

A multi-methodological study of the bastnäsite-synchysite polysomatic series: Tips and tricks of polysome identification and the origin of syntactic intergrowths

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ABSTRACT

In this paper, we evaluated the potentialities of Raman spectroscopy and electron backscattered diffraction (EBSD) in the microscopic characterization of Ca-REE fluorcarbonates (CRFC) belonging to the bastnäsite-synchysite series to provide a “road map” for further investigations with transmission electron microscopy (TEM). EBSD was effective in establishing the sample orientation, setting up the oriented cuts, and ascertaining the effective syntactic relationship among all the detected CRFC phases; however, it failed to distinguish between different polysomes. On samples with different orientations that were preventively ascertained by EBSD and characterized by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), micro-Raman spectroscopy allows for distinguishing between polysomes based on the differences in intensity and position of the symmetric stretching vibration (ν_1) of the carbonate group (CO_3^{2-}) in the region around 1080–1099 cm^{-1} . However, as evidenced by TEM-EDS, what appears as a homogeneous polysome in backscattered electrons (BSE) images may be a disordered intergrowth of compositional faults with a bulk composition being matched with that of a real polysome only by accident. Therefore, we conclude that the Raman signal is sensitive to different Ca/(Ca+REE) ratios but not to any ordered distribution of Ca-poor and Ca-rich lamellae within the analyzed volume, making the unambiguous identification of a polysome tricky. Finally, several ordered polysomes were detected at the TEM scale, including a B_2S and a long-range polytype with a 32 nm repeat distance along c . The possible implications of the detected microstructure for ore mineral formation are discussed.

Keywords: Raman spectroscopy, electron backscattered diffraction, transmission electron microscopy, bastnäsite, synchysite, parisite, polysomatism

INTRODUCTION

The Ca-REE fluorcarbonates (hereafter CRFC) are important minerals for at least two (apparently) distant reasons, one tied to fundamental research and the other to critical raw materials. Indeed, from a crystallographic point of view, CRFC form a polysomatic series (Veblen 1991) with bastnäsite $[\text{REE}(\text{CO}_3)\text{F}]$ and synchysite $[\text{CaREE}(\text{CO}_3)_2\text{F}]$ as the end-members (Fig. 1). Accordingly, intermediate terms can be described by bastnäsite (B) and synchysite (S) modules (B_nS_m) and their composition calculated as $[\text{REE}(\text{CO}_3)\text{F}]_m \cdot [\text{CaREE}(\text{CO}_3)_2\text{F}]_n$ (Donnay and Donnay 1953). Intermediate terms of the series are parisite $[\text{CaREE}_2(\text{CO}_3)_3\text{F}_2]$ (or BS) and röntgenite $[\text{Ca}_2\text{REE}_3(\text{CO}_3)_3\text{F}_3]$ (or BS_2). Possible additional intermediate polysomes have been described by high-resolution transmission electron microscopy (HRTEM) studies (Van Landuyt and Amelinckx 1975; Wu et al. 1998; Meng et al. 2001a, 2001b, 2002; Ciobanu et al. 2017; Capitani 2019, 2020; Zeug et al. 2021). Moreover, the layer sequence within a polysome may be different: a given layer (B or S) may be differently rotated with respect to the ordered sequence, giving rise to polytypism and polytypic disorder as in micas (Banfield et al. 1994). Finally, within a polysome, B and S layers may exchange relative positions, leading to polymorphism (Capitani 2019).

On the other hand, bastnäsite and synchysite are the most important ore minerals for Ce, La, Nd, and Y. The demand for these REEs has spiked in recent years due to their increasing usage in numerous high-technology applications, including electronics and green technologies. For instance, Ce oxide (Ce_2O_3) is used in catalytic converters; La and Nd are used in the manufacturing of hybrid and electric motors and rotors of wind turbines; Nd compounds are used for the manufacturing of the most powerful permanent magnets in microphones, speakers, and hard disks; and synthetic Y garnet ($\text{Y}_3\text{Al}_2\text{O}_{12}$) is used in filters for microwaves, acoustic transmitters and transducers, LEDs, lasers, and even as gems (e.g., Goonan 2011; Charalampides et al. 2015).

In nature, CRFC rarely occur as single crystals. Commonly, they form microscale syntactic (crystallographically oriented) intergrowths (Donnay and Donnay 1953) of different polysomes/polytypes, often with stacking faults at the nanoscale. Due to this recurrent microstructure, definitive structural analyses by single-crystal X-ray diffraction (SCXRD) have been achieved relatively recently and only for some basic polysomes, namely bastnäsite-(Ce) (Ni et al. 1993), synchysite-(Ce) (Wang et al. 1994), and parisite-(Ce) (Ni et al. 2000). Apart from these fortunate cases, for most of the occurrences with intergrowths at the microscale, reliable structural analysis can only be performed via TEM.

Regarding SEM-EDS analysis, which is a relatively faster characterization technique compared to HRTEM, syntactic intergrowths can be revealed by the average atomic number (Z)

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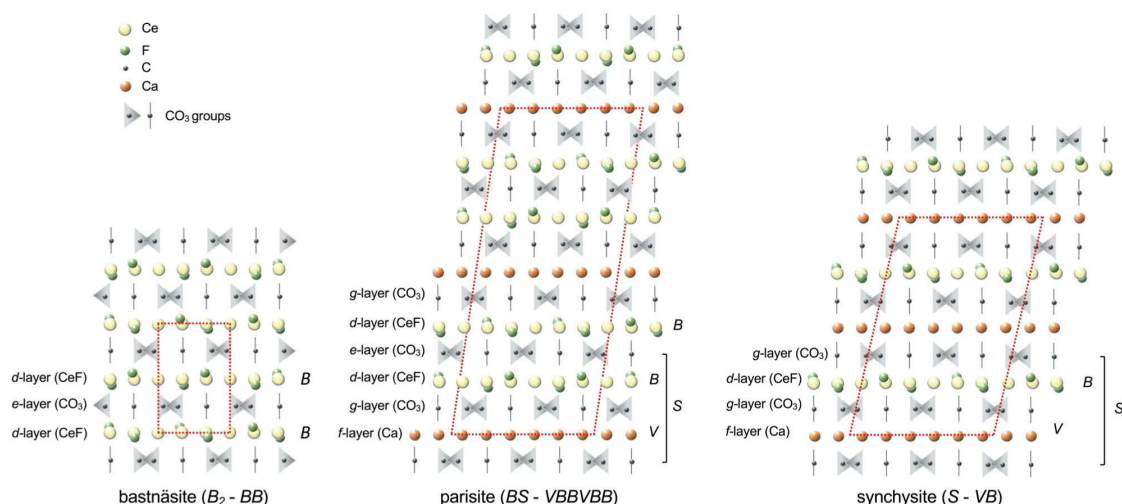


FIGURE 1. Drawings of the basic CRFC structures showing the different building layers [and related names in different coding systems; further details in Capitani (2019)] stacked along the c-axis (vertical). (Color online.)

contrast in BSE images. However, no orientation relationships can be obtained, and submicroscopic intergrowths may be hidden and merged into a uniform-gray-tone microscopic band. Along the same lines, microprobe analysis, whose spatial resolution is on the order of a few micrometers, in the case of submicroscopic lamellae within the analyzed volume can only give an average composition that may accidentally match the composition of a potential polysome.

Raman spectroscopy is another relatively faster characterization technique that has been so far poorly exploited in these minerals. Ce-dominant CRFC has been investigated by Frost and Dickfos (2007), Guastoni et al. (2009), and recently by Zeug et al. (2021), sometimes providing contrasting results. Raman spectroscopy has a spatial resolution comparable to microprobe analysis, and according to Zeug et al. (2021), it can distinguish between some basic

polysomes; however, the influence of submicroscopic lamellae on the Raman response is not clear. On the other hand, electron back-scattered diffraction (EBSD) has, in principle, a spatial resolution that is much better (tens of nanometers) than that of the techniques mentioned above, and it may give orientation relationship information; however, its capability to distinguish between different CRFC has never been tested.

In this study, we investigate well characterized CRFC from Mount Malosa (Malawi) (Guastoni et al. 2009, 2010; Capitani 2019) by combining Raman spectroscopy and EBSD—the latter applied, as far as we know, for the first time to CRFC—to evaluate the potentialities of these two methodologies in the characterization of this material at a microscopic scale and provide a “road map” for further focused investigation, aiming, for instance, to determine

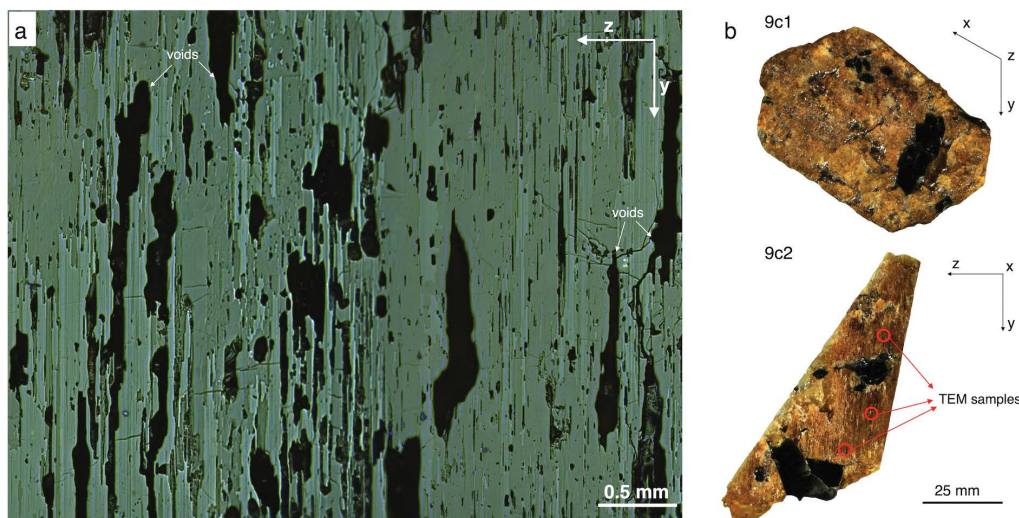


FIGURE 2. (a) Reflected light optical micrograph of sample 9c2 showing the typical banding contrast due to syntactic intergrowths. The black areas are voids. (b) Stereomicroscopy photos of samples 9c2 and 9c1 with their respective orientations obtained through EBSD. Red circles represent the positions where the 3 mm copper rings were placed to extract TEM samples. (Color online.)

new polysomes with TEM.

Investigations at the microscopic and submicroscopic scale of CRFC (or any other ore mineral) may prove to be important for the understanding of the ore mineral formation and possibly for the improvement of downstream processing and REE recovery.

SAMPLES AND METHODS

Samples and sample preparation

The samples studied in this work come from Mount Malosa, Malawi, and were previously described by Guastoni et al. (2009, 2010) and Capitani (2019). All CRFC samples display a yellowish-reddish color and are associated with aegirine (Fig. 2). Before experimental investigations, all samples were embedded in epoxy resin and then cut parallel either to main or generic orientations, first roughly determined by visual inspection of the crystal habit, then following the EBSD results (see below): (1) sample 9c1 sectioned parallel to the x-y (z-axis perpendicular to the section); (2) samples 3 and 9c2 sectioned parallel to the y-z plane (z-axis in the plane of the section); (3) sample 9b and 6 sectioned parallel to a generic orientation (z-axis at a high angle and a low angle to the section, respectively). All samples were mechanically polished with a rotational system using alumina with a nominal grain diameter of 0.3 μm as the last polishing step. Those designated for EBSD investigations were further etch-polished with a Saphir Vibro vibratory polishing device using 0.06 μm colloidal silica. Electron transparent TEM mounts were prepared from sample 9c2, i.e., the one with the optimal orientation to study syntactic intergrowths, which alternate along the c-axis (Donnay and Donnay 1953). After SEM analyses, a double-polished 30 μm thick section stuck with cyanoacrylate adhesive to a glass slide was obtained from the same samples. Copper rings, 3 mm in diameter, were stuck with epoxy resin on the selected sample areas, removed from the glass along with the attached minerals by acetone dissolution of the cyanoacrylate adhesive, and ion-milled down to electron transparency by a Gatan PIPS II Cool instrument. All samples were carbon coated with a 20 nm C-film before SEM observations and with a 5 nm C-film before EBSD and TEM investigations. The C-film was removed before Raman spectroscopy to avoid fluorescence.

Experimental analyses

SEM imaging and analysis were performed at the Platform of Microscopy of the University of Milano-Bicocca (PMiB) with a field emission gun (FEG) SEM Zeiss Gemini 500, operating at 20 keV and equipped with a Bruker XFlash EDS. The standardless method and ZAF correction were used for semi-qualitative analysis. EBSD investigations were performed with a high-resolution Bruker eFlash detector mounted on the same FEG-SEM Zeiss Gemini 500.

Raman spectroscopy analyses were performed at the Department of Earth Science "Ardito Desio" of the University of Milan. The analyses were obtained at room temperature using a LabRAM HR Evolution spectrometer. The system is equipped with an Olympus BX series optical microscope, a diffraction grating of 1800 grooves per millimeter, and a Si-based Peltier-cooled CCD detector. Spectra were excited with the 633 nm emission of a He-Ne laser and were obtained using a 100 $\times$ objective with an acquisition time of 3 $\times$ 30 s. All the spectra were collected close to SEM analysis spots. Fitting of Raman spectra was done after background correction assuming Lorentzian band shapes. The system was calibrated using the 520.7 cm^{-1} line of a silicon wafer. A $\frac{1}{2}\lambda$ wave plate was used to polarize the light. Spectra were obtained with two different polarization directions of the incident electron field vector (**E**): **E** $\perp$ z and **E** $\parallel$ z in samples 3 and 9c2; **E** $\parallel$ y and **E** $\approx$ $\parallel$ x in sample 9c1.

TEM observations were performed at the PMiB with a Jeol JEM2100Plus, supplied with a LaB_6 source and operating at 200 kV. The instrument is equipped with an Oxford EDS system and a Gatan Rio CMOS camera. The Digital Micrograph software (Gatan) was used for image acquisition and processing. The HRTEM filter developed by D.R. Mitchell (2007) was employed to reduce the inelastic scattering in HR images. EDS analyses were collected and quantified with Aztec (Oxford) software using the standardless method and correction for absorption. The method developed by Van Cappellen and Doukhan (1994) was used to estimate the thickness of the TEM mount at the point analysis spots. The estimated beam diameter at the sample surface was 3.5 nm.

RESULTS

Microstructure and composition determined by SEM-EDS

Syntactic intergrowths in CRFC were first studied by SEM-EDS for a first glimpse of the microstructure and the chemical variability at a microscopic scale. As expected, BSE images demonstrate the parallel banding typical of CRFC syntactic intergrowths (Fig. 3). EDS spot analyses were acquired within bands showing homogeneous gray tones. These analyses align with those acquired by wave-dispersive X-ray spectroscopy (WDS) in a previous study of different crystals from the same samples (Guastoni et al. 2009). Therefore, this indicates that EDS is sufficiently accurate for the identification of microscopic CRFC polysomes; at the same time, it is much faster than WDS (Table 1). The EDS analyses display an inverse correlation of the $\text{Ca}/(\text{Ca}+\text{REE})$ ratio with the BSE intensity (brightness)

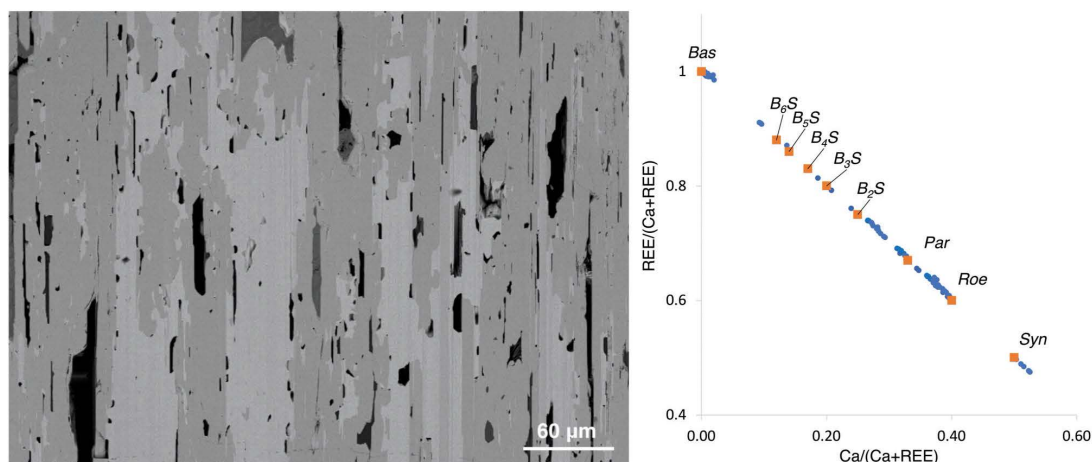
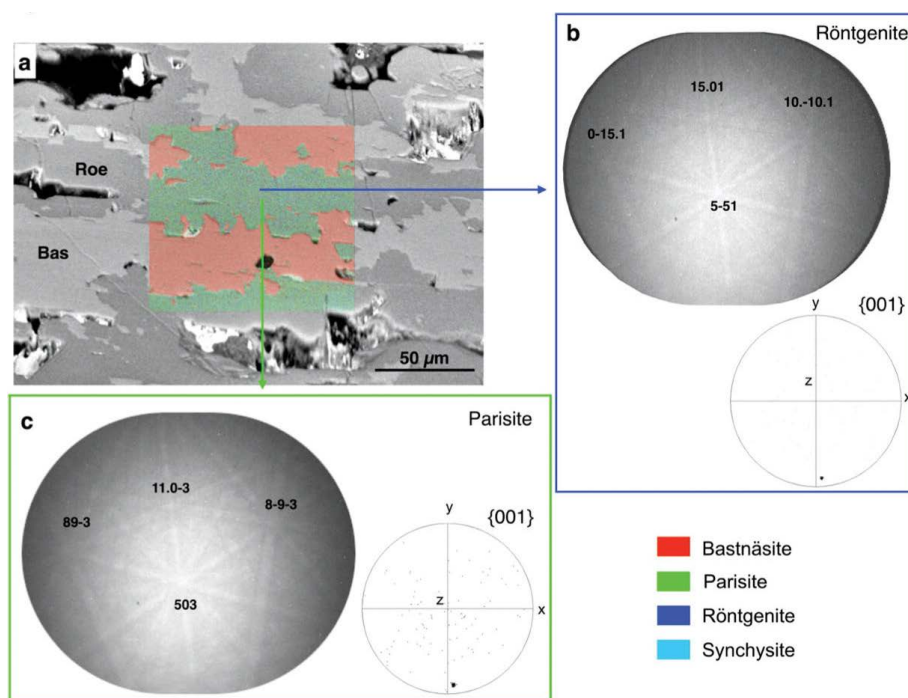


FIGURE 3. (left) SEM-BSE image of sample 9c2 showing the syntactic intergrowths of different CRFC minerals. The compositional contrast is consistent with the average Z-number of the analyzed phases: dark gray corresponds to röntgenite, light gray to bastnäsite, and intermediate gray tones to parisite and other intermediate polysomes (black areas are voids). (right) $\text{Ca}/(\text{Ca}+\text{REE})$ vs. $\text{REE}/(\text{Ca}+\text{REE})$ plot of EDS analyses (blue dots) along with ideal compositions of basic and theoretical polysomes (orange squares). Most of the analyzed lamellae show a composition within the B_2S -röntgenite join. Compositions deviating from the ideal ratios (but also those matching the ideal ratios!) may be due to compositional faults (see the TEM section). (Color online.)

TABLE 1. Comparison between semiquantitative (EDS) and quantitative (EMPA) analyses of bastnäsite, parisite, and synchysite

Mineral phase	EDS (this study)	WDS (Guastoni et al. 2009)
Bastnäsite	$(\text{Ce}_{0.52}\text{La}_{0.27}\text{Nd}_{0.13}\text{Pr}_{0.04}\text{Sm}_{0.01}\text{Gd}_{0.01})_{0.98}(\text{CO}_3)\text{F}_{0.63}$	$(\text{Ce}_{0.51}\text{La}_{0.32}\text{Nd}_{0.09}\text{Y}_{0.01}\text{Pr}_{0.04}\text{Sm}_{0.01}\text{Gd}_{0.01})_{0.98}(\text{CO}_3)(\text{F}_{0.95}\text{OH}_{0.07})_{1.02}$
Parisite	$\text{Ca}_{0.96}(\text{Ce}_{1.04}\text{La}_{0.56}\text{Nd}_{0.27}\text{Y}_{0.01}\text{Pr}_{0.09}\text{Sm}_{0.02}\text{Gd}_{0.01})_{2.00}(\text{CO}_3)_3\text{F}_{1.33}$	$\text{Ca}_{0.92}(\text{Ce}_{1.03}\text{La}_{0.53}\text{Nd}_{0.27}\text{Y}_{0.04}\text{Pr}_{0.10}\text{Sm}_{0.04})_{2.01}(\text{CO}_3)_3(\text{F}_{1.70}\text{OH}_{0.30})_2$
Synchysite	$\text{Ca}_{1.04}(\text{Ce}_{0.35}\text{La}_{0.17}\text{Nd}_{0.13}\text{Y}_{0.21}\text{Pr}_{0.03}\text{Sm}_{0.02}\text{Gd}_{0.03})_{0.94}(\text{CO}_3)_2\text{F}_{0.97}$	$\text{Ca}_{0.99}(\text{Ce}_{0.42}\text{La}_{0.22}\text{Nd}_{0.13}\text{Y}_{0.19}\text{Pr}_{0.04}\text{Sm}_{0.03}\text{Th}_{0.01})_{1.04}(\text{CO}_3)_2(\text{F}_{0.76}\text{OH}_{0.21})_1$

FIGURE 4. (a) BSE image with superposed EBSD phase map of sample 9c2. The legend reports the coloring scheme of all phases considered by the program. The EBSD system indexes correctly bastnäsite (Bas, red) but fails to identify röntgenite (Roe, blue), which is mostly misinterpreted as parisite (green). As a matter of fact, the electron backscattered patterns of röntgenite (b) and parisite (c) are geometrically indistinguishable, leading to ambiguous zone-axis indexing (black numbers). However, as reported in the stereographic projections, EBSD gives consistent and useful information about the crystal orientation relationship. (Color online.)



of the bands. All the measured phases are Ce-dominant and contain La and Nd as other major REEs, whereas Sm, Y, Pr, and Gd may be present as minor components. An exception is represented by synchysite, where Y is more abundant than La and Nd. Fluorine is underestimated in SEM-EDS analyses due to its tendency to diffuse under the influence of a highly focused electron beam. Overall, the chemical compositions of lamellae span from bastnäsite to synchysite depending on the sample and align almost continuously between röntgenite, parisite, and the B_2S polysome (Fig. 3). In particular, other than compositions close to bastnäsite, parisite, röntgenite, and synchysite [ideal $\text{Ca}/(\text{Ca}+\text{REE})$ ratio of 0, 0.33, 0.40, and 0.50, respectively], lamellae with $\text{Ca}/(\text{Ca}+\text{REE})$ of 0.23 and 0.27, which are close to the B_2S polysome (0.25), and lamellae with a $\text{Ca}/(\text{Ca}+\text{REE})$ of 0.36 (Online Materials¹ Table S1) have been often encountered. Moreover, a few analyses with a $\text{Ca}/(\text{Ca}+\text{REE})$ ratio of 0.20, theoretically corresponding to polysomes B_3S , 0.14 (B_5S), and 0.29 (intermediate between parisite and B_2S), have also been collected. At this level, it is unknown whether or not the determined compositions correspond to ordered polysomes or arise from disordered intergrowths at the nanoscale.

Lamellae orientation determined by EBSD

EBSD analyses were undertaken to: (1) establish the initial orientation of the samples; (2) align the sample for oriented cuts for both Raman and TEM investigations; and (3) test the method's capability to discriminate different polysomes. Unsurprisingly, the

EBSD results allowed us to establish the sample orientation, set up the oriented cuts, and ascertain the effective syntactic relationship among all the detected CRFC phases; however, it failed to distinguish between different polysomes (Fig. 4). This drawback can be easily understood if one considers that electron diffraction (similar to X-ray diffraction) is dominated by heavy atoms and that CRFC of the BS series, although monoclinic, have a hexagonal stacking of heavy atoms (Ca and REE) that is identical to that in bastnäsite, the only effective hexagonal term (Ni et al. 1993, 2000; Wang et al. 1994). Different polysomes can be actually distinguished through EBSD maps if EDS chemical information is acquired at the same time and if the map is elaborated with both contributions (50% EDS and 50% EBSD). In this case, the syntactic intergrowths are correctly indexed, but the method is unsuitable since EDS has a spatial resolution (a few micrometers) two orders of magnitude lower than EBSD (tens of nanometers).

Raman spectroscopy

Raman spectroscopic analyses were taken on lamellae previously characterized by SEM-EDS in an attempt to correlate the Raman signal with the chemical composition, aiming to distinguish between different polysomes. Peak assignment was done according to White (1974), Buzgar and Apopei (2009), and Zeug et al. (2021). In particular, the following internal vibrational modes of the carbonate group were identified: (1) symmetric stretching [$\nu_1(\text{CO}_3)$]; (2) out-of-plane bending [$\nu_2(\text{CO}_3)$]; (3) antisymmetric stretching [$\nu_3(\text{CO}_3)$]; (4) in-plane bending [$\nu_4(\text{CO}_3)$] (Table 2; Fig. 5).

Since the intensity of Raman peaks changes in relation to both

TABLE 2. Summary of the (CO₃) vibrational modes in CRFC and their positions as determined in this study

Mode	Bastnäsite	Intermediate polysomes		Synchysite
ν_1 , symmetric stretching	~1095 cm ⁻¹	~1081 cm ⁻¹	~1091–1095 cm ⁻¹ ~1099 cm ⁻¹	~1081 cm ⁻¹ ~1099 cm ⁻¹
ν_2 , out-of-plane bending			~870 cm ⁻¹	
ν_3 , antisymmetric stretching			~1440 cm ⁻¹	
ν_4 , in-plane bending			665–754 cm ⁻¹	

crystal orientation and laser polarization, four different configurations whose details and related Porto's notations (Damen et al. 1966) are reported in Table 3 were investigated. The highest intensity of the ν_1 (CO₃) stretching vibration was obtained in sample 9c2 with the $x(z_y^z)\bar{x}$ configuration. Conversely, the lowest intensity was obtained with the $z(y_x^z)\bar{z}$ setting (Fig. 6). Orientation of the polysomes and laser polarization influence the intensity of the bands only, not their positions.

In agreement with Zeug et al. (2021), we found that the ν_4 (CO₃) in-plane bending is in the range of 665–754 cm⁻¹ and seems separated into two sub-regions. The ν_2 (CO₃) out-of-plane bending is around 870 cm⁻¹. The ν_3 (CO₃) antisymmetric stretching is around 1440 cm⁻¹ and is orientation dependent. The ν_1 (CO₃) symmetric stretching is around 1100 cm⁻¹ and is split into three bands in intermediate polysomes: ~1081, 1091–1095, and ~1099 cm⁻¹, whose relative intensities vary with composition (i.e., Ca/REE ratio, Fig. 15). End-members behave somewhat differently: bastnäsite demonstrates only one intense peak at ~1095 cm⁻¹ and synchysite two bands at 1081 and 1099 cm⁻¹ (Table 2; Fig. 7). As observed in Zeug et al. (2021), we also detected other bands at 598, 1564, and 1738 cm⁻¹, whose origin remains unclear (Fig. 5).

Nanostructure determined by TEM

The sample studied by SEM-EDS and Raman spectroscopy with a favorable orientation for the study of syntactic intergrowths (i.e., with the z -axis laying on the observation plane, sample 9c2) was prepared for TEM to elucidate the structural state associated with the encountered compositions. Ordered regions in sample 9c2 are rare and limited to <1 μ m along the stacking direction. Indeed, the most recurrent microstructure is given by a pervasive occurrence of stacking faults (e.g., Fig. 8a) affecting bastnäsite and parisite, the most abundant phases

detected in the sample (Figs. 8 and 9). Limited regions of B_2S and B_3S showing consistent compositions (Online Materials¹ Table S2) were also detected (Fig. 10), in agreement with SEM-EDS. As for SEM-EDS, a few point analyses with a Ca/(Ca+REE) ratio of 0.29—unrelated to any basic polysome—were measured by TEM-EDS; however, they could not be connected with the underlying structure/microstructure. Moreover, a long-range polytype with a repeat distance of ~32 nm was also observed (Fig. 11). Conversely, even if SEM-EDS and Raman spectroscopy suggest abundant röntgenite, clear evidence of this polysome has not been confirmed by TEM. Along the same lines, the abundant lamellae with a Ca/(Ca+REE) ratio of 0.36 detected by SEM-EDS (Online Materials¹ Table S1) were not detected by TEM. Finally, a new parisite-(Ce) polymorph was detected, and it distinguishes from normal parisite (Ni et al. 2000) and the other polymorphs described by Capitani (2019) by twice the repeat distance along c^* (~56 vs. ~28 Å, respectively), suggesting a repetition of four basic BS modules (~14 Å) along the stacking direction (Fig. 12).

Even considering that using TEM, it is not possible to explore the whole area explored by SEM and that we could have missed some compositions, our findings seem to indicate that, at least in part, the intermediate compositions detected by SEM-EDS on apparently homogeneous lamellae may result from sub-microscopic compositional faults (polysomatic faults), not resolved in BSE images, matching only by accident the composition of a theoretical polysome.

Compositional faults in bastnäsite can only be Ca-rich through the local insertion of vaterite-like slabs, whereas in parisite, they can be either Ca-rich or Ca-poor, i.e., through the insertion of bastnäsite-like slabs. As a matter of fact, in the studied samples, compositional faults in parisite are mostly Ca-poor. These conclusions are supported by nanoscale EDS analysis and HRTEM imaging (Capitani 2019). The Ca/(Ca+REE) ratio that is slightly higher than 0 in bastnäsite and lower than 0.33 in parisite (Online Materials¹ Table S2) now have an explanation.

TABLE 3. Crystal and laser beam settings and related Porto's notations

Mineral section	Beam direction	E polarization	Porto's notation	
1	yz	x	z	$x(z_y^z)\bar{x}$
2	yz	x	y	$x(y_z^y)\bar{x}$
3	yx	z	y	$z(y_x^z)\bar{z}$
4	yx	z	x	$z(x_y^z)\bar{z}$

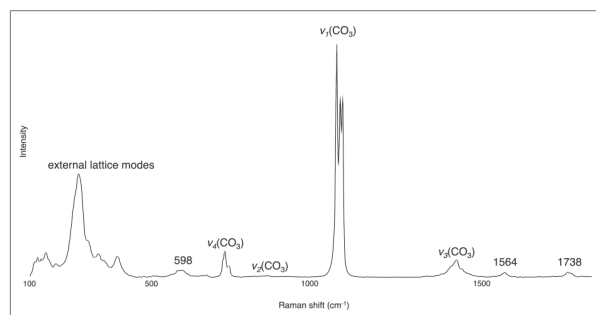
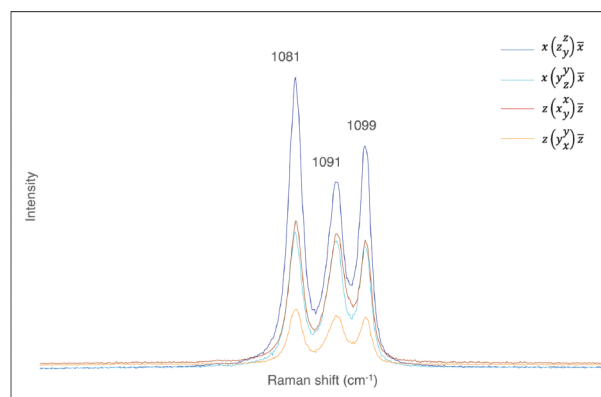
**FIGURE 5.** Raman spectrum of röntgenite showing the main vibrational modes of CRFC.**FIGURE 6.** ν_1 (CO₃) intensity variation in röntgenite as a function of the crystal orientation and laser polarization.

FIGURE 7. (a to f) Symmetric stretching vibration [$\nu_1(\text{CO}_3)$] in the different polysomes, from the poorest Ca-phase bastnäsite (**a**), nominally Ca-free, to the richest Ca-phase synchysite with an ideal $\text{Ca}/(\text{Ca}+\text{REE}) = 0.50$ (**f**). (**b** and **c**) were obtained on lamellae homogeneous in BSE images and with $\text{Ca}/(\text{Ca}+\text{REE})$ ratios of 0.23 and 0.28, respectively, close to the B_2S polysome (0.25). Note the strong orientation dependence of the intensity: $\nu_1(\text{CO}_3)$ is maximal when the laser is polarized parallel to the z-axis [$x(z_y^z)\bar{x}$, solid line] and minimal when the laser is polarized perpendicular to the z-axis [$x(y_y^y)\bar{x}$, dotted line].

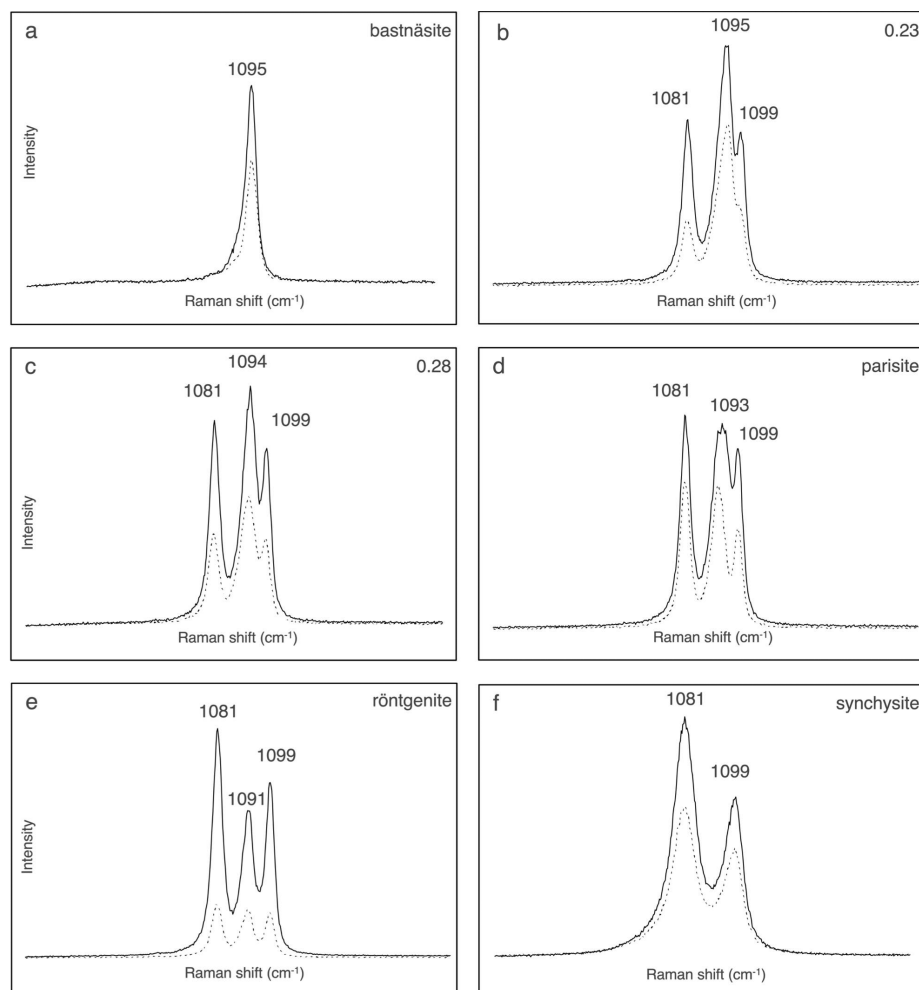


Figure 13 shows bright-field (BF) scanning transmission electron microscopy (STEM) images and related compositional line scans across a Ca-poor lamella hosted in parisite and Ca-rich lamellae in disordered bastnäsite. In both cases, a clear inverse correlation between Ca and Ce can be observed.

Figure 14 is an HRTEM image of bastnäsite ($c \sim 10 \text{ \AA}$), includ-

ing some compositional faults, consistent with B_2S and B_3S single slabs, with a thickness of ~ 19 and $\sim 24 \text{ \AA}$, respectively. The random occurrence of Ca-bearing compositional faults may explain the minor Ca content sometimes detected in bastnäsite and may cause an accidental matching of SEM-EDS analyses with intermediate polysome compositions, causing misinterpretation.

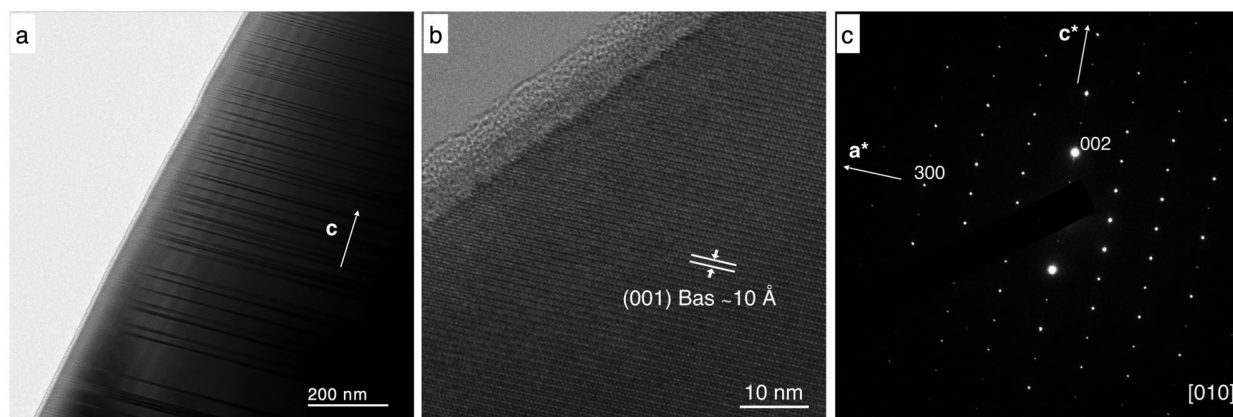


FIGURE 8. (a) Recurrent microstructure in CRFC from Malawi (sample 9c2), made of dense stacking faults. **(b)** Ordered region of bastnäsite as seen down $[010]$ and related SAED pattern **(c)**.

DISCUSSION

Polysome detectability through Raman spectroscopy

According to Raman results, the identification of the basic CRFC is possible through the symmetric $\nu_1(\text{CO}_3)$ stretching vibration at $\sim 1100\text{ cm}^{-1}$ (Fig. 5). Bastnäsite and synchysite can be easily distinguished from other polysomes by the strong Raman band at 1095 cm^{-1} present in the former and the two bands at 1081 and 1099 cm^{-1} present in the latter. Parisite, B_2S , and röntgenite all have three different bands at $\sim 1081\text{ cm}^{-1}$, $\sim 1091\text{--}1095\text{ cm}^{-1}$ (hereafter 1091 cm^{-1}), and $\sim 1099\text{ cm}^{-1}$, which only differ in intensity. According to Zeug et al. (2021), the identification of these intermediate polysomes is possible through the $1091\text{ cm}^{-1}/1081\text{ cm}^{-1}$ intensity ratio. We found this ratio to decrease linearly with the $\text{Ca}/(\text{Ca}+\text{REE})$ ratio for samples with $\mathbf{E} \parallel \mathbf{z}$ and with a parabolic

shape for samples with $\mathbf{E} \perp \mathbf{z}$ (Fig. 15).

The number and position of the symmetric $\nu_1(\text{CO}_3)$ stretching vibration Raman bands depend on the valence and ionic radius (Adler and Kerr 1963) of the neighboring CO_3^{2-} groups. Actually, two different types of CO_3^{2-} -layers are present in the CRFC structure: those in contact on both sides with CeF-layers (or *e*-layers) and those in contact with one CeF-layer on one side and one Ca-layer (or *g*-layers) on the other side (Donnay and Donnay 1953). Only (symmetric) *e*-layers are present in bastnäsite (Yang et al. 2008), resulting in one strong band at 1095 cm^{-1} , whereas only (asymmetric) *g*-layers are present in synchysite (Wang et al. 1994), resulting in two different bands at 1081 and 1099 cm^{-1} . Both *e*- and *g*-layers are present in intermediate polysomes such as parisite, B_2S , and röntgenite (Ni et al. 1993, 2000), leading to a tripartition of the symmetric $\nu_1(\text{CO}_3)$ stretching vibration.

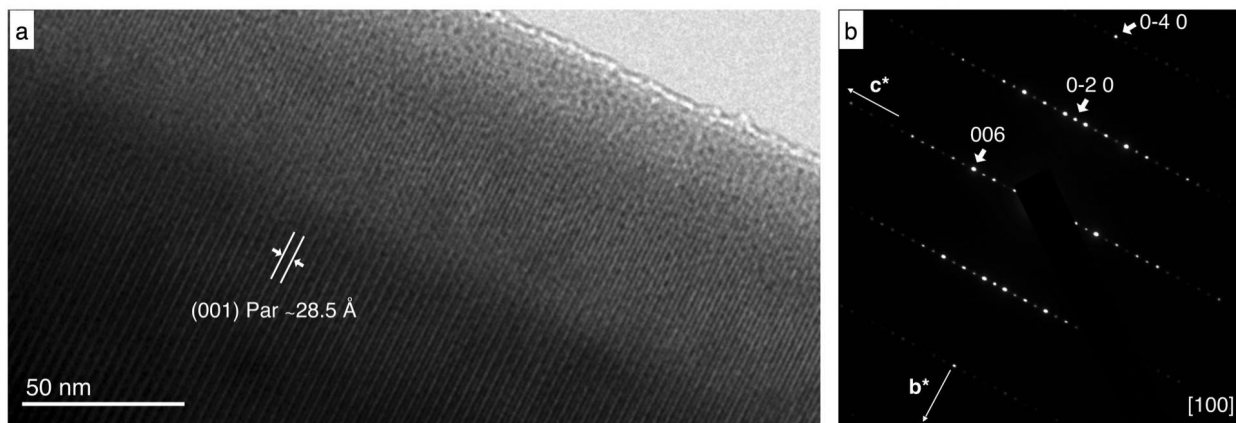


FIGURE 9. Ordered region of parisite (free of compositional faults) as seen down $[100]$ and corresponding SAED pattern (b).

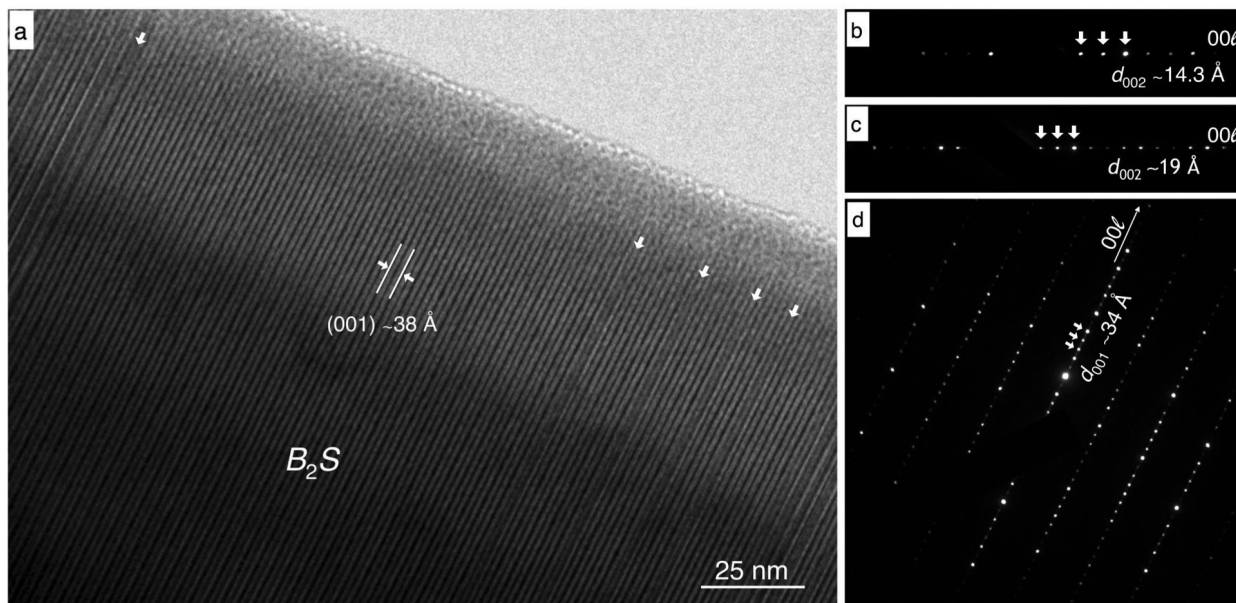


FIGURE 10. (a) Lamella $\sim 140\text{ nm}$ thick with a *c*-spacing of $\sim 38\text{ Å}$, consistent with the B_2S polysome. Some stacking faults delimiting the ordered region are indicated by arrows. (b) $00l$ row of parisite as compared to the $00l$ row of the B_2S polysome (c) to emphasize the different periodicities of the 002 half-cell. (d) SAED pattern of a further polysome with 001 periodicity of $\sim 34\text{ Å}$, consistent with B_5S , whose structure, however, needs to be confirmed.

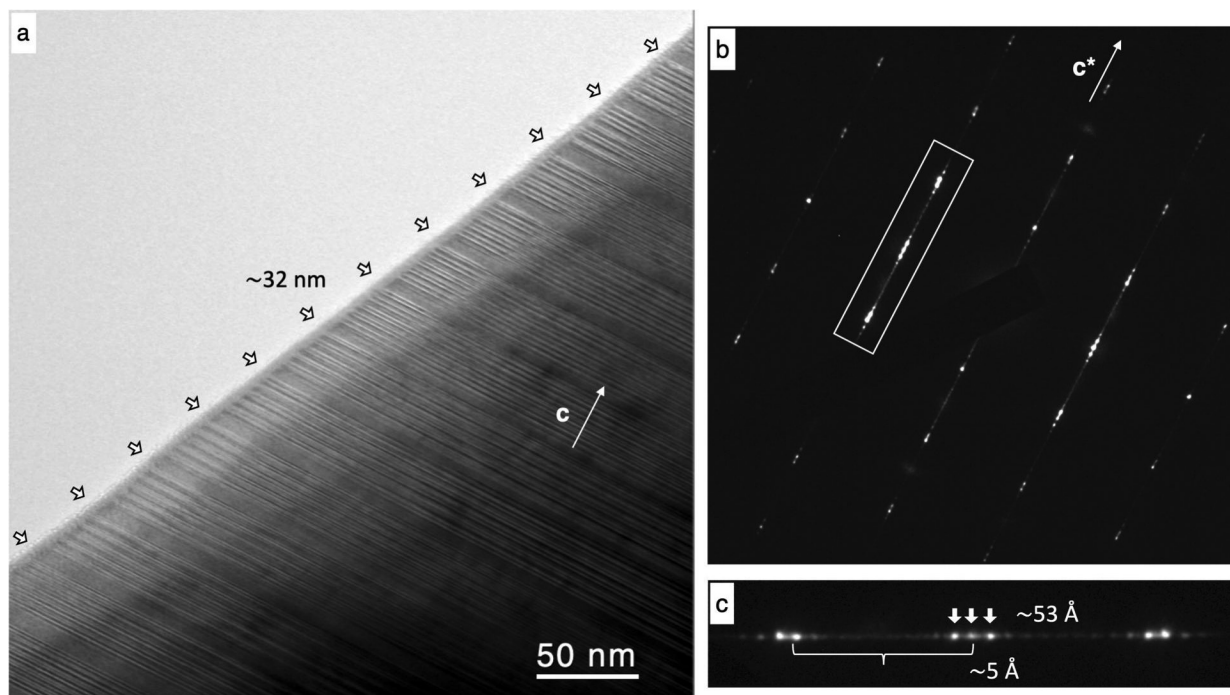


FIGURE 11. (a) Long-range polytype with a repeat distance of ~ 32 nm (the periodic region extends beyond the observed field of view, up to ~ 500 nm in total). (b) Related SAED pattern. The supercell reflections cannot be resolved, because they are too weak and superposed. The strongest subcell reflections showing a periodicity of ~ 53 Å (c), whose intensity is further modulated at ~ 5 Å (brace), suggest a main building block of ~ 53 Å based on single *B*-layers, which may be regarded as the thick, darker lamellae in a (arrows).

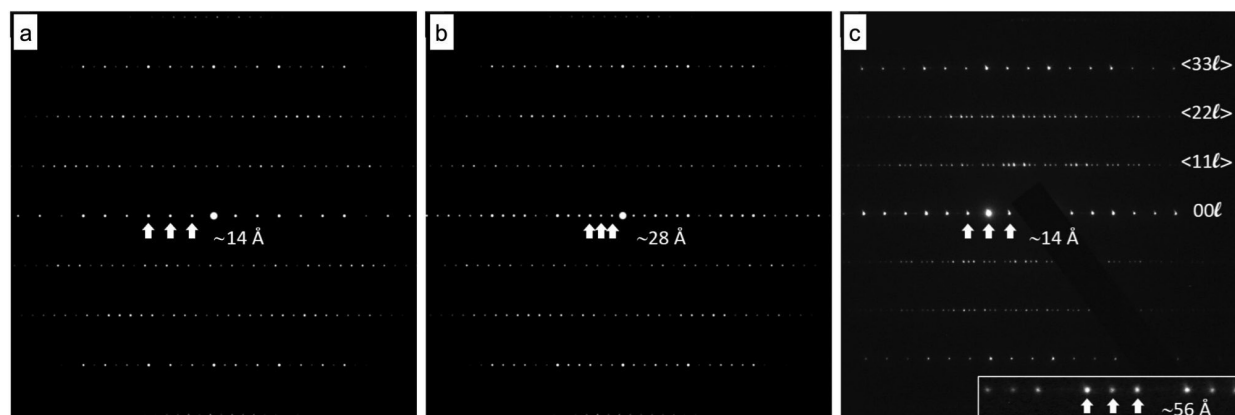


FIGURE 12. SAED patterns of parisite-(Ce) structures along $[1\bar{1}0]$: (a) Ni et al. (2000); (b) Capitani (2019) (both are simulations obtained with the CrystalMaker X software); (c) experimental pattern of the new parisite polymorph detected in this study; inset: zooming of the $11l$ row to highlight the ~ 56 Å periodicity along c^* , which distinguishes the last from the former two structures (~ 28 Å), suggesting a new polymorph with a doubled *c* parameter and a stacking of four *BS* single units (~ 14 Å).

TEM-EDS analyses show that ordered regions in CRFC syntactic intergrowths from Malawi are smaller than expected based on SEM-EDS imaging. Consequently, compositional faults at the nanoscale in bastnäsite and parisite—not resolved in SEM-BSE images—may affect the $\text{Ca}/(\text{Ca}+\text{REE})$ ratio, which can match the composition of a real polysome only by accident. In light of these results, Raman spectroscopy, whose spatial resolution is ~ 1 μm , needs to be critically re-examined. We believe that

the Raman signal is sensitive to different abundances of *e*- and *g*-layers in the structure, whose proportions vary with composition and thus also with the polysome, but not to the order of the layers within the analyzed volume. Therefore, while Raman spectroscopy could be a valid and faster method to probe the $\text{Ca}/(\text{Ca}+\text{REE})$ content of fluorcarbonates, it does not appear to be suitable for distinguishing between ordered and disordered intergrowths with similar compositions.

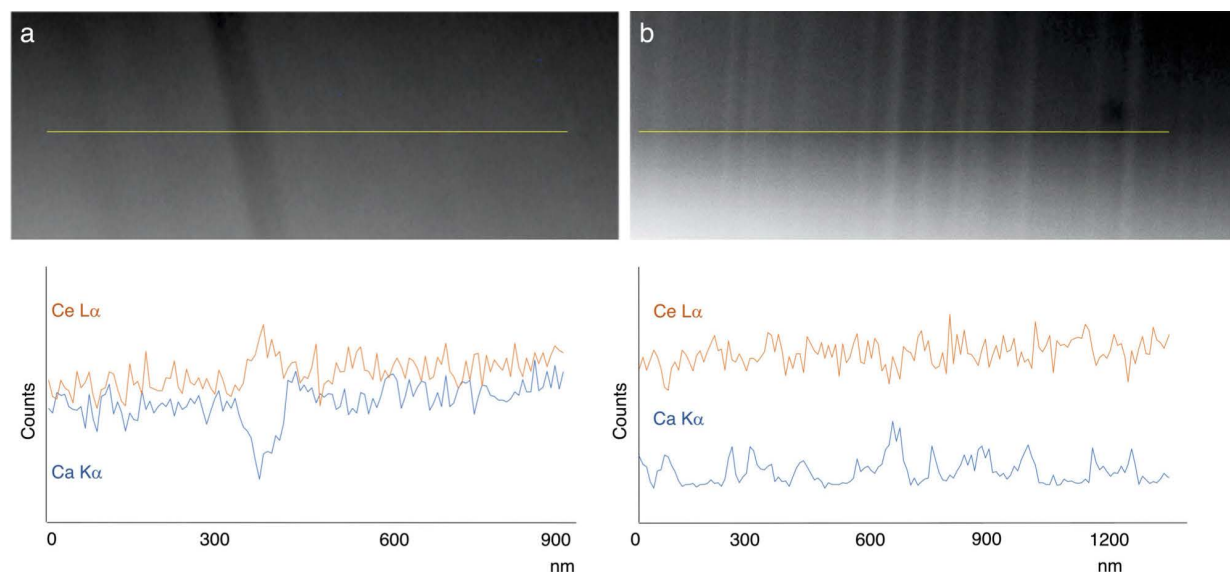


FIGURE 13. BF-STEM images (top) and corresponding compositional line scans (bottom) across a thick lamella within parasite (a) and disordered bastnäsite (b). Note the Ca decrease and the Ce increase at the lamella in parasite and the Ca-Ce inverse correlation in bastnäsite. (Color online.)

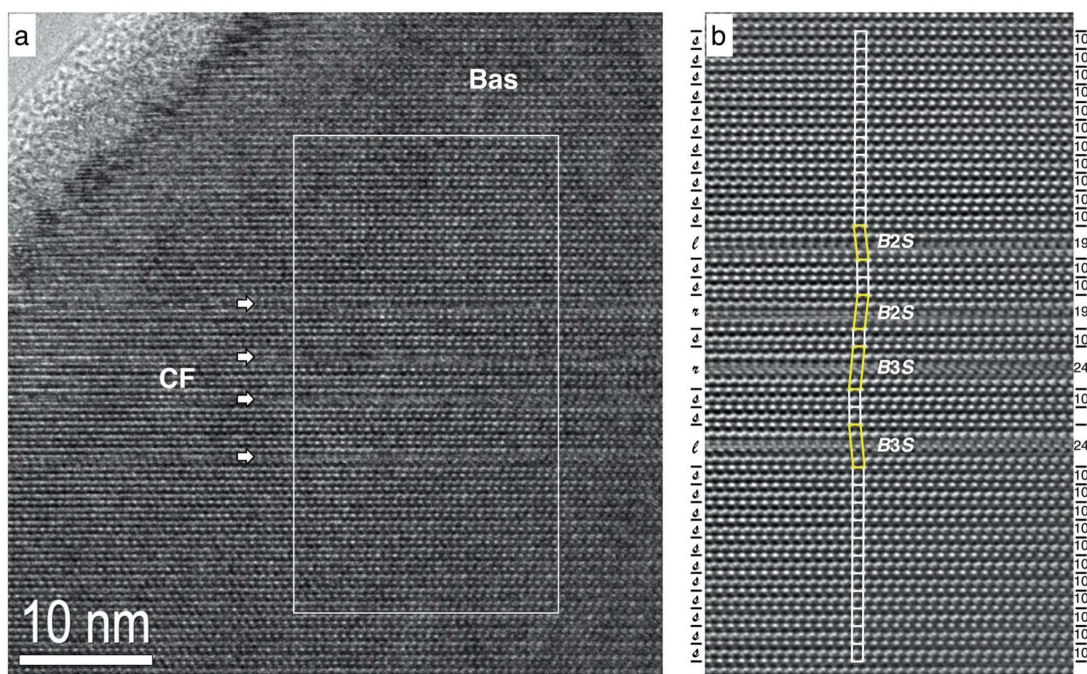


FIGURE 14. (a) HRTEM image of bastnäsite down [010] (SAED pattern similar to Fig. 8c) including some compositional faults (CF, arrows). (b) Fourier filtered image of the rectangular area in a. The unit-cell-scale analysis reveals that these CF can be explained by the insertion of single B_2S and B_3S slabs with thicknesses along c of ~ 19 and ~ 24 Å, respectively. Other than affecting the slab thickness (approximate values in Å on the right), the CF causes a shift on the (001) plane (s = straight, l = left, r = right shift). (Color online.)

Polysome detectability through electron-beam-related techniques

Although the nanoscale disorder can be overlooked, SEM-EDS is the fastest technique for polysome identification. TEM-EDS remains the ultimate technique for polysome identification; however, it is time-consuming and provides only local information. Since most high-resolution TEMs have a limited tilt range,

the sample needs to be pre-oriented before preparation; in this case, EBSD can be very useful. In this regard, EBSD can easily distinguish CRFC among other phases and correctly provides their orientation relationship; however, under routine application, it fails to distinguish between different polysomes.

At the TEM scale, other than basic CRFC, intermediate polytypes that have not yet been fully described in the literature

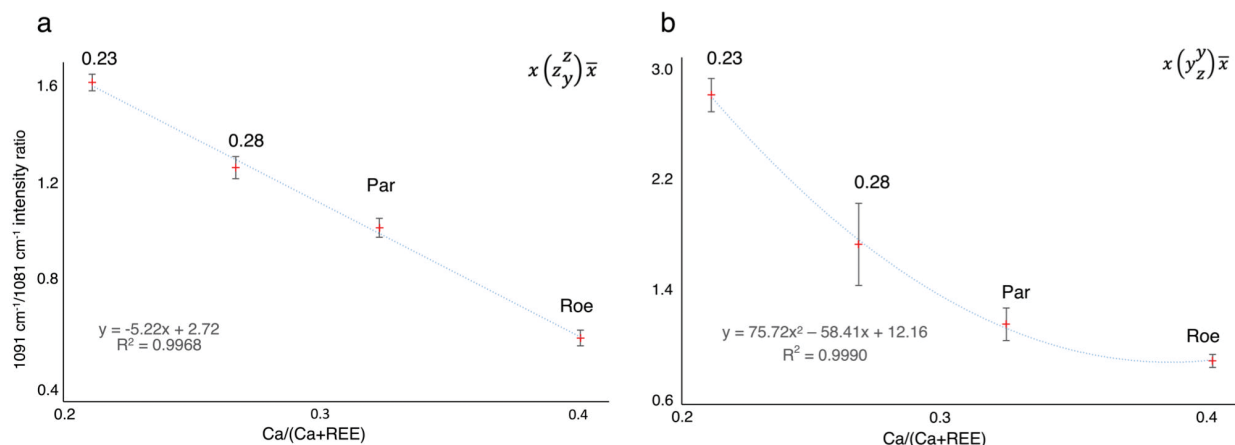


FIGURE 15. 1091 cm⁻¹/1081 cm⁻¹ Raman intensity ratio for röntgenite (Roe), parisite (Par), and B₂S for E // z(a) and E ⊥ z(b). (Color online.)

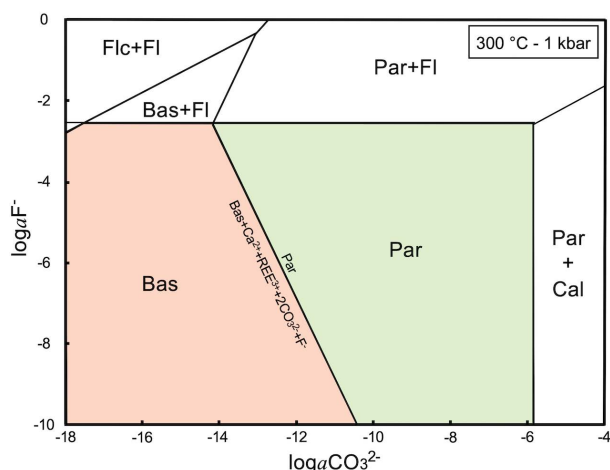


FIGURE 16. Calculated mineral–fluid equilibria at 300 and 1 kbar for the stability of bastnäsite-(Ce) and parisite-(Ce) as a function of aF^- and aCO_3^{2-} (Gysi and Williams-Jones 2015). (Color online.)

have been identified. Among these are a B₂S polysome, a 32 nm long-range polytype, and a new parisite polymorph with a doubled *c* parameter compared to the normal parisite. Further investigations are required for the full characterization of all these new structures.

IMPLICATIONS FOR REE ORE FORMATION

In principle, under equilibrium crystallization conditions, every single fluid composition falling within the bastnäsite-synchysite series can be accommodated by a proper proportion of *B* and *S* layers; therefore, this situation opposes the simultaneous crystallization of two similar phases of different compositions, as in the well-known case of the alkali feldspar system at high pressure (e.g., Winter 2001) when the fluid composition falls within the miscibility gap, promoting the simultaneous crystallization of a Na-rich and a K-rich feldspar upon cooling.

The inability of the system CeFCO₃-CaCO₃ to form solid solutions was considered a factor explaining the presence of syntactic intergrowths in CRFC (Donnay and Donnay 1953). One crystal precipitates until the conditions in the solution have changed sufficiently for the next compound to separate out, which then

crystallizes on the original crystal. Since the two species alternate, periodic and discontinuous changes in the conditions of the system must be postulated. Variations in the aCa^{2+} , $aREE^{3+}$, $a(CO_3)^{2-}$, aF^- , and *T* of the solution may well be the controlling factors during crystal growth (Gysi and Williams-Jones 2015). Therefore, it appears that syntactic intergrowths are the equivalent of zoning in crystal-chemical systems that cannot form solid solutions.

Bastnäsite-(Ce) and synchysite-(Ce) both occur at Mt. Malosa (Malawi), but in separate samples, i.e., they are never observed in contact. Moreover, the chemical composition is remarkably different in terms of REE partitioning, i.e., synchysite is richer in Y (and poorer in Ce, La, and Nd) than bastnäsite and all the other intermediate terms (Table 1; Online Materials¹ Table S1). This could indicate that synchysite formed under different time-space physicochemical conditions than the other polysomes.

The most recurrent microstructure in Mt. Malosa CRFC is represented by rhythmic parisite-bastnäsite intergrowths with several more or less ordered intermediate polysomes. This microstructure is similar to that of the Olympic Dam Australia deposit (Ciobanu et al. 2022); however, a clear trend of compositions varying gradually from a basic polysome to the next through disordered domains has not been observed at Mt. Malosa. The observed microstructure suggests a primary growth mechanism in which fluorocarbonates crystallize from a fluid close to thermodynamic equilibrium whose conditions quickly and repeatedly crossed the parisite–bastnäsite stability boundary rather than a stepwise approach toward the thermodynamic equilibrium.

According to Secco et al. (2007), the crystallization of CRFC at Mount Malosa occurred at ~1 kbar and 300–400 °C. These data are fully consistent with the mineral-fluid stability diagrams for the Ca-REE-C-O-H-F system of Gysi and Williams-Jones (2015). From these stability diagrams, it appears that the boundary between parisite–bastnäsite, which has a negative slope on the $\log aF^-$ vs. $\log a(CO_3)^{2-}$ diagram, can be easily crossed after small variations of either $a(CO_3)^{2-}$ or aF^- , thus representing the most probable reasons for the departure from equilibrium conditions. It should be noted, however, that an increase of $a(CO_3)^{2-}$ in the fluid (or aF^- , or both), for instance, would cause the crystallization of parisite at the expense of bastnäsite (Fig. 16). The protracting of this situation, however, would cause an increase of $aREE^{3+}$ in the remaining fluid, therefore realizing the conditions for the

crystallization of bastnäsite (or some other polysomes poorer in Ca than parisite). In other words, the crystallization itself may induce rhythmic changes in the fluid composition at the crystallization front leading to syntactic intergrowths, which therefore appear as an unavoidable fact in Ca-REE fluorcarbonates.

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