Author(s): Laakso, Kati; Kangas, Lasse; Häkkänen, Heikki; Kaski, Saara; Leveinen, Jussi

Title: Enhanced quantification of wollastonite and calcite in limestone using fluorescence correction based on continuous wavelet transformation for Raman

Year: 2021

Version: Accepted version (Final draft)

Please cite the original version:

Laakso, K., Kangas, L., Häkkänen, H., Kaski, S., & Leveinen, J. (2021). Enhanced quantification of wollastonite and calcite in limestone using fluorescence correction based on continuous wavelet transformation for Raman. Applied Spectroscopy Reviews, 56(1), 67-84. https://doi.org/10.1080/05704928.2020.1729170

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

Kati Laakso[a]*[†], Lasse Kangas[a], Heikki Häkkänen[b], Saara Kaski[c], Jussi Leveinen[a]

[a]*Department of Civil Engineering, Aalto University, Espoo, Finland;*

[b]*Department of Biological and Environmental Science, University of Jyväskylä, Jyväskylä, Finland;*

[c]*Department of Chemistry, University of Jyväskylä, Jyväskylä, Finland;*

*corresponding author: laakso@ualberta.ca

[†]Currently at Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada

Dr. Kati Laakso, ORCID: https://orcid.org/0000-0002-4160-3452

Dr. Heikki Häkkänen, ORCID: https://orcid.org/0000-0002-2931-1545

Dr. Saara Kaski, ORCID: https://orcid.org/0000-0001-9989-4224

January 9, 2020

Abstract

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

Keywords: Raman, fluorescence, wavelets, wollastonite, calcite

1. Introduction

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

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

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

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

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

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

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

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

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

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

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

2. Materials and Methods

2.1. The Study Site

The 3 km long and 0.8 km wide Paleoproterozoic (1.9 Ga) Ihalainen deposit (61° 2'0.60" N, 28°10'52.96" E; in Lappeenranta, southeastern Finland, Fig. 1) is one of the most important calcite-marble deposits in Svecofennia and one of the few wollastonite mines in Europe (Lehtinen, 2015). The deposit hosts significant reserves of wollastonite ($Ca[SiO_3]$), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). The deposit is currently being exploited by Nordkalk Ltd. that has owned the site since 1910 (Lehtinen, 1999). Wollastonite occurs as lath-shaped, 0.5 x 0.1-0.2 mm crystals, comprising 20-24% of the ore (Keeling, 1963, Dumont, 2005). Wollastonite as a commercial mineral is being used to substitute asbestos (Maxim and McConnell, 2005) and to increasing the durability and strength of concrete (Kalla et al., 2015), among other uses.

The study area mainly comprises calcite-rich limestone rocks that are surrounded by younger (1.6 Ga) rapakivi granites. Wollastonite is principally sourced from the limestone rocks where the mineral occurs in association with diopside and quartz bands surrounded by a calcite matrix (Lehtinen, 1999). The wollastonite occurrences are located in a 1.5 km, N-S conforming 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

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

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

2.3. Raman Data Acquisition

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

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

To record the mineralogy and mineral proportions of the samples, the polished samples were analysed in the Field Emission Scanning Electron Microscope (FE-SEM) Laboratory of the Geological Survey of Finland (Espoo, Finland). For this end, a JEOL JSM-7100F Schottky instrument, equipped with an Oxford Instruments energy dispersive X-ray spectroscopy (EDS) with a X-Max 80 mm^2 silicon drift detector (SDD) was applied. The SEM data were acquired with a 20 kV acceleration voltage and 0.5 nA probe current.

The mineral phases were characterized using the Oxford INCA feature phase detection and 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 ramaining 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***

In this paper, the focus is on wollastonite and calcite, the ore minerals of the study site. The chosen minerals have a set of characteristic Raman spectral features, described by Urmos et al. (1991), Richet et al. (1998) and Prencipe et al. (2012). Of these features, the following were selected for data analysis due to their pronounced nature and unique position in the electromagnetic spectrum that minimizes potential confusion with other minerals in the sample set: i) 281 cm^{-1} (*f1* from herein), ii) 414 cm^{-1} (*f2* from herein), iii) 972 cm^{-1} (*f3* from herein) and iv) 1092 cm^{-1} (*f4* from herein). The first spectral feature, *f1*, is a translational lattice mode T(Ca, CO_3) in calcite. The second and third (*f2 and f3*) spectral features are induced by the deformation of the Si-O-Si bonds (Richet et al., 1998) in wollastonite. The fourth spectral feature (*f4*) is a prominent vibrational mode, induced by the v_1 symmetric CO_3 stretching mode in calcite (Urmos et al. 1991). It should be noted that wollastonite has a pronounced feature near 637 cm^{-1} (Richet et al., 1998), also present in the dataset, but this feature was left out of analysis to avoid confusion with diopside that is abundant in the sample set and that has a potentially overlapping spectral feature in the same wavelength range (Prencipe et al. 2012).

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

2.6. Continuous wavelet transformation (CWT)

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

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

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

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

2.7 Linear regression analysis

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

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

3. Results

3.1 The effects of the fluorescence removal

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

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

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

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

3.2. Linear regression analysis

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

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

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

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

4. Discussion

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

4.1 The accuracy of mineral abundance prediction using Raman spectroscopy

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

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

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

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

4. Conclusions

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

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

--

Acknowledgements

The authors are indebted to Mr. Markku Lehtinen for his invaluable help with the sample collection, and for generously sharing his abundant knowledge of the study area. The authors would also like to thank Dr. Sari Lukkari and Dr. Bo Johanson from the Geological Survey of Finland for their help with the scanning electron microscope data acquisition.

This work was supported by the Mineral Resources and Material Substitution program (project: New laser and spectral field methods for in situ mining and raw material investigations) by the Academy of Finland.

Disclosure statement

The authors report no potential conflicts of interest.

References

Andò, S. and Garzanti, E. 2014. Raman spectrscopy in heavy-mineral studies. In (Scott, R.A., Smyth, H.R., Morton, A.C. and Richardson, N., Eds.): Sediment provenance studies in hydrocarbon exploration and production. Geological Society, London, Special Publications 386, 395-412.

Barman, I., Kong, C.-R., Singh, G.P. and Dasari, R.R., 2011. Effect of photobleaching on calibration model development in biological Raman spectroscopy. Journal of Biomedical Optics 16(1). doi: 10.1117/1.3520131.

Becker, R.S., 1969. Theory and interpretation of fluorescence and phosphorescence. Wiley Interscience. 283 pp.

Bozlee, B.J., Misra, A.K., Sharma, S.K. and Ingram, M., 2005. Remote Raman and fluorescence studies of mineral samples. Spectrochimica Acta Part A 61(10), 2342-2348.

Brown, M.B. and Forsythe, A.B., 1974. The Anova and multiple comparisons for data with heterogenous variances. Biometrics 30(4), 719-724.

Burke, E.A.J., 2001. Raman microspectrometry of fluid inclusions. Lithos 55 (1-4), 139-158.

Cadush, P.J., Hlaing, M.M., Wade, S.A., McArthur, S.L. and Stoddart, P.R., 2013. Improved methods for background subtraction from Raman spectra. Journal of Raman Spectroscopy 44, 1587-1595.

Cai, W., Wang, L., Pan, Z., Zuo, J., Xu, C. and Shao, X., 2001. Application of the wavelet transform method in quantitative analysis of Raman spectra. Journal of Raman Spectroscopy 32, 207-209.

Dumont, M. 2005. Wollastonite. Canadian minerals yearbook, 2005. Wollastonite. Natural Resources Canada. pp. 61.1-61.5.

Dörfer, T., Schumacher, W., Tarcea, N., Schmitt, M. and Popp, J., 2009. Quantitative mineral analysis using Raman spectroscopy and chemometric techniques. Journal of Raman Spectroscopy 41(6), 684-689.

Efremov, E.V., Buijs, J.B., Gooijer, C. and Ariese, F., 2007. Fluorescence rejection in resonance Raman spectroscopy using a picosecond-gated intensified charge-coupled device camera. Applied Spectroscopy 61(6), 571-578.

Esposito, A.P., Talley, C.E., Huser, T., Hollars, C.W., Schaldach, C.M. and Lane, S.M., 2003. Analysis of single bacterial spores by micro-Raman spectroscopy. Applied Spectroscopy 57(7), 868-871.

Frosch, T., Tarcea, N., Schmitt, M., Thiele, H., Langenhorst, F. and Popp, J., 2007. UV Raman imaging – A promising tool for astrobiology: Comparative Raman studies with different excitation wavelengths on SNC Martian meteorites. Analytical Chemistry 79(3), 1101-1108.

453 Gaft, M., Panczer, G., Reisfeld, R. and Uspensky, E., 2001. Laser-induced time-resolved
454 luminescence as a tool for rare-earth element identification in minerals. Physics and Chemistry
455 of Minerals 28, 347-363.

456 Hauke, J. and T. Kossowski, 2011. Comparison of values of Pearson's and Spearman's
457 correlation coefficients on the same sets of data. Quaestiones Geographicae 30(2), 87-93.

458 Hoang, V.D., 2014. Wavelet-based spectral analysis. TrAC Trends in Analytical Chemistry 62,
459 144-153.

460 Hope, G.A., Woods, R. and C.G. Munce, 2001. Raman microprobe mineral identification.
461 Minerals Engineering 14(12), 1565-1577.

462 Hu, Y., Jiang, T., Shen, A., Li, W., Wang, X. and Hu, J., 2007. A background elimination
463 method based on wavelet transform for Raman spectra. Chemometrics and Intelligent
464 Laboratory Systems 85(1), 94–101.

465 Irish, D.E. and H. Chen, 1971. The application of Raman spectroscopy to chemical analysis.
466 Applied Spectroscopy 25(1), 1-6.

467 Johnson, C.R. and Asher, S.A., 1984. A new selective technique for characterization of
468 polycyclic aromatic hydrocarbons in complex samples: UV resonance Raman spectrometry of
469 coal liquids. Anal Chem 56, 2258-2261.

470 Kalla, P., Rana, A., Chad, Y.B., Misra, A. and Csetenyi, L., 2015. Durability studies on concrete
471 containing wollastonite. Journal of Cleaner Production 87, 726-734.

472 Keeling, P.S., 1963. The wollastonite deposit at Lappeenranta (Willmanstrand), S.E. Finland.
473 Trans. British Ceram. Soc. 62(10), 877-894.

Landsberg, G. and Mandelstam, L., 1928. Űber die Liehtzerstreuung in Kristallen. Zeitschrift für Physik 50, 769-780.

Lau, K.-M. and Weng, H., 1995. Climate signal detection using wavelet transform: How to make a time series sing. Bulletin of the American Meteorological Society 76(12), 2391-2402.

Lehtinen, M.J., 1999. The crystalline limestone deposits of Ihalainen (Lappeenranta) and Louhi (Kerimäki) in SE Finland and their production history. In: Industrial Minerals: Deposits and New Developments in Fennoscandia. Proceedings of the International Conference. Institute of Geology, Karelian Research Center, Petrozavodsk, 41-43.

Lehtinen, M.J., 2015. Industrial minerals and rocks. In: Maier, W.D., Lahtinen, R. and O'Brien, H., (Eds.). Mineral Deposits of Finland, 685-710. Elsevier Science Publishing Co Inc, Amsterdam, Netherlands. 802 pp.

Levene, H., 1960. Robust tests for equality of variances. In Ingram Olkin and Harold Hotelling (eds.). Contributions to Probability and Statistics: Essays in Honor of Harold Hotelling. Stanford University Press. pp. 278-292.

Li, C. and Stair, P.C., 1996. Ultraviolet Raman spectroscopy characterization of sulfated zirconia catalysts: fresh, deactivated and regenerated. Catalysis Letters 36, 119-123.

Liu, P., Deng, X., Tan, X. and Shen, S., 2017. A wavelet-based Gaussian method for energy dispersive X-ray fluorescence spectrum. Heliyon 3(5), e00311.

Ma, C. and Shao, X., 2004. Continuous wavelet transform applied to removing the fluctuating background in near-infrared spectra. Journal of Chemical Information and Computer Sciences 44, 907-911.

495 Macdonald, A.M. and Wyeth, P., 2006. On the use of photobleaching to reduce fluorescence
496 background in Raman spectroscopy to improve the reliability of pigment identification on
497 painted textiles. Journal of Raman Spectroscopy 37, 830-835.

498 Matousek, P., Towrie, M., Ma, C., Kwok, W.M., Phillips, D., Toner, W.T. and Parker, A.W.,
499 2001. Fluorescence suppression in resonance Raman specroscopy using high-performance
500 picosecond Kerr gate. Journal of Raman Specroscopy 32(12), 983-988.

501 Maxim, L.D. and McConnell, E.E., 2005. A review of the toxicology and epidemiology of
502 wollastonite. Inhalation Toxicology 17(9), 451-466.

503 Misra, A.K., Sharma, S.K., Chio, C.H., Lucey, P.G. and Lienert, B., 2005. Pulsed remote
504 Raman system for daytime measurements of mineral spectra. Spectrochimica Acta Part A
505 61(1), 2281-2287.

506 Nasdala, L., Smith, D.C., Kaindl, R. and Ziemann, M.A., 2004. Raman spectroscopy:
507 Analytical perspectives in mineralogical research, 281-344. In: Beran, A. and Libowitzky, E.
508 (Eds.): Spectroscopic methods in mineralogy 6. European Mineralogical Union.

509 Pekkala, Y. 1988. Suomen karbonaattikivet. In: Haapala, I. (Ed.): Suomen teollisuusmineraalit
510 ja teollisuuskivet. Yliopistopaino, Helsinki. 168 pp.

511 Prencipe, M., Mantovani, L., Tribaudino, M., Bersani, D., Lottici, P.P., 2012. The Raman
512 spectrum of diopside: A comparison between ab initio calculated and experimentally measured
513 frequencies. European Journal of Mineralogy 24(3): 457-464.

514 Reisfeld, R., Gaft, M., Boulon, G., Panczer, C. and Jørgensen, C.K., 1996. Laser-induced
515 luminescence of rare-earth elements in natural fluor-apatites. Journal of Luminescence 69(5-6),
516 343-353.

517 Richet, P., Mysen, B.O., Ingrin, J., 1998. High-temperature X-ray diffraction and Raman
518 spectroscopy of diopside and pseudowollastonite. Physics and Chemistry of Minerals 25(6),
519 401-414.

520 Rivard, B., Feng, J., Gallie, A. and Sanchez-Azofeifa, A., 2008. Continuous wavelet for the
521 improved use of spectral libraries and hyperspectral data. Remote Sensing of Environment
522 112(6), 2850-2862.

523 Romppanen, S., Häkkänen, H., Kekkonen, J., Nissinen, J., Nissinen, I., Kostamovaara, J. and
524 Kaski, S., 2019. Time-gated Raman and laser-induced breakdown spectroscopy in mapping of
525 eudialyte and catapleiite. Journal of Raman Spectroscopy 2019, 1-8.
526 https://doi.org/10.1002/jrs.5622.

527 Shapiro, S.S. and Wilk, M.B., 1965. An analysis of variance test for normality (complete
528 samples). Biometrika 52(3-4), 591-611.

529 Sharma, S.K., Misra, A.K., Clegg, S.M., Barefield, J.E., Wiens, R.C. and Acosta, T., 2010.
530 Time-resolved remote Raman study of minerals under supercritical CO_2 and high temperatures
531 relevant to Venus exploration. Philosophical Transactions of the Royal Society A.
532 Mathematical, Physical and Engineering Sciences 368, 3167-3191.

533 Sharma, S.K., Misra, A.K., Acosta, T.E., Lucey, P.G., 2012. Time-resolved remote Raman and
534 fluorescence spectrometers for planetary exploration. Proceedings SPIE 8379, Laser Radar
535 Technology and Applications XVII, 83790J, doi: 10.1117/12.920955.

536 Smith, D.C., and Carabatos-Nédelec, C., 2001. Raman spectroscopy applied to crystals:
537 Phenomena and principles, concepts and conventions. In (Lewis, I.R. and Edwards, H.G.M.,
538 eds.): Handbook of Raman Spectroscopy, Marcel Dekker Inc., New York, 349-422.

539 Sobron, P., Sobron, F., Sanz, A. and Rull, F., 2008. Raman signal processing software for
540 automated identification of mineral phases and biosignatures on Mars. Applied Spectroscopy
541 62(4), 364-370.

542 United States Geological Survey, 2001. Wollastonite – A versatile industrial mineral. USGS
543 Fact Sheet FS-002-01. Available at: https://pubs.usgs.gov/fs/fs-0002-01/fs-0002-
544 01textonly.pdf.

545 Urmos, J., Sharma, S.K. and Mackenzie, F.T., 1991. Characterization of some biogenic
546 carbonates with Raman spectroscopy. American Mineralogist 76(3-4), 641-646.

547 Vítek, P., Ali, E.M.A., Edwards, H.G.M., Jehlička, J., Cox, R. and Page, K., 2012. Evaluation
548 of portable Raman spectrometer with 1064 nm excitation for geological and forensic
549 applications. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 86, 320-
550 327.

551 Wan, B. and Small, G.W., 2010. Wavelet analysis used for spectral background removal in the
552 determination of glucose from near-infrared single-beam spectra. Analytica Chimica Acta
553 681(1-2), 63–70.

554 Wang, A., Haskin, L.A. and Cortez, E., 1998. Prototype Raman spectroscopic sensor for in situ
555 mineral characterization on planetary surfaces. Applied Spectroscopy 52(4), 477-487.

556 Wang, A., Jolliff, B.L. and Haskin, L.A., 1995. Raman spectroscopy as a method for mineral
557 identification on lunar robotic exploration missions. Journal of Geophysical Research
558 100(E10), 21189-21199.

559 Wang, J. and Mullins, O.C., 1997. Fluorescence of limestones and limestone components.
560 Applied Spectroscopy 51(12), 1890-1895.

Williams, M.N., Gómez Grajales, C.A. and Kurkiewicz, D, 2013. Assumptions of multiple regression: Correcting two misconceptions. Practical Assessment, Research & Evaluation 18(11).

Zhang, Z.-M., Chen, S., Liang, Y.-Z., Liu, Z.-X., Zhang, Q.-M., Ding, L.-X., Ye, F. and Zhou, H., 2009. An intelligent background-correction algorithm for highly fluorescent samples in Raman spectroscopy. Journal of Raman Spectroscopy 41(6), 659-669.

TABLES

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

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

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

FIGURES

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

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

598

599

600