
Si(3)-O(1)*	1.61	Na-2 O(3)	2.65
Si(3)-O(5)	1.67	Na-2 O(5)	2.72
Si(3)-O(6)	1.56	Na-2 O(6)*	2.36
Si(3)-O(9)	1.67		

cal considerations, in special position 8e at 1/4,0.22,1/4.

The trial model was tested by a structure factor calculation. The reliability index (R) for the 369 observed reflections was 0.39. Five cycles of full-matrix least-squares refinement lowered the R value to 0.081. Unit weights were attributed to all the reflections, and the form factors for the dominant ion in the various structure groups (that is, Na, Fe, Si, and O) were used. Positional coordinates and isotropic temperature factors at the present stage of refinement are presented in Table 1.

A description of the main features of the structure (Fig. 1) is implicit in



Fig. 1. Projection along [100] of one-half of the unit cell (x = 0 to $x = \frac{1}{2}$). The second half is obtained by reflection in a mirror plane at $x = \frac{1}{2}$; this mirror plane passes through the O(7), O(8), and O(9) oxygen ions and doubles the silicate chain.

the preceding construction of the trial model. In the conventional classification of silicates developed by Bragg, tuhualite should take its place among the chain silicates, opening a new subgroup characterized by six-repeat double chains of silicon tetrahedrons. The chains are winding and link together four chains of edge-sharing iron polyhedrons. These last chains in turn connect, by corner sharing, four double chains of silicon tetrahedrons.

Zoltai (6) has proposed a classification of tetrahedral structures based on the degree of polymerization of tetrahedral units irrespective of their chemistry. With Fe(1) in the system of linked tetrahedrons, tuhualite displays a framework-like structure, with a ratio between the number of tetrahedral cations and oxygen anions of 14:30. The tetrahedral framework is interrupted in only 2 out of 15 oxygen atoms; they are two symmetry related O(6) atoms. Whereas the silicon tetrahedrons are regular, the tetrahedron around Fe(1)is highly distorted because of the sharing of edges with the Fe(2) octahedron, which in turn is markedly flattened. The sodium cations are placed in the open channels paralleling a, with an irregular sixfold coordination. As in the structure of osumilite, the water molecule should be randomly distributed in these channels.

A feature of the crystal structure of tuhualite arose in connection with the analysis of the bond lengths (Table 2). The chemistry of the mineral suggested an ordering of Fe⁺² and Fe⁺³ cations among the tetrahedral and octahedral sites; for the normal ordering, with Fe⁺³ in tetrahedral and Fe⁺² in octahedral sites, as suggested by crystal field stabilization energies, Fe(1)-O and Fe(2)-O should have mean bond lengths of 1.86 and 2.13 Å, respectively (7). The observed values, 2.00 and 2.02 Å, match those calculated for Fe⁺² in tetrahedral coordination and for Fe+3 in octahedral coordination, 1.99 and 2.00 Å, respectively (7). This anomalous distribution of Fe⁺² and Fe⁺³ cations appears to be reasonable on the basis of its conformity with Pauling's electrostatic valence rule (8). The normal distribution, with Fe⁺² in octahedral sites, should result in a highly undersaturated O(6) anion, with an electrostatic valence bond strength $\zeta = 1.50$. The underbonding is partly removed by the ordering of Fe⁺³ cations in octahedral sites, thus giving ζ a value of 1.67 for O(6) anion, The remaining undersaturation is compensated by shortening of metal-oxygen interatomic distances involving O(6) atom (Table 2).

The formula inferred from the microprobe analysis presented by Nicholls and Carmichael (3) was confirmed by the crystal structure analysis, which revealed the crystallochemical formula

 $(Na,K)_2^{VI} (Fe^{+3})_2^{VI} (Fe^{+2})_2^{IV} Si_{12}O_{30} \cdot H_2O$ Stefano Merlino

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Interstellar Scintillations of Pulsar Radiation

Abstract. Time fluctuations in the intensity of pulsed radiation from CP 0834, CP 1133, AP 1237, and CP 1919 have been investigated. Power spectra, modulation indices, frequency distributions, and decorrelation frequencies are consistent with scintillation theory. If it is assumed that these scintillations are due to irregularities in the interstellar medium that travel at a velocity of 20 kilometers per second, the irregularities have a scale size on the order of 10⁴ kilometers and a distance from the earth of approximately 70 parsecs. These interstellar scintillations would not have been observed if the apparent angular diameters of the pulsars were larger than 0.3×10^{-5} second of arc, and they would cause even a point radio source to have an apparent angular diameter of approximately 10^{-3} second of arc at 318 megahertz.

Recent observations of the time fluctuations in the intensity of pulsar radiation are consistent with the predictions of scintillation theory. These observations reinforce the evidence (1) for an interstellar plasma between the earth and the pulsars. If we assume that the scintillations are interstellar (2), the size of the diffracting irregularities and their distance from the earth may be calculated.

Pulsars CP 0834, CP 1133, AP 1237, and CP 1919 were observed at Arecibo Ionospheric Observatory. Radiometers were used with 10-msec time constants and the following combinations of radio frequency and bandwidth: 111 Mhz-125 khz, 195 Mhz-500 khz, 318 Mhz-500 khz, and 430 Mhz-1 Mhz. The 111- and 430-Mhz antennas were circularly polarized, and the 195- and 318-Mhz antennas were linearly polarized.

Pulse intensities (ON intensities) were calculated by integrating the power within windows of data which were 200 msec wide and centered on each pulse. Intensities due to system noise (OFF intensities) were similarly calculated for windows centered midway between pulses. A more complete description of the method of calculating these intensities is given by Lovelace and Craft (3).

In order to minimize the noise contribution to the ON intensities, the intensity data were smoothed by replacing each intensity point with the average of the 50 succeeding points. Power spectra of the fluctuations of the ON intensities about the mean value were then measured on arrays of 4096 points of intensity (Fig. 1). A similar spectrum for the oFF intensities was undetectable on the scale of Fig. 1. The spectra of CP 1133, AP 1237, and CP 1919 have widths which are proportional to $\lambda^{1.0 \pm 0.2}$, where λ is the wavelength. These widths give time scales for the fluctuations which are in agreement with the more qualitative results of other observers (3-6). A study of other features in the spectra of CP 1919 has also been made (7).

Some examples of the frequency histograms calculated for the ON and OFF intensities are shown in Fig. 2. After calculating the average intensity of the on data, \overline{I}_{ON} , I formulated these histograms by counting the number of times an intensity I fell within the interval $I \pm (\bar{I}_{ON}/20.0)$. Although the ON frequency distribution is actually the convolution of the pulse frequency distribution with the OFF frequency distribution, the OFF histogram is narrow enough to show that an exponential distribution of pulse intensities is consistent with the observed data. Also shown in Fig. 2 is the relative rootmean-square value M of the intensity fluctuations about the mean intensity. This modulation index and the parameter ξ , which measures the skewness of the on distribution, were calculated according to the procedure of Cohen et al. (8). An exponential distribution of intensities, and values of M and ξ



Fig. 1. Power spectra of the fluctuations in the pulse intensity of pulsars about the mean intensity. The frequency resolution is approximately 0.00025 hz, and the effective Nyquist frequency is approximately 0.01 hz.

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