

HRTEM investigation of bastnäsite–parisite intergrowths from Mount Malosa (Malawi): ordered sequences, polysomatic faults, polytypic disorder, and a new parisite-(Ce) polymorph

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Abstract: This high-resolution transmission electron microscopy (HRTEM) investigation of (Ca, REE)-fluorcarbonates from Mount Malosa (Malawi), previously characterized by bulk techniques, is aimed at elucidating the pervasive syntactic intergrowths that commonly affect these minerals. The studied samples are dominated by bastnäsite-(Ce)–parisite-(Ce) intergrowth with rhythmic repetitions along the *c* axis from the microscale to the nanoscale. Whereas bastnäsite is always structurally and compositionally homogeneous, parisite-(Ce) may be either ordered or disordered, in the latter case showing polysomatic faults (compositional faults) that locally change the composition towards bastnäsite-(Ce). The HRTEM image contrast of ordered and disordered intergrowths is interpreted and discussed in terms of layer shifts on (001) of ~ 2.37 Å of the bastnäsite portions (*B*) above the Ca-layers (*V*) along stacking vectors rotated by $n \times 60^\circ$ ($n = \text{odd}$) with respect to each other. In a few cases, sequential faults (conjugate polysomatic faults that locally alter the layer sequence without altering the overall composition) occur periodically, leading to a new parisite-(Ce) polymorph, described in terms of *V* and *B* stacking sequences. HRTEM images and associated simulations show that the new parisite-(Ce) polymorph has *C*₁ symmetry and cell parameters similar to those of normal parisite. The detected nanostructure is consistent with a primary growth mechanism in which bastnäsite and parisite crystallize directly from a fluid whose thermodynamic (close to) equilibrium conditions quickly and repeatedly crossed their stability boundary. Polysomatic disorder in the compositional interval between parisite and bastnäsite, as occurred in the studied samples, is indicative of growth rates faster than those leading to the formation of long-range polysomes detected in other occurrences. Finally, the present study demonstrates how HRTEM techniques can elucidate polysomatic and polytypic disorder in a comprehensive way, since the contrast is sensitive to the different stacking of CO₃ layers that appears with different slants in HR images, revealing the actual crystal system symmetry and any polytypic disorder.

Key-words: REE deposits; bastnäsite-(Ce); parisite-(Ce); polysomatism; polytypism; fluorocarbonates; HRTEM.

1. Introduction

Calcium and rare earth element (REE) fluorcarbonates are minerals that generate considerable interest because of their importance as ore for REEs (Morteani, 1991) and because of the pervasive syntaxial intergrowths among the phases (Donnay & Donnay, 1953). The most recurrent in nature are (Ca, Ce)-fluorcarbonates, notably bastnäsite-(Ce) [Ce(CO₃)F], synchysite-(Ce) [CaCe(CO₃)₂F], parisite-(Ce) [CaCe₂(CO₃)₃F₂], and röntgenite-(Ce) [Ca₂Ce₃(CO₃)₅F₃]. These fluorcarbonates have layered topology with planar carbonate groups “standing-on-edge” with respect to the overall structural layering (Grice *et al.*, 2007). As consequence of the layered structure, (Ca,REE) fluorcarbonates show polytypism as micas (Wang *et al.*, 1994; Ni *et al.*, 2000) and are generally described as polysomatic *B_mS_n* series built up of bastnäsite (*B*) and synchysite (*S*) basic units. Their chemical formula can be expressed as [Ce(CO₃)F]_{*m*}·[CaCe(CO₃)₂F]_{*n*} (van Landuyt & Amelinckx, 1975;

Wu *et al.*, 1998). In addition to the four most common mineral species of the series, additional *B_mS_n* ordered stacking sequences have been reported on the basis of transmission electron microscopy (TEM) studies (van Landuyt & Amelinckx, 1975; Wu *et al.*, 1998; Meng *et al.*, 2001a, b, 2002). However, the limited resolution of the TEM images did not provide the orientation of the stacking sequences, which is fundamental in order to define the polytypic ordered/disordered nature of the series.

In this study, we undertook a high-resolution (HR) TEM study of (Ca, REE)-fluorcarbonates from Mount Malosa (Malawi) that were previously characterized by bulk techniques (Guastoni *et al.*, 2009) in order to push down to the nanoscale the mineral characterization and to bring to light any new ordered layer sequence. The understanding of the syntaxial intergrowth at the nanoscale will provide further insight into the *B_mS_n* polysomatic series and can potentially provide insights into the formation and processing of mineral deposits that are the primary source of REEs for industrial use.

Table 1. Crystallographic and EMP compositional data for (Ca, REE)-fluorcarbonates from Mount Malosa (Malawi).

Mineral	Sample	<i>S.G.</i>	Cell parameters (Å, °)*	Composition*
Bastnäsite-(Ce)	7C	<i>P6₂c</i>	<i>a</i> = 7.110(1) <i>c</i> = 9.771(2)	(Ce _{0.51} La _{0.32} Nd _{0.09} Pr _{0.04} Y _{0.01} Sm _{0.01}) Σ =0.98 (CO ₃)(F _{0.95} OH _{0.07}) Σ =1.02
Parisite-(Ce)	9A	<i>Cc</i>	<i>a</i> = 12.337(3) <i>b</i> = 7.126(1) <i>c</i> = 28.504(8) β = 98.29(2)	(Ca _{0.92} Ce _{1.03} La _{0.53} Nd _{0.27} Pr _{0.10} Y _{0.04} Sm _{0.04}) Σ =2.93 (CO ₃) ₃ (F _{1.70} OH _{0.30}) Σ =2.00
Synchysite-(Ce)	3L	<i>C2c</i>	<i>a</i> = 12.255(1) <i>b</i> = 7.080(1) <i>c</i> = 18.665(3) β = 102.68(2)	(Ca _{0.99} Ce _{0.42} La _{0.22} Y _{0.19} Nd _{0.13} Pr _{0.04} Sm _{0.03} Th _{0.01}) Σ =2.03 (CO ₃) ₃ (F _{0.79} OH _{0.21}) Σ =1.00

*Guastoni *et al.* (2009).

2. Samples and methods

The (Ca, REE)-fluorcarbonate samples employed in this study come from the same suite of samples studied by Guastoni *et al.* (2009). They were previously characterized by single-crystal X-ray diffraction (SCXRD), electron microprobe (EMP) analysis, thermogravimetric (TG) and differential thermogravimetric (DT) analyses, and CHNS elemental analysis. Bastnäsite-(Ce), parisite-(Ce), and synchysite-(Ce) have been described in these samples, although synchysite-(Ce) was not detected in the present study. Their principal compositional and crystallographic data are reported in Table 1.

For investigations by scanning electron microscopy (SEM) and TEM, mineral fragments of Malawi fluorcarbonates were embedded in epoxy resin and sectioned parallel to the *c*-axis direction with the aim of obtaining pre-oriented samples suitable for study of the syntaxial intergrowth, which is known to occur along the *c*-axis (Donnay & Donnay, 1953). Double polished petrographic thin sections were obtained from the fragments, preliminarily studied by SEM-EDS techniques, and then prepared for TEM observations. Electron transparent TEM mounts were obtained through ion milling using a Gatan precision ion polishing system (PIPS) at the Department of Earth Sciences of the University of Milan.

The SEM investigations were performed at the Department of Earth and Environmental Sciences of the University of Milano-Bicocca with a Tescan VEGA TS 5136XM instrument operating at 20 keV and equipped with an EDAX GENESIS 4000XMS energy dispersive spectroscopy (EDS). The standardless method and the ZAF correction method were used for semi-quantitative analysis.

The TEM observations were performed at the Department of Physical Sciences, Earth and Environment of the University of Siena with a Jeol JEM 2010 instrument operating at 200 keV and equipped with an Oxford Link EDS and an Olympus Tengra 2.3k × 2.3k × 14-bit slow-scan CCD camera. To remove noise contrast due to amorphous materials, HRTEM images were rotationally filtered (Kilaas, 1998) with the HRTEM filter (Mitchell, 2007), as implemented in the Gatan Digital Micrograph version 3.9. High-resolution image simulations were performed with JEMS[®], Java version Electron Microscopy Software, by P. Stadelmann (CIME-EPFL, Switzerland). Finally, semi-quantitative EDS analyses were obtained with the standardless method within the Cliff & Lorimer (1975) approximation.

3. Theoretical background

The precise crystal structures of bastnäsite-(Ce), synchysite-(Ce), and parisite-(Ce) have been obtained by SCXRD (Ni *et al.*, 1993, 2000; Wang *et al.*, 1994). These structures can be taken as reference for the interpretation of HRTEM images of mixed-layer fluorcarbonate minerals. Their stacking sequences and thickness and the ideal Ca/(Ca + REE) ratios are reported in Table 2. The structure of this family of minerals has been described quantitatively in terms of layers parallel to (001) of the hexagonal or pseudo-hexagonal (monoclinic) cell. Diverse layer definitions in terms of composition, thickness, position (within the sequence), and symmetry have been employed so far, making the situation quite confusing. Donnay & Donnay (1953) described the structures of bastnäsite-group minerals in terms of CeF-ionic layers (*d*-layers), layers of Ca ions (*f*-layers), layers of CO₃ groups between CeF-layers (*e*-layers), and layers of CO₃ groups between a CeF-layer and a Ca-layer (*g*-layers). Later, van Landuyt & Amelinckx (1975) used this notation to describe other ordered polysomes detected by TEM and also used another description of blocks of (*de*) bastnäsite (*B*) and (*dgfg*) synchysite (*S*), leading to the *B_mS_n* notation code, which is the most widely used, probably because of its conciseness. More recently, Yang *et al.* (1998) introduced another notation code in which the four different symmetry states of the two basic building units, the CaO₈ and the CeO₆F₃ polyhedral layers, are distinguished by the letters *u*, *n*, $\bar{u}$, and $\bar{n}$ and *b*, *d*, *p*, and *q*, respectively. In this notation code, *n* and $\bar{n}$, and also *u* and $\bar{u}$, are related by a mirror plane parallel to the layer, and *n* and *u*, as well as $\bar{n}$ and $\bar{u}$, are related by a two-fold rotation axis. Analogously, *b* and *d*, as well as *p* and *q*, are related by a mirror plane, and *b* and *q*, as well as *d* and *p*, are related by an inversion center.

The *defg* notation code and, even more so, the *un $\bar{u}$ $\bar{n}$ bdpq* one are exhaustive but fail to be concise and intuitive and are prone to errors. On the other hand, the *B_mS_n* notation code is concise but cannot distinguish among different stacking arrangements of the same polysome. Moreover, the *B* and *S* modules cannot be straightforwardly separated in HR images. A fourth notation code, which was found to be suitable for the interpretation of our HR images, can be defined in terms of a pure Ca carbonate end-member (*V*) and bastnäsite (*B*). However, the pure Ca carbonate end-member should connect adjacent Ca-layers as in vaterite, which is not stable in normal geological conditions. As a

Table 2. Stacking sequences, stack thickness and ideal Ca/(Ca + REE) ratio for the most common (Ca, REE)-fluorcarbonates and for the polysomatic faults and ordered sequences described in this study.

Mineral name	Ideal Ca/(Ca + REE)	<i>defg</i> code	<i>unūnbdpq</i> code	<i>VB</i> code	<i>B_mS_n</i> code	Theoretical stack thickness (Å)
Vaterite	1	<i>fg</i>	<i>nn</i>	<i>V</i>	–	4.25
Synchysite	0.50	<i>fgdg</i>	<i>nbuq</i>	<i>VB</i>	<i>S</i>	9.13
Röntgenite	0.40	<i>fgdgfgdedg</i>	<i>nbuqp</i>	<i>VBVBB</i>	<i>BS₂</i>	23.14
Parisite	0.33	<i>fgdedg</i>	<i>nbdnpq</i>	<i>VBBVBB</i>	<i>BS</i>	14.01 (×2)
Bastnäsité	0	<i>de</i>	<i>bd</i>	<i>BB</i>	<i>B₂</i>	4.88 (×2)
	0.33	<i>fgdgfgdedgedg</i>	<i>nbuqpq</i>	<i>VBVBBB</i>	<i>BS</i>	28.02
	0.25	<i>fgdededg</i>	<i>nbdb</i>	<i>VBBB</i>	<i>B₂S</i>	18.89
	0.20	<i>fgdededgedg</i>	<i>nbdbd</i>	<i>VBBBB</i>	<i>B₃S</i>	23.77
	0.17	<i>fgdededgedgedg</i>	<i>nbdbdb</i>	<i>VBBBBB</i>	<i>B₄S</i>	28.65
	0.14	<i>fgdededgedgedgedg</i>	<i>nbdbdbd</i>	<i>VBBBBBB</i>	<i>B₅S</i>	33.53
	0.12	<i>fgdededgedgedgedgedg</i>	<i>nbdbbdbb</i>	<i>VBBBBBBB</i>	<i>B₆S</i>	38.41

matter of fact, no fluorcarbonate phase has been found hitherto, even at the microscopic scale, with a composition richer in Ca than synchysite. For this reason, Ni *et al.* (2000) suggested that synchysite should be considered the Ca-richest end-member of the (Ca, REE)-fluorcarbonate polysomatic series and bastnäsité should be considered the Ca-poorest (nominally Ca-free) end-member. For these reasons, the *VB* code has not been widely used in past literature.

It turns out that in all our HR images, even taken at different thickness and defocus conditions, the Ca-layer can be easily recognized and distinguished from the CeF-layers. For this reason, throughout the text, we adopt the vaterite–bastnäsité (*VB*) notation code. Written in extended form, this code can account for different stacking sequences of the same polysome (*e.g.*, *VBBVBB* vs. *VBVBBB*, *etc.*). For the sake of consistency with previous works, however, the correspondence between the *VB* code and the other codes is given in Table 2 and throughout the text whenever required.

A specific sequence of compositionally different layers defines a polysome, which is thus distinguished from another polysome by a different structure and composition (*e.g.*, *ababab* ..., *abbabb* ..., and *aabaab* ..., where “*a*” and “*b*” are layers of distinct structure and composition). A specific sequence of compositionally and structurally similar layers defines a polytype, which is thus distinguished from another polytype that has a different structure but maintains the same (or a very similar) composition (*e.g.*, Veblen, 1991). In the case of (Ca, REE)-fluorcarbonates, however, phases with different stacking arrangements of the same number of compositionally diverse layers (*e.g.*, *abababab* ..., *aabbaabb* ...) are also considered polytypes.

Polysomatic faults within ordered sequences in (Ca, REE)-fluorcarbonates have been indicated in past literature as “compositional faults” if they entail a compositional change or as “sequential faults” if they entail only a different layer sequence without affecting the composition (van Landuyt & Amelinckx, 1975). Both compositional and sequential faults are easily recognized in HR images by a lattice fringe spacing variation. The periodic occurrence of compositional faults may lead to the formation of a new polysome, whereas the periodic occurrence of sequential faults may lead to the formation of a new polytype.

A special kind of “polytypic faults”, which fulfils the definition of Veblen (1991), concerns just different stacking arrangements of the same compositional layer within the sequence (*e.g.*, *abbabb* ..., *abpabp* ..., and *abdabd* ..., where *b*, *p*, and *d* refer to the same layer but in different orientations). Polytypic faults of this kind do not entail any lattice fringe spacing or compositional variation but have only an altered stacking of analogous compositional layers. They can be recognized on two-dimensional HR images by the different slants of similar structural units, and for this reason they have been overlooked in past studies on (Ca, REE)-fluorcarbonates. In the following, we use the terms “polytypic fault” or “polytypic disorder” to refer only to this kind of faulting. All the other cases are covered by the term “polysomatic fault”, either “compositional” or “sequential”.

4. Results

Backscattered electron (BSE) images of (Ca, REE)-fluorcarbonates show zones of different grey tones due to their different compositions. Bright grey lamellae, irregular in shape and size, alternate with one another, in a parallel way, within a matrix of darker grey tone (Fig. 1a).

The SEM-EDS analyses of the studied samples (Table S1 in the Supplementary Material linked to this article and freely available on the GSW website of the journal: <https://pubs.geoscienceworld.org/eurjmin>) show compositions consistent with bastnäsité (bright grey) and parisité (dark grey), and within the accuracy allowed by SEM-EDS analysis and the recurrent chemical variability affecting these minerals, are consistent with EMP analyses (Table 1). Ca is close to 1 atom per formula unit (*apfu*) in parisité, whereas it is very low or absent in bastnäsité. Sm, Gd, Y, and Th are very low or absent in bastnäsité, whereas they can reach significant levels in parisité. Gd was not reported in EMP analysis, probably because it was not measured. Nd shows similar contents in parisité and bastnäsité, as well as Pr.

The syntactic intergrowth described above is easily recognized in TEM in low-magnification bright-field (BF) images by the presence of planar faults (Fig. 1b) that separate domains with distinct compositions (Table S1).

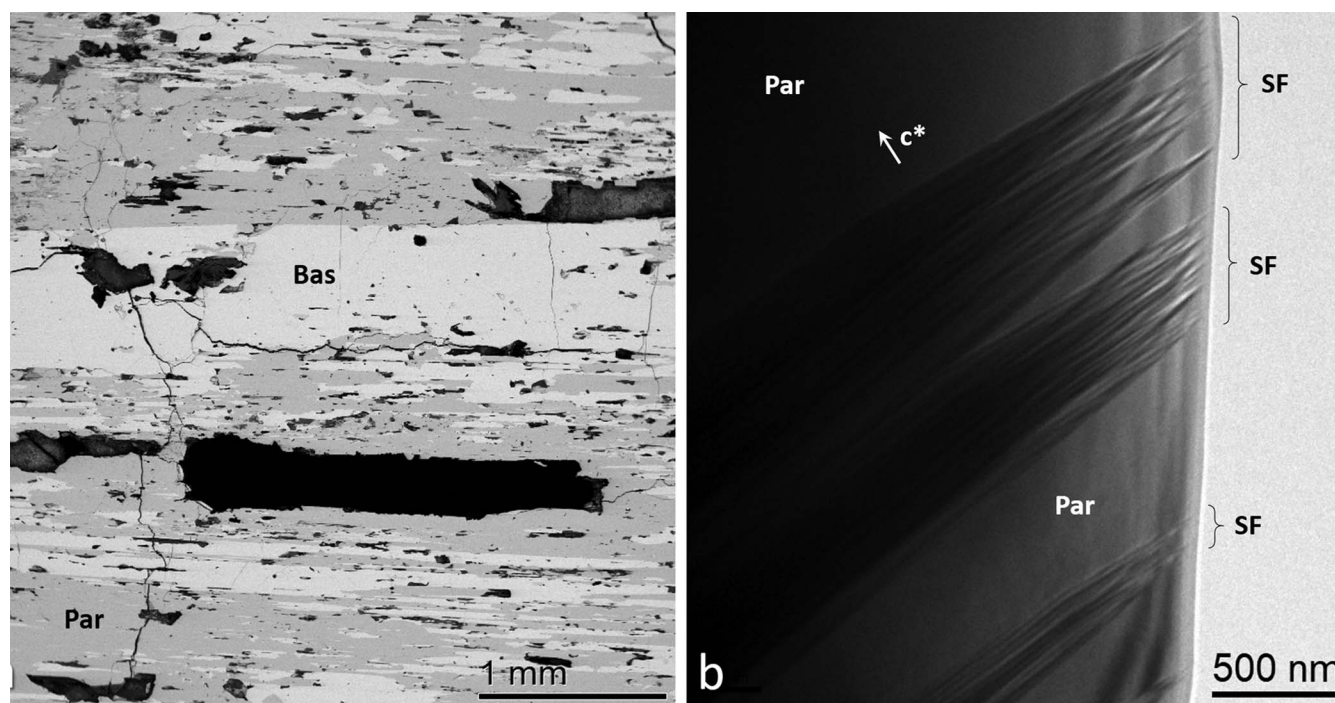


Fig. 1. (a) SEM-BSE image of a syntactic intergrowth of parsite (Par, intermediate grey) and bastnäsite (Bas, bright grey). Darker areas are voids, sometimes filled by secondary material; (b) BF-TEM image of parsite (Par) showing stacking faults (SF) that separate ordered domains.

The TEM-EDS major-element composition is consistent with the SEM-EDS results, although minor elements such as Sm, Gd, Y, Th, and Pr could not be detected at significant level because of the lower sensitivity of TEM-EDS with respect to SEM-EDS, and F^- diffuses quickly under the highly focused TEM probe.

Three types of ordered diffraction patterns were observed, which could be successfully indexed as hexagonal $P\bar{6}2c$ bastnäsite and monoclinic Cc parsite (Fig. 2). The latter occurs within the same syntactic intergrowth in two different orientations that entail a rotation of the structure by $\sim 120^\circ$. In addition to these ordered patterns, diffraction patterns with abundant streaking along c^* and hhl rows, suggesting parsite with polysomatic and/or polytypic disorder, are common (Fig. 3). On the contrary, bastnäsite is always perfectly ordered (Fig. 4). The following crystallographic orientations were determined: $(001)_{\text{Bas}}$ parallel to $(001)_{\text{Par}}$; $[010]_{\text{Bas}}$ parallel either to $[010]_{\text{Par}}$ or $[1\bar{1}0]_{\text{Par}}$; and $(100)_{\text{Bas}}$ parallel to either $(602)_{\text{Par}}$ or $(331)_{\text{Par}}$ (Fig. 2).

Most HR images of parsite can be interpreted in terms of alternating compositional layers (e.g., Fig. 5a). Although HR images show a variable contrast due to different thickness and/or defocus and/or misalignment of the sample, most HR images of ordered parsite and parsite disordered intergrowths can be interpreted in terms of the d , e , f , and g layers defined above. In particular, REE-F-layers (d) appear as heavy dark lines; two of these layers are separated by a CO_3 -layer (e) forming a thin array of bright dots; the Ca-layer (f) forms a wide grey band delimited by two arrays of bright dots, which represent the second type of CO_3 -layer (g) between an REE-F-layer and a Ca-layer (Fig. 5b).

As remarked above, this notation is cumbersome and prone to errors. Moreover, there is no need to distinguish the two types of CO_3 -layers to correctly interpret the HR images. Therefore, in the following, HR images are commented on and labelled in terms of VB layers, and the correspondence with the *defg* code is given in Fig. 5b.

In the syntactic intergrowth studied here, parsite shows a significant nano-structural variability. In addition to ordered domains with two different orientations within the same intergrowth, parsite also shows polysomatic faults and polytypic disorder. An ordered VBB domain with a periodicity of ~ 14 Å bordered by two polysomatic faults with $VBBB$ and $VBBBB$ sequences and widths of ~ 19 and ~ 24 Å is reported in Fig. 5, and wider faults with $VBBBBBB$ (~ 34 Å) and $VBBBBBBB$ (~ 39 Å) sequences are reported in Figs. 6 and 7, respectively.

It turns out that in $[1\bar{1}0]$ HR images of ordered parsite, although the contrast is dominated by a ~ 14 -Å periodicity of (002) lattice fringes corresponding to the VBB sequence, the actual ~ 28 -Å periodicity and $VBBVBB$ stacking sequence is revealed by the different setting of white dots in carbonate g -layers bordering the vaterite V -layer. If one V -layer shows white dots arranged in a rectangular pattern, the next one will show white dots arranged in a rhombic pattern, such that rectangles and rhombs will alternate in an ordered fashion (Figs. 5–7). Therefore, whereas variation in lattice fringe spacing may reveal any polysomatic faults, the breaking of the alternation of rectangles and rhombs within a polysome may reveal the presence of polytypic faults. Depending on the presence and type of the polytypic disorder, parsite VBB half-cells along the stack may appear

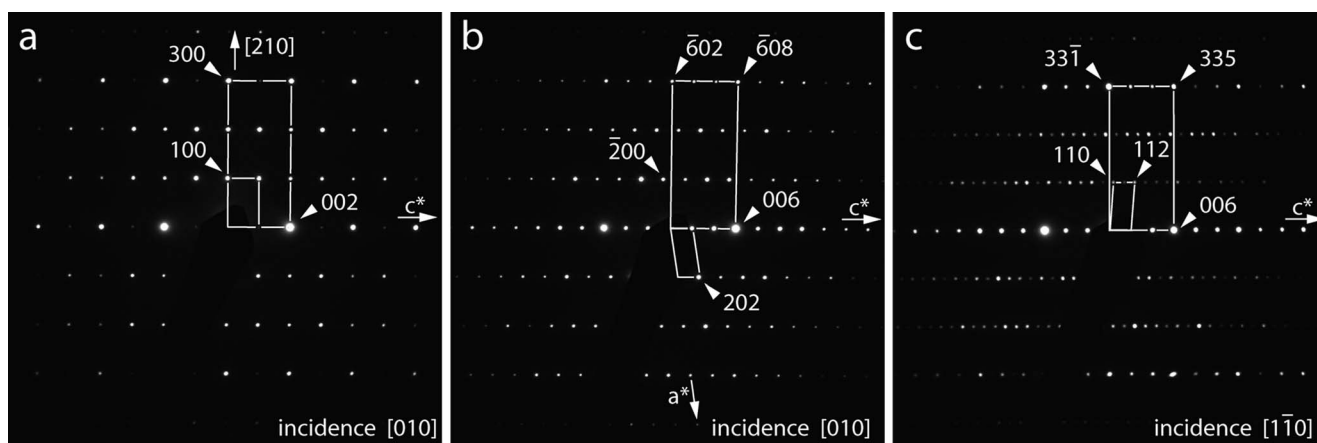


Fig. 2. SAED patterns taken along $[010]$ for (a) bastnäsite and (b) parasite; c) SAED pattern of parasite taken along $[1\bar{1}0]$. The patterns refer to three adjacent areas within the same syntaxial intergrowth and were acquired without rotating the specimen holder – or just a little to compensate local bending of the thin foil – *i.e.*, the intergrowth forms coherent boundaries with the following crystallographic orientation: $(001)_{\text{Bas}}$ parallel to $(001)_{\text{Par}}$; $[010]_{\text{Bas}}$ parallel either to $[010]_{\text{Par}}$ (a) or $[1\bar{1}0]_{\text{Par}}$ (b); and $(100)_{\text{Bas}}$ parallel to either $(\bar{6}02)_{\text{Par}}$ (a) or $(33\bar{1})_{\text{Par}}$ (b). The two-dimensional primitive unit cells and a multiple orthogonal cell are shown. The latter emphasize the almost commensurate substructures.

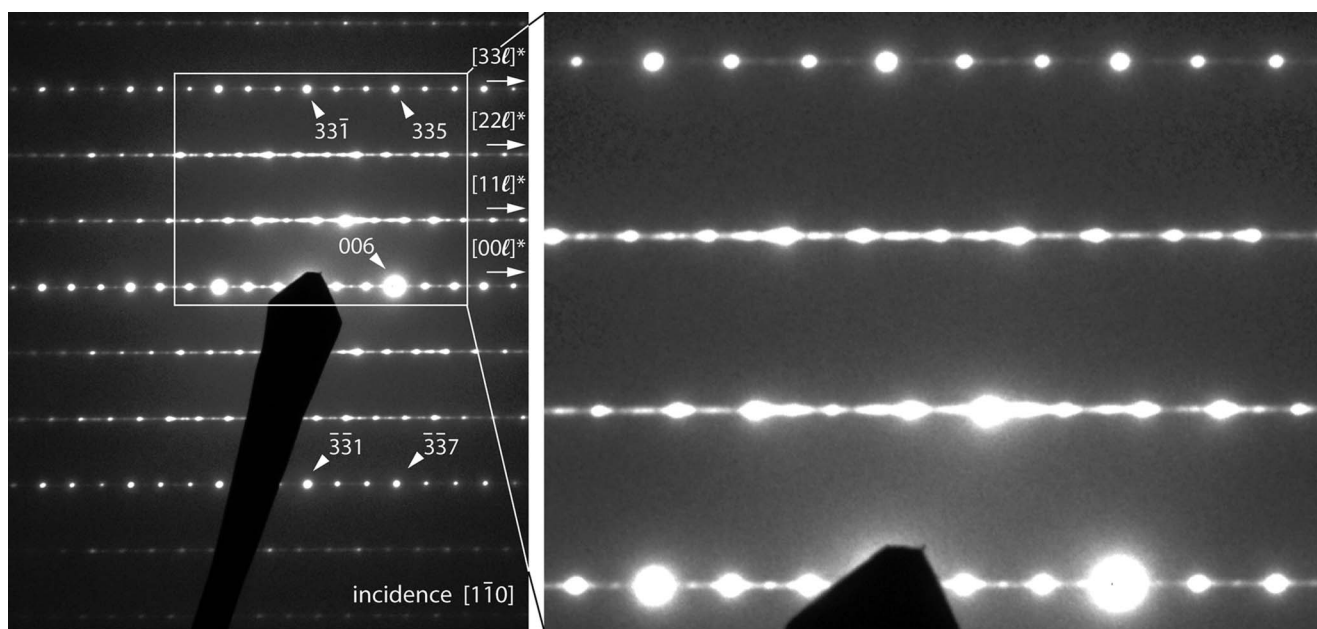


Fig. 3. SAED pattern taken along $[1\bar{1}0]$ for parasite showing streaking along hhl rows (left), indicative of long-range disorder. The enlargement of the central upper part (right) shows that disorder affects seriously $[11l]$ and $[22l]$ rows, and moderately $[00l]$ and $[33l]$ rows, meaning that, within the examined area, polytypic disorder is widespread and polysomatic disorder relatively low, consistently with HR observations (see ahead).

with positive, neutral, or negative slants (Fig. 6). Polytypic disorder is frequently observed between polysomatic faults and does not entail significant structural stress – that is, it is not energetically hindered – since HR images do not show significant strain bands (Figs. 6 and 8).

Polysomatic and polytypic disorder can be recognized and distinguished, as well as in HR images, in SAED patterns and their synthetic analogue: the Fast Fourier Transform (FFT) of the HR images. Figure 8 shows a HR image of parasite along $[010]$ showing two ordered regions

separated by a polysomatic fault with a width of ~ 19 Å, which is consistent with a *VBBB* sequence. Next, three contiguous *VBBB* faults separate one parasite ordered region from a region affected by polytypic disorder. By comparing the FFTs taken in these different regions, that is, ordered parasite, parasite with polysomatic faults, and parasite affected only by polytypic disorder, it is found that polytypic disorder affects only $20l$ and $40l$ rows, which thus appear streaked, whereas polysomatic disorder also affects $00l$. Consistently, in $[110]$ projections, polytypic disorder affects

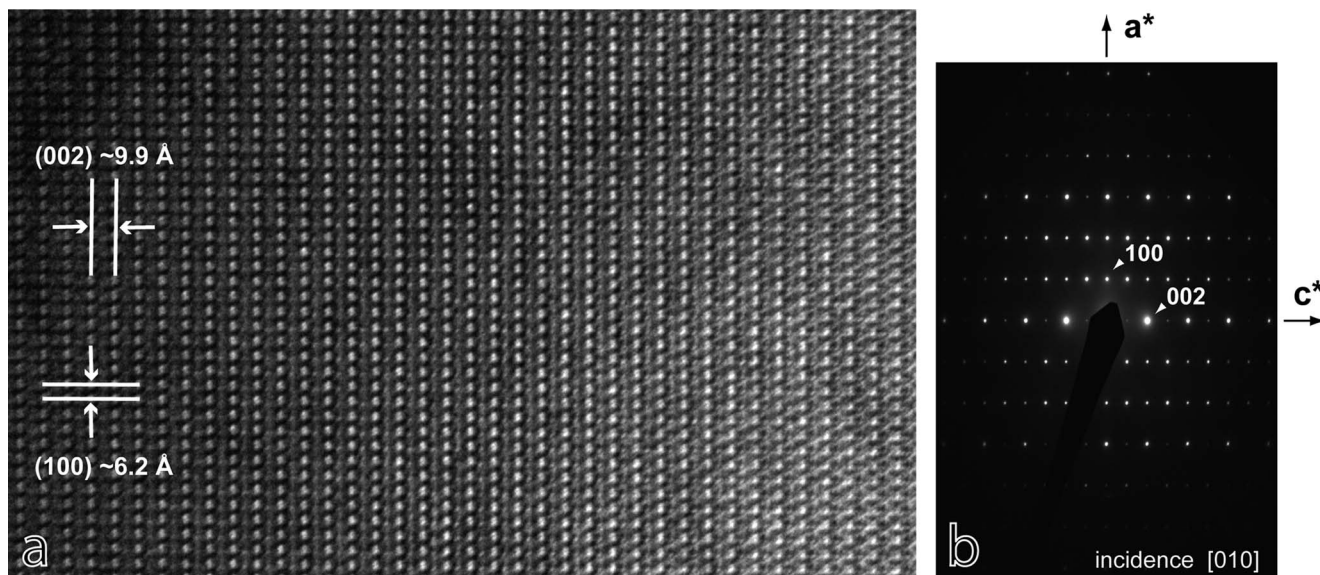


Fig. 4. HR image of ordered bastnäsite as seen down [010] (a) and related SAED pattern (b). No polysomatic faults have been observed in bastnäsite, which occurs always in syntactic intergrowth with parisite with $(001)_{\text{Bas}}$ parallel to $(001)_{\text{Par}}$ and $(100)_{\text{Bas}}$ parallel to either $(\bar{6}02)_{\text{Par}}$ or $(33\bar{1})_{\text{Par}}$.

only $11l$ and $22l$ rows, which thus appear streaked, whereas polysomatic disorder also affects hhl rows (Fig. 6b).

Polysomatic faults are generally single lamellae which extend seamlessly parallel to (001). In a few cases, however, fault offsets were observed. In those cases, lattice fringe bending and strain may be locally significant (Fig. 9). Similar offsets have been observed in other polysomatic series, such as Ca–Mn pyroxenoids (Capitani *et al.*, 2003).

Polysomatic faults within a polysomatic series may occur periodically, in that case originating a new ordered sequence, as has already been observed in REE-fluorocarbonates (van Landuyt & Amelinckx, 1975; Wu *et al.*, 1998; Meng *et al.*, 2001a, b, 2002), and other polysomatic series such as antigorite (Capitani & Mellini, 2005). In the present case, we found a few lamellae, ~200 Å wide, in which the $VBBVBB$ ordered sequence of parisite switches to $VBVBBB$. The cell length along c^* remains the same (~28 Å), as does the composition, since the number of different compositional layers does not change; only their position within the sequence changes (Fig. 10). An ordered sequence is considered to be non-random when the observable repetition of basic units fulfills the statistical criterion given by Veblen & Buseck (1979):

$$p = \frac{n_1! \cdot n_2! \cdot \dots \cdot n_i!}{(n_1 + n_2 + \dots + n_i)!} < 0.001,$$

where p is the probability of a sequence being randomly produced and n_i is the number of lamellae with width i in the sequence. In the present study, in two distinct cases we observed a $VBVB$ sequence (or S_2) alternating with a BB sequence (or B_2) seven times, leading to $n_1 = n_2 = 7$ and $p \approx 0.0003$. Therefore, the $VBVBBB$ sequence is significant and represents a new parisite polytype/polymorph.

5. Discussion

5.1. Polysomatic and polytypic disorder

Single polysomatic faults (compositional faults) with thicknesses from ~19 to ~39 Å, corresponding to sequences from $VBBB$ to $VBBBBBBB$, respectively, were frequently observed in the studied samples. Sequential faults (conjugate polysomatic faults that alter the layer sequence locally without altering the overall composition) are occasional in the studied samples. A noticeable example is represented by the new parisite polymorph described above and discussed below. In this case, sequential faults occur periodically, giving rise to an ordered sequence of layers. Polysomatic faults are usually observed by TEM, extending throughout the sample. The viewing field, however, is limited in this case, suggesting that polysomatic faults may terminate within the sample, as has been observed in SEM images for bastnäsite domains within parisite (Fig. 1). In a few cases, polysomatic faults are laterally offset, a feature previously observed in other polysomatic series, such as pyroxenoids (Capitani *et al.*, 2003), formed under fast growing conditions at low pressure and temperature (Capitani & Mellini, 2000).

Polysomatic faults can be easily recognized in TEM images because they alter the lattice fringe spacing. Polytypic disorder is more elusive since it does not affect the lattice fringe spacing but only affects the orientation of the layers and can be recognized in HR images from the different slants of projected structural units (*e.g.*, Figs. 6 and 8). Similarly, whereas polysomatic disorder produces streaking on any reciprocal lattice rows parallel to the central $00l$ row, including the central $00l$ row itself, polytypic disorder does not affect the central $00l$ row. For these reasons, polytypic disorder might have been underestimated in previous TEM

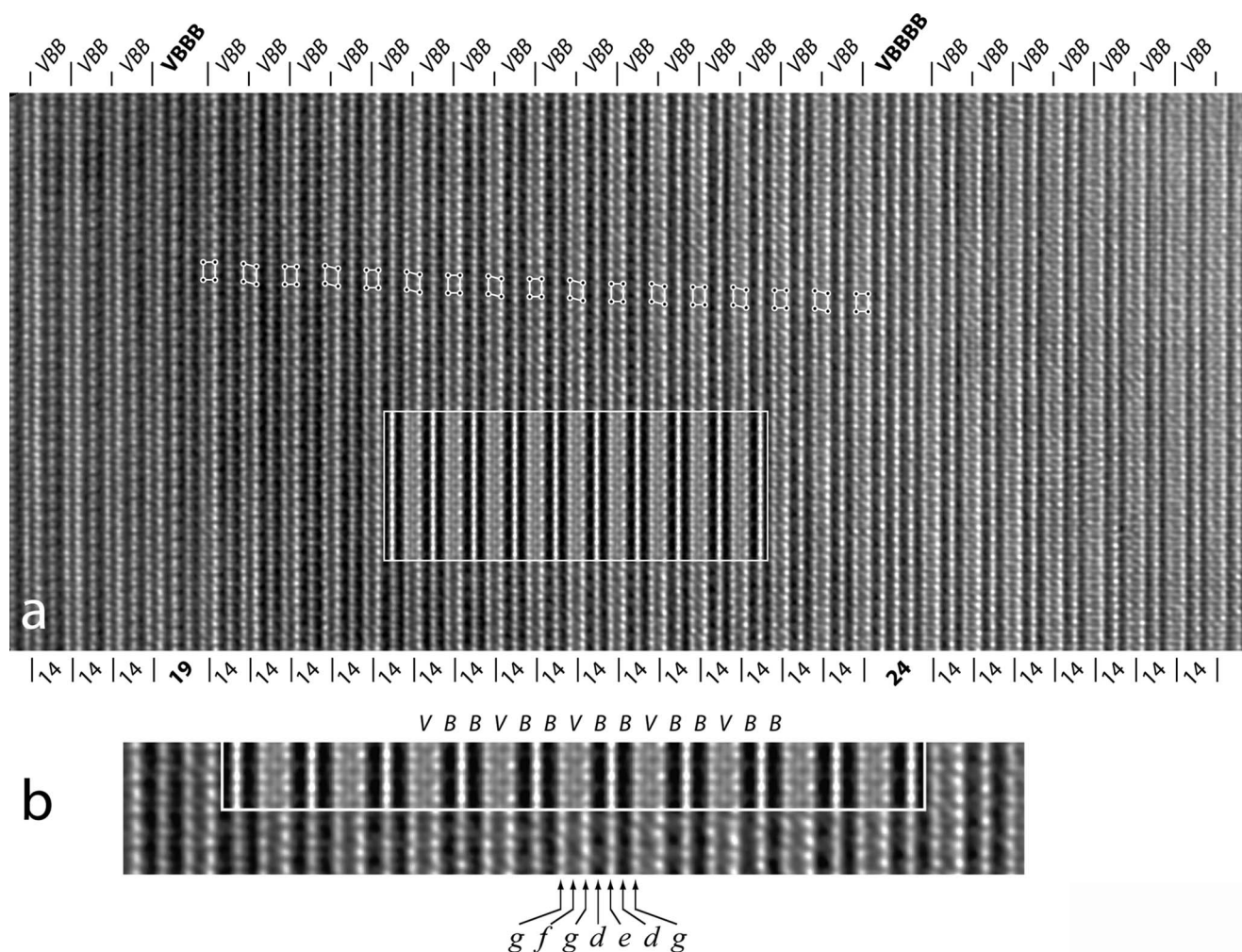


Fig. 5. HR image of parasite along $[1\bar{1}0]$ (a) and simulation that matches the experimental image for a thickness of 50 Å and a defocus of -50 Å (inset). (b) Enlargement of the lower central part of (a) showing the correspondence among lattice fringes and sequence codes. The central ordered region (VBB) shows a prominent periodicity of ~ 14 Å, bordered by two polysomatic faults with VBBB (left) and VBBBB (right) sequences, ~ 19 -Å and ~ 24 -Å wide, respectively. In the ordered VBB sequence, vaterite layers (V) are not all equivalent, since the bordering CO_3 layers (g) alternate with two different settings, as emphasized by the black and white dots, which in one layer are aligned horizontally, but offset vertically in the subsequent one. This leads to a VBBVBB sequence and an actual (001) spacing of ~ 28 Å.

investigations with limited resolution and focus on only the central 00l row.

Polytypism in (Ca, REE)-fluorcarbonates results from the insertion of a Ca-layer between bastnäsite portions and the different types of linkages it forms with the bastnäsite portions above and below it (Ni *et al.*, 2000). Consistently, no polytypic stacking faults have been observed in the Ca-free bastnäsite described in this study (*e.g.*, Fig. 4). In parasite-(Ce), the anionic layers (CO_3 and F layers) in the bastnäsite portion above the Ca-layer shifts on (001) by ~ 2.37 Å ($b/3$) along $[\bar{1}\bar{1}0]$ and those in the next bastnäsite portion shifts another ~ 2.37 Å along $[\bar{1}\bar{1}0]$, which is rotated by $\sim 60^\circ$ from the former shift. The operating stacking vectors between anionic layers in subsequent bastnäsite portions are therefore related by $\pm 60^\circ$ rotations, and the overall shift on the (001) plane in the unit cell results ~ 4.11 Å ($a/3$) along a , which accounts for the monoclinic symmetry of parasite. A consistent bonding pattern, however, is also

obtained for shifts in the upper bastnäsite portion along $[0\bar{1}0]$ and $[110]$, which are rotated by -60° and 180° , respectively, from the former shift. In contrast, shift directions related by either 0° or $\pm 120^\circ$ ($n \times 60^\circ$, $n = \text{even}$) rotations would put the CO_3 groups aligned with the heavy atoms along $[001]$ (hexagonal) columns, impeding a consistent bonding pattern.¹ Therefore, the existence of $n \times 60^\circ$ ($n = \text{odd}$) possible shifts is the reason of polytypism in parasite-(Ce).

When parasite is observed along $[1\bar{1}0]$, the $[\bar{1}\bar{1}0]$ shift projects on the observed plane a component equal to $b/3 \cdot \cos(30^\circ)$, which is ~ 2.05 Å (or $a/6$) perpendicular to the stacking direction (c^*), whereas the $[\bar{1}10]$ shift, which is collinear with the observation direction, has no component

¹ Actually, Ni *et al.* (2000) indicated $\pm 120^\circ$ as possible stacking vectors and $\pm 60^\circ$ as forbidden rotations. A close examination of their structure, however, reveals that the situation is reversed and as described here.

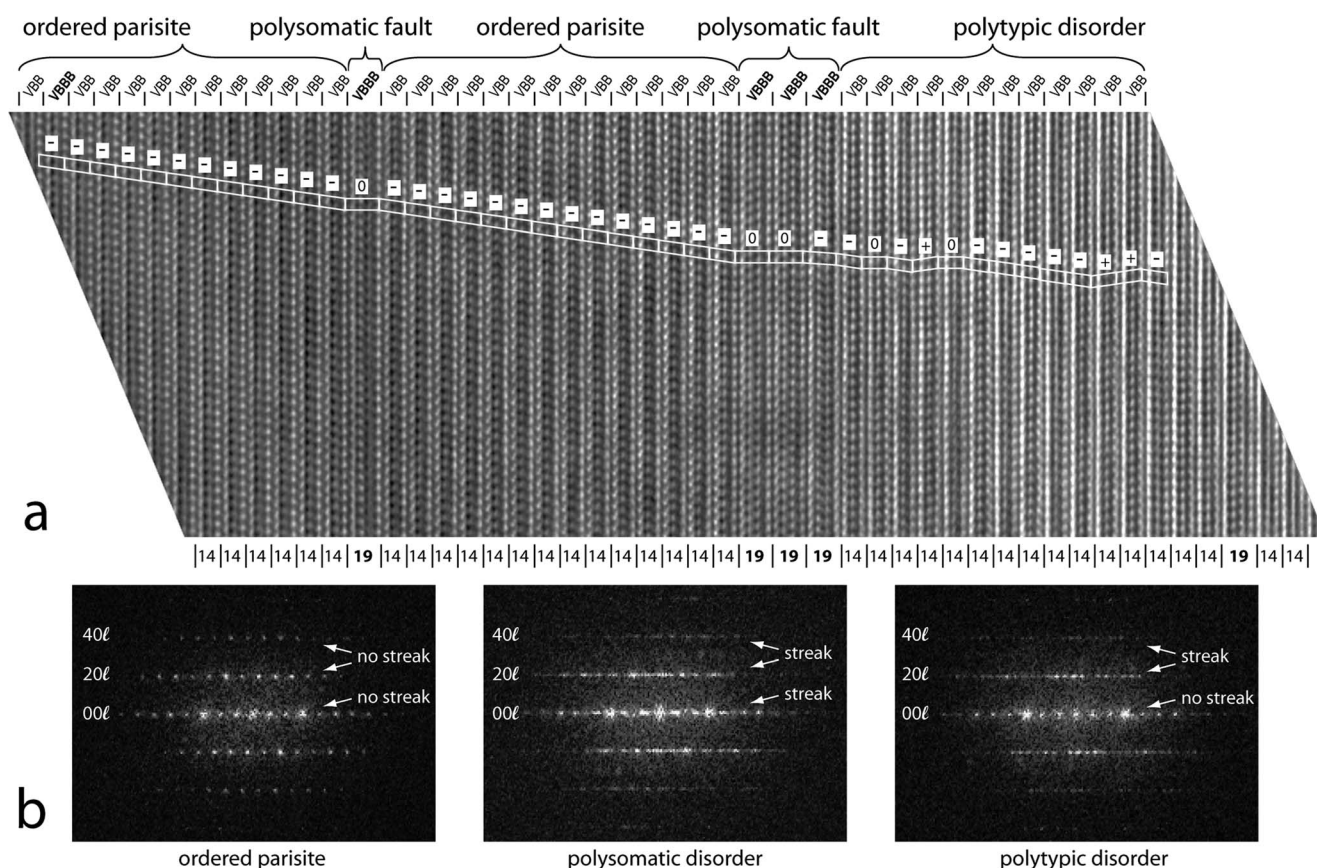


Fig. 8. (a) [010] HR image of parisite showing ordered domains, polysomatic faults and polytypic disorder. The white boxes represent the half-cell stack and the “+”, “0” and “–” signs refer to their slope. It should be noted that in [010] projections ordered parisite shows only the ~ 14 Å periodicity of (002) fringes and a straight sequence along [001]. Therefore, the chaotic sequence of “+”, “0” and “–” signs in regions with ~ 14 Å periodicity represents polytypic disorder. (b) FFTs of ordered parisite (left), parisite affected by polysomatic disorder (center), and parisite affected by polytypic disorder only (right). Note how polysomatic disorder affects all $h0l$ rows, whereas polytypic disorder affects only the $00l$ one.

perpendicular to c^* (Fig. 11). Therefore, VBB half-cells with alternating “–” and “0” slants observed in ordered parisite in $[1\bar{1}0]$ HR images (e.g. Fig. 5) can be explained in this way. Any departure from this scheme, that is, random repetitions of “–”, “0” and “+” slants in $[1\bar{1}0]$ HR images, indicate polytypic disorder (e.g. Fig. 6). When parisite is observed along [010], both the $[1\bar{1}0]$ and $[\bar{1}10]$ shifts project on the observed plane a ~ 2.05 Å component perpendicular to c^* in the same direction (Fig. 11), leading to the apparent halved periodicity along c (e.g., Fig. 8). Again, any departure from this scheme entails polytypic disorder (e.g., Fig. 8, right side). In Table 3 we summarize the complete set of all possible shifts in (Ca, REE)-fluorcarbonates and how they are recognized in HR images along different observation directions of the monoclinic cell.

5.2. The parisite-(Ce) polymorphs

van Landuyt & Amelinckx (1975) reported two parisite polytypes with the same VBB sequence and lattice-fringe periodicity of ~ 14 Å and ~ 28 Å, respectively. The latter corresponds to the monoclinic parisite structure later refined by Ni *et al.* (2000), believed to be rhombohedral by previous

investigators. The other has the same electron diffraction pattern as monoclinic parisite when observed along [010] (Fig. 2b) and the same appearance in [010] HR images (Fig. 8). Therefore, we deduce that van Landuyt & Amelinckx (1975) described the same monoclinic parisite along two different projections, [010] and $[1\bar{1}0]$, which are rotated by $\sim 120^\circ$ around c^* . In a rhombohedral system, these two views are equivalent, but in a monoclinic system they are not. The fact that parisite was considered rhombohedral by earlier investigators may have caused the misinterpretation.

In a recent paper, Ciobanu *et al.* (2017) reported a new 2H hexagonal parisite polytype from the Olympic Dam Deposits (South Australia), with a cell length of ~ 28 Å, that can be added to the 14 parisite polytypes (both hexagonal and rhombohedral) already known from previous TEM studies (van Landuyt & Amelinckx, 1975; Wu *et al.*, 1998; Meng *et al.*, 2001a, b, 2002). As pointed out from previous X-ray structural characterizations (Wang *et al.*, 1994; Ni *et al.*, 2000) and as discussed above, the achievement of a consistent crystal bonding scheme in (Ca, REE)-fluorcarbonates requires a shift of ~ 2.37 Å of the anionic layers above the calcium layer along directions related by

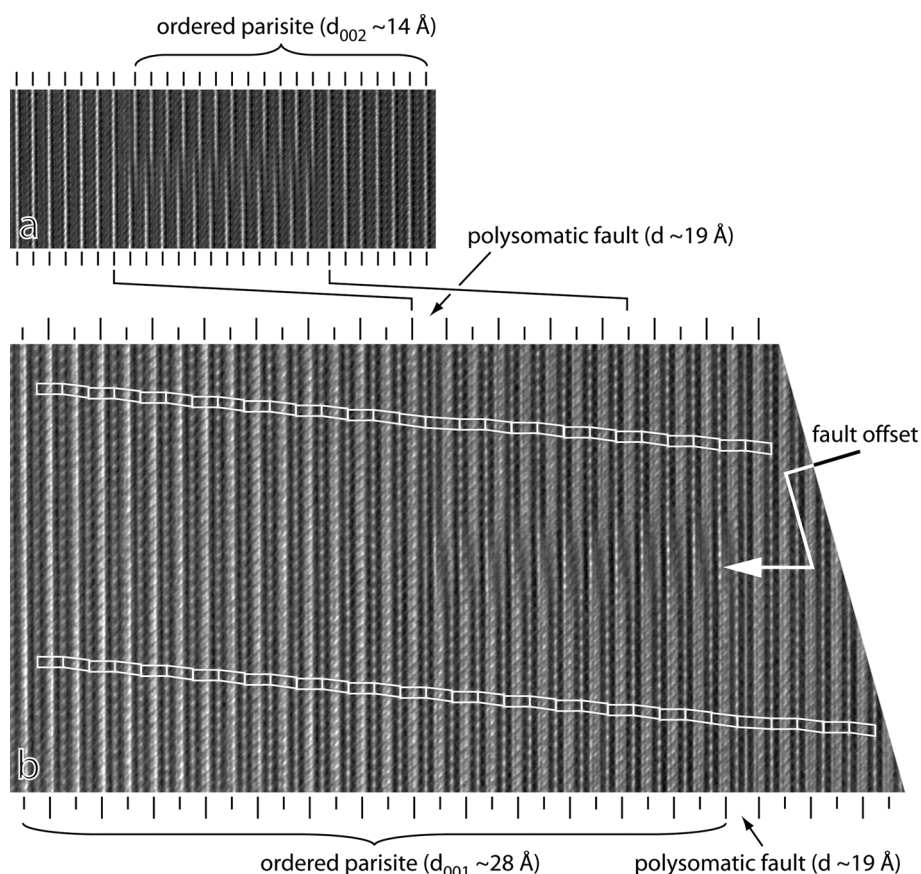


Fig. 9. (a) Ordered paraisite (lattice fringes width $\sim 14 \text{ \AA}$) embedding a *VBBB* lamella ($\sim 19 \text{ \AA}$) laterally offset. In (b), which is a view of the same areas at higher resolution and different defocus, the white dots in the carbonate *e*-layer allows the drawing of the *VBB* paraisite half-cells, which show alternating rectangular and rhombic shapes, consistently with the actual $\sim 28\text{-\AA}$ periodicity of (001) planes (for lattice fringe interpretation see Fig. 5b).

$n \times 60^\circ$ ($n = \text{odd}$) rotations with respect to each other. Therefore, in principle, only $6H$ short-range polytypes ($c \sim 84 \text{ \AA}$) should be possible.

In this study, we report a paraisite polytype/polymorph with a number of compositional layers as for normal paraisite but in a different order. Therefore, the composition and the (001) spacing remain the same, but the layer sequence changes (sequential faults) from *VBBVBB* to *VBVBBB*. The crystal system remains geometrically monoclinic with similar cell parameters, as inferred by the highly coherent boundary interface in HR images (Fig. 10a), but the space group cannot be the same, since the new sequence breaks the *c*-glide. Consequently, $00l$ reflections with l odd, absent by symmetry in the *Cc* space group, become visible with the new sequence (Fig. 10b). Therefore, the new polytype should have *C1* space group and might be indicated as $2M_2$ (assuming as $2M_1$ the polytype described by Ni *et al.*, 2000). To support this hypothesis, we derived a *VBVBBB* trial structure starting from the *VBBVBB* one and carried out HR image simulation for both (Fig. 12).²

² The derived structure in xyz format is provided as Supplementary Material.

Obviously, the derived structure, despite showing reliable crystal bonding, cannot be considered definitive since it could not be refined. Notwithstanding, image simulation under the same experimental conditions of *VBBVBB* and *VBVBBB* intergrowth matches the experimental image well. In particular, the sequence of diverse compositional layers is reproduced well, as is the slant of white dots in carbonate layers between Ca-layers and CeF-layers, suggesting a correct structural topology for the derived *VBVBBB* structure. Fine details within each layer, however, could not be reproduced accurately because of parameters that cannot be simulated, such as crystal bending, local atomic positional disorder, and volatile (H_2O , CO_2) sublimation during observation.

5.3. Nanostructure and genetic considerations

Guastoni *et al.* (2009), comparing their crystal structural data with literature data, suggested an increase in the unit-cell volume as a function of the OH content for paraisite and bastnäs-site. They also described samples with paraisite-(Ce) replaced by bastnäs-site-(Ce) + rhabdophane-(Ce) + cerianite-(Ce). These observations indicate that OH activity (a_{OH}) was significant during the crystallization of (Ca, REE)-fluorcarbonates at Mount Malosa and that it probably increased,

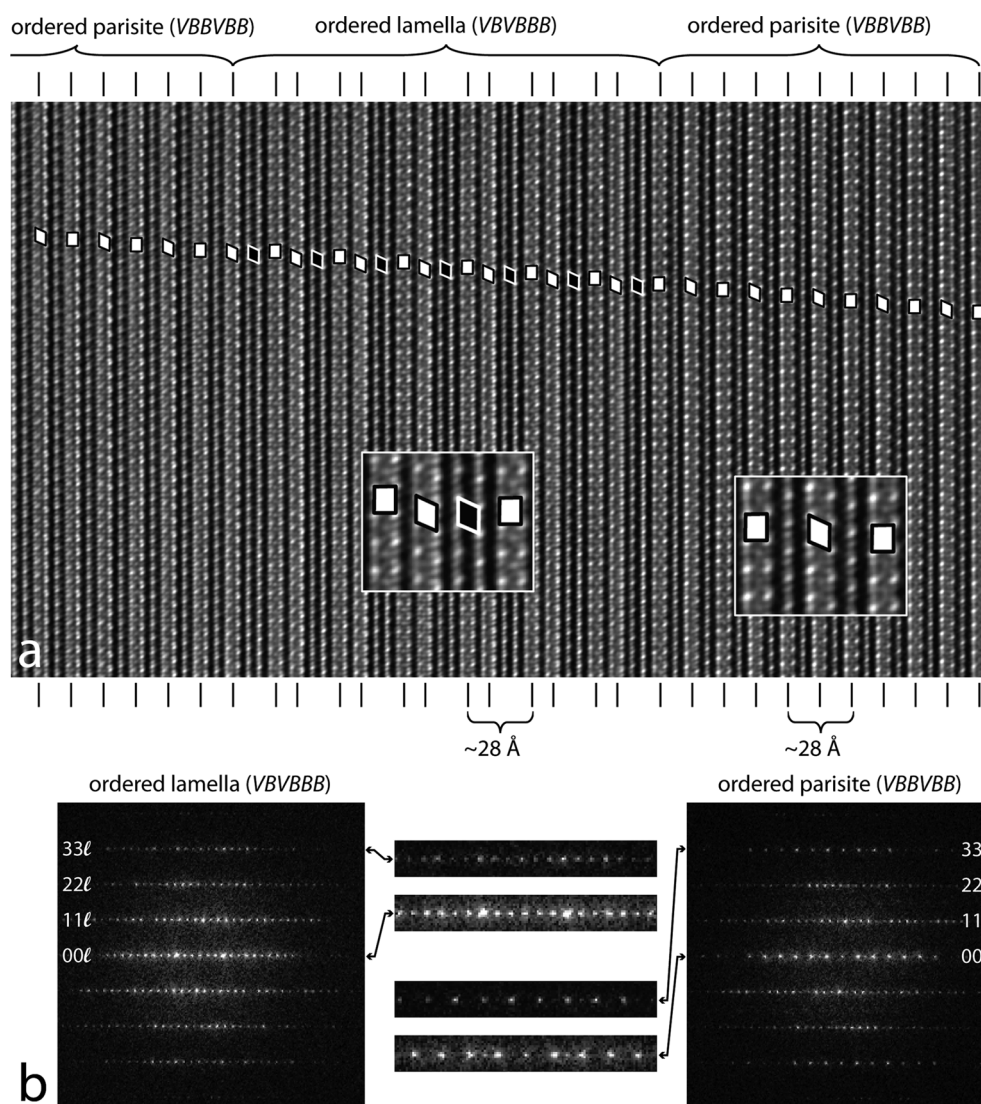


Fig. 10. (a) HR image of ordered parisite (VBBVBB) embedding a lamella about 200-Å thick with sequence a VBVBBB. The white and black boxes in the insets emphasize the different settings of carbonate *g*- and *e*-layers in alternating *V*-layers in both structures (for lattice fringe interpretation see Fig. 5b). The VBVBBB sequence has the same composition as the VBBVBB one (other than the same cell length along *c**), thus it should be considered a polymorph of parisite. (b) FFTs referring to the VBVBBB (left) and VBBVBB (right) sequences, showing halved periodicity in 00*l* and 33*l* rows in the former. In other words, the VBVBBB sequence breaks the *c*-glide and *h*0*l* reflections with *l* odd, absent by symmetry in the VBBVBB sequence, become visible in the VBVBBB one (center).

along with oxygen fugacity ($f\text{O}_2$), during the late stage of crystallization or during a post-crystallization hydrothermal alteration stage. Guastoni *et al.* (2009), however, also described samples where parisite and bastnäsite formed lamellar intergrowths and the replacement process did not occur. Our observations focused on this latter kind of sample.

The studied samples, in addition to ordered parisite (VBB) and bastnäsite (*B*), also contain disordered intergrowths of lamellae with compositions between parisite and bastnäsite. In particular, the local composition may deviate from VBB towards *B* via the intercalation of lamellae with compositions from VBBB to VBBBBBBB. Moreover, SEM-EDS observations show rhythmic bastnäsite–parisite repetitions along the stacking direction (Fig. 1). This nanostructure is

consistent with a primary growth mechanism in which the bastnäsite and parisite intergrowth crystallizes directly from a fluid whose thermodynamic (close to) equilibrium conditions quickly and repeatedly crossed the parisite–bastnäsite stability boundary.

A thermobarometric study performed on associated aegirine (Secco *et al.*, 2007) indicates that the crystallization of (Ca, REE)-fluorocarbonates at Mount Malosa occurred at ~1 kbar and 300–400 °C. Under these conditions, small variations of parameters such as $a\text{Ca}^{2+}$, $a\text{REE}^{3+}$, $a\text{CO}_3^{2-}$, $a\text{F}^-$, and *T* may have caused the crossing of the parisite–bastnäsite boundary and therefore the short-range stacking disorder and the bastnäsite–parisite intergrowth. In particular, all the other parameters being equal, an increase of

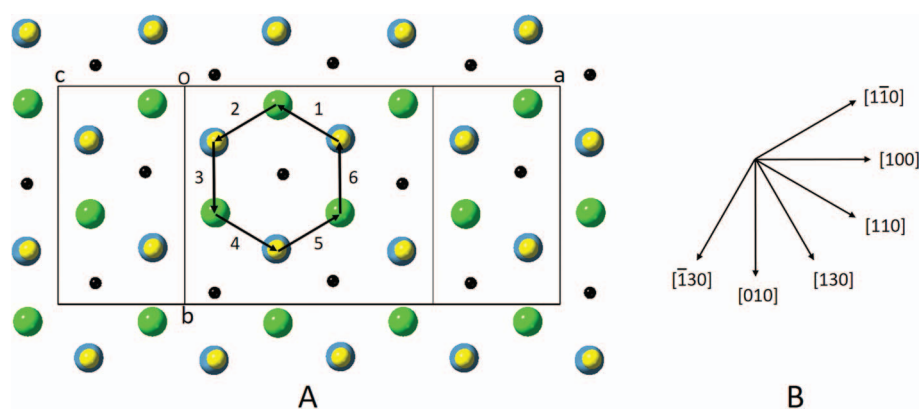


Fig. 11. (a) Projection on (001) of a *dfg*-layer of parisite-(Ce) showing the allowed shifts related by 60° rotations (1–6). Filled circles indicate atom positions (green = F; blue = Ca; yellow = Ce; black = C) and solid lines the monoclinic unit cell. (b) Drawing of the main crystallographic directions along which fluorcarbonates are commonly observed by HRTEM. Note that, depending on the observation direction, on the image plane (perpendicular to it) a given shift may have a component equal to $b/3$ (~2.37 Å); $b/3 \cdot \cos(30^\circ)$ (~2.05 Å, or $a/6$); or $b/3 \cdot \cos(60^\circ)$ (~1.18 Å or $b/6$); or 0 (summary in Table 3).

Table 3. Shift magnitude on the (001) plane of the bastnäsite-like layer in (Ca, REE)-fluorcarbonates as function of both the operating stacking vector (first row) and of the observation direction (left column). The minus sign indicates that the shift has a component along the negative semi-axis of the monoclinic unit cell.

	$[\bar{1}\bar{1}0]$ (1)	$[\bar{1}10]$ (2)	$[010]$ (3)	$[110]$ (4)	$[\bar{1}10]$ (5)	$[0\bar{1}0]$ (6)
$[\bar{1}\bar{1}0]$	$-a/6$	0	$a/6$	$a/6$	0	$-a/6$
$[100]$	$-b/6$	$b/6$	$b/3$	$b/6$	$-b/6$	$-b/3$
$[110]$	0	$a/6$	$a/6$	0	$-a/6$	$-a/6$
$[130]$	$-b/6$	$-b/3$	$-b/6$	$b/6$	$b/3$	$b/6$
$[010]$	$-a/6$	$-a/6$	0	$a/6$	$a/6$	0
$[\bar{1}30]$	$-b/3$	$-b/6$	$b/6$	$b/3$	$b/6$	$-b/6$

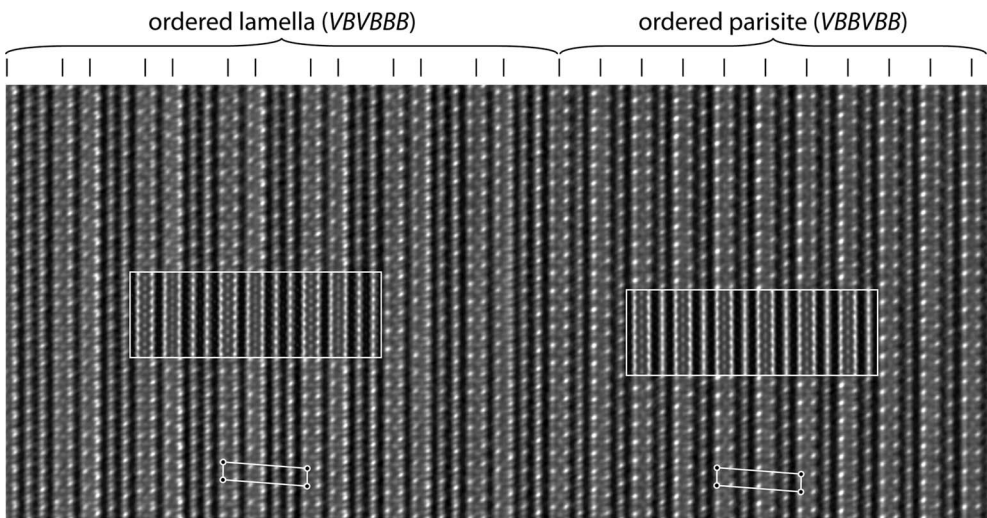


Fig. 12. $[110]$ HR image of adjoining parisite and the new *VBVBVB* parisite-(Ce) polymorph along with image simulation of both structures (inset) and the projected monoclinic unit cells (lower side). Simulation parameters were: accelerating voltage = 200 kV; chromatic aberration = 1.4 mm; spherical aberration = 0.5 mm; beam converge semi-angle = 1 mrad; underfocus = 200 Å; sample thickness = 80 Å.

aF^- and/or of aCO_3^{2-} causes parisite to become stable with respect to bastnäsite, and *vice versa*; an increase of aCa^{2+} and $aREE^{3+}$ and/or an increase in T from 300 °C to 400 °C causes the bastnäsite and parisite stability fields to contract, but the bastnäsite field more than the parisite one (Gysi & Williams-Jones, 2015).

6. Concluding remarks

The present study provides further insight into the definition of species and crystal-structural modularity in mixed-layer (Ca, REE)-fluorcarbonates of the bastnäsitite–synchysite series and the significance of short-range stacking disorder and rhythmic bastnäsitite–parisite repetitions for genetic interpretations.

We report here a new parisite polytype/polymorph characterized by a *VBVBBB* sequence (or *SSBB*, as compared to the *VBBVBB* or *SBSB* sequence of normal parisite). The new parisite polymorph forms lamellae within normal parisite. Two of these are ~200 nm thick, corresponding to seven repetitions along *c*. The intergrowth is perfectly coherent and no strain bands have been observed at the interface, suggesting similar cell parameters between normal parisite and the new polytype. TEM observations, crystal-structure considerations, and HRTEM simulations suggest monoclinic symmetry with space group *C1*.

Two different situations arise from the TEM studies on (Ca, REE)-fluorcarbonates: i) situations where the compositional interval between bastnäsitite and parisite is covered by long-range polysomes, as known from the reported occurrences in China (Wu *et al.*, 1998; Meng *et al.*, 2001a, b, 2002); and ii) situations where such a compositional interval is covered by short-range stacking disorder and rhythmic bastnäsitite–parisite repetitions, as for the Olympic Dam deposit in Australia (Ciobanu *et al.*, 2017) and in the present case. Ciobanu *et al.* (2017) related such differences to different growth rates, slower because of a system closer to thermodynamic equilibrium in the former case and faster in the latter case. Moreover, Ciobanu *et al.* (2017) suggested that such phenomena could be mechanisms for Ca–CO₃ layer adjustment: slower growth rates would promote a monoclinic lattice; faster growth rates a hexagonal/rhombohedral lattice. The results for Mount Malosa (Ca, REE)-fluorcarbonates do not support this hypothesis since, despite belonging to the second type of occurrence, they exhibit only monoclinic species.

As a corollary, the present study demonstrates how HRTEM techniques can elucidate polysomatic and polytypic disorder in a comprehensive way. Advanced high-angle annular dark field scanning transmission electron microscopy techniques, while providing impressive atomic-scale images of heavy elements in minerals (e.g. Ciobanu *et al.*, 2016, 2017), are not at present sensitive to light elements such as C and O. In (Ca, REE)-fluorcarbonates, where Ca and REEs are stacked in a hexagonal lattice and only the lateral shift of interleaving CO₃ layers reveals the actual monoclinic symmetry, this may appear as a limitation. On the contrary, the contrast of HRTEM images is sensitive to the different stacking arrangements of CO₃ layers that appear with different slants, revealing the actual crystal-system symmetry and any polytypic disorder.

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