

## CHEVKINITE, PERRIERITE AND EPIDOTES

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### ABSTRACT

The relationship between perrierite and chevkinite and between these and the epidotes are here re-examined and illustrated on the basis of new data obtained by Jaffe, Evans, Jr. and Chapman on a chevkinite in New Hampshire.

### INTRODUCTION

On the basis of research conducted by myself and G. Gottardi [3], [4] on a new mineral, perrierite, found in the sands of the shore at Nettuno (Roma), we showed that chevkinite represents a family of minerals possessing orthorhombic and monoclinic members with close morphological and structural relationships to the family of epidote. A morphological character common to epidote and chevkinite is shown by the very close angular values in the planes of the zone [010]; a structural character in common is the presence of oxygen chains which develop, in the monoclinic group, along the axis of symmetry; thus the two families of minerals acquire a value of  $b$  very close to 5.6 Å (twice the diameter of oxygen). Other minerals such as rinkite, mosandrite and related silicates which show morphological analogies to epidote and have  $c \sim 5.6$  Å, belong to this category of silicates.

An interesting article by Howard W. Jaffe, Howard T. Evans Jr. and Randolph W. Chapman [6] supplies important new data on chevkinite which support the conclusions of our research [3], [4] and supply experimental evidence for our earlier speculative, though strongly motivated, conclusions.

These authors made an exhaustive study of a chevkinite found in a New Hampshire fayalite-quartz syenite; there is no doubt that this chevkinite is the same mineral described by Boldireff [1], [2] for the Urals. The report by these authors refers several times to the data in our two notes on perrierite; however while the authors concede that many of our statements are convincing (see [6], p. 478 and others), they maintain that our conclusions are not clear to them. That some misunderstanding exists is apparent, apart from the explicit declaration of the authors, by the fact that they still admit the possibility, although with strong reservations, that perrierite and chevkinite might be the same mineral. This is in spite of the fact that, with their own determination of the elementary cell of the New Hampshire chevkinite, different from the perrierite cell, they have proved beyond any doubt that chevkinite and perrierite belong to different mineralogical species.

Most certainly credit must be given to the afore-mentioned authors

for having furnished, after accurate observations, the means for a complete and very interesting clarification of the relationship between epidote, perrierite and chevkinite. I will now try to put this interesting subject of descriptive mineralogy in final and complete form by reexamining our results, adding new data and comparing them with those of the quoted authors.

#### MORPHOLOGICAL CRYSTALLOGRAPHY OF PERRIERITE

Perrierite [3] bears a very close morphological analogy to the epidotes and in particular to allanite. By projecting the most common and frequent forms of allanite stereographically, and by superimposing those of perrierite, thereby identifying poles when they are not more than two degrees apart, we obtain the diagram shown in Fig. 1.

The very close isogonal relationships are evident. Due to the presence of the same zone (112) (012) (indices of allanite), in both minerals, we could have given perrierite an axial ratio almost identical to that of allanite. The crystallographic argument which I consider not worthwhile repeating and to which I refer in the note [3] led us to use the following axial ratio for perrierite:

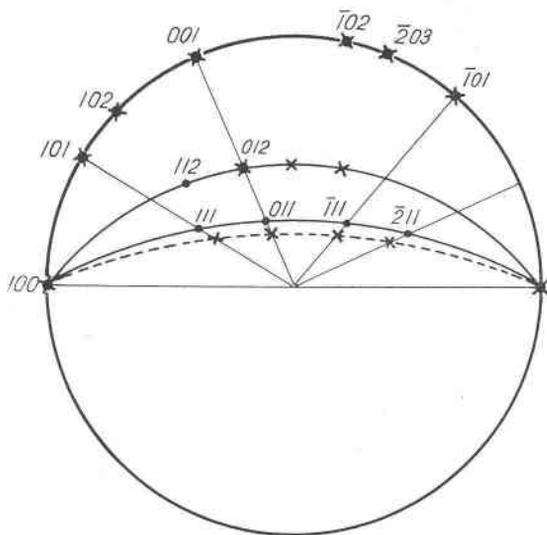


FIG. 1. Allanite and perrierite.

*Points* = poles of the faces of allanite with relative indices.

*Crosses* = poles of the faces of perrierite without indices.

*Points with crosses* = poles of the faces of allanite and perrierite which fall within two degrees of each other. Indices of allanite.

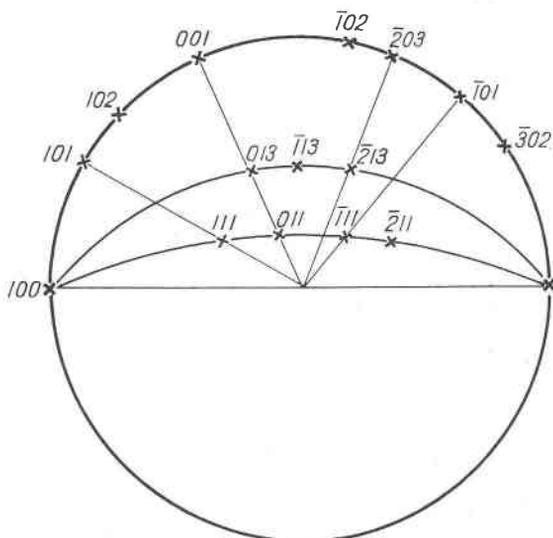


FIG. 2. Crystallographic interpretation of perrierite.

$$a:b:c = 2.047:1:2.380 \quad \text{with } \beta = 113^{\circ}28'$$

in respect to the axial ratio for allanite:

$$a:b:c = 1.551:1:1.769 \quad \text{with } \beta = 115^{\circ}11'.$$

In addition we showed that, if A:B:C is the axial ratio of allanite, then that of perrierite is almost exactly:

$$\frac{4A}{3}:B:\frac{4C}{3}.$$

We predicted that such ratios should apply also to the unit cell of allanite and that of perrierite. Succeeding research permitted the determination of the unit cell of perrierite which, when compared to that of epidote<sup>1</sup> was found to be:

epidote: $\beta = 115^{\circ}24'$	$a = 8.96 \text{ \AA}$	( $\frac{2}{3}a = 11.94$ )
	$b = 5.63 \text{ \AA}$	( $b = 5.63$ )
	$c = 10.30 \text{ \AA}$	( $\frac{2}{3}c = 13.73$ )
perrierite <sup>2</sup> : $\beta = 113^{\circ}28'$	$(a = 11.63 \text{ \AA})$	
	$b = 5.62 \text{ \AA}$	
	$(c = 13.61 \text{ \AA}).$	

<sup>1</sup> The lattice of allanite was not yet known, but it was assumed to be almost identical to that of the common epidote as it actually turned out [14].

<sup>2</sup> The data which in note [4] are expressed in kX are changed here to  $\text{\AA}$ .

The values for perrierite,  $a$  and  $c$ , are expressed in parentheses since the inversion of  $a$  and  $c$  was made necessary by the fact that the crystallographic plane (100) was found to be centered. Therefore the final unit cell of perrierite became:

$$\begin{array}{l} \text{perrierite: } \beta = 113^{\circ}28' \\ a = 13.61 \text{ \AA} \\ b = 5.62 \text{ \AA} \\ c = 11.63 \text{ \AA} \end{array}$$

Notwithstanding the fact that the inversion of  $a$  with  $c$  became structurally necessary, I believe that the orientation used by us must be preserved for the macroscopic crystallography of perrierite; for it demonstrates the close relationship of isogonism between it and the monoclinic epidotes. Other reasons for preserving the orientation given will be formulated in the paragraph where I will give particular treatment to the structural data of perrierite.

#### MORPHOLOGICAL CRYSTALLOGRAPHY OF CHEVKINITE

In 1915–16 Ungemach and Lacroix [11], [12], [15] described chevkinite as a rare earths silico-titanate, and they positively assigned it to the orthorhombic system. They also suggested the possibility of the occurrence of a chevkinite with monoclinic symmetry.

In 1924 Boldireff [1], [2] comprehensively described a monoclinic chevkinite of the Urals and ventured a very reserved opinion that the orthorhombic chevkinite found by Ungemach and Lacroix might be the same monoclinic chevkinite he described. For reasons already given [4] and others to be presented in this paper, the above conjecture cannot be defended. Therefore, to distinguish it from the monoclinic chevkinite of Boldireff, I will call "orthochevkinite" the Ungemach and Lacroix mineral, whose existence must be accepted until new evidence to the contrary.

Boldireff describes the chevkinite of the Urals as monoclinic and gives the following crystallographic elements [1]:

$$a:b:c = 2.426:1:1.955 \quad \text{with } \beta = 79^{\circ}52',$$

where  $79^{\circ}52'$  is the angle between the positive crystallographic axes,  $x$  and  $z$ . This is clearly indicated by the angular values and stereographic projections reported by the above author.

In his crystals Boldireff finds a very frequent and unique twinning with union and twin-plane (001). By applying the method of Fedoroff for the determination of the "symbols of the complex" he finds that allanite is the only mineral similar to chevkinite in form and chemical composition. Consequently, he tries an iso-orientation of the two minerals by bringing (100), the larger face of chevkinite in coincidence with (100) of



Allanite Indices of allanite	Chevkinite Indices of Boldireff	Difference
(100):(101) = 30°06'	face corresponding (101) missing	
(100):(102) = 42°23'	42°45' = (001):(101)	0°22'
(102):(001) = 22°36'	22°57' = (101):(201)	0°21'
(001):(102) = 34°15'	34°26' = (201):(100)	0°11'
(102):(101) = 29°09'	28°50' = (100):(201)	0°19'
(101):(302) = 17°00'	16°14' = (201):(101)	0°46'
(302):(100) = 34°37'	34°48' = (101):(001)	0°11'

Bearing in mind that even perrierite repeats the same series of angles almost exactly, we then have *three minerals which develop a zone around [010] in perfect syngony; they are allanite* (monoclinic epidotes in general), *perrierite*, and *chevkinite*. The only difference worth noting is that chevkinite lacks the form corresponding to the (101) of perrierite and allanite.

Let us now examine the faces of the other zones. We have already spoken of the relationship between perrierite and allanite; it led us to assign to perrierite an axial ratio, as referred to the parameters of allanite (we call A:B:C) nearly equal to  $4A/3:B:4C/3$ ,  $\beta$  being almost the same.

Next we shall compare the morphology of perrierite to that of chevkinite. In the stereographic projection of Fig. 4, the iso-orientation used by us is that which clearly shows the morphological relationships between chevkinite and perrierite, and, consequently, monoclinic epidotes.

For chevkinite we have added, to the forms determined by Boldireff, four new forms reported by Jaffe, *et al.* [6] (indices according to Boldireff), {010}, {012}, {021}, {112}.

In spite of the presence in perrierite of a zone (100) (111) with an inclination almost equal to that of chevkinite, Fig. 4 reveals that only the forms belonging to the zone around [010] find correspondence in the two minerals. *Evidently perrierite is much closer to allanite than to chevkinite*, according to what has already been said and illustrated in Fig. 1.

We started from crystallographic considerations fully given in [4], and which I do not deem worthwhile to repeat here, also because the results of the later investigations of Jaffe, Evans Jr., and Chapman [6] have given us all the relevant facts, where we were only trying to make a forecast. We inferred that for the chevkinite of Boldireff it would also be preferable to adopt the same orientation chosen by us for perrierite, namely by superposing the face of habitual twinning (see Fig. 4). We deemed it would be advisable to assume, for the axial ratio of chevkinite, values very close to those of perrierite, but with  $a$  about twice as great. We thought that this morphological interpretation might have a struc-



It should be clear therefore that, on the basis of the new data now available, the morphological orientation of chevkinite formerly suggested by us, is not acceptable any more; it would be based on a structural cell which is twice the unit one. In this connection however, I wish to make the two following remarks:

1) If one wants to stress the morphological relationships between chevkinite, perrierite and monoclinic epidotes, one has always to keep in mind that (100) and (001) of perrierite and of the epidotes correspond to (001) and (201) of chevkinite.

2) Boldireff, in his crystallographic description of chevkinite, accepted as true  $\beta$  (angle between  $+x$  and  $+z$ )  $79^{\circ}52'$ , and chooses indices accordingly. Jaffe, Evans Jr. and Chapman [4], on the contrary, adopt an obtuse angle for  $\beta$ , for the unit cell, and most probably also for the external morphology. They do not make any mention of this change. There is, however, no possibility of ambiguity, as in chevkinite, for each positive and negative form there exists the corresponding negative and positive; according to Boldireff the negative form corresponding to  $\{112\}$  was missing, but it has now been found by the American authors. I believe that the interpretation of the American authors is the one to be accepted, as it conforms to current usage. Therefore the crystallographic constants of chevkinite are the following:

$$2.329:1:1.926, \beta = 100^{\circ}45' \text{ (according to Jaffe, Evans Jr., Chapman).}$$

They are derived from structural data, surely more reliable than the very imprecise crystallographic measurements of Boldireff (see [1] and [2],  $2.426:1:1.955$ ,  $\beta = 79^{\circ}52'$ , Boldireff).

#### UNIT CELL AND STRUCTURAL DATA OF PERRIERITE AND CHEVKINITE

The unit cell [4] determined by us for perrierite, conforms to the unit cell of monoclinic epidotes, with the already mentioned change in the lengths of  $a$  and of  $c$ . Moreover it has been necessary to exchange  $a$  and  $c$ , because it has been found that the plane (100) is centered. This gives:

$$a = 13.61 \text{ \AA}, \quad b = 5.62 \text{ \AA}, \quad c = 11.63 \text{ \AA}, \quad \beta = 113^{\circ}28'.$$

It should be emphasized that the lattice of perrierite has been found to be of the monoclinic centered type, whereas the lattice of epidote and allanite is of the primitive monoclinic type. In this connection I should like to point out, that:

1) In epidote some of the atoms (e.g. Al, O) are present not only at the corners of unit cell, but also in  $0, \frac{1}{2}, \frac{1}{2}$ ; for these atoms, the cell would be with (100) centered. This does not happen for all atoms, and therefore the cell must be considered primitive monoclinic.

2) It seems that something similar may be the case with perrierite.

On account of the small size of the crystals, the  $x$ -ray photographs are very faint and therefore reveal only the arrangement of the heaviest atoms (mainly the rare earths and titanium). The observed absences could therefore become meaningless if stronger photographs should reveal the arrangement of the lighter atoms also. In such a case perrierite would also have a primitive cell.

At the present stage of the investigations, the unit cell has to be considered as centered. For a correct iso-orientation with the lattices of epidote and of chevkinite, it should be kept in mind that the centered basal plane (structurally (001)) is morphologically the crystallographic plane of very frequent twinning (100).

Jaffe, Evans Jr. and Chapman have determined the unit cell of chevkinite as:

$$a = 13.56 \text{ \AA}, \quad b = 5.82 \text{ \AA}, \quad c = 11.21 \text{ \AA}, \quad \beta = 100^\circ 45'.$$

Also in this unit cell the centered base is the plane of very frequent twinning, the plane which, for chevkinite, is also morphologically the plane (001).

These two cells, although substantially different, are closely related as far as angles and of translations lengths. The relationships, with the iso-orientation as revealed by macroscopic crystallography, are illustrated in Fig. 5.

The centered basal planes are, in both minerals, planes of the usual twinning.

Let us now examine the relationships between these two unit cells and those of epidote, superposing the common planes of usual twinning, in conformity with the morphological iso-orientation suggested by us. See Fig. 6.

Figure 6 is only approximate, because slightly divergent lines are drawn as coincident, and the same is the case for very near points. The approximation is very close. In the case of perrierite and chevkinite this is brought out by the following computation:  $a = 13.56 \text{ \AA}$ ,  $b = 5.82 \text{ \AA}$ ,  $c = 11.21 \text{ \AA}$ ,  $\beta = 100^\circ 45'$  being, according to Jaffe etc. [6], the unit cell of chevkinite; the values for the double cell as drawn on the figure in prolongation (dotted lines) of the cell of perrierite are  $a = 13.56 \text{ \AA}$ ,  $b = 5.82 \text{ \AA}$ ,  $c = 23.94 \text{ \AA}$ ,  $\beta = 113^\circ 04'$ . After doubling  $c$  in the unit cell of perrierite, one obtains  $a = 13.61 \text{ \AA}$ ,  $b = 5.62 \text{ \AA}$ ,  $c = 23.26 \text{ \AA}$ ,  $\beta = 113^\circ 28'$ ; this is in excellent agreement with the computed values, and with what we had predicted. In our note [4], on account of an obvious printing error, there is  $a = 29 \text{ \AA}$ . One should read  $24 \text{ \AA}$  ( $8/3$  of  $a$  of epidote is equal to  $23.89 \text{ \AA}$ ) and should take into account the exchange between  $a$  and  $c$ .

We are faced here with a singular case of relationship between the unit cells of different mineralogical species, which opens new vistas on

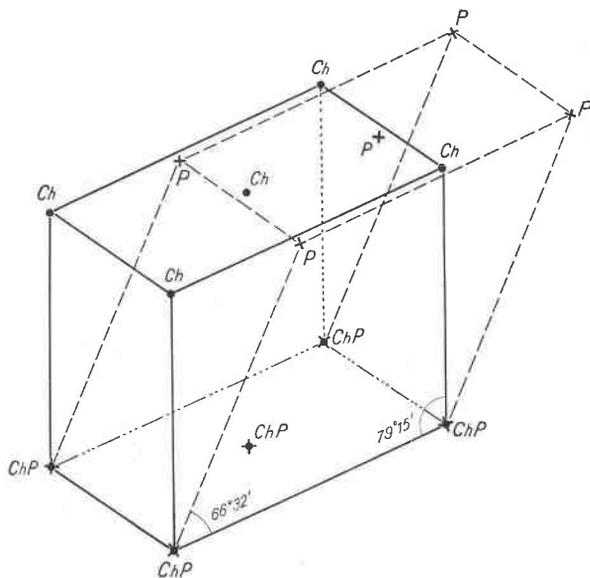


FIG. 5. Relationship between the unit cell of chevkinite (full lines) and of perrierite (dashed lines).

Points *Ch* = equivalent points of chevkinite.

Crosses *P* = equivalent points of perrierite.

polymorphism. It becomes therefore necessary to make an accurate examination of the experimental results, and of the interpretation of the morphological and structural data. The following points are given in confirmation:

(1) On the basis of *x*-ray photographs, the two lattices are clearly different. Equator and first level Weissenberg or Buerger precession photographs about [010] are sufficient to distinguish them. As a consequence of the (001) centering, the patterns for the zero level are almost identical (see dashed lines in Figs. 7 and 8), but the *h*1*l* photograph clearly differentiates them.

Figures 9 and 10 show precession photographs of perrierite around [010], equator and first level.

Figure 11 combines the reflections observed in Figs. 9 and 10, thus showing both the zero and first levels. There is no possibility of confusing the unit cell of perrierite with that of chevkinite [6].

(2) We shall examine next the evidence which can be obtained from the macroscopic crystallographic characters of chevkinite.

Let us compare the stereographic projection of the faces of zone  $(\bar{1}\bar{1}0)$   $(\bar{1}\bar{1}1)$  of chevkinite with the set  $(\bar{1}\bar{1}0)$   $(\bar{1}\bar{1}1)$  of the first layer [010] of the

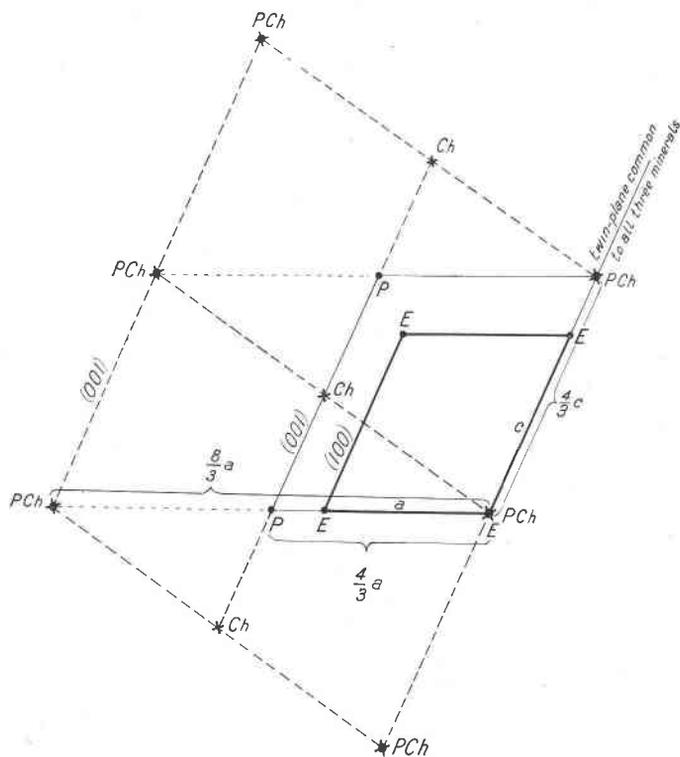


FIG. 6. This scheme gives very closely the relationship, on the plane (010), between the unit cell of epidote (heavy full lines), of perrierite (light full lines), and of chevkinite (dashed lines: four unit cells (010)). Structural indices.

Points *E* = equivalent points of epidote.

Points *P* = equivalent points of perrierite.

Crosses *Ch* = equivalent points of chevkinite.

reciprocal lattice of chevkinite (see Fig. 12). On this figure, besides the crystallographic planes of chevkinite, shown with dots and their indices, are represented also, with crosses, the crystallographic planes of perrierite.

It is clear from the foregoing that the morphological crystallography reflects exactly the relationship of the two lattices. It was on account of this morphological relationship that we had predicted for chevkinite a unit cell which, although of double size, did closely correspond to the real one.

(3) Powder photographs. Data on perrierite from Nettuno, Italy, obtained with a Philips diffractometer, are compared with data for chevkinite from New Hampshire and Arizona, and for a specimen from Japan, called chevkinite, but actually perrierite, in Table 1.

TABLE 1. POWDER PHOTOGRAPH DATA

I Perrierite of Kobe-mura, Japan [13] (called chevkinite)		II Perrierite of Nettuno, Italy			III Chevkinite, New Hampshire [6]			IV Chevkinite, Arizona [10]	
<i>d</i> , Å	I	<i>hkl</i>	<i>d</i> , Å	I	<i>hkl</i>	<i>d</i> , Å	I <sup>1</sup>	<i>d</i> , Å	I <sup>1</sup>
5.399	20	002	5.34	65	002	5.50	W		
5.195	30	110	5.13	25					
4.834	10				$\bar{1}11$	4.92	MW	4.97	M
					111	4.67	M	4.71	M
4.104	20		4.06	20					
3.566	40	003	3.56	20	003	3.67	W	3.68	W
		$31\bar{1}$	3.53	15	310	3.51	MW	3.52	M
3.462	40		3.43	20					
3.405	40								
3.217	20	400	3.15	15	$\bar{3}12$	3.20	Sb	3.20	S
3.045	50		3.03	20	$\bar{4}02$	3.11	M	3.11	W
2.983	100	$31\bar{3}$	2.96	100	203	2.98	W	3.04	M
2.956	100	311	2.93	55					
2.841	70	020	2.82	65	020	2.90	M	2.91	M
					312	2.79	MW	2.77	W
					004	2.74	VS	2.74	S
2.699	60	113	2.73	15					
		004	2.675	20					
					022	2.60	W		
2.579	20	220	2.550	15					
2.513	30	022	2.488	15					
2.458	40							2.38	W
2.247	20		2.229	50					
2.231	20								
2.176	50		2.166	25		2.19	W	2.19	W
2.158	40		2.156	25					
2.108	20		2.095	15					
		600	2.088	15					
1.952	30	024	1.941	50		1.99	MW	1.98	M
			1.779	15					
1.723	20		1.719	10					
1.659	30		1.658	10					
1.612	30		1.649	15					
1.597	20		1.585	15					

<sup>1</sup> VS=Very strong; S=Strong; M=Medium; MW=Medium weak; W=Weak; F=Faint; VF=Very faint; b=Broad.

For perrierite the indices given have been obtained from a comparison of Weissenberg and precession data with powder data.

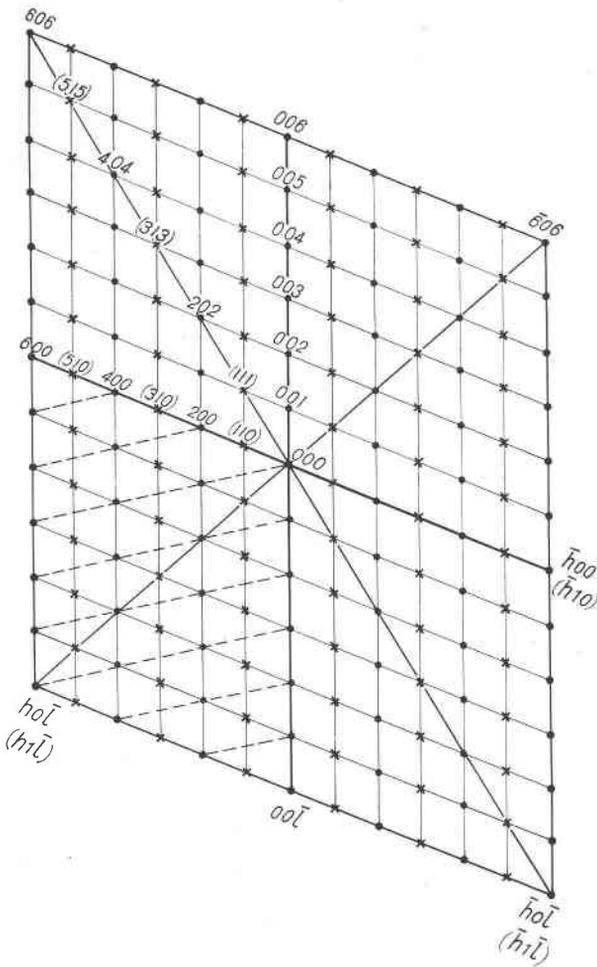


FIG. 7. Reciprocal lattice around [010] of perrierite, equator (dots) and first layer (crosses).

Let us note in the first place that now we are in possession of powder both of perrierite and of chevkinite, which are definitely different; even without morphological data, they allow one to distinguish clearly one mineral from the other, unless these chevkinites be hopelessly metamictic. The chevkinite of Arizona (column IV) is undoubtedly chevkinite; the so-called chevkinite of Kobe-mura (column I) is perrierite.

Now let us examine the powder data of perrierite (column II) and of chevkinite (column III). If the unit cells of perrierite and of chevkinite have been correctly interpreted, we should find the same analogies and



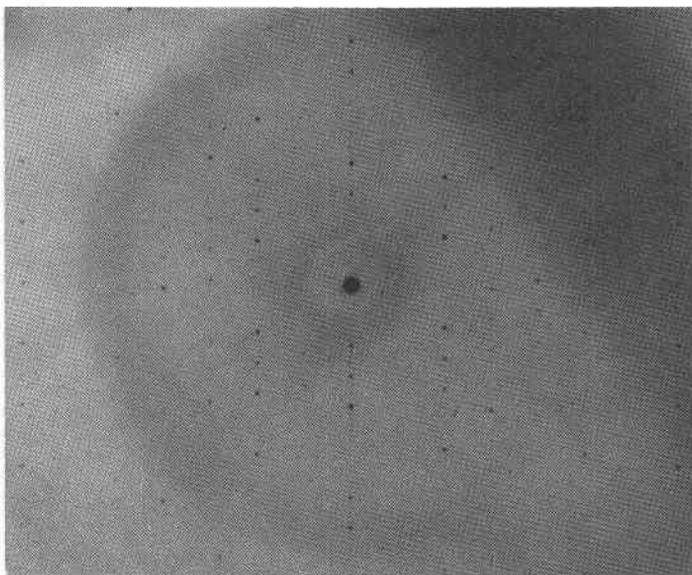


FIG. 9. Buerger precession, 0-level; [010] of perrierite.

than the analogies between chevkinite on one hand, and epidotes and perrierite on the other.

As far as the space group is concerned, the quoted authors [6] give as probable for chevkinite the group  $C2/m$ ; they do not exclude however, the possibility that it may belong to  $C2$  or  $Cm$ , these being groups without a symmetry center. I may add to their convincing remarks, that the analogies with perrierite and epidotes seem to me to exclude the latter possibility. We had assigned perrierite to group  $C2/m$ . In fact, the detailed and easily interpretable morphological crystallography of perrierite does not offer any indication of the lack of a center of symmetry; moreover, repeated endeavors to detect with an extremely sensitive device, any piezoelectricity, have always led to negative results. These data, and the crystallographic relationship with epidote, allow one to conclude with almost absolute certainty that perrierite has a symmetry center.

#### OPTICAL PROPERTIES OF PERRIERITE AND OF CHEVKINITE

Perrierite and chevkinite do not lend themselves to easy optical determinations, on account of their very strong absorption, with exceptional pleochroism. We feel however that the data we have obtained for perrierite deserve confidence; on account of its rather young age (quaternary) [3], it also does not show strong signs of metamict transformations.

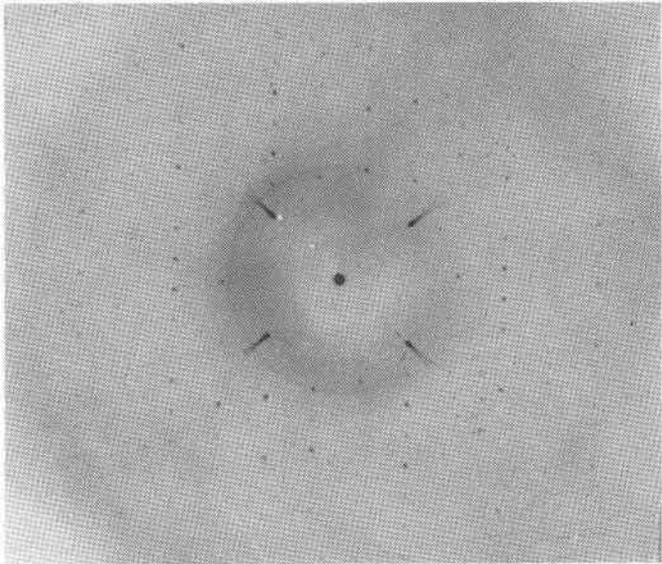


FIG. 10. Buerger precession, first layer [010] of perrierite.

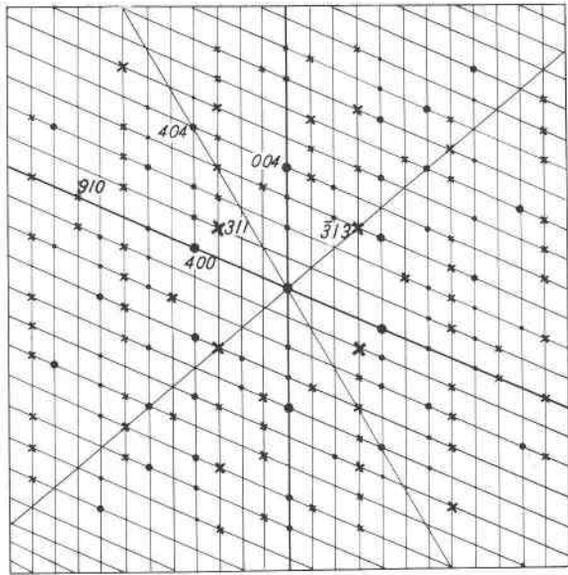


FIG. 11. Diffraction spots observed in the Buerger precession [010] of perrierite, equator (dots) and first layer (crosses).

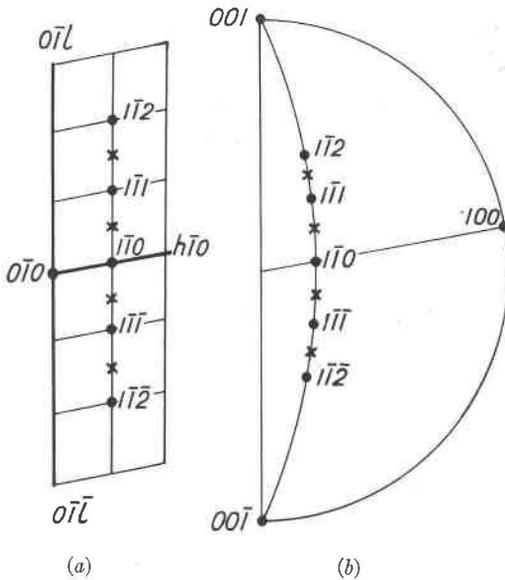


FIG. 12. *a*) Reciprocal lattice first layer of chevkinite (dots with indices), with added lattice planes of perrierite (crosses only).

*b*) Stereographic projection of the corresponding faces of chevkinite (dots with indices) and of perrierite (crosses only).

On the other hand, on account of the quoted difficulties, I have nothing to add to what has already been published in note [4].

Perrierite: Very strong absorption, with  $Z \cong Y \gg X$ ;  $X$  = yellow;  $Y$  = opaque to violet red;  $Z$  = opaque to deep brown;  $a = 1.90-1.95$ ;  $\beta = 2.01$  (computed);  $\gamma = 2.02-2.06$ .

Orientation:  $Z = b$ ;  $X \wedge a =$  about  $24^\circ$  in the obtuse angle;  $2V =$  about  $60^\circ$ , with negative birefringence.

For chevkinite we have Boldireff's data, which however were obtained on strongly metamict material. Therefore he found birefringence around  $0.001-0.002$ , which surely does not fit unaltered material. Boldireff gives: intense pleochroism in reddish brown shades, with  $Z > Y > X$ ; orientation  $Z = b$ ,  $X \wedge c$  from  $11^\circ 30'$  to  $25^\circ 45'$  in the acute angle.

Jaffe, Evans Jr. and Chapman who have studied the chevkinite of New Hampshire, recognized, in the same sample, definitely metamict zones near other more fresh ones. For the latter, they found a minimum index of refraction of  $1.97$  and a maximum of  $2.05$ , with  $2V$  variable from medium to large and optic sign negative. As orientation they give  $Z \wedge$  elongation (*b*)  $6^\circ-9^\circ$ . This last data, for an undoubtedly monoclinic crystal, seems perplexing.

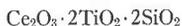
From the examination of these optical characters it is however evident, that it is practically impossible to distinguish between perrierite and chevkinite under the microscope in thin sections. It is also difficult, especially in thin sections, to distinguish the chevkinites from allanite, although, in the unusual case of fresh mineralizations, the chevkinites should be recognizable through higher indices and the stronger birefringence. The diagnostic character which, in my opinion, is easiest to ascertain, is the stronger absorption in violet shades of the chevkinites as compared with allanite. It is very likely that perrierite and chevkinite are far more widespread in rocks than commonly believed, and that in petrographical analyses they have been determined as allanite. The fact that in petrographical treatises one finds, besides the normal data for allanite, also anomalous data (e.g., much higher indices of refraction and an orientation  $Z=b$ ), could be fittingly explained by this possibility of confusion between allanite and the chevkinites.

#### CHEMISTRY

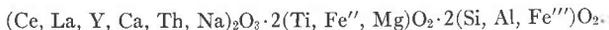
None of the attempts made to assign a chemical formula to the chevkinites, have led to fully satisfactory results. It can be foreseen that it will not be possible to gather under a single formula all the chevkinites for which chemical analyses are available, on account of the wide range of their compositions; this range appears to me to exceed very much the limits of possible isomorphic substitutions. I do not wish to insist on the subject, because I hope to be able to soon give the complete structure of perrierite, which is being studied at present in the Mineralogy Institute of Pisa. It would therefore serve no purpose to offer unwarranted hypotheses, since the knowledge of the structure of at least one mineral of the chevkinite group will be put on a sure basis.

I shall limit myself therefore to a few remarks on crystallochemical criteria, which will have to be respected also when we know the complete structure of chevkinite.

In the first place, I believe that the general crystallochemical rule, according to which calcium is in isomorphic substitution with cerium and with the other rare earths, shall not admit exception in the chevkinites. Keeping together those elements which have the same coordination (8, 6, 4), we gave a formula of the following type:



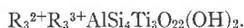
or more in detail



I admit that this formula is not very satisfactory. On account of the great quantity of titanium, and of the difficulty of maintaining the electrical neutrality, it is not easy to accept the association of tetravalent

titanium with bivalent iron and magnesium. On this point the decision will have to be left to the analysis of the structure; should it confirm this grouping, it would contribute valuable data on the possibilities of isomorphous substitution. I believe, however, that it is preferable to the earlier formulas, which by rather naively grouping bivalent, trivalent and quadrivalent elements, lead to results not in harmony with the principles of crystal chemistry.

Also Jaffe, Evans Jr. and Chapman have tried to assign to chevkinite a new formula, while declaring the previously suggested ones are not supported by any convincing evidence ([6], p. 480). Considering that a structural basis would be of help in reaching an exact formula, they have tried to find in their determination of the unit cell the starting point for the solution of the problem. Starting from the assumption that in such compounds the volume is accounted for by the oxygen atoms alone, and taking the value of the oxygen volume as  $18.1 \text{ \AA}^3$ , as in epidote, they come to the result that the number of oxygen atoms in chevkinite (unit cell volume  $873 \text{ \AA}^3$ ) is 48. On this assumption they give the following formula:



Even omitting other crystallochemical considerations, it is perplexing to note, that in this formula, calcium and rare earths are separated. As far as the 48 atoms of oxygen are concerned, I wish to point out that applying the same procedure to perrierite<sup>3</sup> (unit cell volume  $812 \text{ \AA}^3$ ) the number of atoms in the unit cell should be 44.86, nearly equal to the 44 required by our formula. I do not intend, however, to make use of this computation as a support for our interpretation, because it leads to a rough approximation only, with an uncertainty of a few units. For example, assuming as the unit volume of chevkinite the volume found after heat-treatment, the number of oxygen atoms which ought to be present is reduced to 46.

The chemical formula put forward by us for perrierite seems to me the most acceptable, until the day the determination of the structure will supply further data. It should then be possible to decide if perrierite and chevkinite are polymorphs, or if they have to be considered two distinct minerals.

#### ORTHO-CHEVKINITE FROM MADAGASCAR

Ungemach [15], and Lacroix [12] described for the first time the morphology of a chevkinite on samples from Madagascar. They stated

<sup>3</sup> Some of the chemical data and the density of perrierite have been incorrectly reported in the paper by Jaffe, Evans Jr. and Chapman [6].

definitely that it is orthorhombic, although expressing the possibility that a monoclinic form may also exist. In describing chevkinite from the Ural, Boldireff [1], [2] admits, although very doubtfully, the possibility that the orthorhombic crystals described by Ungemach and Lacroix may be morphologically the same as the ones described by himself, simulating through twinning an orthorhombic symmetry. We have already shown in detail why the hypothesis of Boldireff seems indefensible. Let me state three fundamental points in confirmation:

1) The twinning which, according to Boldireff, would transform the monoclinic chevkinite described by him into the orthorhombic chevkinite of Ungemach, would be; twinning plane (100) not coincident with the composition plane. Therefore, a parallel twinning with irrational twinning axis and with composition plane equally irrational (no plane containing the normal to (100), can have a rational index, with the exception naturally of (100)). Such a twinning does not seem acceptable.

2) Even if one admits this strange twinning, one does not obtain the orthorhombic crystals of Ungemach [15] which show, for instance, the association of the three orthogonal pinacoids {100}, {010}, {001}.

3) This twinning has never been found either in the chevkinite of the Urals, in that of New Hampshire, in perrierite, in allanite, or in other monoclinic epidotes. It would therefore be specific, and very common, only in orthochevkinite of Madagascar. One would make use, for proving the crystallographic identity of two minerals, of an evident and important differential character.

I owe to the kindness of Mme. Jérémme of the Minéralogical Laboratory of the Museum of Paris the opportunity to examine three of the original crystals from Madagascar, described by Ungemach and Lacroix. My crystallographic examination fits perfectly the orthorhombic interpretation of the said authors.

With the kind permission of Mme. Jérémme I have broken off a small fragment from a big crystal; with this I have made some Debye-Scherrer photographs. Those obtained with this material before heat treatment are very faint, with broad lines; this confirms the advanced metamict transformation of the mineral. The photographs after heat treatment are more sharp and rich in diffraction lines; but it has been easy to ascertain that, besides the faint lines which correspond almost exactly to the untreated material, there appears the powder pattern of  $Ce_2O_3$ , some of the lines being very strong. Table 2 gives the data so obtained.

With all the uncertainties due to the fact that the material is strongly altered, one can assume as specific for the chevkinite of Madagascar those diffractions common to the spectrograms both of the untreated and

TABLE 2. ORTHOCHEVKINITE OF MADAGASCAR

Untreated		Heat-treated <sup>2</sup>	
d, Å	I <sup>1</sup>	d, Å	I <sup>1</sup>
4.15	VS	4.13	W
3.78	S	3.72	F
3.54	M	3.50	W
		(3.12)	(VS)
		2.96	W
2.875	S	2.831	W
2.699	S	(2.706)	(M)
2.527	M	2.505	W
		2.232	F
		2.159	MW
		2.085	W
		1.959	W
		(1.911)	(S)
		1.738	VF
1.692	S	1.689	F
		(1.632)	(S)
		(1.565)	(W)
1.488	M	1.413	W
		(1.353)	(MW)
		(1.241)	(M)
		(1.210)	(MW)
		(1.104)	(M)
		(1.041)	(M)
		(0.956)	(MW)

<sup>1</sup> VS=Very strong; S=Strong; M=Medium; MW=Medium weak; W=Weak; F=Faint; VF=Very faint.

<sup>2</sup> Spacings in parentheses pertain to the  $Ce_2O_3$  produced by heating.

of the heat-treated material. There is no possibility of correlation with the powder spectrograms of perrierite and of chevkinite (cf. Table 1).

I do not wish to deny that it may be possible to identify the orthorhombic chevkinite with monoclinic chevkinite or with perrierite, through a mimetic twinning (but surely not of the kind suggested by Boldireff). I am more inclined to believe in a structural twinning within the lattice, in keeping with what is already well known in the case of orthorhombic zoisite, with respect to monoclinic epidotes. The close analogies between epidotes and chevkinites hint of the possibility of this further kinship; should this be proved, it would complete in a very satisfactory way the picture of the relationship between epidotes and chevkinites.

## CONCLUSIONS

1) Epidotes and chevkinites form two groups of minerals with close morphological and structural ties. The most significant common character is the development of oxygen chains along the symmetry axis in the monoclinic members ( $b \sim 5.6 \text{ \AA}$ ). Other minerals, like mosandrite, rinkite, etc., are related to these two groups.

2) The chevkinites are not a single mineral species. Well identified are perrierite and monoclinic chevkinite; probably there is also a orthorhombic chevkinite.

3) Perrierite has to be referred to the following crystallographic elements, which give it the same orientation as for the monoclinic epidotes:

Monoclinic system, prismatic class,

$$a:b:c = 2.047:1:2.380, \quad \beta = 113^\circ 28' \text{ (Bonatti and Gottardi).}$$

The values of the unit cell are the following:

$$a = 13.61 \text{ \AA}, \quad b = 5.62 \text{ \AA}, \quad c = 11.63 \text{ \AA}, \quad \beta = 113^\circ 28'$$

where  $a$  and  $c$  are interchanged in respect to the morphological interpretation, the lattice being centered.

Space group:  $C2/m$ .

4) Chevkinite has to be referred to the following elements, in iso-orientation with its unit cell:

Monoclinic system, prismatic class,

$$a:b:c = 2.329:1:1.926, \quad \beta = 100^\circ 45' \text{ (Jaffe, Evans Jr., Chapman)}$$

remembering that, for stressing the isogonal relations with perrierite and with the monoclinic epidotes, the face (001) must be assumed as (100), and (201) as (001).

The values of the unit cell are the following:

$$a = 13.56 \text{ \AA}, \quad b = 5.82 \text{ \AA}, \quad c = 11.21 \text{ \AA}, \quad \beta = 100^\circ 45'$$

in iso-orientation with the morphological elements.

Space group:  $C2/m$ .

5) The unit cell of chevkinite as given above, with  $c$  doubled and with (010) centered, gives:

$$a = 13.56 \text{ \AA}, \quad b = 5.82 \text{ \AA}, \quad c = 23.94 \text{ \AA}, \quad \beta = 113^\circ 04'$$

which repeats with great accuracy the unit cell of perrierite with  $c$  doubled; therefore it is in the following relationship with the unit cell of monoclinic epidotes:

$$\frac{4}{3} c, 1b, \frac{8}{3} a, \text{ with } \beta \text{ similar.}$$

This confirms what had been anticipated, through the morphological comparison of perrierite with chevkinite and the epidotes, by Bonatti and Gottardi [4].

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