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Revision 2

Vaterite – interpretation in terms of OD theory and its next of kin

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ABSTRACT

The polytypic structures of vaterite, $CaCO_3$, described in recent literature, have been reinterpreted in terms of the OD (order-disorder theory) which allows us to explain and systematize all the observed and predicted polytypes of the mineral in a unified fashion. In terms of this theory, the structure consists of OD layers which comprise a layer of calcium coordination polyhedra and the attached halves of the standing CO_3 groups. The two-sided layer group of symmetry of the OD layer is $c2/m$ whereas the interlayer symmetry operations are three two-fold rotation axes at 120° to one another, as well as a mirror plane in the common layer boundaries and partial c glide planes perpendicular to the boundary. Depending on the orientation of the active two-fold rotation axis with respect to the above-defined layer mesh, performed independently in each stacking step, maximally ordered simple stacking sequences $P6_122$, $P6_522$, $C2/c$, $C2/c2/m2_1/m$ and a more complicated sequence $P3_12$ or $P3_22$, as well as a number of complicated or disordered sequences is obtained (before eventual relaxation to a subgroup of a particular space group). A perfect copy of the vaterite OD layer occurs in the structures of the bastnäsite - synchysite polysomatic series of fluorocarbonates. In these structures, the *REE* layers, configurationally analogous to the Ca-based OD layer, have layer symmetry $p32$ and their stacking does not lead to polytypism and OD phenomena; these are generated on the Ca-based OD layers.

Keywords: vaterite, calcium carbonate, polytypes, OD theory

INTRODUCTION

The highly disordered crystal structure of the third polymorph of $CaCO_3$, *vaterite,* has been object of several interpretations, in widely different space groups [e.g., Meyer (1969), the substructure by Kamhi (1963), Medeiros et al. (2007) and Le Bail et al. (2011)]; the bulk of recent information was summarized by Demichelis et al. (2012, 2013). These authors and Mugnaioli et al. (2012) investigated vaterite respectively by *ab initio* calculations and by automated electron diffraction experiments, proposing again different crystal structures. Another group which published the results of *ab initio* calculations is Wang and Becker (2009), with a structure proposal closest to that of Demichelis et al. and a good summary of previous investigations.

All three groups of authors, however, describe the same type of calcium layers and the same type of the loosely configured interspersed CO_3 layers in their proposed structures. Only one type of each layer is present if we disregard small distortions in individual structures, produced by structure relaxation in a particular space group. Mugnaioli et al. (2012) undertook a 'normal-course' crystal structure determination whereas Wang and Becker (2009) and Demichelis et al. (2012, 2013) do not report a potential source of their configurations, concentrating in detail on the structure descriptions by means of layer shifts and changing orientation. These, in principle identical, and very plausible results, and the hitherto generally unacknowledged presence of such layers in the fluorocarbonates of the batnäsite-synchisite polysomatic series are the rationale behind this contribution.

Perusal of these results led the present author to the application of the OD (order-disorder) theory initiated by Dornberger (1956,1966) and further advanced by, e.g., Ďurovič (1997) and Merlino (1997). A short review of fundamental notions of the OD theory is given in the appendix; we shall not repeat them here, and it is recommended to start reading the appendix before the paper itself. The crystal structure of vaterite lends itself both to one-layer and two-layer OD description. The 3D results of the description in terms of one OD layer type are easier to comprehend and it is the approach adopted here.

THE OD LAYERS AND THEIR STACKING SEQUENCES

The crystal structure of vaterite consists of alternating layers of Ca polyhedra (CN = 6 – 8) and 'standing' CO_3 groups, the latter with one edge of every coordination triangle parallel to the layer stacking direction (Fig. 1). Calcium cations form a fairly regular hexagonal net, and on both sides of it every second triangle of the Ca net is accompanied by a CO_3 group. In their own 'carbonate' layer, these groups are disposed along three sides of a hexagonal prism with a height equal to the O – O edge of the CO_3 triangle and with alternating sides of the prism unoccupied, with overall point group symmetry -6 (Fig. 2). The hexagons form an openwork layer by sharing their sides but six of them always surround and enclose a smaller ditrigon, which has three CO_3 triangles pointing toward its center, and three alternate triangles pointing outward, positioned in its vertices (Fig. 2). The cation sheet alone approximates closely the two-sided *p*6/*mmm* layer group of symmetry; the CO_3 layer alone approximates symmetry *p*-6*2m* (with 2_1 axes and *g* planes situated between, and parallel to, the twofold rotation axes of the two-sided layer group of symmetry).

The periodicities of the idealized carbonate layer, and of the carbonate – Ca pair of layers, form a supercell of the idealized periodicity of the Ca net itself; the former are related to the latter by the matrix

$$\begin{pmatrix} 1 & -1 \\ 2 & 1 \end{pmatrix}$$

and the orientation of the respective mesh differs by 30°. This is the two-dimensional cell used in the subsequent text.

The *OD layer* will be modeled as the central plane of Ca ions, with the 'inner' halves of the standing CO_3 groups on both sides added (Fig. 3). The 'outer' or peripheral halves of CO_3 belong to the adjacent OD layers; the C atoms, and the oxygen atoms at the same height levels, are shared by two adjacent OD layers, i.e., they represent a layer boundary. The CO_3 configurations across the Ca plane are not mirror-related; they are related by 'horizontal' two-fold axes in the Ca plane, and preserve one of the vertical mirror planes of the Ca plane, which becomes common to all three just mentioned subunits of the OD layer (i.e., to the Ca net and two halves of adjacent carbonate layers) (Fig. 3). The resulting layer symmetry group of the OD layer is *c*2/*m*; the centration results from application of a rectangular cell to a hexagonal motif of the Ca layer. If we select *m* as (10.0) of the hexagonal net of the carbonate – Ca pair, defined in the previous paragraph, then the *a* parameter of the *centred* rectangular OD layer cell will be the next longer Ca-Ca distance (a_2 of the carbonate hexagonal motif), and the *b* parameter will ideally be equal to $2a\cos 30^\circ$, i.e., the vector $2\mathbf{a_1}+\mathbf{a_2}$ of the 2D hexagonal cell. Layer group symmetry 2/*m* of *lambda* (i.e., intralayer; see the appendix) operations is significantly reduced in comparison to the symmetries of the three individual parts which together constitute the OD layer.

The interlayer *sigma* operations, which transform the *n*th OD layer into (*n*+1)st OD layer, are determined by the configurations of the CO_3 layer straddling the boundary of two OD layers. In the ideal model, without relaxation pertinent to a particular polytype, its vertical mirror planes are (10.0), (01.0) and (1-1.0) of the carbonate net, and two-fold axes are in the direction of its crystallographic a_1, a_2 and a_3 axes (Fig. 4). These axes are polar, the $+a_i$ ad the $-a_i$ direction is always different. The *p*-6 2 *m* symmetry includes three-fold axes, and a 'horizontal' reflection plane. In terms of the layer-reversing *rho* operations, it is the actions of the latter reflection plane, and of the twofold axes, which propagate the *n*th layer into the (*n*+1)st layer.

With respect to the *lambda* mirror plane in the OD layer (symmetry 2/*m*), there are two possible orientations of the *sigma* two-fold axes (and associated vertical mirror planes) situated in the layer boundary. When the two-fold axis follows one of the diagonals of the centered cell of the OD layer, which in the above defined orientation of the OD layer, $m \parallel (10.0)$, can be a hexagonal a_1 or a_3 axis, a combination of the 2-fold rotation with the internal symmetry of the OD layer results in the (n+1)st layer being rotated by 60° against the nth one (Fig. 4). An additional, *tau-sigma* operation results from these operations; it is a partial glide plane c_2 *(this symbol indicates a full translation period from a layer to a layer as a translation component)* which is perpendicular to the two-fold axis performing the transformation.

Application of the same orientation of the acting (*sigma*) two-fold rotation axis *to each consecutive OD layer* results in the generalization of the partial 6_1 or 6_5 operation (one 60° turn) into a general one, producing a *six-layer polytype* $P6_{1\ (or\ 5)}22$, one of the vaterite polytypes *with a maximum degree of order* (MDO polytype). The MDO polytype is defined as a polytype in which the same *sigma* operation is applied at each derivation step. The $P6_522$ structure is the polytype derived by Wang and Becker (2009) and Demichaelis et al. (2012, 2013).

Application of the two-fold axis which has the a_1 orientation on the nth level, followed by the axis in the a_3 orientation in the (n+1)st level, then a_1 again, etc., always defined for the new orientation of the layer mesh, results in a *two-layer* $C2/c$ structure, this being another MDO polytype. Mugnaioli et al. (2012) determined the $C2/c$ structure from electron diffraction data. They chose a monoclinic two-layer unit cell in which each OD layer has the *m* direction as a cell diagonal, with the resulting cell dimensions equal to *a* 12.17 Å, *b* 7.12 Å, *c* 9.47 Å, β 118.94°, d_{001} 8.29 Å. Because of the pseudohexagonality of the individual components of the OD layer, the dimensions of their centered *a* x *b* cell are actually equal to those of the here described OD layer cell.Thus far, it is the only successful structure determination on vaterite, even if the R_1 factor for the electron diffraction data was as high as 37.6 %. This $C2/c$ sequence can be complicated by stacking errors when, in some instances, a 'wrong' orientation of the two-fold axis (twice the a_i orientation with the same i) is active on a certain level, turning a consecutive part of the layer stack by 60° off the periodic sequence and eventually resulting in a quasi-random sequence of small $C2/c$ blocks.

For the OD layer with the *c*2/*m* layer mesh oriented with the short $a_{OD\ layer}$ parameter parallel to the a_2 axis of the hexagonal mesh of the carbonate interlayer (Fig.4), and the interlayer two-fold rotation axis also parallel to a_2, the action of the latter axis, combined with the symmetry of the OD layer, results in the same effect as the action of the 'horizontal' reflection plane. With the same naming of axes, a *two-layer* orthorhombic structure results, $C2/c2/m2_1/m$ for an unrelaxed MDO structure. It should be noted that in this case, relation between two adjacent 'OD layers' differs from the previous case.

A one-layer polytype with a simple translational stacking of OD layers does not exist because the ditrigonal configurations of the carbonate half-layer on the bottom face of the OD layer are inverted against those on the top face by the action of the 2/*m* symmetry of the OD layer. A threefold twinning *inside an individual OD sheet* is hindered by steric problems. When, in a given orientation, a set of triangular CO_3 groups is aligned coincident with the mirror plane of the c2/*m* group, the corresponding sets at ± 120° to the former one decompose into two parallel, fairly distant subsets, those from the top and from the bottom of the OD layer, respectively. It means that three orientations of the OD layer at 120° to one another will have incompatible contacts.

The $P3_12$ structure is not an MDO polytype because it is generated by two above outlined categories of operations in alternation, but it is a highly ordered structure: the *nth* layer in the above defined starting orientation is propagated by the $2//a_{OD\ layer}$ operation into (*n*+1)st layer, followed by the propagation of the (*n*+1)st layer into (*n*+2)nd layer by the $2//(110)_{OD\ layer}$ (or $2//(1\text{-}10)_{OD\ layer}$ for the enantiomorph) operation, *defined for the new orientation of the layer mesh.* Then the (*n*+2)nd layer is oriented towards the *n*th one by 120°. Continuing this two-term sequence of symmetry operations, we obtain a $P3_12$ or $P3_22$ structure with a *six layer period*.

To summarize the preceding derivations, the crystal structure of vaterite is an OD (order-disorder) structure composed of Ca-based OD layers with the symmetry *c*2/*m.* These OD layers comprise the coordination polyhedra of calcium plus 1/2 of the height of the 'standing' CO_3 groups which interconnect two adjacent Ca-based layers, both from the 'top' and from the 'bottom'. Based on the configurations in the carbonate layers (*p*-62*m*), the interlayer set of *sigma rho* operations relating the two OD layers are three two-fold axes and the horizontal mirror of this layer group. *Sigma tau* operations of the OD groupoid are *c* glide planes perpendicular to the particular

two-fold rotation axis. The resulting layer stackings with maximum degree of order are $C2/c$, $P6_122$ and $P6_522$, $C2/c2/m2_1/m$ and a more complex variant, $P3_12$ ($P3_22$). These maximally or highly ordered polytypes can be accompanied by more complicated layer sequences and disordered variants which result from actions of interlayer *sigma* symmetry operations with non-uniform or random orientations in the layer stacking process.

Demichelis et al. (2013, Fig. 3) demonstrate that the ideal structures with the $C2/c$ and $P6_122$ symmetry have slightly higher internal free energy than $P3_121$, and they undergo room-temperature distortions by means of minor rotation of carbonate groups, to Cc, $C2$, $P6_1$ and $P2_1$, connected with a drop in internal free energy. The energy differences they calculated, however, are small and they can be further modified by presence of stacking faults so that they believe that natural vaterite is a mixture of structures with different symmetries – which is a perfect expression of an OD structure composed of layers.

As mentioned in the introduction, an alternative OD description of vaterite is possible, as a structure composed of two kinds of OD layers, the Ca net alone as one OD layer and the rest of the structure as another OD layer. The description as an OD structure composed of two types of OD layers might be more universal but such a description of vaterite is much more complicated and *less transparent* for a non-specialist.

Some data quoted in the compilation of literature sources in Table 1 of Demichelis (2013), none of which is concerned with their own work, are contradictory. The *Pbnm* structure (Meyer 1969) has c = 8.5 Å, but all cases with 6_3 screw axes (e.g., Meyer 1969) should have two-layer stacking periods. However, these cases cannot exist with the here described OD layer. The *Pbnm* proposal obtained through *ab initio* calculations by Medeiros et al. (2007) differs in many substantial features from the results of Wang and Becker (2009), Demichelis et al. (2012, 2013) and Mugnaioli et al. (2012), and will not be treated here. The same is true for a different configuration proposed by Le Bail et al. (2011) from powder diffraction data. The 4.1 Å a (i.e., one-layer) parameter of this $Ama2$ structure is strange.

During the time this paper was in preparation and review, several papers appeared which appear to confirm our derivations. Kabalah-Amitai et al. (2013) found that

vaterite forming the spicules of the *Herdmania momus* ascidians predominantly represents a hexagonal matrix with intervals of highly disordered layered structure containing a component with unknown symmetry. This is a model in full agreement with our derivations and with the suggestions by Demichelis et al. (2013). Wang et al. (2014) performed molecular dynamics simulations which show that the $P6_522$ structure of Wang and Becker (2009) with ordered carbonate ions has internal energy lower than the disordered structure. Their X-ray powder diffraction data fitted best with this structure, although the reliability indices for the $C2/c$ and $P3_121$ were within the acceptable range as well. Consistency with the $P6_522$ structure was also found for the HRTEM observations. Burgess and Bryce (2015) used a combined ^{43}Ca solid-state nuclear magnetic resonance spectroscopic and computational approach on synthetic, ^{43}Ca – enriched vaterite samples, in combination with X-ray powder diffraction. They suggest that their NMR and diffraction data favor the $P3_221$ structure and/or the monoclinic $C2$ structure whereas the $C2/c$ model yields an excessively complicated powder pattern in comparison with the observed one. De La Pierre et al. (2014) studied Raman spectra of vaterite, comparing the calculated and experimental ones from a variety of materials. They found excellent agreement of these spectra for the $P3_221$ structure and/or the monoclinic C2(?) structure (these two choices were practically indistinguishable) whereas the other symmetries yielded additional minor Raman peaks not observed in the experimental material. If we accept the $C2$ structure as a distorted derivative of the $C2/c$ model, the agreement of all these observations with the OD derivations is very satisfactory.

The crystal structure of $YbBO_3$ (Bradley et al. 1966) is a distant homeotype of vaterite. Yb cations form a hexagonal net, surrounded by the trigonal openwork of BO_3 groups. The latter form hexagonal prisms which have 3 sides occupied by triangles in a 'rotation' configuration, symmetry $3/m$, in combination with ditrigons which house in- and out-pointing BO_3 triangles. Thus, $YbBO_3$ displays the same basic scheme as vaterite. Cation coordination is different, however, pulling the centers of ditrigons on one side of OD layer over the same type of centers on the opposite side of the layer; they are related by inversion. This structure is an introduction to the next group, from which it differs in important details.

NEXT OF KIN: THE BATNÄSITE-SYNCHYSITE POLYSOMATIC SERIES

The protracted efforts to solve the crystal structure of vaterite could have been shortened by a close look at the known structures of the members of the bastnäsite - synchysite polysomatic series of flourocarbonates. This series, $Ca_m(REE)_n(CO_3)_{n+m}(F,OH)_n$ (Ferraris et al. 2008), with four well defined members (bastnäsite, m = 0, n = 1; synchysite, m = 1, n = 1; parisite, m = 1, n = 2; röntgenite, m = 2, n = 3), has been defined structurally by Donnay and Donnay (1953) and subsequently refined by a number of researchers (Van Landuyt and Amelinckx 1975, Yang et al. 1994, 1998, Ni et al. 2000). It became popular recently, in connection with the world-wide exploration for *REE*. In these structures, all of which contain the 'standing' CO_3 groups, a calcium-based layer alternates with a packet of one or several *REE*-based layers. Yang et al. (1994, 1998) already noticed a relationship between the Ca layers from the fluorocarbonates and vaterite, but as it was long before the refinements by Demichelis et al. (2012, 2013) and Mugnaioli et al. (2012), this observation did not receive due attention. We shall use the structure refinement for *parisite* (Ni et al. 2000) to illustrate the relationship to the vaterite structure in detail, in terms of layers configurationally close to those in vaterite.

In parisite (Fig. 5), a calcium-based layer alternates with a pack of two *REE*-based layers. The Ca layer is identical with that described above as the vaterite OD layer. At $z = 0$, the mirror plane of this *c*2/*m* layer is parallel to (110) of the parisite cell. Unlike the Ca layer, the *REE* layer also contains F atoms situated approximately (i.e., slightly above or below) in every triangle of the hexagonal *REE* net of cations. The carbonate configurations surrounding the *REE* (i.e., cerium) layer are the same as those surrounding the Ca layer but their mutual displacement across the hexagonal *REE* net differs (Fig.6). The hexagons and ditrigons of the carbonate openwork on the two sides of the *REE* layer are situated above one another in two settings: in two thirds of cases, the 3/*m* 2 *m* ditrigons with in- and outwards orientation of CO_3 groups lie above or below the distorted 3/*m* hexagons with a 'rotational' arrangement of CO_3 groups, and in one third of cases, two oppositely pointing 'rotational' arrangements share the same *x*,*y* coordinates, in a -3 arrangement (Fig. 6). The resulting layer symmetry of the *REE layer* (configurationally analogous to the Ca-based OD layer) is *p32* whereas the general scheme according to which the different types of hexagons/ditrigons are disposed is *p* -3 2/m 1 when we ignore the orientation of triangular CO_3 groups.

The action of the potential OD *sigma rho* operations in the median plane of each carbonate layer (the same as in vaterite), from which we can mention the three

twofold rotation axes at 120° to one another, does not lead to a polytypism in a Ca-free sequence, as already stressed by Ni et al. (2000). For an *REE layer pair*, the openwork hexagons of the (*n*+1)st layer lie above those of the *n*th layer. The hexagon sequences with counter-rotation of three CO_3 groups in the walls lie above one another and the sequences of alternatively centripetal and rotational CO_3 arrangement in the walls again follow one another along the stacking direction. For the Ca-free bastnäsite, this layer stacking symmetry results in the *P*-32*c* space group. As already suggested by Ni et al. (2000), a linkage of two *REE* layers by a Ca layer generates an offset between slabs; this offset is the origin of the observed polytypism in the Ca-*REE* fluorocarbonates (Ferraris et al. 2008). Detailed treatment of the polytypism of this series lies outside the scope of this paper. We should mention that the stacking of different ditrigonal elements of the carbonate openwork in the fluorocarbonate series and of the borate openwork in $YbBO_3$ (Bradley et al. 1966) is completely different.

IMPLICATIONS

The derivations presented here demonstrate that polytypism and occurrence of random stacking is an inherent property of vaterite.

Different polytypes will have very similar free energies, further reduced by relaxation by slight distortions allowed by a particular space group or its subgroup. Stacking faults produced in the OD process do not substantially alter the energy situation either. Thus, the kinetics of random nucleation will have profound influence on the resulting layer stacking, especially because vaterite is a result of (relatively) low-temperature processes at (often) high reaction rates. The resulting crystals will have high configurational entropy.

Although resulting in the same set of derived or potential vaterite polytype structures as the study of Demichelis et al. (2012, 2013), the one-layer OD approach gives a simpler and more transparent picture of vaterite polytypism than the scheme of carbonate layer shifts and rotations used in the previous studies.

A fully developed vaterite-like 'OD' layer of the type defined and used in this study, different from the rest of the structure, is present in the Ca-*REE* fluorocarbonates of the bastnäsite - synchysite polysomatic series. On the one hand, it is *a cause of polytypism* in this series and on the other hand it shows that *vaterite is, in all respects, the extreme end-member of this series*, with the number of *REE* layers reduced to nil,

as already suggested by Yang et al. (1998). At present, no fluorocarbonates with multiple vaterite-like layers, or vaterite with intercalated *REE* layers, are known but their existence and character, especially as synthetic products, is predictable from the current model.

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APPENDIX: BASIC NOTIONS OF THE THEORY OF OD PHENOMENA

All crystal structures can be sectioned into equivalent slabs. For the majority of structures, the orientation and position of the (n+1)st slab after the nth slab is unambiguously determined. The less frequent cases when these rules are relaxed but still deterministic, are dealt with by the OD (order-disorder) theory. In the sense used in this contribution, OD (order-disorder) phenomena describe ambiguity in the position (and orientation) of the (n+1)st slab of the structure after every nth slab. In the OD structures, the two (or more) positional/orientational choices give rise to two or several *geometrically (and thus also crystal-chemically) equivalent pairs of slabs*, which differ from one another only by their orientation. These slabs are purely geometrical and not always identical with crystal chemically defined layers. They are called *OD layers*, with their own crystallographic (pseudo)symmetry, described by one of the eighty layer groups [consisting of the so-called *intralayer* (or λ-) *partial operations* (POs); the partial character of the operations means that they are not necessarily valid for the whole structure; they may be valid only for the OD layer]. Another set of operations (the so-called *interlayer partial operations* or σ-POs) transforms an OD layer into the adjacent one. Together these two kinds of operations

do not form a symmetry group but a weaker combination of symmetry operations, a *groupoid* (Dornberger-Schiff, 1964). The above-mentioned positional ambiguity means that – although all layer pairs are equivalent - layer triples, quadruples, etc., are not automatically identical even in one and the same structure or in various crystals of the same substance. All OD-structures with the same set of λ-POs and σ-POs to the exclusion of translations belong to one *OD-groupoid family*. Our case, vaterite, is described as one of the families of OD structures composed of *one kind of OD layers* but ample examples of OD structures composed of two (or more) kinds of OD layers in regular alternation exist as well (e.g., Ferraris et al. 2008).

The partial character of interlayer operations (glide-reflection planes and screw axes) in the OD structures involves unusual translation components with special notation rules. In all cases the translation component is referred to the basis vectors of the OD layer. Generalized notation rules for partial symmetry operations which interconnect an *n*th layer with the (*n*+1)st layer (σ-POs**)** are as follows: for a glide plane, *the translation component* is the value of the subscript attached to the symbol divided by two: n ($\equiv n_1$) has translation equal to ½ of the full translation vector, $n_{½}$ has translation component equal to ¼ of the translation vector, n_2 has a translation component equal to a full translation period (from one OD layer to the next one), etc. In a similar way, 2_1 has the translation component equal to ½ of the full translation period parallel to the axis, 2_2 is a partial operation with the translation equal to a full translation period of the lattice along the given axis, etc.

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FIGURE CAPTIONS

FIGURE 1. The *C*2/*c* structure of vaterite according to Mugnaioli et al. (2012). Large spheres: Ca, triangles: CO_3 groups. (001) plane is horizontal, *c* axis subvertical.

FIGURE 2. Configuration of the carbonate layer on one side of the calcium net of vaterite (from the $P6_522$ structure defined by Demichelis *et al.* (2012)). Grey spheres: Ca, triangles: CO_3 groups. Oblique view was selected in order to make the 'standing' CO_3 groups visible. The carbonate layer consists of a trigonal openwork of

419 CO_3 groups with distorted hexagons decorated by three triangles in a rotating
420 arrangement and of ditrigons with three inward and three outward oriented CO_3
421 triangles. The latter surround on three sides the configuration in which the axial cross
422 has been placed.

423 **FIGURE 3.** The OD layer derived from the $P6_522$ crystal structure variant of vaterite
424 (Demichelis et al. 2012), valid for all polytypes treated in this paper. It consists from
425 the central net of Ca atoms and the adjacent halves of standing triangular CO_3 groups.
426 However, for the sake of legibility, entire CO_3 groups are shown. In the present
427 orientation, the mirror plane of the *c*2/*m* layer group of the OD layer is parallel to (1-
428 100) of the hexagonal cell. Oblique view was selected in order to make the 'standing'
429 CO_3 groups visible.

430 **FIGURE 4A,B.** Different orientations of the interlayer symmetry operations (*sigma*
431 operations; here the horizontal polar two-fold rotation axes indicated by short arrows)
432 in relation to the centered unit mesh and the symmetry elements of the adjacent OD
433 layer. (a) Action of a *sigma* operation (a two-fold rotation axis indicated by an arrow)
434 generating the 6_5 and *C*2/*c polytypes,* and (b) action of the *sigma* operation (right-left
435 oriented two-fold axis) generating the orthorhombic 2-layer polytype. Compare with
436 description in the text.

437 **FIGURE 5.** The crystal structure of parisite (Ni et al. 2000). Grey spheres: Ca, black
438 spheres: *REE*, white large spheres: F, and triangles: 'standing' CO_3 groups with
439 oxygen as small spheres in the corners. (001) planes are viewed edge-on, the *a* axis
440 points approximately to the left, *c* axis is subvertical

441 **FIGURE 6.** The *REE*-based layer from the crystal structure of parisite: the cation net
442 with halves of attached carbonate groups. For clarity of design, however, entire CO_3
443 groups are shown. For conventions see Fig. 5.

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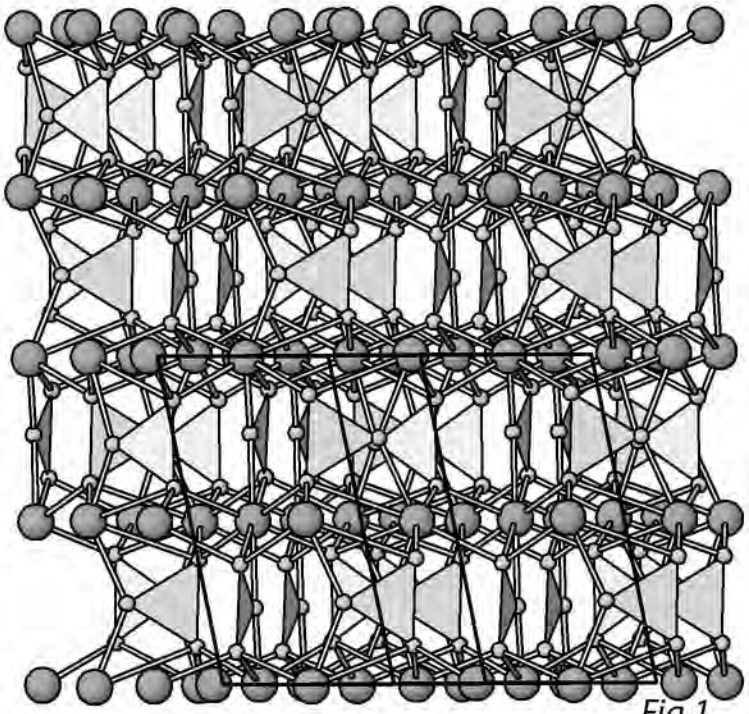
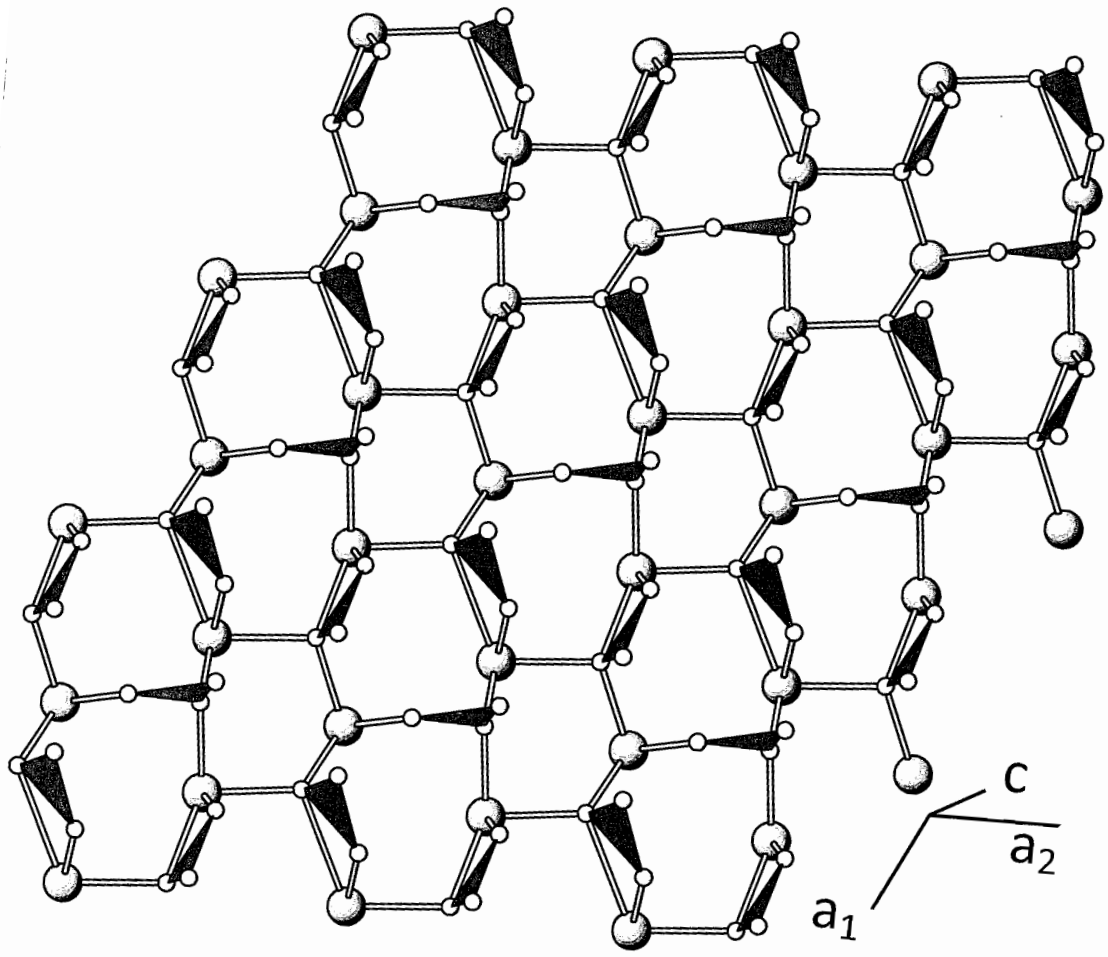
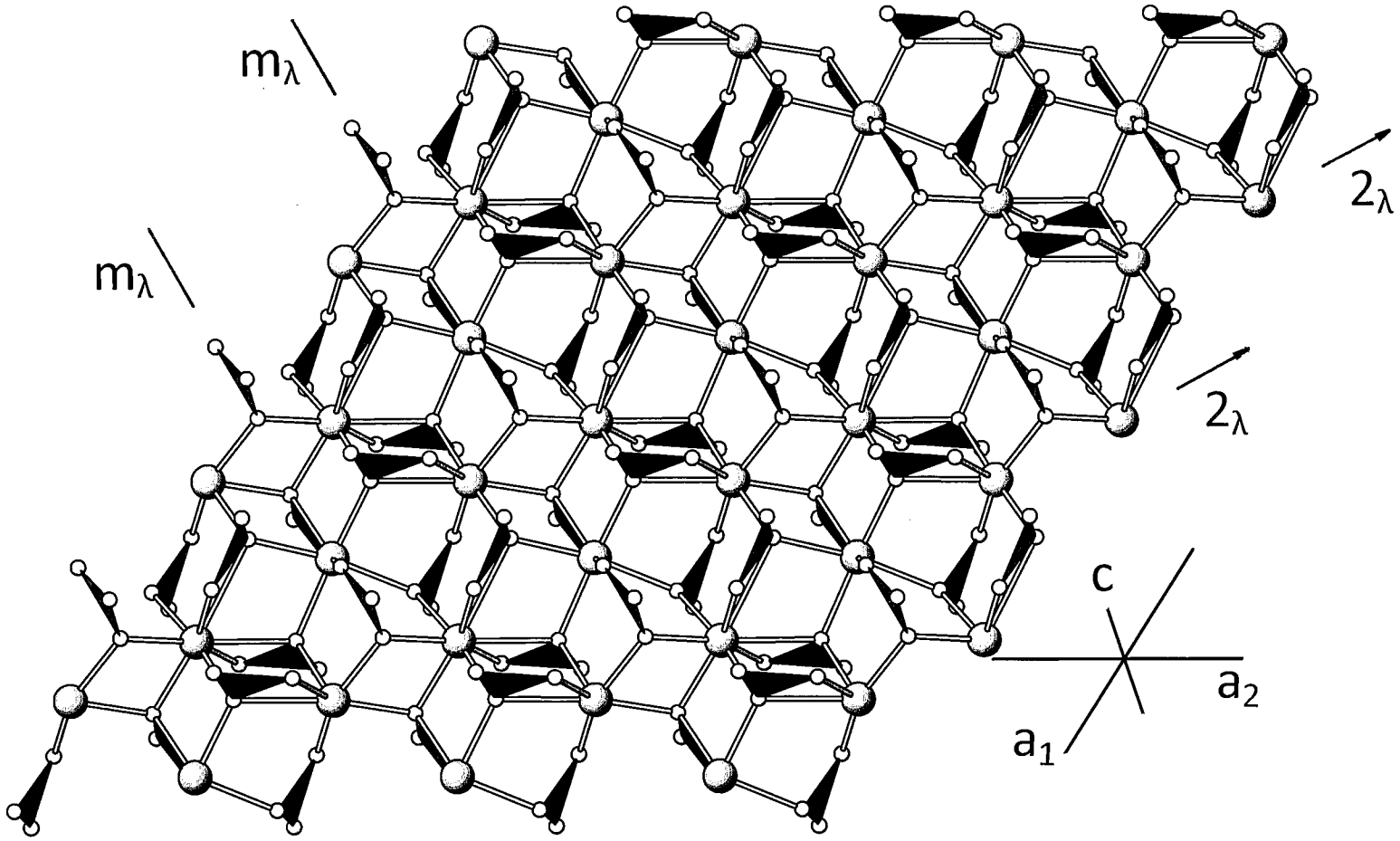
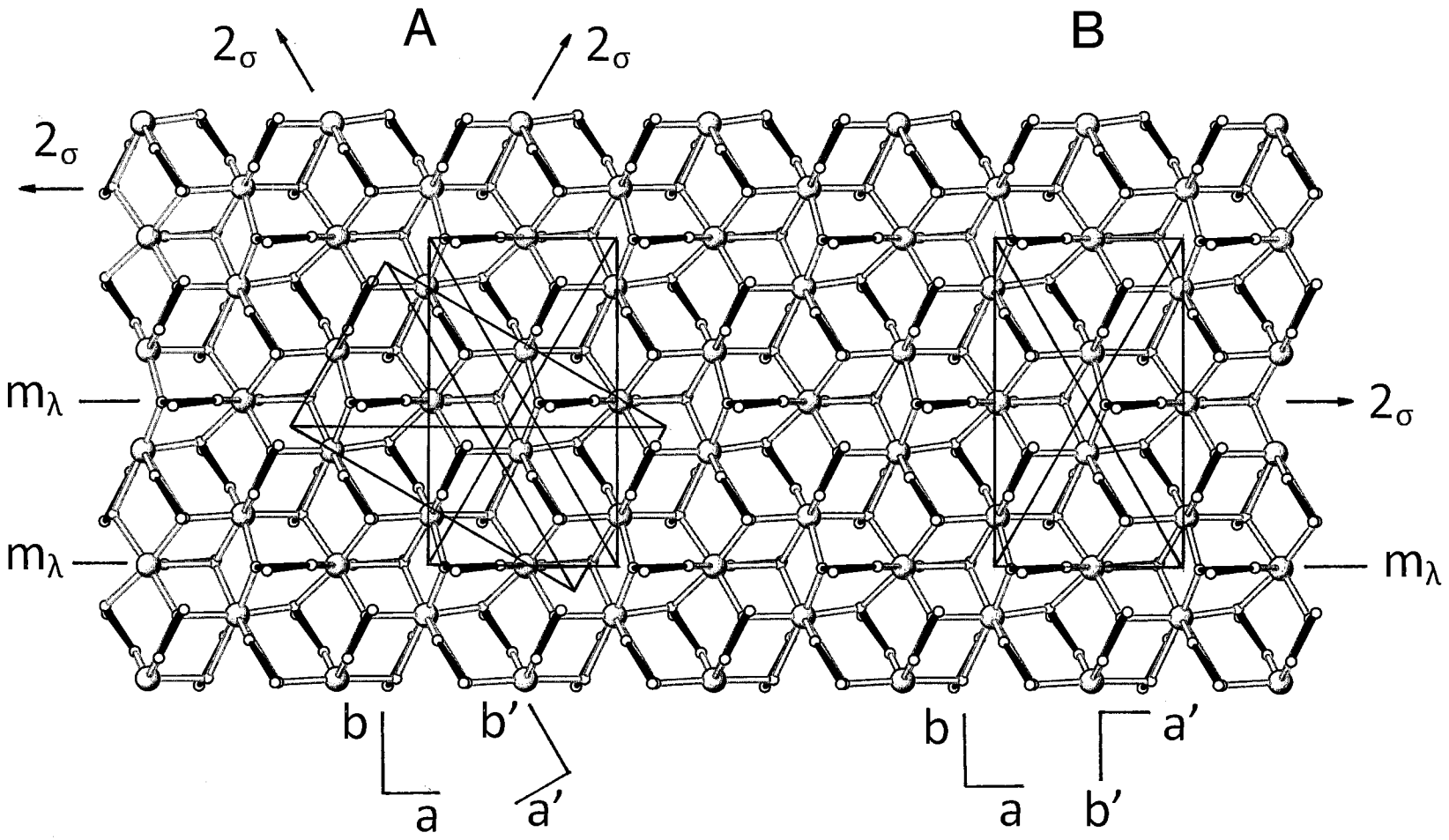


Fig.1


c
a2
a1


m_λ
m_λ
2_λ
2_λ
c
a_2
a_1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B
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2_σ
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b'

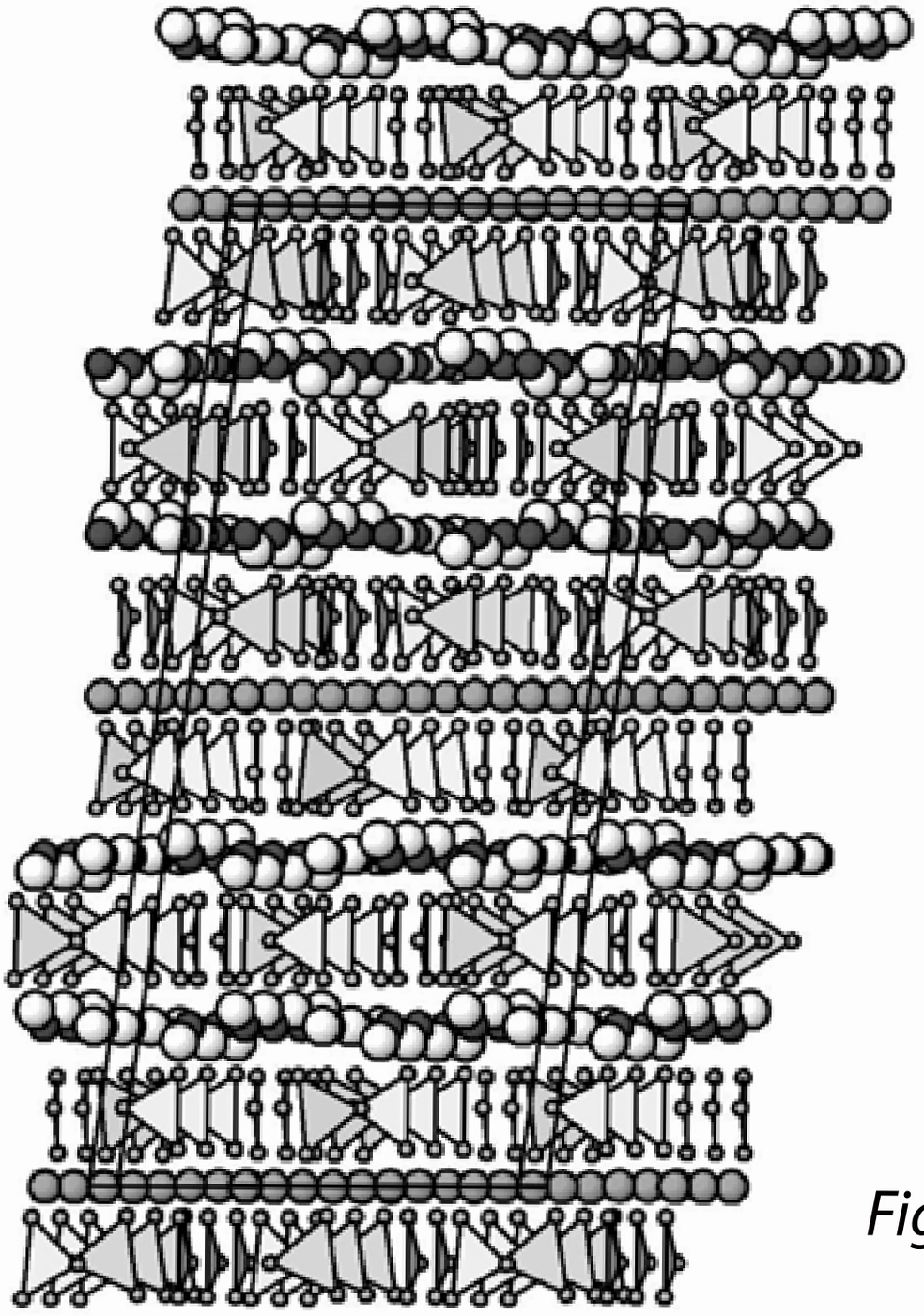

Fig.5

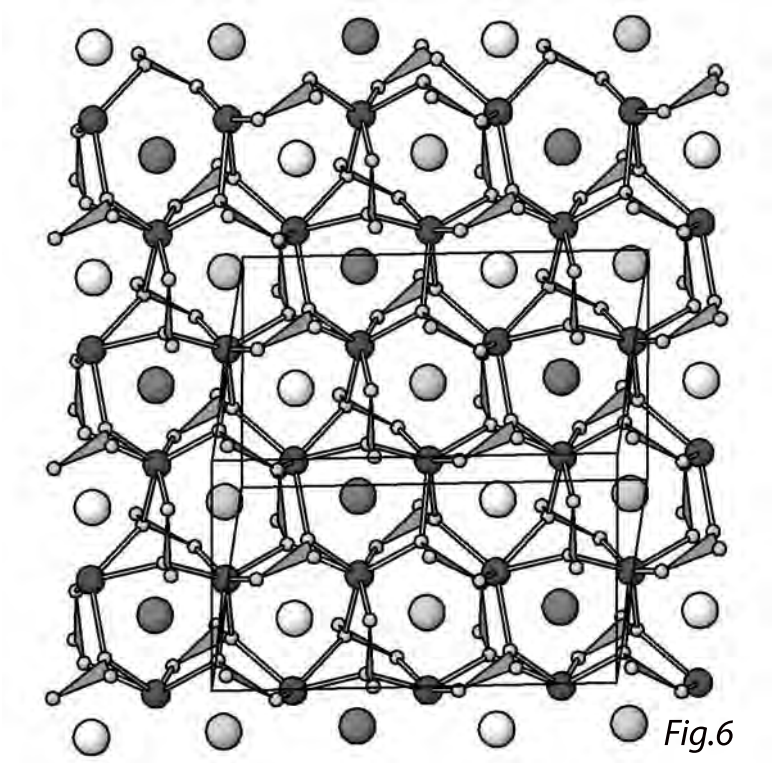

Fig.6