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# POLYTYPISM IN HANJIANGITE, SHEET SILICATE-CARBONATE-FLUORIDE OF CALCIUM, ALUMINIUM, VANADIUM AND BARIUM

Abstract - Polytypism in Hanjiangite, sheet silicate-carbonate-fluoride of calcium, aluminium, vanadium and barium. The crystal structure of hanjiangite, sheet silicate-carbonate-fluoride of calcium, aluminium, vanadium and barium is described and its polytypic character is indicated. It is shown that hanjiagite is built up by two distinct structural layers (building layers BL1 and BL2) which alternate along the direction normal to the layers. The analysis of the possible sequences shows that there are three main polytypes: one, hanjiangite-2M, corresponding to the structure of the phase found in nature and studied by Liu et al. (2012), in which two layers of each type alternate for two times in a monoclinic cell; the two other polytypes, hanjiangite-1M and hanjiangite-3T, present a single alternation of BL1 and BL2 layers in a monoclinic cell (hanjiangite-1M) and a triple alternation of BL1 and BL2 in a trigonal cell (hanjiangite-3T). The close metrical and compositional relationships of hanjiangite-1M with a pair of other complex layered minerals are discussed.

Key words - hanjiangite, polytypism, layer mineral, main polytypes, surite, niksergievite.

Riassunto - Politipismo della hanjiangite, silicato-carbonato-fluoruro di calcio, alluminio, vanadio e bario. La struttura cristallina della hanjiangite, silicato-carbonato-fluoruro di calcio, alluminio, vanadio e bario viene descritta, mettendo in evidenza il suo carattere politipico. Infatti la hanjiangite è costituita da due distinti strati strutturali ('building layers' BL1 e BL2) che si alternano regolarmente lungo la direzione della normale agli strati. L'analisi delle possibili sequenze mostra che ci sono tre principali politipi: il primo, hanjiangite-2M, corrispondente alla struttura della fase trovata in natura e studiata da Liu et al. (2012), nel quale politipo due strati di ciascun tipo si alternano in una cella monoclina; gli altri due politipi, hanjiangite-1M and hanjiangite-3T, presentano una singola alternanza di BL1 e BL2 in una cella monoclina (hanjiangite-1M) ed una tripla alternanza di BL1 e BL2 in una cella trigonale (hanjiangite-3T). Vengono infine discusse le strette relazioni metriche e composizionali di hanjiangite-1M con due altri complessi minerali a strati.

**Parole chiave -** hanjiangite, politipismo, politipi principali, minerale a strati, surite, niksergievite.

## INTRODUCTION

Hanjiangite has been found as a new mineral in the Shiti barium deposit in the Dabashan region, China, by Liu *et al.* (2012), who presented an accurate study of its chemical, crystallographic and structural properties.



Fig. 1 - Crystal structure of hanjiangite as seen down **a**, **b** horizontal. The calcium trigonal prisms are green; in the octahedral layer the vanadium and aluminium octahedra are lilac and light green, respectively, the silicon tetrahedra are red; small yellow circles represent barium, whereas small blue circles represent fluorine; carbonate groups are represented as blue triangles.

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From the chemical point of view hanjiangite is a silicate-carbonate-fluoride of calcium, aluminium, vanadium and barium, with crystal chemical formula Ba<sub>2</sub>Ca(AlV<sup>3+</sup>)[Si<sub>3</sub>AlO<sub>10</sub>(OH)<sub>2</sub>]F(CO<sub>3</sub>)<sub>2</sub>. It was found as monoclinic crystals with unit cell parameters a = 5.2050 (12), b = 9.033 (2), c = 32.077 (8) Å,  $\beta = 93.49(8)^\circ$ , space group symmetry *C*2.

Its crystal structure may be described as built up by two distinct structural layers (Fig. 1): a TOT layer of pyrophyllite type but containing, beside aluminium, also vanadium in the octahedral sheet, with composition  $[(AIV^{3+})Si_3AIO_{10}(OH)_2]^{-}$ ; and a layer presenting a tessellation of calcium trigonal prisms, connected by corner-sharing carbonate groups, with fluoride anions in the resulting cavities, with composition  $[Ca(CO_3)_2F]^{-}$  (Fig. 2). The two layers are linked together by 10-coordinated barium cations.



Fig. 2 - The structure of the  $[Ca(CO_3)_2F]^-$  layer (central block of the BL1 layer) presenting a tessellation of calcium trigonal prisms (light grey), connected by corner-sharing carbonate groups (black), with fluoride anions in the cavities (light grey), as seen down **a** (**b** horizontal).

In the paper by Liu *et al.* (2012) we read the statement: 'A subset of reflections accounting for nearly half of the total number of reflections was identified that obeyed a single orientation matrix and gave a monoclinic unit cell with a = 5.205, b = 9.033, c = 32.077 Å,  $\beta = 93.49^{\circ}...$ '

This statement suggests that part of the collected reflections did not correspond to the indicated cell. This feature may be related to possible twinning or to the presence of other polytypes in the studied crystal. The last possibility is also suggested by the structural arrangement found by Liu *et al.* (2012), characterized by the presence of two pyrophyllite-like layers and two layers of calcium prisms and carbonate groups in the unit translation along **c**; an aspect that points to possible more simple arrangements.

### CONSTRUCTION OF THE POLYTYPES

To derive the possible polytypes it is now useful to describe the structure of hanjiangite as built up by two structural layers different from those previously introduced to illustrate its crystal chemical features. The new layers, which alternate along the direction normal to the layers, are the following: the first one (BL1 – building layer 1) is built up by a central block with composition Ba2Ca(CO3)2F, with tetrahedral sheets  $[Si_3AlO_{10}(OH)_2]$  on both sides, with the tetrahedral apices oriented outside (Fig. 3a); the second one (BL2) is a dioctahedral pyrophyllite-type layer, characterized by the regular alternation of Al and V octahedra (Fig. 3b); in the Figure a silicate sheet has been added, just to show the kind of connection between successive layers; obviously some oxygen atoms belong to both layers).

The two distinct layers are shown in Fig. 4, as seen in direction normal to them.

In Fig. 4 trigonal symmetries for both layers are indicated. Actually the layer BL1 (Fig. 4b) has layer group symmetry *P*312 (nearly *P-6m2* symmetry; the light grey triangles correspond to the upper base of the trigonal prisms around Ca cation; the white circles correspond to Ba cations, the light green ones correspond to the F anions); also the layer BL2 (Fig. 4a) has layer group symmetry *P*312 (the dark grey octahedra are centered by V, whereas light grey octahedra are centered by Al). The superposition of the layer BL2 with respect to the layer BL1 is illustrated in Fig. 5.

In this Figure (which was built up on the basis of the results obtained by Liu *et al.* (2012) in their structural study)  $\mathbf{a_T}$  and  $\mathbf{b_T}$  indicate the axes of the basal 'hexagonal' cell, common to both layers;  $\mathbf{a_{2M}} \in \mathbf{b_{2M}}$  are the axes of the cell of hanjiangite reported in the study by Liu *et al.* (the meaning of the symbols will be clarified in the following);  $\boldsymbol{\sigma_1}$  indicates the shift (in projection on the basal plane) of the origin of the first layer. As layer BL1 has P312 (nearly *P*-6*m*2) symmetry, the shifts  $\boldsymbol{\sigma_2} \in \boldsymbol{\sigma_3}$  (obtained through rotations by 120°) are geometrically (and therefore also energetically) equivalent.



Fig. 3 - a. Layer BL1 (left); b. Layer BL2 (right).



Fig. 4 - a. Layers BL2 (left), with V octahedra (dark grey) and Fe octahedra (light grey); b. Layers BL1 (right) with Si tetrahedra (dark grey), Ca trigonal prisms (light grey) and carbonate triagles (black). Both BL1 and BL2 are seen in direction normal to the layers.



Fig. 5 - Superposition of layer BL2 with respect to the layer BL1.  $\mathbf{a}_T$  and  $\mathbf{b}_T$  (dark grey vectors) indicate the axes of the basal 'hexagonal' cell, common to both layers;  $\mathbf{a}_{2M} \in \mathbf{b}_{2M}$  (black vectors) are the axes of the cell of hanjiangite reported in the study by Liu et al.;  $\sigma_1$ ,  $\sigma_2$  and  $\sigma_3$  (light grey vectors) indicate the three geometrically equivalent shifts (in projection on the basal plane) of the origin of the second layer with respect to the origin of the first layer



Fig. 6 - Connections of BL1 layers on both sides of BL2 layer, with indication of the axes of the basal hexagonal cell and of the translation vector with component  $t_1$  (light grey) on the basal plane.

As regards the positioning of the layers BL1 on both sides of the dioctahedral layer BL2, the arrangement shown in Fig. 6 is energetically favoured; it corresponds to the arrangement of the tetrahedral sheets on both sides of the dioctahedral layer in pyrophyllite-*1A* and pyrophyllite-*2M1*, the only polytypes of pyrophyllite which have been sofar found in nature or synthesised in the laboratory. An alternative type of connection – not favoured from an energetic point of view – is illustrated in Fig. 7.



Fig. 7 - Energetically unfavoured connection of tetrahedral sheets on both sides of a dioctahedral layer.

On the basis of the arrangement illustrated in Fig. 6, it appears evident that, with a shift vector  $\mathbf{\sigma}_1$ , the whole block of layers 1 and 2 will present a translation vector with component  $\mathbf{t}_1$  on the basal plane, with  $\mathbf{t}_1 = -\mathbf{a}_T/3$ . In general, the translation vectors with components  $\mathbf{t}_1$ ,  $\mathbf{t}_2$ ,  $\mathbf{t}_3$  will correspond to the shift vectors  $\mathbf{\sigma}_1$ ,  $\mathbf{\sigma}_2$  and  $\mathbf{\sigma}_3$ , respectively:

$$\mathbf{t}_1 = -\mathbf{a}_T/3;$$
  $\mathbf{t}_2 = -\mathbf{b}_T/3;$   $\mathbf{t}_3 = \mathbf{a}_T/3 + \mathbf{b}_T/3$ 

Infinite possible polytypes correspond to the infinite possible sequences of the vectors  $\mathbf{t}_1$ ,  $\mathbf{t}_2$  and  $\mathbf{t}_3$ . The most simple polytypes correspond to the sequences  $\mathbf{t}_1$   $\mathbf{t}_1$   $\mathbf{t}_1$  ... (the sequences  $\mathbf{t}_2$   $\mathbf{t}_2$   $\mathbf{t}_2$  ...,  $\mathbf{t}_3$   $\mathbf{t}_3$   $\mathbf{t}_3$  ... have the same structural arrangement of the sequence  $\mathbf{t}_1$   $\mathbf{t}_1$   $\mathbf{t}_1$  ... in different orientation; if they occur in the same crystal, they give rise to twinning);  $\mathbf{t}_1$   $\mathbf{t}_2$   $\mathbf{t}_1$   $\mathbf{t}_2$  ... (obviously sequences of the same type with two different stacking vectors will present the same structural arrangement);  $\mathbf{t}_1$   $\mathbf{t}_2$   $\mathbf{t}_3$  ... ( $\mathbf{t}_1$   $\mathbf{t}_3$   $\mathbf{t}_2$  ... has enantiomorphous arrangement).

The sequence  $\mathbf{t_1} \mathbf{t_2} \mathbf{t_1} \mathbf{t_2} \dots$  is realized in the structure of hanjiangite studied by Liu *et al.* (2012); the space group is *C*2. In Fig. 8 the stacking sequence  $\mathbf{t_1} \mathbf{t_2}$  is shown; the Figure indicates that the vector  $\mathbf{c_{2M}}$  has horizontal component  $-\mathbf{a}_{T}/3 - \mathbf{b}_{T}/3$  (module 1.735 Å), with a vertical component corresponding to the sum of the widths of two layers of type 1 and two layers of type 2, calculated as 32.02 Å. Therefore c = 32.067Å,  $\beta = 93.10^{\circ}$ , in good agreement with the values observed by Liu *et al.* (2012); only the twofold axes of the layer BL1 are symmetry elements of the whole structure, which has space group *C*2, with a cell in which layers of types BL1 and BL2 alternate for two times; therefore the phase may be correctly indicated as hanjiangite-2*M*.

The sequence  $\mathbf{t_1} \mathbf{t_1} \mathbf{t_1}$ ... gives rise to a structure with a single alternation of the layers BL1 and BL2 within the repeat period; therefore it may be correctly defined as hanjiangite -1*M*. In fact it is monoclinic and – due to the iso-orientation of the subsequent stackings – both the twofold axes of the layers BL1 and BL2 are symmetry elements of the whole structure, which has space group C2. Fig. 8 presents the orientation of the cell of hanjiangite-2*M* (black coloured vectors) and that of the cell of hanjiangite-1*M* (light grey coloured vectors).



Fig. 8 - Cell orientation of the polytypes 1M and 2M of hanjiangite.

The basis vectors of polytype *1M* may be obtained from those of polytype *2M*:

$$a_{1M} = a_{2M}/2 + b_{2M}/2$$
  

$$b_{1M} = -3a_{2M}/2 - b_{2M}/2$$
  

$$c_{1M} = c_{2M}/2 - b_{2M}/6$$

On the basis of the values of the parameters of polytype 2*M*, those of polytype 1*M* are:

$$a_{1\mathrm{M}} = 5.205, b_{1\mathrm{M}} = 9.033, c_{1\mathrm{M}} = 16.10$$
 Å,  $\beta = 96.19^{\circ}$ 

It is also possible to obtain the atom coordinates in polytype *1M* from those of polytype *2M*:

$$x_{1M} = x_{2M}/2 + 3y_{2M}/2 + z_{2M}/2$$
  

$$y_{1M} = -x_{2M}/2 + y_{2M}/2 + z_{2M}/6$$
  

$$z_{1M} = 2z_{2M}$$

The indicated transformations are applied to all the atoms of polytype 2M with coordinate z between 0 e 0.25, after changing their coordinates y by -0.0627, so as to bring the atom Ca in 0.0, 0.0, 0.0. The coordinates of atoms in hanjiangite-1M are given in Table 1 and the structure is represented in Fig. 9.

Table 1. Atomic coordinates of polytype hanjiangite-1M.

Atom	$x_{1M}$	$y_{1M}$	$z_{1M}$
Ca	0.0	0.0	0.0
C2	0.0327	-0.3331	0.0988
Ba2	0.5551	-0.1662	0.1691
F	0.5	-0.1789	0.0
V1	0.5	-0.0023	0.5
Al	0.5	-0.3348	0.5
O7	0.5913	-0.1683	0.4350
O8	0.1344	0.0201	0.433
O9	0.6419	0.1486	0.4316
O13	-0.1740	-0.4047	0.0984
O14	0.0384	-0.1939	0.1018
O15	0.2431	-0.4157	0.0924
Si3	0.0924	0.0081	0.3282
Si4	0.6008	0.1633	0.3298
O10	0.3540	0.0587	0.2882
O11	0.8538	0.1106	0.2872
O12	0.5245	0.3335	0.2982

The sequence  $\mathbf{t}_1 \mathbf{t}_2 \mathbf{t}_3 \dots$  gives rise to a structure which repeats after three pairs of alternating layers BL1 and BL2. It therefore may be correctly defined as hanjiangite-*3T*, because it presents trigonal symmetry, due to the presence of a  $3_1$  axis. Only the twofold axes of the layer BL1 are symmetry elements of the whole structure, which has space group  $P3_112$ .

The basis vectors of the polytype 3T may be obtained from those of the polytype 2M:

$$\begin{aligned} a_{\rm T} &= a_{\rm 2M}/2 + b_{\rm 2M}/2 \\ b_{\rm T} &= a_{\rm 2M}/2 - b_{\rm 2M}/2 \\ c_{\rm T} &= 3c_{\rm 2M}/2 + a_{\rm 2M}/2 \end{aligned}$$

On the basis of the values of the parameters of polytype 2M, those of polytype 3T are:

$$a_{\rm T} = b_{\rm T} = 5.205, c_{\rm T} = 48.03$$
 Å.



Fig. 9 - Crystal structure of polytype hanjiangite-1M, as seen down **a**, **c** vertical. The various polyhedra and atoms are represented with the same colours as in Fig. 1.

To obtain the atomic coordinates for polytype 3T, we have to proceed as here indicated.

a) The coordinates of the polytype 2M (after the indicated shift of all the *y* coordinates by -0.0627) are transformed according to the relationships between the cell vectors of the two polytypes, namely according to the equations:

$$x_{\rm T} = x_{\rm 2M} + y_{\rm 2M} - z_{\rm 2M}/3$$
  

$$y_{\rm T} = x_{\rm 2M} - y_{\rm 2M} - z_{\rm 2M}/3$$
  

$$z_{\rm T} = 2z_{\rm 2M}/3$$

b) Afterwards, the origin is displaced by  $2t_1/3 + t_2/3$ , corresponding to  $-2a_T/9 - b_T/9$ ; namely the coordinates  $x_T e y_T$  of all the atoms are increased by 0.2222 and 0.1111, respectively, just to account for the position of the  $3_1$  axis, which is located at centre of the small triangle formed by the three stacking vectors  $t_1$ ,  $t_2$ ,  $t_3$  (Fig. 8).

The coordinates of atoms in hanjiangite-3T are given in Table 2.

As already said, infinite distinct polytypes (as well as disordered sequences of the vectors  $\mathbf{t}_1$ ,  $\mathbf{t}_2$ ,  $\mathbf{t}_3$ ) are possible. In all the polytypic families a small group of 'main' polytypes exist, which are called 'simple', 'standard', 'regular', corresponding to those which are defined as MDO (maximum degree of order) polytypes in OD theory. These are those polytypes in which not only pairs of adjacent layers, but also triples, quadruples,...*n*-tuples of layers are geometrically equivalent.

Table 2. Atomic coordinates of polytype hanjiangite-3T

Atom	x <sub>3T</sub>	y <sub>3T</sub>	z <sub>3T</sub>
Са	0.2222	0.1111	0.0
C2	0.5550	0.7773	0.0329
Ba2	0.8823	0.4431	0.0564
F	0.8645	0.4688	0.0
V1	0.5316	0.1157	0.1662
Al	0.8798	0.7802	0.1666
O7	0.8367	0.4476	0.1450
O8	0.1921	0.0708	0.1443
O9	0.5716	-0.1861	0.1439
O13	0.4201	0.9204	0.0329
O14	0.4205	0.4988	0.0339
O15	0.8501	0.9424	0.0309
Si3	0.1971	0.0950	0.1094
Si4	0.5497	-0.2156	0.1099
O10	0.4215	-0.0062	0.0961
O11	0.8696	-0.1101	0.0957
O12	0.3138	-0.5559	0.0994

We have just constructed and described those polytypes and the corresponding schemes are illustrated in Fig. 10. They are characterized by the following sequences of stacking vectors: a) sequences of only one type of stacking vectors; b) sequences of alternating vectors of only two type  $(t_1 t_2..., t_1 t_3..., t_2 t_3...)$ ; ordered sequences of the three stacking vectors  $(t_1 t_2 t_3...; or the enatiomorphous one t_3 t_2 t_1...)$ .



Fig. 10 - Scheme of the stacking sequences in the three polytypes *1M*, *2M*, *3T* of hanjiangite.

#### Possibly related compounds

The polytypic character of hanjiangite indicates that a re-examination of the material from the Shiti barium deposit studied by Liu *et al.* (2012) should be appropriate. Several crystals should be studied to look for the possible presence of other polytypes, beside the 2*M* one, and also for possible twinning.

Moreover we observe very close relationships between the crystallographic data of surite (Hayase *et al.*, 1978), which presents a unit cell with a = 5.22, b = 8.97, c =16.3 Å,  $\beta = 96.3^{\circ}$  and those reported for the polytype *1M* of hanjiangite. The similarity is strengthened by the close crystal chemical relationships, here reported:

hanjiangite  $Ba_2$  Ca (AlV<sup>3+</sup>) [Si\_3AlO\_{10}(OH)\_2] (CO\_3)\_2 F surite Pb<sub>1.8</sub> (Ca, Na) (Al, Fe<sup>3+</sup>, Mg) [Si\_3AlO\_{10}(OH)\_2] (CO\_3)\_2 (H\_2O)

Surite was found as a new mineral in lead-zinc-copper deposit of the Cruz del Sur mine, in Argentina, by Hayase *et al.* (1978), who proposed a structural model built up by 'a lead carbonate layer intercalated with the repetitive 2:1 silicate layers' and indicated  $P2_1$  as possible space group. Surite was subsequently studied by Uehara *et al.* (1997) who assumed a pseudo-orthorhombic cell with a = 5.219, b = 8.968, c = 16.19 Å,  $\beta$ = 90.13° and proposed – on the basis of one dimensional Fourier syntheses – a model of the mineral as 'a 2:1 dioctahedral smectite interlayered with basic lead calcium carbonate'. The two models differ in the positioning of the various components of the intermediate lead-calcium-carbonate layer.

Notwithstanding the close relationships between the cell parameters derived for hanjiangite-1M and those determined by Hayase *et al.* (1978) for surite, and the very similar chemical composition of the two phases, marked differences have been observed between the X-ray powder patterns experimentally determined by Hayase *et al.* (1978) and Uehara *et al.* (1997) and the powder pattern calculated on the basis of the atomic parameters reported in Table 1 for hanjiangite-1M.

I think that new attempts should be made to look for a specimen of surite which may be amenable to a single crystal investigation, through X-ray diffraction with synchrotron radiation or electron diffraction with ADT (Automated Diffraction Tomography) technique, with the aim to reliably define its crystal structure and its possible relationships with that of hanjiangite-1*M*.

Finally, I add here that there is another compound

which could be structurally related to the *1M* polytype of hanjiangite, the mineral niksergievite (Saburov *et al.,* 2005), with chemical composition given by the authors as

$$(Ba_{1,33}Ca_{0,67}Al) Al_2 [Si_3AlO_{10}(OH)_2] [(CO_3) (OH)_4 nH_2O]$$

and crystal data:

$$a = 5.176$$
,  $b = 8.989$ ,  $c = 16.166$  Å,  $\beta = 96.44^{\circ}$ ,

with space group C2/c, C2 or Cm.

This compound too deserves a careful re-examination.

#### ACKNOWLEDGEMENTS

I am grateful to Cristian Biagioni for helpful discussions and assistance in the preparation of the text.

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(ms. pres. il 10 ottobre 2014, ult. bozze il 20 dicembre 2014)