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RESEARCH ARTICLE



Empirical Raman calibration of trioctahedral ferromagnesium chlorite minerals

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Abstract

Chlorite is a common hydrated-aluminous phyllosilicate mineral group that forms in most geological environments (e.g., hydrothermal, igneous, sedimentary, and metamorphic). The chemical composition of chlorite depends on several factors including temperature, pressure, fluid, and bulk rock composition. Raman spectroscopy is proposed as a quick and cost-effective alternative to scanning electron microscopy and electron probe micro-analysis, which involve complex sample preparation. In this paper, we demonstrate that Raman spectroscopy is a viable technique to determine the chemical composition of chlorite. Our results show that chlorite's Raman spectra changes quantitatively as a function of its chemical composition. Iron (Fe) and magnesium (Mg) content (APFU) is linearly correlated with the peak positions of three bands: Band 1 (99-104 cm⁻¹), Band 8 (546-553 cm⁻¹), and Band D (3,570-3,580 cm⁻¹). In contrast, silicon (Si) and tetrahedral aluminum (Al^{IV}) are correlated with a single band's position, Band 9b ($663-679 \text{ cm}^{-1}$). We derived 18 empirical rules from these correlations, aiding geoscientists in accurately identifying and determining chlorite composition using Raman spectroscopy. Moreover, this technique holds potential for determining chlorite's chemical composition during planetary exploration, leveraging existing Raman spectrometers deployed on Mars and for future space missions.

KEYWORDS

calibration, chemical composition, chlorite, Fe-Mg chlorite, ferromagnesium

1 INTRODUCTION

Chlorites form a group of complex hydrous phyllosilicates that occur in most geological settings including igneous, sedimentary (diagenetic), metamorphic, and hydrothermal environments.¹⁻⁶ It is a common alteration product from water-rock interactions of a variety of minerals such as biotite,⁷ hornblende,⁸ pyroxenes,⁹ kaoliniteserpentine group,^{10–12} smectite group,^{13–15} tourmaline,¹⁶ and cordierite.¹⁷ Therefore, understanding the chemical composition of chlorite can be important for documenting mineralogical processes that occur within the crust, particularly those associated with water-rock interactions,¹⁸⁻²⁰ diagenetic and metamorphic reactions, ^{3,4,13} and ore formations.^{21,22} Moreover, its presence on extraterrestrial surfaces, such as Mars, may

constitute a paleo-indicator of the presence of water, which may have implications for past Martian habitability.²³ In this context, it is intriguing that the presence of chlorite has been inferred in clay units in Mars' crust based on visible and near infrared spectroscopy data from the Mars Reconnaissance Orbiter.^{24–26}

The chemical composition of chlorite is generally determined using electron probe micro- analyses (EPMA), which can be time consuming and expensive.²⁷ Recent improvements in sensitivity of Raman spectroscopy detectors²⁸ allows for the detection of cationic substitutions in different solid-solution mineral and mineraloids, such as plagioclase,²⁹ garnet,³⁰ and volcanic glasses.³¹

Therefore, we propose that Raman spectroscopy can be a suitable alternative technique for determining the chemical composition of chlorite under circumstances where EPMA is impractical, for example, in the exploration of extraterrestrial bodies. Raman spectroscopy is an ideal tool because it can analyze samples without specific sample preparation, is generally non-destructive, and produces spectra composed of bands that are sharper than near or mid-range infrared spectroscopy.^{30,32}

Previous studies of Raman spectral characteristics of chlorite have been conducted by Prieto et al.,² Kleppe et al.,³³ and Wang et al.³⁴ Although based on limited sample numbers, these studies reported measurable change in the Raman spectra in response to compositional changes in chlorites. They specifically report that analyzed chlorite minerals are characterized by a series of intense Raman bands in the 600–750 cm^{-1} region and a set of weak bands in the $800-1,100 \text{ cm}^{-1}$ region. These authors also demonstrated the presence of a composite band in the 3,683–3,610 cm⁻¹ spectral region corresponding to OH⁻ vibrational modes that seems to be influenced by the amount of XFe (XFe = Fe/[Fe + Mg]) in the chlorite. Although these results are encouraging, more samples reflecting a larger range of chemical compositions are needed to extract empirical equations for a Raman spectroscopic calibration.

Raman spectroscopy is widely accessible in laboratories worldwide, and its utility is enhanced by the presence of flight-proven miniaturized systems currently in operation on Mars. NASA's Perseverance Rover carries two Raman systems: a pulsed 532 nm laser and a pulsed 248.6 nm laser.^{35,36} The planned ESA's Mars Rover Rosalind Franklin will also be equipped with a continuous wave 532 nm Raman laser.³⁷ *In situ* analysis using Raman spectroscopy following Mars orbiter studies can lead to further information about planetary past geological and climate processes. Additionally, the inclusion of a Raman laser is recommended for a proposed NASA lander mission to Europa, given its versatile capabilities and extensive usage.³⁸ In this paper, we report new microprobe and Raman spectroscopic data from 19 chlorite samples collected from several geological and geographical settings. This collection of chlorites offers a wide range of compositions of trioctahedral ferromagnesium chlorites to demonstrate that chemical composition can be accurately measured using Raman spectroscopy. The Raman spectral features are compared with high-resolution electron probe microanalyses to derived chlorite composition empirical rules. We demonstrate that Raman spectroscopy can be used to quantify Fe, Mg, Al (IV), and Si.

1.1 | Chlorite background

Chlorite is composed of four layers, also referred to as a 2:1:1 layered mineral, which include two tetrahedral sheets. one octahedral sheet between the tetrahedral sheets, and an interlayer sheet (a brucite-like layer) (Figure 1).^{6,39,40} The general chlorite formula is $(R^{2+}, R^{3+}, \Box)_6$ (Si_{4-x}, Al_x) O₁₀(OH)₈, where R²⁺ is an octahedral divalent atom, R^{3+} is an octahedral trivalent atom, and \square is a cation vacancy.^{6,41} Tetrahedral lavers are dominated by Si⁴⁺ or Al³⁺ (also referred to as Al^{IV}, which corresponds to the Al partitioned into the tetrahedral layer),^{39,41} though B^{3+} has been also reported in Borocookeite.⁴² In contrast, the octahedral layer is dominated by Fe^{2+} , Mg^{2+} , Mn^{2+} , Fe^{3+} , and $Al^{3+[6]}$ although Mn^{3+} , Ni^{2+} , Ti^{2+} , Zn^{2+} , and Li^{1+} may also be present.^{16,41,43,44} The tetrahedral Al is denoted by Al^{IV}, and the octahedral Al is denoted by Al^{VI}. The 2:1 layers and interlayer are connected through hydrogen bonding, which stabilizes the mineral over a large P-T range.^{33,45}



FIGURE 1 Chlorite structure represented as two-dimensional ball and stick model. Oxygen atoms (O²-) are represented by blue circles, cations in the tetrahedral layer are depicted by purple circles, hydroxyl ions (OH⁻) by green circles, and cations in the octahedral layer by yellow circles. Modified from Wiewióra and Weiss.⁴¹

Chlorite can have up to two cation vacancies in either the octahedral layer or the interlayer.⁴¹

Vacancies in chlorite can be determined by subtracting the total trivalent atoms (such as aluminum or ferric iron) in the octahedral layers by total trivalent atoms in the tetrahedral layers and dividing by two.40 The complexity of chlorite's chemical composition can be described using three main substitutions: (1) Tschermak, (2) di-trioctahedral, and (3) ferromagnesian.^{4,6,45,46} The Tschermak exchange substitutes a tetrahedral Si⁴⁺ atom and a divalent octahedral atom (either Fe^{2+} or Mg $^{2+}$) for two Al atoms, one in the tetrahedral sheet and one in the octahedral sheet. Di-trioctahedral substitution occurs when two Al³⁺ atoms and a vacancy are substituted for three divalent cations, either Mg^{2+} or Fe^{2+} . The ferromagnesian substitution involves Fe and Mg in the octahedral laver. Iron-rich chlorites have a lower range of temperature stability than magnesium-rich chlorites.⁴⁷ These substitutions are sensitive to temperature (T), pressure (P) of equilibration, and bulk composition (X) of the parent rock.^{4,6,45,48} The ferromagnesian substitution (i.e., the Fe/[Fe + Mg] ratio, also known as XFe) is dependent on temperature and pressure conditions at time of formation.^{2,49} The sensitivity of these substitutions to T, P, and X, in addition to the fact that chlorite is widespread in different geological environments, makes chlorite an excellent geothermometer.3,4,19,20,45,48-51 As such, knowing the chemical composition of chlorite is essential for determining temperatures condition of metamorphism.

2 | METHODOLOGY

2.1 | Sample collection and preparation

This study consists of 19 natural polycrystalline chlorite samples from four broad localities: Alps, Ardennes, Corsica, and Pyrenees. Out of our 19 samples, the EPMA composition of 10 (samples Ba05, Cookeite [Nav01], KS47, MB03-EV, Ne02, Ne04, PPV26, Tri04, Tri07, and SM01) are from Lacroix and Vennemann.⁵ Other samples include Ca02 and CAXX (Queyras schist lustrés, Alps), KS45 (Ardennes massif), Ne05 (Neouvielle massif, Pyrenees), Nev01 (Neves Area, Alps), Tri01 and Tri03 (Trimous massif, Pyrenees), 16SS02 (Seynijes-pass, Alps), and Ga0904 (Gavere, Alps). Four samples were reserved to use as unknowns to test the resulting calibration. These samples include SM03 (Piedmont, Western Alps), 407900, 407904, and 407916 (French Guinea). All samples have been made into polished thin sections.

To evaluate the potential effect of di-trioctahedral substitution as well as the effects of vacancies content

(\Box) on Raman features, we also analyzed a cookeite sample (Nav01) (Al-rich chlorite) from Navette Valley, Alps. Cookeite is a lithium-rich di-trioctahedral chlorite with a formula of (LiAl₄) (Si₃Al) O₁₀ (OH)₈.^{52–55}

2.2 | EPMA characterization

Chlorite samples were analyzed for Si, Al, Fe, Mg, Mn, Na, Ca, K, and Ti composition with a JEOL electron probe micro-analyzer at University of Lausanne and University of Bern. The instrument has five X-ray spectrometers, and operating conditions included 15 keV accelerating voltage, 10 nA current intensity, and a beam diameter of 5–6 μ m. The microprobe analyses were calibrated using common standards: orthoclase (K), albite (Na), andalusite (Al), forsterite (Mg), fayalite (Fe, Si), wollastonite (Ca), chromium oxide (Cr), and MnTi metal (Mn and Ti).

Chlorite analyses with K₂O, Na₂O, or CaO values higher than 0.1 wt% were discarded, to avoid contamination by another mineral phases (e.g., mineral inclusions and polymineral grain boundaries). Oxides mass fractions were converted to chlorite structural formula (APFU) based on 14 oxygen equivalents, assuming that all Fe is in the ferrous (Fe²⁺) state. The justification for assuming that all iron (Fe) exists as Fe^{2+} is supported by the crystallographic constraints commonly observed in chlorites. which generally prevent high concentrations of Fe³⁺ concentrations.^{46,56} Therefore, the oxidation state of Fe in chlorites has historically been assumed to be ferrous iron, unless direct measurements of the Fe oxidation state available by other methods, for example, from a synchrotron, which is outside the scope of this study. The selected chlorite compositions are also assumed to have zero vacancies. The exception to this is the cookeite sample, which is a di-trioctahedral chlorite with a single vacancy in the octahedral layer. Ferromagnesium chlorites have Al in both its tetrahedral layer, Al^{IV}, and octahedral layer, Al^{VI}. Therefore, total Al must be distributed between the two layers. The tetrahedral aluminum, Al^{IV}, is calculated by (4 - Si APFU). The octahedral aluminum, Al^{VI} , is calculated by $Al_{total} - Al^{VI}$.

2.3 | Raman spectroscopy

Raman spectroscopy is used to determine molecular structure and is typically a non-destructive technique, though certain materials are susceptible to photooxidation depending on laser wavelength and laser power.⁵⁷ Relative intensity in Raman spectroscopy is based on numerous factors including amount of material, laser -WILEY-RAMA CTROSCOPY

power, time of irradiation, sample orientation, excitation wavelength, the material's Raman cross-section, and number of acquisitions.⁵⁸ Frequencies of the atom vibrations are based on the masses of the atoms and strength of the bonds.⁵⁹ Shifting of peak positions is due to different stresses in the molecular geometry, including cationic substitutions.58

Raman analyses of chlorite samples were conducted at the Kansas State University Department of Geology using a Renishaw InVia Reflex spectrometer with a spectral resolution of 1.0 cm⁻¹ and an axial spatial resolution of $<1 \mu m$. Ten to 20 spectra per sample were obtained on polished thin sections under 100X objective (numerical aperture = 0.9) on a DM25—Leica microscope. The Raman scattering was excited by a 532 nm wavelength (green) laser with a power of 22.5 mW (50% power of this laser) on the sample surface over a 5 s analysis time (two accumulations each). These experimental conditions have been set up to prevent destruction of samples, lower the chances of fluorescence, and boost signal-to-noise ratio. Raman analyses were performed at different locations on the chlorite sample, generally from different chlorite grains in the same thin sections. Before each session of measurements, the spectrometer was calibrated using the 520.5 cm⁻¹ line of an internal and external silicon standard. This calibration process-ensured accurate and reliable measurements were obtained.

Raman spectra were processed with SpectraGryph software and WiRE 5 software, and background was removed by intelligent fitting mode. This was done by excluding regions with peaks determined by WiRE 5, then fitting the baseline to the remaining spectra. Both regions were normalized separately in SpectraGryph, with the highest band of each region set to one. The highest band in the 80–1,200 cm^{-1} and 3,200–3,750 cm^{-1} ranges were Band 8 (\sim 550 cm⁻¹) and the composite Band II $(\sim 3,560 \text{ cm}^{-1})$, respectively. Each region of each sample was curve fit separately in WiRE 5.

Curve fitting for each chlorite spectra used a 50% mixed Gaussian-Lorentzian routine, which included many combinations of bands. Multiple iterations were performed to achieve the optimum reduced chi-squared value for all samples. The lower region was only fitted between 80 and $1,200 \text{ cm}^{-1}$ to prevent any additional noise to be counted against the reduced chi-squared, while the upper region was only fitted between 3,200 and 3,750 cm⁻¹. All reduced chi-squared values were calculated to a tolerance of 10^{-8} and had a max iteration of 10,000. After all spectra for a sample were curve fitted to the best possible reduced chi square, then the average value for peak position, relative intensity, full width at half maximum (FWHM), and area was calculated for

each peak in a sample. The second derivative was taken of each chlorite spectrum as a validity check of the number of bands. The position of the peaks in the secondderivative spectrum corresponds to the Raman bands, which can be used to identify the vibrational modes of the molecule being studied.

3 RESULTS

Composition of chlorite 3.1

Average EPMA chemical compositions of the analyzed chlorite samples are presented in Figure 2. Table S1 reports the average EPMA values for the chlorites of this study, including the 10 samples previously reported in Lacroix and Vennemann.⁵ Most of the analyzed chlorites correspond to Fe-Mg chlorite with XFe varying from 0.04 and 0.64 (Table S1). The calculated cation values are in the range of 2.3-3.7 APFU (atoms per formula unit) for Si, 0.3–1.7 APFU for Al^{IV}, 0.8–5.1 APFU for Al^{VI}, 0.1–2.7 APFU for Fe, and 0.1–4.8 APFU for Mg (Table S1).

The compositions of analyzed chlorites are plotted in the R²⁺-Si diagram of Wiewióra and Weiss,⁴¹ which is a projection of a generalized chlorite chemical composition (Figure 2). This figure shows the relationship between Si and R^{2+} (the octahedral cations with a 2+ charge). The slanted \square and \mathbb{R}^{3+} lines correspond to the proportion of vacancies and trivalent cations, respectively. Most of our samples plot close to the zero-vacancy line, indicating these are likely trioctahderal. Cookeite chlorite plots further away from the other samples due to high tetrahedral silica content, and its octahedral layers were dominated by Al and a vacancy.

Raman characteristics of chlorite 3.2

Raman spectra obtained from the analyzed chlorites show several common spectral features, characterized by several strong and moderately strong bands in the range $80-1,200 \text{ cm}^{-1}$ and $3,200-3,700 \text{ cm}^{-1}$, respectively (Figures 3 and 4). Distinct Raman bands in the lower wavenumber spectral range are found at 100 cm⁻¹ (Band 1), 205 cm^{-1} (Bands 3a and 3b), 548 cm^{-1} (Bands 8), and 670 cm^{-1} (Bands 9a and 9b) (Figure 3; Table 1), while bands in the higher wavenumber spectral region are found at 3,440 cm^{-1} (Band A), 3,570 cm^{-1} (Bands C and D), and $3,650 \text{ cm}^{-1}$ (Bands E–G) (Figure 4, Table 1). For ease of reference, the lower spectral range $(80-1,200 \text{ cm}^{-1})$ and higher spectral range $(3,200-3,750 \text{ cm}^{-1})$ are referred to in this study as regions 600 and $3,500 \text{ cm}^{-1}$, respectively.

FIGURE 2 Silicon APFU values plotted against the concentration of divalent octahedral cations ($R^{2+} = Fe^{2+}$ [APFU] + Mg²⁺ [APFU]). Diagonal lines with positive slopes indicate vacancy values, while diagonal lines with negative slopes represent the APFU of trivalent cations such as aluminum or ferric iron. The standard error was calculated for all samples, except for PPV26, which values came from Lacroix and Vennemann⁵ without reporting the associated error. This diagram is derived from Wiewióra and Weiss.⁴¹







There is a scarcity of literature of phonon assignments for the Raman spectroscopy of chlorites, and moreover, what literature that is available, there is no consensus on the phonon assignments of these bands. For example, Band 1 in Prieto et al.² was assigned to octahedral movements (the MO_6 octahedron) while Ulian et al.⁶⁰ assigned as an tetrahedral movements

(Si–O[b] triangle rotation). In other papers, Band 1 was outside the range of the spectrometers and therefore not always mentioned in studies. Composite Band 3 was assigned to the T-O-T lattice modes in one study⁶¹ and then octahedral symmetric stretching in two studies.^{2,60} Possibly, the lack of consensus for Band 3 is because this was found to be a composite band in

TABLE 1 Ranges of the average band characteristics of all the chlorite samples in regions 600 and 3,500 cm⁻¹.

	Peak positio	Peak position (cm $^{-1}$)		Width (cm $^{-1}$)		Relative intensity		Area	
Band	Min	Max	Min	Max	Min	Max	Min	Max	
1	99.00	104.21	5.53	18.51	0.10	0.19	0.76	4.65	
2a	122.50	138.65	11.39	23.02	0.01	0.22	0.80	5.51	
2b	130.43	152.48	16.39	32.60	0.02	0.23	0.49	5.67	
3a	199.02	209.89	10.28	18.79	0.17	0.61	2.27	10.59	
3b	194.02	212.15	19.60	45.39	0.12	0.38	4.71	9.49	
4	271.36	290.08	15.61	43.28	0.03	0.25	0.65	4.53	
5	356.44	377.19	16.86	52.88	0.05	0.34	1.34	8.96	
6	385.76	559.26	2.87	38.50	0.02	0.07	0.10	3.17	
7	466.79	569.20	12.61	32.87	0.02	0.16	0.39	5.06	
8	546.19	552.78	9.20	12.19	0.88	1.02	12.10	18.47	
9a	665.08	679.54	50.98	68.86	0.17	0.48	11.40	28.99	
9b	663.39	678.69	21.22	27.91	0.26	0.74	5.97	27.43	
10 and 11	745.79	808.49	47.55	78.14	0.03	0.08	1.46	6.26	
12	891.80	942.87	23.41	83.73	0.02	0.13	1.10	8.65	
13	940.96	995.06	33.00	111.74	0.04	0.13	2.14	16.50	
14	983.56	1,047.49	17.65	72.84	0.04	0.19	0.99	13.56	
15	1,018.85	1,086.76	6.41	97.13	0.06	0.28	1.00	31.19	
А	3,438.71	3,457.53	105.59	142.74	0.27	0.68	38.70	147.30	
В	3,444.59	3,518.88	32.19	62.00	0.05	0.19	2.17	12.65	
С	3,540.49	3,564.44	44.90	75.98	0.42	0.71	20.59	56.68	
D	3,570.21	3,580.30	31.64	40.88	0.25	0.76	8.42	34.12	
Е	3,614.46	3,643.35	18.41	39.36	0.08	0.45	1.68	15.01	
F	3,631.93	3,666.37	14.60	31.07	0.09	0.44	2.37	10.05	
G	3,653.10	3,677.41	14.16	29.74	0.06	0.30	0.98	8.79	

Note: Band characteristics mentioned are the position, width, intensity, and area.

our study instead of assuming to be a single band. In addition, Band 8 has also been related to the overall T-O-T lattice modes⁶¹ and the tetrahedral sheet (T_2O_5) .² Composite Band 9 has been assigned to being controlled by both tetrahedral atoms and combination of OH vibrations.^{2,61} Therefore, given this lack of consensus in literature pertaining to band assignments, we are nominally assigning these bands as numbers.

3.2.1 | Region 600 cm⁻¹

Region 600 cm^{-1} generally includes between 18 and 19 bands for each sample (Figure 3): two strong bands (548 and 670 cm⁻¹) and several moderate to weak bands. Three composite bands are present in this region: Bands 2, 3, and 9 (Figure 5). These composite bands can be decomposed in the sub-bands 2a and 2b for composite

Band 2, 3a and 3b for composite Band 3, and 9a and 9b for composite Band 9 (Figure 5).

In analyzed samples, Bands 1, 3a, 3b, 8, 9a, and 9b are systematically present and can be easily separated from other bands. Bands 12–15 are present and compose a wide composite band, though these bands are difficult to differentiate from each other (Figure 3). In contrast, weak to moderate Bands 2a, 2b, 4–7, 10, and 11 are not systematically present, which could be due to low signal/noise (S/N) in this spectral range or based on chemical composition. For example, in a past study, Band 5 was found to be present in clinochlore (Mg-rich), but not present in chamosite (Fe-rich).⁶¹

Band 1, a moderate band, is located between 99 and 104 cm⁻¹ and has a narrow peak (FWHM between 5 and 11 cm⁻¹). Our EPMA results show a strong correlation between the Band 1 position, Fe APFU content ($R^2 = 0.93$), Mg APFU content ($R^2 = 0.85$), and XFe



FIGURE 6 Scatter plots depicting the correlation between the average peak position (in wavenumbers/cm⁻¹) of Band 1 (A–C), Band 8 (D-F), and Band D (G-I) in each sample (excluding cookeite) and the EMPA values of iron, magnesium, and XFe (Fe/Fe + Mg). (A) Band 1 position versus iron APFU (Equation (1), $R^2 = 0.93$), (B) Band 1 position versus magnesium APFU (Equation (4), $R^2 = 0.85$), (C) Band 1 position versus XFe (Equation (7), $R^2 = 0.91$), (D) Band 8 position versus iron APFU (Equation (2), $R^2 = 0.95$), (E) Band 8 position versus magnesium APFU (Equation (5), $R^2 = 0.87$), (F) Band 8 position versus XFe (Equation (8), $R^2 = 0.93$), (G) Band D position versus iron APFU (Equation (3), $R^2 = 0.85$), (H) Band D position versus magnesium APFU (Equation (6), $R^2 = 0.86$), and (I) Band D position versus XFe (Equation (9), $R^2 = 0.88$). Error bars are included, although in many cases, the error bars are smaller than the spot size. The standard errors are reported in Table S1.

 $(R^2 = 0.91)$ (Figure 6A–C). Note that these correlations do not include the cookeite sample. Band 1 position also has a linear relationship with the positions of Band 8 ($R^2 = 0.98$). As Fe content increases, positions of Bands 1 and 8 shift toward lower relative wavenumbers (Figure 6A,D). In contrast, the band positions shift to higher relative wavenumbers as Mg content rises (Figure 6B,E). Using a limited number of samples for simplicity, Figure 7 demonstrates with three samples (Ca02, KS45, and Tri04) how Band 8 shifts based on amount of Fe and Mg. Prieto et al.² suggest that Band 1 is

associated with octahedral cations and is not present in Fe -rich chlorites (XFe range between 0.8 and 0.9). In this study, all the analyzed samples feature Band 1, consistent with XFe values between 0.0 and 0.6.

Raman Bands 3a and 3b both compose the 200 cm^{-1} composite band (Figure 5). The two bands can be distinguished by their peak FWHM. Band 3b $(23-37 \text{ cm}^{-1})$ is wider than the narrow 3a band (10–20 cm^{-1}). Generally, Band 3a is characterized by higher relative intensity and is located at lower wavenumbers $(199-210 \text{ cm}^{-1})$ than Band 3b (201–217 cm^{-1}). It has a normalized intensity in



FIGURE 7 The average peak positions of Band 8 for a subset of the 18 samples, specifically Ca02 (blue line), KS45 (green line), and Tri04 (purple line). Among these three samples, Ca02 has the highest Fe content (2.59 APFU), the lowest Mg content (1.63 APFU), and the lowest relative wavenumber for the peak position of Band 8 (546.2 cm⁻¹). On the other hand, Tri04 has the lowest Fe content (0.16 APFU), the highest Mg content (4.91 APFU), and the highest relative wavenumber for the peak position of Band 8 (552.7 cm⁻¹). KS45 falls within the middle range for Fe, Mg, and

the peak position of Band 8.

the range 0.17–0.5, while Band 3b location ranges between 0.07 and 0.34.

Composite Band 8 (\sim 550 cm⁻¹) is the strongest in the 600 cm^{-1} region (Figure 3). Band 8 corresponds to a narrow FWHM band located in the 546–553 cm⁻¹ spectral range (Figure 7). In some cases, this band may be asymmetrical, with the presence of a left shoulder suggesting the presence of a short and broad band (Figure 8). It is possible that the band on the left shoulder represents the same vibrational mode shifted to a lower relative wavenumber due to substitution of a heavier element into the chlorite lattice. Band 8's position is negatively correlated with Fe content ($R^2 = 0.95$) and XFe ($R^2 = 0.93$): As the elemental values increase, Band 8 position shifts to lower wavenumber (Figure 6D,F). Band 8 also exhibits a positive correlation with Mg ($R^2 = 0.87$), indicating that as Mg content increases the band shifts toward a higher wavenumber (Figure 6E).

Composite Band 9 (\sim 670 cm⁻¹), the second strongest band in the 600 cm⁻¹ region, can be subdivided in Bands 9a and 9b (Figure 5). These bands are characterized by their FWHM, with 9a having a larger FWHM than 9b (Figure 5). Band 9b was found to be correlated with Si and Al^{IV} (R² = 0.76) (Figure 9A,B). In addition to being correlated with the tetrahedral cations, Band 9b seems to have some correlation with the di-trioctahedral



FIGURE 8 Two examples of Band 8 (\sim 550 cm⁻¹) are provided for comparison. The first example is represented by the black curve, which does not exhibit a left shoulder. In contrast, the second example, depicted by the red curve, displays the presence of a left shoulder. These distinct examples highlight the variations in the shape and characteristics of Band 8.



FIGURE 9 Relationship between the peak position of Band 9b and (A) Si APFU, (Equation (10), $R^2 = 0.76$), (B) AlIV APFU (Equation (11), $R^2 = 0.76$), and (C) di-trioctahedral substitution = $(2^*AITotal + \Box) / 3^*(Fe + Mg)$, (Equation (15), $R^2 = 0.77$). The standard errors are reported in Table S1.

substitution $(2*Al_{Total} + \Box) /3*(Fe + Mg)$ (Figure 9C). Band 9b is located between 663 and 678 cm⁻¹, its FWHM is 18–33 cm⁻¹, and its normalized intensity is 0.27–0.73. It was found in Prieto et al.,² Band 9 splits when XFe is greater than >0.5, though our study did not see any correlation between XFe and the positions of Bands 9a and 9b.

The chlorite Raman spectra in the 600 cm^{-1} region were analyzed using the cosine similarity technique. Cosine similarity measures the similarity between two spectra and ranges from 0 (no similarity) to 1 (perfect *match*).⁶² The average cosine similarity of all the spectra in this region is 0.94. The chlorite samples that were least similar were the Mg-rich sample Tri04, with an average cosine similarity of 0.80, compared to the Fe-rich samples CA02 and MB03-EV. In addition to the octahedral cations, Tri04 has the highest amount of Si (excluding cookeite) among the selected chlorites. Furthermore, CA02 and MB03-EV have the highest amount of Al^{IV} among the other chlorites. Therefore, it is unclear whether the dissimilarity of the spectra is primarily influenced by octahedral cations or tetrahedral cations. Overall, a cosine similarity of 0.80 to 0.99 indicates a high level of similarity between the spectra, meaning the Raman bands in the analyzed chlorites are highly alike.

3.2.2 | Region 3,500 cm⁻¹

Region 3,500 cm⁻¹ is characterized by three broad composite bands (denoted with Roman Numerals I, II, and III), which can be decomposed into seven bands (Bands A–G) (Figure 4; Table 1). Composite Band I (3,300– 3,500 cm⁻¹), composite Band II (3,500–3,600 cm⁻¹), and composite Band III (3,600–3,700 cm⁻¹). The overall region has been attributed to H₂O or OH bonds.^{2,32,33,61}

Composite Band I is characterized by Band A and more rarely by Band B. Band A is the main band from Composite Band I, and its peak position is between 3,438 and 3,458 cm⁻¹ (Table 2). Band B is located between 3,444 and 3,517 cm⁻¹ and can shift significantly. Consequently, Band B could be either found in composite Band I, or on the boundary between composite Bands I and II. Composite Band II is the most intense band of 3,500 cm⁻¹ region and can be subdivided in Bands C and D, both located between 3,540 and 3,565 cm⁻¹ and between 3,570 and 3,580 cm⁻¹, respectively (Table 2). Band D peak position shows some good correlations with Fe ($R^2 = 0.85$), Mg ($R^2 = 0.86$), and XFe ($R^2 = 0.88$) (Figure 6G–I). Finally, Composite Band III is constituted by Bands E–G with band positions 3,614–3,635, 3,631– 3,655, and 3,653–3,674 cm⁻¹, respectively. Prieto et al.² suggest that Band III is controlled by Fe (APFU).

The cosine similarity technique was also employed to analyze chlorite spectra within the $3,500 \text{ cm}^{-1}$ region, (limited to 3,200 to $3,750 \text{ cm}^{-1}$). The average cosine similarity for this spectral region was found to be 0.98. A comparison between the Mg-rich sample Tri04 and the Fe-rich samples CA02 and MB03-EV revealed higher cosine similarity scores of 0.93 and 0.94, respectively. These scores were significantly higher than the observed similarity range of 0.80 in the 600 cm⁻¹ region. Therefore, in terms of cosine similarity, the spectra in the 600 cm^{-1} exhibit more dissimilarity based on cation substitutions than the 3,500 cm⁻¹ region.

3.3 | Empirical rules for extracting chemical composition of chlorite

The following empirical rules are those with the highest R^2 value (≥ 0.75) for correlations between chlorite composition derived from the EPMA data and Raman spectral features discussed above. These empirical rules are based on bands systematically present in all the analyzed samples and, preferably, those with strong relative intensities to reduce the impacts from background noise. To do so, we used an average value for each band characteristic (minimum of 10 spectra averaged) and correlated them with the chlorite elemental compositions. We listed multiple relationships for individual elements, along with a single equation that combines the peak positions of Bands 1, 8, and D for each octahedral cation. This approach addresses the limitations that can arise when certain Raman spectral features are unavailable, such as when using spectrometers with shorter ranges. However, averaging the values derived from all equations listed for a given element may provide a more precise compositional estimate.

Among the samples analyzed, cookeite is unique because it is an Al-rich chlorite with virtually no Fe and

TABLE 2Average peak position ofBands 1, 8, 9b, and D for SamplesSM03, 407900, 407904, and 407916.

Samples	Band 1 (cm $^{-1}$)	Band 8 (cm $^{-1}$)	Band 9b (cm^{-1})	Band D (cm^{-1})
SM03	101.82	549.45	674.72	3,576.42
407900	99.43	546.88	669.84	3,569.75
407904	100.31	547.90	673.98	3,572.95
407916	98.37	547.40	673.27	3,573.69

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Mg in its crystal structure and formed from a different solid solution. Therefore, this sample has been excluded from the dataset used to derive the following empirical equations. The equations below are for trioctahedral ferromagnesium chlorites, only.

3.3.1 | Octahedral cations

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Iron content (APFU) can be estimated using the spectral Raman characteristic of Bands 1, 8, and D. As Bands 1 and 8 show that highest correlations (0.93 and 0.95, respectively), they should be favored to constrain Fe content of analyzed chlorite (Figure 6A,D,G).

Fe (APFU)
$$\pm 0.183 =$$
 (Band 1 position * -0.4229 + 44.47); [R² = 0.93]
(1)

Fe (APFU) \pm 0.150 = (Band 8 position * -0.3338 + 184.97); [R² = 0.95] (2)

Fe (APFU) \pm 0.258 = (Band D position * -0.2193+785.67); [R² = 0.85]

(3)

(5)

Mg content (APFU) in chlorite can be determined using the following correlation equations between Mg content and spectral features of Bands 1, 8, and D. Note that Equation (6) gives the best R^2 value and should be favored (Figure 6B,E,H).

Mg (APFU)
$$\pm 0.322 =$$
 (Band 1 position $*0.5112 - 48.93$); [R² = 0.85]
(4)

Mg (APFU)
$$\pm 0.311 =$$
 (Band 8 position $*0.4008 - 217.28$);
[R² = 0.87]

Mg (APFU)
$$\pm$$
 0.319 = (Band D position $*$ 0.2767 – 986.44); [R² = 0.86]
(6)

XFe (XFe = Fe/[Fe + Mg]) can represent the ferromagnesium substitution in chlorite. We found three correlations with high R^2 values that can be used to calculate the XFe in chlorite (Figure 6C,F,I).

XFe
$$\pm$$
 0.047 = (Band 1 position * -0.0992 + 10.42); [R² = 0.91]
(7)

XFe \pm 0.041 = (Band 8 position * -0.0783 + 43.38); [R² = 0.93] (8)

$$XFe \pm 0.054 = (Band D \text{ position} * -0.0528 + 189.10); [R^2 = 0.88]$$
 (9)

3.3.2 | Tetrahedral cations

As described above, the best empirical rule to derive AI^{IV} content of analyzed chlorite samples involved Band 9b. Note that this correlation is characterized by a low R^2 value ($R^2 = 0.79$) (Figure 9A).

Al^{IV}(APFU)
$$\pm 0.094 =$$
 (Band 9b position $* -0.0482 + 33.57$);
[R² = 0.76] (10)

Because Al^{IV} is generally calculated using the relationship $Al^{IV} = 4$ – Si, the following equation to determine Si content of chlorite is associated with Equation (10) (Figure 9B).

Si (APFU) \pm 0.094 = (Band 9b position * 0.0482 - 29.57); [R² = 0.76] (11)

3.3.3 | Calculating tetrahedral aluminum and vacancies

Based on the higher R^2 values (0.85–0.95) from multiple bands, our results suggest that Raman band positions (Bands 1, 8, and D) are strongly correlated with octahedral Fe and Mg cation contents. Tetrahedral Si and Al^{IV} also show relatively high correlations with Band Position 9b ($R^2 = 0.76$), although lower than the correlations for Bands 1, 8, and D. We did not find a substantial relationship between octahedral aluminum (Al^{VI}) and any Raman spectral features, such as band positions, intensity, width, or area. Although using the values of the divalent octahedral atoms and the silicon values, on the R^{2+} -Si diagram of Wiewióra and Weiss,⁴¹ the vacancy and total Al content can be calculated. Therefore, Al^{VI} can be calculated by subtracting tetrahedral Al from total Al.

The Wiewióra and Weiss⁴¹ diagram (Figure 2) is based on four assumptions: (1) the tetrahedral layer has four cation sites to fill with either trivalent or Si atoms; (2) the octahedral sheet and interlayer have a total of six cation sites that are divalent, trivalent, or vacancies; (3) there are never more than two vacancies; and (4) chlorite is overall neutrally charged; the total positive electric charges equals 28 to balance the negative electric charges from the 10 oxygen atoms (2⁻ charge) and the eight hydroxyl ions (1⁻ charge). Chlorite has a total of 10 cation sites (4 tetrahedral cations and 6 octahedral cations) that theoretically equal 28 positive electric charge:

10 cations sites =
$$Si^{4+} + R^{3+} + R^{2+} + V^0$$
,
28 positive electric charges = $4 * Si^{4+} + 3 * R^{3+} + 2 * R^{2+} + 0 * V$.

By rearranging these equations, it is possible to cancel out the trivalent atoms and produce an empirical rule to determine vacancies (Equation (12)). Repeating those steps, but instead canceling out trivalent atoms (\mathbb{R}^{3+}), produces Equation (13), which can be used to obtain \mathbb{Al}^{3+} Total.

Vacancy (APFU) =
$$0.666 + 0.333$$

* $[Si (APFU) - R^{2+} (APFU)]$ (12)

$$\begin{aligned} Al_{Total} \left(APFU \right) &= 9.333 + -1.333 \\ &* \left[Si \left(APFU \right) + \left(0.5 * R^{2+} \left(APFU \right) \right) \right] \end{aligned} \tag{13}$$

Recalling that the total Al is the sum of the Al in the tetrahedral layer and the octahedral layer yields Equation (14):

$$Al^{VI}(APFU) = [Al_{Total}(APFU)] - [Al^{IV}(APFU)]$$
(14)

3.3.4 | Di-trioctahedral substitution

The di-trioctahedral substitution replaces two Al atoms and a vacancy with three divalent atoms (Fe^{2+} and Mg^{2+}). This can be represented using the following equation (Figure 9C):

$$(2 * Al_{Total} + \Box)/3 * (Fe + Mg) = (Band 9b position * -0.0184 + 12.75); [R2 = 0.77] (15)$$

3.3.5 | Combined octahedral cations equations

Raman spectrometers with a full spectral range of 80– 3.800 cm⁻¹ can achieve greater accuracy by utilizing a combination of band peak positions. Equations (16)–(18) presented here pertain to the octahedral cations Fe, Mg, and XFe, and their relationship to the sum of Bands 1, 8, and D's positions (Figure 10). These equations exhibit strong correlations with high R² values (\geq 0.91). Notably, the combined Mg Equation (17) demonstrates a higher



FIGURE 10 Correlation between the sum of peak positions of Bands 1, 8, and D. (A) Fe APFU (Equation (16), $R^2 = 0.95$), (B) Mg APFU (Equation (17), $R^2 = 0.91$), and (C) XFe (Equation (18), $R^2 = 0.96$). The standard errors are reported in Table S1.

 R^2 compared to the individual equations (4–6, with R^2 ranging from 0.85 to 0.87). Thus, whenever possible, the combined equations should be favored (Figure 10A–C).

Fe (APFU)
$$\pm 0.149 = ($$
Sum of Bands 1, 8, and D's position $)$
*-0.1065+451.77; [R² = 0.95] (16)

$$Mg (APFU) \pm 0.257 = \left(Sum of Bands 1, 8, and D's position \right) *0.1309 - 550.53; [R^2 = 0.91]$$
(17)

XFe
$$\pm$$
 0.033 = (Sum of Bands 1, 8, and D's position)
*-0.0252 + 107.18; [R² = 0.96] (18)

4 | DISCUSSION

4.1 | Calibration

The calibrations proposed in this study are suited for trioctahedral Fe-Mg chlorite samples with Si^{4+} APFU of

2.3–3.7, Mg^{2+} APFU 0.01–4.8, Fe^{2+} APFU 0.1–2.7, and Al^{3+}_{total} APFU 2.3–5.4. For chlorite samples that fall outside this compositional range, the proposed calibrations should be used with caution. Peak positions that also fall outside spectral ranges of Bands 1, 8, 9b, and D stated in (Table 1) should be used with caution, as they likely reflect chlorite compositions that lie outside the range of the dataset we used to generate the calibrations.

Our results show that octahedral cations act as the main control over the positions of Bands 1, 8, and D among the analyzed samples. These three bands likely represent similar vibrational modes for the octahedral sites. As Fe or XFe increases, band's relative wavenumbers decrease because Fe is a heavier element than Al or Mg, that is, elements that commonly substitute on the octahedral sites. According to the anharmonic oscillator equation originally derived from Hooke's Law, heavier atoms downshift relative wavenumbers when being substituted for lighter elements.⁶³ It is reasonable to assume that Fe exhibits a better correlation with these same bands than Mg and Al^{VI}, because of the mass differences. Iron has an atomic weight of 55.8 amu (atomic mass unit), whereas Mg and AlVI are 24.305 and 26.98 amu, respectively. The relative wavenumber is proportional to the inverse square root of the reduced mass $[(m_1m_2)/(m_1 + m_2)]$.⁶² Cationic substitutions are subtle in Raman spectroscopy, but a larger difference in mass would result in a greater change in the Raman spectra than substitutions of elements of similar mass. Substitution of Al for Mg would result in a relatively smaller shift to the right in the spectrum and substitution of Fe for Mg a relatively larger shift to the left. For example, a substitution of Fe^{2+} for $Mg^{2+}(0.00 \text{ XFe to } 0.91 \text{ XFe})$ between the pure endmembers in olivine results in a 9 cm^{-1} shift to the left for the 820 cm^{-1} peak.⁶⁴ Though we did not have pure endmembers of chlorite, Band 1 ($\sim 100 \text{ cm}^{-1}$) shifted by 5 cm⁻¹, and Band 8 (\sim 548 cm⁻¹) shifted by about 7 cm^{-1} based on a change from 0.03 XFe to 0.64 XFe.

We have also demonstrated that Band 9b has a relationship with the tetrahedral atoms (Si and Al^{IV}). As Si content increases in chlorite, the position of Band 9b shifts to higher relative wavenumbers. In contrast, as Al increases, the band shifts to a lower relative wavenumber. Unlike the octahedral cations, these relationships are based on bond strength and not on atomic mass. Silicon (28.09 amu) and aluminum (26.98 amu) have similar masses.⁶⁵ A stronger bond will shift the vibrational frequencies to higher relative wavenumbers. The bond between silicon and oxygen is stronger than that between aluminum and oxygen.⁶⁶

Band 9b was also weakly correlated to the octahedral divalent atoms Fe and Mg. Arbiol and Layne⁶¹ saw a shift

of the composite Band 9 between Mg-rich chlorite and Fe-rich chlorite and hypothesized that this band could be used to estimate Fe^{2+} content. Our data show a shift in the bands based on Mg and Fe amounts, though neither Band 9a or 9b produced an equation with particularly high accuracy; Bands 1, 8, and D had better accuracy and should be prioritized over either Band 9a or 9b. More studies are necessary to fully understand the complex relationship between octahedral divalent atoms and Band 9.

The results of cosine similarity indicated that the 600 cm^{-1} region was more sensitive cation substitutions compared to the $3,500 \text{ cm}^{-1}$ region. The majority of the bands (Band 1, 8, and 9b) used as the foundation of the empirical rules were observed in the 600 cm^{-1} spectral region; only one of the bands (Band D) used in the empirical rules was in the $3,500 \text{ cm}^{-1}$. On the other hand, the $3,500 \text{ cm}^{-1}$ region was found to be more uniform and could potentially be more suitable for overall mineral identification. To optimize both mineral identification and determination of chemical composition, it is recommended that spectrometer detectors have a spectral range that encompasses both regions, particularly the full 600 cm^{-1} region (80–1200 cm⁻¹), which could provide valuable information about the chemical composition of chlorite.

While our proposed Raman calibration is suitable for chlorite compositions within the range of composition used in this study (see above), potential errors in the estimation of Al composition could be induced by either the presence of other tetrahedral cations (e.g., Li³⁺, Mn²⁺, and Ni³⁺) or the presence of vacancies. As a result of these substitutions, our calculation of the Al distribution between the octahedral and tetrahedral layers could be inaccurate. While we did not find a strong relationship between octahedral aluminum (AlVI) and any spectral features, Al^{VI} can be determined by Equations (14) and (15) (Section 3.3.5) derived from the $Si-R^{2+}$ diagram of Wiewióra and Weiss.⁴¹ It is also important to note that all Fe is assumed to be ferrous (Fe^{2+}) , which could result in a miscalculation of Fe APFU if a significant proportion of Fe is in the ferric state (Fe^{3+}).

4.2 | Testing the calibration

In order to test the accuracy of the proposed calibration, we applied our calibrations to the Raman spectra of chlorite samples also analyzed by EPMA (407900, 407904, 407916, and SM03) but not included in the dataset used to generate the calibration equations. The average Raman values of the positions of Bands 1, 8, 9b, and D are provided in (Table 2). For this, we used the first 15 empirical rules equations from Section 3.3 to convert Raman spectral features into chemical composition.

Equations (1)–(3) were used to calculate the average APFU value for Fe. Subsequently, Equations (4)–(6) and (7)–(9) were used to calculate the average of Mg and XFe, respectively. The average AI^{IV} and Si values are based on Band 9b (Equations (10) and (11)), respectively. Equation (13) (Fe/Al^{IV}) and the average Fe value were used to calculate another value for AI^{IV} and Si.

 R^{2+} was calculated by summing the averages of Fe and Mg. Equations (12) and (13) need the average Si value and the R^{2+} as inputs. Equation (14) (Al^{VI}) used the value of Equation (13) minus the average value of tetrahedral aluminum (IV).

The average EPMA values compared to the calculated APFU values from the Raman empirical rules are displayed in (Table 3). The concentrations estimated from the Raman calibrations are closest to the EPMA measured values for iron, silicon, tetrahedral aluminum (IV), and total aluminum (0–5% error, 0–3%, 0–8%, and 0–17% error, respectively). XFe, Mg, and Al^{VI} are the next closest to their EPMA values (7–18% error, 6–23% error, and 8–50% error, respectively). Calculation of vacancies shows the greatest deviation from the measured values (13–270% error).

4.3 | Spectral Raman characteristics of Li-rich Cookeite

Sample cookeite is the only sample from our study to contain lithium, high aluminum, and vacancy $(\Box = \sim 1)$.⁵ It corresponds to a lithium-bearing aluminum-rich chlorite with an ideal formula of $(\text{LiAl}_4\Box)(\text{Si}_3 \text{ Al})O_{10}(\text{OH})_{8.}^{44,54}$ Whereas lithium was not directly measured in the cookeite sample used in this study, Jullien et al.⁴⁴ reported Li contents in the range 0.6–1.5 APFU for a cookeite sample collected from the same geographic area (Vanoise Massif, Alps). As cookeite is not a ferromagnesium chlorite, this sample was excluded from the present calibration. However, its spectral features are discussed below.

Unlike any other chlorite samples we analyzed, cookeite presents a distinct band at \sim 1,080 cm⁻¹ (Figure 11). This band has been theorized in a past study to be quartz contamination, due to the presence of doublet at about 780–798 cm⁻¹.² However, in this cookeite sample, it was not possible to ascertain the presence of any additional bands in the 780–798 cm⁻¹ region, as Bands 10 and 11 are located in that range. Moreover, it should be noted that quartz's band at ~1,080 cm⁻¹ is relatively weak compared to the quartz A1 mode typically observed at ~465 cm⁻¹.⁶⁷ The cookeite sample in this study had no RAMAN SPECTROSCOPY WILEY

distinct peak located at ~465 cm⁻¹. Therefore, in the absence of the A1 mode at 465 cm⁻¹, the band at 1,080 cm⁻¹ cannot be attributed to quartz. Therefore, we remain unconvinced that the observed band can be attributed to quartz contamination. It is also possible that this distinct band is produced by a shift of Band 15 toward higher relative wavenumbers due to the presence of lithium instead of Al, Mg, and Fe. In the other analyzed samples, Band 15 is a weak band and hard to differentiate from Bands 12 through 14 (Figure 11). Lithium has a lower atomic mass (6.94 amu) than other typical octahedral atoms (Mg 24.31 amu; Al 26.98 amu; and Fe 55.85 amu).⁶⁵ We infer that this significant change in mass could shift the band to higher relative wavenumbers.

In addition to band at \sim 1,080 cm⁻¹, the widths of Bands 9a and 9b may be used to determine whether the analyzed chlorite is ferromagnesian (Fe-Mg substitution) or from another solid-solution model. For cookeite sample, the FWHM ratio between Bands 9a and 9b is smaller (1.9) than the Fe-Mg chlorites (2.3–2.7). It may be possible to use Bands 9a and 9b FWHM ratio as a test of whether the chlorite in question is ferromagnesium. If the ratio is below 2, it could indicate the chlorite is not ferromagnesium. Though more samples would be needed to test this.

It is not yet fully understood how vacancies affect the Raman spectral features of chlorite, such as shifting positions or changing relative intensity. The presence of lithium and vacancy could significantly affect the vibrational modes in cookeite, which could explain why the spectra for cookeite are distinct from the other analyzed samples. Therefore, we infer that this new band is associated with the presence of lithium or vacancy. These observations support the conclusion that the calibrations reported in this study are only suitable for identification of Fe-Mg trioctahedral chlorites.

4.4 | Raman lasers on Mars

On board NASA's Perseverance Rover, there is a Raman laser suite known as SuperCam, which operates at a pulsed wavelength of 532 nm.³⁶ SuperCam's spectrometers have a spectral range of $105-7,070 \text{ cm}^{-1}$ and a FWHM resolution of 12 cm^{-1} .³⁶ This spectral range falls outside Band 1 (99–104 cm⁻¹), suggesting that the empirical rules derived from Bands 1 (Equations (1) [Fe], 4 [Mg], and 10 [XFe], and the combined Equations (16)–(18)) cannot be used to derive chlorite compositions, though these elemental values can be determined using other Fe, Mg, and XFe empirical rules that utilize Bands 8 and D. The equations to determine Si and Al^{IV} can also

Element		SM03	407900	407904	407916
Si	EPMA	2.8	2.7	3.0	2.8
	Raman	2.9	2.7	2.9	2.9
	Abs. Diff.	0.1	0.0	0.1	0.1
	% Error	3%	0%	3%	3%
Al (IV)	EPMA	1.2	1.3	1.0	1.2
	Raman	1.1	1.3	1.1	1.1
	Abs. Diff.	0.1	0.0	0.1	0.1
	% Error	7%	0%	8%	7%
Fe	EPMA	1.5	2.5	2.1	2.3
	Raman	1.4	2.5	2.1	2.3
	Abs. Diff.	0.1	0.0	0.0	0.0
	% Error	5%	0%	0%	0%
Mg	EPMA	3.3	2.2	2.6	2.5
	Raman	3.1	1.7	2.3	2.0
	Abs. Diff.	0.2	0.5	0.3	0.5
	% Error	5%	22%	13%	19%
Al (VI)	EPMA	1.2	1.2	1.3	1.1
	Raman	1.1	1.6	1.2	1.4
	Abs. Diff.	0.1	0.4	0.1	0.3
	% Error	8%	32%	10%	25%
XFe	EPMA	0.3	0.5	0.5	0.5
	Raman	0.3	0.6	0.5	0.5
	Abs. Diff.	0.0	0.1	0.0	0.1
	% Error	3%	11%	4%	13%
Al (total)	EPMA	2.4	2.5	2.4	2.3
	Raman	2.4	2.9	2.5	2.7
	Abs. Diff.	0.0	0.4	0.1	0.4
	% Error	1%	17%	6%	17%
Vacancy 🗌	EPMA	0.1	0.2	-0.1	0.1
	Raman	0.1	0.2	0.2	0.2
	Abs. Diff.	0.1	0.0	0.3	0.1
	% Error	180%	13%	270%	58%

TABLE 3 The average EPMA values compared to the calculated APFU values from the Raman empirical rules.

Note: Absolute difference and percent error are also displayed.

be used to since Band 9b falls in the spectral range. In addition to the 532 nm Raman on board, Perseverance is also carrying a laser-induced breakdown spectroscopy system that can determine elemental abundance as another confirmation.³⁶

In addition to SuperCam, the Perseverance rover is equipped with a second Raman instrument suite known as SHERLOC.³⁵ SHERLOC is a pulsed 248.6 nm laser and spectrometers with a spectral range of \sim 800–4,000 cm⁻¹ and a FWHM resolution of 40.3 cm⁻¹.^{35,68} However, due

to the starting point of the SHERLOC spectral range at 800 cm^{-1} , it is not possible to utilize equations associated with Bands 1–9b. Although Band D falls within the SHERLOC spectral range, it is a composite band, and the spectral resolution may not be sufficient for its deconvolution. In the event that Band D could be deconvoluted, caution must be exercised since our calibration was performed using a green 532 nm laser, rather than a deep UV 248.6 nm laser. Therefore, the SHERLOC instrument could be used to calculate the concentrations

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for Fe, Mg, and XFe using a single equation (Equations (3), (6), and (9)). However, it does not allow for the determination of silicon and aluminum concentrations.

The upcoming ESA Rosalind Franklin Rover, set to launch in 2028, will carry a continuous wave 532 nm Raman laser. These spectrometers will be able to detect relative wavenumbers between 150 and 3.800 cm^{-1} and has a spectral resolution between 6 and 10 cm^{-1} .³⁷ Potential chlorite measurements with this rover will be unable to use Bands 1, 2a, and 2b. Like NASA's SuperCam, all elemental APFU values can still be calculated without Band 1, and Bands 2a and 2b were not even used for our empirical rules. Therefore, Bands 8, 9b, and D can still be used to calculate Fe, Mg, Si, and Al with the Rosalind Franklin Rover.

Since this work could help determine the chemical composition of chlorite on other planets, it can also be used as the input for geothermometry models to constrain the temperature range for formation of chlorite. In order to detect and accurately analyze the spectral bands of planetary surfaces, we recommend equipping future planetary Raman instruments with certain specifications ideal for this calibration. If possible, we advise that future Raman payloads have a minimum spectral range of 80- $3,800 \text{ cm}^{-1}$, encompassing Bands 1 to D, to effectively capture the desired spectral information for this chlorite calibration. Though, it must be noted, it might not be feasible for a spaceflight Raman payload to be able to detect the spectral bands below 100 cm⁻¹. Thus, using this calibration on other planets or celestial bodies might inherently have limitations, potentially restricting the calibration to Bands 8, 9b, and D exclusively. Additionally, a minimum spectral resolution of 6 cm^{-1} should be implemented to ensure ample sensitivity for detecting subtle shifts in the positions of these spectral bands. These parameters will lead to a greater understanding of the past Martian environment.

Potential ferric iron and vacancies 4.5 studies

Based on Raman spectra, Wang et al.³⁴ suggest that it is possible to distinguish dioctahedral from trioctahedral phyllosilicates, including chlorite, which would have implications for determining vacancies in chlorite. Except for the cookeite sample, all the samples from this study are assumed to have zero vacancies (Figure 2). In order to study the effect of the number of vacancies, a series of samples with known Fe³⁺ APFU and calculated vacancies is required to quantify the effects vacancies on chlorite spectral features. Theoretically, the presence of vacancies would shift bands controlled by the octahedral sites to lower values or have lower relative intensity. A study like this would also give a greater understanding of the vibrational modes' controls in chlorite.

Ferric iron (Fe^{3+}) and ferrous iron (Fe^{2+}) might be difficult to differentiate directly with Raman spectroscopy, as these ions have negligible mass differences (0.00055 amu) but have different electronegativity that affects bond strength. The change in bond strength associated with XFe³⁺ might be detected by Raman spectroscopy, if the detectors have a high spectral resolution. Enough ferric iron creates a charge imbalance in the octahedral layer that is counterbalanced with vacancies. Of course, these hypotheses are neither supported nor refuted by our analyses. A more rigorous study focusing on the relationship between ferric iron and vacancies would be required.

The presence of ferric iron (Fe^{3+}), noted as XFe^{3+} , has been reported in chlorite from several studies.^{6,19} In diagenetic and metamorphic rocks, the XFe³⁺ content of chlorite depends on the temperature and the oxygen fugacity that control chlorite formation.^{6,69} Therefore, the determination of XFe³⁺ is critical for understanding chlorite condition of formation.

WILEY-RAMAN SPECTROSCOPY

5 | CONCLUSION

This study demonstrates the feasibility of using Raman spectroscopy to determine chlorite composition. We found that chlorites have between 25 and 26 bands between two regions $(80-1,200 \text{ cm}^{-1}; 3,200-3,700 \text{ cm}^{-1})$. We also found that Fe, Mg, Al^{IV}, and Si concentrations can be related to at least one Raman spectral characteristic. In contrast, the relationship between octahedral aluminum and Raman spectral features is not strong; nonetheless, it is still possible to calculate AlVI based on the Si and divalent octahedral cation (Fe and Mg) values. Iron shows the best correlation of the remaining elements (Si, Al^{IV}, and Mg). Bands 1, 8, 9b, and D have strong relationships with Fe, Mg, and XFe, indicating that these bands are controlled by substitutions on the octahedral site. Although the proposed calibration cannot fully address specific compositions of chlorites like cookeite, this work demonstrates the feasibility of the approach in principle. Additional work on a wider range of compositions will be required to refine the calibration. This calibration may also open several opportunities for future planetary exploration programs.

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