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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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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 fluorescence 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 ($\text{Ca}[\text{SiO}_3]$), calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). 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

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

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

2.2. Sample Set

The sample set comprises 26 rock samples that were collected from different parts of the study site (rock piles). Because the original locations of the samples are uncertain, their coordinates were not recorded. The samples were selected to represent the different wollastonite types of the study area, discussed in section 2.1. Here, the objective was to have wollastonite and calcite -rich samples to compare the effects of fluorescence removal on mineralogically distinct samples. Petrographic analysis of the samples 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 mm² 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

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

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

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

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 ν_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 quantities 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 strengthens 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 homogeneity 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

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

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

4.2 The effects of applying CWT for background removal

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

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Disclosure statement

The authors report no potential conflicts of interest.

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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.

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

Figure 4. The average Raman spectra of Type 1 (wollastonite) and Type 2 (calcite) samples.

Labels *f1-f4* refer to the spectral features of calcite and wollastonite.

Figure 5. An average spectrum of all the samples of the CWT 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.

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

Figure 7. Raman intensities of the spectral features a) *f1* (calcite), b) *f2* (wollastonite), c) *f3* (wollastonite) and d) *f4* (calcite) against the mineral percentages of the SEM data.

Abbreviations: a.u.=arbitrary units.

Figure 8. CWT Raman intensities of the spectral features a) *f1* (calcite), b) *f2* (wollastonite), c) *f3* (wollastonite) and d) *f4* (calcite) against the mineral percentages of the SEM data.

Abbreviations: a.u.=arbitrary units.