

Determination and refinement of the crystal structure of turquoise, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$

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With 7 figures

(Received June 9, 1964)

Auszug

Der Türkis hat die Raumgruppe $P\bar{1}$, die Gitterkonstanten $a = 7,424 \text{ \AA}$, $b = 7,629 \text{ \AA}$, $c = 9,910 \text{ \AA}$, $\alpha = 68,61^\circ$, $\beta = 79,71^\circ$, $\gamma = 65,08^\circ$ und eine Formel-einheit in der Elementarzelle, so daß Cu an das Inversionszentrum gebunden ist. Die Reflex-Intensitäten wurden mit einem Proportionalzähler registriert und mit dem Lorentz-Polarisations-Faktor und auf Absorption korrigiert. Aus einer dreidimensionalen Patterson- und einer ebenfalls dreidimensionalen Elektronendichte-Funktion, beruhend allein auf den Vorzeichen der Cu-Beiträge, folgte ein Strukturvorschlag, der durch Fourier- und Ausgleichs-Methoden bis zu $R = 0,07$ verfeinert wurde.

Die Struktur kann beschrieben werden als aufgebaut aus Ebenen von O-Atomen in nahezu dichtester Kugelpackung parallel (001). Zwischen diesen Ebenen sind abwechselnd Schichten von Al in oktaedrischer Koordination und von Cu in (4+2)-Koordination eingelagert. Die oktaedrischen Aniongruppen um die Al-Atome sind einfach oder doppelt; zwei Tetraeder um Phosphoratome verbinden jede Doppelgruppe mit dazu identischen unter Bildung von Tetraeder-Oktaeder-Ketten parallel zur b -Achse. Die PO_4 -Tetraeder ergeben zusammen mit den einfachen Oktaedern um Al-Atome zickzackförmige Ketten in Richtung der c -Achse. Es wurden vier Moleküle H_2O pro Zelle festgestellt.

Abstract

Turquoise is triclinic, space group $P\bar{1}$, with cell dimensions $a = 7.424 \text{ \AA}$, $b = 7.629 \text{ \AA}$, $c = 9.910 \text{ \AA}$, $\alpha = 68.61^\circ$, $\beta = 79.71^\circ$, $\gamma = 65.08^\circ$. The cell contains one formula of $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, so the Cu atom is fixed in an inversion center. Three-dimensional intensity data were collected on a single-crystal diffractometer using a proportional counter as detector, and were corrected for Lorentz-polarization factors and absorption. The interpretation of a three-dimensional Patterson function and of a three-dimensional electron-density function based on signs due to the Cu contribution only, gave a trial

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structure that was refined by Fourier methods and then by least-squares methods to an R factor of 7⁰/₆.

The structure can be described in terms of planes of approximately close-packed oxygen atoms oriented parallel to (001). Planes containing the Al in octahedral coordination and planes containing the Cu in a 4+2 octahedral coordination alternate between two oxygen layers. The octahedral groups of anions around the aluminum are single and double; two phosphorus tetrahedra link each double group to its translational equivalent, building a tetrahedra-octahedra chain parallel to the b axis. The PO₄ tetrahedra together with the simple aluminum octahedra constitute a zig-zag chain in the direction of the c axis. The water content has been determined to be four molecules per cell.

Introduction

The turquoise group is one of the few examples of a well known mineral family whose crystal structures have not been worked out up to the present time. Two isomorphous series can be distinguished in this group. One is the turquoise-chalcociderite series, characterized by isomorphous substitution of Al₂O₃ by Fe₂O₃; this includes as members turquoise¹, henwoodite², rashleighite³, alumo-chalcociderite⁴, and chalcociderite⁵. The other series is formed by isomorphous substitution of Cu by Zn and only the two end members, turquoise and faustite⁶, are known.

Of the whole group, single crystals suitable for x-ray structure determination have been reported only for chalcociderite and turquoise. A recent x-ray study of chalcociderite crystals⁷, has shown a curious feature that can be explained as a very thin epitaxial growth of turquoise on all crystals examined. This fact made chalcociderite an unfavorable case for structure determination.

For almost eighty centuries turquoise had only been known to occur in the cryptocrystalline state. It was not until 1912 that the first single crystals of turquoise were described by SCHALLER¹. Crystals

¹ WALDEMAR T. SCHALLER, Crystallized turquoise from Virginia. *Amer. Jour. Sci.* **33** (1912) 35—40.

² E. FISCHER, Henwoodit, ein Glied der Türkis-Chalkociderit-Reihe. *Chemie der Erde* **21** (1961) 97—100.

³ ARTHUR RUSSEL, On rashleighite, a new mineral from Cornwall, intermediate between turquoise and chalcociderite. *Min. Mag.* **28** (1948) 353—383.

⁴ A. JAHN und E. GRUNER, Alumo-Chalkociderit, ein neues Mineral vom Schneckenstein i. V. *Mitt. Vogtld. Ges. Naturf. Nr. 8*, 1933. (Taken from Ref. ².)

⁵ N. S. MASKELYNE, On andrewsite and chalcociderite. *Jour. Chem. Soc. [London]* **28** (1875) 586—691.

⁶ RICHARD C. ERD, MARGARET D. FOSTER and PAUL D. PROCTOR, Faustite, a new mineral, the zinc analogue of turquoise. *Amer. Min.* **38** (1953) 964—971.

⁷ HILDA CID-DRESDNER, X-ray study of chalcociderite. *Amer. Min.* (in press).

from SCHALLER's original sample were kindly provided by Professor CLIFFORD FRONDEL, of Harvard University, and by Dr. GEORGE SWITZER, of the U. S. National Museum, for use in the crystal-structure determination reported here.

Unit cell and space group

Turquoise is triclinic and the space group is $P\bar{1}$, as reported by SCHALLER¹ and GRAHAM⁸. The determination of the unit cell was based on data from two precession photographs, GRAHAM's a and b axes being the precession axes. As is customarily done for triclinic crystals, a reduced cell was chosen according to BUERGER's and BALASHOV's convention^{9,10}. This convention uses the three shortest non-coplanar translations of the lattice as crystallographic axes and requires the interaxial angles to be all-acute or all-obtuse. The orientation of the set is completely defined by the condition $a < b < c$.

The relations of the chosen reduced cell to the previous work of SCHALLER and GRAHAM are given below. It should be noted that GRAHAM's cell is a reduced cell that satisfied PEACOCK's conventions for the setting of a triclinic crystal¹¹. His set includes the three shortest non-coplanar translations of the lattice and satisfies the relations $a < c < b$; $\alpha, \beta > 90^\circ$, $\gamma < 90^\circ$.

	Direct transformation	Inverse transformation
SCHALLER to GRAHAM	$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 1 & 0 \\ -1 & -1 & -1 \\ 0 & 0 & 1 \end{bmatrix}$
GRAHAM to CID-DRESDNER	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}$
SCHALLER to CID-DRESDNER	$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & -1 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 1 \\ -1 & 1 & -1 \\ 0 & -1 & 0 \end{bmatrix}$

⁸ A. R. GRAHAM, X-ray study of chalcocyanite and turquoise. Univ. Toronto, Stud. Geol. Soc. **52** (1948) 39–53.

⁹ M. J. BUERGER, Reduced cells. Z. Kristallogr. **109** (1957) 42–60. — M. J. BUERGER, Note on reduced cells. Z. Kristallogr. **113** (1960) 52–56.

¹⁰ V. BALASHOV, The choice of the unit cell in the triclinic system. Acta Crystallogr. **9** (1956) 319–320.

¹¹ M. A. PEACOCK, On the crystallography of axinite and the normal setting of triclinic crystals. Amer. Min. **22** (1937) 588–620, 987–989.

Final cell constants were obtained by refinement of data from three axial photographs taken with a precision back-reflection Weissenberg camera¹². Five cycles of least-squares refinement using BURNHAM's LCLSQ 3 program¹³ for the IBM 7094 computer yielded the lattice constants listed in Table 1, where they are compared with GRAHAM's values. The centro-symmetric space group was confirmed by a piezoelectric test.

Table 1. *Turquoise cell constants*

	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ
GRAHAM's values for the all-acute cell	7.46 Å	7.65 Å	9.91 Å	68.35°	69.43°	64.62°
This work	7.424 ±.004 Å	7.629 ±.003 Å	9.910 ±.004 Å	68.61 ±.03°	69.71 ±.04°	65.08 ±.03°

The refined cell parameters of Table 1 and SCHALLER's analysis of crystalline turquoise from Virginia¹ were used to determine the unit-cell contents. The original formula of turquoise¹ was given as $\text{CuAl}_6(\text{PO}_4)_4\text{O}_4 \cdot 9\text{H}_2\text{O}$, since the chemical analysis reported 20 non-water oxygens. The values listed below have been normalized to 20 oxygens since the available values of the specific gravity¹⁰ were not considered satisfactory.

Cu	0.94
P	4.02
Al	5.99
Fe	0.02
O	20.00
H ₂ O	9.33

This formula corresponds to the ideal composition $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot (4\text{H}_2\text{O} + \text{H}_2\text{O})$. Whether or not this extra water molecule belonged in the atomic arrangement of turquoise was to be elucidated from the structure determination.

Intensity data

A small turquoise crystal of average dimension 0.18 mm was selected for intensity measurements. The shape of the crystal was an irregular tetrahedron with truncated corners. Although this irregular

¹² M. J. BUEGER, The precision determination of the linear and angular lattice constants of single crystals. *Z. Kristallogr. (A)* **97** (1937) 433–468.

¹³ CHARLES W. BURNHAM, Lattice constants refinement. *Carnegie Inst. of Washington Ann. Rept.* **61** (1962) 132–135.

shape precluded an accurate absorption correction, the choice of this particular crystal was made on account of its transparency, perfect extinction under the polarizing microscope, and the good shape of the x-ray diffraction spots that were obtained with it.

Of the 2600 reflections in the positive hemisphere of the Ewald sphere for CuK radiation, 1650 which were within the instrument limit, were measured on a single-crystal counter diffractometer. The instrument was based on equi-inclination, Weissenberg geometry¹⁴, and the parameters γ and φ as well as the Lorentz-polarization factor for each reflection were obtained using a program written by PREWITT¹⁵ for the IBM 7094 computer. A proportional counter was used as a detector.

Counter-intensity data for each reflection consisted of the scan count [i.e., the total number of counts while the crystal was rotated through the maxima, from a position φ_1 to φ_2 , where $\varphi_1 < \varphi(hkl) < \varphi_2$] and fixed-time background counts for the positions φ_1 and φ_2 . The average background count from these last two measurements was subtracted from the total scan count.

The calibration of the absorbing foil was made in the following way. The integrated intensities of ten medium-sized reflections were measured twice; first with the Al foil and then without it. The ratio between the two measurements gave a good approximation of the factor by which the strongest reflection had been reduced. In addition, a separate scale factor for these reflections was allowed in the last cycles of refinement.

The calculation of the observed structure factors was made through two data-reduction programs¹⁶ written for the IBM 7094 computer. The first computed the integrated intensities, allowing appropriate scaling adjustments for the reflections measured with Al foils; the second one applied Lorentz-polarization and absorption corrections to the integrated intensities. In this case an approximation to the absorption correction was made by applying a spherical-absorption correction since the lack of well-developed crystal faces made it impossible to use a prismatic correction¹⁶. Since the product

¹⁴ M. J. BUERGER, New single-crystal counter-tube technique. *Acta Crystallogr.* **9** (1956) 834.

¹⁵ C. T. PREWITT, The parameters γ and φ for equi-inclination with application to the single crystal-counter diffractometer. *Z. Kristallogr.* **114** (1960) 355–360.

¹⁶ CHARLES W. BURNHAM, The structures and crystal chemistry of the aluminum-silicate minerals. Ph. D. thesis (1961) Mass. Inst. of Technology, Cambridge, Mass.

of the linear-absorption coefficient and the average radius of the "sphere" was 0.835, the error introduced by this approximation was not expected to affect the results greatly, even if it showed up as a temperature effect.

Structure determination

a) Two-dimensional work

An attempt was made to solve the structure in projections. The three Patterson projections $P(xy)$, $P(xz)$ and $P(yz)$ were calculated with the FORTRAN program ERFR2 on the IBM 7094 computer¹⁷. The

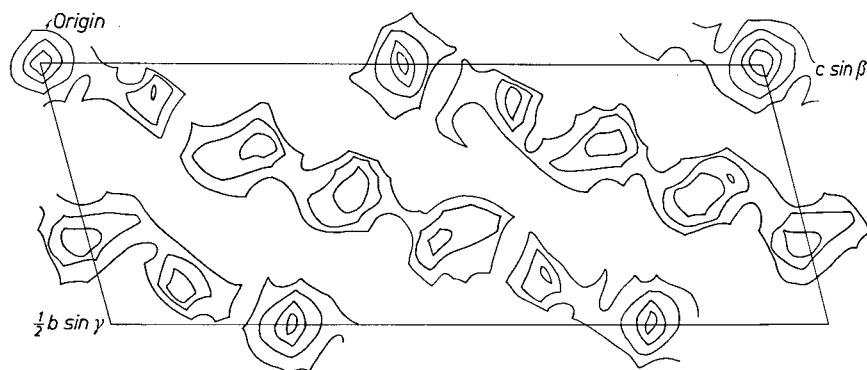


Fig. 1. Minimum function $M_4(yz)$

projection $P(yz)$ was studied first since it should show less superposition. The two strongest peaks were assumed to define the interatomic vectors from the copper atom to two other cations. Two minimum function $M_2(yz)$, based on the corresponding inversion peaks, were calculated and combined to produce the function $M_4(yz)$ which is illustrated in Fig. 1. The maxima from $M_4(yz)$ provided the coordinates y and z for a model structure, the x coordinates being obtained by correlation of $M_4(yz)$ with the other two Patterson projections. This model structure was refined independently in the three projections by successive Fourier syntheses followed by structure-factor calculations to discrepancy factors $R = 49.3\%$ for $\rho(xy)$, $R = 53.0\%$ for $\rho(xz)$, and $R = 36.5\%$ for $\rho(yz)$. At this stage the three projections

¹⁷ W. G. SLY, D. P. SHOEMAKER and J. H. VAN DER HENDE, ERFR2, a two and three-dimensional crystallographic Fourier summation program for the IBM 7090 computer. Esso Research and Engineering Co., Londen, N. J. Publication No. CBRL-22m-62.

could not be correlated any longer, and neither the Fourier refinement nor least-squares refinement succeeded in attaining further convergence. It was decided then that full three-dimensional data were necessary to solve the structure. Accordingly the model structure was discarded and a new start in three dimensions was made.

b) Three-dimensional work

A three-dimensional Patterson function, based on the 1600 intensities collected, was calculated. In the interpretation of the Patterson function the following features were taken into consideration:

1. Turquoise can be treated as a structure composed of a heavy atom at the origin and a residual structure of atoms randomly distributed through the unit cell. The ratio of the contribution from the heavy atom and the maximum contribution of the residue is only 12%. Nevertheless the heavy atom is always making a maximum positive contribution. On the other hand, the contribution of residual atoms will never attain more than a fraction of their maximum value due to the fact that they are randomly distributed. Hence, in spite of the small ratio, the probabilities are that most of the structure-factor signs will be positive. If so, an electron-density function calculated with $|F_{o,hkl}|$ as coefficients will approximate the real structure.

2. In the absence of a substructure the strongest peaks in the Patterson map should correspond to vectors from the Cu atom to the Al and P atoms. The next highest peaks should be the Cu—O interactions of approximately the same height as an Al—P peak, but both about half of the Cu—Al peak. (Actually it was not expected that this would hold rigorously since structures based on oxygen are likely to show some kind of a substructure.)

3. The Cu is expected to be in a distorted octahedral coordination¹⁸ with four oxygens at an approximate distance of 2 Å and the other two at a distance of 2.5 Å. The Al is expected to be in octahedral coordination with approximate Al—O distances of 1.9 Å, and the P will be surrounded by an oxygen tetrahedron with approximate P—O distances of 1.5 Å.

4. At least the peaks chosen as the cations in the structure should project as a peak in the old $M_4(yz)$ function.

¹⁸ F. ALBERT COTTON and G. WILKINSON, *Advanced inorganic chemistry*. Interscience Publishers (1962) 560—610.

An electron-density function, with all signs positive, was calculated, and from it a model structure which fulfilled all the preceding conditions was chosen. This model was refined by four successive electron-density functions followed by structure-factor calculations from the original discrepancy factor $R = 62\%$ to $R = 27\%$. In the course of the Fourier refinement five of the oxygens and one of the phosphorus atoms from the original model were found to be incorrect. The peak erroneously assumed to be a phosphorus was a substructure peak due to the superposition of the almost identical Al(1)—P(1) and Al(2)—P(2) vectors.

At this point the Fourier refinement had converged. The electron-density function whose atomic coordinates gave an R of 27% showed round peaks of correct relative heights in the atomic locations and no spurious peaks. Consequently the structure was considered solved and the model was submitted to least-squares refinement. Only four water molecules were included in the structure, since no extra peak that could be attributed to the other oxygen had been found. On the other hand, the 28 oxygens per cell fulfilled the coordination requirements of all the cations, and if a fifth water molecule were to be placed in the unit cell it could not be attached to the cations in any of the usual ways.

Refinement of the structure

Least-squares refinement of the turquoise structure was done on an IBM 7094 computer using the full-matrix program written by PREWITT¹⁹. Atomic scattering factors for Cu^{+2} , O, Al^{+1} , P, together with individual isotropic-temperature factors, were used in the first four cycles of least-squares refinement. The initial temperature coefficients were taken from the pseudomalachite structure²⁰, for Cu, O and P, and from the andalusite²¹ structure for Al. These values were 0.5 for Cu, 0.15 for P, 0.6 for O and 0.25 for Al.

Only one scale factor for all reflections was used in the initial stages of the refinement. No rejection test was included, but, at this point, a special weighting scheme was used. The product of the discrepancy factor of a group of reflections and the weight of these reflections

¹⁹ C. T. PREWITT, Structures and crystal chemistry of wollastonite and pectolite. Ph. D. thesis (1962) Mass. Inst. of Technology, Cambridge, Mass.

²⁰ SUBRATA GHOSE, The crystal structure of pseudomalachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$. Acta Crystallogr. **16** (1963) 124—128.

²¹ CHARLES W. BURNHAM and M. J. BUERGER, Refinement of the crystal structure of andalusite. Z. Kristallogr. **115** (1961) 269—290.

was maintained constant by this weighting scheme²². It was designed to give a larger weight to those structure factors that showed a better agreement, because this is desirable in the initial stages of the refinement.

One cycle of least-squares refinement, varying the atomic coordinates and the scale factor but not the temperature factors, improved the R factor from 27% to 14.2%. Three more cycles in the same conditions gave an R of 13.5% and no movement in the atomic positions larger than the standard deviation was observed.

At this point the weighting scheme was changed. All reflections were given the same weight in order to allow more reflections to influence the refinement. Three more cycles of refinement only improved the R factor to 13.2%.

Two scale factors, one for the reflections measured with an Al absorber and one for all the rest, were used from this point on. One cycle, varying isotropic temperature factors together with both scale factors, was run in order to study the interaction among these parameters. This was done through the Geller matrix coefficients²³ obtained from the least-squares refinement program. Rather large correlation coefficients were obtained for interactions between scale factor (1) and scale factor (2), and for interactions between scale factors and temperature factors. Accordingly, the scale factors and temperature factors were varied in consecutive independent cycles.

After three cycles of refinement of the isotropic temperature coefficients the discrepancy index R had attained 10%. A three-dimensional difference-Fourier synthesis was calculated in order to see the hydrogen atoms. There are eight hydrogens in the asymmetric unit of turquoise, four are attached to two water molecules and the other four belong to OH radicals. If those hydrogens were found, it would be the best way to differentiate an OH radical from an H₂O molecule.

The difference-synthesis maps showed two types of anomalies; these were, peaks in six out of the eight expected locations of the hydrogens, and also the characteristic combination of positive and negative peaks attributed to anisotropic motion of the atoms. Again,

²² BERNHARDT J. WUENSCH, The nature of the crystal structures of some sulfide minerals with substructures. Ph. D. thesis (1963) Mass. Inst. of Technology, Cambridge, Mass.

²³ S. GELLER, Parameter interaction in least-squares structure refinement. *Acta Crystallogr.* **14** (1961) 1026–1035.

no peak that could be interpreted as the fifth water molecule was found. When the six hydrogens were included, but not varied in a final cycle of isotropic refinement, the resulting R factor became 9.5%.

Four cycles of anisotropic refinement with the six hydrogens, included but not varied, converged to an R factor of 7.2%. During this refinement five oxygens did not maintain a definite positive character, even though their equivalent isotropic temperature factors

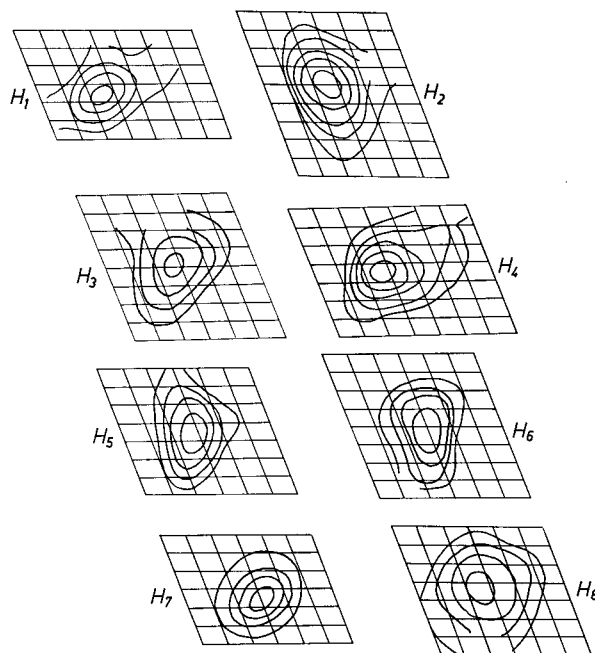


Fig. 2. The eight hydrogens of the turquoise structure

were always positive. This was attributed to errors in the absorption correction due to the deviation of the shape of the crystal from a sphere.

A final three-dimensional difference-Fourier synthesis, using the results from the final cycle of anisotropic refinement, with the six hydrogens excluded, was calculated. The positions from the six hydrogens plus two others were recovered from it. The eight hydrogen peaks are shown in Fig. 2. When the hydrogen coordinates obtained from the last three-dimensional difference-Fourier synthesis were included in the refinement, a final discrepancy index of 7% was attained.

