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THE OD NATURE OF PERRIERITE AND CHEVKINITE

Abstract - S. Merlino, *The OD nature of perrierite and chevkinite.*
The structure-types of perrierite and chevkinite display OD character. Those structure-types are built up by two distinct layers which may succeed each other in different ways, pairs of adjacent layers being geometrically equivalent, giving rise to a whole family of OD structures. The symmetry properties of the two layers are described and the four MDO (Maximum Degree of Order) structures in the family are derived: two of them correspond to perrierite and chevkinite structure-types; the other two MDO structures, with orthorhombic symmetry and presenting double cell volumes, correspond to new possible polytypes in the family.

Key words - chevkinite, perrierite, OD structures, polytypism, MDO structures

Riassunto - S. Merlino, *La natura OD di perrierite e chevkinite.*
Le fasi naturali perrierite e chevkinite, o più correttamente i loro tipi strutturali, dispiegano carattere OD. Invero essi sono costituiti da due distinti strati strutturali che possono susseguirsi l'un l'altro in modi differenti, coppie di strati adiacenti risultando, comunque, sempre geometricamente equivalenti, dando in tal modo origine ad una intera famiglia di strutture OD. Sono descritte le proprietà di simmetria dei due strati e sono derivate le quattro strutture MDO (Maximum Degree of Order) della famiglia: due di esse corrispondono a perrierite e chevkinite; le altre due strutture MDO, con simmetria ortorombica e con raddoppiato volume di cella, corrispondono a nuovi possibili politipi nella famiglia.

Parole chiave - chevkinite, perrierite, strutture OD, politipismo, strutture MDO

Introduction

Chevkinite group minerals (CGM) occur "in a very wide range of igneous and metamorphic parageneses. We know of 250 localities world-wide where members of the group have been recorded…" (Bagiński & Macdonald, 2013).
The twelve members of the group currently known are divided in the chevkinite and perrierite subgroups. Chevkinite [presently redefined as chevkinite-(Ce)] has been firstly named by Gustav Rose in 1839 (Dana, 1892), whereas perrierite [currently redefined as perrierite-(Ce)] has been found by Bonatti & Gottardi (1950). Its peculiar characters and clear distinction from chevkinite were presented and discussed by Bonatti & Gottardi (1954) and Bonatti (1959); it appears therefore incorrect the statement "Originally chevkinite-(Ce) was described as perrierite by Bonatti and Gottardi (1950)" by Sokolova *et al.* (2004) in their careful study of the structure and crystal chemistry of chevkinite-(Ce).
The composition of the minerals in the chevkinite and perrierite subgroups correspond to the formula $A_4BC_2D_2Si_4O_{22}$, where A = REE, Y, Ca, Sr, Th; B = Fe^{2+}; C = Fe^{2+}, Fe^{3+}, Mg, Mn, Ti, Al, Zr, Nb; D = Ti (Gottardi, 1960; Bonatti & Gottardi, 1966; Ito, 1967; Ito & Arem, 1971; Macdonald *et al.*, 2019).
The minerals in both subgroups display monoclinic symmetry and the most unequivocal way to discriminate between the two subgroups is the value of the angle β, ~100° and ~113° for the minerals in the chevkinite and perrierite subgroups, respectively.
The structures of perrierite and chevkinite are represented in Figs 1 (perrierite) and 2 (chevkinite).
Unit-cell parameters and space groups (s.g.) are the following:

perrierite-(Ce)
a = 13.61,   b = 5.62,   c = 11.63 Å,
β = 113.47°,   s.g. *C2/m*
(Bonatti & Gottardi, 1954);

chevkinite-(Ce)
a = 13.400,   b = 5.7232,   c = 11.0573 Å,
β = 100.537°,   s.g. *C2/m*
(Sokolova *et al.*, 2004).

The structure types of all the phases in the group are built up by two distinct layers, indicated as L1 and L2 in Figs 1 and 2. L1 octahedral layers display D octahedral columns with the apical corners pointing along **a**, connected with C octahedral columns with apical corners in the direction normal to (001). L2 layers are built up by Si_2O_7 groups interconnected with B octahedral columns. The structures are completed by large A cations placed in cavities within the resulting framework. It seems proper to recall that "in the asymmetric unit of the perrierite-type structure there are two A sites (A1 and A2), one B site, one C site, and one D site. In chevkinite the D site splits in D1 and D2" (Macdonald *et al.*, 2019). The unique sites B, C, D1 and D2 are denoted M1-M4 by Popov *et al.* (2001), Sokolova *et al.* (2004) and Holtstam *et al.* (2017).

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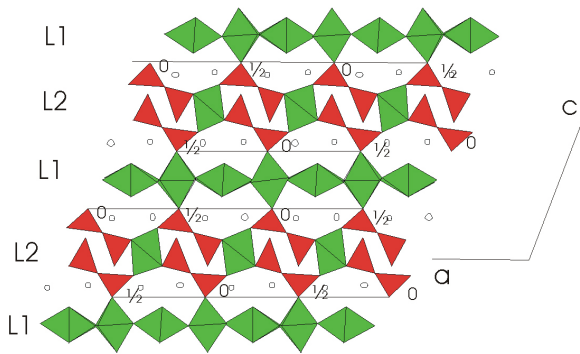
Figure 1. Structure of perrierite as seen along [010]. B, C, D octahedra are green coloured. The A sites are indicated with small circles. The *y* coordinates of the silicon atoms placed at the border between L1 and L2 layers are indicated.
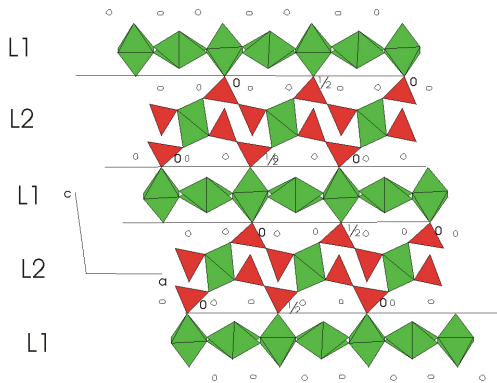

Figure 2. Structure of chevkinite as seen along [010]. B, C, D octahedra are green coloured. The A sites are indicated with small circles. The *y* coordinates of the silicon atoms placed at the border between L1 and L2 layers are indicated.

CGM of both subgroups occur in different space groups, *C2/m* and *P2₁/a*. Stachowitz *et al.* (2019) described Nb-rich chevkinite-(Ce) from the Biruya rare metal deposit (Transbaikalia, Russia), occurring in both space groups but with "nearly identical crystal structure topologies". In the following discussion we shall constantly assume *C2/m* space group for both structure-types.

The aim of the present paper is to present a description of the relationships between the chevkinite and perrierite structure-types, based on the OD theory (Dornberger-Schiff, 1956, 1964; Ferraris *et al.*, 2008; Merlino, 2016). In the following discussion we shall constantly assume *C2/m* space group for both structure-types.

POLYTYPES IN CHEVKINITE GROUP MINERALS AS MDO STRUCTURES

The two structures may be described as belonging to one family of OD structures built up with two distinct types of layer, L1 and L2 (each of them presenting one of the 80 layer group symmetries), indicated in Fig. 1.

Layer L1 has orthorhombic symmetry, layer group *P2/m 2/m* (2/m) and translations:

$$\mathbf{a}_{L1} = \mathbf{a}_p/2 \qquad \mathbf{b}_{L1} = \mathbf{b}_P/2$$

[$\mathbf{a}_p$, $\mathbf{b}_p$ are the translation vectors of the perrierite structure-type (as well as of the chevkinite structure-type)].

Layer L2 has monoclinic symmetry, space group *C 1 2/m* (1) and translations:

$$\mathbf{a}_{L2} = \mathbf{a}_p \qquad \mathbf{b}_{L2} = \mathbf{b}_P$$

The parentheses in the last position of each layer group symbol indicate the missing periodicity.
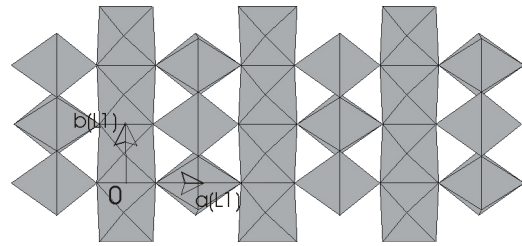
Figure 3. Layer L1 as seen normal to (001).

The fact that the symmetry of the L1 layer is higher than that of layer L2 points to the possibility of polytypic relationships.

The kind of connection of L1 layers on opposite sides of L2 is unique, similarly realized through the action of the operators [- - 2]$_{x=0}$, [- - 2₁]$_{x=1/4}$, as well as through the inversion centres, all representing partial operations (POs) of the layer L2.

On the other side different possible ways exist for connecting layers L2 on opposite sides of a layer L1. It is proper to remark that – for all the distinct possible ways (four ways as we shall see in the following) – pairs of adjacent L1-L2 layers are geometrically equivalent, wherever taken in the structure (**principle of OD structures**).

An infinite number of possible polytypes or of disordered structures is possible, corresponding to the various sequences of operators which may be active in the L1 layer. The symmetry relations common to all the polytypes in this family are embodied in the

so called OD groupoid family symbol, which, if we assume the origin of the layer L1 as indicated in Fig. 3 (structure of the L1 layer), will be:

$$D\ 2/m\ 2/m\ (2/m) \qquad\qquad C\ 1\ 2/m\ (1)$$
$$[-0.17 \qquad 0.0]$$

In this symbol the first line presents the symmetries of the two layers L1 and L2. The letter D (as suggested by Dornberger-Schiff) indicates that the cell is doubled if we refer to the common cell of both layers. More precisely the parameters of the two cells are related as indicated in the following:

$$\mathbf{a}_{L2} = 2\ \mathbf{a}_{L1} \qquad \mathbf{b}_{L2} = 2\ \mathbf{b}_{L1}.$$

Therefore the 'two-dimensional' cell L1 corresponds to ¼ of that of L2, but due to the C centring of L2 (which is therefore a double cell), the correct indication for the cell L1 is D. The parentheses in the last position of the symbol of each layer group indicate the direction of missing periodicity.

In the second line the positional relationships between the adjacent layers are indicated: the origin of L2 is shifted by 0.17 $\mathbf{a}$ + 0.0 $\mathbf{b}$ with respect to that of L1 (with reference to the vectors of the common cell).

Among the infinite possible polytypes, OD theory singles out those polytypes with maximum degree of order (MDO structures), namely those which contain the smallest number of different kinds of triples (**principle of MDO structures**). In the present case, in which there is only one way to connect L1 layers on both sides of L2 (and so only one kind of triple L1-L2-L1) and different possible ways (actually four as it will be shown) for L2-L1-L2 triples, the smallest number of distinct triples is two.

THE FOUR POSSIBLE MDO STRUCTURES

When pairs of layers L2 on opposite sides of L1 are always related by a symmetry axis $[\,\text{-}\ \text{-}\ 2\,]_{x=0}$, the structure-type of perrierite (Polytype 1 – MDO1) is obtained. When the pairs of layers L2 on opposite sides of L1 are always related by a symmetry axis $[\,\text{-}\ \text{-}\ 2\,]_{x=1/2}$ (the x coordinates are referred to the translation $\mathbf{a}$ of the cell L1), the structure-type of chevkinite (Polytype 2 – MDO2) is obtained.

Similarly, the action of the inversion centres in L1 at 0, 0 and ½, ½ gives rise to the structure-type of perrierite, whereas the action of the inversion centres in L1 at 0, ½ and ½, 0 gives rise to the structure-type of chevkinite.

Perrierite is obtained also through the composition of the operations which give rise to the chevkinite structure-type with the translations $\mathbf{a}_{L1}$ and $\mathbf{b}_{L1}$ (both are symmetry operations of the layer L1). Chevkinite is obtained also through the composition of the operations which give rise to the perrierite structure-type

with the translations $\mathbf{a}_{L1}$ and $\mathbf{b}_{L1}$ (both are symmetry operations of the layer L1).

In conclusion the constant application of the operator $[\,\text{-}\ \text{-}\ 2\,]$ in L2 and the operator $[\,\text{-}\ \text{-}\ 2\,]_{x=0}$ (or the other 'equivalent' operators) in L1 gives rise to the structure-type of perrierite. The constant application of the operator $[\,\text{-}\ \text{-}\ 2\,]$ in L2 and the operator $[\,\text{-}\ \text{-}\ 2\,]_{x=1/2}$ (or the other 'equivalent' operators) in L1 gives rise to the structure-type of chevkinite.

However there are other POs in L1:

1) $[\ 2\ \text{-}\ \text{-}\ ]_{y=0}$
2) $[\ 2\ \text{-}\ \text{-}\ ]_{y=1/2}$
3) $[\ \text{-}\ \text{-}\ m\,]$.

The application of 1) and 3) gives rise to another polytype, polytype 3 (MDO3) with space group $Ccmm$ and $\mathbf{a} = \mathbf{a}_P$, $\mathbf{b} = \mathbf{b}_P$, $\mathbf{c} = 2\mathbf{c}_P\sin\beta_P$ (Fig. 4)

The application of 2) gives rise to the polytype 4 (MDO4), with space group $Ccmb$ and the same basis vectors as in the previous case (Fig. 5).

In the polytype MDO3 tetrahedra are connected, on both sides of the layer L1, according to the perrierite way; in polytype MDO4 the tetrahedra are connected, on both sides of the layer L1, according to the chevkinite way.
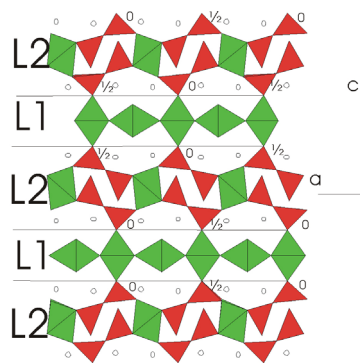

Figure 4. The structure of the polytype MDO3, s.g. $Ccmm$. The tetrahedra on opposite sides of the L1 layer are placed according to the 'perrierite' way.
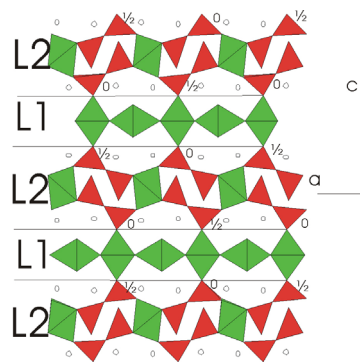

Figure 5. The structure of the polytype MDO4, s.g. $Ccmb$. The tetrahedra on opposite sides of the L1 layer are placed according to the 'chevkinite' way.

Table 1. Atomic coordinates in polytype MDO3 and MDO4. It is assumed that A sites are occupied by cerium atoms and the octahedral sites are occupied by titanium atoms.

MDO3	x	y	z	MDO4	x	y	z
Ce1	0.3173	½	-0.1164	Ce1	0.3173	½	-0.1164
Ce2	-0.0333	½	0.1223	Ce2	-0.0333	½	0.1223
Si1	0.3332	½	0.1171	Si1	0.3332	½	0.1171
Si2	0.1452	½	0.0238	Si2	0.1452	½	0.0238
Ti1	0.1704	-0.2560	-¼	Ti1	0.1704	-0.2560	-¼
Ti2	0.4454	½	-¼	Ti2	0.4454	½	-¼
Ti3	0	0	0	Ti3	0	0	0
O1	0.1796	-0.2525	-0.1532	O1	0.1796	-0.2525	-0.1532
O2	0.4174	-0.2300	-0.1882	O2	0.4174	-0.2300	-0.1882
O3	0.4143	-0.2350	-0.0457	O3	0.4143	-0.2350	-0.0457
O4	0.2736	½	-¼	O4	0.2736	½	-¼
O5	0.5750	½	-¼	O5	0.5750	½	-¼
O6	0.4374	½	0.0815	O6	0.4374	½	0.0815
O7	0.2403	½	0	O7	0.2403	½	0
O8	0.1717	½	-0.0497	O8	0.1717	½	-0.0497
Ti21	0.4454	0	-¼				
O41	0.2736	0	-¼				
O51	0.5750	0	-¼				

Table 1 presents the atomic coordinates corresponding to the structure-types illustrated in Figs 4 and 5, assuming that the A positions are occupied by cerium and that all the octahedral positions are occupied by titanium.

ORTHORHOMBIC POLYTYPES

MDO3 and MDO4 structures correspond to possible orthorhombic polytypes in the chevkinite family. Some indications exist in the literature for the actual existence of similar polytypes in this family. An orthorhombic polytype of rengeite, which presents the structure-type of perrierite and composition $Sr_4ZrTi_4(Si_2O_7)_2O_8$, has been described by Mashima *et al.* (2008). It was found as microdomains inside crystals of monoclinic rengeite. According to these authors an orthorhombic unit cell can be constructed by twinning operation on a mirror plane (001) in the L1 layer (Figs 4b and 4c in Mashima *et al.*, 2008), namely exactly operating as in the derivation of the MDO3 polytype. Lacroix (1915) and Ungemach (1916) described, through morphological studies, an 'orthorhombic chevkinite' from Madagascar. Original crystals from that locality were also studied by Bonatti (1959) who confirmed the orthorhombic interpretation of those authors. Bonatti (1959) also tried to obtain Debye-Scherrer photo-graphs. However, the diffraction patterns, due to the advanced metamict transformations of the samples, do not consent an unequivocal comparison with the calculated patterns of MDO3 and MDO4.

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