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Khinite, parakhinite, and dugganite, three new tellurates from Tombstone, Arizona

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Abstract

Khinite was found at the Old Guard mine, one piece known. It is $Cu_3PbTeO_4(OH)_6$, orthorhombic, *Fddd*, with $a = 5.740$, $b = 9.983$, $c = 23.960$A. Strongest lines are 2.491 (10), 3.451 (9), 4.866 (8), 2.996 (7), 2.204 (7), 2.818 (6), 1.916 (6), 1.558 (6). Dark green, H = 3½, D calc = 6.69g/cm^3; $\alpha = 2.110$, $\beta = 2.112$, $\gamma = 2.165$, $2V_z = 20°$.

Two pieces of parakhinite were found at the Emerald mine. Formula also $Cu_3PbTeO_4(OH)_6$, hexagonal $P6_222$ with $a = 5.753$, $c = 17.958$A, thus $c = \frac{3}{4}c$ of khinite. Strongest lines are 3.336 (10), 2.490 (10), 4.800 (8), 1.558 (8), 2.913 (7), 2.245 (6), 2.994 (5), 1.997 (5). Color, H, and D calc are identical to khinite; $\epsilon = 2.120$, $\omega = 2.155$.

Several pieces of dugganite were found at three mines. Analysis gave $Pb_3Zn_3(TeO_6)_x(AsO_4)_{2-x}(OH)_{6-3x}$ with $x = 0.94$ to 1.33. Hexagonal, perhaps *P6/mmm*, with $a = 8.472$, $c = 5.208$A; strongest lines are 3.284 (10), 2.997 (8), 2.446 (6), 1.896 (6), 1.603 (6), 2.773 (5), 1.177 (5), 5.204 (4). Colorless to various greens (with CuO = 0–1.5 percent), H = 3, G = 6.33, D calc = 6.33g/cm^3; $\omega = 1.977$, $\epsilon = 1.967$.

IMA approval of these species is pending.

Introduction

This study began with a visit by R. W. Thomssen in the summer of 1977. He brought a spectacular unknown, subsequently identified as rodalquilarite, that he had found on a mine dump at Tombstone. Spurred on by this discovery, I began an exhaustive search of all mine dumps in the district. This very quickly yielded more than twenty new tellurium species as well as rare ones such as sonoraite, quetzalcoatlite, and xocomecatlite.

The occurrence of tellurium minerals at Tombstone has long been known. Hessite was found in early workings, and Tombstone is the type locality for emmonsite, first described by Hillebrand (1885), probably from the same locality where rodalquilarite occurs. Rasor (1937) noted the occurrence of emmonsite, and discussed two unknown tellurites. His suite of samples, preserved at the University of Arizona, was kindly loaned for study by Dr. John Anthony. It contains several new and rare tellurium oxysalts.

On a second visit to Tombstone, the dumps of the Old Guard mine were examined. This dump has been almost entirely removed for heap leaching, only scattered debris remaining. One piece was immediately found, the type specimen of khinite. This piece carries two other new species as well. Khinite occurs as corroded, deep green crystals that form rings on fracture surfaces. Massive chlorargyrite occupies the center of the rings, and khinite shows replacement on the outside by a sparkling druse of minute dugganite crystals. The matrix is coarse glassy quartz (intensely silicified granodiorite). There are a few pockets of granular quetzalcoatlite hosting grains of gold, and chrysocolla and tenorite staining is common. This is the only specimen of khinite known.

As examination of dumps in the district continued, the Emerald mine quickly yielded several pieces of dugganite with a bewildering variety of other new tellurates/tellurites. During this time, removal of the dump to the leach pad was begun, so efforts were redoubled to visit the rapidly vanishing supply as often as possible. Several pieces rich in unknowns were found, including two pieces of massive vein quartz containing parakhinite. The first of these was found by BaSaw Khin, mineralogist for Phelps Dodge Corporation.

Parakhinite is identical in color to khinite, occurring as thin crystalline films of fractures in the quartz gangue or as tabular hexagonal euhedra in vugs; crystals may attain 0.5mm in largest dimension. Like khinite, parakhinite may alter to dugganite. Other associated species are xocomecatlite, bromargyrite, and a host of unknown tellurates/tellurites.

Dugganite at both localities occurs in either quartz or manganese oxide gangue. Most of the associated species are tellurates/tellurites yet to be described. Bromargyrite and chlorargyrite are also common accessories. Dugganite was also finally found at a third locality, the Joe Shaft, in a portion of the dump rich in emmonsite and rodalquilarite. One specimen was found with minute druses of dugganite, cerussite, emmonsite, and yet two more unknown tellurates/tellurites.

Physical properties

Crystals on the khinite specimen reach 0.15mm in maximum dimension. They are curved or barrel-shaped bipyramids bounded by a series of {*hkl*} forms, but supergene corrosion has etched them deeply, rendering measurement impossible. Crystals are brittle, showing a fair cleavage on {001}, and the Mohs hardness is 3½. The color is a lovely dark green close to bottle green (RHS 135A), with a vivid green streak. No fluorescence was observed. There was far too little material for the Berman balance, and the specific gravity is greatly in excess of Clerici solution. Using alcohol and beeswax, Thoulet's method was employed with 178μg of material. Several trials indicated G = 6.5–7.0.

The properties of parakhinite are identical to those described above for khinite. An estimate of the specific gravity (Thoulet method) using 222μg is also 6.5–7.0. Crystals are brilliant hexagonal tablets or equant prisms that reach 0.2mm in maximum, and single crystals occurring as fracture fillings may be considerably larger (0.5mm). One perfect crystal measured on the two-circle goniometer showed $\{0001\}$, $\{11\bar{2}0\}$, and $\{11\bar{2}4\}$ in approximately equal rank.

The color of dugganite is variable for two reasons. Crystals in some specimens are rich in inclusions of an unknown Cu–tellurate, and this imparts a yellow-green color. Even when perfectly pure, however, the color is easily influenced by minor amounts of copper in substitution for zinc. The best sample found (and used for most analytical work) carries sparkling water green (RHS 132D) crystals up to 0.3mm in length. The streak is white, the luster adamantine, and the crystals could be mistaken for willemite. The Mohs hardness is 3, and crystals are exceedingly brittle with a poor cleavage on $\{11\bar{2}0\}$. No fluorescence was noted. The specific gravity was determined by Berman balance using 5mg at 23°C. It is 6.33±0.15.

No crystals were suitable for measurement. They are slightly curved, stubby prisms, with a length to width ratio near 2:1. Thin sections show $\{0001\}$ and $\{11\bar{2}0\}$ dominant with tiny $\{11\bar{2}1\}$.

Chemistry

Khinite shows behavior in reagents that closely matches that of parakhinite. Testing for SO_3, Cl, Br, and I gave no response, but owing to extreme paucity of material, and the suspicion that its chemistry would be identical to parakhinite, no material was sacrificed for spectrographic examination. Instead, material was submitted directly for analysis, and the results for Cu, Pb, and Te^{6+} (see Table 1A) appear to justify this caution. In addition, water was not determined, but was calculated on the basis of the average ratio obtained for Cu/Pb/Te. The low sum reflects the presence of traces of chlorargyrite and quartz, too small in amount to recover and weigh as insol. The formula is thus $Cu_3PbTeO_4(OH)_6$.

Spectrographic analysis of parakhinite showed major Cu, Pb, and Te, with traces of Ca. Analytical methods employed were those used for dugganite, leading to the results shown in Table 1A, or a formula $Cu_3Pb(TeO_4)(OH)_6$. Determination of Ca showed negligible amounts present. Microchemical testing showed no CO_2, NO_2, SO_3, or Cl, Br, I.

Parakhinite is easily soluble in cold dilute acids but

Table 1A. Chemistry of khinite and parakhinite

	1	2	3	4	5
CuO	33.2%	0.417	32.8%	0.412	34.5%
PbO	32.4	0.145	31.9	0.143	32.3
TeO_3	24.5	0.139	25.7	0.146	25.4
H_2O	(7.6)	(0.421)	7.8	0.428	7.8
	97.7		98.2		100.0

(1) Khinite. Cu and Pb on 160μg, Te^{+6} on 284μg; H_2O calculated from average ratio obtained for other constituents. Low sum reflects traces of quartz and chlorargyrite.

(2) Ratios for Khinite, calculated for H_2O

(3) Parakhinite. Cu and Pb on 670μg, Te^{+6} on 450 and 674μg; water by Penfield method on 842μg. Traces of quartz noted as insol.

(4) Ratios for parakhinite

(5) Theory for $Cu_3PbTeO_4(OH)_6$

Table 1B. Chemistry of dugganite

	1	2	3	4
PbO	55.3%	0.248	54.4%	54.5%
ZnO	17.6	0.231	19.8	19.9
CuO	1.2			
TeO_3	14.0	0.080	14.3	13.4
As_2O_5	10.4	0.045	9.3	9.9
H_2O	1.5	0.083	2.2	2.3
	100.0		100.0	100.0

(1) Averaged for four analyses for Pb, Zn, Cu; 3 for Te, and 2 for As on samples ranging from 889 to 1555μg, reset to 100% to compensate for insol which averaged 3.63%. Water by Penfield method on 11.882mg.

(2) Rations

(3) Theory for $Pb_3Zn_3TeO_6(AsO_4)(OH)_3$

(4) Theory for $Pb_3Zn_3(TeO_6)_x(AsO_4)_{2-x}(OH)_{6-3x}$ with x = 0.94.

may coat with $PbCl_2$ or $Pb(NO_3)_2$ if heated, or in strong acid. In the closed tube, it fuses readily to a syrupy brown slag (after evolving water).

Preliminary spectrographic analysis of dugganite showed major Pb, Zn, Te, and As, with traces of Cd, Ag, Mo, Cu, and Ca. The Pb, Cu, and Zn were determined by atomic absorption prior to analysis of Te^{6+} by visible spectroscopy. Arsenate was found by UV spectroscopy as AsI_3. Subsequent analysis for Ca and Cl were run, both constituents proving to be negligible. Microchemical tests showed traces of CO_2 and gave negative reaction for nitrate, chloride, and sulfate. Subsequent analysis of one sample by Schwartzkopf Microanalytical Laboratories indicated only traces of CO_2.

The results of analysis of crystalline dugganite from the Emerald mine are shown in Table 1B, and lead to the formula $Pb_3Zn_3TeO_6(AsO_4)(OH)_3$. Other partial analyses performed on a different sample from this mine, and from one sample found at the Joe shaft, however, show some substitution of TeO_4^{2-} for AsO_4^{3-}, and the formula is better written $Pb_3Zn_3(TeO_6)_x(AsO_4)_{2-x}(OH)_{6-3x}$, with Cu substitution for Zn probably quite limited. Analyses done to date show x varies from 0.94 to 1.33.

Dugganite is soluble in cold dilute HNO_3 or HCl, but if more concentrated acid is used, or heating employed, it coats with $Pb(NO_3)_2$ or $PbCl_2$. Taken to ignition, it fuses to a brown slag with difficulty, evolving a white sublimate of TeO_2 and As_2O_3.

All samples were of course checked for both Te^{4+} and Te^{6+}. For further discussion of the analytical method, the reader is referred to Williams (1975).

X-ray study

All three species provided good single crystals for Weissenberg and rotation patterns, and all give excellent, clear powder patterns. The results of the powder study are shown in Tables 2–4.

A fragment of khinite was rotated on two axes and yielded the following cell: a = 5.740 (±0.005), b = 9.983 (±0.009), c = 23.960A (±0.09). The space group is *Fddd*. The calculated density, based on Z = 8, is 6.69g/cm³, in agreement with the measured estimate of G = 6.5–7.0.

Parakhinite provided the following hexagonal cell: a = 5.753 (±0.009), c = 17.958A (±0.092); the space group is $P6_222$ or $P6_422$. Etch testing in 10 percent HCl seems to confirm this choice. If Z = 3, the calculated density is 6.69g/cm³. The c axis of khinite is $\frac{4}{3}$ that of parakhinite, and thus the cell volume is $\frac{8}{3}$ as large.

Dugganite is also hexagonal, *P6/mmm*. Single-crystal work showed a = 8.472 (±0.005), c = 5.208A (±0.005). The cell dimensions were refined from powder data. If Z = 1, the calculated density is 6.33g/cm³, in agreement with the measured value.

Optics

Khinite and parakhinite resemble one another strongly in thin section but are unlike any other minerals I have ever seen. Indices for both were measured in white light using S-Se melts that were immediately uncovered and checked by the Brewster method. Khinite is biaxial (+) with a measured $2V$ of 20° and indices are α = 2.110, β = 2.112, γ = 2.165 (all

Table 2. X-ray powder data for khinite—Cr$K\alpha$ radiation, 114 mm camera

$I/I_{o\,est.}$	$d_{meas.}$	$d_{calc.}$	hkl	$I/I_{o\,est.}$	$d_{meas.}$
4	5.976	5.990	004	5	1.997
8	4.866	4.872	111	6	1.916
5	4.607	4.608	022		
½	4.225	4.223	113	1	1.877
9	3.451	3.452	115	1	1.860
5	3.116	3.118	026	½	1.837
7	2.996	2.995	008	2	1.753
2	2.860	2.858	131	3	1.730
6	2.818	2.820	117	1	1.702
½	2.785	2.791	202	4B	1.650
½	2.706	2.708	133		
10	2.491	2.496	040	6	1.558
		2.488	220	4	1.446
3	2.466	2.468	135		
1	2.330	2.331	206		
7	2.204	2.203	137		

±0.004). Pleochroism is in rich yellowish green (Z and Y) with X a vivid emerald green; $Z = Y > X$. Parakhinite shows identical colors, ω = rich yellowish green, ϵ = clear emerald green, with $\omega > \epsilon$. Although pleochroic, the change in intensity of color is slight in both species. Parakhinite is perfectly uniaxial (−) showing no optically anomalous behavior. Dispersion is strong (it was not measured) and indices are $\epsilon = 2.120$, $\omega = 2.155$.

In thin section, dugganite resembles hidalgoite closely in overall appearance and mode of occurrence. Refractive indices are higher, however, and measured for the Na*D* line are $\omega = 1.977$ (±0.002), $\epsilon = 1.967$. Crystals may show sectoring or zoning features and exhibit a small (−) $2V$, but more perfectly formed, isolated crystals are usually not sectored and are perfectly uniaxial.

Discussion

All three minerals are clearly unlike tellurates that have been found previously. Their continued rarity doubtless is due to several factors. All are formed only by severe oxidation in acid waters, and if the oxide zone is penetrated by even mildly alkaline waters, the effect upon tellurates such as these is fatal; they quickly dissolve. Another reason for rarity is that the bonanza ores found at Tombstone were those carrying tellurides, and little material found its way to the waste dumps.

Khinite is named to honor BaSaw Khin, longtime mineralogist for Phelps Dodge Corporation, who found the first parakhinite. This latter mineral is named in allusion to its close relation to khinite. Dugganite is to honor Marjorie Duggan, the accomplished analytical chemist, and reflects her discovery of the first Te^{6+} in nature, and development of microanalytical techniques for Te^{4+}/Te^{6+}.

Type specimens of parakhinite and dugganite will be provided the British Museum (Natural History) and the University of Arizona Geological Museum. A fragment of khinite will be given to the British Museum (N.H.). There are about two dozen pieces of dugganite comprising an estimated 50mg, 6 pieces of parakhinite with perhaps 5mg, and two chips of khinite with, at most, 200μg remaining (but clearly visible).

Table 3. X-ray powder data for parakhinite—Cr$K\alpha$ radiation, 114 mm camera

I/Io	$d_{meas.}$	$d_{calc.}$	hkl	I/Io	$d_{meas.}$
2	5.973	5.986	003	5	1.997
2	4.986	4.982	100	5	1.915
8	4.800	4.801	101	3	1.874
2	4.352	4.356	102	2	1.853
3	3.830	3.829	103	4	1.739
10	3.336	3.335	104	4	1.691
5	2.994	2.993	006	4	1.669
7	2.913	2.913	105	8	1.558
3	2.838	2.840	111	4	1.438
1	2.740	2.739	112	+ 12 additional	
10	2.490	2.491	200	lines to d=1.2	
4	2.424	2.422	114		
6	2.245	2.245	115		
2	2.076	2.074	116		

Table 4. X-ray powder data for dugganite—Cr$K\alpha$ radiation, 114 mm camera

$I/Io_{est.}$	$d_{meas.}$	$d_{calc.}$	hkl	$I/Io_{est.}$	$d_{meas.}$
4	5.204	5.208	001	1	1.687
4	4.233	4.236	110	1	1.644
3	3.666	3.669	200	6	1.603
10	3.284	3.286	111	3	1.569
8	2.997	2.999	201	½	1.530
5	2.773	2.773	120	2	1.469
4	2.603	2.604	002	3	1.413
6	2.446	2.448	121	1	1.387
		2.446	300		
		2.454	102	1	1.364
				2	1.341
4	2.215	2.218	112	3	1.321
		2.214	301	1	1.303
4	2.121	2.118	220	3	1.279
		2.123	202	1	1.242
4	2.035	2.035	130	3	1.225
½	1.963	1.962	221	4	1.209
6	1.896	1.895	131	5	1.177
		1.898	122		
4	1.783	1.783	302		
½	1.734	1.736	003		

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These new species and names have been submitted to the IMA for approval.

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