

Visible and short-wave infrared reflectance spectroscopy of REE fluorocarbonates

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ABSTRACT

An understanding of the mineralogy and petrogenesis of rare earth element deposits has significant implications for their economic viability. Lanthanide-bearing compounds are known to produce sharp absorption features in the visible to short-wave infrared region (VIS-SWIR), however, a significant knowledge gap exists between the fields of hyperspectral reflectance spectroscopy and rare earth element mineralogy. Reflectance spectra were collected from four bastnäsite samples, two parisite samples, and one synchysite sample from the visible into the short-wave infrared. These REE fluorocarbonate mineral samples were characterized via scanning electron microscopy and electron probe microanalysis. Sharp absorptions of REE-bearing minerals are mostly the result of $4f-4f$ intraconfigurational electron transitions and for the light REE-enriched fluorocarbonates, the bulk of the features can be ascribed to Nd^{3+} , Pr^{3+} , Sm^{3+} , and Eu^{3+} . The lanthanide-related spectral responses of the REE fluorocarbonates are consistent across the group, supporting the notion that the REE cation site is very similar in each of these minerals. Carbonate-related spectral responses differed between these minerals, supporting the notion that the crystallographic sites for the carbonate radical differ between bastnäsite, synchysite, and parisite. Exploitable spectral differences include a distinct absorption band at 2243 nm that separates bastnäsite from synchysite and parisite. Similarly, for bastnäsite a dominantly Pr^{3+} -related absorption band located is at 1968 nm, while in synchysite and parisite it occurs at 1961 nm.

Keywords: Mineral spectroscopy, rare earth elements, hyperspectral, bastnäsite, parisite, synchysite

INTRODUCTION

The mineralogy of rare earth element deposits is critical in understanding their petrogenesis and has significant implications for their economic viability. Rapid determination of ore modal mineralogy for these deposit types by hyperspectral reflectance spectroscopy would provide immediate feedback on the strength, type, and relevance of mineralization. Lanthanide-bearing compounds are known to produce sharp absorption features in the visible to short-wave infrared region (VIS-SWIR) and have been conventionally viewed as unchanging features in the field of remote sensing (e.g., Clark 1999); however, a significant knowledge gap exists between the fields of hyperspectral reflectance spectroscopy and rare earth element mineralogy.

The lanthanides (Ln) are a series of 15 elements belonging to the $4f$ block of the periodic table, and from lightest to heaviest are lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). In geological environments the lanthanides are commonly found together in their trivalent state, with the exception of divalent europium (Eu^{2+}) and sometimes tetravalent cerium (Ce^{4+}). The term “rare earth elements” (REE) comprises the lanthanides, commonly yttrium (Y) and sometimes scandium (Sc) due to similar chemical characteristics. Coordination states of the REE

cations in the assorted mineral structures can be quite variable (e.g., Miyawaki and Nakai 1996), ranging from a reasonably symmetrical 8-coordinated site in xenotime, to britholite with two distinct sites with coordination numbers of 7 and 9, and the REE fluorocarbonates with multiple bonding anions (oxygen and fluorine) with a coordination number of 9 ($6\text{O}+3\text{F}$).

The mineralogy of REE ore deposits is important because the metallurgy of only certain REE-bearing phases is well established. Namely, most global REE production is derived from REE fluorocarbonate minerals (e.g., bastnäsite, parisite, and synchysite), REE phosphate minerals (e.g., monazite and xenotime) and from ion-absorbed clays, however, recent advances have been made in the treatment of REE silicate mineral ore (e.g., eudialyte and britholite) (e.g., Mariano and Mariano 2012). Furthermore, REE deposits can show a complex mineral paragenesis with REE-mineral assemblages varying significantly across a single geological system. Consequently, there exists significant potential for reflectance spectroscopy to play an important role in the exploration and exploitation of REE ore deposits.

The objectives of this study are to present mineralogical characterization and reflectance spectra in the visible to short-wave infrared region of the main rare earth element fluorocarbonate minerals; bastnäsite, parisite, and synchysite. Following mineralogical and spectroscopic background of REE bearing minerals we provide a band registry for these minerals as well as interpretations of spectral absorption features related to the lanthanides. The spectral features of the registry will be the focus of further study in the development of hyperspectral reflectance

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imaging spectroscopy to carry out REE mineral identification, REE mineral abundance estimates and rare earth element abundance estimates.

GENERAL SPECTROSCOPY OF THE LANTHANIDES

The outer radius of the $4f$ electron shells (~ 0.3 Å) for the lanthanides is much less than that of their filled $5s$ and $5p$ shells (~ 2 and ~ 1 Å). It can then be approximated that the local electronic environment of Ln^{3+} cations interacts primarily with those outer shells, leaving the $4f$ electrons “relatively sheltered” but not completely non-participatory in bonding (e.g., Liu 2005). Electrostatic repulsion of the base ion generates a first level splitting of spectroscopic states, ^{2S+1}L (e.g., ^5I). Next, spin-orbit coupling splits these into multiplets, or “J-levels” (e.g., $^5I_8$), and once placed into a crystal field the J-levels are then split into “Stark Sublevels”. Crystal field interactions for the Ln cation include variables such as ligand type, coordination number, and polyhedron asymmetry, which all play a role in the location and intensity of energy levels and the associated absorption (Görlner-Walrand and Binnemans 1998). Each of the resulting sublevels provides the potential for promotion of a relaxed electron into an excited state, giving rise to absorption of electromagnetic radiation (e.g., light) at a specific energy level (e.g., wavelength).

The spectroscopy of REE-bearing phases is well established in the fields of physics and chemistry, however, the well-understood principles and well-studied doped compounds do not lend to direct translation into mineralogy and hyperspectral remote sensing. For example, the Dieke Diagram (Dieke et al. 1968) details intraconfigurational $4f$ - $4f$ transitions for “free ions” as deduced through studies of largely mono-lanthanide synthetic compounds, however, the transitions shown do not include splitting of energy levels due to a crystal field nor the complexities of naturally occurring REE minerals with variable REE distributions and other elemental substitutions. Consequently, this diagram and other band registries can only act as proxies to help identify origins of absorption features in reflectance spectra from minerals.

In general, and excluding other physical parameters such as grain size, the strength of absorption features by the lanthanides will be primarily a function of the concentration of the ion as well as the specific absorptivity of that ion’s intraconfigurational transitions within a given crystal structure. The location of lanthanide-related absorption features will be primarily a function of the cation’s specific coordination and asymmetry in the host crystal structure.

REVIEW OF REE-RELATED REFLECTANCE SPECTROSCOPY STUDIES

Few studies have been published addressing rare earth element bearing minerals and rocks in the field of reflectance spectroscopy. Surveys of carbonatites and alkaline intrusive complexes in the literature can be divided into coarse spectral resolution spaceborne studies (e.g., Oppenheimer 1998; Rowan and Mars 2003; Mars and Rowan 2011), fine spectral resolution airborne studies (e.g., Crowley et al. 1988; Rowan et al. 1995; Bowers and Rowan 1996; Bedini 2009), and fine resolution ground and lab-based studies (e.g., Rowan et al. 1986; McHugh et al. 2000). The early work by Rowan, Crowley, and Mars rec-

ognized the potential of exploiting REE absorption features with hyperspectral imaging, however, focus of their future research shifted to other geological systems, use of ASTER multispectral satellite imagery, and planetary remote sensing.

The studies with coarse resolution used ASTER imagery and were focused on lithological mapping via end-member extraction and band ratios. The general results are that lithologies of carbonatite complexes can be identified with moderate confidence using ASTER satellite data from areas with well-established geological maps (e.g., Khanneshin, Mountain Pass, Ol Doinio Lengai). Remote sensing using the finer resolution AVIRIS airborne system shows improved classification of rock types and even interpreted detection of REE from Mountain Pass (e.g., Crowley et al. 1988). Bedini (2009) investigated the REE-mineralized Sarfatoq carbonatite complex of Greenland using the HyMap airborne hyperspectral imager focusing on the classification of rock type and predictive mapping, however, there was no mention of any specific REE phases being detected from the airborne platform. Similar results were achieved by Bowers and Rowan (1996) at the Ice River Complex using AVIRIS data. Ground and laboratory based studies by Rowan et al. (1986) of four carbonatite hosted rare metal deposits focused on rock type classification and were able to discriminate between several carbonatite phases, as well as identify the sharp absorption features caused by Nd^{3+} in field samples. This earliest work is referenced in all of the above literature and has served as a base for the spectral classification of rock types at carbonatite and alkaline intrusive igneous complexes.

Early infrared spectroscopy investigations of carbonate minerals by Adler and Kerr (1963) included bastnäsite and parisite because of their distinct carbonate arrangements, but did not investigate the influence of the lanthanides and stopped short of the short-wave infrared region. The benchmark mineral spectroscopy paper of Hunt (1977) lists monazite (misspelled as monzonite) in his tabulation of common minerals and respective spectral signatures, however, La^{2+} is listed as the origin of absorptions but La would have 3+ valence in monazite and would therefore not have spectral features in the VIS-SWIR (e.g., Liu 2005). Clark (1999) covers several REE oxides in his Spectroscopy of Rocks and Minerals review and recognizes that the patterns seen in REE minerals are a combination of several lanthanides but states that absorptions are independent of mineralogy. Reflectance spectra in the VNIR-SWIR of bastnäsite and parisite with limited discussions have been presented by Kerr et al. (2011) and Morin Ka (2012), with both publications stating that REE signatures are present in these REE minerals and that more detailed documentation is warranted.

CRYSTAL STRUCTURE REVIEWS OF BASTNÄSITE, PARASITE, AND SYNCHYSITE

Bastnäsite, parisite, and synchysite are rare earth element fluorocarbonate minerals of economic significance in many REE deposits and occurrences. Bastnäsite, $CeCO_3F$, is the most commonly reported of these minerals, however, it is also the most familiar of the group. Synchysite, $CaCe(CO_3)_2F$, is the most Ca-enriched of the REE fluorocarbonates, sometimes forms euhedral prismatic crystals and is the second most reported. Parisite, $CaCe_2(CO_3)_3F_2$, can form distinct doubly terminated

pyramidal crystals and is the least reported of these rare earth fluorocarbonate minerals. Rontgenite, $\text{Ca}_2\text{Ce}_3(\text{CO}_3)_3\text{F}_3$, is another rare REE fluorocarbonate mineral with a similar structure but was not addressed in this study.

Total rare earth oxide (REE_2O_3) content increases from ~52 wt% in Ca-rich synchysite, to ~60 wt% in parisite and up to ~75 wt% in Ca-absent bastnäsité. These minerals show preference for the light rare earth elements (LREE) and have similar slopes and trends in chondrite-normalized diagrams. These three minerals are commonly found together, are structurally related, can show syntaxial intergrowth and are also commonly found together in secondary mineral mixtures.

Structurally, each of the phases can be assembled using a common set of building blocks (Ni et al. 1993), which include layers of CeF , CO_3 , and Ca. On an atom basis, bastnäsité is Ca-absent, parisite shows $\text{REE}:\text{Ca} = 2:1$ and synchysite shows $\text{REE}:\text{Ca} = 1:1$. Accordingly, the stacking order of the blocks gives rise to the different compositional proportions and mineral species (Fig. 1). Polytypism has been documented for these minerals (e.g., Meng et al. 2001). It is important to note that all of the REE will occur in the Ce site, but only Ce will be listed

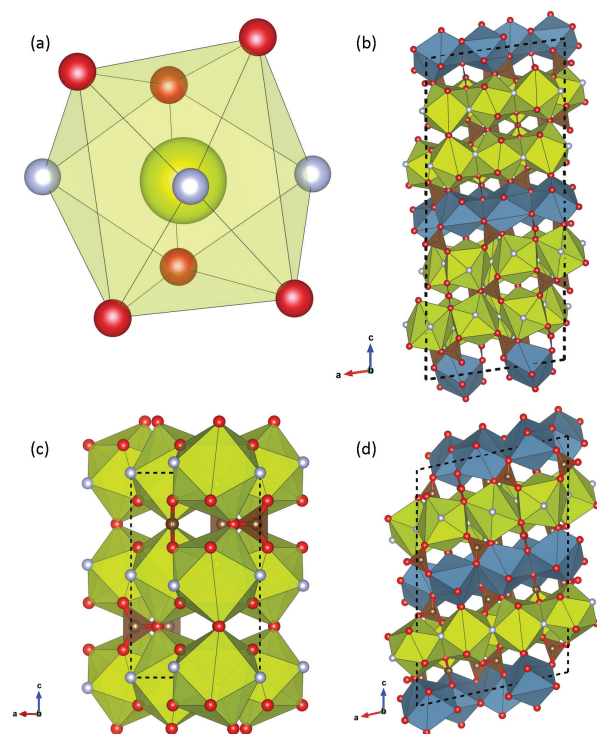


FIGURE 1. (a) Coordination polyhedron for the Ce1 site in parisite (Ni et al. 2000); also applicable to bastnäsité and synchysite. Ce1 (green) atom is coordinated with F1, F2, and F3 (lavender) atoms, whose plane is roughly perpendicular to *c*-axis, and 6 oxygen (red) atoms O11, O23, O32, O42, O53, and O61. Overall coordination number of 9 in a distorted tricapped trigonal prismatic arrangement. (b) Parisite crystal structure from Ni et al. (2000), (c) bastnäsité crystal structure from Ni et al. (1993), and (d) synchysite crystal structure from Wang et al. (1994). Atom coloring: red = oxygen, green = REE, lavender = F, brown = C. Polyhedra coloring: green = REEO_6F_3 , dark blue = CaO_8 , brown = CO_3 . (Color online.)

TABLE 1. Some basic properties of the REE fluorocarbonates

Mineral	Bastnäsité	Parisite	Synchysite
Reference	Ni et al. (1993)	Ni et al. (2000)	Wang et al. (1994)
Formula	REECO_3F	$\text{CaREE}_2(\text{CO}_3)_3\text{F}_2$	$\text{CaREE}(\text{CO}_3)_2\text{F}$
Symmetry	Hexagonal	Monoclinic	Monoclinic
Space group	$P6_2c$	Cc	$C2/c$
<i>a</i> (Å)	7.1175	12.305	12.329
<i>b</i> (Å)		7.1053	7.110
<i>c</i> (Å)	9.7619	28.25	18.741
β (°)		98.257	102.68
Structure			
REE coordination	9: 3×F, 6×O	9: 3×F, 6×O	9: 3×F, 6×O
REE site shape	tricapped trigonal	tricapped trigonal	tricapped trigonal
Number of unique REE cation sites	1	6	2
REE-O (Min, Å)	2.542	2.466	2.497
REE-O (Mean, Å)	2.571	2.564	2.558
REE-O (Max, Å)	2.591	2.631	2.619
REE-F (Min, Å)	2.403	2.370	2.376
REE-F (Mean, Å)	2.407	2.397	2.399
REE-F (Max, Å)	2.416	2.445	2.417
CO_3 influences	Each CO_3 layer influenced by REE only	3 distinct CO_3 layers, one influenced by REE only, two influenced by REE and Ca	Each CO_3 layer influenced by Ca and REE
Number of unique CO_3 polyhedra	1	9	3
Average C-O bond lengths (Å)			
CO_3 #1	1.287	1.2478	1.2817
CO_3 #2		1.2728	1.2854
CO_3 #3		1.2718	1.2752
CO_3 #4		1.2636 ^a	
CO_3 #5		1.2646 ^a	
CO_3 #6		1.2736 ^a	
CO_3 #7		1.3004	
CO_3 #8		1.2887	
CO_3 #9		1.2945	
Average CO_3 polyhedra <i>V</i> (Å ³)	0.0017	0.0223	0.0146
Average CO_3 polyhedra distortion index	0.0094	0.0282	0.0159
General chemistry			
REE_2O_3 wt%	73	59	51
CaO wt%	0	10.5	17
F wt%	5	4.5	2.6
CO_3 wt%	20	24	28

^a These CO_3 polyhedra in parisite are coordinated only to REE.

for brevity. Table 1 documents some basic crystallographic data for the REE fluorocarbonates.

In bastnäsité Ni et al. (1993) described the hexagonal crystal structure as being built by layers of REE-F alternating with layers of CO_3 in (0001) arrangement. There is one REE site, which is coordinated with 3 in-plane fluorine (F) atoms and two sets of 3 oxygen (O) atoms from bordering CO_3 layers. Bond lengths of REE with O are reported at 2.591, 2.542, and 2.579 Å while lengths with F are shorter and between 2.403 and 2.416 Å. The resulting 9-coordinated tricapped trigonal prismatic REE site is therefore asymmetrical with two distinct sets of bonding ligands and lengths.

Ni et al. (2000) studied the crystal structure of parisite and determined that, unlike bastnäsité, it is monoclinic. The structure was described as being built of two portions of bastnäsité layers connected by a Ca layer, stacked along the *c*-axis (i.e., CeF-CO_3 , CeF-CO_3 , Ca-CO_3). Coordination for REE is similar to bastnäsité ($3 \times \text{Ce-F}$, $6 \times \text{Ce-O}$) with Ce-O mean lengths between 2.55 and 2.57 Å and Ce-F means between 2.38 and 2.41 Å. Minimum and maximum Ce-O bond lengths are 2.47 and 2.63 Å, while

for Ce-F they are 2.37 and 2.45 Å. The resulting 9-coordinated tricapped trigonal prismatic REE site is therefore asymmetrical with two distinct sets of bonding ligands and lengths. The unit cell for parisite contains three carbonate radical layers, two of which are influenced by both the REE-F and Ca layers and one of which is influenced only by REE-F layers.

The crystal structure of synchysite, $\text{CaCe}(\text{CO}_3)_2\text{F}$, was investigated by Liben et al. (1994) and expanded upon by Ni et al. (2000). Synchysite is also monoclinic and is built by stacking layers of $\text{CeF}\cdot\text{CO}_3$ and $\text{Ca}\cdot\text{CO}_3$ in a one-to-one ratio along (001), making it the most Ca-rich member of the REE fluorocarbonate group. Coordination for REE is similar to bastnäsite and parisite ($3 \times \text{Ce-F}$, $6 \times \text{Ce-O}$) with Ce-O mean lengths between 2.557 and 2.567 Å and Ce-F means between 2.394 and 2.407 Å. Minimum and maximum Ce-O bond lengths are 2.50 and 2.62 Å, while for Ce-F they are 2.38 and 2.41 Å. The resulting 9-coordinated tricapped trigonal prismatic REE site is therefore asymmetrical with two distinct sets of bonding ligands and lengths. In the case of synchysite, the carbonate layer is now always influenced by bonding with both Ca and REE-F layers.

Each of the REE fluorocarbonate minerals hosts REE in ninefold tricapped trigonal prismatic coordination with 6 oxygen atoms at the apices of the prism and 3 fluorine atoms in planar configuration through the faces of the prism (Fig. 1). Minor differences in the bond lengths of REE-F and REE-O among the REE fluorocarbonates are reported in the literature, however, a significant difference between each of the minerals is the local environment surrounding the carbonate radical. In bastnäsite, the oxygen apices of the CO_3 radical interact only with REE cations both below and above the CO_3 plane. In parisite, two of the three repeating CO_3 layers interact with REE and Ca above and below the plane while the third repeating CO_3 layer interacts only with REE. For synchysite, the apices of the CO_3 radical always interact with both REE and Ca on either side of the plane. Consequently, bastnäsite and synchysite show only one configuration for cation bonding with the CO_3 radical, whereas parisite shows two configurations that are unevenly populated. Furthermore, the geometry of the CO_3 polyhedra is much more variable for parisite than for synchysite or bastnäsite (Fig. 2, Table 1).

The cation sites for REE in these minerals are very similar and one would therefore expect that the spectral features due to intraconfigurational electron transitions of the REE would also be very similar. It would then be expected that *variations between spectra of the same mineral* would be predominantly in the relative strengths of REE-specific absorption features while *variations of REE-related spectral features between the different minerals* might include slight shifts in the locations of REE-related absorption features as well as the strength of some of these features. The coordination environment of the carbonate radical is quite different for each of these minerals, relatively speaking, and one would expect to see a difference in the carbonate-related absorption features between the minerals. Other variables that may influence spectra include the signal to noise ratio of the spectral data, crystallographic orientation, variations in other trace elements, and possibly syntaxial intergrowths with other REE fluorocarbonates.

The infrared spectra of bastnäsite and parisite were presented in Adler and Kerr (1963). Bastnäsite is characterized by carbon-

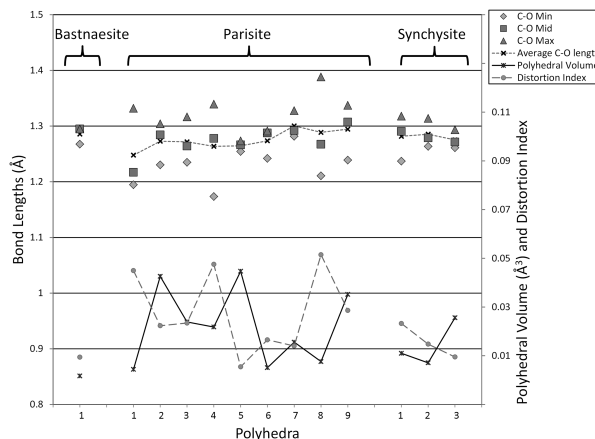


FIGURE 2. Bond characteristics for the CO_3 radical polyhedra in REE fluorocarbonate. Data from Table 1 and references therein, Min = minimum, Mid = middle, Max = maximum.

ate related absorptions common to what is seen in calcite and dolomite, however, the strongest features for bastnäsite are the $\nu_2(\text{CO}_3)$ and $\nu_3(\text{CO}_3)$ modes at 11.52 μm (868 cm^{-1}) and 6.93 μm (1443 cm^{-1}), respectively, and are asymmetric. The $\nu_2(\text{CO}_3)$ and $\nu_3(\text{CO}_3)$ modes in parisite are the most prominent and are located at 11.49 μm (870 cm^{-1}) and 6.90 μm (1449 cm^{-1}), respectively, and are asymmetric. Both the $\nu_2(\text{CO}_3)$ and $\nu_3(\text{CO}_3)$ absorption features are broader for parisite than for bastnäsite. For parisite Adler and Kerr (1963) also made note of the multiple non-equivalent carbonate radicals and observed doublets for the $\nu_1(\text{CO}_3)$ (9.19 and 9.27 μm , or 1088 and 1079 cm^{-1}) and $\nu_4(\text{CO}_3)$ (13.40 and 13.62 μm , or 746 and 734 cm^{-1}) vibrational modes while the $\nu_1(\text{CO}_3)$ and $\nu_4(\text{CO}_3)$ modes for bastnäsite occur at 9.21 and 13.74 μm (1086 and 728 cm^{-1}). Raman and infrared spectroscopy studies by Frost and Dickfos (2007) and Yang et al. (2008) revealed that OH stretching bands are present in most REE-fluorocarbonate samples studied, although the bands recorded are variable in number and position.

EXPERIMENTAL METHODS

Samples

Three bastnäsite samples were borrowed from the Canadian Museum of Nature's Mineral Collection (CMNMC) and were labeled as originating from Burundi (no. 39382), the Karonga Mine (Congo, no. 56255), and Madagascar (no. 50588). These samples were all single-crystal fragments, honey brown in color, and approximately 1 cm^3 . A fourth bastnäsite crystal sample from the Diao Lou Shan area in Sichuan (China) was obtained from A. Mariano, was light brown in color and measured $3 \times 3 \times 2\text{ cm}$. Two sample sets of parisite crystals from Snowbird (Montana, U.S.A.) and Muzo (Colombia) were obtained from A. Mariano. The Snowbird set comprised four euhedral elongate tapering prismatic crystal fragments, each approximately $1 \times 1 \times 2.5\text{ cm}$ and light gray-brown in color. The Muzo set comprised two euhedral tapering prismatic crystal fragments, each approximately $0.5 \times 0.5 \times 0.5\text{ cm}$ and golden brown with high translucency. Scanning electron microscopy (SEM) investigations showed that all the bastnäsite and parisite samples were not compositionally zoned, did not show syntaxy, and did not show any other mineral inclusions. Three samples of synchysite were studied, originating from Narsarsuk (Southwest Greenland, no. UBC-3376), the White Cloud Mine (Colorado, U.S.A.) and Morris County (New Jersey, U.S.A.). Both the White Cloud Mine (from CMNMC, no. 37320) and Morris County (from CMNMC, no. 37321) samples were fine grained and SEM investigations showed that the complex mineralogy was not suitable for baseline spectroscopic characterization.

studies. The Narsarsuk hand sample (from UBC Museum Collection) included a cluster of ~25 light brown elongate prismatic euhedral synchysite grains up to ~1 mm long, hosted on a feldspar-biotite dominated matrix. SEM examination and electron microprobe analyses (EMPA) data also revealed very minor amounts of ancyllite and an unknown REE-Ca-Sr-Ba phase. Reagent-grade lanthanide oxide powders and REE-doped spectralon wavelength calibration samples were also investigated to aid in band assignment.

Reflectance spectroscopy

Reflectance spectroscopy was primarily carried out using the *sisuROCK* instrumentation (manufactured by SPECIM Spectral Imaging Ltd.) at the University of Alberta's CoreSensing Facility, and data was handled using ENVI 4.4, a widely used and commercially available software package. Two imaging spectrometers ("cameras") acquired reflectance spectra in the visible-near infrared (VNIR, 396 to 1003 nm over 784 channels for an average spectral resolution of 0.77 nm) and short-wave infrared (SWIR, 928 to 2530 nm over 256 channels for an average spectral resolution of 6.26 nm) portions of the electromagnetic spectrum in high spatial resolution mode. Spatial resolution of the cameras in this mode was approximately 0.079 mm/pixel in the VNIR and 0.241 mm/pixel in the SWIR. Noise was very prevalent in the shortest wavelength portion of the VNIR camera below ~550 nm and moderate from 550 to ~650 nm. In the high spatial resolution mode, averaging ~16 pixels resulted in reliable spectra in the noisier ranges that would be useable in spectral libraries. Spectra presented originate from single crystals for parisite and bastnäsite. The synchysite spectrum is an aggregate of multiple single crystals. The euhedral crystals of bastnäsite from Sichuan, parisite from Muzo, and parisite from Snowbird were also large enough to permit imaging both parallel and perpendicular to the grains' *c*-axis. Spectra documented here are nominally an average of 2004 pixels for the VNIR camera and 1029 pixels for the SWIR camera. Samples were placed on a matte black surface that translates the samples under the camera and has very low reflectance across the sampled wavelength range. Some samples were propped up with foam blocks to ensure surfaces of interest faced the spectrometers. All samples were also substantially thick enough to assume the reflectance spectra are representative of the mineral target.

A TerraSpec Pro point spectrometer manufactured by Analytical Spectral Devices Inc. (ASD) was used in the earliest studies and records 2151 channels from 350 to 2500 nm, for a spectral resolution of ~1 nm. Spot size of the point spectrometer is approximately 1 cm in diameter, which significantly restricted the use of this instrument. Methodology of acquiring spectra followed the manufacturer's recommendation of ~30 s acquisition time with periodic dark-field and white reference spectralon panel normalization and wavelength calibrations using Ho, Er, and Dy doped spectralon samples (manufactured by Labsphere). Though the ASD instrument provided limited spectra (e.g., for bastnäsite from Mountain Pass), they were valuable for confidence in band assignment below 600 nm because of lower noise levels than using the *sisuROCK* system.

Averaged spectra from the imaging spectrometer were preferred over spectra from the spot spectrometer because some of the samples investigated had grain sizes smaller than were confidently resolvable by the point spectrometer. This allowed for non-destructive testing of mineral specimens and the ability to exclude spectral effects from other minerals that would have otherwise been in the field of view of the spot spectrometer. For larger single-crystal samples, a simple region of interest (ROI) was used to select the target mineral's pixels for averaging. For finer grained samples, a priori knowledge about the sample allowed several baseline spectra to be isolated from single pixels. These spectra were then used to run mixture tuned matched filtering within the ENVI software package on the entire scene, from which a strict qualitative threshold allowed a discrete selection of pixels to be averaged (see Fig. 3). Reflectance spectra did not have the continuum removed so as to present the data unmodified and to facilitate comparison against other earlier publications.

Scanning electron microscopy and electron microprobe analysis

The Philips XL30 scanning electron microscope (SEM) at the University of British Columbia, which is equipped with an energy-dispersion X-ray spectrometer (EDS), was used for preliminary examination of mineral mounts of selected minerals and rock fragments studied by reflectance spectroscopy.

Selected samples were then analyzed by electron microprobe at the Saskatchewan Research Council's Advanced Microanalysis Centre using a Cameca SX-100 equipped with 5 tunable wavelength dispersive spectrometers. Operating conditions were: 40° takeoff angle, beam energy of 15 keV, beam current of 20 nA, beam diameter of 5 µm. The MAN background intensity data was calibrated

and continuum absorption corrected. Elements were acquired using analyzing crystals: LLIF for FeK α , TaL α , PrL α , EuL α , DyL α , TmL α , MnK α , LaL α , NdL α , GdL α , HoL α , YbL α , BaL α , CeL α , SmL α , TbL α , ErL α , LuL α ; PET for CaK α , KK α , ClK α , TiK α , NbL α , YL α , SrL α , ZrL α , PK α , UMa, ThMa; and LTAP for MgK α , FK α , NaK α , SiK α , AlK α . Counting times were 10 s for Zr and P and 15 s for all other elements, with off peak count times of 10 s. The standards (with elements) were SPI-barite (Ba), SPI-celestite (Sr), SPI-YAG (Y, Al), Smithsonian Cr-augite (Mg, Ca), Smithsonian ilmenite (Fe, Ti), Smithsonian apatite (F, P), Smithsonian microcline (K), Smithsonian zircon (Zr), Harvard albite (Si, Na), Cameca Mn (Mn), SPI2-TiCl (Cl), SPI2-Nb (Nb), SPI2-La (La), SPI2-Ce (Ce), SPI2-Pr (Pr), SPI2-Nd (Nd), SPI2-Sm (Sm), SPI2-Eu (Eu), SPI2-Gd (Gd), SPI2-Tb (Tb), SPI2-Dy (Dy), SPI2-Ho (Ho), SPI2-Er (Er), SPI2-Tm (Tm), SPI2-Yb (Yb), SPI2-Lu (Lu), SPI2-Ta (Ta), SPI2-Th (Th), and SPI2-U (U). Amounts of CO₂ (as CO₃) and OH⁻ (as H₂O) were determined by stoichiometry based on 4, 11, and 7 anions for bastnäsite, parisite, and synchysite, and for full occupation of the F atomic site by F⁻, Cl⁻, and OH⁻.

RESULTS

Samples described here were selected from a larger set and were characterized by imaging reflectance spectroscopy, scanning electron microscopy and microprobe analysis. Several samples have spectra collected from a point spectrometer. Table 2 documents electron microprobe results for the REE fluorocarbonates in this study and Figure 4 shows chondrite-normalized patterns of the samples. Tables 3 and 4 document prominent absorption features for the REE fluorocarbonates and includes probable origins of the features, as chosen through comparison with reflectance spectra from unpublished reagent grade lanthanide oxide spectra, REE-doped calibration standard spectra, and other REE-bearing mineral spectra for which compositional data exists, as well as REE spectroscopy literature. The position and shape of these features were recorded using reflectance spectra (i.e., not continuum removed spectra). Tables 5 and 6 compare significant chemical and spectral differences among the bastnäsite and parisite sample sets, respectively, and include the number of pixels averaged from the *sisuROCK* imaging scenes by the VNIR and SWIR cameras. (Data sets available on deposit¹.)

Bastnäsite

Chemical variability among the four samples is moderate, with the samples from Burundi (no. 39382) and Karonga (no. 56255) showing greater amounts of heavier REE, such as Nd, Sm, and Gd (Table 2 and Fig. 4). None of the crystals show unusual concentrations of other cations or notable compositional zoning. Published analyses of bastnäsite from other localities are comparable to the samples analyzed here (e.g., Zaitsev et al. 1998; Holtstam and Andersson 2007).

Comparing the spectra (Fig. 5) of the four bastnäsite samples in both the VNIR and SWIR ranges, differences are primarily the relative strengths of absorption features generated by lanthanides. The sample from Sichuan is taken as the baseline because it shows the cleanest spectrum, is derived from the most number of pixels, and has supporting spectra from a point spectrometer. The sample from Madagascar shows the largest differences in that, in general, its features are more subdued than its peers. Spectra

¹ Deposit item AM-14-714, Data sets. Deposit items are stored on the MSA web site and available via the American Mineralogist Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

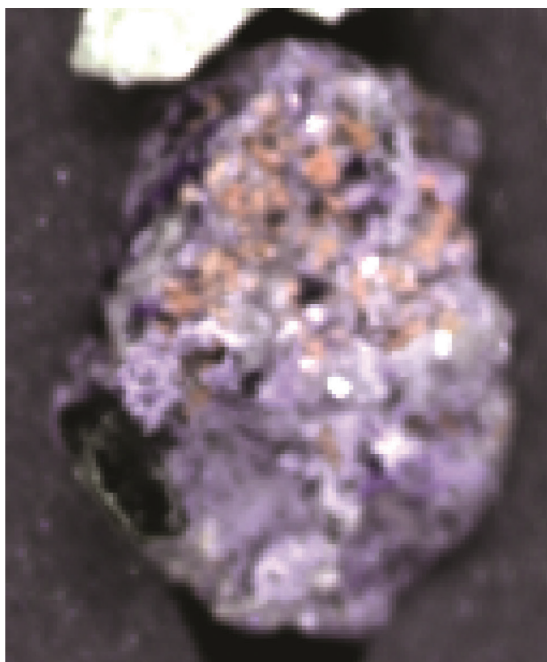
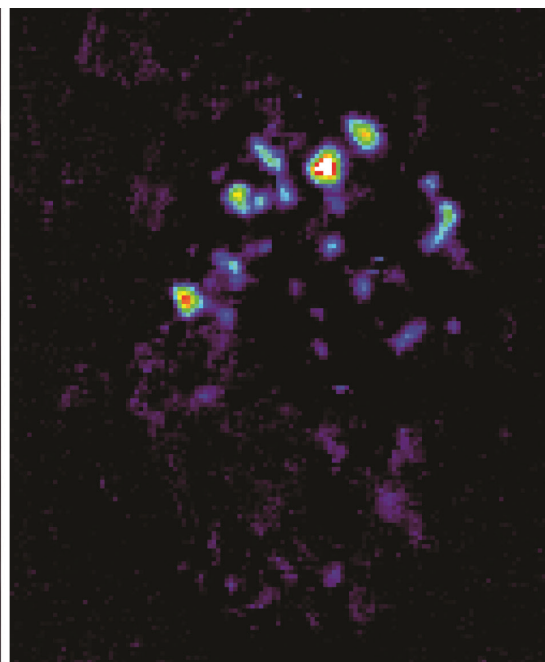
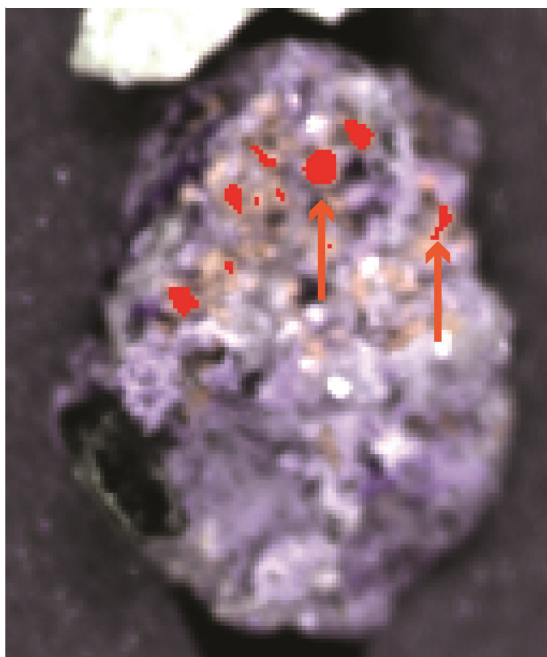
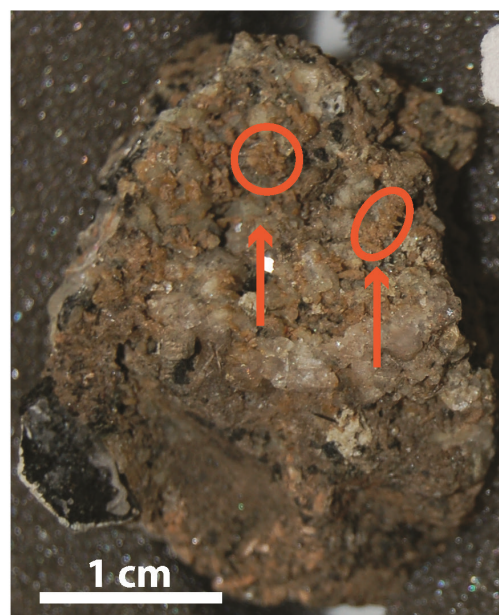
(a) SWIR False Color**(b) MTMF Value Color Ramp****(c) SWIR with ROI from MTMF****(d) Digital Photo**

FIGURE 3. (a) Hyperspectral imagery of the synchysite-bearing sample from Narsarsuk in the short wave infrared (SWIR). (b) Mixture tuned matched filtering (MTMF) results for synchysite in SWIR scene and (c) regions of interest (ROI) derived from thresholded MTMF results for generating an average spectrum. (d) Annotated digital photograph of the same sample from nominally the same perspective. Arrows in **c** and **d** point to the same patches of synchysite. Monomineralic patches of synchysite are on the order of 2 mm by 2 mm, large enough for successful imaging with a spatial resolution of 0.241 mm by 0.241 mm, to enable isolation of pure monomineralic pixels with confidence for averaging of their spectra. (Color online.)

TABLE 2. Average EMPA compositions of REE fluorocarbonate samples in wt%

Mineral Sample ID Locality	Bastnäsite Sichuan Diao Lou Shan, China		Bastnäsite 39382 Burundi		Bastnäsite 50588 Madagascar Congo		Bastnäsite 56255 Karonga, U.S.A.		Parisite Muzo Colombia		Parisite Snowbird Montana, U.S.A.		Synchysite UBC3376 Narsarsuk, Greenland		Detection limits
<i>n</i>	10	2σ	5	2σ	5	2σ	5	2σ	6	2σ	5	2σ	3	2σ	(average)
Nb ₂ O ₅	0.01	0.02	0.00	0.00	0.01	0.03	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.04
P ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.05	0.17	0.02
SiO ₂	0.05	0.01	0.11	0.02	0.06	0.00	0.11	0.01	0.06	0.01	0.08	0.08	0.38	0.52	0.01
ZrO ₂	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.03	0.00	0.00	0.00	0.00	0.01	0.03	0.04
UO ₂	0.53	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.13	0.34	0.19	0.00	0.00	0.07
ThO ₂	0.14	0.13	0.00	0.00	0.37	0.48	0.00	0.00	0.83	0.64	1.62	0.26	0.54	0.12	0.06
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.15	0.01
La ₂ O ₃	27.77	1.88	19.44	1.00	25.22	0.64	20.76	0.75	14.03	0.53	12.87	0.37	12.17	1.33	0.03
Ce ₂ O ₃	31.14	0.67	32.58	0.31	32.95	0.11	32.47	0.48	26.11	0.90	24.77	0.77	22.29	0.99	0.02
Pr ₂ O ₃	2.50	0.32	3.07	0.33	2.38	0.19	2.98	0.15	2.90	0.19	2.71	0.19	2.17	0.29	0.02
Nd ₂ O ₃	7.25	1.18	11.05	1.07	6.62	0.15	10.28	0.20	11.90	0.59	12.14	0.17	8.25	0.57	0.02
Sm ₂ O ₃	0.47	0.18	1.18	0.14	0.29	0.07	1.02	0.01	1.85	0.14	2.64	0.23	1.42	0.05	0.02
Eu ₂ O ₃	0.00	0.02	0.16	0.08	0.02	0.05	0.11	0.05	0.03	0.07	0.10	0.10	0.17	0.01	0.02
Gd ₂ O ₃	0.20	0.18	0.53	0.14	0.08	0.10	0.40	0.10	1.06	0.19	1.70	0.25	1.03	0.08	0.02
Tb ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.08	0.04	0.02	0.02
Dy ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.35	0.16	0.38	0.08	0.02
Ho ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.001	0.00	0.02
Er ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Tm ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Yb ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
Lu ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Y ₂ O ₃	0.01	0.03	0.17	0.12	0.01	0.01	0.11	0.06	0.74	0.32	1.69	0.13	1.47	0.53	0.04
SrO	0.01	0.04	0.02	0.06	0.08	0.13	0.02	0.05	0.00	0.00	0.00	0.00	0.22	0.36	0.03
MgO	0.00	0.00	0.02	0.02	0.01	0.02	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01
FeO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.43	0.01
CaO	0.11	0.10	0.00	0.00	0.05	0.02	0.00	0.00	10.48	1.06	10.23	0.16	16.49	2.69	0.01
Na ₂ O	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.01	0.10	0.04	0.01
Cl	0.01	0.02	0.08	0.02	0.06	0.02	0.08	0.04	0.02	0.01	0.02	0.01	0.12	0.05	0.01
F	5.22	0.42	4.42	0.22	4.56	0.15	4.27	0.23	4.48	0.20	4.12	0.57	2.87	1.04	0.02
CO ₂ ^a	18.86		18.36		18.32		18.35		24.2		24.46		27.26		
H ₂ O ^b	1.38		1.64		1.57		1.17		1.17		1.38		1.4		
-O=Cl	0.00		-0.02		-0.01		-0.02		0.00		0.00		-0.03		
-O=F	-2.20		-1.86		-1.92		-1.80		-1.89		-1.73		-1.21		
Total	93.50		90.96		90.73		90.32		98.37		99.51		97.80		
[REE+Y] ₂ O ₃	69.35		68.19		67.57		68.12		58.61		58.99		49.38		

Note: Ta, Ti, Mn, K, and Ba were sought but not detected.

^a Determined by stoichiometry, on the basis of 4, 11, and 7 anions, respectively.

^b H₂O calculated assuming ideal occupation of "F" site (F, Cl, OH).

were collected both perpendicular and parallel to the *c*-axis for the Sichuan sample, however, no differences were noted.

Parisite

Chemically, the Snowbird sample shows a greater proportion of heavy rare earth elements (Table 2 and Fig. 4) and especially thorium than the sample from Muzo and neither shows notable compositional zoning. Published analyses of parisite from other localities are comparable to the samples analyzed here (e.g., Zaitsev et al. 1998; Ni et al. 2000).

Spectra of the two samples show strong similarities (Fig. 6) with variations predominantly in the strength of absorption features and relative depths between specific features. Spectra from Muzo samples also show narrower absorption features. Spectra were collected both perpendicular and parallel to the *c*-axis for both parisite samples, however, no differences were noted.

Synchysite

Three samples of synchysite were studied, however, only the sample from Narsarsuk (Greenland) produced reliable and unambiguous spectra. Spectra indicative of REE-fluorocarbonates could be resolved from the White Cloud Mine (Colorado, U.S.A.) and Morris County (New Jersey, U.S.A.) samples, however, SEM investigations of both revealed complex REE

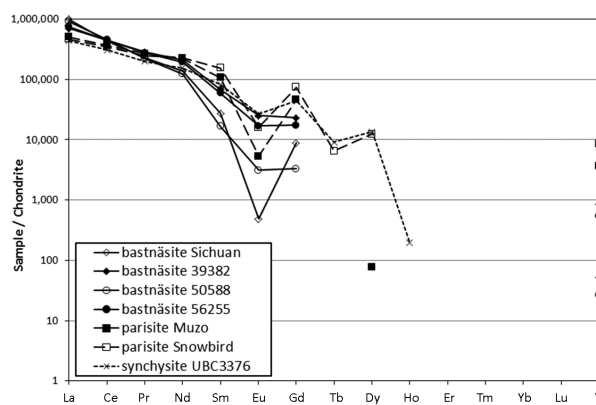
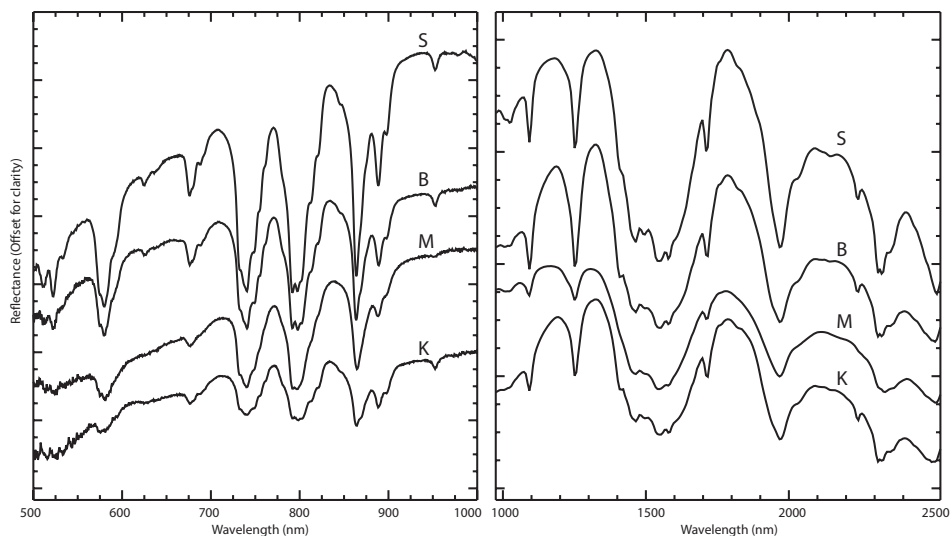
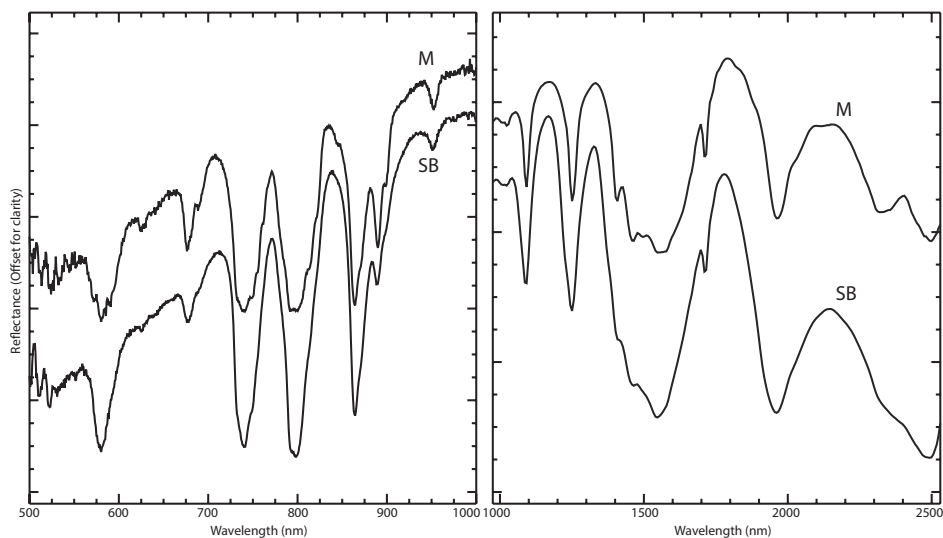


FIGURE 4. Chondrite-normalized REE plot from microprobe results. Normalization values from McDonough and Sun (1995). Er, Tm, Yb, and Lu are below detection for all samples.

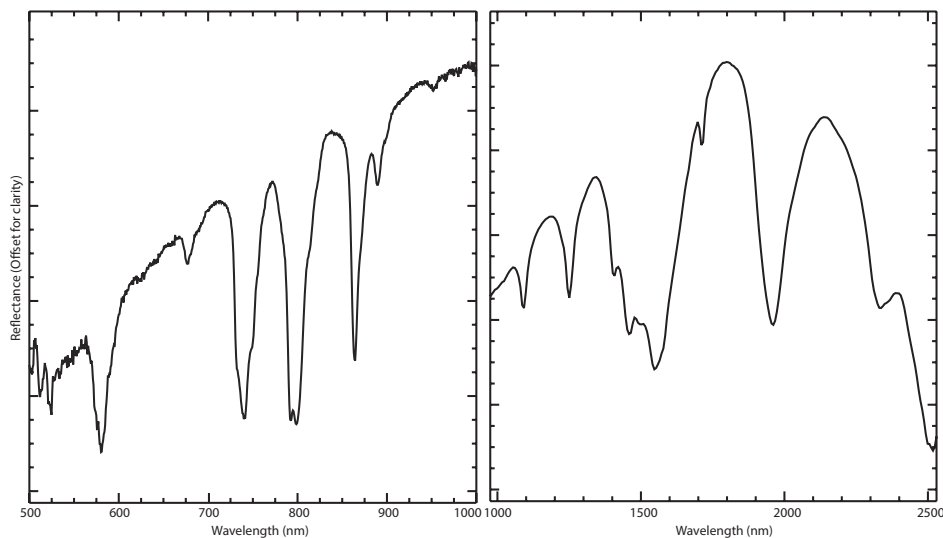
mineralogy, including synchysite, and very fine-grained material. Consequently only the Narsarsuk sample is suitable for baseline characterization and discussed in detail. Microprobe results are in accordance with other published analyses (e.g., Förster 2001; Guastoni et al. 2009).



◀ **FIGURE 5.** Stacked spectra of bastnaesite in VNIR (left, 500 to 1000 nm) and SWIR (right, 975 to 2530 nm) from the two sisuROCK instrument cameras. Spectra from top to bottom: Sichuan (S), Burundi (B), Madagascar (M), Karonga (K).



◀ **FIGURE 6.** Stacked spectra of parisite in VNIR (left, 500 to 1000 nm) and SWIR (right, 975 to 2530 nm) from the two sisuROCK instrument cameras. Spectra from top to bottom: Muzo (M), Snowbird (SB).



◀ **FIGURE 7.** Spectra of synchysite from Narsarsuk in VNIR (left, 500 to 1000 nm) and SWIR (right, 975 to 2530 nm) from the two sisuROCK instrument cameras.

The VNIR and SWIR spectra included 1651 and 175 pixels, respectively. The spectrum (Fig. 7) of the Narsarsuk sample is dominated by the high relative concentrations of spectrally active lanthanides and resembles spectra of bastnäsite and parisite. Synchysite shows carbonate related minima at 2337 and 2518 nm with a shoulder at 2499 nm.

DISCUSSION ON THE SPECTRAL VARIABILITY OF REE-FLUOROCARBONATE MINERALS

The reflectance spectra from samples of bastnäsite, parisite, and synchysite, all members of the REE-fluorocarbonate mineral group, are consistent among their respective mineral species. The location of absorption features related to the lanthanides will be a function of the specific REE coordination and asymmetry of crystal structure; because all three minerals have very similar cation sites for the REE consistent patterns were observed. As alluded to in the review of these minerals' crystal structures, the differences in coordination of the CO₃ radical result in the greatest distinction between the REE fluorocarbonates.

In general, 15 “clusters” of spectral features are present between 500 and 2500 nm in bastnäsite, the REE-fluorocarbonate with the highest concentration of REE and simplest crystal structure. Spectra from parisite and synchysite show strong similarities to bastnäsite spectra, however, noise at shorter wavelengths reduces confidence in this region for these two minerals. Tables 3 and 4 document resolvable absorption features of the fluorocarbonates based primarily on spectra from the Sichuan (bastnäsite), Snowbird (parisite), and Narsarsuk (synchysite) localities. Figures 8 and 9 show representative VNIR and SWIR spectra of bastnäsite, parisite, and synchysite with bolded index lines and approximate full-width at half max regions for the dominant absorptions of each group. Probable origins for absorptions are described in Tables 3 and 4.

TABLE 3. Prominent absorption features of the REE fluorocarbonates in the VNIR range

Group	Bastnäsite		Parisite		Synchysite		Probable origin
	λ (nm)	Shape	λ (nm)	Shape	λ (nm)	Shape	
1	500	MIN	501	MIN-n	503	MIN-n	Nd ³⁺
	511	MIN	510	MIN-n	512	MIN-n	Nd ³⁺
	523	MIN	523	MIN	525	MIN-n	Nd³⁺
	533	MIN-w	533	MIN-n	534	MIN-n	Nd ³⁺ >Eu ³⁺
	545	SH	545	SH-n			Nd ³⁺
2	557	MIN-w					Sm ³⁺
	575	SH	574	SH-n	576	SH-n	Nd ³⁺
	580	MIN-st	580	MIN-st	580	MIN-st	Nd³⁺
3	595	SH	595	SH	595	SH	Nd ³⁺ >Pr ³⁺
	625	MIN	625	MIN-w	625	MIN-w, n	Nd³⁺
	636	MIN-w	637	MIN-w, n			Nd ³⁺
4	642	SH-w					Nd ³⁺
	676	MIN	676	MIN	678	MIN	Nd³⁺
	681	SH	681	MIN-w, n	680	SH	Nd ³⁺
	689	MIN-w	689	MIN-w	691	SH	Nd ³⁺
5	693	SH					Nd ³⁺
	734	SH	732	SH	732	SH	Nd ³⁺
	738	SH	738	SH	738	SH	Nd ³⁺
	741	MIN-st	741	MIN-st	740	MIN-st	Nd³⁺
	749	MIN-w	749	SH	749	SH	Nd ³⁺
	755	SH	755	SH	756	SH	Nd ³⁺
	761	SH	762	SH	762	SH	Nd ³⁺
	768	SH	770	SH	770	SH	Nd ³⁺
6	781	SH	781	SH	780	SH	Nd ³⁺
	784	SH-w	784	SH-w	784	SH-w	Nd ³⁺
	792	MIN-db	792	MIN-db	792	MIN-db	Nd³⁺
	797	MIN-db	798	MIN-db	799	MIN-db	Nd³⁺
	803	SH	804	SH	804	SH	Nd ³⁺
	813	SH	813	SH	813	SH	Nd ³⁺
	821	SH	822	SH	822	SH	Nd ³⁺
7	845	SH	845	SH			Nd ³⁺
	864	MIN-st	864	MIN-st	864	MIN-st	Nd³⁺
	871	SH	871	SH	871	SH	Nd ³⁺
	889	MIN	889	MIN	889	MIN	Nd³⁺
	898	MIN-w	899	SH	899	SH	Nd ³⁺
8	953	MIN	953	MIN	953	MIN-w	Sm³⁺
	978	MIN-w	978	SH-w			Nd ³⁺ >Pr ³⁺

Notes: Bold values are indexed on Figure 8. Shape and modifier abbreviations: MIN, local minimum; SH, shoulder; -n, noisy; -w, weak; -st, strong; -db, doublet.

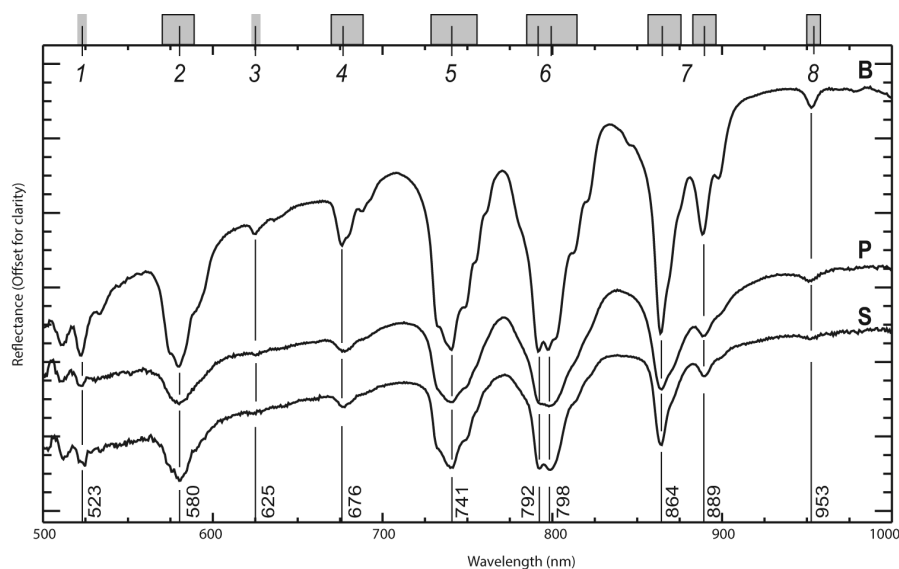


FIGURE 8. VNIR (500 to 1000 nm) spectra of bastnäsite (B, top), parisite (P, middle) and synchysite (S, bottom). Italic numbers denote groups with probable origin described in Table 3. Lines denote prominent absorption features with wavelength position, shaded boxes represent the approximate full-width at half max for each absorption or absorption cluster, borderless box indicates narrow feature. Stacked spectra from sisuROCK instrument.

TABLE 4. Prominent absorption features of the REE fluorocarbonates in the SWIR range

Group	Bastnäsité		Parisite		Synchysite		Probable origin
	λ (nm)	Shape	λ (nm)	Shape	λ (nm)	Shape	
9	1004	MIN-w	1004	SH-w	998	SH-w	Pr ³⁺
	1023	MIN	1023	MIN-w	1023	SH	Pr ³⁺
	1093	MIN-st	1093	MIN-st	1093	MIN-st	Sm³⁺
10	1225	SH-w	1225	SH-w	1225	SH-w	Sm ³⁺
	1251	MIN-st	1251	MIN-st	1251	MIN-st	Sm³⁺
	1314	SH-w	1314	SH-w	1301	SH-w	Pr ³⁺ ?
11	1408	SH	1408	MIN-w	1408	MIN-w	H ₂ O
	1465	MIN	1465	MIN	1459	MIN	Pr ³⁺
	1496	MIN-w	1496	MIN-w	1496	MIN-w	Pr ³⁺ >Sm ³⁺
	1547	MIN-st	1547	MIN	1547	MIN-st	Pr ³⁺ >Sm ³⁺
	1578	MIN	1578	SH	1578	SH	Pr ³⁺ >Sm ³⁺ >Nd ³⁺
	1666	SH-w	1666	SH-w	1666	SH-w	Nd ³⁺
	1710	MIN	1710	MIN	1710	MIN	Nd ³⁺
	1742	SH-w	1742	SH-w	1742	SH-w	Nd ³⁺
	1761	SH-w	1767	SH-w	1767	SH-w	Nd ³⁺
	1817	SH-w	1817	SH-w	1817	SH-w	Nd ³⁺
12	1886	SH-w	1880	SH-w			Pr ³⁺ ?
	1943	SH-w					Pr ³⁺
	1968	MIN-st	1961	MIN-st	1961	MIN-st	Pr ³⁺ >Sm ³⁺ & H ₂ O
	2037	SH	2037	SH-w	2037	SH-w	Pr ³⁺ >Eu ³⁺
	2112	SH-w	2118	SH-w	2105	SH-w	CO ₃ ?
	2143	MIN-w	2143	SH-w			Pr ³⁺
13	2243	MIN-st	ABSENT	ABSENT	ABSENT	ABSENT	CO ₃
14	2312	MIN-db	2312	SH	2312	SH-w	CO ₃ >Pr ³⁺ >Nd ³⁺ >Sm ³⁺
	2324	MIN-db	2324	MIN / SH	2337	MIN	CO ₃ >Pr ³⁺ >Nd ³⁺ >Sm ³⁺
	2355	SH	2355	SH-w	2368	SH-w	CO ₃ >Pr ³⁺ >Nd ³⁺ >Sm ³⁺
			2393	SH-w	2393	MIN-w	CO ₃
15	2437	SH	2443	SH-w			CO ₃ >Pr ³⁺ >Nd ³⁺ >Sm ³⁺
	2480	SH-w	2474	SH	2474	SH-w	CO ₃
	2499	SH-w	2499	MIN	2499	SH	CO ₃
	2518	MIN	2518	SH-w	2518	MIN	CO ₃

Notes: Bold values are indexed on Figure 9. Shape and modifier abbreviations: MIN, local minimum; SH, shoulder; -n, noisy; -w, weak; -st, strong; -db, doublet.

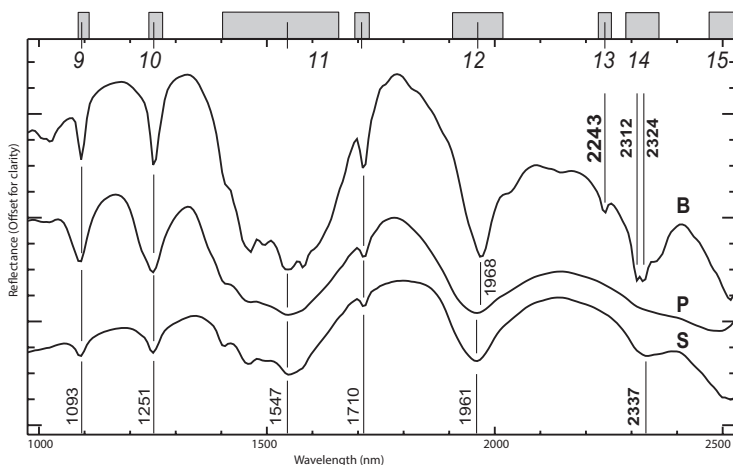


FIGURE 9. SWIR (975 to 2530 nm) spectra of bastnäsité (B, top), parisite (P, middle), and synchysite (S, bottom). Italic numbers denote groups with probable origin described in Table 4. Lines denote prominent absorption features with wavelength position, shaded boxes represent the approximate full-width at half max for each absorption or absorption cluster, borderless box indicates narrow feature. Stacked spectra from sisuROCK instrument.

Intraconfigurational 4f-4f electronic transitions

The REE-related absorptions in the VNIR-SWIR for these LREE-enriched minerals can be largely attributed to Pr³⁺, Nd³⁺, and Sm³⁺, with Eu³⁺ having much less influence. Y³⁺, La³⁺, and Lu³⁺ do not have free electrons in the *f* orbitals to generate absorptions, and absorptions related to Ce³⁺ do not fall within the VNIR-SWIR range. Similarly, Gd³⁺ shows absorptions at too high of energy levels, and Dy³⁺, Tb³⁺, Ho³⁺, Er³⁺, Tm³⁺, and Yb³⁺ are either too low in concentration and/or overlapping with other stronger absorption bands to have a noticeable effect in the spectra of the studied minerals.

Most differences between the REE fluorocarbonate mineral

spectra are small shifts in the location of the absorption minima or apparent strengths of overlapping absorptions represented as shoulders or weak local minima. Most of the differences in absorption minima locations are usually on the scale of one or two spectral channels suggesting that in some cases it may be the result of noise or a function of spectrum slope. Noise at shorter wavelengths in spectra from the sisuROCK imaging spectrometer precludes delineation of some features below ~650 nm, however, data from the ASD point spectrometer with greater signal to noise performance supports subtle features from 650 nm down to 450 nm. Better resolution of local minima as opposed to overlapping absorptions or shoulders in spectra is primarily observed for bast-

TABLE 5. Significant chemical and spectral differences between bastnäsite samples

Sample	VNIR pixels	SWIR pixels	Notes
Diao Loa Shan – Sichuan, China	5715	4379	Chemically, shows intermediate values for REE. Spectrally, shows the most resolved features in the VNIR.
Burundi	2312	173	Chemically, shows the highest values for heavier REE, such as Gd. Spectrally, is very similar to the Sichuan sample. The 1093 nm and 1251 nm absorptions (Sm ³⁺ related) are particularly pronounced in the suite, which is correlative with this sample having the highest Sm content. Accordingly, the Sm ³⁺ related 1408 nm feature is represented as a local minimum rather than a shoulder.
Madagascar	613	387	Chemically, shows higher La and Ce but lower middle REE within the bastnäsite suite. Spectrally, it generally shows subdued REE absorptions as compared to other samples. However, a significant difference is that the carbonate related 2243 nm and 2312/2324 nm doublet features are very subdued.
Karonga Mine, Congo	1341	135	Chemically, shows intermediate values for REE with a greater abundance of middle REE than the Sichuan sample. Spectrally, it is similar to the Burundi sample with respect to the 1093, 1251 and 1408 nm Sm ³⁺ features, however, it displays less resolved Nd ³⁺ -related features at 741, 792/797, and 864 nm.

TABLE 6. Significant chemical and spectral differences between parisite samples

Sample	VNIR pixels	SWIR pixels	Notes
Muzo, Colombia	265	162	Chemically, more enriched in La, Ce and Pr. Spectrally, tends to show better resolved and narrower features than for the Snowbird sample.
Snowbird, U.S.A.	2130	1790	Chemically, shows greater values for heavier REE, from Nd to Lu, but is still LREE-enriched. Spectrally, it shows broadened features and finer structure is generally subdued (e.g., clusters near 580 and 1500 nm). The carbonate-related features near 2324 and 2474 nm are also less resolved. The sample's greater amount of Th will have subjected these crystals to greater radioactivity, which might contribute to broadening of spectral features as the crystal loses crystallinity.

näsite over synchysite and parisite, likely because of the greater concentration of REE in the Ca-absent bastnäsite. For example, the local minima at 689 and 898 nm (Fig. 8) are generally better defined in the bastnäsite samples, and two resolved absorptions are prevalent with minima at 1547 and 1578 nm (Fig. 9). Parisite from Muzo and synchysite from Narsarsuk do, however, show more resolved features than parisite from Snowbird near 676, 889, and 1547 nm (Figs. 6 and 7). Bastnäsite consistently shows a deep and relatively broad absorption centered at 1968 nm, while parisite and synchysite both show the minimum of this absorption at 1961 nm. A water combination band occurs in this region and likely plays a role, however, Pr³⁺ also exhibits a strong absorption here. This wavelength shift is consistent with Görrler-Walrand and Binnemans (1996) listing this intraconfigurational transition (excitation from ground to the ⁷F₂ multiplet) as being particularly sensitive to the crystal field.

Vibrational bands of the carbonate radical

The most important observation among the spectra of REE fluorocarbonates is that a distinct absorption at 2243 nm (4458 cm⁻¹) distinguishes bastnäsite from parisite and synchysite, neither of which have this feature (Fig. 8). Bastnäsite also shows a well-resolved doublet with absorption bands at 2312 and 2324 nm (4325 and 4303 cm⁻¹), a shoulder at 2355 nm (4246 cm⁻¹) and an additional band at 2518 nm (3971 cm⁻¹). Notable is that the bastnäsite sample from Madagascar only shows a weak shoulder at 2243 nm and at present the reason for this is uncertain (Fig. 5). It is possible that structurally bound hydroxyl present in the bastnäsite samples may be the origin of the 2243 nm feature, however, the same substitution of fluorine could be said for both parisite and synchysite and neither show this absorption. Furthermore, EMPA composition of the Madagascar sample does not suggest it as being OH-absent and F-rich. Moreover, our unpublished spectra of uncharacterized bastnäsite from other localities do show the

2243 nm absorption feature.

Both parisite and synchysite have broader absorption features that are likely related to the carbonate radical. Parisite shows a weak absorption band at 2324 nm (4303 cm⁻¹) and another near 2499 nm (4002 cm⁻¹) (Fig. 9). Synchysite shows a more resolved absorption band at 2337 nm (4279 cm⁻¹) and another at 2518 nm (3971 cm⁻¹).

Spectral effects of the actinides

Most REE minerals will also host the actinide elements Th⁴⁺ and U⁴⁺. The electronic structure of Th⁴⁺ is similar to La³⁺, and so has no spectral response related to *f*-orbital transitions. Tetravalent U has a similar structure to Pr³⁺ and Binnemans et al. (1999) show that although similar, U⁴⁺ shows stronger but broader absorption features than Pr³⁺ because the 5*f* electrons are less efficiently shielded in actinides than the 4*f* electrons in lanthanides. Dominant absorptions of U⁴⁺ have been recorded near ~1111 nm (~9000 cm⁻¹) and ~666 nm (15 000 cm⁻¹). For the REE fluorocarbonate minerals studied here, Th and U contents were low enough that no actinide-related spectral features were observed. Unpublished spectra of Th-U-bearing zircon do, however, show spectral features in these regions.

IMPLICATIONS

The REE are strategic elements in many high-tech industries due to their special properties in permanent magnets, metal alloys, catalysts, and phosphors, among other applications. Recent volatility in supply and demand has increased exploration in North America for these critical elements but ore mineralogy can be significantly variable, with significant implications for later beneficiation (e.g., Mariano and Mariano 2012).

The reflectance spectra of bastnäsite, parisite, and synchysite presented and discussed here form the first systematic spectral characterization and comparison of these three important REE minerals. Their spectra are feature-rich, distinct, and comprise

many narrow overlapping absorption bands that can be mostly attributed to 4*f*-4*f* intraconfigurational electron transitions of Nd³⁺, Pr³⁺, and Sm³⁺, and possibly Eu³⁺.

Consistent lanthanide-related spectral responses of the REE fluorocarbonates support the notion that their REE cation site is very similar. Variations in these consistent lanthanide-related responses suggest REE concentration information could be extrapolated from reflectance spectra. Variable carbonate-related spectral responses support the notion that the crystallographic sites for the carbonate radical differ between bastnäsité, synchysite, and parisite.

Exploitable differences for mineral identification using hyperspectral imaging include the carbonate-related absorption at 2243 nm for bastnäsité, as well as a resolved doublet with minima at 2312 and 2324 nm. Synchysite shows a carbonate-related minimum at 2337 nm and parisite shows a less-resolved carbonate-related minimum near 2324 nm. A Pr³⁺ and water related absorption is exhibited at 1968 nm for bastnäsité while in synchysite and parisite it occurs at 1961 nm. Collectively, the spectral patterns of this mineral grouping are distinct from other REE minerals phases, such as monazite, xenotime, and eudialyte, among others.

This work starts to address the knowledge gap that exists between reflectance spectroscopy and rare earth element mineralogy and future research will include continued characterization and comparison of other important REE-bearing minerals. Accordingly, although hyperspectral remote sensing is becoming increasingly prevalent in the mining and mineral exploration industries, its adoption into REE-focused programs could be of particularly great benefit, such as in defining and assessing ore mineralogy or rapidly logging diamond drill core. Incorporating these spectra into larger spectral databases harnessed by various users will also facilitate the identification of REE fluorocarbonate minerals that may have otherwise gone unnoticed.

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