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Visible and short wave infrared reflectance spectroscopy of REE phosphate minerals

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ABSTRACT

Reflectance spectroscopy in the visible to short-wave infrared regions (500 nm to 2500 nm) was
carried out using natural samples of the rare earth element (REE) phosphate minerals monazite,
xenotime and britholite. Samples were characterized by scanning electron microscopy and electron
microprobe analysis. Absorption band positions were recorded with their probable origins, and spectral
variability amongst the samples is discussed. Spectral features of these minerals are driven primarily by
$4f$-$4f$ intraconfigurational electronic transitions of trivalent lanthanides. The distinct REE distributions of
monazite, xenotime and britholite drive their bulk spectral patterns, which in turn are sufficiently distinct
to enable spectral classification. Spectral variability of some specific REE-related absorptions are
interpreted to be driven by differences of the coordination polyhedra for the lanthanide cations between
the crystal structures. Spectra of these minerals were also compared against carbonatite-hosted REE
bearing fluorapatite. The work presented here strengthens the growing foundation for the interpretation
of reflectance spectra of these REE phosphate minerals and enables exploitation of the observed features

24   by the remote sensing community for detection, identification and quantification of REE phosphate

25   minerals. This is especially relevant for hyperspectral imaging spectroscopy with high spatial resolution,

26   where the spectral response of a pixel becomes increasingly dominated by mineralogy.

27   **INTRODUCTION**

28   The rare earth element (REE) -bearing phosphate minerals monazite, xenotime and britholite are

29   important phases in certain REE deposits and can also be important for geochronology. Monazite and

30   xenotime are found in a wide range of rocks, whereas britholite is more commonly restricted to alkaline

31   igneous complexes, although its distribution is comparatively less well documented. Fluorapatite is a

32   common accessory mineral in many rocks and is also a common host to minor amounts of REE,

33   sometimes reaching substantial concentrations (e.g., up to ~19 wt. % REE_2O_3 at Pajarito Mountain,

34   Roeder et al 1987, Hughes et al. 1991).

35   Monazite, LnPO$_4$, is composed primarily of the light rare earth elements (LREE) from La

36   through to Gd. Xenotime, also LnPO$_4$, is composed primarily of the heavy rare earth elements (HREE)

37   from Gd through to Lu and including Y. Despite their similar compositions, monazite and xenotime

38   crystallize in different space groups. Monazite is monoclinic ($P2_1/n$) and xenotime is tetragonal

39   ($I4_1/amd$), in part due to the decreasing ionic radii of the lanthanides from La to Lu and the resulting

40   effect on the coordination polyhedra of the Ln^{3+} and the overall crystal structure. Britholite-(Ce) has the

41   general formula $(Ce,Ca)_5(SiO_4)_3(OH)$ and has been reported with both hexagonal and monoclinic

42   symmetry, however, Oberti et al. (2001) suggest the correct space group is $P6_3$. Fluorapatite,

43    $Ca_5(PO_4)_3F$, accepts REE^{3+} in place of Ca^{2+} and is generally LREE enriched (e.g., Roeder et al. 1987,

44   Hughes *et al.* 1991). The term Ln represents any of the lanthanide elements (La to Lu) while the term

45   REE also includes the geochemically similar element yttrium (Y) and often scandium (Sc).

46   Reflectance spectroscopy, a rapid non-destructive analytical technique requiring little sample

47   preparation, has been used to study the reflectance of these minerals in the visible to short-wave infrared

48   regions. This research builds on the study by Turner et al. (2014) that documented the reflectance spectra

49   of the REE fluorocarbonate minerals bastnaesite, parisite and synchysite. Mineralogical and

50   spectroscopic background of REE-bearing minerals is provided here, followed by a band registry for

51   these phosphate minerals as well as interpretations of spectral absorption features related to the

52   lanthanides. The spectral features of the registry will be the focus of further study in the development of

53   hyperspectral reflectance imaging spectroscopy to carry out REE mineral identification and REE

54   abundance estimates.

55   **GENERAL SPECTROSCOPY OF THE LANTHANIDE ELEMENTS**

56   The outer radius of the $4f$ electron shells (~0.3 Å) for the lanthanides is much less than that of

57   their filled $5s$ and $5p$ shells (~2 Å, ~1 Å). It can then be approximated that the local electronic

58   environment of Ln^{3+} cations interacts primarily with those outer shells, leaving the $4f$ electrons relatively

59   sheltered but not completely non-participatory in bonding (e.g., Liu 2005). Electrostatic repulsion of the

60   base ion generates a first-level splitting of spectroscopic states, 2S+1L (e.g., ^5I). Next, spin-orbit

61   coupling splits these into multiplets, or "J-levels" (e.g., $^5I_8$), and once placed into a crystal field the J-

62   levels are then split into Stark Sublevels. Crystal field interactions for the Ln cation include variables

63   such as ligand type, coordination number and polyhedron asymmetry which all play roles in the location

64   and intensity of energy levels and the associated absorptions (Görller-Walrand and Binnemans 1998).

65   Each of the resulting sublevels provides the potential for promotion of a relaxed electron into an excited

66   state, giving rise to absorption of electromagnetic radiation (light) at a specific energy level (wavelength

67   or wavenumber).

68   The Dieke Diagram (Dieke et al. 1968) details intraconfigurational $4f$-$4f$ transitions for 'free

69   ions' as deduced through studies of largely mono-lanthanide synthetic compounds. The transitions

70   shown do not include splitting of energy levels due to a crystal field nor the complexities of naturally

71   occurring REE minerals with variable REE distributions and other elemental substitutions.

72   Consequently, this diagram and other band registries (e.g., White 1967) can only act as proxies to help

73   identify origins of absorption features in reflectance spectra of REE minerals. The strength of absorption

74   features due to the lanthanides will primarily be a function of the concentration of the ion as well as the

75   specific absorptivity of that ion's intraconfigurational transitions within a given crystal structure. The

76   location of lanthanide-related absorption features will be primarily a function of the cation's specific

77   coordination and asymmetry in the host crystal structure.

78   Synthetic lanthanide and actinide orthophosphates and silicophosphates have also been studied in

79   fairly good detail in research fields such as ceramics, nuclear waste, phosphors and nanotechnology and

80   some studies do include natural samples (e.g., Hayhurst et al. 1981, Bernstein 1982, Becker et al. 1984,

81   Rapaport et al. 1999, Assaaoudi et al. 2001, Cantelar et al. 2001, Carpena et al. 2001, Boatner 2002,

82   Silva et al. 2006, Hernadez and Martin 2007, Zhang and Vance 2008, Ardanova et al. 2010, Savchyn et

83   al. 2012, Lenz et al. 2013, Heuser et al. 2014). These studies generally focus on infrared spectroscopy

84   (400 to 4000 cm^{-1}), Raman spectroscopy and UV-VIS luminescence spectroscopy, however, information

85   can be gathered to help understand and assign absorption bands of natural samples in reflectance spectra.

86   **REVIEW OF REFLECTANCE SPECTROSCOPY STUDIES OF REE-BEARING PHOSPHATE**

87   **MINERALS**

88   The earliest report of reflectance data from REE phosphate minerals is for monazite from 350 to

89   2500 nm (Gerharz 1965), for which no conclusive origin was resolved. In his benchmark mineral

90   spectroscopy paper, Hunt (1977) lists monazite (misspelled as monzonite) in his tabulation of common

91   minerals and respective spectral signatures. However, La^{2+} is listed as the origin of absorptions but La

92   would have a 3+ valence in monazite and would therefore not have spectral features in the VIS-SWIR

93   (e.g., Liu 2005). Amongst many REE-bearing rock sample spectra, Rowan et al. (1986) include a

94   spectrum (400 to 2500 nm) of britholite from Oka (Quebec) and ascribe bands in the VNIR to Nd^{3+} and

95   suggest that a series of bands in the SWIR are related to Sm^{3+}. It is unclear if this is a mineral sample or

96   a britholite-dominant rock sample. Clark (1999) covers several REE oxides in his "Spectroscopy of

97   Rocks and Minerals" review and recognizes that the patterns seen in REE minerals are a combination of

98   several lanthanides, but states that absorptions are independent of mineralogy.

99   The widely used USGS Spectral Library (Clark et al. 2007) contains spectra for fluorapatite,

100   chlorapatite, hydroxylapatite and monazite. The F- and Cl-bearing apatite samples both contain spectral

101   features in the VNIR suggesting minor Nd^{3+} content, whereas the monazite spectrum clearly shows

102   REE^{3+} spectral features. The fluorapatite and monazite spectra are similar to those studied here,

103   however, the data presented here has higher spectral resolution. No xenotime spectra are included in the

104   USGS Spectral Library Version 06.

105   Morin Ka (2012) provides some partial spectra (original data likely collected between 380 and

106   2500 nm) for monazite, xenotime and REE-bearing apatite, but no detailed investigations were carried

107   out. Similarly, Kerr et al. (2011) present spectra from 350 to 2500 nm of monazite, xenotime and REE-

108   bearing apatite but provide no chemical data or interpretation of the spectra. Abstracts by Swayze et al.

109   (2013), Hoefen et al. (2013, 2014) and Huntington and Laukamp (2015) indicate that baseline and

110   applied research is being conducted on REE minerals and deposits, however, no detailed information is

111   available.

112   Thus, there remains an information gap of published material for the interpretation of REE

113   phosphate reflectance spectra, with respect to identifying and explaining spectral features as well as in

114   supporting the discrimination of these phosphate minerals based on their spectral characteristics.

115   **CRYSTAL STRUCTURE REVIEWS**

116   The phosphate classes of REE-bearing minerals show a range of coordination states for REE

117   from eight to 12 with bond lengths as short as 2.25 and as long as ~2.8 Å. Cation and anion substitutions

118   in these minerals can be substantial with complex crystal chemical implications, such as in the alunite

119   supergroup. On the other hand, the crystal structures of monazite, xenotime and fluorapatite have been

120   well studied and are well understood.

121   Monazite-(Ce), $CePO_4$, and xenotime-(Y), YPO_4, are very common REE orthophosphate

122   minerals that occur in a wide range of rocks. Despite their similar compositions they have different

123   crystal structures and coordination geometry for the REE site, owing primarily to the size reduction of

124   lanthanides towards Lu. Ni et al. (1995) and Clavier et al. (2011) carried out detailed studies on

125   synthetic $REEPO_4$ and showed that monazite hosts LREE at a distorted nine-coordinated site whereas

126   xenotime hosts HREE at a higher symmetry eight-coordinated site (Fig. 1). These studies also

127   demonstrated that the $REEPO_4$ crystals show a systematic decrease in REE-O bond distances when

128   moving from $LaPO_4$ through to $LuPO_4$. Eight of the LREE-O bond lengths for synthetic monazite

129   cluster into three groups between ~2.35 and 2.65 Å, with a ninth outlier having a considerably greater

130   length of ~2.77 Å (Fig. 2). Mullica et al. (1984) studied the ninefold coordination polyhedron of La in

131   synthetic $LaPO_4$ and determined that it most closely resembled a distorted pentagonal interpenetrating

132   tetrahedral polyhedron. In xenotime, the bonds are organized into a tighter and more symmetrical

133   structure where four short bonds of ~2.25 Å and four medium bonds of ~2.35 Å create an $HREO_8$

134   dodecahedron. The total REO content of natural monazite and xenotime attains 70%.

135   Britholite's more general formula, $(Ce,Ca,Th,La,Nd)_5(SiO_4,PO_4)_3(OH,F)$, is chemically and

136   structurally similar to apatite, whereby Si replaces P and REE replaces Ca (Mariano 1989, Oberti et al.

137   2001). Studies of britholite have reported both monoclinic ($P2_1$) and hexagonal ($P6_3$ and $P6_3/m$)

138   symmetry (e.g., Oberti et al. 2001, Pekov et al. 2007). According to refinements by Oberti et al. (2001),

139   the REE can occupy three distinct sites with either nine- (REE1 and REE1a sites, distorted tricapped

140   trigonal prism) or eight- (REE2 site, distorted dodecahedron) coordination (Fig. 1). Bond lengths to the

141   nine-coordinated sites cluster into 2.389, 2.510 and 2.700 Å sets of three each, and for the eight-

142   coordinated site they range from 2.377 to 3.180 Å, averaging ~2.467 Å (Fig. 2). The shortest of these

143   eight bonds is to an OH group. Although the REE1 and REE1a sites are not particularly symmetrical,

144   the REE2 site is highly asymmetrical and is also characterized by two ligand types, hydroxyl and

145   oxygen. Total REO content attains 55%.

146   Fluorapatite, $Ca_5(PO_4)_3F$, has been well studied in a wide range of fields. Its crystal structure is

147   well accepted, and numerous exchange mechanisms have been postulated for the wide variety of

148   substitutions in various rock types. Generally, fluorapatite accepts REE^{3+} in place of Ca^{2+} and Hughes et

149   al (1991) suggest the following dominant coupled substitutions to accommodate charge balancing;

150     $REE^{3+} + Si^{4+} = Ca^{2+} + P^{5+}$ and $REE^{3+} + Na^+ = 2Ca^{2+}$. Two distinct Ca sites exist (Fig. 1) and the REE

151   have been shown to populate both but have a preference for the Ca(2) site over the Ca(1) site (Fleet and

152   Pan 1995). Using cell refinements of REE-bearing fluorapatite from the Kipawa Complex in Hughes et

153   al. (1991), we see that the Ca(1) site is nine-coordinated with three sets of three oxygen atoms with bond

154   lengths of 2.404, 2.458 and 2.807 Å. The Ca(2) site is seven-coordinated with six Ca-O bonds between

155   2.352 and 2.680 Å, and a bond to F of 2.298 Å (Fig. 2).

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EXPERIMENTAL METHODS

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157 **Samples**

158   Three monazite, four xenotime and two britholite samples from a larger suite were studied in

159 detail with the scanning electron microscope and none showed compositional zoning. One honey-brown

160 monazite crystal (1 × 1 × 1 cm) from an unknown location was obtained from the Mineralogy/Petrology

161 Museum at the University of Alberta ("537-542 SE Quadrant") and one similarly sized pinkish-brown

162 monazite fragment from Elk Mountain (Nebraska) was obtained from A. Mariano. The third monazite

163 sample comprising multiple smaller grains is from Serra Verde, Brazil, and was also obtained from A.

164 Mariano. A xenotime sample from Serra Verde that is composed of multiple smaller grains was also

165 obtained. Two euhedral xenotime crystals from Novo Horizonte, Brazil, measured 2.25 × 0.75 × 0.75 cm

166 (sample C) and 2.5 × 1.4 × 1 cm (sample J) and were dark purple in color with patches of transparency.

167 The xenotime sample from Gunter Quarry is a fragment, measures 1.75 × 2.5 × 2 cm, and is opaque and

168 dark brown. Both britholite samples came from the Kipawa deposit in Ontario. One sample was

169 obtained from A. Mariano and comprised several small grains while the second was borrowed from the

170 Canadian Museum of Nature (sample CMNOC F90-8). Hand sample CMNOC F90-8 contains britholite

171 grains measuring on average ~1 × 1 × 1 mm. Reagent-grade lanthanide oxide powders, REE-doped

172 Spectralon wavelength calibration samples and other REE mineral phases were also investigated using

173 EMPA in order to aid in band assignment. Hand samples of dolomitic magnesio-carbonatite from the Fir

174 carbonatite system were used to study spectra from unprobed fluorapatite grains up to 6 × 3 mm (Chudy

175 2013).

176 **Scanning electron microscopy and electron microprobe analysis**

177   The Philips XL30 scanning electron microscope (SEM) at the University of British Columbia,

178 which is equipped with an energy-dispersion X-ray spectrometer (EDS), was used for preliminary

179 examination of mineral mounts of selected minerals and rock fragments studied by reflectance

180 spectroscopy.

181   Selected samples were then analyzed by electron microprobe at the Saskatchewan Research

182 Council's Advanced Microanalysis Centre using a Cameca SX-100 instrument equipped with five

183 tunable wavelength dispersive spectrometers. Operating conditions were: 40° takeoff angle, beam

184 energy of 15 keV, beam current of 20 nA, beam diameter of 5 μm. The MAN background intensity data

185 was calibrated and continuum absorption corrected. Elements were acquired using analyzing crystals

186 **LLIF** for Fe$K\alpha$, Ta$L\alpha$, Pr$L\alpha$, Eu$L\alpha$, Dy$L\alpha$, Tm$L\alpha$, Mn$K\alpha$, La$L\alpha$, Nd$L\alpha$, Gd$L\alpha$, Ho$L\alpha$, Yb$L\alpha$, Ba$L\alpha$,

187 Ce$L\alpha$, Sm$L\alpha$, Tb$L\alpha$, Er$L\alpha$, Lu$L\alpha$, **PET** for Ca$K\alpha$, K$K\alpha$, Cl$K\alpha$, Ti$K\alpha$, Nb$L\alpha$, Y$L\alpha$, Sr$L\alpha$, Zr$L\alpha$, P$K\alpha$,

188 U$M\alpha$, Th$M\alpha$, and **LTAP** for Mg$K\alpha$, F$K\alpha$, Na$K\alpha$, Si$K\alpha$, Al$K\alpha$. Counting times were 10 seconds for Zr

189 and P and 15 seconds for all other elements, with off-peak count times of 10 seconds. The standards

190 (with elements) were SPI-barite (Ba), SPI-celestite (Sr), SPI-YAG (Y, Al), Smithsonian Cr-augite (Mg,

191 Ca), Smithsonian ilmenite (Fe, Ti), Smithsonian apatite (F, P), Smithsonian microcline (K), Smithsonian

192 zircon (Zr), Harvard albite (Si, Na), Cameca Mn (Mn), SPI2-TlCl (Cl), SPI2-Nb (Nb), SPI2-La (La),

193 SPI2-Ce (Ce), SPI2-Pr (Pr), SPI2-Nd (Nd), SPI2-Sm (Sm), SPI2-Eu (Eu), SPI2-Gd (Gd), SPI2-Tb (Tb),

194 SPI2-Dy (Dy), SPI2-Ho (Ho), SPI2-Er (Er), SPI2-Tm (Tm), SPI2-Yb (Yb), SPI2-Lu (Lu), SPI2-Ta (Ta),

195 SPI2-Th (Th) and SPI2-U (U). Formulae were calculated based on four anions for monazite and

196 xenotime, and 26 anions (O+F+Cl) for britholite. Iron was assumed to be FeO in the one xenotime

197 sample that showed a concentration above detection limit. The amount of OH (as H_2O) was determined

198 by stoichiometry based on full occupation of the "O4" atomic site by two atoms of F, Cl and OH as per

199 Oberti et al. (2001).

Reflectance spectroscopy

201 Reflectance spectroscopy was primarily carried out using the sisuROCK instrumentation

202 (manufactured by SPECIM Spectral Imaging Ltd.) at the University of Alberta's CoreSensing Facility,

203 and data were handled using ENVI 4.4, a widely used and commercially available software package.

204 Two imaging spectrometers ("cameras") acquired reflectance spectra in the visible-near infrared (VNIR,

205 396 nm to 1003 nm over 784 channels for an average spectral resolution of 0.77 nm) and short-wave

206 infrared (SWIR, 928 nm to 2530 nm over 256 channels for an average spectral resolution of 6.26 nm)

207 portions of the electromagnetic spectrum in high spatial resolution mode. Spectralon-based white and

208 striped panels are placed at the head of the imaging table for spectral calibration and camera focusing,

209 and QA/QC procedures carried out automatically by the instrument for each imaging scan. Spatial

210 resolution of the cameras in this mode was approximately 0.079 mm / pixel in the VNIR and 0.241 mm /

211 pixel in the SWIR (Fig. 3). Noise was very prevalent in the shortest wavelength portion of the VNIR

212 camera below ~550 nm and moderate from 550 nm to ~650 nm. In the high spatial resolution mode,

213 averaging spectra of ~16 neighboring pixels resulted in reliable spectra in the noisier ranges that would

214 be useable in spectral libraries. Spectra presented here originate from single crystals, multiple crystals

215 within a single rock sample and from multiple loose single crystals. Spectra documented here are

216 nominally an average of 3215 pixels for the VNIR camera and 1018 pixels for the SWIR camera.

217 Uncommon specular reflections (e.g., as in Fig 3) that saturated detectors were avoided in the selection

218 of pixels. Samples were placed on a matte black surface that translates the samples under the camera and

219 has very low reflectance across the sampled wavelength range. Some samples were propped up with

220 foam blocks to ensure the surfaces of interest faced the spectrometers and were in focus. All samples

221   were thick enough that we could assume that the reflectance spectra are representative of the mineral

222   target.

223   Simple Regions Of Interest (ROI) were used on most samples to select target pixels for

224   averaging. For the loose grains and crystals in hand samples, a priori knowledge of the sample allowed

225   several single-pixel baseline spectra to be isolated. These spectra were then used to apply mixture-tuned

226   matched filtering within the ENVI software package to an entire hyperspectral image, from which a

227   strict qualitative threshold allowed a discrete selection of pixels to be averaged. This process enabled the

228   averaging of tens to hundreds of pixels per sample (Table 1) to produce a representative spectrum as

229   stated above. Reflectance spectra did not have the continuum removed so as to present the data

230   unmodified and to facilitate comparison against data from other publications.

231   **ELECTRON MICROPROBE COMPOSITIONS**

232   Samples described here were selected from a larger set and were characterized by imaging

233   reflectance spectroscopy, scanning electron microscopy and microprobe analysis. Tables 2, 3 and 4

234   document electron microprobe compositions for the REE phosphate minerals in this study and Figure 4

235   shows chondrite-normalized patterns for the samples.

236   Monazite microprobe compositions show similar chemical distributions of the REE for all

237   samples (Table 2), however, the Elk Mountain sample showed slightly higher rare earth elements from

238   Sm onwards. Totals for the Serra Verde and UofA Unk samples are satisfactory, while those for the

239   analyses of the Elk Mountain sample are lower and show high Th and Si contents, indicating

240   substitutions moreso related to huttonite than cheralite (Linthout 2007, Clavier et al. 2011).

241   Xenotime microprobe compositions for the two Novo Horizonte samples show elevated Eu-Gd-

242   Tb-Dy and lesser Yb, Lu and U as compared to the samples from Gunter Quarry and Serra Verde,

243   resulting in two main groups (Table 3). Neodymium and Sm concentrations are roughly equivalent in all

244   four samples, and La, Ce and Pr contents are either very low or below detection. Analytical totals are

245   satisfactory.

246   The two britholite samples originated from different collections but the same ore deposit

247   (Kipawa) and show similar concentrations of REEs (Table 4). Britholite is commonly noted to be at least

248   partially metamict (e.g., Pasero et al. 2010) and in general this is true for samples from Kipawa (e.g.,

249   Noe et al. 1993). The Mariano-001 sample displays a low analytical total while sample CMNOC F90-8

250   is satisfactory for a mineral species commonly reported as metamict. Microprobe compositions show

251   that Ce is the most abundant REE, REE>Ca, Si>P and F>OH,Cl, therefore these samples are

252   fluorbritholite-(Ce).

253   Figure 4 shows the chondrite-normalized EMPA results for selected samples of each mineral to

254   demonstrate relative total REE contents and patterns. Xenotime is strongly enriched in the heavy rare

255   earth elements (HREE) and monazite is enriched in the light rare earth elements (LREE), while

256   britholite contains moderate amounts of all REE.

257   In the case of fluorapatite, published (e.g., Hughes et al. 1991) and unpublished analyses of

258   LREE-enriched fluorapatite from the Fir carbonatite show total rare earth contents near ~5500 ppm. Of

259   the spectrally active REE^{3+}, the measured Pr content is ~300 ppm, Nd ~1200 ppm and Sm ~200 ppm.

260   **SPECTRA AND SPECTRAL VARIABILITY OF REE-PHOSPHATE MINERALS**

261   Each of the three REE-phosphate minerals exhibits its own characteristic distribution of rare

262   earth elements and therefore spectral patterns derived from $4f$-$4f$ intraconfigurational electronic

263   transitions. As seen from microprobe compositions, xenotime is populated by the heavy rare earths (Gd

264   to Lu), monazite by the light rare earths (La to Sm) and britholite accommodates both lights and heavies

265   yet has lower overall REE contents (Fig. 4 and Tables 2 to 4). Fluorapatite is generally enriched in

266   LREE (e.g., Hughes et al. 1991).

267   Figures 5, 6, 7 and 8 document the spectra from samples of each mineral and show the location

268   of prominent absorptions and absorption clusters listed in Tables 5, 6 and 7.These "Band Index Tables"

269   document prominent absorption features for the REE phosphate minerals and include probable origins of

270   the features, as chosen through comparison with reflectance spectra from unpublished reagent-grade

271   lanthanide oxide spectra, REE-doped calibration standard spectra, and other REE-bearing mineral

272   spectra for which compositional data exists, as well as REE spectroscopy literature. Clusters are

273   numbered and denoted in the Tables by horizontal line breaks and important absorptions are bolded. As a

274   set of summary figures, clusters and main absorption features are shown on "Index Figures" 9 (VNIR

275   range) and 10 (SWIR range) for representative spectra of monazite, britholite and xenotime.

276   The UofA Unk monazite, CMNOC Kipawa britholite, Gunter Quarry and Novo Horizonte J

277   xenotime samples were used in the Index Tables because of their superior microprobe results. Band

278   indices for all samples can be found in Turner (2015).

279

Monazite reflectance spectra

281   The Serra Verde and UofA Unk monazite samples have fairly similar elemental distributions,

282   however, the sample from Elk Mountain shows higher medium REE values and considerably higher Th

283   and Si and lower P than the other two samples.

284   The VNIR spectral range is divided into seven main clusters of absorptions (Fig. 5, Table 5). The

285   most notable differences in the VNIR spectra of the three monazite samples are the strengths of the 652

286   and 671 nm absorptions of Cluster 2, which are strongest in the sample from Serra Verde. The

287   absorption band at 978 nm (Cluster 7) also shows some variability in strength, being most pronounced in

288   the spectrum of the Elk Mountain sample and weakest in the spectrum of the UofA Unk sample.

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289   The SWIR spectral range is divided into five main clusters of absorptions starting after Clusters

290   6 and 7, which are better resolved in the VNIR range (Fig. 5, Table 6). Spectra for the monazite samples

291   in the SWIR range are very consistent. Subtle differences include a shift in the ~1960 nm feature and the

292   relative intensities of absorption bands at ~2424 and ~2499 nm.

293   **Xenotime reflectance spectra**

294   Chemical differences separate the two xenotime samples from Novo Horizonte (higher Eu, Gd,

295   Tb, Dy) from those from Serra Verde and Gunter Quarry (higher Yb, Lu, U). Bulk patterns are consistent

296   across all xenotime samples, however, the notable chemical distributions give rise to spectral differences

297   in both the VNIR and SWIR.

298   The VNIR spectral range is divided into six main clusters of absorptions (Fig. 6, Table 7).

299   Differences in the VNIR spectra across the two groups of xenotime samples are typically slight, such as

300   the presence or absence of a shoulder feature or the relative depth of a specific absorption. The Novo

301   Horizonte samples show stronger absorptions at 643, 690, 760, 827, 932 and 961 nm while the Gunter

302   Quarry and Serra Verde samples show stronger absorptions at 669, 678 and 803 nm. These two groups

303   hold true for other unpublished xenotime VNIR spectra that show similar spectral patterns but that do

304   not have supporting microprobe compositions.

305   The SWIR spectral range is divided into eight clusters beyond 978 nm, where Cluster 6 is better

306   described in the VNIR range (Fig. 6, Table 7). Differences in the SWIR spectra across the two groups of

307   xenotime samples are most prominent in clusters 7, 12 and 14. Cluster 7 differences are driven by

308   relative contents of Dy and U in the two groups. The high U content of the Gunter Quarry and Serra

309   Verde samples results in the prominent absorption being at 1143 nm, while the high Dy content of the

310   Novo Horizonte C and J samples results in the prominent absorption being at 1099 nm. For Cluster 12,

311   the prominent absorption at 1880 nm is consistent with the relative proportions of Tb in the xenotime

312   samples. Cluster 14 comprises absorptions from 2150 nm to the end of the detection range of the

313   spectrometer at 2530 nm, and is discussed in more detail later.

314   **Britholite reflectance spectra**

315   The two britholite samples have very similar REE distributions, however, their bulk

316   compositions differ. The CMNOC F90-8 sample shows totals closer to 100% and better cation

317   populations after formula normalization by anion content. This sample shows lower La and Ce contents,

318   equivalent Pr through Lu and higher Y, as well as higher P, Si, Th, Ca and OH contents.

319   The VNIR spectral range is divided into six main clusters of absorptions (Fig. 7, Table 5). The

320   only significant difference between the two spectra is how Cluster 1 is resolved into two features in

321   sample "001-Mariano", which generally shows stronger absorptions elsewhere.

322   The SWIR spectral range is divided into six clusters beyond the 978 nm absorption, which is

323   ascribed to Cluster 6 in the VNIR range (Fig. 7, Table 6). Absorptions in Clusters 11 and 12 show slight

324   variations.

325   **Fluorapatite reflectance spectrum**

326   The fluorapatite spectrum was derived from one crystal with distinct grain boundaries in a cut

327   rock slab with an abundance of fluorescent fluorapatite, all of which show spectra with equivalent

328   absorptions in the VNIR and SWIR. Although the absorptions were weaker in fluorapatite, general

329   cluster locations were consistent with the LREE-enriched monazite and britholite sample spectra (Tables

330   5 and 6).

331   Generally, the reflectance spectrum of pure fluorapatite in the SWIR range is featureless (e.g., as

332   in the USGS Spectral Library, Clark et al. 2007), however, the SWIR reflectance spectrum for this

333   sample is dominated by absorption bands consistent with ferroan dolomite (e.g., minima at 2318 and

334   2499 nm with continuum removed; Gaffey 1986). Subtle but narrow absorptions in this fluorapatite

335   spectrum occur within the broader ~1200 nm Fe-related absorption, and are likely associated with

336   REE^{3+}. The ferroan dolomite signals are likely due to microscopic inclusions within the fluorapatite

337   crystal, however, carbonate has also been shown to exist as a minor component in some hydroxylapatite

338   and fluorapatite (e.g., Fleet and Liu, 2008).

339   **DISCUSSION OF SPECTRA AND SPECTRAL VARIATIONS**

340   **REE compositional controls on reflectance spectra**

341   The typical distribution of rare earth elements in monazite (LREE), xenotime (HREE), britholite

342   (LREE and HREE) and fluorapatite (LREE) directly affects their spectral signatures. For naturally

343   occurring minerals the most important LREE that are spectrally active in the VNIR-SWIR range are

344   Pr^{3+}, Nd^{3+} and Sm^{3+}. Similarly, the most important spectrally active HREE for minerals are Dy^{3+}, Er^{3+}

345   and Yb^{3+} but Tb^{3+}, Ho^{3+} and Tm^{3+} still need to be considered. Therefore, typical REE distribution for a

346   given mineral means that it will also display a typical distribution of *spectrally active* REE^{3+}. This

347   allows for quick recognition of a mineral's bulk REE distribution but more subtle spectral features then

348   need to be considered when addressing mineral identification.

349   Accordingly, the most notable differences between the mineral samples are driven by the relative

350   distributions of light versus heavy rare earth elements. Monazite is LREE-enriched and thus its spectral

351   signature is driven primarily by Nd^{3+} with lesser influence by Pr^{+3} and Sm^{+3}, while HREE-enriched

352   xenotime has spectral features driven primarily by Yb^{+3}, Er^{+3} and Dy^{+3}. The britholite spectrum is

353   dominated by Nd^{+3} with lesser influence by Pr^{+3} and Sm^{+3} but signals of Dy^{+3}, Er^{+3} and Yb^{+3} are

354   observed. Consequently, britholite spectra more closely resemble spectra of monazite than xenotime and

355   a good understanding of the spectral characteristics of britholite can be derived by 'modifying' monazite

356 spectra with minor input from Dy^{+3}, Er^{+3} and Yb^{+3}. The fluorapatite spectrum shows absorptions related

357 to Nd^{3+} in the VNIR, and possible weak absorptions related to Sm^{3+} and Pr^{3+} in the SWIR.

358   Spectral differences between xenotime samples are minor, usually only a variation in the strength

359 of a feature. Unlike LREE minerals dominated by Pr^{3+}, Nd^{3+} and Sm^{3+} spectral features, in minerals with

360 abundant HREE it is harder to definitively assign individual features to individual lanthanide elements

361 because many of the multiplet levels from Sm^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+} overlap. Some of

362 the multiplet levels can produce many absorptions of varying strength as deduced through mono-

363 lanthanide doping studies of various compounds (e.g., Ho^{3+}:YGG by Gruber et al. 2009).

364 **Comparison of absorption patterns for monazite, xenotime, britholite and fluorapatite**

365   Figures 9 and 10 show representative spectra for xenotime, britholite and monazite in the VNIR

366 and SWIR ranges with absorption clusters and distinct absorptions labeled. Samples "UofA Unk" for

367 monazite, "Gunter Quarry" for xenotime and "Kipawa CMNOC F90-8" for britholite are used as the

368 base lines for describing intermineral variations. The monazite sample shows the nearest chemical

369 composition to ideal monazite, the xenotime sample represents one of the two spectral-chemical

370 populations and the britholite sample shows the highest total from microprobe data and better atomic

371 site assignments.

372   When comparing spectra of monazite to britholite, which have similar LREE concentration

373 patterns, trends of shifting band minima and band broadening emerge (Figs. 9 and 10). Many absorption

374 minima related to Nd^{3+} undergo systematic shifts to longer wavelengths in britholite as compared to

375 monazite. Shifted bands (from monazite to britholite) in the VNIR include 679 nm to 685 nm, 745 nm to

376 747 nm, 800 nm to 805 nm, 863 nm to 867 nm and 871 nm to 879 nm.

377   The absorptions for britholite are generally broader and show less structure, most likely

378 attributable to multiple REE sites and therefore multiple overlapping bands in close proximity. For

379   example, the fine structure of the Nd^{3+}-related 745 nm absorption of monazite is lost in britholite except

380   for a weak shoulder at 743 nm. The many local minima from 871 to ~900 nm in monazite are also lost in

381   britholite, likely due to REE site multiplicity and resulting fine band shifts and overlap.

382   Turner et al. (2014) described the reflectance spectra of REE fluorocarbonate minerals and noted

383   that the Sm^{3+}-related features at 1093 nm and 1251 nm are quite sharp. In monazite, these two features

384   are each consistently split into two discrete absorptions at 1074 and 1105 nm and at 1232 and 1257 nm

385   (Fig. 10). The barycenter of the absorptions in monazite remains close to that of the REE

386   fluorocarbonate minerals. In britholite, concentrations of Sm are lower, however, the splitting appears

387   greater near 1251 nm with a strong band minima at 1225 and a shoulder at 1257 nm (Fig. 10). Near 1093

388   nm, the absorptions in britholite broaden with minima at 1074 nm and a weak shoulder at 1105 nm. The

389   weaker Sm^{3+}-related absorption at 953 nm in bastnaesite is similarly split to 941 nm and 957 nm in

390   monazite (Fig. 9). In britholite, however, this absorption is not seen due to again lower Sm contents.

391   Fluorapatite absorptions can all be attributed to Nd^{3+} in the VNIR and occur in the same regions

392   as for monazite and britholite, however, the absorptions near 870 nm are much more subdued, possibly

393   due to the influence of an Fe^{2+} band from ferroan dolomite (Gaffey 1986), and the Cluster 2 Nd^{3+}

394   absorptions seen in the monazite spectra are not resolvable in the fluorapatite spectrum. The most

395   notable aspect of the fluorapatite spectrum is the pronounced pair of minima at 576 and 585 nm, which

396   is not seen as a resolved pair in either monazite or britholite (Fig. 11).

397   **The Yb-Er related absorption near 978 nm**

398   Britholite and xenotime show an absorption feature at 978 nm that is related to both Yb^{3+} ($^2F_{7/2}$

399    $\rightarrow ^2F_{5/2}$) and Er^{3+} ($^4I_{5/2} \rightarrow ^4I_{11/2}$). This particular Yb^{3+} transition is known to be hypersensitive to its

400   immediate coordination polyhedron and also absorbs more strongly than Er^{3+} at this wavelength (e.g.,

401   Zou and Toratani 1995, Strohhofer and Polman 2003). In britholite, the strength of the 978 nm

402   absorption is equal to or stronger than in xenotime (Fig. 12), despite the concentrations of Er and Yb

403   being *lower* by a factor of ~4 in britholite (Tables 3 and 4, and Fig. 4). Thus, the absorption coefficient

404   for this particular Yb^{3+} hypersensitive transition is much stronger in britholite than in xenotime. This is

405   most probably due to the REE site in britholite being more asymmetric than in xenotime (Figs. 1 and 2),

406   as well as being better suited to host REE^{3+} cations with larger ionic radii, such as Ce^{3+}, rather than the

407   smaller Yb^{3+}.

Spectral effects of the actinides

409   Electronic absorption bands for the $5f$ energy levels of $U^{4+, 5+}$ are reported to be strongest near

410   ~2069, ~1500, ~1330 and ~1111 nm in the SWIR and ~666 nm in the VNIR (e.g., Binnemans et al.

411   1999, Zhang et al. 2002, 2003), however, all of these bands are also within the ranges of various other

412   REE^{3+} absorptions. Xenotime from Serra Verde contains the most uranium of all the samples studied

413   with 1.59 wt.% UO_2 while those from Novo Horizonte have ~0.05 wt.% UO_2. Probable resolvable

414   absorptions related to U in xenotime were noted at 653, 1118, 1143 and 1503 nm, as interpreted through

415   comparison with zircon spectra (e.g., Zhang et al. 2002, 2003, and Turner 2015) and considering EMPA

416   data.

Hydroxyl and water bands of the REE phosphate minerals

418   Xenotime and monazite can accommodate minor amounts of OH in their crystal structures, trap

419   fluid inclusions during growth, and become metamict through radiation damage related to decay of U

420   and Th which can then lead to hydration (e.g., Talla et al. 2011). The xenotime samples studied here

421   contain low amounts of charge-balancing anions and are not considered to be appreciably metamict.

422   Monazite shows generally higher calculated OH content and also considerably more Th. Britholite

423   normally accommodates OH and some samples from Kipawa studied by others have been shown to be

424   partially metamict (e.g., Noe et al. 1993). Consequently, the monazite and britholite samples show

425   absorption bands at 1377 nm that are related to OH and near ~1950 nm that are related to water and

426   REE. Xenotime spectra show bands from 1408 to 1415 nm that are related to an OH overtone, which is

427   consistent with Talla et al. (2011) who identified stretching vibrations near 3500 cm^{-1} in xenotime. The

428   bands near 1936 nm are more likely tied to the Ho^{3+} and Tb^{3+} content but may also be influenced by

429   water.

Absorptions from 2150 nm to 2530 nm

431   Spectra of the REE phosphate minerals display a number of overlapping absorptions expressed

432   as minima and shoulders between 2150 nm (~4650 cm^{-1}) and 2530 nm (~3953 cm^{-1}). As a general

433   statement, each mineral shows moderate consistency between the samples, but significant differences

434   are observed in the two classes of xenotime samples (Figs. 5, 6 and 7). The exact origin of these

435   absorption bands remains unclear.

436   In their study of hydrated and hydroxylated phosphate minerals [e.g., childrenite –

437    $FeAlPO_4(OH)_2 \cdot H_2O$], Lane et al. (2011) show reflectance spectra with sharp absorptions in the 2100 to

438   2500 nm range, which they attribute to overtones and combinations of OH and PO_4 vibrations. In a

439   similarly themed study of hydrated hydroxylated phosphate minerals [e.g., wardite –

440    $NaAl_3(PO_4)_2(OH)_4 \cdot 2H_2O$], Frost and Erickson (2005) ascribed bands from ~4600 to 4000 cm^{-1} (2174 to

441   2500 nm) to combinations of OH stretching and OH deformational vibrations. Assaaoudi et al. (2001)

442   and Onac et al. (2005) reported that amongst different hydrated orthophosphates (e.g., churchite,

443    $YPO_4 \cdot 2H_2O$), small band shifts of the fundamental vibrations for P-O, O-H and H-O-H are potentially

444   related to variable REE content. Talla et al. (2011) studied OH defects in xenotime and identified an OH-

445   stretching mode near 3500 cm^{-1} (~2850 nm). Combining that stretching mode with a fundamental PO_4

446   vibration near 1000 cm^{-1} (e.g., Farmer 1974) results in a potential combination band near 4500 cm^{-1}

447   (2222 nm). Small absorptions near 4500 cm^{-1} can been seen in one IR spectral plot of xenotime from

448   Talla et al. (2011), but are not discussed in the paper. Pekov et al. (2007) recorded overlapping Si-O and

449   P-O bands for metamict fluorcalciobritholite at 930 and 1070 cm^{-1} (10753 and 9346 nm), respectively,

450   and Oberti et al. (2001) recorded a broad OH-stretching band at 3437 cm^{-1} (2910 nm) in fluorbritholite

451   but no spectrum was provided. Thus, theoretical calculations of combination bands for the REE

452   phosphate minerals support the notion of their influence in this region between 2150 and 2530 nm,

453   however, neither xenotime nor monazite have structural OH or H_2O in any great amounts and

454   reflectance spectra consistently show more than one resolved band.

455   Trivalent lanthanide elements with electronic energy levels in the ~2150 to 2500 nm range (4650

456   cm^{-1} to 3953 cm^{-1}) include Pr^{3+} (~2310 nm, $^3H_6$) and Tb^{3+} (~2200 nm, $^7F_3$) with potential influence from

457   Nd^{3+} (~2500 nm, $^4I_{13/2}$) and Eu^{3+} (~2100 nm, $^7F_6$) when placed in a crystal field, according to energy

458   levels recorded by Dieke et al. (1968) and Carnall et al. (1989). Reflectance spectra for REE_2O_3 reagents

459   and reflectance and transmission data available from the literature in this range suggest that REE-related

460   absorptions could be responsible for the patterns seen in the REE phosphate minerals. In particular, Talla

461   et al. (2011) synthesized REE-doped xenotime with Pr, Nd, Sm, Dy, Ho and Er and collected polarized

462   IR absorption spectra from 7000 to 2500 cm^{-1} (1429 – 4000 nm). Of these synthetic xenotime crystals,

463   the Nd-doped sample exhibits two (possibly three) bands at approximately2400 and 2475 nm (the third

464   near 2500 nm) and the Pr-doped sample exhibits only one band near 2375 nm. Unfortunately neither

465   Eu_2O_3 nor Tb_2O_3 were included in their EMPA results for their natural samples and they did not

466   synthesize Eu- or Tb-doped xenotime. It is unlikely that Eu would play a significant role due to

467   relatively low contents, however, Tb_2O_3 concentrations in xenotime can be appreciable. Focusing just on

468   xenotime, the two samples from Novo Horizonte have the highest Tb_2O_3 contents and show the

469   strongest absorptions near 2262 nm and 2312 nm, suggesting that at least these two bands are linked to

470   Tb^{3+}. Looking back at the one natural sample shown by Talla et al. (2011) in this range (their Fig. 7),

471   two more small absorption features can be seen near 2247 and 2325 nm. Thus, with the spectra from

472   Talla et al. (2011) but without spectra from Tb-doped xenotime it is still difficult to conclusively tie

473   intramineral chemical variations to spectral variations.

474   A spectrum from reagent grade La powder [qualitatively determined as $La(OH)_3 \gg La_2O_2(CO_3)$

475   through powder X-ray diffraction, see Turner 2015] shows absorption bands in the 2300 to 2500 nm

476   range (in addition to water related absorptions at ~1420 nm and ~1950) but La^{3+} should not show $4f$-$4f$

477   electronic transitions as it has no electrons in the f orbital. Conversely, reagent grade Gd_2O_3, Y_2O_3 and

478   Yb_2O_3 powders show minor absorptions near 1420 and 1950 nm but no distinct absorptions between

479   2300 and 2500 nm. Consequently, it is apparent that at least *some* REE reagents are generating

480   absorptions related to REE-OH bonding (with possible CO_3 absorptions), thus making interpretations of

481   other REE-related absorptions in this region difficult.

482   If absorptions in this region were solely attributable to PO_4 / OH vibrational combinations we

483   would expect more coherency between the PO_4 minerals, less variability in the xenotime spectra, and

484   weaker absorptions where OH is minimal (i.e., xenotime and monazite vs. britholite). If these

485   absorptions were solely the result of REE^{3+} electronic transitions we would expect greater support from

486   the existing REE-spectroscopy literature and not observe absorptions in La_2O_3. If they were solely the

487   result of REE-OH vibrational bands we would expect to see more systematic variations within and

488   across the phosphate groups. It is therefore most likely that each of these factors plays a role in

489   absorptions from 2150 to 2530 nm, but without further investigations using additional techniques it is

490   difficult to determine the exact origins of these absorption bands across monazite, britholite and

491   xenotime.

IMPLICATIONS

492

493 This work is the first published systematic study of the REE-phosphate minerals monazite,

494 xenotime and britholite using reflectance spectroscopy in the VNIR-SWIR range. Spectra coupled with

495 microprobe compositions indicate that spectra of monazite and britholite are dominated by Nd^{3+}, Pr^{3+},

496 and Sm^{3+}-related absorption bands. The multiple atomic sites with mixed coordination for Ln^{3+} in

497 britholite allows for easy incorporation of Tb, Dy, Ho, Er, Tm and Yb. The mixed coordination of cation

498 sites REE1/REE1a (nine-coordinated) and REE2 (eight-coordinated) results in multiple sets of crystal

499 field splitting for the Ln^{3+}, thus potentially broadening each absorption band related to electronic

500 transitions. The xenotime spectrum is dominated by the distribution of HREE, namely Tb^{3+}, Dy^{3+}, Ho^{3+},

501 Er^{3+}, Tm^{3+} and Yb^{3+}. Many of the energy levels for these elements overlap, making definitive

502 assignments of probable origin difficult; however, absorption clusters are consistent across samples. The

503 reflectance spectrum of LREE-bearing fluorapatite was shown to have strong similarities to monazite

504 and britholite spectra in the VNIR range, however, the Nd^{3+}-related absorptions near 576 and 585 nm

505 show distinct differences in band positions.

506 The sensitive nature of the Yb^{3+} and Er^{3+} transitions near 978 nm are well illustrated between

507 xenotime and britholite. Despite xenotime having significantly higher concentrations of Yb and Er,

508 britholite exhibits an equally strong absorption band at this wavelength because of the greater

509 asymmetry of the coordination polyhedra compared to xenotime.

510 These data provide the diverse geological remote sensing community with a benchmark to which

511 comparison can be made regarding spectra with Ln^{3+}-related electronic absorptions. Diagnostic

512 variations between the REE phosphate minerals can also be exploited in a number of circumstances,

513 such as remote predictive mapping, petrology of thin sections and rocks, identifying potential mineral

514 grains for geochronology, drill core and chip logging, mine wall imaging or ore sorting.

515   Future work should include a systematic study of mono-lanthanide doped phosphate crystals, as

516   well as continuing to add other REE phosphate minerals with variable REE content. Spectral range

517   should be expanded to include regions of fundamental vibrations in the same mineral suites (i.e., 400 to

518   4000 cm^{-1}). This will enhance the growing database of REE mineral reflectance spectra and help clarify

519   ambiguity for assigning absorptions to specific lanthanides across the entire VNIR-SWIR range, but

520   especially from 2150 to 2530 nm.

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657   **FIGURE CAPTIONS**

658 Figure 1. Coordination polyhedra for rare earth element cations in monazite, xenotime, britholite and

659 fluorapatite. Data for polyhedra from Oberti et al. (2001), Ni et al. (1995), and Hughes et al. (1991).

660

661 Figure 2. Bond distances for REE polyhedra in monazite, xenotime, britholite and fluorapatite, as

662 described in the text. Multiple bond lengths are indicated where found (e.g., O × 4), the OH bond of

663 REE2 in britholite and F bond in fluorapatite are labeled, and the vertical bars illustrate the minimum,

664 mean and maximum bond lengths. Data for polyhedra lengths from Oberti et al. (2001), Ni et al. (1995)

665 and Hughes et al. (1991).

666

667   Figure 3. Example of false colour VNIR hyperspectral reflectance imagery (inset, Novo Horizonte "C"),

668   single pixel spectrum (lower spectrum) and average spectrum (upper spectrum). For this particular

669   scene, 2097 pixels were included in a ROI for calculating the averaged spectrum. Crystal measures 0.75

670   × 2.25 cm.

671

672   Figure 4. Chondrite-normalized REE plots for selected samples of monazite (triangles), britholite

673   (squares), and xenotime (×'s).

674

675   Figure 5. Absorption spectra of characterized monazite samples in the VNIR (left, 500 to 1000 nm) and

676   SWIR (right, 950 to 2530 nm) with absorption band clusters shown and the prominent absorption lines

677   of the UofA sample indicated with tick marks. From the top down the spectra are from the Serra Verde,

678   UofA Unk and Elk Mountain samples.

679

680   Figure 6. Spectra of characterized xenotime samples in the VNIR (left, 500 to 1000 nm) and SWIR

681   (right, 950 to 2530 nm) with absorption band clusters shown and the prominent absorption lines of the

682   GQ sample identified with tick marks. From the top down the spectra are from Serra Verde, Gunter

683   Quarry, Novo Horizonte-J and Novo Horizonte-C.

684

685   Figure 7. Spectra of characterized britholite samples in the VNIR (left, 500 to 1000 nm) and SWIR

686   (right, 950 to 2530 nm) with absorption band clusters shown and prominent absorption lines of the

687   CMNOC sample indicated with tick marks. The upper spectrum is from the 001-Mariano sample and the

688   lower is from the CMNOC F90-8 sample.

689

690   Figure 8. Spectrum of fluorapatite in the VNIR (left, 500 to 1000 nm) and SWIR (right, 1000 to 2530

691   nm) with REE-related absorption band clusters shown and prominent absorption lines indicated by tick

692   marks.

693

694   Figure 9. Representative spectra for xenotime (X, top, red), britholite (B, middle, green) and monazite

695   (M, bottom, black) samples in the VNIR range (500 to 1000 nm). Absorption band clusters are shown

696   with bars and prominent absorptions are labeled according to text descriptions.

697

698   Figure 10. Representative spectra for xenotime (X, top, red), britholite (B, middle, green) and monazite

699   (M, bottom, black) samples in the SWIR range (950 to 2530 nm). Absorption band clusters are shown

700   with bars and prominent absorptions are labeled according to text descriptions.

701

702   Figure 11. Fluorapatite (black, FAP), monazite (blue, MON) and britholite (red, BR) reflectance spectra

703   in the VNIR (left) and SWIR (right, only from 1000 nm to 1800 nm). Note the consistent location of

704   Nd-related absorptions in the VNIR but different morphology and relative inensities, as well as the lack

705   of other REE^{3+} features such as the 978 nm absorption in britholite. Subtle absorptions that are related to

706   bands ascribed to Sm^{3+} and Pr^{3+} in monazite and britholite can also be seen in the SWIR range of the

707   fluorapatite spectrum.

708

709   Figure 12. Reflectance spectra (left) and continuum-removed spectra (right) near 978 nm for samples

710   showing absorptions at this wavelength. Spectra are labeled and Er and Yb contents are given in

711   parentheses (Er_2O_3 wt.% / Yb_2O_3 wt.%). The continuum-removed plot shows britholite samples with a

712   heavier line weight and "B" labels as well as an "M" label for the single monazite spectrum.

Figure 1

Xenotime
8 coordinated

Monazite
9 coordinated

Britholite
REE1 and REE1a sites
9 coordinated
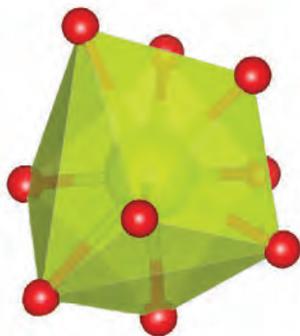
Britholite
REE2 site
8 coordinated

Fluorapatite
Ca1 site
9 coordinated
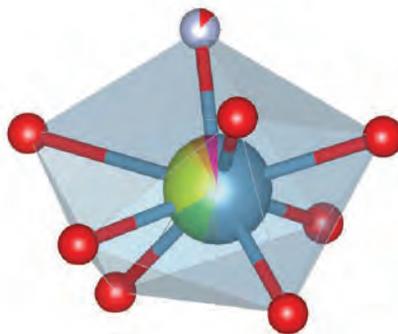
Fluorapatite
Ca2 site
7 coordinated
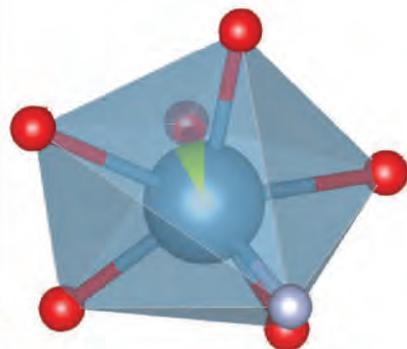
Figure 2
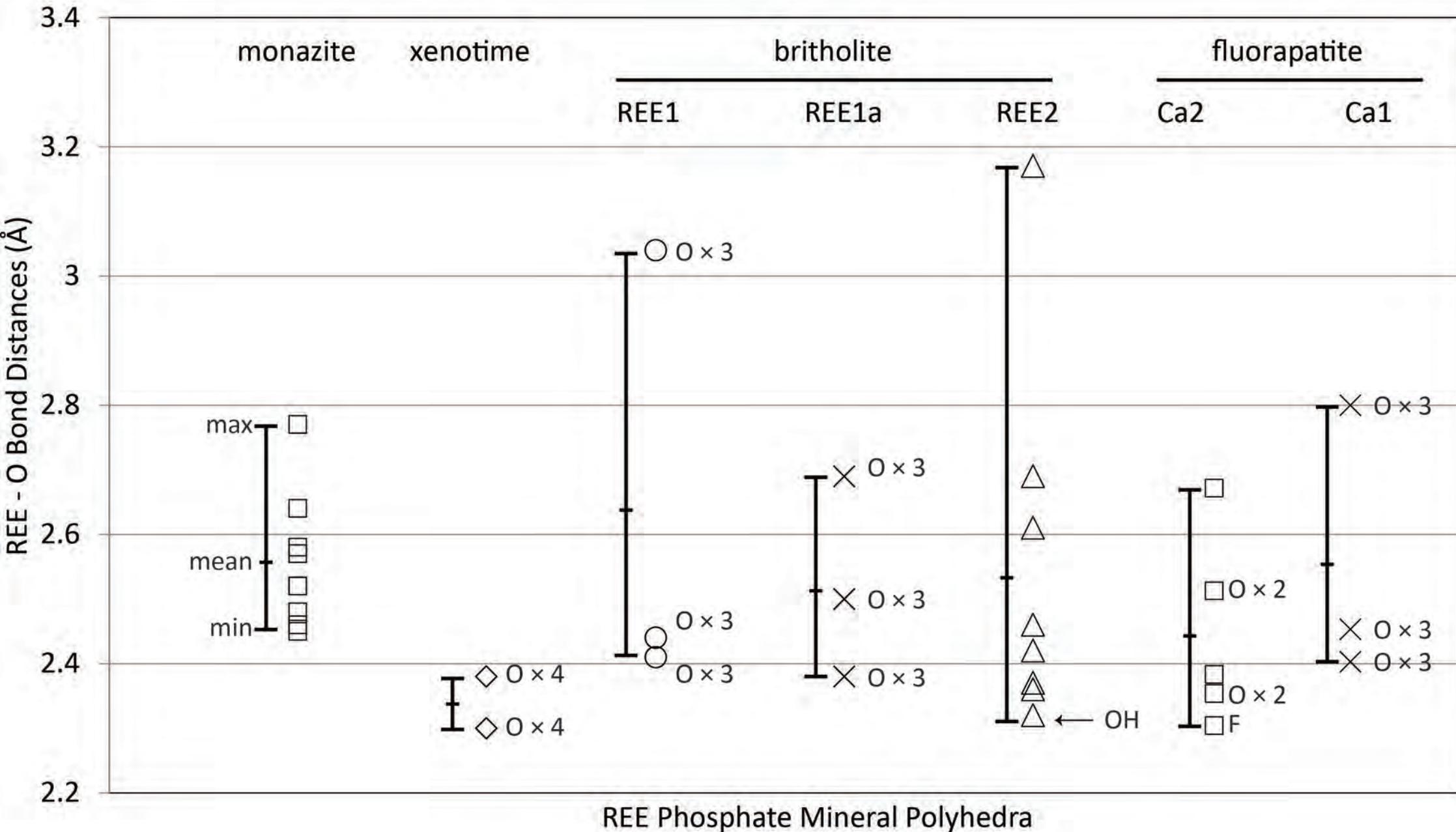
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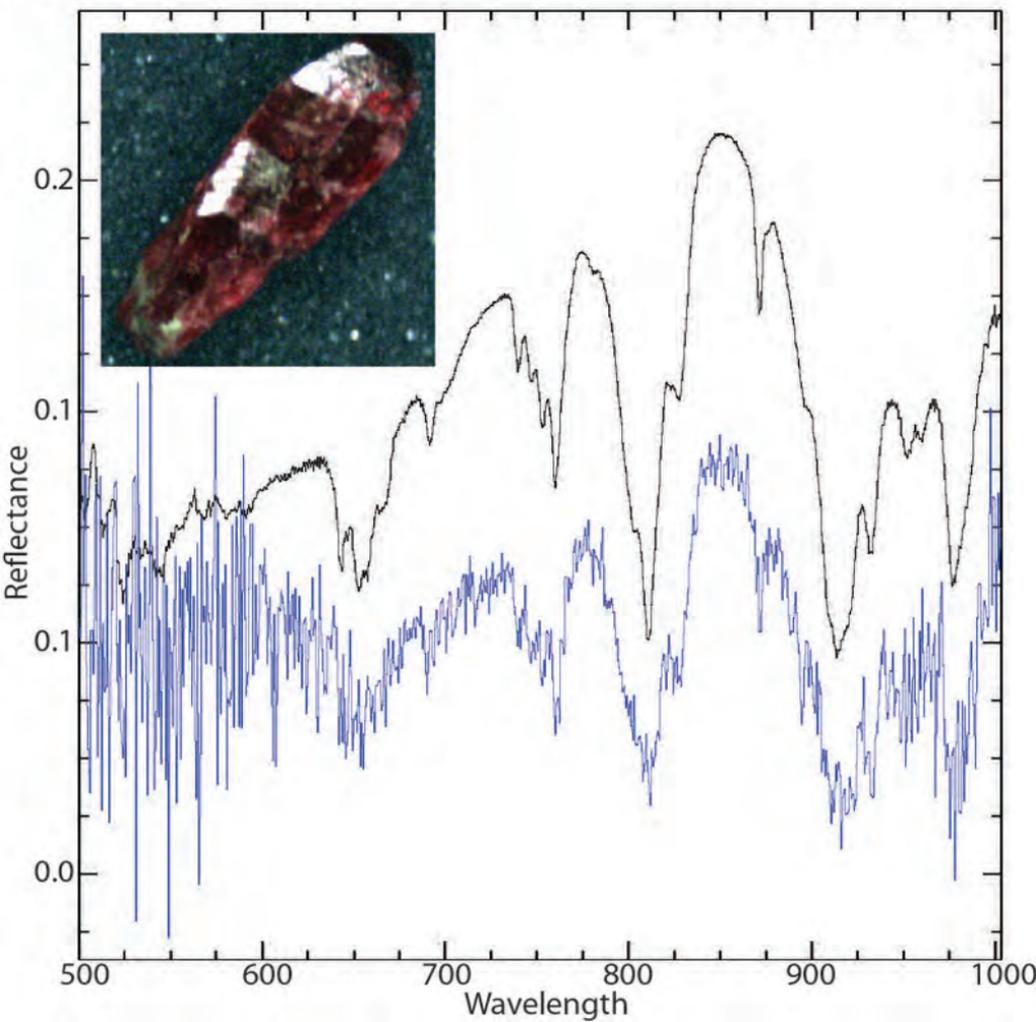
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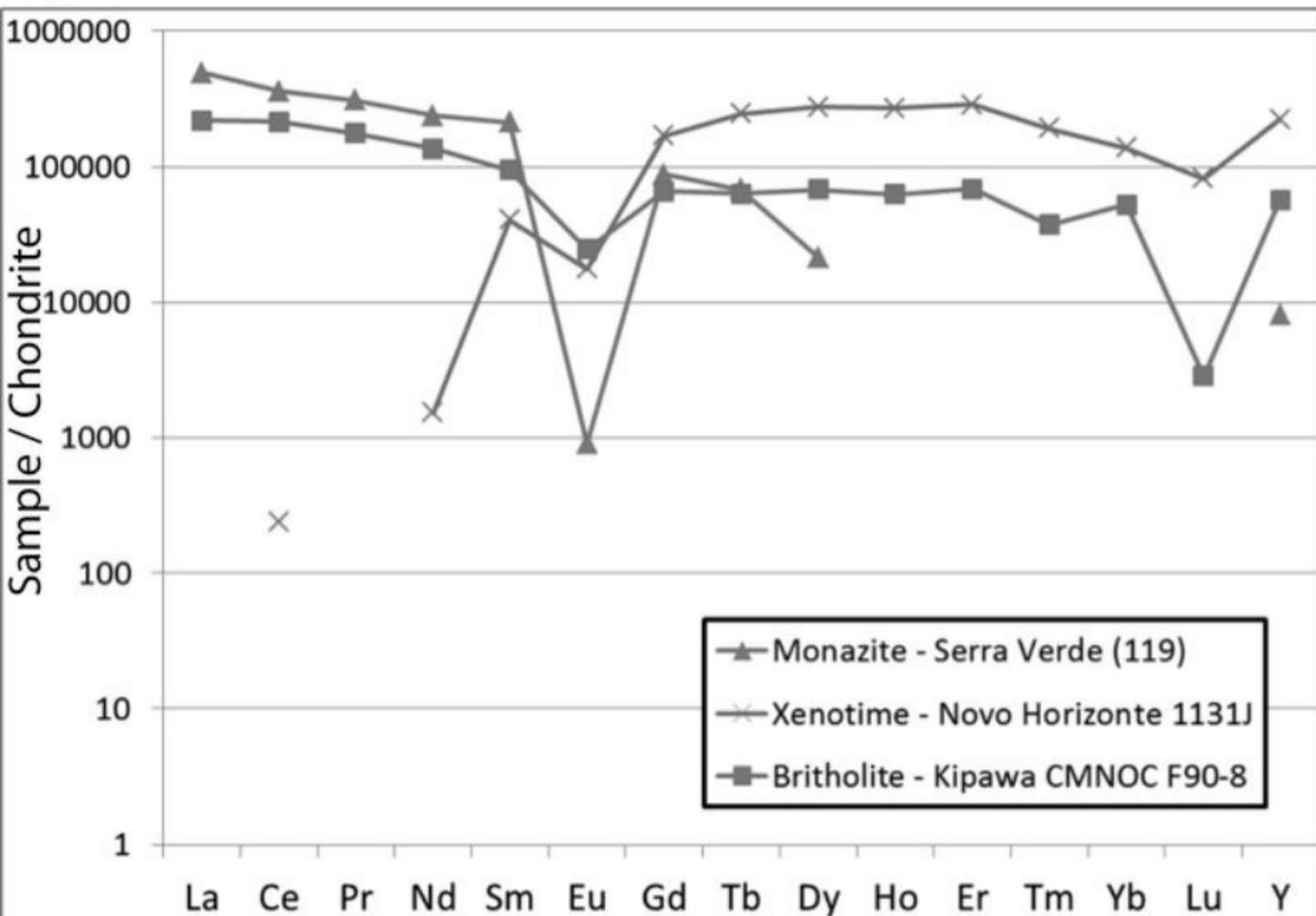
Figure 5
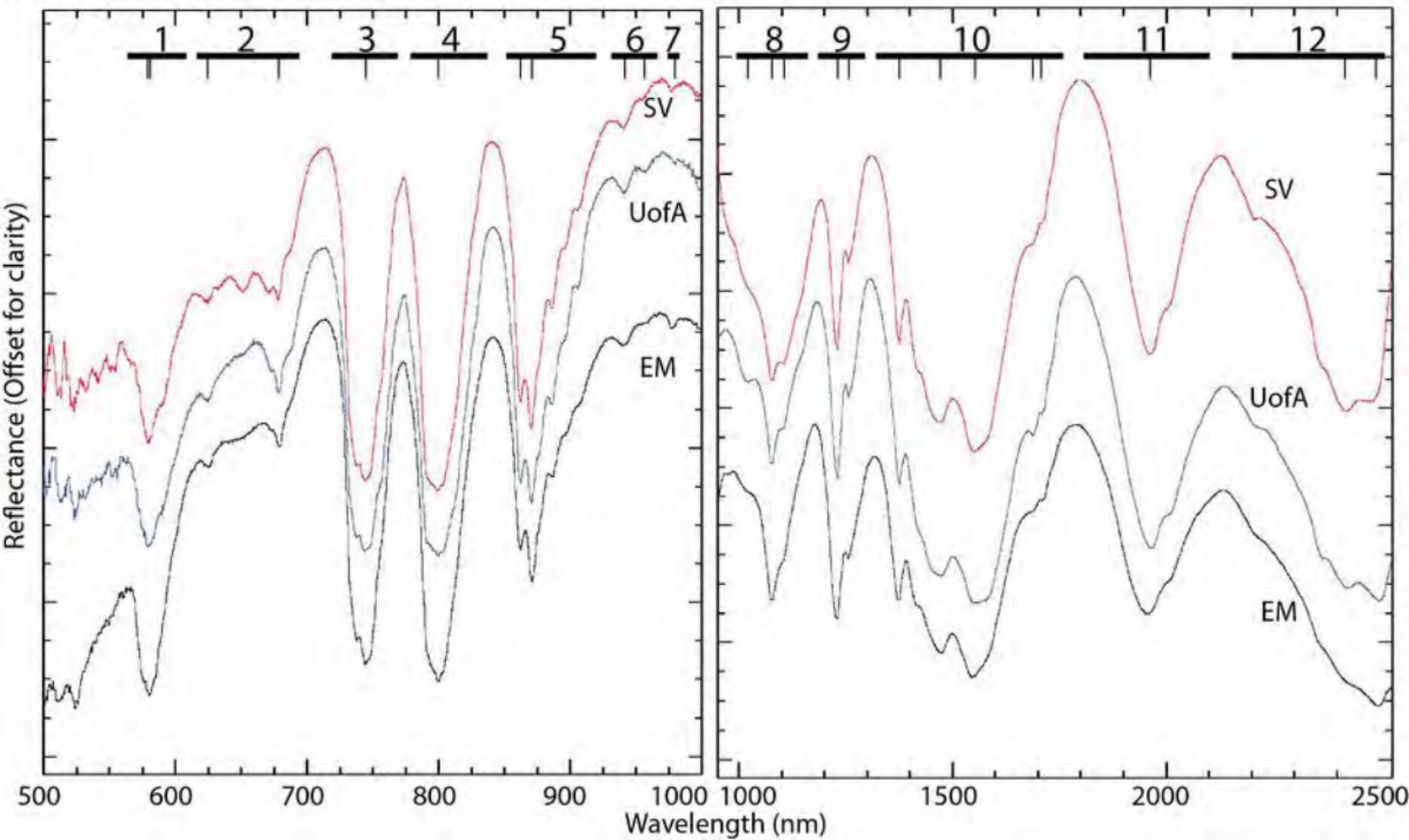
Figure 6
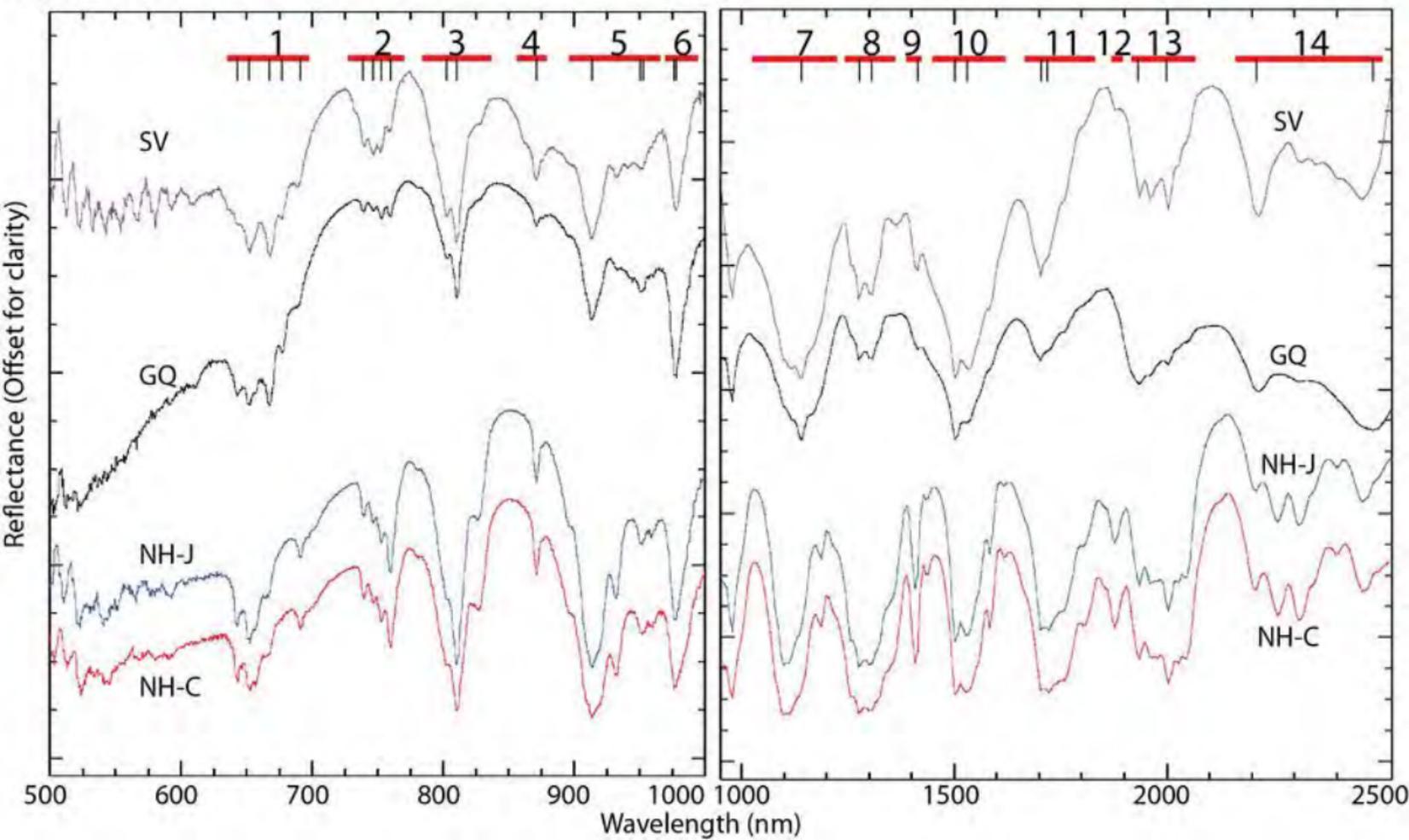
Figure 7
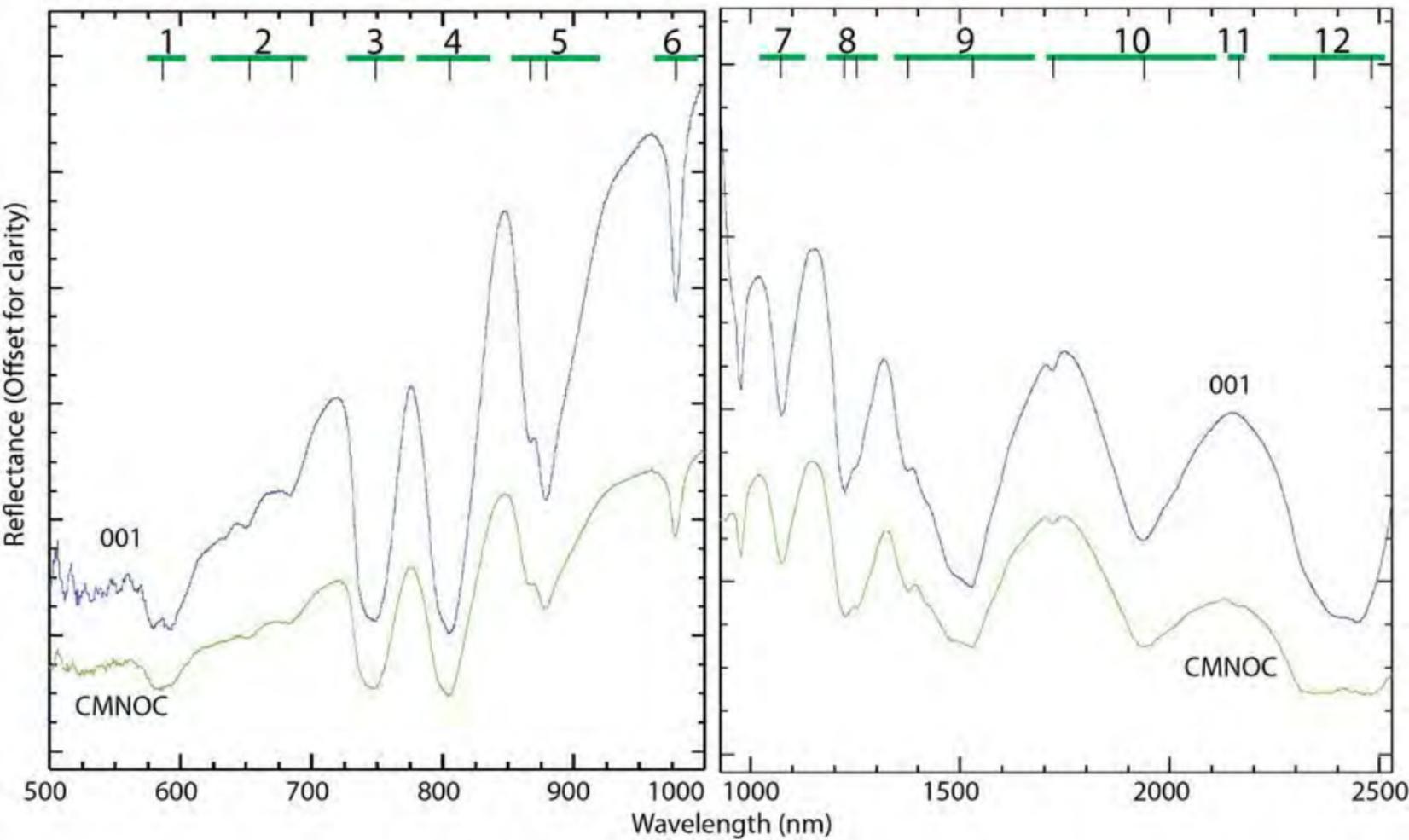
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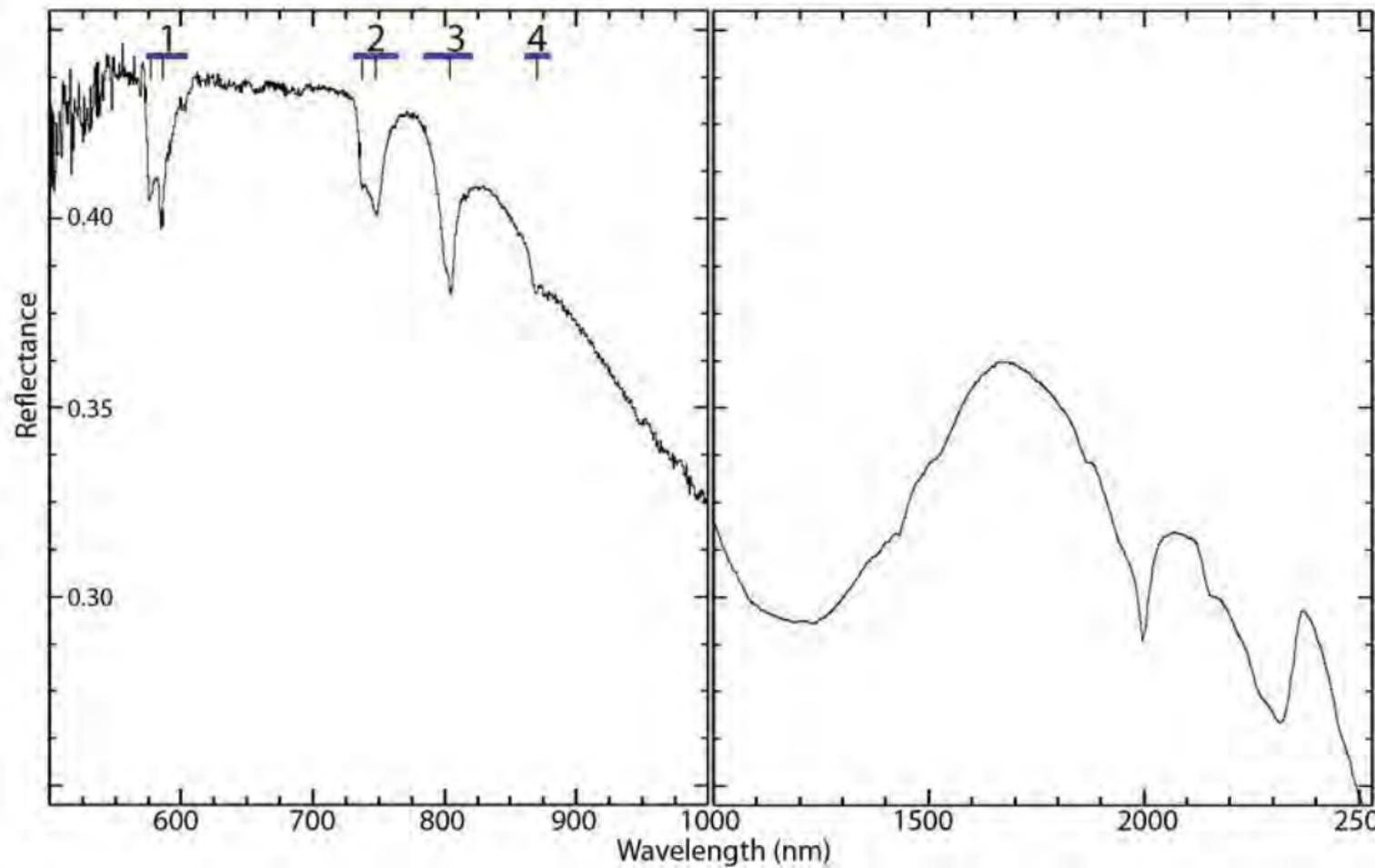
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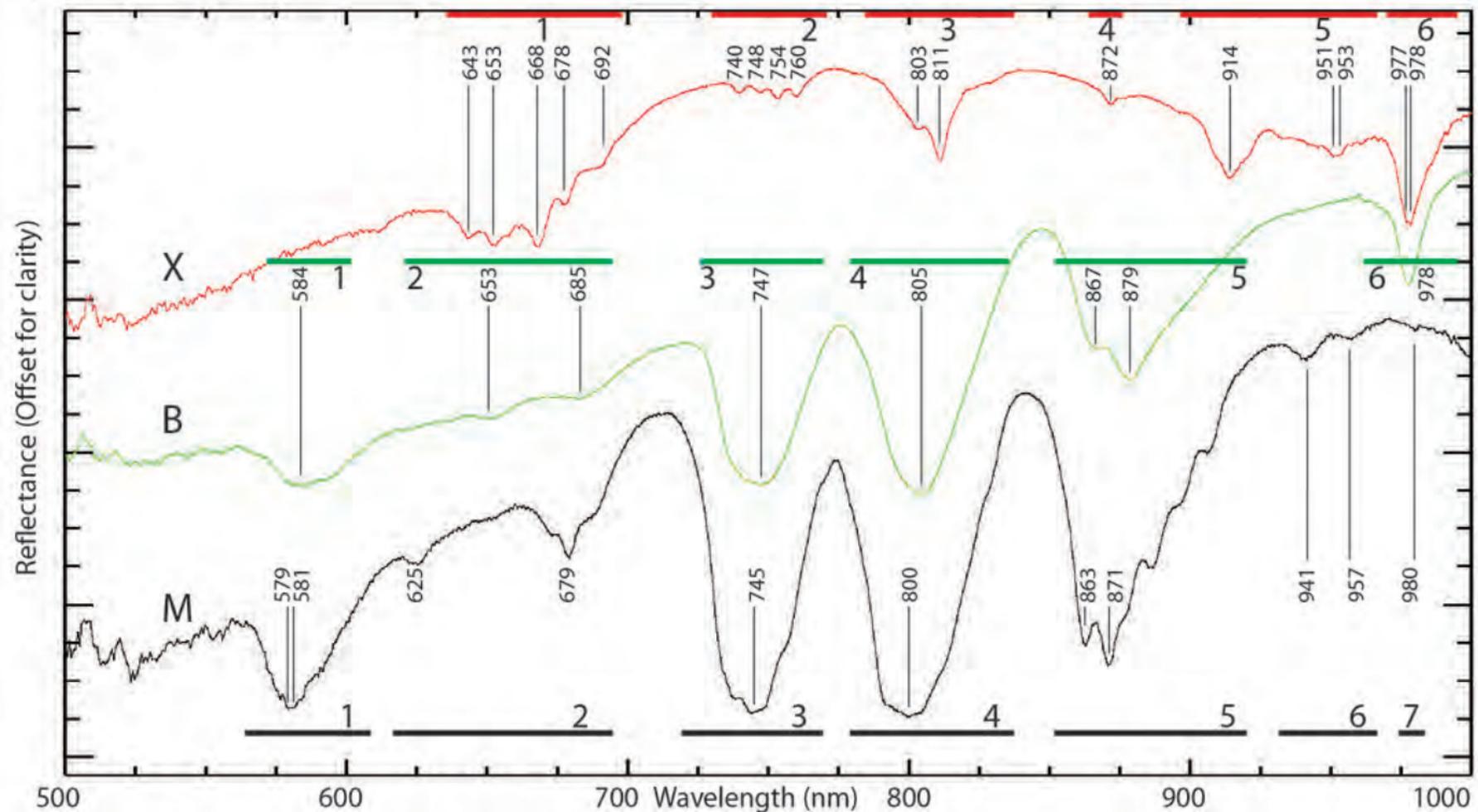
Figure 10
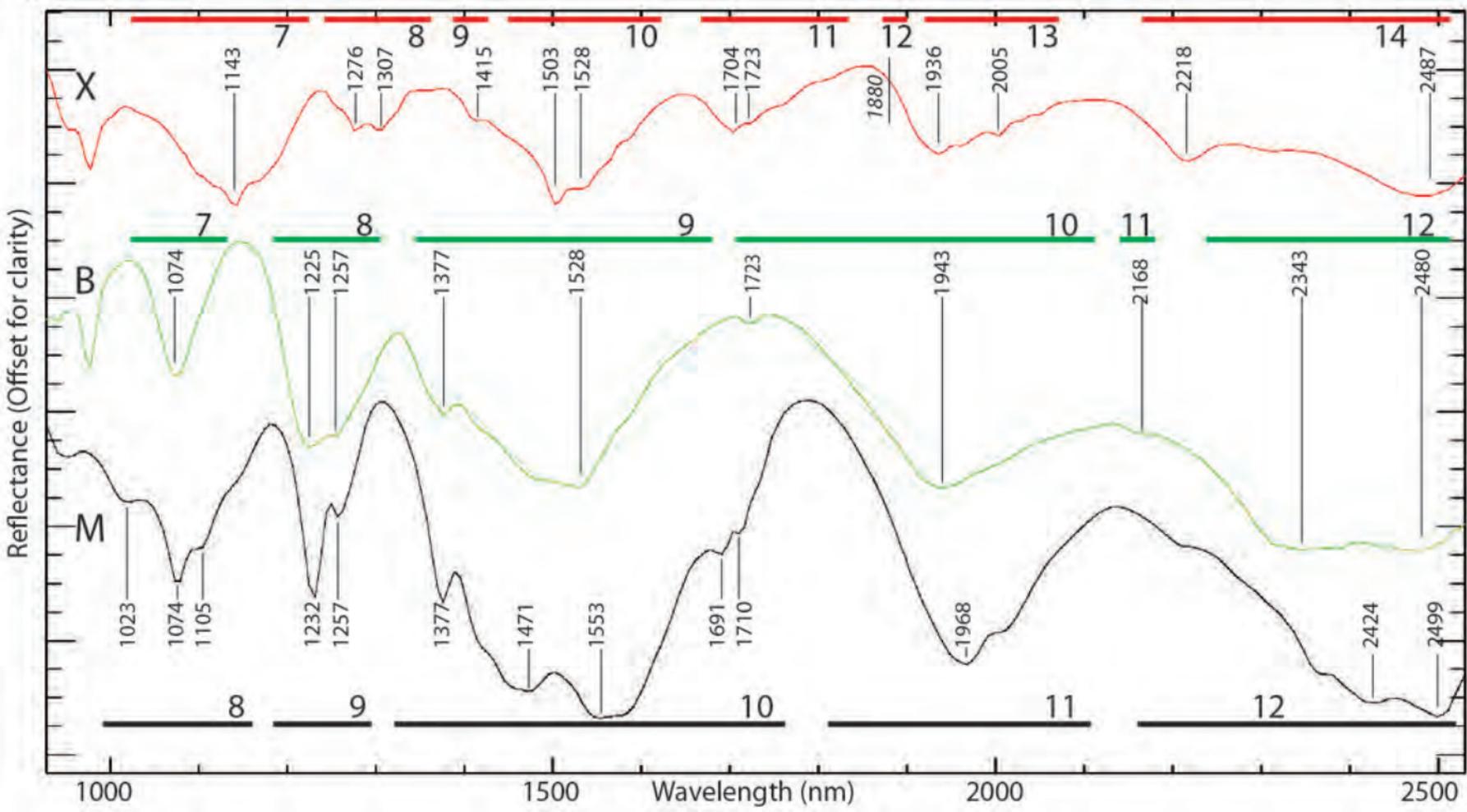
Figure 11
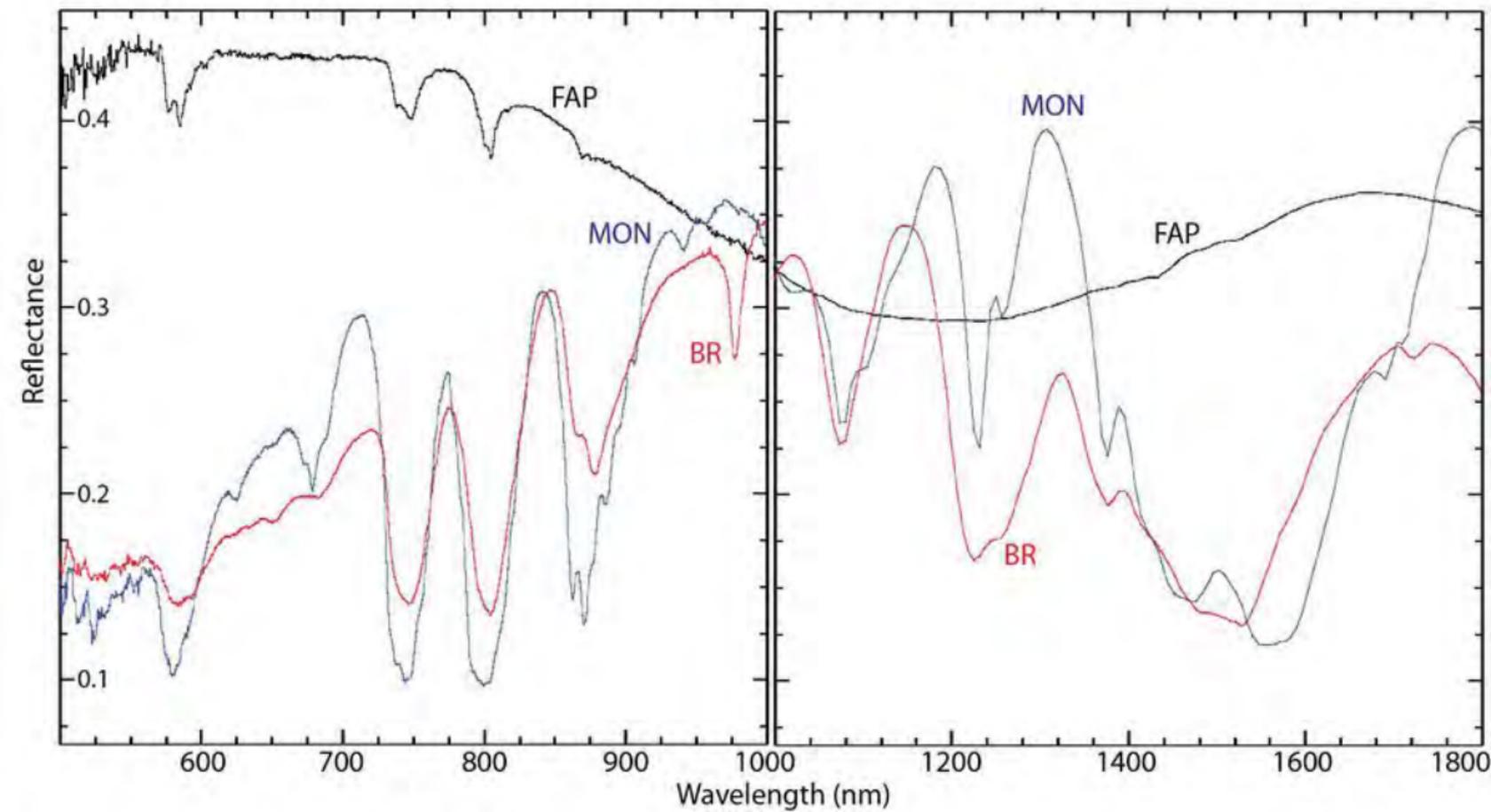
Figure 12
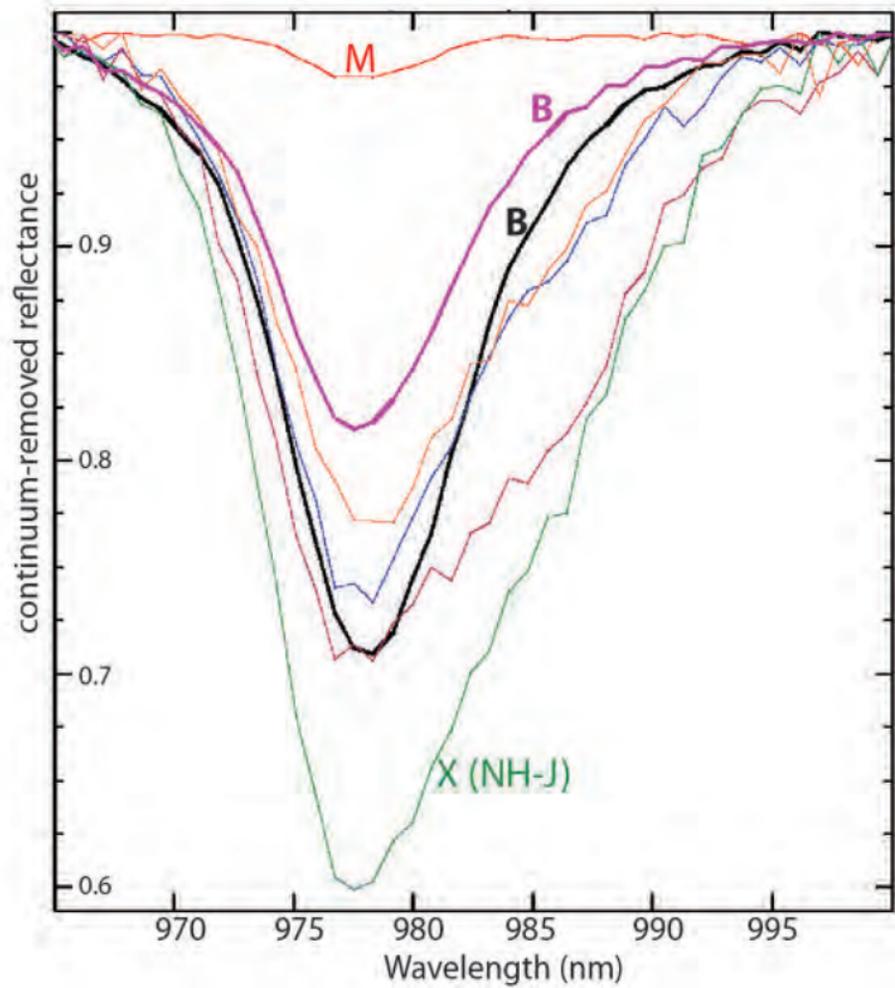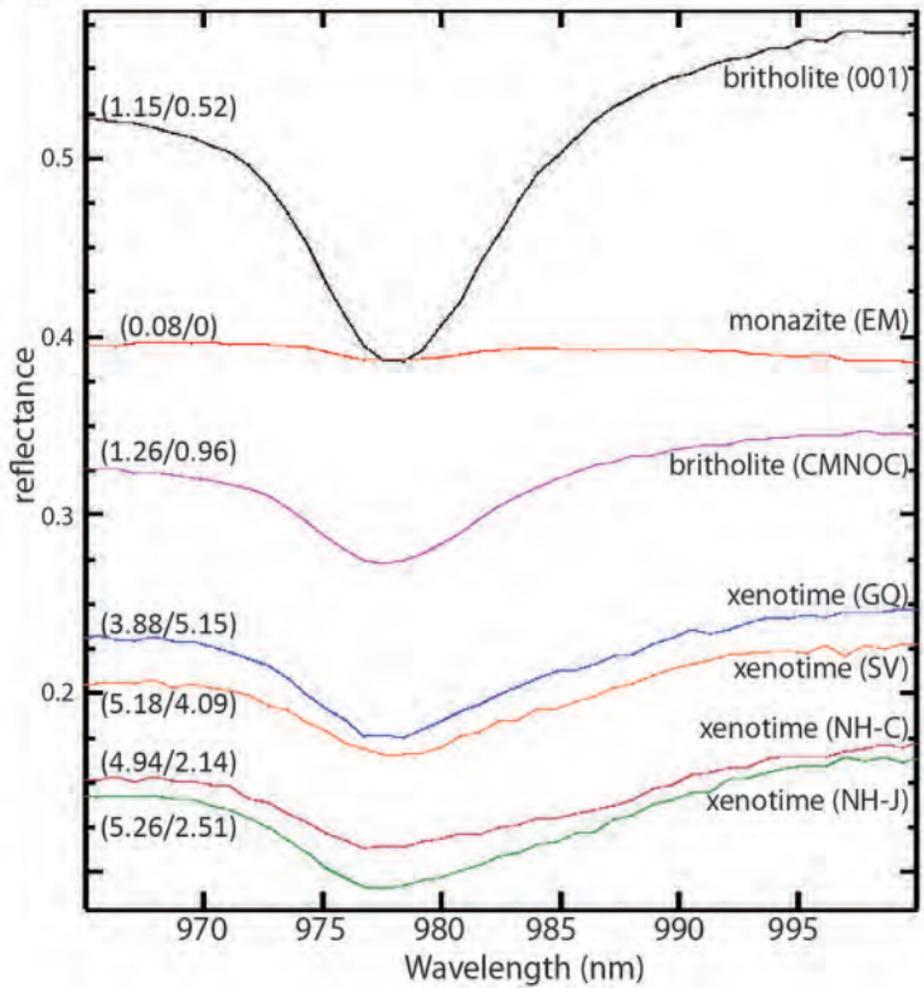
Table 1. Pixel counts per sample used to produce an average spectrum.

Mineral	Sample	VNIR ROI Pixels	SWIR ROI Pixels
monazite	Serra Verde	1995	180
	Elk Mountain	1283	1121
	UofA Unknown	6226	848
xenotime	Serra Verde	1848	215
	Gunter Quarry	2826	419
	Novo Horizonte C	2097	1931
	Novo Horizonte J	5240	4955
britholite	Kipawa CMNOC F90-8	4001	186
	Kipawa Mariano 001	3727	122
fluorapatite	Fir Carbonatite	2898	202

Table 2. Electron microprobe compositions for monazite.

Sample #	119	15-H-7	UofA Unk		119	15-H-7	UofA 537-542 SE
Locality	Serra Verde	Elk Mountain	Unknown		Serra Verde	Elk Mountain	Unknown
# Analyses	5	5	5				
Nb_2O_5 (wt.%)	0.01	0.00	0.09	Nb^{5+} (apfu)	0.00	0.00	0.00
P_2O_5	25.78	22.62	27.77	P^{5+}	0.91	0.85	0.96
SiO_2	1.08	1.90	0.79	Si^{4+}	0.05	0.08	0.03
TiO_2	0.01	0.00	0.00	Ti^{4+}	0.00	0.00	0.00
ZrO_2	0.04	0.02	0.03	Zr^{4+}	0.00	0.00	0.00
UO_2	0.39	0.32	0.05	U^{4+}	0.00	0.00	0.00
ThO_2	7.36	12.15	3.55	Th^{4+}	0.07	0.12	0.03
La_2O_3	13.56	10.60	14.33	La^{3+}	0.21	0.17	0.22
Ce_2O_3	25.91	22.98	33.16	Ce^{3+}	0.39	0.37	0.49
Pr_2O_3	3.35	3.03	3.84	Pr^{3+}	0.05	0.05	0.06
Nd_2O_3	12.72	11.86	11.42	Nd^{3+}	0.19	0.19	0.17
Sm_2O_3	3.64	4.94	1.90	Sm^{3+}	0.05	0.08	0.03
Eu_2O_3	0.01	0.12	0.02	Eu^{3+}	0.00	0.00	0.00
Gd_2O_3	2.01	2.83	0.42	Gd^{3+}	0.03	0.04	0.01
Tb_2O_3	0.28	0.48	0.00	Tb^{3+}	0.00	0.01	0.00
Dy_2O_3	0.61	1.64	0.08	Dy^{3+}	0.01	0.02	0.00
Ho_2O_3	0.00	0.00	0.00	Ho^{3+}	0.00	0.00	0.00
Er_2O_3	0.00	0.08	0.00	Er^{3+}	0.00	0.00	0.00
Tm_2O_3	0.00	0.00	0.00	Tm^{3+}	0.00	0.00	0.00
Yb_2O_3	0.00	0.00	0.00	Yb^{3+}	0.00	0.00	0.00
Lu_2O_3	0.00	0.00	0.00	Lu^{3+}	0.00	0.00	0.00
Y_2O_3	1.62	0.45	0.11	Y^{3+}	0.04	0.01	0.00
MnO	0.00	0.00	0.02	Mn^{2+}	0.00	0.00	0.00
CaO	0.46	0.64	0.03	Ca^{2+}	0.02	0.03	0.00
Na_2O	0.01	0.02	0.00	Na^+	0.00	0.00	0.00
Cl	0.01	0.02	0.03	Cl^-	0.00	0.00	0.00
F	0.39	0.36	0.36	F^-	0.05	0.05	0.05
O=Cl	0.00	0.00	-0.01	O^{2-}	3.95	3.95	3.95
O=F	-0.16	-0.15	-0.15				
TOTAL	99.08	96.90	97.84	CATSUM	2.01	2.03	1.99
[REE+Y]₂O₃	*63.71*	*59.01*	*65.28*	AN SUM	4.00	4.00	4.00

*Ta, Al, Sr, Mg, Fe, Ba and K were sought but not detected.
*Formula contents on a basis of 4 anions pfu.

Table 3. Electron microprobe compositions for xenotime.

Sample #	1131 C	1131 J	119	CMN F92-15		1131 C	1131 J	119	CMN F92-15
Locality	Novo Horizonte	Novo Horizonte	Serra Verde	Gunter Quarry		Novo Horizonte	Novo Horizonte	Serra Verde	Gunter Quarry
# Analyses	5	5	6	5					
Nb_2O_5 (wt.%)	0.07	0.08	0.06	0.08	Nb^{5+} (apfu)	0.001	0.001	0.001	0.001
P_2O_5	29.12	30.83	32.18	34.16	P^{5+}	0.899	0.919	0.938	0.967
SiO_2	0.2	0.23	0.46	0.53	Si^{4+}	0.007	0.008	0.016	0.018
TiO_2	0	0.01	0	0	Ti^{4+}	0	0	0	0
ZrO_2	0.13	0.11	0.16	0.17	Zr^{4+}	0.002	0.002	0.003	0.003
UO_2	0.07	0.01	1.59	0.58	U^{4+}	0.001	0	0.012	0.004
ThO_2	0.07	0.33	0.33	0.53	Th^{4+}	0.001	0.003	0.003	0.004
Al_2O_3	0	0	0	0.01	Al^{3+}	0	0	0	0
La_2O_3	0	0	0	0	La^{3+}	0	0	0	0
Ce_2O_3	0	0.02	0.04	0	Ce^{3+}	0	0	0.001	0
Pr_2O_3	0	0	0	0.01	Pr^{3+}	0	0	0	0
Nd_2O_3	0.05	0.08	0.29	0.15	Nd^{3+}	0.001	0.001	0.004	0.002
Sm_2O_3	1.05	0.7	0.77	0.34	Sm^{3+}	0.013	0.008	0.009	0.004
Eu_2O_3	0.35	0.12	0	0	Eu^{3+}	0.004	0.001	0	0
Gd_2O_3	5.71	3.88	2.74	1.46	Gd^{3+}	0.069	0.045	0.031	0.016
Tb_2O_3	1.48	1.02	0.87	0.33	Tb^{3+}	0.018	0.012	0.01	0.004
Dy_2O_3	9.75	7.73	6.93	3.58	Dy^{3+}	0.115	0.088	0.077	0.039
Ho_2O_3	1.72	1.67	1.51	1.02	Ho^{3+}	0.02	0.019	0.017	0.011
Er_2O_3	4.94	5.26	5.18	3.88	Er^{3+}	0.057	0.058	0.056	0.041
Tm_2O_3	0.51	0.54	0.66	0.61	Tm^{3+}	0.006	0.006	0.007	0.006
Yb_2O_3	2.14	2.51	4.09	5.15	Yb^{3+}	0.024	0.027	0.043	0.052
Lu_2O_3	0.11	0.23	0.6	0.82	Lu^{3+}	0.001	0.002	0.006	0.008
Y_2O_3	41.82	44.51	42.87	45.72	Y^{3+}	0.812	0.834	0.785	0.813
FeO	0.02	0	0	0	Fe^{2+}	0.001	0	0	0
BaO	0	0	0	0.01	Ba^{2+}	0	0	0	0
CaO	0	0	0.01	0.01	Ca^{2+}	0	0	0	0
Na_2O	0.01	0	0	0	Na^{+}	0.001	0	0	0
Cl	0	0	0	0.02	Cl^{-}	0	0	0	0.001
F	0.3	0.33	0.35	0.51	F^{-}	0.035	0.037	0.038	0.054
O=Cl	0	0	0	0	O^{2-}	3.965	3.963	3.962	3.945
O=F	-0.13	-0.14	-0.15	-0.21					
TOTAL	99.49	100.06	101.54	99.46	CATSUM	2.052	2.036	2.017	1.994
$[REE+Y]_2O_3$	69.63	68.27	66.55	63.07	AN SUM	4	4	4	4

*Ta, Sr, Mg, Mn, and K were sought but not detected

*Formula contents on a basis of 4 anions pfu.

Table 4. Electron microprobe compositions for britholite.

Sample #	Mariano 001	CMNOC F90-8		Mariano 001	CMNOC F90-8
Locality	Kipawa	Kipawa		Kipawa	Kipawa
# Analyses	5	6			
Nb_2O_5			Nb^{5+}		
(wt.%)	0.01	0.02	(apfu)	0.001	0.002
P_2O_5	3.03	3.99	P^{5+}	0.708	0.854
SiO_2	17.23	20.12	Si^{4+}	4.758	5.088
ZrO_2	0.01	0.02	Zr^{4+}	0.001	0.002
UO_2	0.22	0	U^{4+}	0.014	0
ThO_2	1.26	3.24	Th^{4+}	0.079	0.186
La_2O_3	9.01	6.09	La^{3+}	0.918	0.568
Ce_2O_3	17.29	15.4	Ce^{3+}	1.748	1.426
Pr_2O_3	2.04	1.91	Pr^{3+}	0.205	0.176
Nd_2O_3	7.75	7.22	Nd^{3+}	0.764	0.652
Sm_2O_3	1.91	1.63	Sm^{3+}	0.182	0.142
Eu_2O_3	0.07	0.16	Eu^{3+}	0.007	0.014
Gd_2O_3	1.53	1.52	Gd^{3+}	0.14	0.127
Tb_2O_3	0.33	0.26	Tb^{3+}	0.03	0.022
Dy_2O_3	1.93	1.92	Dy^{3+}	0.172	0.156
Ho_2O_3	0.22	0.39	Ho^{3+}	0.019	0.031
Er_2O_3	1.15	1.26	Er^{3+}	0.1	0.1
Tm_2O_3	0.02	0.1	Tm^{3+}	0.002	0.008
Yb_2O_3	0.52	0.96	Yb^{3+}	0.044	0.074
Lu_2O_3	0	0.01	Lu^{3+}	0	0.001
Y_2O_3	9.81	11.35	Y^{3+}	1.442	1.527
SrO	0.03	0.03	Sr^{2+}	0.005	0.004
MnO	0.03	0.02	Mn^{2+}	0.007	0.004
BaO	0	0.01	Ba^{2+}	0	0.001
CaO	16.33	17.57	Ca^{2+}	4.832	4.76
Na_2O	0.08	0	Na^+	0.043	0
Cl	0.01	0.05	Cl^-	0.005	0.021
F	1.59	1.28	F^-	1.389	1.024
H_2O *	0.33	0.57	OH^-	0.607	0.955
O=Cl	0	-0.01	O^{2-}	24	24
O=F	-0.67	-0.54			
TOTAL	**93.07**	**96.55**	Sum [Si]	5.466	5.942
[REE+Y]$_2O_3$	*53.58*	*50.18*	Sum [REE1, 2]	10.755	9.983
			Sum (F, Cl, OH)	2.001	2
			CATSUM	16.219	15.927
			AN SUM	26	26

*Determined by stoichiometry, H_2O calculated assuming 2 (OH^-, Cl^-, F^-) pfu.
**Formula contents on a basis of 26 anions (O+F) pfu.
***Ta, Ti, Al, Mg, Fe and K were sought but not detected.

Table 5. Prominent absorption features of REE-bearing phosphate minerals enriched in LREE in the VNIR range

monazite: UofA_UnkSE			Probable Origin	fluorapatite: Fir			Probable Origin	britholite: CMNOC			Probable Origin
C#	λ (nm)	shape		C#	λ (nm)	shape		C#	λ (nm)	shape	
1	575	SH	Nd								
	576	MIN - n	Nd								
	579	**MIN - st**	**Nd**	1	**576**	**MIN - st**	**Nd**				
	581	**MIN - st**	**Nd**								
	584	MIN - w, n	Nd		**585**	**MIN - st**	**Nd**	1	**584**	**MIN - b, n**	**Nd**
	592	MIN - w, n	Nd, Pr		602	MIN - w, n	Nd				
2	622	MIN - n	Nd					2	621	SH - n	Nd
	624	MIN - n	Nd								
	625	**MIN - n**	**Nd**						635	SH - n	Nd
	653	SH - w, n, b	Ho, Er, U?						**653**	**MIN - n**	**Er, Ho**
	673	MIN	Nd								
	676	SH	Nd								
	679	**MIN**	**Nd**						**685**	**MIN - n**	**Nd**
	689	SH	Nd								
3	734	SH	Nd								
	738	MIN	Nd	2	738	**MIN**	**Nd**				
	745	**MIN - st**	**Nd**					3	743	SH	Nd>Dy
	747	SH	Nd		747	SH	Nd		**747**	**MIN - st, b**	**Nd>Dy**
	749	SH	Nd		**749**	**MIN - st**	**Nd**				
	757	SH	Nd		763	MIN	Nd				
	770	SH	Nd								
4	792	MIN - w	Nd								
	796	MIN - w	Nd	3	795	SH	Nd	4	797	SH	Nd>Dy, Er
	800	**MIN - st**	**Nd**		800	MIN	Nd		799	SH	Nd>Dy, Er
	804	MIN - w	Nd		**805**	**MIN - st**	**Nd**		805	**MIN - st, b**	**Nd>Dy, Er**
	814	SH	Nd		817	MIN - w, b, n	Nd				
	830	SH	Nd								
5	**863**	**MIN**	**Nd**					5	867	MIN	Nd
	871	**MIN - st**	**Nd**	4	**870**	**MIN**	**Nd**		879	MIN - st	Nd
	877	SH	Nd								
	887	MIN	Nd								
	896	SH	Nd								
	906	MIN - w	Nd								
6	**941**	**MIN**	**Sm**								
	957	**MIN - w**	**Sm**								
7	**980**	**MIN - n**	**Yb>Er**					6	**978**	**MIN - st**	**Yb>Er**

*All lanthanides are considered to be trivalent (Ln^{3+})
C# denotes Cluster Number, as referred to in the text

Table 6. Prominent absorption features of REE-bearing phosphate minerals enriched in LREE in the SWIR range

monazite: UofA_UnkSE			Probable Origin	fluorapatite: Fir			Probable Origin	britholite: CMNOC			Probable Origin
C#	λ (nm)	shape		C#	λ (nm)	shape		C#	λ (nm)	shape	
8	1023	MIN	Pr								
	1074	MIN - st	Sm		1086	SH	Sm	7	1074	MIN - st	Sm
	1105	SH	Sm		1112	SH	Sm		1105	SH	Sm
	1150	SH	Pr								
9	1232	MIN - st	Sm		1232	MIN	Sm	8	1225	MIN - st	Sm
	1257	MIN	Sm						1257	SH	Sm > Dy
									1288	SH	Dy
10	1377	MIN	Sm		1382	SH	Sm	9	1377	MIN	Sm, Dy
	1415	SH	H_2O		1433	MIN - w	H_2O		1415	SH	H_2O
	1452	SH	Pr								
	1471	MIN	Pr						1478	SH	Pr
	1553	MIN	Sm?		1522	SH	Sm > Er		1528	MIN - st	Sm > Er
	1578	SH	Pr						1559	SH	Pr
									1591	SH	Sm, Pr
	1691	MIN	Dy, Nd								
	1710	MIN	Nd					10	1723	MIN	Nd, Dy
	1717	SH	Nd								
	1735	SH	Nd								
11	1968	MIN - st	Pr, Sm, H_2O						1943	MIN - st	Pr, Sm, H_2O
									1986	SH	Pr, Sm
	2011	SH	Pr, Sm						2018	SH	Pr, Sm, Ho
12	2212	SH	REE/OH/PO_4					11	2168	MIN	REE/OH/PO_4
			REE/OH/PO_4					12	2318	MIN	REE/OH/PO_4
	2368	MIN	REE/OH/PO_4						2343	MIN	REE/OH/PO_4
	2393	SH	REE/OH/PO_4						2387	MIN	REE/OH/PO_4
	2424	MIN	REE/OH/PO_4						2405	SH	REE/OH/PO_4
	2499	MIN	REE/OH/PO_4						2437	SH	REE/OH/PO_4
									2462	MIN	REE/OH/PO_4
									2480	MIN	REE/OH/PO_4

*Note that dolomite-related absorptions for the fluorapatite spectrum are not listed.

**All lanthanides are considered to be trivalent (Ln^{3+})

C# denotes Cluster Number, as referred to in the text

Table 7. Prominent absorption features of xenotime in the VNIR (left) and SWIR (right) ranges

C#	Novo Horizonte J λ (nm)	shape	Gunter Quarry λ (nm)	shape	Probable Origin
1	**643**	**MIN**	**643**	**MIN**	**Ho>Er**
	647	MIN	648	MIN	Ho, Er
	651	MIN	651	MIN	Ho, Er
	653	**MIN**	**653**	**MIN**	**Ho, Er, U^{4+}**
	657	MIN	658	MIN	Ho, Er
	661	SH	661	MIN	Ho, Er
	665	MIN	665	SH	Ho, Er
	667	MIN - n	667	SH	Ho, Er
	668	**SH**	**668**	**MIN**	**Er>Ho**
	678	**SH - n**	**678**	**MIN**	**Er>Ho, Nd**
	689	SH	689	MIN - w	Er>Ho, Nd
	692	**MIN**	**692**	**SH**	**Tm > Nd**
2	**740**	**MIN**	**740**	**MIN**	**Dy>Ho, Nd?**
	742	SH	742	SH	Dy>Ho, Nd?
	747	**MIN**	**748**	**MIN**	**Dy>Ho, Nd?**
	753	**MIN**	**754**	**MIN**	**Dy>Ho, Nd?**
	760	**MIN**	**760**	**MIN**	**Dy>Ho, Nd?**
	767	SH - w	767	SH - w	Nd?
3	781	MIN - w	781	MIN - w	Tm
	803	**MIN**	**803**	**MIN**	**Dy>Er, Nd?**
	811	**MIN - st**	**811**	**MIN -st**	**Dy>Er, Nd?**
	817	SH	817	SH	Dy, Er, Nd?
	822	SH	822	MIN	Dy, Er, Nd?
	823	MIN	823	SH	Dy, Er, Nd?
	826	MIN	826	MIN	Dy, Er, Nd?
	828	SH	829	MIN	Dy, Er, Nd?
4	**872**	**MIN**	**872**	**MIN**	**Nd**
	876	SH	876	MIN - w	Nd
	877	SH	877	MIN - w	Nd
5	896	SH	896	MIN	Dy, Yb, Ho
	909	SH	909	SH	Dy, Yb, Ho
	914	**MIN - st**	**914**	**MIN - st**	**Dy, Yb, Ho**
	920	SH	920	SH	Dy, Yb
	932	MIN	933	MIN	Dy, Yb
	951	**MIN - n**	**951**	**MIN - n**	**Dy, Yb, Sm**
	953	**MIN - n**	**953**	**MIN - n**	**Dy, Yb, Sm**
	961	MIN - n	961	MIN - n	Dy, Er, Yb
6			**977**	**MIN - st**	**Yb, Er**
	978	**MIN - st**	**978**	**MIN - st**	**Yb, Er**

C#	Novo Horizonte J λ (nm)	shape	Gunter Quarry λ (nm)	shape	Probable Origin
	1004	SH			Yb, Er
7			1036	SH	Yb, Er
			1080	SH	Sm
	1099	**MIN - st**	1099	SH	**Dy**
	1112	MIN	1118	SH	Dy, U^{5+}
	1143	SH	1143	MIN - st	Ho, Dy, U^{4+}
			1168	SH	Dy>Ho
	1187	MIN	1193	SH	Ho, Dy
8	1213	SH			Dy, Tm
	1257	SH	1257	SH	Dy, Sm
	1276	**MIN**	**1276**	**MIN**	**Dy**
	1301	**MIN**	**1307**	**MIN**	**Dy**
	1320	SH	1326	SH	Dy
	1358	SH	1358	MIN	Dy
9	**1408**	**MIN**	**1415**	**MIN**	**H$_2$O**
10	1433	MIN	1452	SH	Er
	1503	**MIN**	**1503**	**MIN - st**	**Er>Sm, U^{5+}**
	1528	**MIN**	**1528**	**MIN**	**Er>Sm**
	1559	SH	1559	SH	Er
	1585	MIN	1585	SH	Er
11	1616	MIN			Dy>Sm, Tm
	1660	SH			Dy
	1704	**MIN**	**1704**	**MIN - st**	**Dy**
	1723	**MIN**	**1723**	**SH**	**Dy, Tb**
	1761	SH	1761	SH	Dy, Tb
	1805	MIN	1805	SH	Dy
12	1848	SH			Tb, Ho
	1880	**MIN**			**Tb, Ho**
13	**1936**	**MIN**	**1936**	**MIN - st**	**Ho, Tb, H$_2$O**
	1961	MIN	1961	MIN	Ho
	1980	MIN	1980	SH	Ho, Sm
	2005	**MIN - st**	**2005**	**MIN**	**Ho, Sm, Tb**
	2030	MIN	2030	SH	Ho, Sm
	2043	MIN	2049	SH	Ho, Sm
	2130	SH			Ho, Sm, Tb
14	**2212**	**MIN - st**	**2218**	**MIN**	**REE/OH/PO$_4$**
	2262	MIN - st			REE/OH/PO$_4$
	2312	MIN - st	2312	MIN	REE/OH/PO$_4$
	2349	SH			REE/OH/PO$_4$
	2399	MIN			REE/OH/PO$_4$
	2462	MIN	2462	SH	REE/OH/PO$_4$
			2474	SH	REE/OH/PO$_4$
	2499	SH	**2487**	**MIN - st**	**REE/OH/PO$_4$**

*All lanthanides are considered to be trivalent (Ln^{3+})

C# denotes Cluster Number, as referred to in the text