THE AMERICAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 47 MAY–JUNE, 1962 Nos. 5 and 6

THE DETERMINATION AND REFINEMENT OF THE STRUCTURE OF NARSARSUKITE, $Na_2TiOSi_4O_{10}$

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ABSTRACT

The symmetry of narsarsukite is $I4/m$ with $a=10.726_9$ Å and $c=7.947_6$ Å. The unit-cell content is ideally $4(Na_2TiOSi_4O_{10})$. Intensity data obtained with the single-crystal Geiger-counter diffractometer were used to compute the three-dimensional Patterson synthesis. Restrictions placed on the location of titanium enabled a set of minimum function maps based on images in titanium to be constructed. Despite ambiguities, these maps, in conjunction with an implication diagram and the Patterson synthesis, provided the location of the titanium and silicon atoms. The silicon inversion peak was thus located on the Patterson maps and a complete set of minimum-function maps based on silicon was prepared. This revealed all atoms with no ambiguities. The structure, so determined, was refined by the method of least-squares.

The structure is based on a new arrangement of silicon tetrahedra. It can be described as made up of tubes having composition Si_4O_{10} parallel to the c axis. Chains of titanium octahedra run parallel to the c axis and bond together the Si_4O_{10} tubes. Sodium atoms occupy voids between the tubes and chains, and have an irregular coordination of oxygen atoms.

INTRODUCTION

The rare tetragonal silicate mineral, narsarsukite, has two perfect cleavages, (100) and (110). This combination of symmetry and cleavage suggested a new silicate type, and this encouraged us to investigate its structure. After we had finished our determination of the structure and were in the process of refining it, Pyatenko and Pudovkina (1959) published a note indicating that they had determined the structure and in a fuller account (1960) described their investigation and their results. Although the general arrangement of atoms in the narsarsukite structure had been published, we felt it desirable for several reasons to continue our work and publish it. In the first place, Pyatenko and Pudovkina used photographic film with a 30-point blackening scale to determine intensities. We determined our intensities with a single-crystal counter diffractometer, and were able to reproduce our measurements to between 1–2%. Our data were therefore much more precise than those of Pya-

TABLE 1. CELL DIMENSIONS AND SPACE GROUP OF NARSARSUKITE

	a	c	Space group
Gossner and Strunz (1932)	10.80 Å[1]	8.01 Å[1]	$I4/m$
Warren and Amberg (1934)	10.76[1]	7.92[1]	$I4$, $I\bar{4}$ or $I4/m$
Stewart (1959)	10.72_0	7.94_8	$I4/m$
Pyatenko and Pudovkina (1960)	10.72 ± 0.04	7.99 ± 0.02	$I4$, $I\bar{4}$ or $I4/m$
Peacor and Buerger	10.726_9	7.947_6	$I4/m$

[1] kX converted to Å.

tenko and Pudovkina. Secondly, they determined their structure by projections, whereas we determined our structure directly in three dimensions. Finally, our structure was highly refined by least-squares and difference maps. In all, our work has lead to a much more precise knowledge of the structure, and this, in turn, has permitted better understanding of the crystal chemistry and physical properties of narsarsukite.

UNIT CELL AND SPACE GROUP

Gossner and Strunz (1932), Warren and Amberg (1934), Stewart (1959) and Pyatenko and Pudovkina (1960) have studied the unit cell and space group of narsarsukite. Their results are listed in Table 1, together with the results of this investigation.

Precession photographs of narsarsukite display diffraction symmetry $4/mI\text{-}/\text{-}$, which is consistent with space groups $I4$, $I\bar{4}$ and $I4/m$. Form development and etch-pit symmetry strongly suggest that the space group is $I4/m$, in agreement with Stewart's (1959) results on material from the same locality.

Unit-cell dimensions were determined using data from precision back-reflection Weissenberg photographs in conjunction with a least-squares IBM 704 program (Burnham, 1960). The following unit-cell contents were obtained using the resulting precise unit-cell dimensions, a specific gravity of 2.783±.014 g/cc as determined by Stewart (1959), and an analysis on Halfbreed Creek, Montana, material by Ellestad (quoted by Graham, 1935):

$$\begin{array}{cccc}
\left|\begin{array}{l}\mathrm{Na}_{7.58}\\ \mathrm{K}_{0.14}\\ \mathrm{Ca}_{0.05}\end{array}\right| & \left|\begin{array}{l}\mathrm{Ti}_{3.22}\\ \mathrm{Fe}^{3+}_{0.60}\\ \mathrm{Mg}_{0.18}\\ \mathrm{Fe}^{2+}_{0.10}\end{array}\right| & \left|\begin{array}{l}\mathrm{Si}_{15.90}\\ \mathrm{Al}_{0.10}\end{array}\right| & \mathrm{O}_{43.48} \\
\overline{7.77} & \overline{4.10} & \overline{16.00} &
\end{array}$$

INTENSITY DETERMINATION

The specimen used for initial intensity measurement was a cleavage prism with a nearly rectangular cross-section of .016×.031 mm and a length of .250 mm. All intensities were graphically recorded using a single-crystal Geiger-counter diffractometer. Values of Υ, ϕ, $\sin \theta$ and $1/Lp$ were obtained with a standard IBM 704 program. The asymmetric unit of the copper reciprocal sphere contains approximately 610 reflections of which 469 were within recording range of the apparatus. The intensities of these reflections were corrected for Lorentz and polarization factors, and approximate absorption corrections were made according to the method of Buerger and Niizeki (1958).

STRUCTURE ANALYSIS

Patterson synthesis. The three-dimensional Patterson synthesis was computed using MIFR1 (a standard IBM 704 program for computing Fourier series (Sly and Shoemaker, 1960)). The function was obtained in sections normal to c, at intervals of 1/60 along all three axes.

Preliminary considerations. Equipoints of space group $I4/m$ have ranks 2, 4, 8 or 16. It has been noted that the cell contains 44 oxygen atoms. Since combinations of 16 and 8 can be devised to yield 40 and 48, but not 44, at least four oxygen atoms must be located on an equipoint of rank four, or on the two equipoints of rank two. Thus at least four oxygen atoms must occupy equipoint $4e$, $4d$, $4c$, or $2a+2b$. Since there are only four titanium atoms in the unit cell, titanium must also occupy one of these equipoint combinations. Equipoints $4c$ and $4d$ are on the $\bar{4}$ axes, while $4e$, $2a$ and $2b$ are on the 4-fold axes. Coordinates of these equipoints are outlined in Table 2.

A possible distribution of oxygen and titanium would be such that they both occupy the same set of axes. A consideration of equipoint and space requirements shows that such a distribution would consist of a string of alternating titanium and oxygen atoms along either the 4-fold or $\bar{4}$ axes. The interval between titanium and oxygen would be $c/4$. The

TABLE 2. EQUIPOINTS OF RANKS 2 AND 4 IN $I4/m$

	Equipoint	Coordinates
on 4-fold axes	$2a$	000
	$2b$	$00\frac{1}{2}$
	$4e$	$00z;\ 00\bar{z}$
on $\bar{4}$ axes	$4c$	$0\frac{1}{2}0;\ \frac{1}{2}00$
	$4d$	$0\frac{1}{2}\frac{1}{4};\ \frac{1}{2}0\frac{1}{4}$

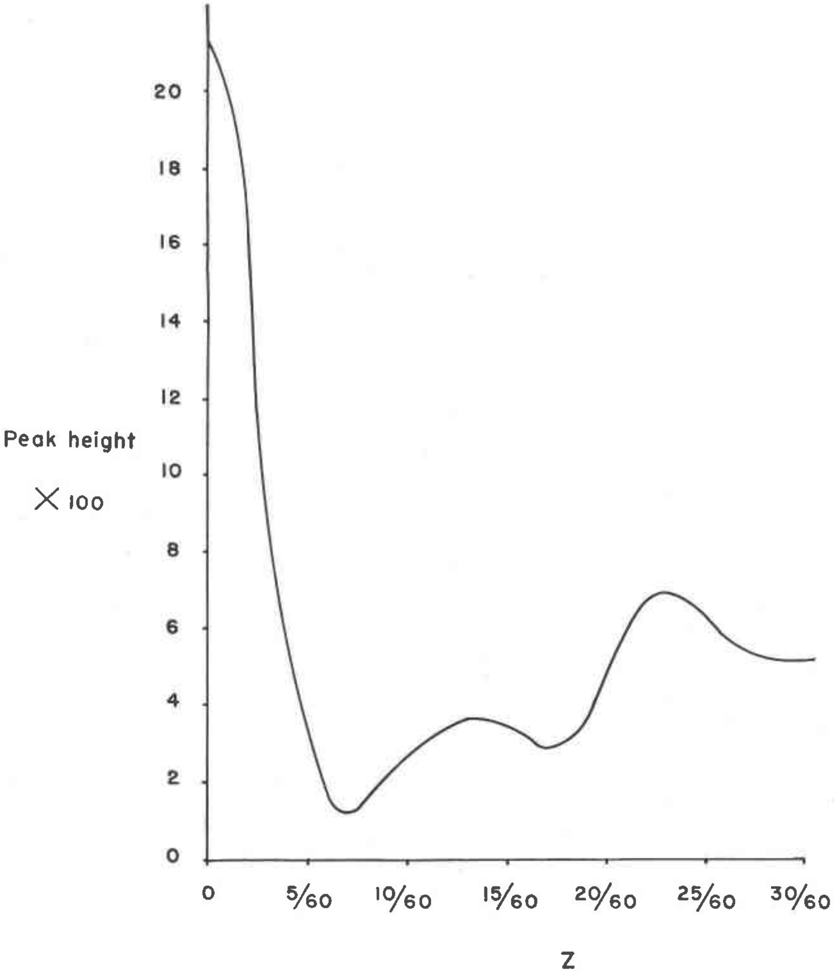

FIG. 1. Harker line [00*z*].

observed $c/4$ distance, 1.99 Å, compares favorably with known Ti-O distances, strongly suggesting that this type of titanium-oxygen distribution occurs in narsarsukite. Further evidence for such a distribution is found in the peaks observed on the Harker line 00*z* (Fig. 1). Peaks are found only at $z=0$, 23/60, 14/60 and 30/60. The chain distribution described above requires Patterson peaks on the Harker line of weight $4Z_{\mathrm{Ti}}Z_{\mathrm{O}}$ at $z=\frac{1}{4}$, and of weight $2(Z_{\mathrm{Ti}}^2+Z_{\mathrm{O}}^2)$ at $z=\frac{1}{2}$. The weights of the observed peaks (372, 520) are approximately equal to the predicted weights (380, 496).

Of the possible equipoints which titanium may occupy, only the z coordinate of equipoint $4e$ is variable. As shown above, the titanium-oxygen chain distribution requires this coordinate to be approximately $\frac{1}{4}$ since titanium atoms are approximately equally spaced along the c axis. With this qualification, all four possible titanium equipoint distributions differ from each other only in the location of the origin. This requires that the Patterson-peak distribution resulting only from Ti:Ti vectors be the same for all four cases.

Theory of the use of the minimum function. Since, in all four possible distributions (with the possible exception of equipoint $4e$) titanium atoms lie on the 4 or $\bar{4}$ axes separated by an interval of $z=\frac{1}{2}$, a method is available for readily solving the structure. Consider, first, only two of the titanium atoms on either 4 or $\bar{4}$, separated by an interval of $z=\frac{1}{2}$. The Patterson maps are dominated by images of the structure in both of these atoms (Buerger, 1959). If these two images can be brought together and the minimum function mapped, the result should be an approximation to the crystal structure. In particular, if all Patterson maps differing by an interval $z=\frac{1}{2}$ are exactly superimposed and the minimum function mapped, the correct solution will result. It is unimportant where the two titanium atoms are located in the actual structure, so long as they lie one above the other and are separated by the interval $c/2$.

An ambiguity is caused by the presence in the unit cell of two sets of titanium-atom pairs related by the body-centering translation. The minimum-function solution will therefore contain two images of the structure in titanium superimposed on each other. The pairs of titanium atoms are related by the component of the centering translation, t, normal to c. Therefore the two images of the structure are related by this translation. The combination of this translation and the 2-fold operation of the 4-fold axis in the origin results in a 2-fold operation at $t/2$ from the origin. Where this 2-fold axis pierces each section, namely at $\frac{1}{4}\frac{1}{4}$, it appears to be an inversion center. Thus the two images of the structure in titanium are related by what appears to be an inversion center in each level of the minimum function at $\frac{1}{4}\frac{1}{4}$.

A further problem is the lack of knowledge of the correct origin of such minimum-function maps because there are four equipoint combinations available for locating 4Ti. The set of minimum-function maps thus contains the true solution to the structure, with an ambiguity, but the coordinates of the atoms will depend on the proper placement of this set of maps with respect to the origin.

Analysis with the minimum function. All Patterson maps differing by an interval of $z=\frac{1}{2}$ were exactly superimposed and the minimum function mapped, as outlined above. The resulting solution showed a very high

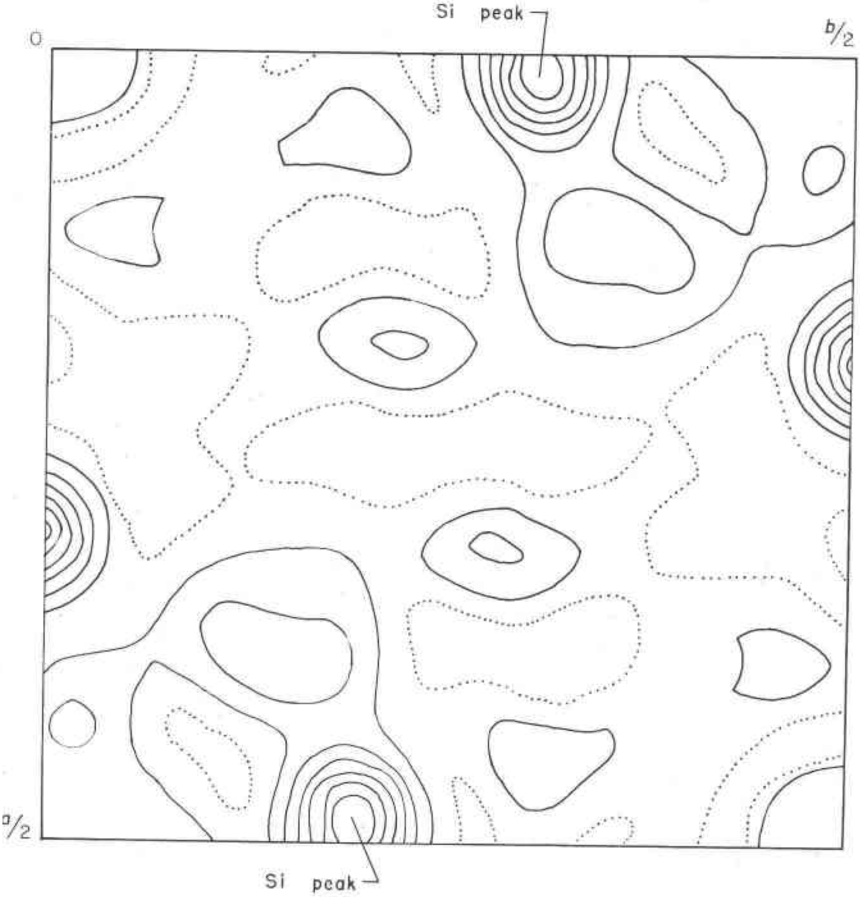

FIG. 2. Level $\frac{11}{60}$ of the minimum-function based on images of the structure in titanium, showing Si peaks.

peak, representing titanium, at the origin. In addition, only one high peak with general coordinates and its inversion equivalent were present (Fig. 2). The weight of this peak compared well with the expected weight of silicon, and comparison of the unit-cell contents and equipoint ranks shows that silicon is the only relatively dense atom with possible general coordinates. The peak was therefore assumed to represent silicon. The location of silicon relative to the titanium peak at the minimum-function origin was thus established, with the exception of the two-fold inversion ambiguity.

An implication map $I4(xy0)$ was next prepared (Fig. 3). This is a pro-

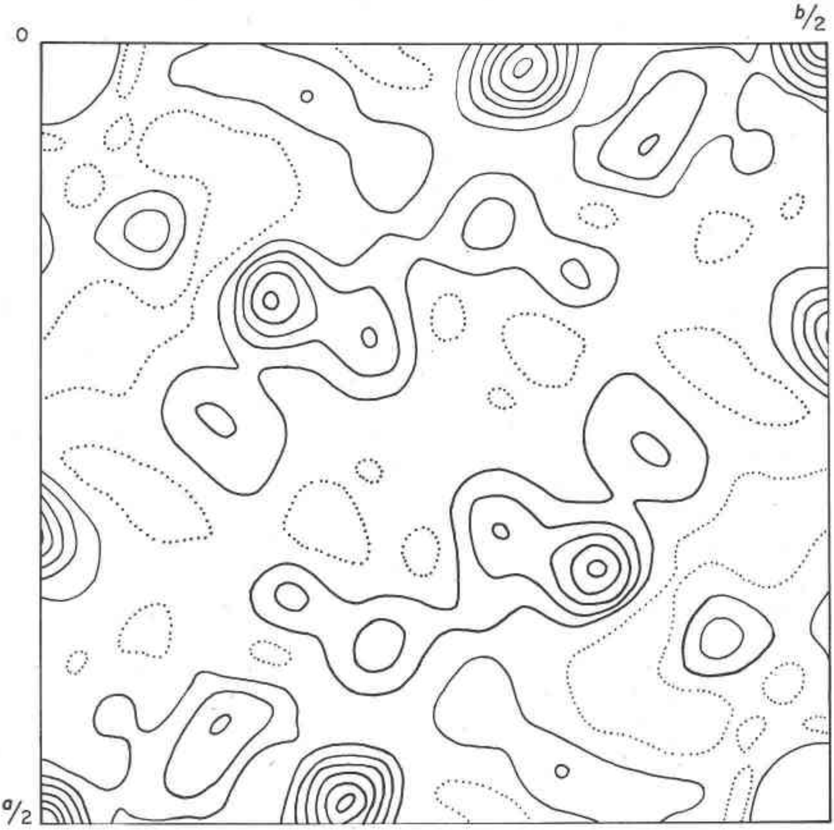

FIG. 3. Implication map $I_4(xy0)$, contours omitted from origin peak.

jection of an approximation to the crystal structure, with ambiguities, on (001). There are high peaks on this map corresponding to all possible projected titanium positions. Two possible titanium positions, 4*c* and 4*d*, occur on the $\bar{4}$ axis at $0\frac{1}{2}$. The set of minimum-function maps was accordingly placed so that the high titanium peak of these maps was superimposed on the high peak at $0\frac{1}{2}$ of the implication map. Since each type of map is an approximation to the crystal structure, with ambiguities, there should be good correlation of high peaks if the titanium atom is actually on equipoint 4*c* or 4*d*. No peak on the implication map was found to correspond to either of the possible silicon peaks on the minimum-function maps with this placement of maps. This eliminated 4*c* and 4*d* as possible titanium locations. The other positions which titanium may occupy, namely, $2a+2b$ or 4*e*, are located on the 4-fold axis at 00 of the implication map. If the minimum-function maps are placed over the implication maps so that the high titanium peak is superimposed on the high peak at 00 of the implication map, there is good correlation with implication peaks, not only of the silicon peaks of Fig. 2, but of all minimum-function peaks. The titanium atoms must therefore be located either on equipoint $4e$ or on $2a+2b$.

It can be easily seen from the minimum-function maps that the silicon and titanium atoms are separated by an interval of $z=4/60$. If titanium is on equipoint $4e$ with $z=\frac{1}{4}$, the silicon atom is on level $15/60-4/60=11/60$. This results in a high silicon reflection peak on the Harker line $00z$ at $z=22/60$. The only peak on the Harker line so far unaccounted for is located at $z=23/60$. On the other hand if the titanium atom is located on equipoint $2a$, the silicon atom would be on a level $0/60\pm 4/60=4/60$, and a high peak would appear on the Harker line at $z=8/60$. The trough in the Patterson function at this position eliminates this possibility. The titanium atom is thus definitely located at $00\frac{1}{4}$, equipoint $4e$. The levels of the minimum function can therefore be given their proper location z. This fixes the location of the silicon atom, which had previously been known only relative to that of titanium.

Minimum function based on a silicon inversion peak. The location of the silicon inversion peak on the Patterson maps was easily derived from the location of the silicon atom. A complete set of three-dimensional minimum-function maps containing an image of the structure as seen from silicon was constructed. Both of the ambiguous inversion-related peaks yielded the same solution.

Initial Patterson-map comparison yielded an M_2 function, but an M_8 function was formed using the 4-fold axis in each M_2 function. A projection of the peaks of the three-dimensional M_8 function is shown in Fig. 4. A comparison of relative peak heights, interpeak distances and coordination numbers with known electron densities, interatomic distances and coordination numbers readily yielded correct identification of the peaks. Only one small false peak remains unlabelled.

REFINEMENT

Refinement of atom parameters was carried out with the Busing and Levy (1959) least-squares IBM 704 program. Input data for the program included the coordinates obtained from the minimum-function maps (Table 3), an arbitrary value of 0.7 for all individual anisotropic temperature factors, and form factors assuming half-ionization of all atoms.

Eleven cycles of refinement were carried out. During the final cycles all data with $F_o=0$ and $|F_o-F_c|/F_o\geq 0.25$ were excluded from the refinement process. The resulting discrepancy factor was $R=0.142$ for all reflections, and 0.115 when reflections with $F_o=0$ were excluded from the calculation.

An electron-density map $\rho(xy)$ was prepared using phases based on the final cycle of refinement. This map contained the expected peaks with correct weights, but many peaks were not perfectly round and regions of very low electron density showed small unexplained peaks. It was thought that these features might be caused by faulty data, so that a decision was made to remeasure all intensities.

A new prismatic cleavage fragment with a cross-section of .028×.033 mm and a length of .203 mm was chosen. Intensities were again collected with the single-crystal Geiger-counter diffractometer, but were measured by a direct-count method. Absorption was graphically corrected for according to the method of Rogers and Moffett (1956). Values of the transmission factor were obtained at 20 degree intervals of Υ and ϕ. Intermediate values were obtained by linear interpolation using an IBM 704 program prepared by Mr. Charles Burnham.

Using these new intensity data and final parameters obtained from the previous refinement, the refinement was continued. Two cycles were executed varying all coordinates and a separate scale factor for each level. Isotropic temperature factors were used but were not varied. Final values for the separate scale factors indicated that there was no systematic variation with level. Cycles three and four were accordingly executed with a single scale factor. After cycle 4, R attained a value of 0.099. All coordinate changes were less than .0004, and the change in scale factor was negligible. The isotropic temperature factors of O_I and O_{II} attained slightly negative values, however.

In an attempt to understand the meaning of the negative temperature factors, we carried out two procedures. In the first place, all of the structure determination had been carried out assuming space group $I4/m$. One cycle of refinement was carried out with symmetry common to all possible space groups consistent with the diffraction symbol. The coordinates of the atoms retained symmetry $I4/m$ during refinement.

Secondly, a difference map, $\Delta\rho(xyz)$ was computed. This indicated that all coordinates and temperature factors were well refined except in the following instances. Anisotropic temperature motion was indicated for Na, and variation of $\Delta\rho(00z)$ along the axis of the titanium-oxygen chain included a negative trough at the titanium position flanked by positive peaks. Such a situation might be accounted for either by disorder of titanium in two positions, or by an extremely large anisotropic temperature motion of Ti. Refinement was therefore continued in the following ways. First, three cycles (cycles 5, 6 and 7) were completed with the titanium atom split into two equal halves. The positions of these "half-

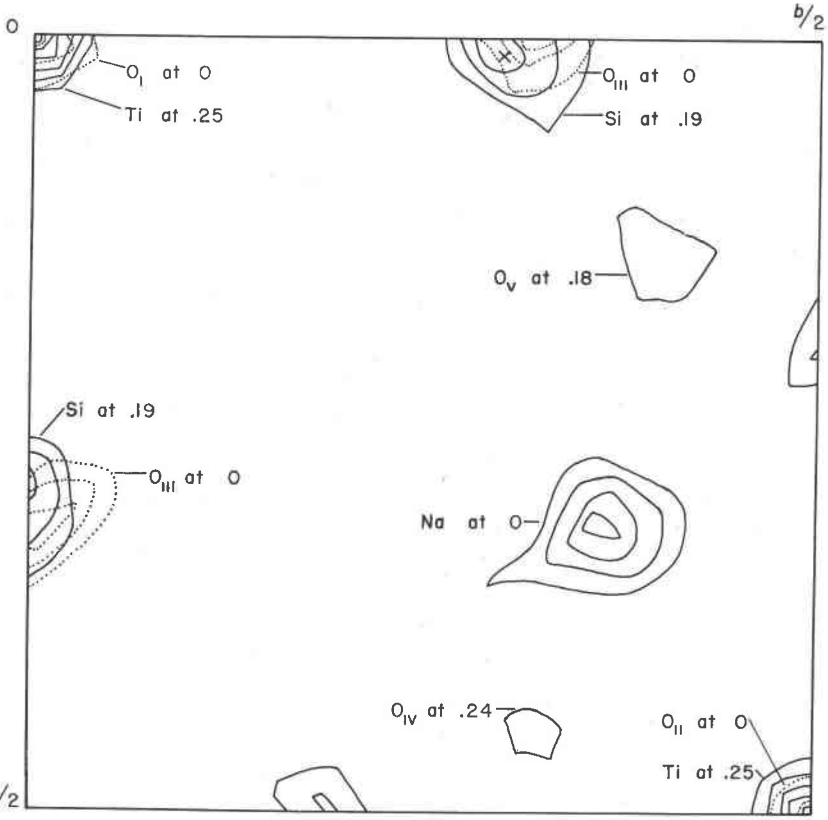

FIG. 4. Projection on (001) of the peaks of the asymmetric unit of the three-dimensional minimum-function which is based on the silicon inversion peak.

titanium" atoms and the anisotropic temperature factors of Ti, O_I, O_{II} and Na were allowed to vary. The titanium-atom coordinates readily refined to positions on the *c* axis whose average was the former value for the single titanium atom. This treatment led to an *R* of 0.085 for all reflections and an *R* of 0.082 for those reflections with $F_o \neq 0$. The negative temperature factors, however, remained.

Secondly, three cycles of refinement were completed during which all anisotropic temperature factors were allowed to vary, titanium being again treated as an individual atom. In an attempt to cause the temperature factors of O_I and O_{II} to become positive, it was assumed that they were more than half ionized. In three subsequent cycles of refinement the temperature factors readily refined. Although several anisotropic temperature factors retained negative values, all equivalent isotropic temperature factors except that of silicon are positive. Since the composition of a site influences its form factor there was a possibility that the negative anisotropic temperature factors were caused by incorrect form-factor curves. However this effect had actually been tested by assuming a different ionization for oxygen, and found not to affect the results noticeably. The final discrepancy factor, R, for all reflections with $F_o \neq 0$ is 0.080.

Since the refinement had converged, we wished to test the result by an electron-density synthesis. Accordingly, structure factors based on parameters obtained from cycle 7 were computed using small positive values for the temperature factors of O_I and O_{II}. (The signs of only 16 reflections

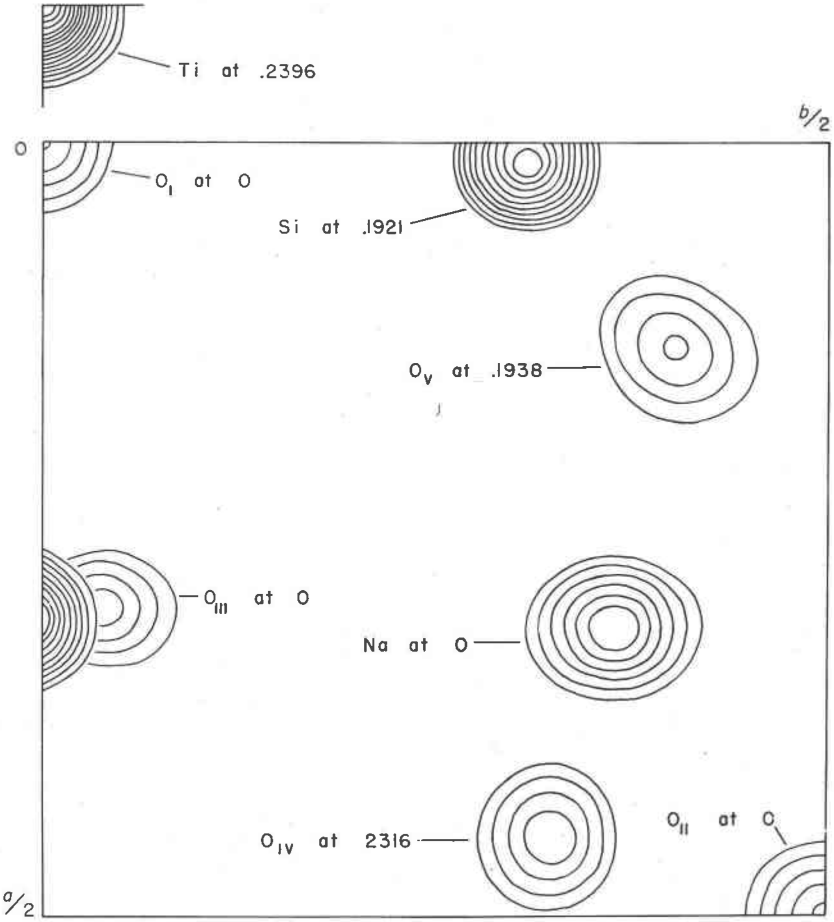

FIG. 5. Projection on (001) of the peaks of $\rho(xyz)$, arbitrary scale, zero contour omitted.

TABLE 3. COMPARISON OF COORDINATES OF ATOMS IN NARSARSUKITE

Atom	x	y	z	B[1]	
Ti	0	0	.250		(from minimum function maps)
	0	0	.250		(given by Pyatenko and Pudovkina)
	0	0	.2396	.130	(from least-squares refinement)
Na	.186	.141	$\frac{1}{2}$		
	.185	.135	$\frac{1}{2}$		
	.1858	.1378	$\frac{1}{2}$	1.38	
Si	.008	.294	.192		
	.013	.307	.202		
	.0118	.3085	.1921	−0.09	
O_I	0	0	0		
	0	0	0		
	0	0	0	0.05	
O_{II}	0	0	$\frac{1}{2}$		
	0	0	$\frac{1}{2}$		
	0	0	$\frac{1}{2}$	0.20	
O_{III}	−.009	.316	0		
	−.025	.299	0		
	−.0400	.3024	0	0.17	
O_{IV}	.055	.179	.250		
	.049	.178	.275		
	.0488	.1754	.2684	0.37	
O_V	.128	.392	.183		
	.134	.402	.198		
	.1324	.4023	.1938	0.32	

[1] Equivalent isotropic temperature factor computed from anisotropic parameters β_{11}, β_{22}, β_{33}, β_{12}, β_{23}, β_{31}.

of low intensity were found to have changed since the commencement of refinement with split titanium atoms.) Final electron-density sections $\rho(xyz)$ were then computed. These contain all of the expected peaks with only the usual minor background fluctuations. A projection on (001) of the peaks of $\rho(xyz)$ is shown in Fig. 5. For comparison with Pyatenko and Pudovkina's Fig. 2, we also computed an electron-density projection

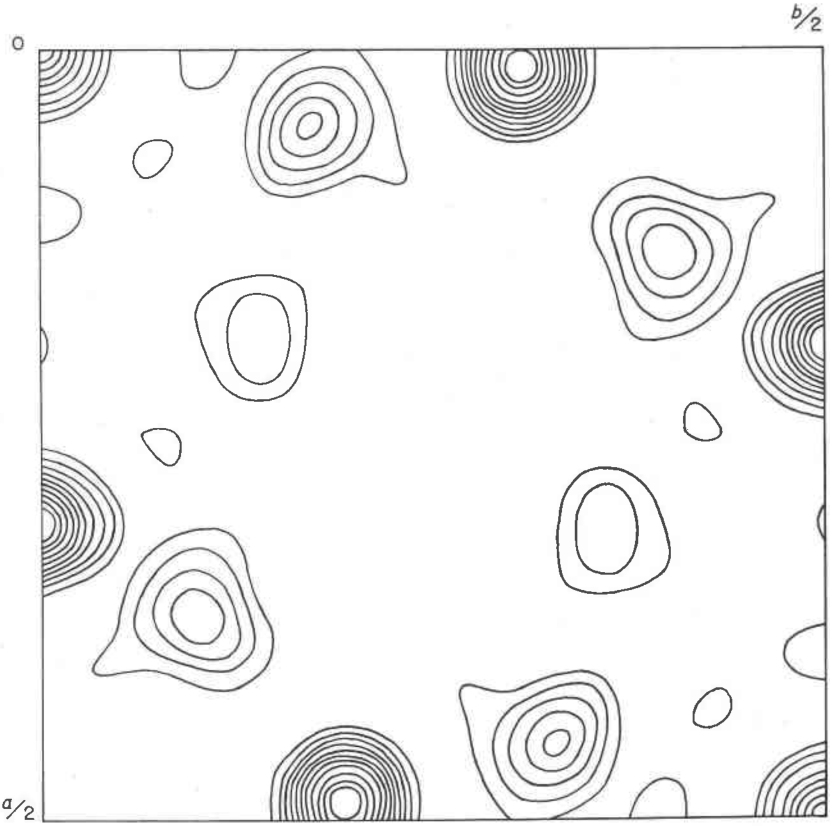

FIG. 6. Electron-density projection $\rho(xy)$, arbitrary scale, zero contour omitted: contour interval on $Ti+O_I+O_{II}$ is 3 times the interval of the rest of the map.

$\rho(xy)$ which is shown in Fig. 6. The somewhat noncircular shapes of the lower contours are obviously caused by series-termination effects. The generally smooth, rounded contours confirm the improvement over the Pyatenko and Pudovkina (1960) structure. Final coordinates are listed in Table 3.

DESCRIPTION OF THE NARSARSUKITE STRUCTURE

The narsarsukite structure is seen in projection along the *c* axis in Fig. 7. The structure can be described as a network having large interstices in which the Na atoms occur. The most striking feature of the network is a multiple chain of linked silicon tetrahedra parallel to the *c* axis of a type unknown except in narsarsukite. The chain is shown in idealized form in Fig. 8*A*. There are a number of ways of describing this unique chain. In

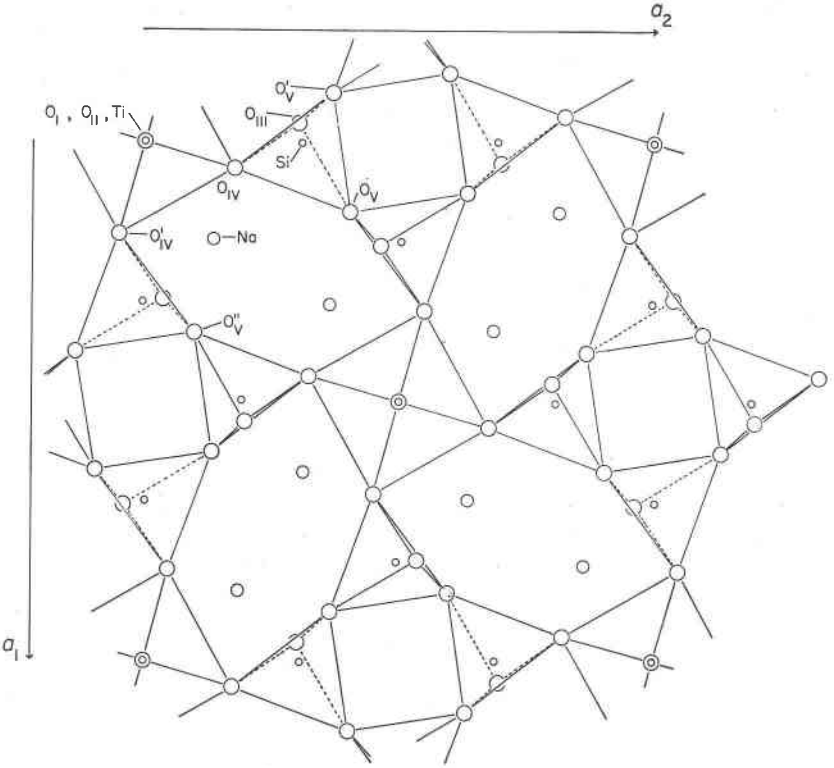

FIG. 7. The narsarsukite structure from $z=0$ to $z=\frac{1}{2}$, as seen looking down the c axis.

the first place, it can be roughly described as a sequence of rings of 4 tetrahedra, linked together in the direction of the c axis to form a tube. It is also useful to note that the tube can be formed by rolling up a hexagonal sheet of composition Si_4O_{10} of the type that occurs in the phyllosilicates. In such sheets the silicon atoms occur at the points of nested hexagons. If the sheet is cut into a ribbon parallel to the long diagonal of the hexagon and four tetrahedra wide, and this is rolled into the form of a tube, the chain shown in Fig. 8*A* is formed. The idealized symmetry of the tube shown in Fig. 8*A* is lowered by distortion in narsarsukite to that shown in Fig. 8*B*. This distortion has the important function of causing all Si—O—Si bond angles to attain values of 140°.

The Si_4O_{10} chains are bonded together by titanium atoms as shown in Fig. 8*B*, and also in projection in Fig. 7. Fig. 8*B* shows that the titanium atoms are part of a chain of alternating Ti and O atoms running parallel to the c axis. The titanium atoms are surrounded by six oxygen atoms in

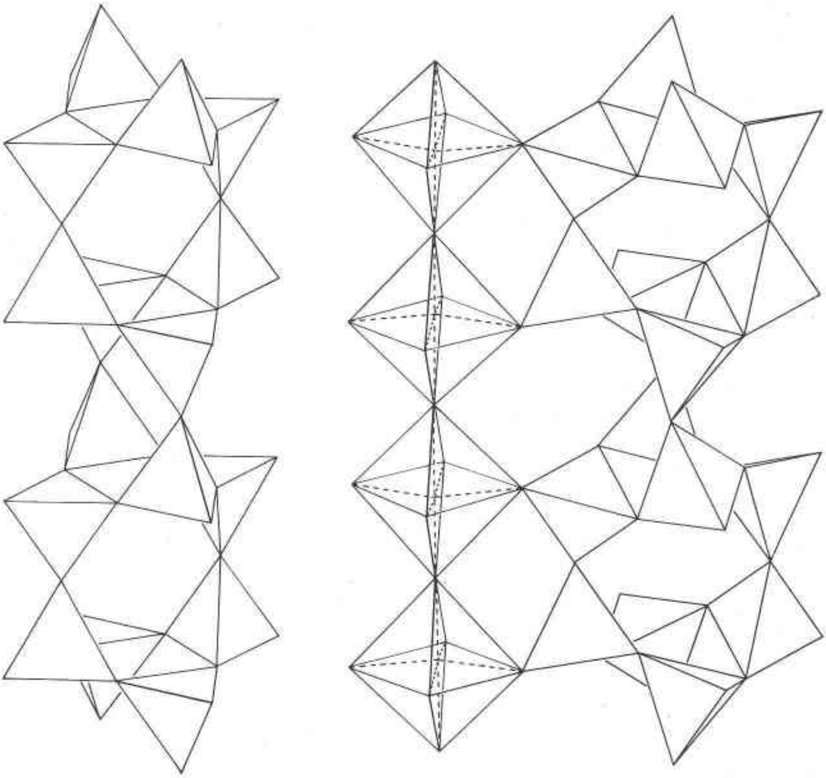

FIG. 8A. (left) Idealized version of the tube of silica tetrahedra found in narsarsukite. B. (right) Tube of silica tetrahedra and chain of titanium octahedra showing actual distortion found in narsarsukite.

approximately octahedral coordination, and the octahedra are linked to compose a straight chain parallel to the *c* axis as seen in projection in Fig. 7. Each Ti—O chain bonds together four Si_4O_{10} chains, and each Si_4O_{10} chain, in turn, bonds together four Ti—O chains. The result is a space network shown in projection in Fig. 7. The network is characterized by rather large void spaces in which the sodium atoms are housed.

Because the atoms O_I and O_{II} are associated only with the Ti atoms, and not with the Si_4O_{10} chain, it is appropriate to write the composition of narsarsukite as $NaTiOSi_4O_{10}$. If the oxygen atoms are lumped together so that the composition is written $NaTiSi_4O_{11}$, this formula suggests a similarity to amphibole, which is not borne out by the structure.

The interatomic distances for narsarsukite are listed in Table 4, and the important bond angles are given in Table 5. The silicon tetrahedron is regular, with average edge length of 2.639 Å and average Si—O dis-

TABLE 4. IMPORTANT INTERATOMIC DISTANCES IN NARSARSUKITE

Si tetrahedron					
Si	x, y, z	1	O_{III}	x, y, z	1.626 Å
		1	O_{IV}	x, y, z	1.601
		1	O_{V}	x, y, z	1.639
		1	O_{V}'	$y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$	1.614
O_{III}	x, y, z	1	O_{IV}	x, y, z	2.672
		1	O_{V}	x, y, z	2.634
		1	O_{V}'	$y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$	2.607
O_{IV}	x, y, z	1	O_{V}	x, y, z	2.661
		1	O_{V}'	$y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$	2.610
O_{V}	x, y, z	1	O_{V}'	$y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$	2.651
Ti octahedron					
Ti	x, y, z	1	O_{I}	x, y, z	1.904
		1	O_{II}	x, y, z	2.070
		4	O_{IV}	x, y, z	1.966
O_{IV}	x, y, z	4	O_{I}	x, y, z	2.892
		4	O_{II}	x, y, z	2.682
		4	O_{IV}'	$y, \bar{x}, z$	2.761
Na polyhedron					
Na	x, y, z	1	O_{II}	x, y, z	2.481
		2	O_{IV}	x, y, z	2.389
		2	O_{IV}'	$y, \bar{x}, z$	2.723
		2	O_{V}''	$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$	2.522
O_{IV}	x, y, z	2	O_{IV}	x, y, 1−z	3.974
		2	O_{IV}'	$y, \bar{x}, z$	2.761
		4	O_{II}	x, y, z	2.682
O_{V}''	$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$	1	O_{V}	$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$	3.080
		2	O_{IV}'	$y, \bar{x}, z$	2.610

tance of 1.620 Å. The octahedron of oxygen atoms surrounding the titanium atoms is almost exactly regular. On the other hand, the titanium atoms are not centered in the octahedra, but are displaced by 0.083 Å towards one another in pairs as brought out in Fig. 8*B*. The displacement results in a Ti—O—Si angle of 138°, and would appear to be caused by the requirement that this angle attain approximately 140°.

The Na atoms are located in interstices of the network, and in the vicinity of O_{II}. A sodium atom has about seven close oxygen neighbors. Six of these are located approximately at six of the eight corners of a cube,

TABLE 5. BOND ANGLES IN NARSARSUKITE

Atoms	Coordinates of Atoms			Bond angle
Si—O_{III}—Si	xyz	xyz	$xy\bar{z}$	139.9°
Si—O_V—Si	xyz	xyz	$\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z$	139.8°
Si—O_{IV}—Ti	xyz	xyz	xyz	137.9°
Ti—O_I—Ti	xyz	xyz	$xy\bar{z}$	180°
Ti—O_{II}—Ti	xyz	xyz	x, y, 1−z	180°
O_I—Ti—O_{IV}	xyz	xyz	xyz	96.6°

while the seventh, namely O_2, is outside the cube.

The oxygen atoms of the Si_4O_{10} tubes are of two types: O_{III} and O_V are between pairs of Si atoms and can be regarded as saturated. Of these, O_{III} is not near Na, but two O_V's are, and comprise two corners of the partial cubic coordination. The exterior points of chains in Fig. 8 are O_{IV} atoms. These are unsaturated, and so are the O_I and O_{II} atoms of the TiO chains. The Na atoms are localized in this region of unsaturated oxygen atoms.

If the titanium octahedra are regarded as regular, then the TiO bond has an electrostatic valence strength of $\frac{2}{3}$. Since O_I receives two such bonds, Pauling's rule would be unsatisfied at this point. But the Ti—O_I distance is shorter than Ti—O_{II} and Ti—O_{IV}, so Ti may be crudely regarded as having a coordination number of 5. If so, the sum of the bonds on O_I is $\frac{4}{5}+\frac{4}{5}=1\frac{3}{5}$, so Pauling's rule is still not satisfied. Presumably a homopolar bond must be attributed to Ti:O_I, because of the short length of this bond.

If the bond Ti—O_{II} is ionic, its general strength may be estimated by the lack of saturation of O_{II} due to nearby Na. Each Na has five unsaturated neighbors. If it contributes $\frac{1}{5}$ to each, O_{II} receives four of these, or $\frac{4}{5}$ total; the residue $\frac{6}{5}$ is divided between the two surrounding Ti atoms, suggesting $\frac{3}{5}$ from each. This is consistent with a five-coordinated Ti($4O_{IV}+1O_{II}$) of ionic valence 3. If this argument is followed, then the valence bonds reaching O_{IV} (on the titanium octahedron equator) are two bonds from Na of strength $\frac{1}{5}$, plus 1 bond from Ti of strength $\frac{3}{5}$, plus one bond from Si of strength 1, giving the sum $2\frac{1}{5}+\frac{3}{5}+1=2$. This scheme perfectly satisfies Pauling's electrostatic valence rule.

ACKNOWLEDGMENTS

This work was supported by a grant from the National Science Foundation. The facilities of the M.I.T. Computation Center were used in conjunction with IBM 704 programs. Dr. David B. Stewart of the U. S.

Geological Survey kindly provided Sage Creek, Montana, material for this study.

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Manuscript received, July 26, 1961.