

KHINITE-4O [= KHINITE] AND KHINITE-3T [= PARAKHINITE]

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ABSTRACT

Comparison of the crystal structures of khinite, $\text{Pb}^{2+}\text{Cu}^{2+}_3\text{Te}^{6+}\text{O}_6(\text{OH})_2$, orthorhombic, a 5.7491(10), b 10.0176(14), c 24.022(3) Å, V 1383.6(4) Å³, space group $Fdd2$, $Z = 8$, and parakhinite, $\text{Pb}^{2+}\text{Cu}^{2+}_3\text{Te}^{6+}\text{O}_6(\text{OH})_2$, trigonal, a 5.765(2), c 18.001(9) Å, V 518.0(4) Å³, $Z = 3$, space group $P3_2$, show that these minerals are polytypic. They consist of layers of composition $[\text{TeCu}_3\text{O}_6]$ that stack along the c axis at 6 Å intervals, with Pb atoms between the layers. The only difference is the relative displacement of adjacent layers in each structure, *i.e.*, the relative stacking of the layers. Hence, khinite and parakhinite are polytypes and should be renamed as follows: khinite becomes khinite-4O and parakhinite becomes khinite-3T. These changes in nomenclature have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-08-C).

Keywords: khinite-4O, khinite-3T, polytypes.

SOMMAIRE

Une comparaison des structures cristallines de la khinite, $\text{Pb}^{2+}\text{Cu}^{2+}_3\text{Te}^{6+}\text{O}_6(\text{OH})_2$, orthorhombique, a 5.7491(10), b 10.0176(14), c 24.022(3) Å, V 1383.6(4) Å³, groupe spatial $Fdd2$, $Z = 8$, et de la parakhinite, $\text{Pb}^{2+}\text{Cu}^{2+}_3\text{Te}^{6+}\text{O}_6(\text{OH})_2$, trigonale, a 5.765(2), c 18.001(9) Å, V 518.0(4) Å³, $Z = 3$, groupe spatial $P3_2$, démontre que ces minéraux sont polytypiques. Ils sont construits de couches de composition $[\text{TeCu}_3\text{O}_6]$ empilées le long de l'axe c à intervalles de 6 Å, avec des atomes de Pb entre les couches. La seule différence est le déplacement relatif entre couches adjacentes dans ces deux structures, c'est-à-dire le mode d'empilement relatif des couches. La khinite et la parakhinite sont donc des polytypes qui devraient être renommés comme suit: la khinite devient la khinite-4O, et la parakhinite devient la khinite-3T. Ces changements en nomenclature ont été entérinés par la Commission des Nouveaux Minéraux, de la Nomenclature et de la Classification de l'Association minéralogique internationale (IMA-08-C).

Mots-clés: khinite-4O, khinite-3T, polytypes.

INTRODUCTION

Khinite and parakhinite are tellurate minerals of lead and copper discovered at Tombstone, Arizona, U.S.A., and described as new species by Williams (1978). Khinite was discovered on the dumps of the Old Guard mine. It is a rare secondary mineral that occurs as corroded deep green crystals on fracture surfaces in quartz (intensely silicified granodiorite), adjacent to massive chlorargyrite and altered to minute crystals of dugganite, and associated with pockets of quetzalcoatlite, gold and chrysocolla, and stained with

tenorite. Khinite formed through oxidation of gold-telluride ores by highly acid minewaters. Parakhinite was found in the dumps of the Emerald mine, where it occurs in vugs in massive vein quartz. It may alter to dugganite $[\text{Pb}_3\text{Zn}_3(\text{Te}^{6+}\text{O}_6)(\text{AsO}_4)_2]$, and it is associated with xocomecatlite $[\text{Cu}^{2+}(\text{Te}^{6+}\text{O}_4)(\text{OH})_4]$, bromargyrite $[\text{AgBr}]$ and various unknown tellurates and tellurites. Williams (1978) gave the formula of both khinite and parakhinite as $\text{Pb}^{2+}\text{Cu}^{2+}_3\text{Te}^{6+}\text{O}_4(\text{OH})_6$.

The crystal structure of khinite was reported by Cooper *et al.* (2008), and the chemical formula of khinite was revised to $\text{Pb}^{2+}\text{Cu}^{2+}_3\text{Te}^{6+}\text{O}_6(\text{OH})_2$ as a

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result of that work. The crystal structure of parakhinite was reported by Burns *et al.* (1995), who revised its chemical formula to $\text{Pb}^{2+}\text{Cu}^{2+}_3\text{Te}^{6+}\text{O}_6(\text{OH})_2$.

CRYSTAL STRUCTURE

Cell dimensions and space groups for khinite and parakhinite are given in Table 1.

Khinite

In the structure of khinite, there is one Pb atom coordinated by eight anions. There is one Te site occupied by Te, with a coordination number of [6] and a $\langle\text{Te}-\text{O}\rangle$ distance of 1.962 Å, indicating that Te is hexavalent in khinite. There are three Cu sites, all of which are occupied by [6]-coordinated Cu^{2+} ; the resulting octahedra show strong $[4 + 2]$ Jahn–Teller distortion. Khinite contains TeO_6 and $\text{Cu}(3)\text{O}_6$ octahedra that share *trans* edges to form rutile-like $[\text{MO}_4]$ chains that extend parallel to [110] (Fig. 1, layer 1, right). The $\text{Cu}(1)\text{O}_6$ and $\text{Cu}(2)\text{O}_6$ octahedra link similarly to form adjacent parallel $[\text{M}\Phi_4]$ chains that share corners with the $[\text{TeCu}(3)\text{O}_4]$ chains to form an $[\text{M}\Phi_2]$ layer of composition $[\text{TeCu}_3\Phi_8]$ (Fig. 1, layer 1, right). These layers stack along the *c* axis at 6 Å intervals with Pb atoms located between the layers (Fig. 2, right). The $[\text{TeCu}_3\Phi_8]$ layers are related by 2_1 screw axes along [001] and *d*-glide planes parallel to (100) and (010). The successive layers along [001] are shown in Figure 1 (right), where it can be seen that layers adjacent along *c* are offset laterally relative to adjacent layers.

Parakhinite

In the structure, there is one unique Pb atom that bonds to six oxygen anions and two hydroxyl groups, forming an irregular $\text{PbO}_6(\text{OH})_2$ polyhedron. There is one unique Te atom that is octahedrally coordinated by six oxygen anions, indicating that the tellurium is present as Te^{6+} . There are three unique Cu positions: Cu(1) and Cu(2) are both octahedrally coordinated by four oxygen atoms and two hydroxyl groups in a *cis* arrangement. Both the $\text{Cu}(1)\text{O}_6$ and $\text{Cu}(2)\text{O}_6$ octahedra are strongly distorted owing to the Jahn–Teller effect associated with a d^9 cation in an octahedral ligand field. The Cu(3) atom bonds to four oxygen anions with Cu–O distances of ~1.92 Å, and two apical O atoms at distances of 2.95 and 3.23 Å from Cu(3). The TeO_6 and $\text{Cu}(3)\text{O}_6$ octahedra share *trans* edges to form rutile-like $[\text{M}\Phi_4]$ chains that extend parallel to [110]. These $[\text{M}\Phi_4]$ chains link by octahedra sharing corners to form a $[\text{M}\Phi_3]$ sheet of composition $\text{TeCu}\Phi_6$ in the (100) plane. The $\text{Cu}(1)\text{O}_6$ and $\text{Cu}(2)\text{O}_6$ octahedra link in a similar fashion to form a $\text{CuCu}\Phi_6$ sheet. These two sheets then link by octahedra sharing edges, the octahedra of one sheet matching to the interstices of the

other sheet to form an interrupted $[\text{M}\Phi_2]$ sheet (Fig. 1, layer 1, left) of composition $\text{TeCu}_3\Phi_8$. These sheets are repeated along the *c* axis through the 3_2 screw operator, and there is an interesting difference in appearance with viewing direction (Fig. 2, left). Interstitial linkage between adjacent sheets is provided by Pb atoms, which link to four anions in each of the adjacent sheets, and by hydrogen bonds.

POLYTYPISM IN KHINITE AND PARAKHINITE

In khinite, the $[\text{TeCu}_3\Phi_8]$ layers are related by 2_1 screw axes along [001] and *d*-glide planes parallel to (100) and (010). The successive layers along [001] are shown in Figure 1 (right), where it can be seen that layers adjacent along *c* are offset laterally relative to adjacent layers. In parakhinite (Fig. 1, left), the $[\text{TeCu}_3\Phi_8]$ layers are related by a 3_2 screw axis along [001], without the lateral offsets that characterize the structure of khinite.

The structures of khinite and parakhinite contain the same layer of polyhedra of composition $[\text{TeCu}_3\Phi_8]$, and the same linkage between layers is provided by interstitial Pb atoms and hydrogen bonding. It is only the relative stacking of the $\text{TeCu}_3\Phi_8$ layers in the *c* direction that distinguishes the two structures (Figs. 1, 2), and hence khinite and parakhinite are polytypes. Application of the standard nomenclature for polytypes (Bailey *et al.* 1978, Nickel & Mandarino 1987, Nickel 1993) produces the following changes: khinite becomes khinite-4*O*, and parakhinite becomes khinite-3*T*. These changes have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-08–C).

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TABLE 1. CRYSTALLOGRAPHIC DATA FOR KHINITE AND PARAKHINITE

	Khinite	Parakhinite
	orthorhombic	trigonal
<i>a</i> (Å)	5.7491(10)	5.765(2)
<i>b</i>	10.0176(14)	<i>a</i>
<i>c</i>	24.022(3)	18.001(9)
<i>V</i> (Å ³)	1383.6(4)	518.0(4)
Space group	<i>Fdd2</i>	<i>P3₂</i>
<i>Z</i>	8	3

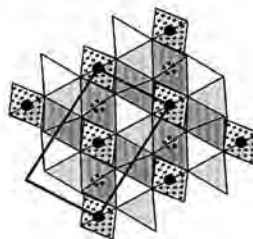
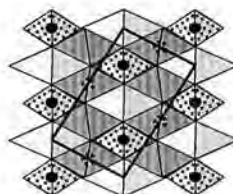
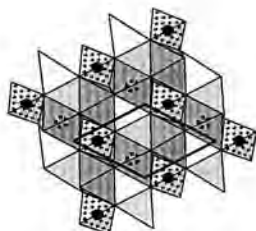
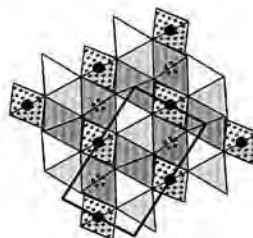
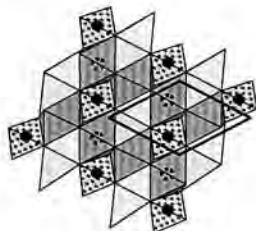
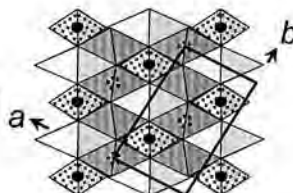
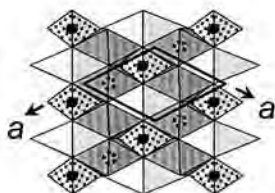
PARAKHINITE**KHINITE****layer 4****layer 3****layer 2****layer 1****KHINITE-3T****KHINITE-4O**

FIG. 1. The $\text{TeCu}_3\Phi_8$ layers in khinite-3T [= parakhinite] and khinite-4O [= khinite] projected down [001]. The *Te* polyhedra are shaded light grey with additional small crosses; *Cu*(3) polyhedra are light grey shaded; *Cu*(1) and *Cu*(2) polyhedra are dark grey shaded. The Pb atoms lying above the layer are shown as black filled circles, and as dashed circles below the layer. In khinite-4O, the Pb atoms lie under the *Cu*(2) polyhedra, and in khinite-3T, they lie under the *Cu*(1) polyhedra. The position of the unit cell is outlined in black.

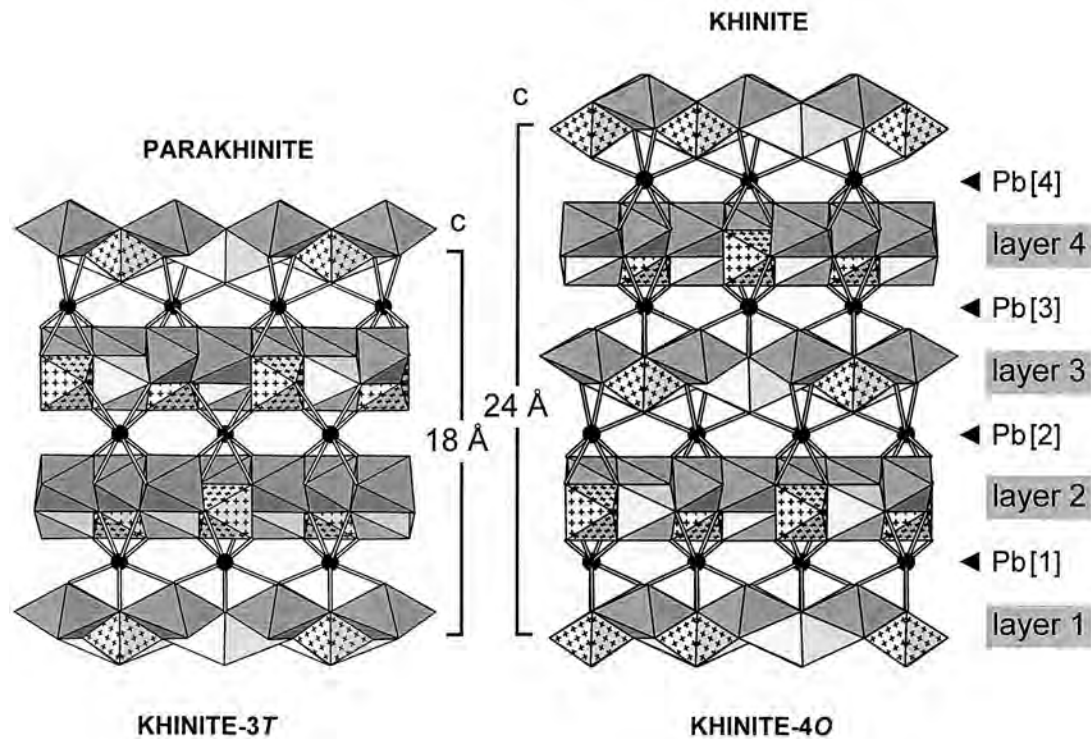


FIG. 2. The structures of khinite-3T [= parakhinite] and khinite-4O [= khinite] projected down $[110]$ and $[1\bar{1}0]$ respectively; legend as in Figure 1.

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