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**Enhanced Quantification of Wollastonite and Calcite in Limestone using Fluorescence
Correction Based on Continuous Wavelet Transformation for Raman**

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22 **Abstract**

23 Raman spectroscopy offers a non-destructive means to identify minerals in rocks, but the
24 ability to use the technology for quantitative mineralogical analysis is limited by fluorescence
25 that can mask the spectral features of minerals. In this paper we apply continuous wavelet
26 transformation (CWT) to remove fluorescence from Raman data acquired from 26 carbonate
27 rock samples. We then record the intensity values of individual spectral features, proxies for
28 mineral abundances, using the original Raman data and the thus inferred CWT data. The
29 intensity values are then compared against the known mineral abundances determined using the
30 scanning electron microscope (SEM) technology. This comparison is conducted using a linear
31 regression model to determine whether fluorescence removal enhances the mineral abundance
32 predictions. Our results suggest that CWT enhances the accuracy of mineral abundance
33 estimates, thus highlighting the importance of fluorescence removal when using Raman for
34 quantitative mineralogical analysis.

35 **Keywords:** Raman, fluorescence, wavelets, wollastonite, calcite

36 **1. Introduction**

37 Raman provides spectral fingerprints unique to many minerals thus enabling their detection
38 and identification. This characteristic has been used for mineral identification since the advent
39 of the technology (Landsberg and Mandelstam, 1928; and references therein). The technology
40 is based on irradiating the material of interest and subsequently recording the resulting photons.
41 Most photons have the same frequency as the laser beam, but a small fraction have shifted
42 frequencies due to changes in the vibrational or rotational energy stages in molecules or crystals
43 (Hope et al., 2001). In a Raman spectrum, these shifted frequencies are expressed as spectral
44 features (commonly called “peaks”) that correspond to the energies of the vibrational modes of
45 minerals (Burke, 2001). The sharp and generally non-overlapping Raman spectral features are

46 well suited for the identification of minerals (Wang et al., 1995; Smith and Carabatos-Nédelec,
47 2001) and for specific applications such as the determination of the composition of fluid
48 inclusions (Nasdala et al., 2004). Being rapid and nondestructive, the technology offers many
49 essential applications for geosciences (Vítek et al., 2012), including mineral quantification.

50 The ability to estimate mineral abundances using Raman is based on the linear relationship
51 between the intensity of the spectral features of the mineral and the solution concentration (Cai
52 et al., 2001). This ability that has been known since the 1970s (see Irish and Chen, 1971; and
53 references therein) can be reduced by luminescence emissions (also called “the background”)
54 that are generally the main source of noise in Raman data. As luminescence is in general 10^6 -
55 10^8 times stronger than the signal (Matousek et al., 2001, Vítek et al., 2012), the phenomenon
56 can severely impair the ability to detect Raman fingerprints. Luminescence, or
57 photoluminescence, as the material is excited by laser light, has two components: the short-life
58 (10^{-8} - 10^{-9} s⁻¹) fluorescence and the longer-life (10^{-6} s⁻¹) phosphorescence (Becker, 1969). In
59 minerals, the prevailing process is fluorescence that is induced by the presence of transition
60 metals, rare-earth elements, actinides, color centers and organic residues (Urmos et al., 1991;
61 Reisfeld et al., 1996; Wang and Mullins, 1997). Fluorescence can also result from residues (e.g.
62 fingerprints) or fluid inclusions (Burke, 2001). To be able to analyze the mineral-related signal,
63 it is essential to separate fluorescence and Raman signals. For this end, hardware and software-
64 oriented approaches have been devised.

65 Regarding hardware-related approaches that aim to subdue fluorescence, it is a common
66 practice to lower the energy of the excitation by selecting a laser operating at longer wavelength,
67 commonly 785 nm or even 1064 nm (Efremov et al., 2007). When using these relatively long
68 wavelengths, it is less probable to excite the material to the higher electronic states, which is
69 prerequisite for the fluorescence to occur (Frosch et al., 2007). The approach has the
70 disadvantage of the Raman scattering intensity being inversely proportional to the laser

71 wavelength by λ^{-4} (Efremov et al., 2007) and thus, longer excitation wavelengths inducing a
72 weaker signal response. Also, minerals can contain small amounts of rare earth elements as
73 impurities, and since some of these elements are excited at relatively low energy levels, they
74 can nevertheless induce fluorescence. As an alternative to long excitation wavelengths, short
75 ultraviolet (UV; wavelengths below 250 and up to 280 nm) excitation wavelengths have been
76 used to suppress fluorescence (Johnson and Asher, 1984, Li and Stair, 1996). The use of the
77 UV excitation wavelengths is based on the fluorescence emissions being rare or absent in this
78 wavelength domain, thus enabling a complete spectral separation between Raman and
79 fluorescence emissions (Frosch et al., 2007). Furthermore, when using this excitation
80 wavelength range, Raman excitation may occur within a highly excited electronic resonance
81 band, thus resulting in a strong signal (Frosch et al., 2007).

82 Another hardware-related approach that has gained momentum in recent years is time
83 gating. Conventional Raman systems apply continuous-wave lasers to excite the sample with a
84 continuous beam of photons. Of these photons, only a small fraction (circa. 10^{-7}) is Raman
85 scattered, and to strengthen the Raman signal, integration times of several seconds typically
86 take place (Sharma et al., 2010). This approach can result in Raman fingerprints being
87 superimposed on a fluorescence background. To overcome this problem, the signal is recorded
88 before it is subdued by the fluorescence signal (Bozlee et al., 2005; Efremov et al., 2007).
89 technology has been successfully used to eliminate fluorescence in mineral samples by a
90 number of studies (see e.g. Bozlee et al., 2005; Misra et al., 2005; Romppanen et al., 2019).

91 Fluorescence has also been subdued using the photobleaching approach, a technique of
92 keeping a sample under a sustained laser exposure (Barman et al., 2011). However, some
93 researchers (e.g. Esposito et al., 2003; Cadush et al., 2013) argue that fluorescence may not be
94 completely removed using this approach and moreover, alterations in the intensity of the

95 spectral features can take place due to the long laser exposure that can change the physico-
96 chemical properties of the sample (Macdonald and Wyeth, 2006).

97 As choosing specific excitation wavelengths or using a specific data acquisition approach
98 is not always feasible, computational approaches of removing fluorescence have received
99 attention. Wavelet transformation, a technique of decomposing the signal into localized
100 contributions (details and approximations) labeled as scales (Hoang, 2014), is one of the most
101 popular advanced background-correction methods in the field of Raman spectroscopy (Sobron
102 et al. 2008, Zhang et al., 2009). The popularity of the method is based on the known ability of
103 the wavelet transformation to de-noise Raman spectra without changing the wavelength
104 positions of the spectral features of materials (Cai et al., 2001). Because the background has a
105 lower frequency than the material (Hu et al., 2007), background can be eliminated without a
106 significant loss of spectral information (Ma and Shao, 2004). As reviewed by Ma and Shao
107 (2004), the ability to use wavelet transformation for background removal is due to the concept
108 of vanishing moments. With certain vanishing moments, the ratio between the intensity of the
109 background and the intensity of the analytical signal is large enough for the background to be
110 negligible. In addition to its ability to remove the background from the signal, wavelet
111 transformation has the benefit that it does not require *a priori* information about the composition
112 or the background signal of the samples (Hu et al., 2007), an important characteristic when
113 analyzing often incompletely known rock samples. Wavelet transformation can be implemented
114 as continuous (CWT) or discrete (DWT).

115 Our research was motivated by the observation that despite a body of research on the use of
116 Raman spectroscopy for quantitative mineralogy (e.g. Dörfer et al., 2009), the ability to use
117 computational methods to mask fluorescence are not well established in that field of research.
118 To partially fill this knowledge gap, we acquired high spatial resolution Raman data from a set
119 of 26 rock samples. Using these data, CWT was conducted to remove the background signal.

120 Energy-dispersive-scanning electron microscope (EDS-SEM; for simplicity "SEM" from
121 herein) was then used to determine the mineralogy of the samples. These data were used as a
122 benchmark against which the mineral abundances extracted from the original Raman data and
123 the thus derived CWT data were assessed. The accuracy of the Raman-inferred mineral
124 abundances was evaluated using correlation coefficients and linear regression. In this context,
125 we aim to respond the following question: does computational fluorescence removal improve
126 the accuracy of Raman-based quantifications of minerals in rocks?

127 **2. Materials and Methods**

128 ***2.1. The Study Site***

129 The 3 km long and 0.8 km wide Paleoproterozoic (1.9 Ga) Ihalainen deposit (61° 2'0.60"
130 N, 28°10'52.96" E; in Lappeenranta, southeastern Finland, Fig. 1) is one of the most important
131 calcite-marble deposits in Svecofennia and one of the few wollastonite mines in Europe
132 (Lehtinen, 2015). The deposit hosts significant reserves of wollastonite ($\text{Ca}[\text{SiO}_3]$), calcite
133 (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). The deposit is currently being exploited by Nordkalk
134 Ltd. that has owned the site since 1910 (Lehtinen, 1999). Wollastonite occurs as lath-shaped,
135 0.5 x 0.1-0.2 mm crystals, comprising 20-24% of the ore (Keeling, 1963, Dumont, 2005).
136 Wollastonite as a commercial mineral is being used to substitute asbestos (Maxim and
137 McConnell, 2005) and to increasing the durability and strength of concrete (Kalla et al., 2015),
138 among other uses.

139 The study area mainly comprises calcite-rich limestone rocks that are surrounded by
140 younger (1.6 Ga) rapakivi granites. Wollastonite is principally sourced from the limestone rocks
141 where the mineral occurs in association with diopside and quartz bands surrounded by a calcite
142 matrix (Lehtinen, 1999). The wollastonite occurrences are located in a 1.5 km, N-S conforming
143 strike of a 65% eastward dip (Lehtinen, 2015). The limestone body of the study area is cut by

144 rapakivi dykes and NW-SE running diabase (amphibolite) dykes (Keeling, 1963), and mixtures
145 of the two (Lehtinen, 1999). There are also leptitic dykes that follow the dip and strike of the
146 limestone rocks (Pekkala, 1988). The bedrock has undergone strong deformation.

147 Wollastonite formed during two stages. The first, older stage, occurred 1.858 Ga ago during
148 medium-to high grade metamorphism when water infiltrated the silicious beds of the carbonate-
149 rich sediments (Lehtinen, 1999; Lehtinen, 2015). The second, younger event, occurred when
150 wollastonite skarns formed during contact metamorphism of the granitic rocks in the vicinity
151 of the limestone body (Lehtinen, 1999, Lehtinen, 2015). During these metamorphic stages, two
152 types of wollastonite developed (Lehtinen, 2015). The first type comprises wollastonite and
153 diopside-containing calc-silicate bands (+/- quartz) in a matrix of bluish calcite (Lehtinen,
154 2015). Here, calcite is the main ore mineral with abundances of 55-75% and the amount of
155 wollastonite seldom exceeds 30% (Lehtinen, 2015). This type of wollastonite formed during
156 the older, regional event that precedes the rapakivi magmatism that occurred around 1.6 Ga ago
157 (Lehtinen, 2015). The second type of is a skarn-type wollastonite ore where the wollastonite
158 content typically exceeds 30% (Lehtinen, 2015). This rock type is associated with the younger
159 contact metamorphic event.

160 **2.2. Sample Set**

161 The sample set comprises 26 rock samples that were collected from different parts of the
162 study site (rock piles). Because the original locations of the samples are uncertain, their
163 coordinates were not recorded. The samples were selected to represent the different wollastonite
164 types of the study area, discussed in section 2.1.
165 Here, the objective was to have wollastonite and calcite -rich samples to compare the effects of
166 fluorescence removal on mineralogically distinct samples. Petrographic analysis of the samples
167 confirmed that the average grain size of the samples is approximately 0.5 mm. The

168 crystallographic orientations of the samples were furthermore observed to be random and not
169 to have a preferred orientation.

170 To prepare the samples for SEM analysis, a 2.5 cm drill core was extracted from each
171 sample. Next, one surface of each sample was cut and polished. Using these polished sample
172 surfaces, a 1x1 cm area was marked using Cu-tape. This was done to help align the Raman and
173 SEM data and to acquire them from the same surface area of each sample.

174 ***2.3. Raman Data Acquisition***

175 The Raman data were acquired at the University of Jyväskylä with an in-house Raman setup
176 (backscattering geometry). The data were acquired using a solid state continuous wave laser by
177 CNI (excitation wavelength: 532 nm, laser power: 200 mW). Raman signal was collected to
178 imaging spectrograph (Princeton Instruments, Acton SP2500i), coupled to a CCD detector
179 (Andor Newton) using a 0.1 s integration time. Dark noise and the spectral features induced by
180 the foreoptics were subtracted from the data. Care was taken to only acquire data from the inside
181 of the areas marked with the Cu-tape, resulting in 4900 analyses per sample and a 100 μm
182 spatial resolution.

183 ***2.4. Scanning Electron Microscope (SEM) Data Acquisition and Results***

184 To record the mineralogy and mineral proportions of the samples, the polished samples
185 were analysed in the Field Emission Scanning Electron Microscope (FE-SEM) Laboratory of
186 the Geological Survey of Finland (Espoo, Finland). For this end, a JEOL JSM-7100F Schottky
187 instrument, equipped with an Oxford Instruments energy dispersive X-ray spectroscopy (EDS)
188 with a X-Max 80 mm² silicon drift detector (SDD) was applied. The SEM data were acquired
189 with a 20 kV acceleration voltage and 0.5 nA probe current.

190 The mineral phases were characterized using the Oxford INCA feature phase detection and
191 classification software. Next, the elemental compositions of the samples were recorded using

192 the EDS. A number of analyses were obtained from each sample such that data were acquired
193 only from areas that fell inside the ones marked with a Cu-tape. The spatial resolution of the
194 analyses is ca. 102 μm . Here, the objective was to achieve a spatial resolution that would be as
195 close to the Raman data as possible. The exact number of analyses per sample is given in Table
196 1. The amount of analyses varies in the sample set because the boundaries for the data
197 acquisition were set manually, and care was taken not to go outside of the taped areas. This
198 resulted in an average number of analyses of 5205 per sample, which is slightly higher than the
199 number of analyses of the Raman data (4900 analyses).

200 The results, listed in Table 1, suggest that the majority of the samples have a high
201 wollastonite content (average: 69.2%), moderate calcite and diopside contents (averages: 15.9%
202 and 11.1%, respectively) and low contents of all other minerals (average: 0.3%). Using the 30%
203 wollastonite content threshold, discussed in section 2.1, to divide the samples into two
204 categories, 80.8% (21 out of 26) of the samples fall into Type 1 category that represents the
205 wollastonite ore. Of the remaining 5 samples, samples 15, 17, 21 and 22 fall into Type 2
206 category where calcite content is 55% or higher, and hence these samples represent the calcite
207 ore. Sample 20 does not clearly fall into either of the two categories. Also, even if the samples
208 represent one or the other category, they can still contain a relatively large amount of the other
209 mineral. For instance, sample 2 contains 75% of wollastonite, but nevertheless has 17.2% of
210 calcite.

211 It should be noted that zero values in Table 1 represent analyses where the mineral in
212 question has been detected, but the total percentage falls below the number of decimal digits
213 shown in Table 1. Also, although not specifically listed in the table, the SEM results suggest
214 that sample 6 contains two grains (features) of an unidentified Cu-mineral.

215 *2.5 Spectral features*

216 In this paper, the focus is on wollastonite and calcite, the ore minerals of the study site. The
217 chosen minerals have a set of characteristic Raman spectral features, described by Urmos et al.
218 (1991), Richet et al. (1998) and Prencipe et al. (2012). Of these features, the following were
219 selected for data analysis due to their pronounced nature and unique position in the
220 electromagnetic spectrum that minimizes potential confusion with other minerals in the sample
221 set: i) 281 cm^{-1} ($f1$ from herein), ii) 414 cm^{-1} ($f2$ from herein), iii) 972 cm^{-1} ($f3$ from herein) and
222 iv) 1092 cm^{-1} ($f4$ from herein). The first spectral feature, $f1$, is a translational lattice mode T(Ca,
223 CO_3) in calcite. The second and third ($f2$ and $f3$) spectral features are induced by the
224 deformation of the Si-O-Si bonds (Richet et al., 1998) in wollastonite. The fourth spectral
225 feature ($f4$) is a prominent vibrational mode, induced by the ν_1 symmetric CO_3 stretching mode
226 in calcite (Urmos et al. 1991). It should be noted that wollastonite has a pronounced feature
227 near 637 cm^{-1} (Richet et al., 1998), also present in the dataset, but this feature was left out of
228 analysis to avoid confusion with diopside that is abundant in the sample set and that has a
229 potentially overlapping spectral feature in the same wavelength range (Prencipe et al. 2012).

230 The spectral features $f1$ - $f4$ were analyzed as follows. First, the quality of the data were
231 assessed for potential outliers and low signal-to-noise ratios. It was deemed that the data had
232 no underlying quality issues, and hence no data was removed prior to data analysis. Next, an
233 average spectrum was extracted from i) samples that were classified as belonging into Type 1
234 ($n=21$) or Type 2 ($n=4$) sample category and ii) from each sample ($n=26$, Fig. 2). The former
235 analysis was conducted to visually compare the differences between the two types of rock
236 samples. The intensities of the four spectral features of interest ($f1$ - $f4$) were recorded using the
237 results of the latter analysis (the sample average).

238 **2.6. Continuous wavelet transformation (CWT)**

239 Continuous wavelet transformation (CWT) was applied to the original data to remove the
240 background fluorescence. This analysis was carried out using the Anaconda client version 1.6.9.
241 with Python 3.6.4. The Ricker (also called: the “Mexican hat”) as the mother wavelet,
242 decomposed into ten scales using the standard dilation and translation functions described by
243 Lau and Weng (1995). Here, CWT (as opposed to DWT) was chosen because its outputs are
244 directly comparable with the original spectra (Rivard et al., 2008). The Mexican hat wavelet
245 was chosen based on its demonstrated ability for background removal (see e.g. Zhang et al.,
246 2009; Liu et al., 2017). As Ricker is a symmetric function, fluorescence will be automatically
247 removed for as long as it slowly changing and monotonic (Zhang et al., 2009). The number of
248 scales ($n=10$) was chosen using pre-existing knowledge of the feature widths of the spectral
249 features $f1-f4$.

250 The bivariate normal distribution of the SEM data and the Raman data, tested using the
251 Shapiro-Wilk W statistic (Shapiro and Wilk, 1965), suggests that the SEM data ($W=0.764664$,
252 $df=26$ $p=0$) and Raman data associated with the spectral features $f1$ and $f4$ are not normally
253 distributed (for details, see Table S1). Due to the generally non-normal bivariate data
254 distribution, the non-parametric Spearman rank correlation coefficient (R_s), a measure that does
255 not make assumptions about the frequency distribution of the data (Hauke and Kossowski,
256 2011), was used to conduct all of the correlation analyses of this study.

257 To find which wavelet has the highest correlation with the SEM data, bivariate correlation
258 analysis was conducted between the ten scales and the four spectral features of interest. Of the
259 outputs of this analysis, the scale that had the highest correlation coefficient with the SEM data
260 was chosen for further analysis. The correlation analysis results, shown in Figure 3, reveals a
261 generally high correlation between the SEM data and the ten wavelets of the CWT data
262 ($R_s=0.845-0.880$, 99% confidence level, 2-tailed). Of these wavelets, scale 3 has the highest
263 correlation with the SEM data ($R_s=0.880$, $n=26$). Therefore, data associated with this specific

264 scale was selected for all the ensuing data analysis steps, and will simply be referred to as the
265 “CWT data” from herein.

266 *2.7 Linear regression analysis*

267 The relationship between the SEM data (predictor variable) and Raman data (the response
268 variable) was further assessed using Spearman’s rank correlation coefficients and linear
269 regression analysis. This analysis was conducted separately for the original data and the CWT
270 data to determine which dataset is more robust in predicting the quantities of the minerals of
271 interest (wollastonite and calcite).

272 Prior to regression analysis, Levene’s test (Levene, 1960; Brown and Forsythe, 1974) was
273 used to evaluate the homogeneity of variances, a prerequisite of that specific analysis (Williams
274 et al., 2013). The Shapiro-Wilk statistic was used to test the normality of the residuals of the
275 model. All statistical analyses were performed using the IBM® SPSS® Statistics version 25 at
276 a 95% confidence interval, unless otherwise stated.

277 **3. Results**

278 *3.1 The effects of the fluorescence removal*

279 The average spectra of the Type 1 and Type 2 samples show that both sample types have
280 varying degrees of background fluorescence (Figure 4). Of the two sample categories, Type 1
281 (wollastonite ore) appears to have a higher degree of fluorescence than Type 2 (calcite ore).
282 Also, with the exception of spectral feature 2, the spectral features of interest, labeled as *f1-f4*
283 in Figure 4, are detectable irrespective of the sample category, due to the presence of the
284 minerals of interest across the sample set.

285 As can be seen in Figure 5, the CWT transformation has removed the background
286 fluorescence from the Raman spectra. This can also be noted in the boxplot figures of the

287 original and CWT spectra where the median of each spectral feature has a lower intensity than
288 the intensity of the original data (Fig. 6a-b).

289 As noted by Zhang et al. (2009), wavelet transformed Raman spectra can contain negative
290 values that do not bear a physical significance. The coefficients are negative because the
291 product of the chosen wavelet (here: Ricker/Mexican hat) and the unit step is a negative
292 constant. As can be seen in Figure 6a-b, the CWT spectra have negative values in the
293 wavenumber positions of abrupt transitions marking the shift from the background to the signal
294 (i.e. mineral spectral features). Nevertheless, as the spectral feature positions have not shifted
295 from the original, these negative values do not affect data analysis in our study.

296 **3.2. Linear regression analysis**

297 In general, the correlation coefficients are lower between the original Raman data and SEM
298 data ($R_s=0.806$, $n=26$, 99% confidence level, 2-tailed, Figure 7) than between the CWT data
299 and SEM data ($R_s=0.880$, $n=26$, 99% confidence level, 2-tailed, Figure 8). Thus, removing the
300 background strengthens the relationship between the intensity of the spectral features and the
301 abundance of the minerals of interest (calcite and wollastonite). Of the individual spectral
302 features, $f1$ and $f4$, associated with calcite, have slightly higher correlation coefficients than
303 those of the spectral features $f2$ and $f3$, associated with wollastonite. More specifically, the
304 average R_s between the original Raman data and the SEM data is 0.865 in the case of calcite
305 and 0.748 in the case of wollastonite. The corresponding coefficients are 0.932 and 0.829,
306 respectively, for the CWT data.

307 The Levene's test reveals that the assumption of homogeneity of variances is satisfied ($F(1,$
308 $206)= 2.589$, $df1=1$, $df2=206$, $p=0.109$). Furthermore, the Shapiro-Wilk test results suggest that
309 the residuals of the model are not normally distributed ($W=0.885$, $df=208$, $p=0$). As regression
310 analysis is relatively robust against violations against normally distributed errors (Williams et

311 al., 2013) and the relationship between the SEM data and the Raman data can be considered
312 linear based on a visual interpretation (see Figure 7), simple linear regression was used to assess
313 the relationship between the SEM data and the intensity values of the Raman data.

314 When examining the resulting R^2 values of the minerals of interest, given in Table 2, the
315 results suggest that 87% of the average variation of the spectral features of calcite of the original
316 Raman data, and 94% of the CWT data can be explained by the SEM data. The corresponding
317 figures are 66% and 78% for wollastonite. Averaged across all spectral features, the results
318 suggest that 77% of the total variation of the original Raman data, and 86% of the CWT data
319 can be explained by the SEM data. Thus, the CWT treatment enhances the predictive ability of
320 the Raman data by an average of 9 percentage units across all spectral features. However, there
321 is large inter-spectral feature variation and while the enhancement is 14% for spectral feature
322 $f1$, it is only 3% for spectral feature $f4$ even if both features represent calcite. Similarly The
323 enhancement is 5% for spectral feature $f2$ and 31% for spectral feature $f3$. Hence, the average
324 enhancement, induced by the CWT, is higher for wollastonite (average: 18%) than for calcite
325 (average: 8.5%).

326 **4. Discussion**

327 We have applied Raman spectroscopy to assess the quantities of calcite and wollastonite in
328 a set of 26 rock samples collected from the Ihalainen open pit mine in Eastern Finland. Our
329 results suggest that there is a strong positive correlation and thus, a strong relationship, between
330 the intensity values of the individual spectral features and the known mineral abundances
331 determined by the SEM. Similar to previous studies to have created calibration models using
332 Raman data (e.g. Wan and Small, 2010), our results suggest that fluorescence removal can
333 enhance the ability to use Raman data for quantitative mineral analysis.

334 ***4.1 The accuracy of mineral abundance prediction using Raman spectroscopy***

335 The strong positive correlation between the known abundances of wollastonite and calcite
336 and their Raman spectral feature intensities conforms to the results by Cai et al. (2001) who
337 applied Raman data to infer concentrations of ethanolic solutions. However, the intensity values
338 of the individual Raman spectral features are not only related to concentrations, but also to
339 factors such as the crystal orientation with respect to the polarization direction of the light
340 (Andò and Garzanti, 2014), and thus factors such as grain orientation in rocks need to be
341 considered in the context of geological Raman studies. If the average grain size of the sample
342 is smaller than the spot size of the spectrograph, the signal of a single measurement can be a
343 mixture of two or more minerals, thus making interpretations on the mineralogy of the sample
344 more challenging. In this study, the spot size is smaller than the average grain size of the
345 samples (0.1 and 0.5 mm, respectively), thus ensuring that any spectral mixing is negligent and
346 mainly confined to marginal areas of individual mineral grains. Furthermore, if the sample
347 contain minerals that have spectral features in the same wavelength region, interpretations on
348 the presence or absence of a specific mineral can become more challenging. In this study, such
349 confusion was minimized by only analyzing the spectral features that do not overlap with any
350 other spectral features of the sample set.

351 It is important to note that the quantitative information that Raman can provide should be
352 seen as relative, as opposed to absolute, since the intensity values of the spectral features lack
353 universal meaning (Irish and Chen, 1971) due to differences in instrumental response,
354 instrument drift and sample-specific variation (Wan and Small, 2010). Because of this, data
355 obtained using different Raman setups need to be individually calibrated in each study. Also,
356 care should be taken to acquire the calibration data and the Raman data from the same mineral
357 surfaces when there are potential differences in the quantities of individual minerals in different
358 parts of the rock samples. In this study, calibration was conducted using SEM data and

359 furthermore, areas from which the Raman data and the calibration data were acquired were
360 carefully marked using Cu-tape to ensure the ability for cross comparisons.

361 As suggested by our results, some minerals may be more amenable for Raman-based
362 mineral quantification than others. In our study, correlations between calcite and SEM were
363 stronger than those between wollastonite and SEM. Being a strong Raman scatterer (Wang et
364 al., 1998), calcite gives an easily recognizable spectral signature with strong features. In our
365 dataset, these features provide a stronger link between the Raman data and the mineral
366 abundances than in the case of wollastonite. One potential explanation is the stronger signal
367 and lower fluorescence background of calcite when compared to wollastonite.

368 *4.2 The effects of applying CWT for background removal*

369 Fluorescence can completely overwhelm the Raman signal which is several degrees of
370 magnitude weaker (Burke, 2001), and thus removing it can enhance the ability to quantify
371 mineral abundances. Our results suggest that CWT effectively removes the background induced
372 by fluorescence in Raman spectra, which enhances the relationship between the mineral
373 abundances and their Raman intensities. However, this effect varies as a function mineral and
374 specific spectral feature. According to our results, the average enhancement in the predictive
375 power of wollastonite, induced by the CWT treatment, is higher than in the case of wollastonite.
376 As seen in Figure 4, wollastonite appears to have a higher level of background fluorescence
377 than calcite, thus potentially explaining this result. In calcite, Ca can be substituted by rare
378 earth and transition metal ions (Gaft et al., 2001) to induce strong fluorescence in calcite
379 (Sharma et al., 2012). Wollastonite, albeit typically relatively pure CaSiO_3 , can also contain
380 fluorescence-inducing transition elements, such as iron (United States Geological Survey,
381 2001). To the knowledge of the authors, rare earth elements have not been reported in the study
382 area, as also suggested by the generally low amount of fluorescence background in our samples.
383 It is likely that the fluorescence background of the wollastonite-rich samples is caused by

384 transition elements, but the exact chemical composition of the samples is beyond the scope of
385 our study.

386 The methodology discussed in this paper can be a useful tool for a rapid mineral
387 identification. To further test the applicability of our research across a range mineralogical
388 compositions, we suggest a baseline study that spans across mineral samples that represent
389 varying degrees of fluorescence.

390 **4. Conclusions**

391 Raman spectroscopy is an established technology in the field of mineral identification, but
392 thus far has not been widely applied for quantitative mineralogical analysis. One of the reasons
393 for this may be fluorescence, a phenomenon that can completely mask the spectral features of
394 minerals. As the intensities of the spectral features are associated with their abundances,
395 fluorescence can make the use of Raman data for mineral quantification challenging or
396 impossible.

397 Our results suggest that there is a high correlation between the intensity values of the Raman
398 spectral features of calcite and wollastonite and their known abundances. This relationship was
399 made stronger by the removal of fluorescence, conducted using the CWT. Nevertheless, the
400 predictive ability of different minerals and their spectral features varies, thus emphasizing the
401 importance of careful selection of specific spectral features prior to using them from
402 quantitative mineralogical analysis.

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415 **Disclosure statement**

416 The authors report no potential conflicts of interest.

417

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567 TABLES

568 **Table 1.** The scanning electron microscope (SEM) results for the samples of the study. The
569 significance of the letters: A=albite, B=ankerite, C=apatite, D=calcite, E=chrysotile,
570 F=diopside, G=fluorite, H=galena, I=K-feldspar, J=Mg-hornblende, K=Mg-olivine,
571 L=pectolite, M=plagioclase, N=quartz, O=sphene, P=tacl, Q=tremolite, R=vesuvianite,
572 S=wollastonite. Abbreviations: An.=analyses, Nr.=number,

573 **Table 2.** The regression analysis results for the original and CWT treated Raman data of the
574 spectral features *f1-f4*. Abbreviations: Adj.=adjusted, Std.=standard.

575 **Table S1.** The bivariate Shapiro-Wilk (*W*) normality of the original and CWT-treated Raman
576 data of the spectral features *f1-f4*.

577 FIGURES

578 **Figure 1.** A map of southeastern Finland and the location of the study site.

579 **Figure 2.** An average spectrum of all the samples of the original Raman data. The shaded areas
580 depict the maximum and minimum ranges of the individual spectra. Labels *f1-f4* refer to the
581 spectral features of calcite and wollastonite. For details, see section 2.5. Abbreviations:
582 a.u.=arbitrary units.

583 **Figure 3.** The Spearman correlation coefficients (R_s) across the ten wavelet scales.

584 **Figure 4.** The average Raman spectra of Type 1 (wollastonite) and Type 2 (calcite) samples.
585 Labels *f1-f4* refer to the spectral features of calcite and wollastonite.

586 **Figure 5.** An average spectrum of all the samples of the CWT data. The shaded areas depict
587 the maximum and minimum ranges of the individual spectra. Labels *f1-f4* refer to the spectral
588 features of calcite and wollastonite.

589 **Figure 6.** A box plot representation of the intensity variation of a) the individual spectral
590 features *f1-f4* and b) across all of the spectral features. The presentations are given separately
591 for the original Raman data and CWT data.

592 **Figure 7.** Raman intensities of the spectral features a) *f1* (calcite), b) *f2* (wollastonite), c) *f3*
593 (wollastonite) and d) *f4* (calcite) against the mineral percentages of the SEM data.
594 Abbreviations: a.u.=arbitrary units.

595 **Figure 8.** CWT Raman intensities of the spectral features a) *f1* (calcite), b) *f2* (wollastonite), c)
596 *f3* (wollastonite) and d) *f4* (calcite) against the mineral percentages of the SEM data.
597 Abbreviations: a.u.=arbitrary units.

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