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1 Time-resolved Raman and luminescence spectroscopy of synthetic REE- 2 doped hydroxylapatites and natural apatites

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14 Abstract

15 Apatites are phosphate minerals of broad interest in Earth and planetary sciences, and beyond. Using
16 continuous and time-resolved spectroscopy, we investigate the Raman and luminescence signal from
17 synthetic hydroxylapatites doped with trivalent Rare-Earth Elements (REE) dysprosium (Dy³⁺),
18 Europium (Eu³⁺), Neodymium (Nd³⁺) and Samarium (Sm³⁺), as well as from natural apatites, with laser
19 excitation at 532 nm and 785 nm. We demonstrate that time-resolved spectroscopy is extremely efficient
20 to reject luminescence from Raman spectra or, alternatively, to investigate the luminescence signal
21 without the interference of the Raman contribution. Time-resolved luminescence spectroscopy is found
22 powerful to generate specific high-quality luminescence spectra for the REE emission activators in
23 apatites by using appropriate combinations of delay and gate width for the time synchronization of the
24 laser pulse and ICCD detector. This allows unambiguous detection and identification of the activators
25 by avoiding overlapping of various emission signals in the luminescence spectra, which is particularly
26 useful in the case of natural samples that often include several activators for luminescence. In the case
27 of synthetic REE-doped apatites, a quenching process of luminescence due to the activator concentration
28 is evidenced for Eu³⁺ and Sm³⁺: the higher the concentration, the shorter the luminescence decay time.
29 The interpretation of luminescence decay time in natural apatites is promising but more complex
30 because of energy transfers between the various luminescence activators present in the mineral structure.
31 Luminescence is a powerful signal to detect the presence of REE in apatites down to ppm levels, yet it
32 is challenging to quantify the concentration.

33
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37 **Introduction**

38

39 The calcium phosphate apatites with general formula $[\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})]$ are among the
40 most common accessory minerals in terrestrial rocks and in meteorites; they have also recently
41 been identified *in situ* on Mars by the ChemCam LIBS instrument onboard the Curiosity rover
42 (Forni et al. 2020). They are also a very important biomineral constitutive of bones or teeth as
43 well as a primary source of phosphorous, a key element for life and many human activities. In
44 Earth and planetary sciences, apatites are sensitive tracers of volatiles and fluid-rock
45 interactions in terrestrial metamorphic rocks (Harlov 2015), terrestrial magmatic and volcanic
46 rocks (Webster & Piccoli 2015) as well as in meteorites (McCubbin & Jones 2015). They are
47 important minerals for thermochronological and geochronological investigations of processes
48 occurring at various depths and temperatures (Chew & Spikings 2015). Last but not least,
49 apatites offer an unusual range of applications and use for human activity making them a
50 technological gem: this includes ecology, agronomy, biology, medicine, archeology,
51 environmental remediation, and materials science (Rakovan & Pasteris 2015; Gomez-Morales
52 et al. 2013). It is thereby important to constantly improve the tools for the characterization of
53 the structure and chemistry of apatites. To this aim, vibrational spectroscopies like infrared and
54 Raman, as well as luminescence spectroscopy provide rich information, and a number of
55 practical advantages making them nowadays inevitable when exploring the physico-chemical
56 properties of such minerals.

57 Raman spectroscopy is useful for a quick, non-destructive and non-ambiguous
58 identification of apatites down to the microscale (Antonakos et al. 2007). In addition, Raman
59 spectroscopy provides valuable information on the presence of OH⁻ in the halogen site and,
60 more generally, on the type of apatite: hydroxyl- versus fluor- versus chlor- apatites (Antonakos
61 et al. 2007). It can also be used to assess the cristallinity of apatite and to track possible
62 carbonate incorporation in bioapatite through CO₃²⁻ substitution for PO₄³⁻ tetrahedra (Awonusi
63 et al. 2007, and see Pasteris & Beyssac 2020 and references therein). Laser excitation during
64 Raman analysis may also induce emission of luminescence in apatite. Luminescence is used
65 here as a generic term describing all kinds of photoluminescence whatever the mechanism of
66 light emission, e.g., fluorescence, luminescence, or phosphorescence (see Gaft et al. 2015 and
67 Waychunas 2014 for further details). Because the luminescence signal can be extremely strong
68 and can completely overwhelm the Raman signal, it is often considered as a severe limitation
69 for proper Raman analysis. In some cases, the luminescence peaks can be so sharp that they
70 actually may be confused with Raman peaks (Lenz et al. 2015). However, in many cases,

71 luminescence carries a rich and valuable information complementary to Raman (Gaft et al.
72 2015; Nasdala et al. 2004; Panczer et al. 2012; Waychunas 2014), particularly in apatites
73 (Waychunas 2002; Gaft & Panczer 2013). Recent developments in Raman mapping further
74 allow for mapping luminescence patterns in minerals at the microscale opening new avenues
75 for the non-destructive investigation of internal microtexture of minerals (Nasdala et al. 2012;
76 Lenz and Nasdala 2015).

77 One possibility to avoid or limit luminescence is to change the wavelength of the laser
78 excitation used for Raman analysis in the range from the deep ultra-violet (UV) to the near
79 infrared (IR). This approach works well in some cases but it is also limited by severe analytical
80 challenges (e.g. deep UV) or by the poor Raman efficiency at high wavelength in the near IR
81 region (Dubessy 2012; Beyssac 2020 for a review). Another possibility is to use time-resolved
82 (TR) spectroscopy, which uses the different lifetimes of the Raman and luminescence
83 processes. The Raman effect is actually a prompt phenomenon with an extremely short lifetime
84 ($\approx 10^{-15}$ s). By contrast, the lifetime of luminescence processes in minerals is longer, ranging
85 from fractions of nanoseconds to seconds and even more (Panczer et al. 2012; Gaft et al. 2015).
86 By perfectly synchronizing in the time-domain a pulsed-laser (in the nanosecond range) with a
87 gated intensified CCD (ICCD), it is possible to excite effectively the Raman effect and to reject
88 efficiently most of the luminescence especially if it has a long decay time. Furthermore, time-
89 resolved spectroscopy makes possible the exploration of the time decay or lifetime of
90 luminescence, which is a measure of the transition probability between two specific levels.
91 Such lifetime is then a specific and unique property of the luminescence signal (Gaft and
92 Panczer 2013) for a given electronic transition in a precise crystallographic environment.

93 Rare-Earth Elements (REE) also named lanthanides, are a large and very important
94 group of elements in mineralogy and geochemistry. REE can actually be incorporated during
95 mineral formation and evolution as trace elements in various mineral matrices. REE
96 incorporation in minerals and further exchanges are fundamental in geochemistry and have
97 provided key information on many geological processes. Optical properties like luminescence
98 of REE as trace elements in minerals may be treated similarly to those of impurities in crystals.
99 Since they behave as emission centers, here called luminescence activators, in minerals, their
100 luminescence properties are used to track them by photoluminescence or to map them to detect
101 possible internal zoning in minerals using cathodoluminescence (Waychunas 2014; Gaft et al.
102 2015) or photoluminescence (Lenz and Nasdala 2015). Because the apatite structure can
103 accommodate a large variety of elements, it is a well adapted matrix for trapping minor and
104 trace elements, in particular REE. In natural apatites, monitoring REE contents may then inform

105 on the constitution and evolution of local mineralogical grounds. On fossil bones, REE are
106 progressively incorporated in bone apatite during diagenesis, upon enrichment from the
107 surrounding minerals (Suarez et al., 2010). In the field of nanomedicine, the intentional
108 incorporation of luminescent REE as dopants in synthetic apatites allows nanoparticle tracking
109 in medical diagnosis (Mondéjar et al., 2007, Al-Kattan et al., 2014); and their luminescence
110 signal has been recently exploited, coupled to Raman and histology analyses, to follow the skin
111 penetration of apatite-based colloidal nanoparticles for dermatological applications (Choimet
112 et al. 2020). Luminescence spectroscopy is thus a powerful technique to investigate REE in
113 such mineral compounds, however it is still largely under-exploited.

114 Simple yet valuable investigations of luminescence properties in minerals can be done
115 with a conventionnal Raman spectrometer, an instrument largely accessible nowadays in
116 laboratories, and even for field studies (Jehlicka et al. 2017). Notably, there are more and more
117 combined LIBS and Raman investigations often with a single instrument (see Fau et al. 2019
118 and references therein): LIBS provides chemistry and Raman provides mineralogy. LIBS can
119 detect major and many trace elements but is not able to detect REE at low concentration.
120 Luminescence spectroscopy could fill the gap and provide detection of REE for such studies.
121 This is particularly the case for the SuperCam instrument, which is an instrumental suite to be
122 deployed on Mars onboard the NASA Perseverance rover in 2021. SuperCam will combine
123 remote LIBS and time-resolved Raman and luminescence spectroscopy, and could benefit from
124 the detection of REE by luminescence for a better understanding of geochemical processes at
125 the surface of Mars (Wiens et al. 2021, Maurice et al. in press, Beyssac 2020).

126 The purpose of the present study is to investigate (i) the structure by Raman
127 spectroscopy and (ii) the luminescence properties, of synthetic REE-doped apatites used as
128 standards as well as natural apatite specimens. In the case of synthetic hydroxylapatites, they
129 are doped with one single trivalent lanthanide (Eu^{3+} , Sm^{3+} , Nd^{3+} or Dy^{3+}) at relevant geological
130 concentration and we explore the corresponding luminescence spectra. We also document the
131 decay time of the luminescence signal for various concentrations of the doping REE element.
132 The case of natural apatites is interesting but more complex to interpret since several emission
133 centers for luminescence are present within a given sample. Comparison of the time-resolved
134 luminescence spectra of synthetic and natural apatites is first discussed for a better
135 interpretation of the peaks in the emission spectra of luminescence. In addition, we discuss
136 possible factors affecting the luminescence signal of REE in apatites, in particular those
137 controlling the evolution of luminescence in the time domain like quenching and/or sensitizing
138 phenomena.

139

140 **Apatite: an overview on Raman and luminescence**

141 Apart from few exceptions, such as pure chlorapatite (monoclinic system, space group $P2_1/b$),
142 apatites most generally crystallize in a hexagonal structure in the $P6_3/m$ space group symmetry.
143 These compounds contain five crystallographic sites: the Ca1 (9-fold coordination) and Ca2 (7-
144 fold coordination) sites, the P site, the halogen/ OH^- site and “defect” sites following the
145 terminology by Waychunas (2002). More details on the topology of these sites and, more
146 generally, on the crystal structure of apatites may be found in Hughes and Rakovan (2002) or
147 Hughes and Rakovan (2015).

148 The Raman spectrum of apatites has been extensively described by O'Shea et al. (1974)
149 and Antonakos et al. (2007). Interestingly, apatites include the PO_4^{3-} and OH^- ions that can be
150 easily detected by Raman (Rey et al. 2014). The most intense peak, often used for a quick
151 detection of phosphate minerals is located at $\approx 960 \text{ cm}^{-1}$ for apatites and is due to the ν_1
152 symmetric stretching mode of PO_4^{3-} . Additional peaks due to PO_4^{3-} are the doubly degenerate
153 ν_2 bending mode at $\approx 430 \text{ cm}^{-1}$, the triply degenerate antisymmetric ν_3 stretching mode at \approx
154 1060 cm^{-1} and the triply degenerate ν_4 bending mode at $\approx 580 \text{ cm}^{-1}$. OH^- , when present,
155 contributes a large band at $\approx 3570 \text{ cm}^{-1}$ while F^- and Cl^- are not directly detected by Raman.
156 However, the presence of F^- and/or Cl^- in the OH^- site may induce a shift of the various PO_4^{3-}
157 vibration modes as well as modifications in the OH^- domain due to a modified configuration of
158 hydrogen bonds.

159 Luminescence of apatites has been extensively studied from a long time (Blasse 1975).
160 Waychunas (2002) and Gaft et al. (2015) made comprehensive reviews while other studies were
161 dedicated to the specific luminescence of Eu (Kottaisamy et al. 1994; Gaft et al. 1997), or more
162 generally to the REE luminescence patterns in apatites (Reisfeld et al. 1996; Czaja et al. 2010).
163 Some studies are dedicated to other emission centers such as U^{6+} and $(\text{UO}_2)^{2+}$ (Panczer et al.
164 1998) or Mn^{2+} (Gaft et al. 2015) in apatite. Waychunas (2002) provided a detailed description
165 of the type of luminescence activators and described the link with the apatite structure. The five
166 sites of apatites can be occupied by activators, but the most common ones, *i.e.* those observed
167 in natural apatites, in particular REE or Mn^{2+} , actually go in the Ca1 and Ca2 sites (Waychunas
168 2002).

169 One important point to emphasize is that some activators like Mn^{2+} will generate very
170 broad emission bands because of the different symmetries of the ground and excited electronic
171 states. Alternatively, activators for which the change in configurational coordinate between

172 ground and excited state is small, or even null, will generate very narrow emission lines. This
173 is the case for REE³⁺, for which (i) the parity forbidden *4f-4f* transitions should be weak unless
174 being enhanced by symmetry crystal fields establishing a relationship between intensity and
175 site symmetry, and (ii) the allowed *4f-5d* transitions generally lead to slightly broader bands.
176 Activators generally do not behave independently in the apatite structure and some may transfer
177 part or all of their energy to other nearby activators becoming sensitizers. This applies to some
178 REE³⁺ that can be sensitized by Mn²⁺: this triggers and enhances emission by REE³⁺ and
179 decreases that of Mn²⁺ (Marfunin 1979). Conversely, some authors have argued that Eu²⁺ can
180 act as a sensitizer of Mn²⁺ luminescence (Knutson et al. 1985; Kottaisamy et al. 1994). Of
181 course, not only a single but many REE are generally present in natural apatites making very
182 likely the occurrence of transitions with similar energy. This may favor not only single energy
183 transfer but also multiple ones involving several REE (Waychunas 2002).

184 In natural apatites, REE can easily substitute for Ca and become emission centers for
185 luminescence in the crystallographic structure of the host apatite. Most REE can be
186 incorporated in either the Ca1 or Ca2 sites and be luminescent as trivalent or divalent ions.
187 When trivalent REE ions are incorporated in substitution of Ca²⁺, this is necessarily associated
188 to a charge balance mechanism (Hosseini et al., 2014), thus generating other “abnormalities”
189 or defects in the apatitic lattice which may somewhat alter locally the site symmetry (which
190 may have an impact on luminescence features). Studies by steady-state luminescence, *i.e.*
191 continuous excitation in the time domain, in general using UV excitation, have demonstrated
192 that natural apatite luminescence is dominated by divalent Mn²⁺ and Eu²⁺ and trivalent Ce³⁺,
193 Dy³⁺, Nd³⁺ and Sm³⁺ (Gaft et al. 2001). The particular case of Eu in apatites has been
194 extensively studied by Gaft et al. (1997, 2001) and Kottaisamy et al. (1994). These studies give
195 an overview of the complexity of REE luminescence in apatites but also of the rich information
196 that can be extracted with this technique. In apatite, Eu²⁺ luminescence appears as a single band
197 at ≈ 450 nm due to a *4f-5d* transition with a lifetime of 500 ns (Gaft et al. 2001). It has been
198 assigned to the Ca2 sites by Kottaisamy et al. (1994). Eu³⁺ luminescence is characterized by
199 lines at 590, 617, 651 and 695 nm and was assigned to the Ca1 site (Gaft et al. 2001). In
200 synthetic Eu-doped apatites under specific excitation, additional lines were observed at 575,
201 628 and 712 nm and were assigned to Eu³⁺ in the Ca2 site (Morozov et al. 1970).

202

203 **Samples: synthetic and natural apatites**

204 *REE-doped synthetic hydroxylapatites*

205 The REE-doped hydroxylapatites were synthesized at CIRIMAT Toulouse at relevant
206 geological concentrations, following the method described by Hosseini et al. (2014). The REE
207 selected for this study are trivalent Eu^{3+} , Sm^{3+} , Nd^{3+} and Dy^{3+} because they are important
208 geochemical tracers and their luminescence patterns in apatite is known. We selected trivalent
209 REE because they emit luminescence in spectral windows relevant to our instrumental setups
210 and they are also observed in natural samples. The REE salts used were purchased from
211 SIGMA-ALDRICH. First, we prepared a stock solution of each REE doping element with a
212 concentration of 0.04 mol/L by dissolving respectively europium(III) chloride hexahydrate,
213 ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ – molecular weight MW: 366.41 g/mol), samarium(III) nitrate hexahydrate,
214 ($\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ - MW: 444.47 g/mol), dysprosium(III) chloride hexahydrate, ($\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$
215 - MW: 376.95 g/mol) and neodymium(III) nitrate hexahydrate, ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ - MW:
216 438.35 g/mol) in deionized water. Preparation of hydroxylapatites was based on coprecipitation
217 obtained by mixing two starting solutions: solution A contained calcium nitrate tetrahydrate
218 ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ - MW: 236.15 g/mol) dissolved in deionized water to obtain a calcium
219 concentration of 0.4 mol/L, and solution B contained di-ammonium hydrogenphosphate
220 ($(\text{NH}_4)_2 \cdot \text{HPO}_4$ - MW: 132.06 g/mol) dissolved in deionized water at a phosphate concentration
221 of 0.13 mol/L. REE-doped hydroxylapatites at desired concentrations of doping element were
222 finally obtained by mixing solutions A and B and the relevant REE stock solution diluted as
223 necessary and to which 2 mL of 30% NH_4OH ammonia were added to increase the pH of the
224 solution in order to facilitate the hydroxylapatite precipitation. The obtained mixtures are then
225 placed in an oven at 143 °C for a duration of 14 hours. Three successive washing stages with
226 deionized water and centrifugation for 3 minutes at 7500 rpm were carried out in order to
227 remove traces of ammonia and unreacted salts present in the precipitating medium. Finally, the
228 samples were dried in an oven at 80 °C for a minimum of 8 hours.

229

230 *Natural apatites*

231 The natural apatite samples were selected from the collection de Minéraux (Sorbonne
232 Université, Paris) as raw millimetric to centimetric samples. Table 1 summarizes the main
233 information for each apatite specimen studied. These samples are either single crystals or
234 polycrystalline aggregates.

235

236 **Methodology: analytical techniques**

237

238 *Chemical analyses*

239 Major and trace element analyses for natural and synthetic apatites were done by alkali
240 fusion of rock samples (LiBO_2), followed by concentration measurements using an ICP-OES
241 Icap 6500 (Thermoscientific) for major elements, and an ICP-MS X7 (Thermoscientific) for
242 trace elements (protocol by Carignan et al., 2001). Analyses were performed at the Service
243 d'Analyse des Roches et Minéraux (SARM, CNRS, Nancy, France). For Dy^{3+} -doped synthetic
244 apatites, chemical analysis was performed on only one sample as the luminescence signal was
245 not detected for these samples (see below). Table 1 and Table 2 present the major (oxide wt%)
246 and trace element (mg/g) composition of the natural and synthetic REE doped samples
247 respectively. Figure 1 depicts the chondrite normalized REE patterns for the natural apatites.

248

249 *X-ray diffraction*

250 XRD was used to verify the apatitic nature of the synthetic apatites prepared. We used a
251 Panalytical Pro MPD operating at 40 kV, 40 mA with $\text{Co-K}\alpha$ radiation wavelength of $\lambda =$
252 1.788965 \AA . Diffractograms were recorded from 5 to 90° in a 2θ scale and 0.033° step size
253 during 3 cycles of 1.5 hour.

254

255 *Infrared spectroscopy*

256 Fourier transform infrared (FTIR) was used to characterize and verify the cristallinity and
257 molecular structure of the synthetic apatites. We used a Nicolet Magna 560 working under dry
258 air. All measurements were done in transmission mode with a Globar / Nernst lamp source and
259 a DTGS-CsI detector. Spectra were obtained in the $4000\text{-}400 \text{ cm}^{-1}$ range with a resolution of 2
260 cm^{-1} and by averaging 200 spectra. Before analyses, samples were prepared by mixing 1 mg of
261 REE-doped hydroxylapatite with 300 mg of dried KBr.

262

263 *Continuous-wave Raman spectroscopy*

264 All samples were analyzed using a continuous-wave (CW) Raman microspectrometer
265 Renishaw InVia Reflex for point analyses and Raman hyperspectral mapping when needed.
266 Measurements were performed using a green 532 nm solid-state laser focused on the sample
267 through a Leica DM2500 microscope with a long-working distance 50X objective ($\text{NA} = 0.55$).
268 This configuration yields a planar resolution of $\approx 1\text{-}2 \text{ }\mu\text{m}$ for a laser power delivered at the
269 sample surface set at less than 1 mW using neutral density filters to prevent irreversible thermal
270 damages. This corresponds to a laser irradiance in the range of $0.3\text{-}1.3 \text{ }10^9 \text{ W.m}^{-2}$. All
271 measurements were performed with a circularly polarized laser using a $\frac{1}{4}$ -wave plate placed
272 before the microscope in order to minimize polarization effects. The Raman signal was

273 dispersed by a grating with 2400 lines/mm and the signal was analyzed with a RENCAM CCD
274 detector. Some samples (Nd³⁺-doped hydroxylapatites) were also analyzed using a 785 nm
275 diode laser yielding a spot size of a few μm^2 for excitation and a 1200 lines/mm grating for
276 dispersion, the rest of the setup being the same.

277 For Raman mapping and the acquisition of hyperspectral maps, the sample was moved with
278 an appropriate step size using a XYZ Renishaw motorized stage. Laser focus was optimized by
279 correcting topographic variation prior to analysis (surface mode using the Renishaw Wire 4.3
280 software) and all maps were processed using the Wire 4.3 software. More about Raman
281 mapping can be found in Bernard et al. (2008). All measurements were performed at room
282 temperature and spectra were recorded directly on the raw samples without any preparation.

283 Note that CW Raman spectroscopy also provides steady-state luminescence emission
284 spectra in the range 532-720 nm with excitation at 532 nm, or in the range 785-930 nm with
285 excitation at 785 nm.

286

287 *Time-resolved Raman and luminescence spectroscopy*

288 All samples were also analyzed using a custom-built time-resolved Raman and luminescence
289 spectrometer described by Fau et al. (2019). The laser is a nanosecond (1.2 ns FWHM, 1 mJ
290 per pulse) pulsed diode-pumped solid-state (DPSS) laser operating at 532 nm with a 10 to 2000
291 Hz repetition rate. The laser is slightly defocused at the sample surface through a microscope
292 objective (MPlan Apo Mitutoyo 20X, NA= 0.42) and the Raman and luminescence signals are
293 collected in the backscattering geometry. In addition, the laser is circularly polarized thanks to
294 a $\frac{1}{4}$ -wave plate placed before the microscope in order to minimize polarization effects. In this
295 setup, a Notch filter cuts off the Rayleigh scattering at $\approx 90 \text{ cm}^{-1}$ and the signal is collected by
296 an optical fiber and sent into a modified Czerny-Turner spectrometer (Princeton Instruments
297 IsoPlane 320) coupled with an intensified Princeton Instruments PIMAX4 ICCD camera. The
298 fine control of both time delay and gating time of the camera allows sub-nanosecond time
299 resolution experiments thanks to a precise synchronization between the laser pulse and the
300 ICCD. This spectrometer has three motorized gratings which can be selected depending on the
301 spectral window and resolution requested for the experiment. Irradiance associated with a
302 pulsed laser can be estimated as $Q/(\tau S)$, with $Q = P/f$ being the laser energy per pulse, P being
303 the time-integrated laser power measured at the surface of the sample, f the laser repetition rate,
304 τ the pulse duration, and S the surface of the laser spot on the sample. For these experiments,
305 irradiance was set at $\approx 10^{10} \text{ W.m}^{-2}$ which is conservative even in the case of absorbing minerals
306 (Fau et al. 2019).

307

308 **Time-resolved Raman and luminescence spectroscopy: overview**

309 The luminescence signal is generally much stronger than the extremely weak Raman signal.
310 One way to separate the Raman signal from luminescence is to exploit the fact that these two
311 processes have very different lifetimes using time-resolved spectroscopy. Lifetime corresponds
312 to the time spent in any excited state, e.g. vibrational for Raman or electronic for
313 luminescence, before it returns to the ground state. For luminescent compounds, de-excitation
314 is expected to occur by the emission of a photon. However, depending on the energy gap
315 between the excited and ground states of a given luminescent center (e.g. Eu^{3+} or Tb^{3+} ions),
316 de-excitation may partially also occur by a non-radiative process as in the form of vibrational
317 energy (phonon) if a good energetic correspondence is found, as was reported in apatites with
318 O-H vibrations (Al-Kattan et al., 2014). However, even in this case, luminescent signals remain
319 strong. In all cases, light absorption is “immediate” in the range of 10^{-18} seconds, while Raman
320 and emission of luminescence are longer processes. Relaxation from virtual vibrational levels
321 is typically in the range of 10^{-15} seconds for Raman and can be considered as “immediate” at
322 our experimental time scale. On the other hand, going back from excited electronic levels to
323 the ground state is much slower, and the lifetime of luminescence covers a wide time range
324 from the nanosecond (e.g., organic fluorescence, Lakowicz 2006) to milliseconds or even
325 seconds (e.g., Cr^{3+} or REE^{3+} in minerals, Gaft et al. 2015).

326 Time-resolved spectroscopy uses a pulsed excitation signal synchronized with a gated
327 detector. The main idea is that the Raman signal will last only during the excitation pulse, while
328 the luminescence will be excited within the pulse but will continue to emit and decay after the
329 pulse. Using a short time gate perfectly synchronized with the laser pulse and matching it in the
330 time domain allows rejection of most of the luminescence signal and maximization of the
331 collection of the Raman signal. Time-resolved spectroscopy further allows the collection of
332 only the luminescence signal without any Raman contribution by simply opening the detector
333 gate just after the laser pulse. The Raman signal is then completely vanished and is absent in
334 the spectrum while luminescence is still present. In this study, we investigate the emission
335 spectra: all spectra were obtained with an incident excitation laser at 532 nm, or 785 nm in the
336 sole case of Nd^{3+} using the CW spectrometer. Such excitation wavelengths are likely not optimal
337 for triggering absorption and thereby emission of luminescence. Going towards UV would be
338 more efficient, but these wavelengths constitute a good compromise for combining Raman and
339 luminescence investigations.

340 The custom-built time-resolved instrument used for this study offers an excellent
 341 synchronization making possible the exploration of luminescence with various lifetimes. To
 342 this aim, an appropriate combination of delays (moment the detector gate opens with respect to
 343 the laser pulse) and gate width has to be used.

344 Lastly, this technique allows proper characterization of the time decay of luminescence by
 345 doing time sweep experiments: a post-pulse detector gate with appropriate opening duration is
 346 shifted at various time delays, and the integrated intensity of the signal can be plotted versus
 347 the shift time (delay). These data allow calculating the lifetime and give further information on
 348 the nature of the electronic transition and, more practically, on the identification of the emission
 349 center (Lakowicz 2006; Gaft & Panczer 2013; Gaft et al. 2015).

350 Luminescence decay is given by

$$351 \quad I(t) = I_0 e^{-\frac{t-t_0}{\tau}} \quad \text{equation (1)}$$

352 with I_0 the number of photons emitted at time t_0 , τ the lifetime of the considered transition.
 353 The analysis of luminescence decay is done by measuring the number of photons received
 354 during a time period controlled by the gate width and by shifting this gate through time after the
 355 laser pulse. Critical parameters are then the gate width t_g and t_s the time increment by which
 356 the gate is shifted.

357 Using the time-resolved setup one effectively measures:

$$358 \quad F(T) = \int_T^{T+t_g} I_0 e^{-\frac{t-t_0}{\tau}} dt \quad \text{equation (2)}$$

359 in $n+1$ points given by

$$360 \quad T_k = t_0 + k t_s \quad \text{equation (3)}$$

361 After normalisation by the gate width and introduction of equation (3), $F(T)$ becomes

$$362 \quad F(T_k) = I_0 t_g e^{-\frac{kt_s}{\tau}} \left(\frac{1 - e^{-\frac{t_g}{\tau}}}{\frac{t_g}{\tau}} \right) \quad \text{equation (4)}$$

363 Several aspects about methodological information can be retrieved from this equation. First,
 364 the gate width does not influence the experimental evaluation of τ because, whatever τ ,

365 $\left(\frac{1 - e^{-\frac{t_g}{\tau}}}{\frac{t_g}{\tau}} \right)$ is a constant value even if $\frac{t_g}{\tau}$ is large. For a reliable assesment of τ , luminescence

366 must have decayed notably so that $\frac{kt_s}{\tau} > \frac{1}{4}$. To have an acceptable uncertainty, the statistics has

367 to be good so k value has to be large. Lastly, the unpredictable factor is the intensity of

368 luminescence. The lower the intensity, the larger the accumulation of signal required to obtain

369 a correct spectrum. This is an important parameter to consider in such experiments, which has

370 an important effect on the duration of the time decay experimental analysis (time sweep
371 experiment).

372 To exploit efficiently the luminescence spectra and time sweep experiments, a specific
373 script was written using Python. A Voigt function is used for fitting all the peaks and includes
374 a Gaussian component with a fixed FWHM value at 13 cm^{-1} corresponding to the instrument
375 resolution and a Lorentzian component due to the luminescence signal. A linear baseline
376 defined by two points automatically calculated as the lowest points from a predefined region in
377 the spectrum is subtracted prior to luminescence peak fitting, and no normalization is
378 performed before data processing. For each time sweep experiment, the selected peaks are fitted
379 on the first spectrum of each series, when the signal-to-noise ratio is high, by letting free the
380 Lorentzian FWHM as well as the area and position of the Voigt band. A second series of fit is
381 then performed on the whole series of spectra with just the Voigt band area as a free parameter.
382 Lifetime is determined from the semi-logarithmic representation of intensity versus time delay
383 and is taken as the slope of the regression line extracted from the experimental points.

384 In addition, time-resolved spectroscopy allows exciting selectively luminescence
385 emissions from various emission centers if they have different lifetime decays. This is very
386 promising as one challenge in the interpretation of luminescence spectra, especially in the case
387 of natural minerals like apatites, is precisely that emission peaks from various emission centers
388 often overlap in the spectral domain.

389

390 **Results and discussion**

391

392 *Physico-chemical characterisation of the REE-doped synthetic apatites*

393 XRD diffractograms of synthetic hydroxylapatites display all the main characteristic peaks of
394 hydroxylapatite thus confirming the apatitic nature and the good crystallinity of the samples
395 produced (Figure 2). These findings are corroborated by FTIR spectroscopy analyses (Figure 3).
396 All the infrared spectra obtained are very similar among the different samples with various
397 concentrations of the doping element and exhibit the characteristic spectral features of
398 hydroxylapatite (Rey et al., 2014). The presence of an OH^- peak at 3570 cm^{-1} (O-H stretching)
399 and an associated libration band at 632 cm^{-1} confirm that the synthesis yielded hydroxylated
400 apatites. The presence of trace impurities in the form of nitrate NO_3^- ions is detectable as a
401 minor contribution ($\approx 1383\text{ cm}^{-1}$), and hydration of the synthetic apatites is detectable via a wide
402 band due to the vibration of H_2O molecules around 3400 cm^{-1} .

403 Chemical data for major and trace elements obtained on the synthetic apatites are
404 presented in Table 1. Table 1 shows that the range of concentrations obtained is wide for Eu^{3+} ,
405 Sm^{3+} and Nd^{3+} from tens to thousands of ppm, while Dy^{3+} was properly incorporated into the
406 analyzed synthetic apatite as well (although the luminescence signal is not detected, see below).
407 We also note that some samples have been slightly contaminated by the presence of another
408 lanthanide than the one used for synthesis. This is likely due to the imperfect purity level of the
409 initial REE salts. For instance, the sample of hydroxylapatite doped with a concentration of 24
410 ppm of samarium also has a europium concentration of around 5 ppm. Continuous-wave Raman
411 mapping was performed on some synthetic hydroxylapatites to assess their homogeneity by
412 obtaining thousands of spectra on a given sample. These maps showed that the structure of
413 these samples is homogeneous because the FWHM and peak position of the main ν_1 peak is
414 rather constant with only minor variations ($<1 \text{ cm}^{-1}$).

415

416 *Time-resolution: a considerable improvement for Raman spectroscopy*

417

418 Figure 4 depicts representative CW micro-Raman spectra obtained at random positions on the
419 synthetic apatites. Depending on the REE doping element, the Raman peaks characteristic of
420 apatite are clearly visible (Dy^{3+}), more or less visible (Sm^{3+}) or not visible (Eu^{3+}). Note that the
421 case of Nd^{3+} is different: Raman peaks are clearly visible when excited at 532 nm but non-
422 visible with excitation at 785 nm because the luminescence of Nd^{3+} is extremely strong in the
423 near IR region. Indeed, the Raman signal remains constant in Raman shift for all the synthetic
424 samples, while emission of luminescence after light absorption strongly depends on the
425 excitation wavelength for each REE. Eu^{3+} ions are highly excited at 532 nm and luminescence
426 completely masks the Raman signal while for Sm^{3+} luminescence is less strong and the Raman
427 signal is visible. In the case of Dy^{3+} -doped apatites, 532 nm is out of the range of absorption
428 (excitation) and emission of luminescence is not observed while Raman bands are nicely
429 recorded.

430 Alternatively, Figure 5 shows a representative Raman spectrum obtained with the time-
431 resolved Raman instrument with a short gate (5 ns) centered on the laser pulse. This spectrum
432 was obtained with a highly luminescent hydroxylapatite doped with 23,936 ppm Sm^{3+} , but
433 similar spectra were obtained with all other synthetic doped hydroxylapatites. The difference is
434 striking with CW Raman spectroscopy as no luminescence bands are detected while all the
435 Raman peaks are clearly visible, including the OH^- bands. This is due to the efficient rejection
436 of the REE luminescence which has a long lifetime for the REE considered here.

437 The case of the natural apatites is more complex when analyzed with CW Raman
438 spectroscopy (Figure 6): a very strong background including some peaks due to Raman and
439 luminescence is observed in all spectra. In general, only the main ν_1 symmetric stretching mode
440 of PO_4^{3-} is observed in these spectra (e.g., samples Tyrol, Saxe and Renfrew) while the other
441 modes are hardly detected in some samples (Slyudyanka and Imilchil). Clearly, using Time-
442 resolved Raman spectroscopy makes possible the rejection of almost all the luminescence
443 contributions in these natural apatites and the recording of high-quality Raman spectra without
444 any luminescence interference. It is particularly interesting in the case of REE because they
445 generate intense and thin peaks that can be easily confused with Raman peaks in phosphate
446 minerals but also in other mineral phases like zircon as discussed by Lenz et al. (2015).

447 In the REE-doped synthetic hydroxylapatites, the Raman shift of the ν_1 symmetric
448 stretching mode of PO_4^{3-} is nearly constant at about $960 \pm 1 \text{ cm}^{-1}$. In the natural apatites, this
449 PO_4^{3-} mode is in the range 963.8 to 965.4 cm^{-1} . A strong OH^- band is observed in all the
450 synthetic apatites while it is not observed in the natural apatites, even in the time-resolved
451 Raman spectra. The Raman shift of the ν_1 symmetric stretching mode of PO_4^{3-} is actually
452 sensitive to the nature of the apatite (Ashley et al. 2018): it occurs at $\approx 960 \text{ cm}^{-1}$ in pure
453 hydroxylapatite, $\approx 961 \text{ cm}^{-1}$ in pure chlorapatite and $\approx 965 \text{ cm}^{-1}$ in pure fluorapatite. This is due
454 to the fact that Cl^- has a much larger ionic radius compared to F^- . From these observations,
455 Raman investigations confirm that the synthetic apatites are pure hydroxylapatites as assessed
456 from infrared and XRD characterization. The natural apatites are solid solutions in between the
457 three endmembers (OH^- - Cl^- - F^- apatites) and the Raman spectra do not show a notable
458 contribution of OH^- , hence the contribution of the hydroxylapatite endmember is minor in these
459 samples. Based on the Raman shift of the ν_1 symmetric stretching mode of PO_4^{3-} , most natural
460 samples appear to have Raman shift values corresponding to high levels of F^- in the halogen
461 site and these samples likely correspond essentially to fluorapatites. Only the case of the
462 Imilchil sample is slightly different with a lower shift and this sample has likely a higher Cl^-
463 level in the halogen site.

464

465 *Time-resolved luminescence: detecting REE and other emission centers*

466

467 If time-resolved spectroscopy allows to get rid of luminescence features in Raman spectra, it is
468 also powerful to eliminate the Raman contribution from the luminescence spectra, and thereby
469 to unambiguously study the luminescence signal. For this, the ICCD gate just has to be opened

470 after the laser pulse when the Raman signal is completely relaxed and is no longer active. For
471 many minerals including apatites, the main luminescence emission lines can be attributed rather
472 confidently unless there is a strong overlap between various luminescence signals making the
473 interpretation complex (Gaft et al. 2015).

474 In the natural apatites, the total Raman and luminescence spectra obtained in
475 continuous-wave (CW) illumination are actually not straightforward to interpret (Figure 6). This
476 is due to the multiple emission lines of the various REE incorporated in the mineral structure
477 in addition to the contribution of other activators like Mn^{2+} . Mn^{2+} is actually likely partly
478 responsible for the broad background observed in most of these samples. Figures 7 illustrates
479 the capability of time-resolved spectroscopy to separate the Raman and luminescence signals
480 in the Durango apatite. In addition, this technique allows further investigating luminescence by
481 generating spectra specific of activators with various lifetimes by selecting appropriate
482 combinations of delays and gates. In the case of the Durango sample (Figure 7), this technique
483 allows to retrieve a clear spectrum of the short-lifetime luminescence signal from erbium by
484 opening a short gate (1,500 ns) just after the laser pulse (delay 6 ns). Erbium luminescence is
485 otherwise completely covered by longer lifetime emissions in the continuous wave emission
486 spectrum. In a complementary approach, this technique allows to analyze just the contribution
487 of long lifetime emissions by opening a wide gate (450,000 ns) long after the laser pulse (delay
488 1,500 ns). Ideally, if activators are expected in a given sample as well as the approximative
489 lifetime of their emission is known, appropriate combinations of delay and gate should allow
490 maximization of the emission signal for each activator. This makes time-resolved spectroscopy
491 an extremely powerful tool to avoid overlapping of various luminescence contributions from
492 REE and other emission centers in apatites and other mineral phases.

493 Alternatively, at a constant delay (e.g. just after the laser pulse) one can open the gate
494 with increasing values from 10 to thousands of ns (here we limit at 450,000 ns just before the
495 next laser pulse arriving at 500,000 ns at 2 KHz) to test the detection of various emission centers
496 with different lifetimes. This is illustrated on Figure 8 for the Durango apatite. With short gates
497 (<1,000 ns), only the short lifetime emission signal, here Er^{3+} , is visible in the spectrum because
498 of the less efficient rejection for short lifetime luminescence. Increasing the gate width allows
499 for the detection of other peaks corresponding to longer lifetime emission signals from Sm^{3+} ,
500 Eu^{3+} and Dy^{3+} . This approach is useful to obtain neat emission spectra for short lifetime
501 emissions but also to assess the rejection efficiency of the instrumental time resolution.

502 Luminescence spectra retrieved from the synthetic REE-doped hydroxylapatites are
503 easier to interpret (Figure 4). In the case of Eu^{3+} , a strong luminescence signal is observed at

504 all concentrations including the lowest. This signal is composed by several bands with two main
505 massifs centered at 590 and 620 nm corresponding respectively at $^5D_0-^7F_1$ et $^5D_0-^7F_2$
506 transitions. Other less important peaks are observed at ≈ 655 nm and $\approx 570-580$ nm and
507 correspond to $^5D_0-^7F_3$ et $^5D_0-^7F_0$ transitions. The case of Sm^{3+} is very similar to Eu^{3+} with two
508 main massifs occurring at ≈ 600 and 650 nm. Dy^{3+} has no emission bands observed in any of
509 the spectra even at concentrations as high as 500 ppm. It contrasts with the natural apatites in
510 which Dy^{3+} emission bands were observed at ≈ 590 nm. One possible explanation is that
511 emission by Dy^{3+} is sensitized either by another REE and/or by Mn^{2+} in the natural samples.
512 Marfunin (1979) and Waychunas (2002) have actually reported that Mn^{2+} can act as a sensitizer
513 for the luminescence of some REE: Mn^{2+} absorbs incident energy and transfers it to REE which
514 then emit light. In the case of the synthetic REE apatite, Dy^{3+} is alone and not excited therefore
515 it does not emit luminescence. In the case of Nd^{3+} , the luminescence peaks are detected only
516 with a continuous instrument with excitation at 785 nm because it corresponds to the best
517 excitation and the emitted signal occurs in the near infrared part of the spectrum. This sample
518 could not be studied with the time-resolved instrument (excitation at 532 nm). The Nd^{3+}
519 emission is characterized by an intense, broad massif with several peaks in the range 850 to 925
520 nm.

521

522 *Deconvolution of luminescence spectra: a challenging task*

523

524 A simple visual inspection of the spectra shows that (i) luminescence spectroscopy is extremely
525 sensitive down to the ppm level and (ii) the overall intensity of the luminescence signal
526 dramatically increases with the activator concentration. Figure 9 depicts the total intensity (sum
527 of areas for all peaks after peak fitting) of the luminescence signal for the massifs centered at
528 620 nm and 600 nm as a function of Eu^{3+} and Sm^{3+} concentration respectively. For figure 9, the
529 luminescence signal was analyzed with continuous spectroscopy and time-resolved
530 spectroscopy at laser repetition rate of 100 Hz: excitation/collection is continuous in the former
531 case while the latter case corresponds to the signal mostly generated by a single laser pulse (the
532 signal has almost completely decayed between two pulses). There is a sharp increase of the
533 intensity increasing concentration: the higher is the concentration, the stronger is the luminescence
534 signal. However, it is difficult to retrieve any quantitative information from this observation as
535 the absolute intensity of the signal depends on many other parameters like the sample surface
536 state and grain size, the sample effective optical absorption or the sample orientation with
537 respect to the incident laser beam.

538 Using the developed Python script, the Eu^{3+} and Sm^{3+} spectra of synthetic
539 hydroxylapatites at different concentrations and different delays from time sweep experiments
540 were deconvoluted. For Eu^{3+} , the fit was performed on the massif centered at 620 nm with 8
541 bands while it was done on the massif centered at 600 nm for Sm^{3+} with 5 bands. This is a rather
542 challenging task as these massifs are likely generated by a much larger number of electronic
543 transitions. For instance, Sm^{3+} luminescence in apatite results from a large number of f-f
544 electronic transitions. The $4f^5$ configuration of Sm^{3+} ion has at least 73 multiplets yielding 198
545 energy levels via spin-orbit interactions (Axe et Dieke, 1962). Not all these transitions are
546 excited and not all of them will generate emission if excited. The number of bands selected may
547 appear somewhat arbitrary, however it is determined by what is actually observed in the spectra.
548 First, in both the Eu^{3+} and Sm^{3+} cases, it was observed that within the considered massif, all the
549 peaks decay with the same lifetime. Second, to investigate the effect of the activator
550 concentration, several plots of the various peaks FWHM or relative intensities were made. In
551 general, no significant trends were observed except an increase of the 597 nm/604 nm peak area
552 ratio in the case of Sm^{3+} .

553 One purpose of these investigations was to check for possible correlations between any
554 spectral parameter and the luminescence activator concentration. This would provide a proxy
555 for quantification or semi-quantification of the activator thanks to its luminescence signal. No
556 such correlation was found for the spectral parameters. This contrasts with the Cr^{3+}
557 luminescence in ruby glasses. Cr^{3+} luminescence in ruby has been extensively studied and
558 results from optical absorption into the $^4\text{T}_2$ and $^2\text{T}_2$ levels and the two well-known emission
559 bands R1 (at 694.25 nm at 300K) and R2 (at 692.74 nm at 300K) originate from the ^2E level
560 (see Syassen 2008 and references therein). Chervin et al (2001) studied the spectral parameters
561 of emission spectra of ruby glasses spheres doped at various concentrations of Cr^{3+} as pressure
562 gauge for optically transparent high-pressure cells. They established clear correlations between
563 the Cr^{3+} concentration and the FWHM of both the R1 and R2 emission lines at various
564 excitation energies: the higher the concentration, the broader the two lines. Such correlations
565 can be used as a first-order proxy for Cr^{3+} concentration in ruby glasses.

566 In the case of natural apatites, the situation is even more challenging due to the multiple
567 overlapping luminescence signals detected in these samples. If time-resolved spectroscopy can
568 be powerful to discriminate short versus long lifetime signals in the emission spectra, one
569 challenge is that many overlapping REE emission signals have similar lifetimes among them
570 and with other emission signals (e.g. from Mn^{2+}) making a challenge any deconvolution of the
571 spectra.

572

573 *Luminescence lifetime: a powerful yet complex physical parameter to interpret*

574

575 Time sweep experiments were performed on the natural and synthetic apatites to investigate the
576 lifetime of Eu^{3+} and Sm^{3+} emission. For this, the laser repetition rate was set at 200 Hz, and 20
577 spectra with a gate of 1 ms were taken with the first being recorded 200 μs after the laser pulse
578 and the delay being augmented by 200 μs for each successive spectrum with a final spectrum
579 at 4 ms after the pulse. The total intensities of the 8 peaks composing the massif at 620 nm for
580 Eu^{3+} and of the 5 peaks of the massif at 600 nm for Sm^{3+} are plotted against time (here the
581 delay) as represented in figure 10. For both Eu^{3+} and Sm^{3+} , the higher the concentration of the
582 activator, the faster the decay of luminescence. From figure 10, the luminescence lifetime for
583 each decay curve for Eu^{3+} and Sm^{3+} can be calculated from equation (4) and plotted against the
584 activator concentration as shown on Figure 11. In both cases, there is a clear correlation between
585 the luminescence lifetime and the activator concentration, even at low concentration: the higher
586 the concentration, the shorter the luminescence lifetime. Such an acceleration of the decay of
587 the luminescence signal by increasing the concentration of the activator may be a consequence
588 of a concentration quenching effect. By increasing the number of activators in the mineral
589 structure, some activators may directly transfer their excitation energy to a neighbour activator
590 through a non-radiative process, *e.g.* by a vibrational process. Such a correlation has already
591 been observed for other materials like $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystals (Meza et al. 2014). These
592 authors established a clear correlation between the lifetime and Eu^{3+} concentration from
593 experimental data that they were able to model with a simple rate equation model. They
594 interpreted such correlation as the consequence of a concentration quenching involving energy
595 transfer among Eu^{3+} ions but also with O^{2-} . Also, as mentioned previously, in hydroxylated
596 apatites, part of the de-excitation energy may contribute to some O-H stretching, which was
597 evidenced in deuterated experiments (Al-Kattan et al., 2014).

598 Time sweep experiments were run with the natural apatites in the same configuration as
599 the one used for the synthetic samples. The Eu^{3+} massif at 620 nm and Sm^{3+} massif at 600 nm
600 were fitted following the procedure used previously in the case of the synthetic apatites. Time
601 decay figures can be generated for each natural apatite (not represented here) and the lifetime
602 of Eu^{3+} and Sm^{3+} emission signals can be calculated. Several spots were analyzed on each
603 natural apatite to have an insight into the intra-sample chemical and structural heterogeneity.
604 Figure 11 depicts all the calculated lifetimes for both natural and synthetic apatites for Eu^{3+} and
605 Sm^{3+} luminescence versus the concentration in Eu^{3+} and Sm^{3+} measured by ICP-MS. First of

606 all, natural samples show systematically a significant dispersion for the calculated lifetimes
607 compared to synthetic samples. Notably, in the case of Eu^{3+} , the concentrations observed in the
608 natural samples are lower than those of the synthetic ones. In addition, for Eu^{3+} , the scattering
609 of the lifetime values for natural samples covers a range almost similar to the complete range
610 of lifetime values in the synthetic samples. This dispersion may reflect first the intra-sample
611 chemical zoning for REE which is often observed in natural apatite minerals. More generally,
612 there is no clear correlation between the lifetime and the activator concentration for the natural
613 samples and the points retrieved from natural samples do not fall on the correlation observed
614 with the synthetic samples. They are generally above the curve obtained from the synthetic
615 samples, which means that luminescence is generally longer to relax in natural samples
616 compared to synthetic ones.

617 A major difference between natural and synthetic samples is the presence in the former
618 of several REE activators and even sometimes of other activators like Mn^{2+} , while the synthetic
619 samples are doped with a single activator (apart minor impurities mentioned above). There is
620 no easy interpretation for the different behavior but there is likely a complex interplay between
621 the various activators in the natural samples involving sensitizing and/or quenching processes
622 for luminescence among REE and/or with other activators. For instance, using time-resolved
623 spectroscopy, Czaja et al. (2010) demonstrated the effective energy transfer between
624 praseodymium Pr^{3+} and samarium Sm^{3+} in natural apatites and showed its effect on the lifetime
625 of emission luminescence of these crystals. Such effects are absent in the synthetic samples
626 which are doped with a single REE activator.

627 As already mentioned by Gaft and Panczer (2013), it is important to distinguish a
628 theoretical “true” decay time or lifetime from a real effective decay time or lifetime. The true
629 lifetime is an intrinsic physical parameter of a given transition for an activator in a crystal
630 structure in the absence of any non-radiative processes and obtained under precise conditions
631 (e.g. temperature, pressure). The effective lifetime is the one measured in the laboratory that
632 can be close to the true one in the case of “perfect” samples with one single activator and no
633 other impurities. But it can be very different in the case of natural samples. The effective
634 lifetime is actually possibly influenced primarily by external parameters like temperature or
635 analytical parameters, orientation of the crystal with respect to the polarization of the incident
636 laser beam; also irradiance may play a role for instance. Overall, as shown by this study, it can
637 depend on the internal properties of the samples like the presence of other impurities (other
638 activators, defects), which may trigger complex sensitizing and/or quenching phenomena by
639 energy transfer.

640

641 ***Implications***

642

643 Time-resolved spectroscopy is a very powerful tool to combine Raman and luminescence
644 spectroscopy as it allows performing both, separately and without interference in the spectral
645 data. In the case of REE, time-resolved spectroscopy is extremely efficient to detect and identify
646 them in accessory mineral phases like apatites or other phosphate minerals, titanite or zircons.
647 Owing to its capability to scan the time domain and selectively analyze each emission signal,
648 time-resolved spectroscopy provides information that is not accessible to steady-state, *i.e.*
649 continuous-wave, spectroscopy. A major achievement would be to reach some quantification,
650 or at least semi-quantification of luminescence activators in mineral phases from the
651 luminescence signal, either directly from the spectra or through the study of lifetime. This may
652 be possible in the case of systems involving one single activator such like Cr^{3+} in natural or
653 synthetic ruby, or in our synthetic REE-doped hydroxylapatites. It is a complex challenge in
654 systems involving more than one activator as activators are likely to transfer energy among
655 themselves generating complex quenching and/or sensitizing interactions and complexifying
656 the interpretation of the time-resolved data.

657 In a close future, on Mars, the Mars2020 SuperCam time-resolved instrument onboard
658 the Perseverance rover should benefit from time-resolved Raman and luminescence
659 spectroscopy for detecting and investigating REE not only martian phosphates but more
660 generally in martian rocks opening new avenues for our understanding of geochemical processes
661 at work on this planet (Wiens et al. 2021; Maurice et al. 2021).

662

663

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886 **Figures Caption**

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888 **Figure 1:** Chondrite-normalized REE patterns from ICP-MS analysis of natural apatites
889 (normalization factor from Sun and McDonough, 1989).

890 **Figure 2:** XRD diffractograms for the synthetic hydroxylapatites doped with europium at
891 increasing concentration (see table 2 for measured concentration). Similar cristallinity was
892 obtained for the other samples doped with other REE³⁺.

893 **Figure 3:** Fourier Transform Infrared spectra for the synthetic hydroxylapatites doped with
894 europium at increasing concentration (see table 2 for measured concentration). Similar
895 cristallinity was obtained for the other samples doped with other REE³⁺.

896 **Figure 4:** Representative continuous-wave Raman and luminescence spectra of synthetic
897 hydroxylapatites doped with europium (a), samarium (b), dysprosium (c) and neodymium (d).
898 All spectra are raw data, excitation at 532 nm except for neodymium (785 nm) and are acquired
899 with the same acquisition time for each series. Note the strong background affecting the
900 spectrum Sm2. R indicates a Raman peak.

901 **Figure 5:** Representative Raman spectra obtained on an hydroxylapatite doped with 23,936
902 ppm of samarium. The CW spectrum was obtained with the TR instrument by opening the gate
903 for 450,000 ns (nearly pulse to pulse at 2 KHz) and including the laser pulse: the luminescence
904 signal from samarium completely masks the Raman signal. The TR spectrum was obtained with
905 the TR instrument by opening the gate for 5 ns including the laser pulse: the luminescence
906 signal from samarium is completely rejected and the Raman signal is clearly visible.

907 **Figure 6:** Representative continuous-wave (green, ICCD gate of 450,000 ns including the laser
908 pulse) and time-resolved (red, ICCD gate of 5 ns centered on the laser pulse) Raman spectra of
909 some natural apatites. All spectra are raw data.

910 **Figure 7:** Time-resolved Raman and luminescence spectra obtained on the Durango apatite by
911 using various combinations of delay and gates for the ICCD. From top to bottom: green is
912 obtained with a long gate (450,000 ns) including the laser pulse, red is obtained with a short
913 gate (5 ns) including the laser pulse, black is obtained with a long gate (450,000 ns) opened just
914 after the laser pulse (10 ns), pale grey is obtained with a gate of 1,500 ns opened just after the
915 laser pulse (5 ns), dark grey is obtained with long gate (450,000 ns) opened 1,500 ns after the
916 laser pulse

917 **Figure 8:** Time-resolved luminescence spectra obtained on the Durango apatite by using a
918 constant delay and increasing progressively the opening of the ICCD gate.

919 **Figure 9:** Diagrams showing the surface of the luminescence bands versus the doping element
920 concentration for the 620 nm massif for europium (a) and the 600 nm massif for samarium (b).
921 The grey inset depict the same diagram at low concentration (<3,000 ppm).

922 **Figure 10:** Result of the time-sweep experiment for Eu- and Sm-doped hydroxylapatites (see
923 table 2 for measured concentration). The plots depict the normalized intensity of the 620 nm
924 massif for Eu (a) and 600 nm massif for Sm (b) versus the delay of the ICCD gate. This figure
925 illustrates the time decay of luminescence signal for Eu (a) and Sm (b). Lifetime is calculated
926 as the slope of the line going through the experimental points.

927 **Figure 11:** Compilation of lifetime of luminescence for europium (a) and Samarium (b) versus
928 the concentration in activator, europium (a) and samarium (b) respectively for the synthetic
929 REE-doped and natural apatites.

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Table 1: Nd, Sm, Eu and Dy composition of the synthetic hydroxyapatite samples measured by ICP-MS. ($\mu\text{g/g}$ = ppm; < L.D below limit of detection).

Sample reference	Nd $\mu\text{g/g}$	Sm $\mu\text{g/g}$	Eu $\mu\text{g/g}$	Dy $\mu\text{g/g}$	CaO wt%	P₂O₅ wt%
Eu 1	0	0	42	0	53.02	39.01
Eu 2	0	0	128	0	53.06	38.92
Eu 3	0	< L.D.	270	0	53.34	39.36
Eu 4	0	0	1 317	0	52.80	38.63
Eu 5	0	0	2 562	0	52.33	37.87
Eu 6	0	0	25 601	0	50.02	37.36
Sm 1	0	24	5	0	52.77	39.17
Sm 2	0	115	5	0	52.06	37.89
Sm 3	0	240	1	0	53.31	39.82
Sm 4	0	1 251	0	0	52.35	38.47
Sm 5	0	2 450	0	0	52.37	38.31
Sm 6	0	23 936	1	1	50.06	37.13
Nd 1	24	4	< L.D.	0	52.91	38.83
Nd 2	115	1	< L.D.	0	52.46	38.14
Nd 3	228	0	< L.D.	1	52.81	38.84
Nd 4	1 185	3	2	2	53.16	39.03
Nd 5	2 475	0	0	5	52.57	38.45
Nd 6	24 832	2	1	50	50.59	39.91
Dy 4	4	< L.D.	0	1 358	51.89	38.16

Table 2: Major elements (oxide wt%) and REE composition ($\mu\text{g/g}$ or ppm) of the natural apatite samples measured by ICP-MS (< L.D below limit of detection).

	Tyrol	Imilchil	Renfrew	Slyudyanka	Durango
Location	Tyrol – Austria	Imilchil – Morocco	Renfrew, Ontario – USA	Lake Baikal, Russia	Durango – Mexico
Type	fluorapatite	fluorapatite	fluorapatite	unknown	fluorapatite
Form	polycristal	polycristal	polycristal	polycristal	monocristal
Color	dark green	light green – yellow	light green	light blue	yellow
CaO	53.23	53.35	54.11	54.34	53.58
P₂O₅	39.83	41.47	40.72	39.92	40.68
MnO	< L.D.	0.02	0.11	< L.D.	< L.D.
Sc	2	1	1	< L.D.	1
Y	297	1418	1643	46	452
La	992	2590	741	75	3166
Ce	2290	4138	2058	136	4030
Pr	276	438	297	14	332
Nd	994	1794	1264	49	1045
Sm	147	407	302	9	131
Eu	13	41	27	2	16
Gd	94	397	308	8	112
Tb	11	54	55	1	13
Dy	56	286	353	8	72
Ho	10	52	74	2	14
Er	23	119	197	4	37
Tm	3	13	27	1	5
Yb	15	61	141	3	26
Lu	2	6	17	0	4

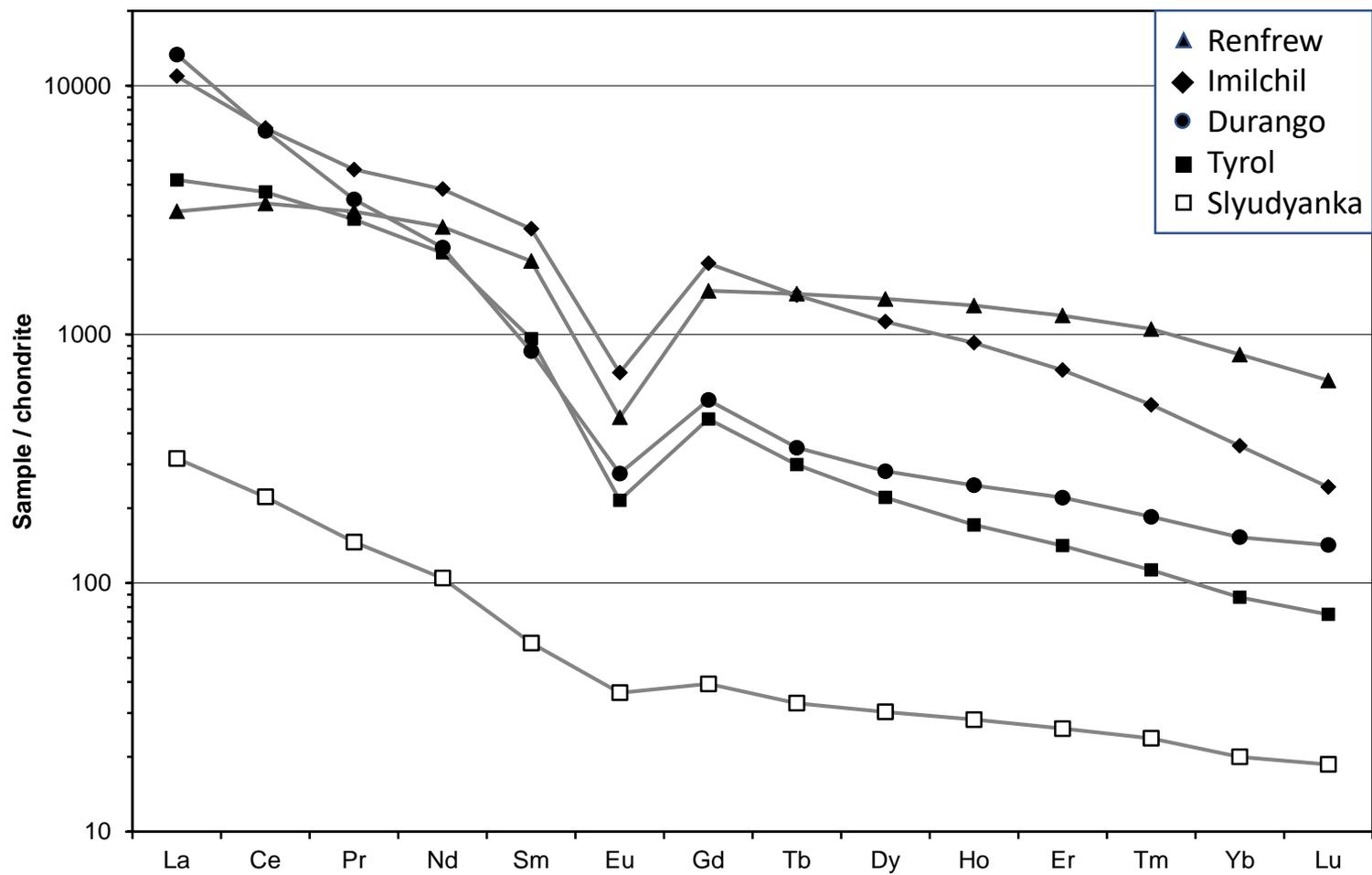


Figure 1

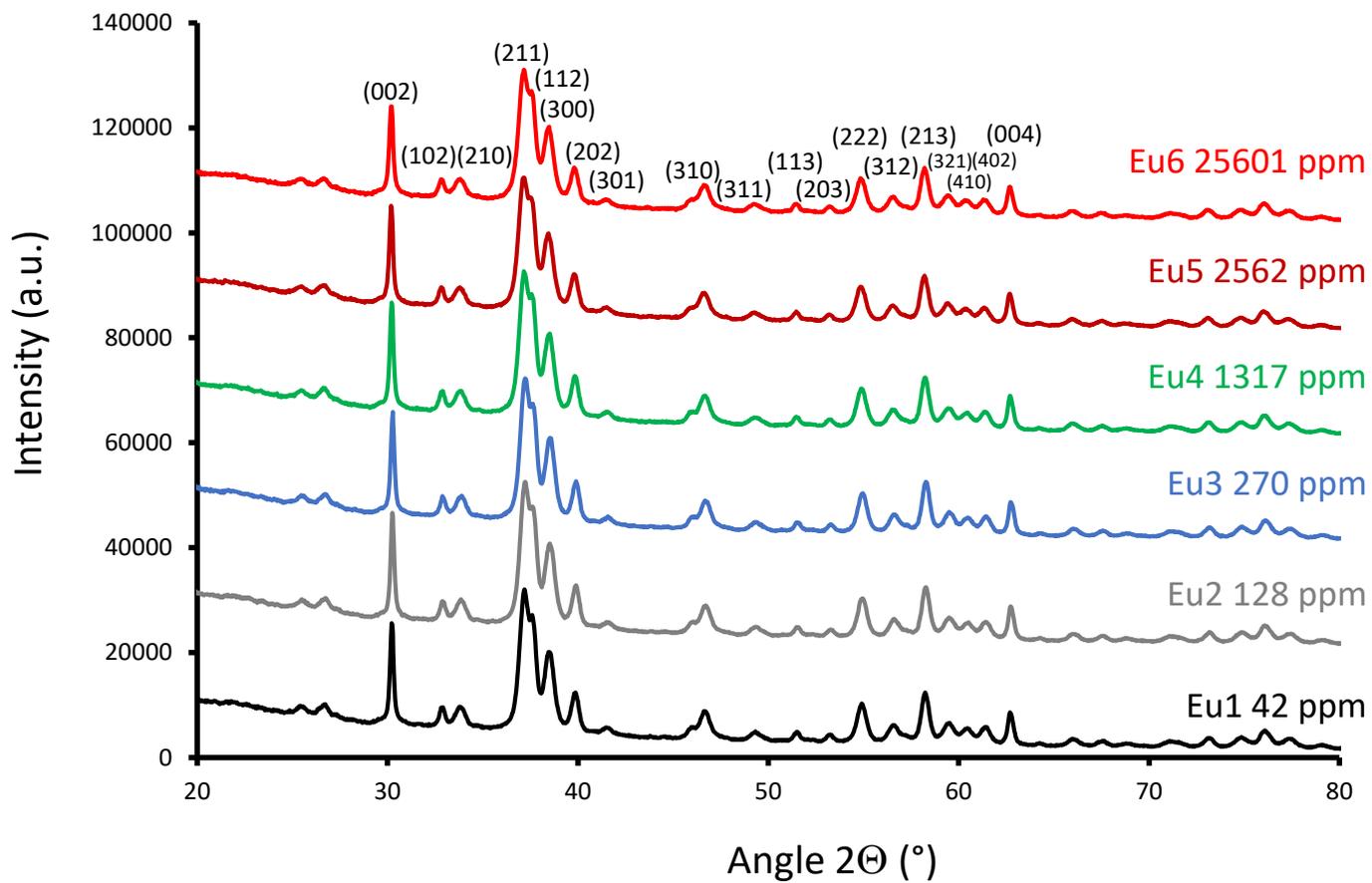


Figure 2

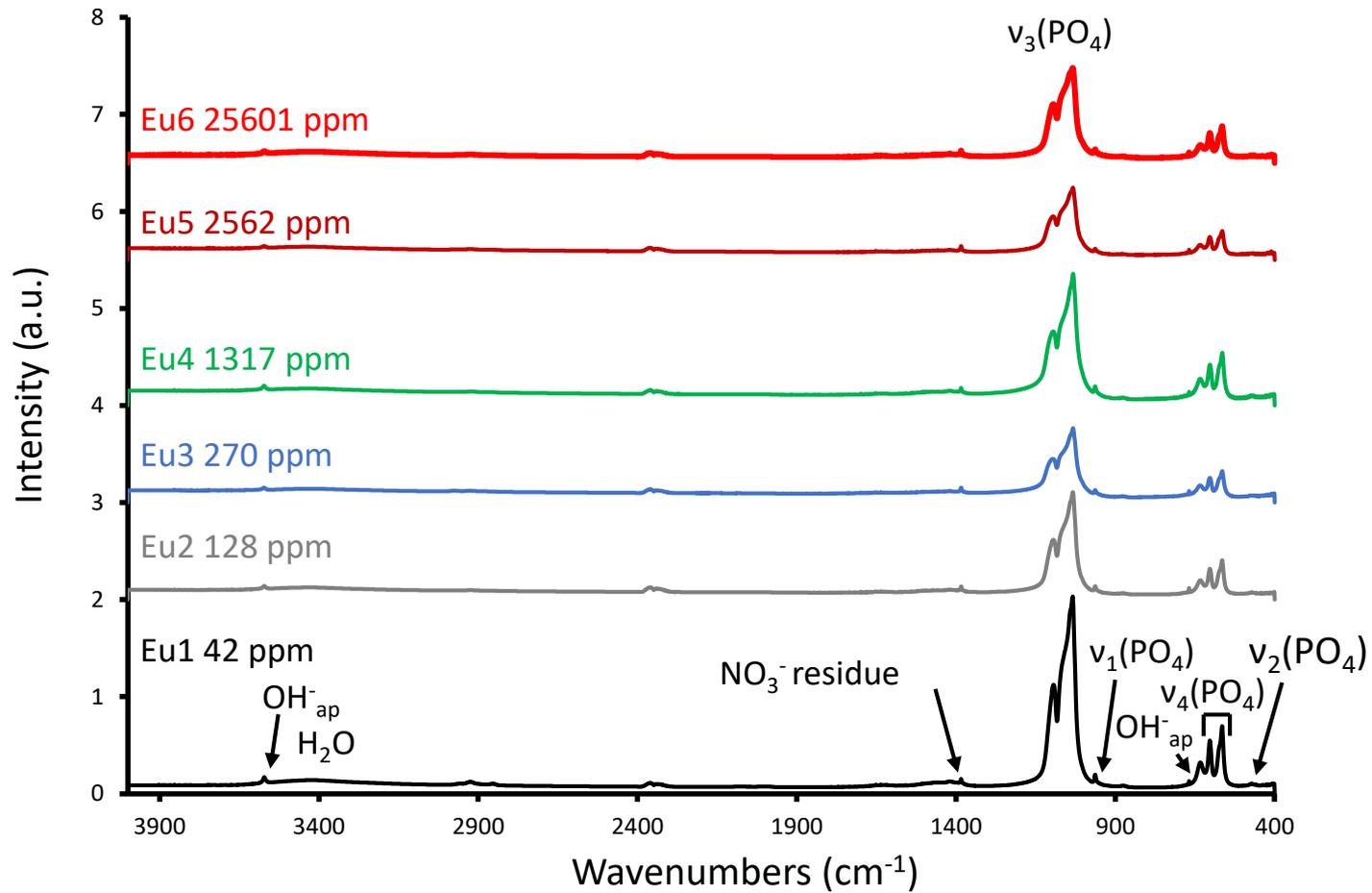


Figure 3

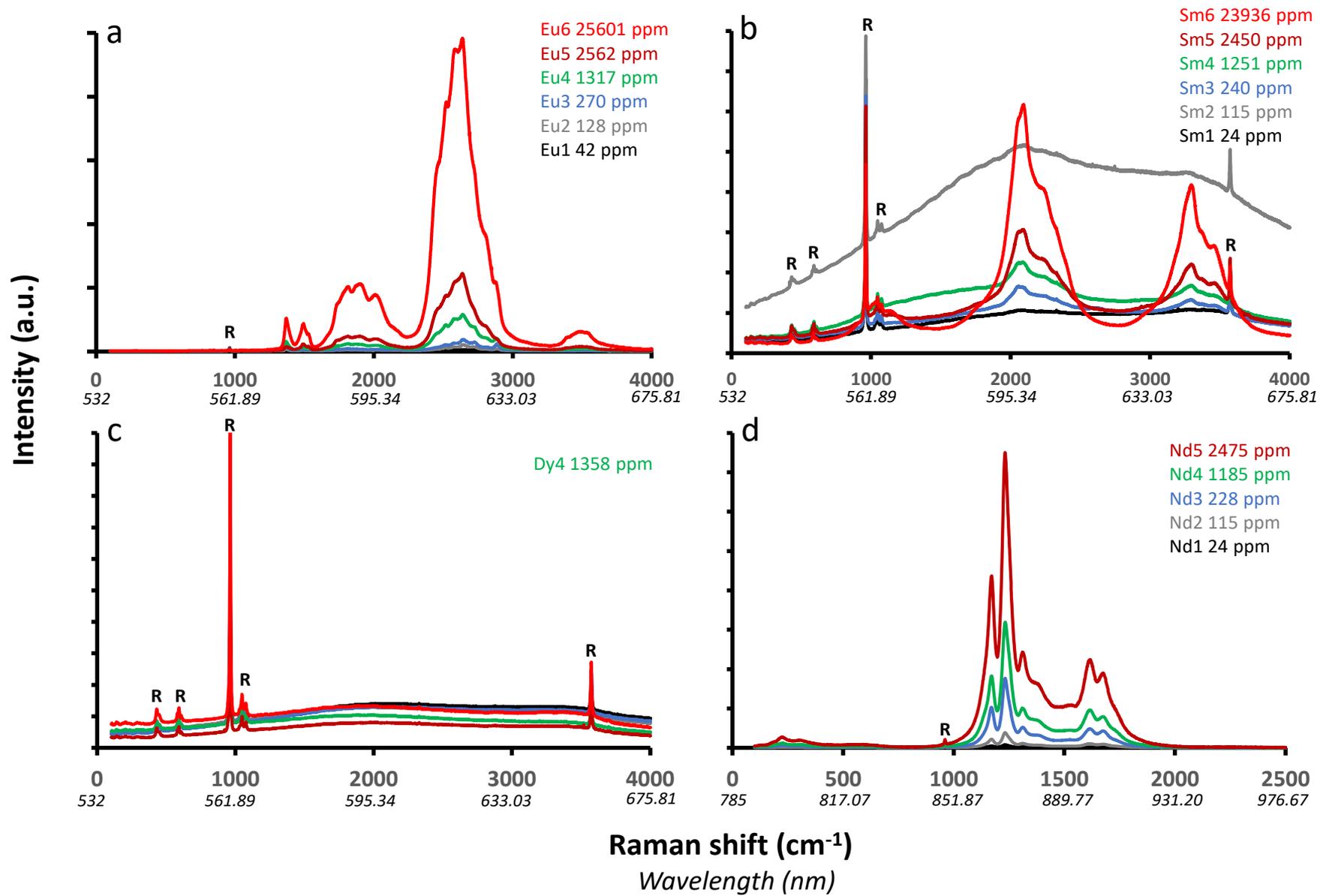


Figure 4

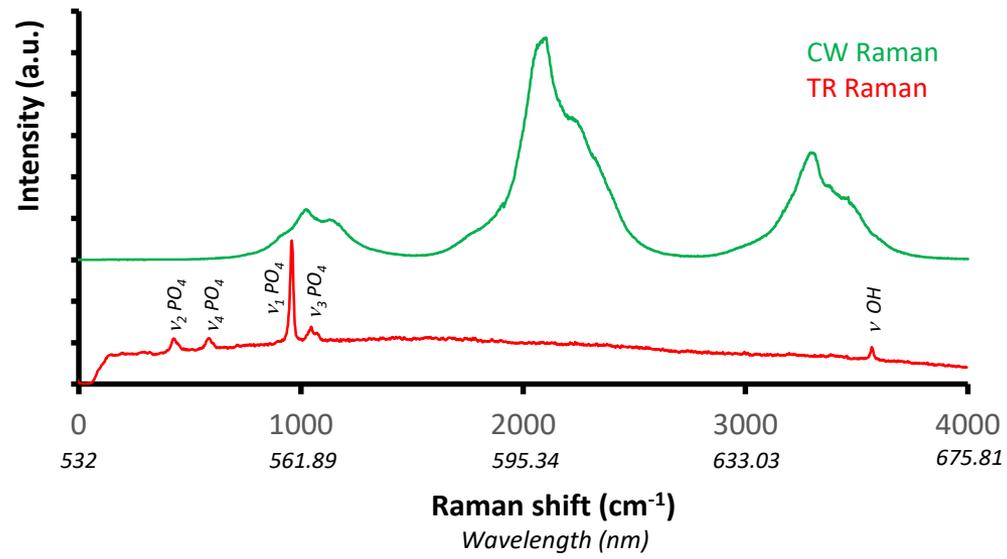


Figure 5

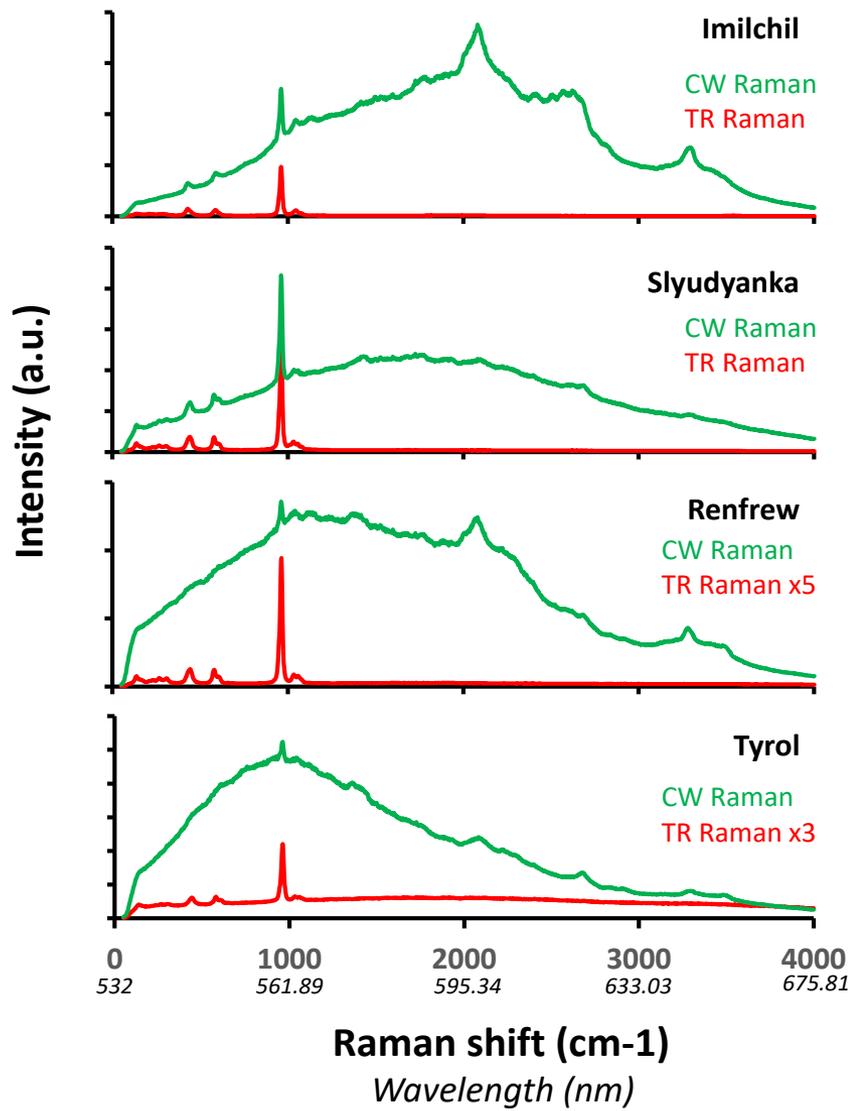


Figure 6

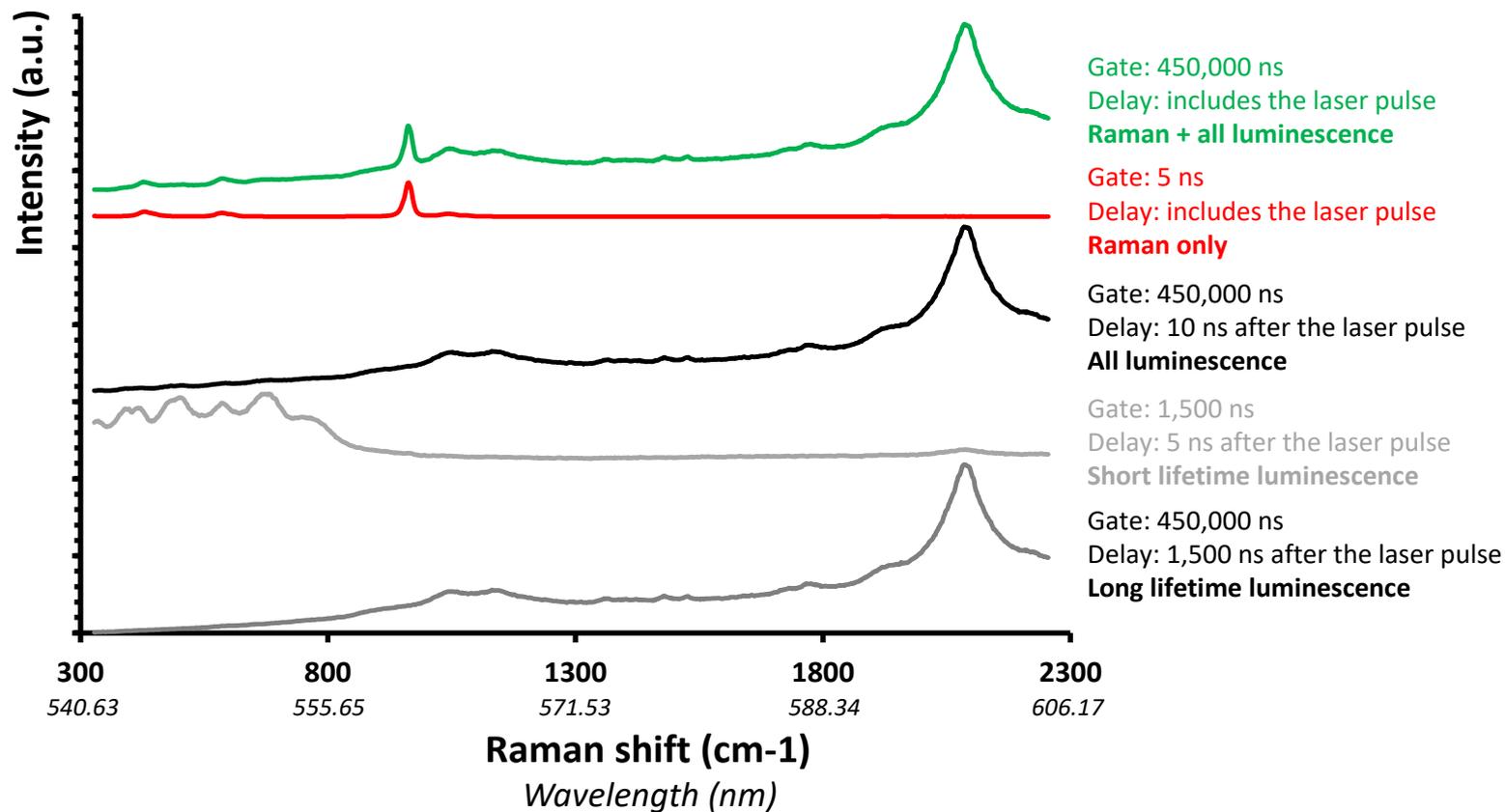


Figure 7

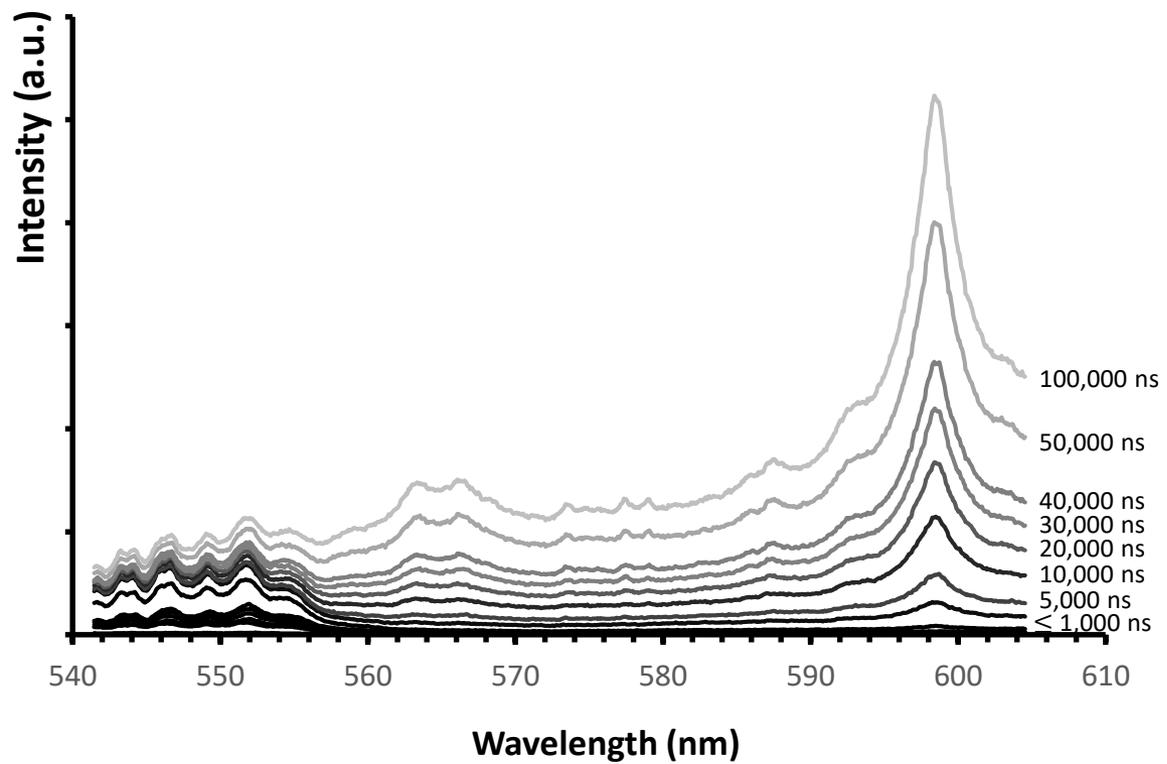


Figure 8

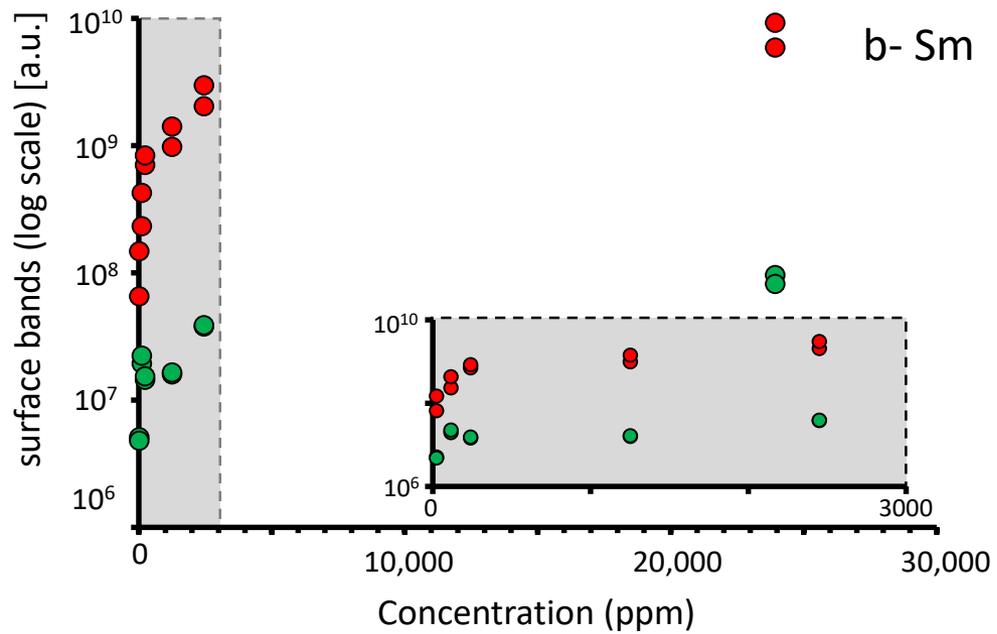
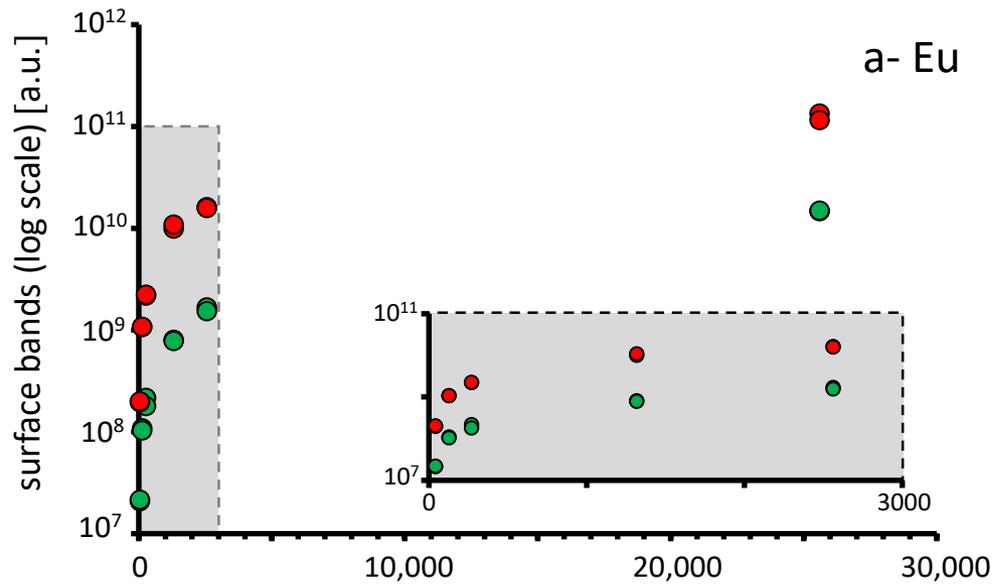


Figure 9

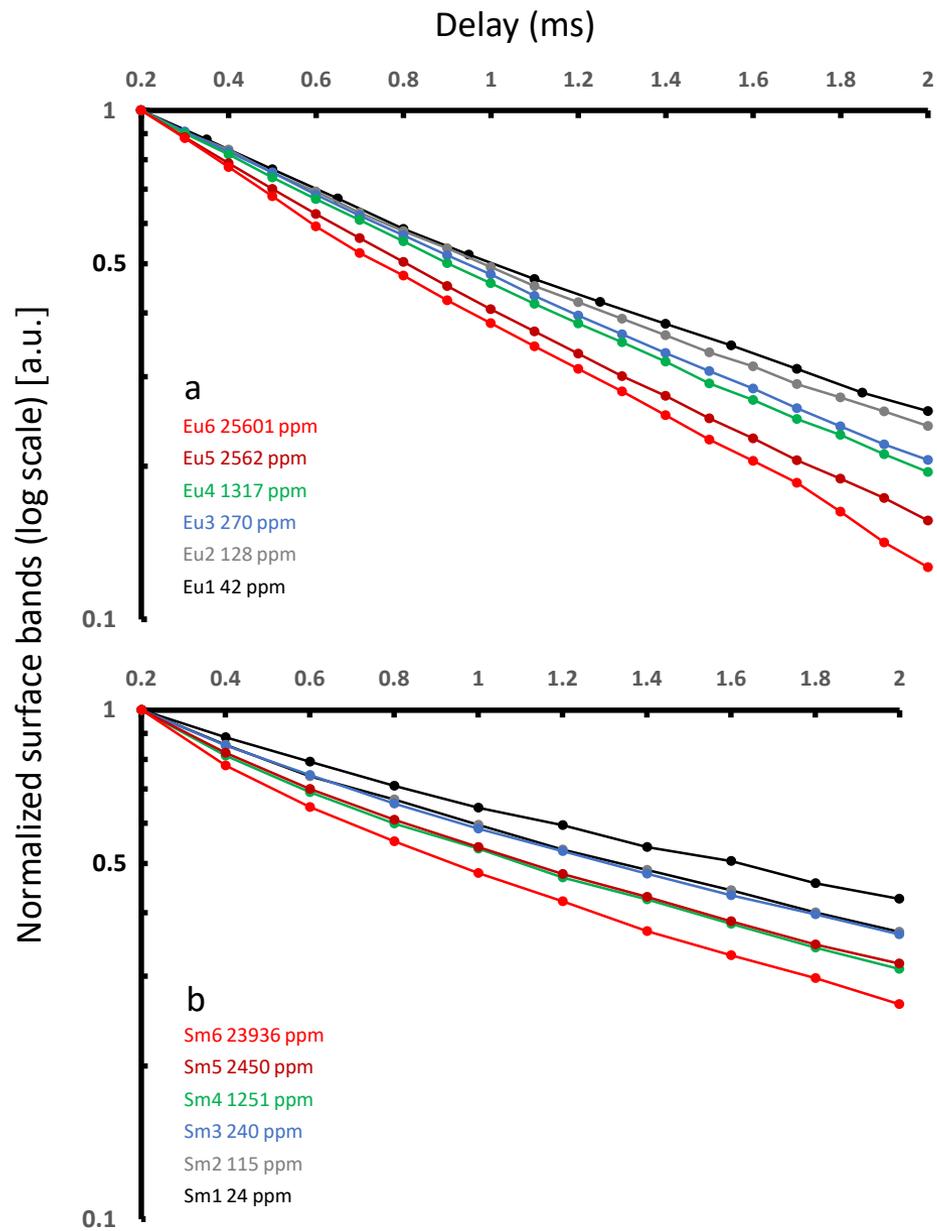


Figure 10

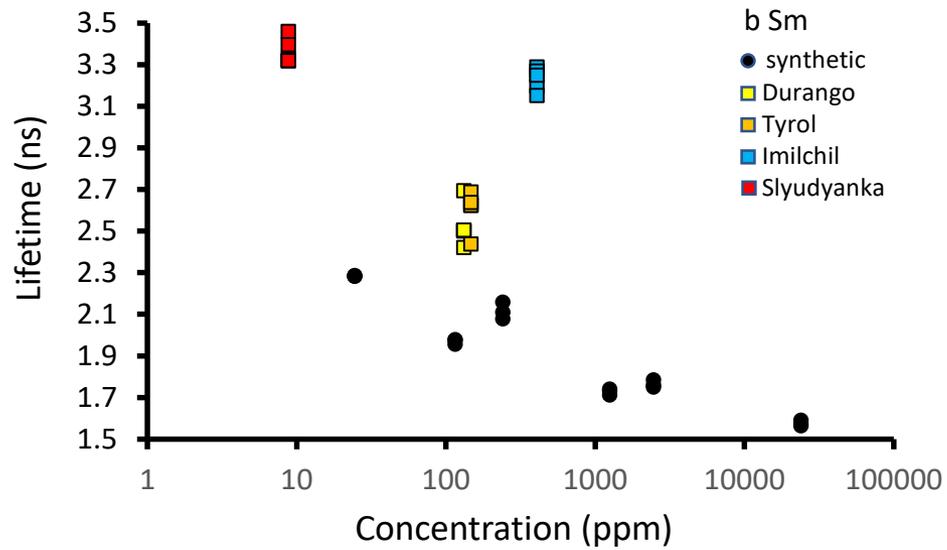
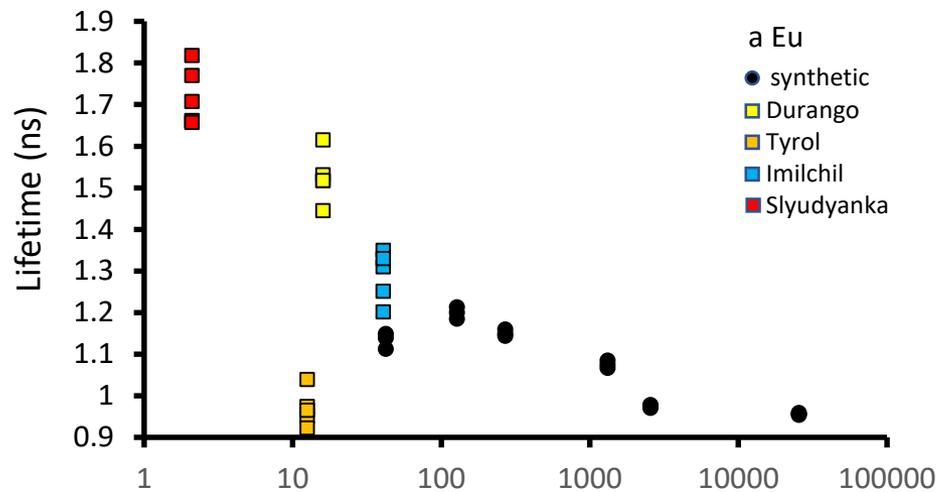


Figure 11