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# KINOITE, A NEW HYDROUS COPPER CALCIUM SILICATE MINERAL FROM ARIZONA

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## ABSTRACT

Kinoite, $Cu_2Ca_2Si_3O_{10}\cdot 2H_2O$, a new species from the northern Santa Rita Mountains, Pima County, Arizona, occurs as single crystals and in veinlets associated with apophyllite, native copper, and copper sulfide minerals. It was found in drill cores which cut skarn developed in a Paleozoic limestone sequence.

X-ray crystallographic data include: $a=6.990\pm.004$, $b=12..890\pm.003$, $c=5.654\pm.002$ Å; $\beta=96°05'\pm04'$; $V=507.097$ Å$^3$; space group, $P2_1/m$. Strongest powder diffraction lines are 4.72 (10), 3.052 (8), 6.441 (7), 2.116 (4), 3.138 (3), 2.951 (3), 2.315 (3), and 2.078 (2) Å.

It is monoclinic with $a:b:c=.542:1:.439$, and $\beta=96°05'$. Crystal morphology is dominated by $\{hk0\}$, and crystals are tabular in the $b$-$c$ plane. {011} is commonly present although terminal forms are poorly developed. It exhibits excellent {010} cleavage and distinct {100} and {001} cleavages. It is deep azurite blue and transparent to translucent. Measured density is $3.16\pm.03$; the calculated value is 3.193 g/cm$^3$ with $Z=2$. Hardness is about 5 on the Mohs scale. Crystals are optically $(-)$; $2V=68°$; $\alpha=1.638$ (pale greenish blue), $\beta=1.665$ (blue), $\gamma=1.676$ (deep blue). $Z\wedge c$ near 0°, $X=b$, $r<v$ distinct.

The mineral is named for Fr. Eusebio Francisco Kino (1645–1711), celebrated Jesuit pioneer of the southwestern United States.

## INTRODUCTION

Examination of core obtained in exploratory diamond drilling by the Anaconda Company in the Santa Rita Mountains, Pima County, Arizona, by Mr. W. F. Mathias, supervising geologist, revealed the presence of a "blue oxidized copper mineral" in BX core from depth. The core was subsequently examined by Mr. G. A. Barber, Chief Geologist of the Southwest Region of the Anaconda Company, who observed that although the mineral superficially resembled azurite, it failed to effervesce with dilute HCl. Mr. Barber referred the mineral to one of us (JWA) for identification. The mineral was also subsequently recognized in core from two near-by drill holes, although no more information is available concerning its spatial distribution. The type locality is on claims held under an agreement between the Anaconda Company and the Banner Mining Company, situated on the east side of the northern Santa Rita Mountains between the old mining camps of Helvetia, to the northwest, and Rosemont, to the southeast. The locality is 30 airline miles south-southeast from Tucson at Lat. 31°51′N., Long. 110°45′W.

The mineral is named in honor of Italian-born Fr. Eusebio Francisco Kino (1645–1711), the remarkable Jesuit missionary who was for a quarter of a century the outstanding figure on the Sonora-Arizona-California frontier (Bolton, 1960).

Kinoite[1] (pronounced Kē′nō-ite) joins four other copper silicate minerals as having been first recognized from Arizona: shattuckite and bisbeeite (Schaller, 1915), ajoite (Schaller and Vlisidis, 1958), and papagoite (Hutton and Vlisidis, 1960).

## OCCURRENCE

The core containing the new mineral is from a diamond drill hole which penetrated contact metamorphosed sedimentary rocks consisting principally of limestones and dolomites corresponding to a Paleozoic series exposed at the surface. In the limited vertical extent of core examined the rock is skarn composed of diopside, garnet, calcite, and quartz. The rock is strongly brecciated and was transected by at least one fault whose gouge consists of calcite, fine diopside, and an aluminous 15 Å expanding-layer smectite. Apophyllite is very abundant in the skarn and occurs characteristically as vuggy, well-crystallized masses as well as along seams filling fractures. Kinoite is embedded in and penetrates the surface of apophyllite crystals. Crystals of Kinoite in this occurrence are typically well-formed and single. The new mineral is also observed in millimeter-thick veinlets filling fracture which cut across both skarn and fault gouge. Djurleite, bornite, and chalcopyrite are irregularly disseminated throughout the skarn. Native copper is present in very small amounts in the skarn and is also embedded in apophyllite crystals with kinoite in the vuggy areas. Where the native copper emerges through the surface of apophyllite the portion within the apophyllite is bright while the free portion is tarnished black.

Kinoite and native copper are clearly contemporaneous with apophyllite and are primary in origin, i.e. not formed under oxidizing conditions related to a supergene process. The apophyllite is interpreted as being of a later generation than the skarn minerals and the solutions which gave rise to kinoite and native copper may also have produced the sulfide minerals.

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[1] The name kinoite has been approved by the Commission on New Mineral Names of the International Mineralogical Association.

## X-RAY DIFFRACTION STUDY

Weissenburg photographs taken about three axial directions show the only systematic omissions to be in $0k0$ with $k=2n$; the space group is $P2_1/m$.[1] The unit cell parameters reported in Table 1 are the result of averaging least squares refined values obtained from 1) 10 axial reflections measured with a single crystal diffractometer, and 2) line measurements on a powder photograph. The powder photograph (Table 2) was made using a Straumanis-type 114.59 mm diameter camera with Ni-filtered copper radiation (CuK$\alpha$=1.5418 Å). The pattern was indexed using the cell parameters obtained from single crystal measurements.

TABLE 1. UNIT CELL CONSTANTS OF KINOITE

| | |
|---|---|
| $a=6.990\pm.004$Å | $\rho$ meas. $=3.16\pm.03$ g/cm$^3$ |
| $b=12.890\pm.003$Å | $\rho$ calc. $=3.193$ g/cm$^3$ |
| $c=5.654\pm.002$Å | $V=507.097$Å$^3$ |
| $\beta=96°05'\pm04'$ | $Z=2$ |
| Space Group: $P2_1/m$ | |

## MORPHOLOGY

Crystals of kinoite are fairly abundant, but no complete euhedra were obtained. Crystal morphology was studied on a Stoe two-circle goniometer but because of the generally inferior development and poor reflectivity of terminal forms the morphological data of Table 3 were calculated from the X-ray cell parameters. Only observed forms are presented in the table. The crystal orientation in agreement with the X-ray cell is followed for the morphological description.

Crystals are invariably tabular in the plane of the *b* and *c* axes and are slightly elongated by extension on *c*. The $[hk0]$ zone is striated and consistently presents a curved aspect because of extensive development of vicinal forms. On a number of crystals examined these show a tendency to cluster in the regions of $\{110\}$ and $\{320\}$. $\{100\}$ and $\{010\}$ are not significantly developed on any crystal. Terminal faces are poorly developed but $\{011\}$ is the principal habit-controlling terminal form (Fig. 1). A pseudoorthorhombic aspect is imparted to some specimens by the presence of $\{\bar{1}33\}$ which with $\{011\}$ suggests an apparent symmetry plane parallel to $\{100\}$. The poor development and inferior quality of the terminal faces may be the result of solution etching.

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[1] Centrosymmetry has been confirmed by a complete structure analysis of kinoite performed by one of us (RBL), refinement having proceeded to R = .06.

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR KINOITE

| *I*est[a] | *d* (meas) | *d* (calc)[b] | *hkl* |
|---|---|---|---|
| 15 | 6.94 | 6.947 | 100 |
| 74 | 6.44 | 6.441 | 020 |
| 4 | 6.14 | 6.115 | 110 |
| 7 | 5.63 | 5.612 | 001 |
| 100 | 4.72 | 4.723 | 120 |
| 19 | 4.35 | 4.345 | $\bar{1}11$ |
| 26 | 3.951 | 3.957 | 111 |
| 7 | 3.741 | 3.752 | $\bar{1}21$ |
| 7 | 3.645 | 3.652 | 130 |
| 11 | 3.489 | 3.493<br>3.474 | 121<br>200 |
| 7 | 3.412 | 3.413 | 031 |
| 11 | 3.344 | 3.354 | 210 |
| 30 | 3.138 | 3.144 | $\bar{1}31$ |
| 81 | 3.052 | 3.057 | 220 |
| 7 | 2.980 | 2.987 | 131 |
| 7 | 2.920 | 2.922 | 140 |
| 15 | 2.799 | 2.798<br>2.794 | $\bar{2}21$<br>041 |
| 4 | 2.751 | 2.758<br>2.745 | 211<br>012 |
| 7 | 2.703 | 2.707 | $\bar{1}02$ |
| 2 | 2.632 | 2.641 | $\bar{1}41$ |
| 11 | 2.573 | 2.575 | 022 |
| 7B | 2.505 | 2.517<br>2.513<br>2.495 | $\bar{2}31$<br>102<br>$\bar{1}22$ |
| 15B | 2.353 | 2.362<br>2.359<br>2.351<br>2.341 | 240<br>231<br>032<br>122 |
| 30 | 2.315 | 2.316 | 300 |
| 2 | 2.285 | 2.290 | $\bar{1}32$ |
| 4 | 2.236 | 2.226 | $\bar{3}01$ |
| 11 | 2.179 | 2.179 | 320 |
| 7 | 2.144 | 2.147 | 060 |
| 41 | 2.116 | 2.117 | 042 |
| 22 | 2.073 | 2.079<br>2.072 | 202<br>$\bar{1}42$ |
| 1 | 1.977 | 1.976 | $\bar{3}31$ |
| 11 | 1.868 | 1.868<br>1.866 | $\bar{3}12$<br>$\bar{1}52$ |
| 4 | 1.810 | 1.812 | $\bar{3}22$ |
| 4 | 1.740 | 1.746<br>1.737 | 113<br>400 |
| 2 | 1.708 | 1.709<br>1.706 | $\bar{1}71$<br>$\bar{1}33$ |
| 9 | 1.681 | 1.683<br>1.682 | 171<br>$\bar{1}62$ |
| 22 | 1.628 | 1.629 | $\bar{3}42$ |
| 4 | 1.610 | 1.610 | 080 |
| 11 | 1.570 | 1.572<br>1.569 | $\bar{2}62$<br>180 |
| 7 | 1.502 | 1.504 | 342 |
| 6 | 1.460 | 1.461<br>1.461 | 280<br>$\bar{4}32$ |
| 4 | 1.418 | 1.418 | $\bar{3}62$ |
| 4B | 1.396 | 1.399 | $\bar{4}42$ |
| 2 | 1.355 | 1.358<br>1.356 | 520<br>182 |
| 4 | 1.339 | 1.337 | $\bar{1}34$ |
| 4 | 1.321 | 1.321 | 124 |
| 2 | 1.289 | 1.289 | 461 |
| 4 | 1.248 | 1.248 | $\bar{2}44$ |
| 4 | 1.208 | 1.208 | 2.10.0 |
| 4 | 1.175 | 1.176<br>1.176 | $\bar{1}64$<br>064 |

[a] Intensities estimated visually with calibrated film strip; measured intensities were compared with intensities obtained on a single crystal diffractometer to assist in indexing.

[b] Only those calculated lines are listed for which there is a match with an observed line.

## PHYSICAL AND OPTICAL PROPERTIES

Kinoite is deep azurite blue in color and transparent in thin fragments. It exhibits excellent cleavage parallel to {010} and distinct cleavages parallel to {001} and {100}. Crystals nearly 1 mm in length were observed, but the average is less than 0.5 mm. Occurrence as single crystals

TABLE 3. CRYSTALLOGRAPHIC DATA FOR KINOITE

Kinoite, Monoclinic—$2/m$

$a{:}b{:}c = .542{:}1{:}.439$ $\beta = 96°05'$ $\mu = 83°55'$

$p_0{:}q_0{:}r_0 = .811{:}.437{:}1$ $r_2{:}p_2{:}q_2 = 2.288{:}1.856{:}1$

$p_0' = .816$ $q_0' = .439$ $x_0' = .107$ $\rho_0 = 6°05'$

| | | $\phi$ | $\rho$ | $\phi_2$ | $\rho_2 = B$ | $C$ | $A$ |
|---|---|---|---|---|---|---|---|
| $c$ | 001 | 90°00′ | 6°05′ | 83°55′ | 90°00′ | — | 83°55′ |
| $b$ | 010 | 0 00 | 90 00 | — | 0 00 | 90°00′ | 90 00 |
| $a$ | 100 | 90 00 | 90 00 | 0 00 | 90 00 | 83 55 | — |
| $m$ | 110 | 61 41 | 90 00 | 0 00 | 61 41 | 84 39 | 28 19 |
| $n$ | 320 | 70 14 | 90 00 | 0 00 | 70 14 | 84 17 | 19 46 |
| $D$ | 011 | 13 39 | 24 19 | 83 55 | 66 25 | 23 35 | 84 26 |
| $d$ | $\bar{1}01$ | −90 00 | 35 18 | 125 18 | 90 00 | 41 23 | 125 18 |
| $k$ | 144 | 35 15 | 28 16 | 72 46 | 67 15 | 25 12 | 74 09 |
| $x$ | $\bar{1}33$ | −20 36 | 25 08 | 99 22 | 66 35 | 27 49 | 98 35 |

is common for the species. The density is $3.16 \pm .03$ g/cm$^3$, the mean of a number of measurements on the Berman density balance of 10 samples ranging in weight from 4 to 47 mg. The calculated density is 3.193 g/cm$^3$.

The small crystal size precludes satisfactory determination of scratch hardness. Penetration hardness measurements with Knoop and diamond pyramid indenters were performed by Dr. Walter W. Walker, Department of Metallurgical Engineering of the University of Arizona. Penetration tests were made on embedded crystals using both types of indenters in three orientations: parallel to $c$ and to $b$, and approximately 45° to these directions. Knoop indentation tests show that the mineral is

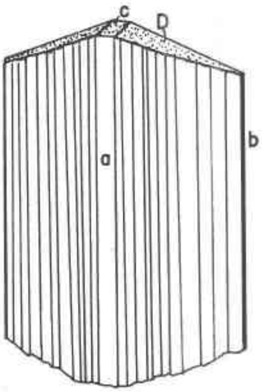

FIG. 1. Appearance of typical kinoite crystal.

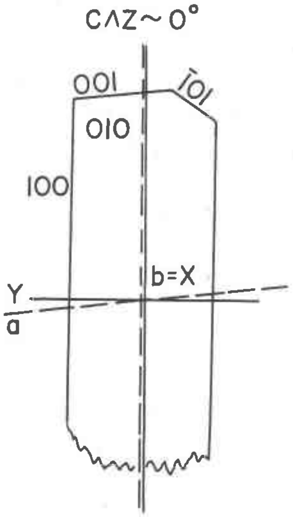

FIG. 2. Optical orientation of Kinoite.

harder in the *b* than in the *c* axial direction. Mohs hardness values equivalent to the Knoop values are 2.0 in the *b* and 2.5 in the *c* direction. (Conversion from Knoop to Mohs hardnesses follows the work of Hays, Kendall, and Hoskins (1965)). Results of similar penetration tests with the diamond indenter yielded somewhat higher Mohs equivalent hardness values, in the range from 4 to 5. Small specimen size, the problem of correlating penetration hardness values with Mohs scale hardness, and variable behavior related to "low load anomaly" effects contribute to the uncertainty of the Mohs hardness.

The optical orientation of kinoite was determined on the universal stage (Fig. 2). Indices of refraction were measured in sodium light. The optical data are presented in Table 4. The mineral is strongly pleochroic in blues and blue-green with $Z>Y>X$.

## CHEMICAL COMPOSITION

The results of a chemical analysis made on a carefully separated sample weighing about 45 mg are presented in Table 3. The analysis leads to the

TABLE 4. OPTICAL PROPERTIES OF KINOITE

| | |
|---|---|
| $\alpha=1.638\pm0.002$ pale greenish blue | Opt (−) |
| $\beta=1.665\pm0.002$ blue | $2V$(meas.) = 68° |
| $\gamma=1.676\pm0.002$ deep blue | $2V$(calc.) = 64° |
| $Z\wedge c$ near 0° | $r<v$ distinct |
| $X=b$ | |

TABLE 5. CHEMICAL ANALYSIS OF KINOITE[a]

| | Wt. % (1) | Mole Proportions | | Wt. % (2) |
|---|---|---|---|---|
| CuO | 31.10 | .391 | 1.964 | 27.90 |
| CaO | 23.55 | .420 | 2.109 | 24.62 |
| MgO | .15 | .004 | .019 | |
| $SiO_2$ | 35.90 | .597 | 3 | 39.58 |
| $H_2O$ | 8.16 | .453 | 2.276 | 7.90 |
| Total | 98.86 | | | 100.00 |

[a] Emission spectrographic analysis showed trace amounts of Ag and Fe.

1. Herbert M. Ochs, Denver, analyst
2. Theoretical weight percentages for $Cu_2Ca_2Si_3O_{10}\cdot 2H_2O$

composition $Cu_{1.96}Ca_{2.11}Mg_{.02}Si_3O_{9.97}\cdot 2.28H_2O$ which is in good agreement with the idealized formula confirmed by structure analysis[1]: $Cu_2Ca_2Si_3O_{10}\cdot 2H_2O$. Kinoite is decomposed in dilute HCl with the development of a white residue.

Type specimens of kinoite will be deposited with the U.S. National Museum and the Department of Geology, University of Arizona.

## ACKNOWLEDGEMENTS

We are indebted to G. Arthur Barber of the Anaconda Company for having brought the mineral to our attention and for providing information regarding its occurrence. Sidney A. Williams kindly verified and corrected the morphological angle table; Victor Hoffman made spectrographic and infrared measurements and was especially helpful during the early stages of the study. W. W. Walker kindly performed the penetration hardness tests. We wish to acknowledge the very helpful criticisms of W. John McLean throughout the work. Dr. McLean assisted with the determination of the precise cell parameters using equipment made available through the courtesy of Professor G. A. Jeffrey of the Crystallography Laboratory, University of Pittsburgh.

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[1] The crystal structure analysis confirms that the Si:O ratio of 3:10 results from independent $Si_3O_{10}$ units within the structure.