RAMAN AND FTIR SPECTROSCOPY OF SYNTHETIC AMPHIBOLES: II. DIVALENT (Mg,Co) SUBSTITUTIONS AT THE OCTAHEDRALLY COORDINATED SITES

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Abstract

Raman spectra were recorded for a set of synthetic amphiboles, Na(NaCa)(Mg_{5-x}Co_x)Si₈O₂₂(OH)₂ with x = 0-5, that have been previously characterized by Rietveld structure refinement and infrared spectroscopy in the principal OH-stretching region. The chemical compositions derived from the intensities of the O-H stretching Raman peaks are in accord with the nominal compositions, as well as with the compositions previously determined by both Rietveld structure refinement and infrared spectroscopy. Detailed peak assignments have been made of the Raman spectra in the low-wavenumber region (50–1200 cm⁻¹) starting from the work of Leissner *et al.* (2015) and Waeselmann *et al.* (2019) and the simulated partial Raman spectra for all the cation-anion pairs in the structure of potassic-magnesio-arfvedsonite given by Ivanov *et al.* (2018). Most Raman peaks exhibit one-mode behavior and shift toward lower wavenumbers for increasing Co in the amphibole.

Keywords: synthetic amphiboles, Co-richterites, FTIR spectroscopy, Raman spectroscopy, octahedral modes.

INTRODUCTION

Amphiboles are geologically important silicate minerals (*e.g.*, Deer *et al.* 1997). Their crystal chemistry is probably the most complicated among the rock-forming silicates due to their very accommodating structure with several different cation/anion sites and the large number of chemical substitutions possible at these sites (*e.g.*, Hawthorne & Oberti 2007). The main structural unit is an I-beam consisting of a strip of M(1), M(2), and M(3) octahedra (containing C-group cations, Fig. 1) sandwiched between two ribbons of tetrahedra [containing T-group cations at the T(1) and T(2) sites]. The I-beams are connected by [6]- to [8]-coordinated B-group cations at the M(4) site (Fig. 1) and large A-group cations at the A(m) and A(2) sites. The O(3) site contains the W- group anions and coordinates a trimer of M(1,3) octahedra overlain by a ring of tetrahedra (Fig. 1). The O(3) site is of particular importance in the crystal chemistry of the amphiboles because different anions [(OH)⁻, F⁻, Cl⁻, O²⁻] may occur at this site, depending on the conditions of growth, which makes them minerals of paramount interest as indicators of the composition and physical conditions (*P*, *T*, and fluid activity) of the system. The possible presence of monovalent and divalent anions at the O(3) site is an additional factor affecting the crystal-chemical flexibility of the amphibole structure, as these anions are effective in allowing incorporation of cations of formal charge from M⁺ (*i.e.*, Li⁺) to M⁴⁺ (*i.e.*, Ti⁴⁺) at the M(1), M(2), and M(3) sites.

There has been significant effort to develop methods for the crystal-chemical analysis of amphi-

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FIG. 1. The monoclinic C2/m amphibole structure viewed along [001].

boles, and it is now clear that the complete chemical and structural definition of these minerals requires the combined use of different analytical techniques (Hawthorne 1983, 2016, Hawthorne & Oberti 2007, Oberti et al. 2007, 2018, Della Ventura et al. 2016, 2018, Susta et al. 2018). Vibrational spectroscopy in the OH-stretching region has proven to be essential in addressing both long-range (LR) and short-range (SR) occupancies in amphiboles. Although much effort has focused on the use of FTIR (e.g., Della Ventura & Robert 1990, Della Ventura et al. 1996, 1998, 1999, Robert et al. 1989, 1999, Hawthorne et al. 2005, Hawthorne & Della Ventura 2007), far fewer studies have addressed the use of Raman spectroscopy (Della Ventura et al. 1991, 1993, Leissner et al. 2015, Sbroscia et al. 2018, Della Ventura et al. 2018, Waeselmann et al. 2019). Sbroscia et al. (2018) examined a series of well-characterized synthetic samples along the potassium-richterite-tremolite join (Hawthorne et al. 1997) and showed that Raman spectroscopy in the OH-stretching region is a rapid and straightforward tool for quantifying the relative occupancy at the A site, an issue that has significant implications for both asbestos and petrological studies (Della Ventura 2017). Here, we show recent results of ongoing work that addresses the detailed characterization of amphiboles using Raman spectroscopy based on the analysis of synthetic solid-solutions. Della Ventura et al. (this volume) has addressed the OH-

librational modes, comparing Raman and IR spectra in the NIR (near infrared) and MIR (medium infrared) for OH-F and D₂O substituted richterites. In this paper, we examine spectra collected from richterites of variable composition at the M(1), M(2), and M(3) sites and show that, as with FTIR spectra, Raman spectra provide a direct measure of the site occupancies of divalent cations at the octahedrally coordinated M sites, at least for simple homovalent substitutions. We use the Mg²⁺–Co²⁺ solid solution at the M(1,2,3) sites as a proxy for the more common Mg-Fe²⁺ solid solution, which is much more difficult to synthesize (e.g., Della Ventura et al. 2016). Moreover, we analyze the framework-mode region in order to test and improve recent models (e.g., Waeselmann et al. 2019) focused on using this spectral region to derive crystal-chemical information on these complex silicates.

EXPERIMENTAL METHODS

We examined synthetic Co-substituted richterite with known compositions and site occupancies. The samples were fully characterized by Della Ventura *et al.* (1997) using a combination of Rietveld structure refinement, SEM-EDS, HRTEM, and FTIR. Singlephase experimental products of amphibole were obtained for all starting compositions, indicating complete Mg–Co solid-solution along the join; no chain-multiplicity faults, chain-arrangement faults, or additional phases were observed by TEM in any of the samples. The FTIR data in the OH-stretching region allowed direct evaluation of the Mg-Co distribution over the M(1), M(2), and M(3) sites, and the values obtained are in accord with the site occupancies derived by Rietveld structure refinement, indicating no difference in molar absorptivity (*cf.* Skogby & Rossman 1991, Hawthorne *et al.* 1996) between the different bands in the spectra.

Raman-scattering data were acquired from powders using a Horiba Jobin-Yvon T64000 triple-monochromator spectrometer equipped with an Olympus BX41 confocal microscope and 50× objective. Data were collected in backscattering geometry with a spectral resolution of 2 cm⁻¹. Two laser lines ($\lambda = 514.532$ and 488.0 nm) were used to verify the absence of photoluminescence peaks. Low laser-power had to be used in the case of Co-rich amphiboles to avoid sample overheating during the data collection; the exact values of the laser power delivered on the sample surface were as follows: 14 mW for x = 0, 7.9 mW for x = 1 and 2, and 0.73 mW for x = 4 and 5. The measured Raman spectra were baseline corrected using spline interpolation and the temperature was reduced to account for the effect of Bose-Einstein population on the peak intensities. Next, the spectra were renormalized to the laser power and acquisition time and fitted with pseudo-Voigt functions to determine the peak positions, widths, and integrated intensities.

The FTIR spectra in the low-frequency region were collected using a Nicolet iS50 spectrometer equipped with a KBr beam splitter and a DTGS detector. Samples were prepared as pellets, with 1 mg of amphibole powder embedded in 150 mg of KBr; data were collected at a nominal resolution of 4 cm⁻¹. Spectra were decomposed using single Gaussian components, as explained in Della Ventura *et al.* (1997).

RESULTS

The OH-stretching region

As discussed by Apopei & Buzgar (2010), Leissner *et al.* (2015), and Della Ventura *et al.* (2018), the same number of bands is expected in both Raman and FTIR OH-stretching spectra of amphiboles. Accordingly, the two series of patterns are almost identical in both multiplicity and relative intensity of the component peaks above $>3650 \text{ cm}^{-1}$, whereas there is a clear difference in the peak intensities at lower wavenumbers. This point will be discussed below; the following discussion pertains to the spectra in the 3650–3750 cm⁻¹ range.

The Raman spectrum of endmember richterite (Fig. 2a, top) shows an intense band at 3730 cm⁻¹ and a weak band near 3677 cm⁻¹ in both the Raman and FTIR spectra. The higher wavenumber band is assigned to the stretching mode of the structural OH groups in the local arrangement $^{M(1)}Mg^{M(1)}Mg^{M(3)}Mg-OH-^{A}Na-^{T}Si^{T}Si$; the minor component is due to stretching vibrations of OH⁻ in the vicinity of vacant *A* sites in the structure (*e.g.*, Robert *et al.* 1989, Della Ventura 1992, Hawthorne *et al.* 1997, Gottschalk *et al.* 1999, Melzer *et al.* 2000, Iezzi *et al.* 2010, 2011), indicating a slight departure of the synthesized amphibole from the nominal composition toward tremolite.

For intermediate (Mg,Co)-amphiboles, each of these two bands can split into four components related to the four local arrangements resulting from the four possible combinations of two divalent cations over the three hydroxyl-coordinated M(1,3) octahedra, a feature originally observed by Strens (1966, 1974) and Burns & Strens (1966) for (Mg,Fe²⁺) in actinolites and later confirmed for other amphibole series (e.g., Della Ventura et al. 1996, 1997, 2016, Hawthorne et al. 1996, Reece et al. 2002, Iezzi et al. 2005, Leissner et al. 2015). In the case of (Mg,Co), the major Raman signal related to filled A sites does split into four components (see Fig. 3), whereas the minor Raman signal related to vacant A only splits into two components (see below). The relative intensities of the hyperfine components in the OH-stretching spectra allow derivation of the Mg/ M^{2+} (M^{2+} = any substituent divalent cation) content at M(1,3) with a high level of accuracy (Hawthorne et al. 1996, Della Ventura et al. 1996, 1997, 2016, Iezzi et al. 2005).

Figure 4a shows that the site occupancies derived by Raman spectroscopy are in excellent agreement with the nominal site-occupancies; this result thus demonstrates the following three points: (1) Similar to what is already known for IR (e.g., Della Ventura et al. 2016 and references therein), Raman spectroscopy is effective in providing quantitative chemical compositions for the octahedrally coordinated sites in amphiboles, at least for simple binary solid-solutions. This is an important point in mineral crystal-chemistry because Raman spectroscopy has a lateral resolution much higher than micro-FTIR (typically 1 µm versus 20 µm, which could be reduced to 2-5 µm by using synchrotron radiation: Della Ventura et al. 2014). In addition, Raman spectroscopy can be used directly on thin sections, an obvious advantage for petrological studies, and for the identification of very acicular crystals, such as asbestos amphiboles, an advantage in environmental or biological studies (Della Ventura 2017 and references therein). (2) As already shown by Hawthorne et al. (1996) and Della Ventura et al. (1996, 1997), the analysis of the relative intensities of



FIG. 2. Raman (a: this work) and FTIR (b: redrawn from the original data of Della Ventura *et al.* 1997) spectra of synthetic (Mg,Co)-richterite: Na(NaCa)(Mg_{5-x}Co_x)Si₈O₂₂(OH)₂ with $0 \le x \le 5$. For clarity, the spectra were vertically offset and normalized to the height of the most intense peak.

the fitted components shows that there is no clustering between Mg and Co throughout the series, an issue that has bearing on the configurational entropy and thus the thermodynamic properties of these amphiboles. (3) A final point worth discussing is that, using the integrated band intensities of the quadruplets associated with OH^- groups next either to empty or occupied *A*-sites, it is possible to calculate the occupancy at the *A* cavities in the structure (Hawthorne *et al.* 1997, Iezzi *et al.* 2007) when the content of ^WF is negligible (Leissner *et al.* 2015). This is another piece of information that is essential in determining the crystal chemistry of the amphiboles. Regarding this point, Hawthorne *et al.* (1997) studied synthetic compositions along the potassium-richterite-tremolite join and found that, due to a difference in the molar absorption coefficient between the full and empty A-site configurations, a correction factor of 2.2 had to be applied to the band intensities in the FTIR spectra to quantitatively determine the tremolite component of the amphibole. The same conclusion was reached by Iezzi *et al.* (2004) for "magnesium richterite" synthesized at different pressure. Sbroscia *et al.* (2018) used Raman spectroscopy to examine the same batch of samples examined using FTIR spectroscopy by Hawthorne *et al.* (1997) and Iezzi *et al.* (2004) and showed that Raman scattering provides a direct measure of the Asite occupancy in these amphiboles, without the need



FIG. 3. The OH-stretching Raman spectrum of Na(Na-Ca)(Mg₂Co₃)Si₈O₂₂(OH)₂ decomposed by using pseudo-Voigt functions; thin gray lines = fitted components, dashed red line = resultant spectrum.

for correction factors for the molar-absorption coefficient. According to these results the quadruplet of bands at lower wavenumbers, which are due to OH groups associated with vacant A-sites, is much more intense in the FTIR spectra than in the Raman spectra collected from the same powders (Fig. 2). For the Raman spectra, calculation of the relative intensities of the fitted components shows that, even considering the fluctuation in the data due to the very low intensity of the scattering, the A-site vacancies are constant across the join, around $0.05-0.1 \ apfu$ (Fig. 4b).

The low-frequency region: Raman scattering

The Raman spectra for the Na(NaCa)(Mg_{5-x}Co_x) Si₈O₂₂(OH)₂ amphiboles are shown in Figure 5. The total integrated intensity Itotal exhibits a minimum near the intermediate compositions (Fig. 5, inset), indicating that the Raman cross-section decreases with increasing substitutional disorder in the solid solution. The overall spectral profile of Raman scattering is completely different from that of IR absorption (see Fig. 6) due to the different selection rules of crystal phonon modes arising from framework vibrations. However, similar to the FTIR spectra, the Raman spectra of amphiboles (e.g., Leissner et al. 2015, Waeselmann et al. 2019) can be conveniently divided into three main regions (Fig. 6): (1) Region 1, between 850 and 1200 cm⁻¹, where mediumto low-intensity peaks due to the T-O stretching mode occur. (2) Region 2, between 550 and 850 cm⁻¹, where the strongest Raman peak for the majority of amphiboles occurs (a notable exception being riebeckite, Susta et al. 2018). This peak, which occurs near 670 \pm 20 cm⁻¹ (Waeselmann et al. 2019), is assigned to deformation of the tetrahedral double-chain, and its position may provide a useful tool for asbestos identification (e.g., Della Ventura 2017 and references therein). As will be discussed below, this peak shifts linearly in position as a function of the Mg-Co substitution. (3) Region 3, in the wavenumber range 100-550 cm⁻¹, is complicated by the presence of many medium- to low-intensity peaks that are strongly polarized (Waeselmann et al. 2019). These peaks have been difficult to assign with confidence because of the overlapping of M-O modes, T-O bendings, and OH libration (Della Ventura et al. this



FIG. 4. (a) Cobalt site-occupancies at M(1,3) derived from the relative intensities of the Raman peaks in the OH-stretching region *versus* the nominal Co (*apfu*) in the amphibole. (b) *A*-site occupancy from the relative intensities of the Raman peaks in the OH-stretching region as a function of the sample composition. For explanation see text.



FIG. 5. The Raman spectra of synthetic richterites along the Na(NaCa)(Mg_{5-x}Co_x)Si₈O₂₂(OH)₂ join; spectra are vertically offset for clarity. The insert on the right-hand side shows, on an enlarged scale, the strongest Raman peak near 680 cm⁻¹, while the insert on the left-hand side displays the area of the entire Raman spectrum (integrated intensity) as a function of the composition *x*. The arrows mark the Raman-active OH-libration modes.

volume). Similar to the major peak near 670 cm⁻¹, most peaks in this range shift linearly toward lower wavenumbers as a function of Mg–Co substitution along the series, thus showing a one-mode behavior (Chang & Mitra 1971). Therefore, the corresponding peak positions can be used to derive the content of Co at the *M* position. For example, Figure 7 shows the compositional evolution of the wavenumber ω for the prominent peak at 398 cm⁻¹ for x = 0 (richterite) that linearly shifts to 382 cm⁻¹ for x = 5 (Co-richterite) according to the equation:

$$(x) = 398.4(5) - 16.7(8)x$$
, where
 $x = Co(apfu)$ at $M(1,3)$

Similarly, the weak peak near 160 for x = 0 linearly shifts to 141 cm⁻¹ for x = 5 (Fig. 7), according to the equation:

$$(x) = 160.4(5) - 20.0(8)x$$

The wavenumber of the latter peak exhibits the same linear behavior as a function of $^{\rm C}({\rm Fe}^{2+}+{\rm Mn}^{2+})$



FIG. 6. The Raman and FTIR spectra of Mg endmember richterite showing the different regions (see text).



Fig. 7. Shift of the Raman peaks around 385 and 160 $\rm cm^{-1}$ as a function of the sample composition.

that is seen in natural Co-free monoclinic amphiboles (Waeselmann et al. 2019).

Finally, the Raman scattering at wavenumbers $<100 \text{ cm}^{-1}$ provides information on amphibole symmetry (Waeselmann *et al.* 2019). Accordingly, monoclinic amphiboles have a strongly polarized peak at 90–100 cm⁻¹ whose position is a function of the M(4)-site occupancy, while orthorhombic amphiboles have a peak at 60–70 cm⁻¹. In accord with this result, all amphiboles studied here have a peak at 100–110 cm⁻¹ whose position is relatively constant along the series, while there is no Raman signal at lower wavenumbers.

The low-frequency region: IR absorption

The FTIR spectra in the low-frequency region $(<1300 \text{ cm}^{-1})$ are shown in Figure 8. Following the work of Ishida et al. (2008) and Della Ventura et al. (this volume), similar to the Raman spectra, the lowfrequency FTIR patterns of richterites can be divided into the same main ranges. In region (1), between 1200 and 850 cm^{-1} (Fig. 8a), the spectra show intense absorptions due to Si-O stretching modes. In region (2), between 800 and 550 cm^{-1} (Fig. 8b), there are relatively weak peaks assigned to chain deformations (Si-O-Si and O-Si-O modes); an OH-libration mode also occurs in this range, around 600 cm^{-1} (Della Ventura et al. this volume). In region (3), between 600 and 400 cm⁻¹ (Fig. 8c), there are several very intense peaks due to O-Si-O bending and M-O (M = Mg, Fe, Al, Ca, Na) stretching modes, as well as a second OHlibration mode (Della Ventura et al. this volume).

Inspection of Figure 8a shows that, in the 1200 and 800 cm^{-1} range, the progressive substitution of Mg by

Co at the M(1,2,3) sites in richterite is correlated with a progressive band shift and broadening. In particular, the higher-wavenumber peak at 1148 cm⁻¹ shifts linearly to 1131 cm⁻¹ for the Co endmember, and similarly the band at 983 shifts to 966 cm^{-1} . The groups of bands in the 1100-1020 and 1000-900 cm⁻¹ intervals merge to give two convolute absorptions centered around 1050 and 950 cm⁻¹ for Co-richterite. In region 2 (Fig. 8b), besides minor band shifts, the most notable feature is the appearance of a new component in the spectra at $\sim 650 \text{ cm}^{-1}$ whose intensity increases as a function of the Co content in the amphibole. Note that, according to the recent work of Della Ventura et al. (this volume), the broad and low-intensity band at 600 cm⁻¹ can be assigned to an OH-libration. In region 3 (Fig. 8c), the spectrum of endmember richterite shows a doublet at 523-509 cm⁻¹ and a relatively intense peak at 450 cm⁻¹. According to Della Ventura et al. (this volume), the shoulder at 478 cm⁻¹ can be assigned to the second OH-libration. For increasing Co along the series, there is a general band broadening and shift, evident in particular for the 523–509 cm^{-1} doublet that, for the Co endmember, overlaps into a broad absorption centered around 450 cm⁻¹.

DISCUSSION

There have been many studies of the lowerfrequency peaks in the Raman spectra of amphiboles, but the assignment of these peaks to specific stretching or bending vibrations in the amphibole structure has been tentative at best. Some more recent studies (Apopei & Buzgar 2010, Leissner et al. 2015, Waeselmann et al. 2019) have examined a wide spectrum of amphiboles previously characterized by crystal-structure refinement and electron-microprobe analysis and have developed some correlations of band intensities with variations in chemical composition (see in particular Waeselmann et al. 2019), with the eventual goal of determining amphibole composition by Raman spectroscopy. However, this work has been hindered by the lack of any rigorous assignment of Raman bands to specific atomic vibrations based on computational modelling of lattice dynamics. Ivanov et al. (2018) made a major step forward with regard to this issue, first by analyzing the polarized Raman spectra of potassicmagnesio-arfvedsonite and second by using a shellmodel force-field with Buckingham pairwise potentials and a bond polarizability model to simulate partial Raman spectra for all cation-anion pairs in the amphibole structure. From the positions of the peaks in the partial spectra, they were able to associate most peaks in the experimental spectrum of potassicmagnesio-arfvedsonite with specific cation-anion



FIG. 8. The FTIR spectra in the low-frequency range for the studied samples along the Na(NaCa)(Mg5-xCox)Si8O22(OH)2 join.

bonds. One should, however, consider that the model used by Ivanov et al. (2018) does not account properly for three-particle interactions, which is critical for modelling the bending-type vibrations of oxygen atoms shared between two different chemical species. Thus the results obtained can only be guidelines to which spectral ranges specific cation-oxygen bond vibrations can contribute, without a proper estimation of the dominant type of atomic vibrations when more than one type of metal-oxygen interaction contributes to the same energy range. Nevertheless, by considering the lattice-dynamics simulations of Ivanov et al. (2018), the data provided by Waeselmann et al. (2019), and the experimental information from the oxidation studies of Della Ventura et al. (2018) on sodic amphiboles, we could assign with confidence most of the Raman signals of (Mg,Co)-richterite to specific cation-oxygen vibrations. The peak assignments of the prominent Raman signals for the studied samples are summarized in Table 1 and a more detailed justification is given below.

The 1200–850 cm⁻¹ range: The Si–O stretching modes

In the calculated partial spectrum of Si^{4+} – O^{2-} there are six peaks that correspond to experimentally observed peaks in the Raman spectrum of potassicmagnesio-arfvedsonite and can be assigned to the TO₄ stretching modes; the mismatch of ~30–70 cm⁻¹ between the calculated and experimental phonon wavenumbers could be due to the simplified model used by Ivanov *et al.* (2018).

A key to understanding the Si-O modes is provided by comparing the FTIR and Raman spectra in the 1200-850 cm⁻¹ region for endmember Mg-richterite. This spectral region can be further subdivided into two sub-ranges (light blue and orange, Fig. 9) having a strong similarity within the same spectral type (Raman or IR). In both sub-ranges the FTIR spectrum shows a well-resolved and relatively sharp peak at higher frequency (marked with an arrow in Fig. 9), followed by a group of overlapping peaks, while the corresponding Raman sub-ranges show only the group of overlapping peaks. In richterite, the T(1) tetrahedron is smaller than the T(2) tetrahedron (e.g., Papike et al. 1969, Cameron et al. 1983), therefore one can anticipate that the range 1200-1020 cm⁻¹ is related to ^{T(1)}Si-O stretching modes, whereas the range 1020-850 cm⁻¹ is related to ^{T(2)}Si–O stretching modes (Fig. 9). This assignment is consistent with the work of Della Ventura et al. (1991) on synthetic titanium-rich potassium richterite, showing that the replacement of Si by Ti at T(2) modifies the 970–900 cm⁻¹ modes of the Raman spectra, whereas those in the 1120-1020 cm⁻¹ range are unaffected.

The strongest Raman peak in each sub-region is dominated by Si-O_{apical} [where O_{apical} are the nonbonded O1 and O2 apical oxygen positions of T(1) and T(2) tetrahedra, respectively] stretching because of two considerations: (1) in silicates the Raman cross-section of Si-O stretching modes involving vibrations of nonbridging oxygen atoms, O_{nb}, is much stronger than that comprising vibrations of bridging oxygen atoms, Obr (*i.e.*, those shared between two SiO_4 tetrahedra) (*e.g.*, Dowty 1987); (2) it is well known, after the work of Waeselmann et al. (2019), that the positions of these peaks are very sensitive to the type of octahedrally coordinated cations, since the M(1,2,3) sites are directly connected with the apical tetrahedral oxygen atoms. This feature is also observed for the studied (Mg,Co)-richterites, where the position of the strongest Raman T-O stretching peak decreases with decreasing Mg content (see Table 1), similar to Mg-Fe²⁺-Mn²⁺ amphiboles (Waeselmann et al. 2019).

As noted above, each sub-region in the IR spectra consists of a sharp, higher-energy peak and a lowerenergy multi-component absorption. We assign the former to infrared-active phonon involving predominantly Si-Oapical stretchings because the corresponding bond is the shortest within the same tetrahedron (Papike et al. 1969). The IR-active phonon mode comprising Si-O_{apical} stretching appears at higher wavenumber than the corresponding Raman-active phonon mode due to different selections rules and consequently different participation ratios of the oxygen atoms, which influences the overall reduced mass of the atoms involved in the vibration. The spectra in Figure 9 suggest that the IR-active T-O mode is strongly localized in vibrations of the apical oxygen atoms, while the Raman-active mode involves, to a certain degree, vibrations of the bridging oxygen atoms as well. However, similar to the Raman-active modes, the IR-active Si-Oapical stretching modes gradually shift in wavenumber towards lower energy with increasing content (see Fig. 8), providing an additional tool to follow the M(1,2,3) site population.

The 800–550 cm^{-1} range: The Si–O deformation modes

The most prominent Raman band in most amphiboles occurs in the range 650–680 cm⁻¹; it has been assigned to a symmetric Si–O–Si bending mode, also referred to as a breathing mode of the bridging oxygen O_{br} atoms of the tetrahedral ring (Leissner *et al.* 2015, Waeselmann *et al.* 2019), because it predominantly involves in-phase O_{br} vibrations. However, lattice dynamics simulations show that this mode also includes an antisymmetric TO₄ bending component (Ivanov *et al.* 2018). The phonon wavenumber ω_{ring} of this mode is sensitive to the composition at all

TABLE 1. RAMAN PEAK POSITIONS (IN cm ⁻¹) AND ASSIGNMENT FOR BOTH ENDMEM	ABERS (x=0 AND x=5)
AND ONE INTERMEDIATE COMPOSITION ($x = 3$) ALONG THE Na(NaCa)(Mg _{5-x} Co	x)Si ₈ O ₂₂ (OH) ₂ JOIN

ω (<i>x</i> = 0)	ω (x = 3)	ω (<i>x</i> = 5)	Dominant type of atomic vibrations
3730.6(1) s - - 3676 5(8) w	3720(3) w 3707(3) w 3690(3) m 3670(3) m overlapped	- - 3673.5(1) s	OH stretching, $\frac{M^{(1,3)}}{M^{(1,3)}}$ (MgMgMg)- ^A Na OH stretching, $\frac{M^{(1,3)}}{M^{(1,3)}}$ (MgMgCo)- ^A Na OH stretching, $\frac{M^{(1,3)}}{M^{(1,3)}}$ (CoCoCo)- ^A Na OH stretching, $\frac{M^{(1,3)}}{M^{(1,3)}}$ (MgMgMg)- ^A
- - -	overlapped 3641(5) vw 3622(7) vw	- - 3624.4(4) w	OH stretching, $M^{(1,3)}$ (MgMgCo)- ^A OH stretching, $M^{(1,3)}$ (MgCoCo)- ^A OH stretching, $M^{(1,3)}$ (CoCoCo)- ^A
1093.0(4) w, 1079.1(1) s, 1046.5(3) m, 1014.6(7) vw	1071.1(3) s, 1041(1) m	1068.9(1) s, 1037.7(6) m	^{<i>T</i>(1)} SiO ₄ stretching
954.8(2) m, 932.1(3) m	949(1) m, 924.6(9) m	947(3) w, 928(1) m	$^{T(2)}SiO_4$ stretching
728.3(5) vw	718(3) vvw	725(5) vvw	$T^{(1)}$ Si motions within the (<i>b</i> , <i>c</i>) plane
682.85(1) vs	678.16(2) vs	676.37(1) vs	TO_4 -ring $O_{bridging}$ breathing $+$ antisymmetric TO_4 bending
589.8(3) w	583(9) vvw	593(3) vvw	(Mg,Co)–OH librations
521.2(5) w, 510.7(4) w	508.7(4) w	500.6(8) w	T-O-T & O-T-O vibrations + (Mg,Co)-O stretching
476.2(7) vw, 465.1(7) vw	470(1) vw	467.1(5) vw	(Mg,Co)–OH librations
432.1(7) vw, 418.8(3) vw, 398.25(3) m, 373.95(6) w, 337.54(9) w	430(4) vw, 401(5) vw, 389.1(9) m, 368(3) w, 326.4(7) w	429(2) vw, 397(1) m, 381.9(5) m, 355.6(7) w, 322.7(5) w	(Mg,Co)O ₆ vibrations
302.9(5) vw	304(3) vw	303.0(7) w	M(4)(Ca,Na)–O vibrations
290.7(5) vw, 260 w, 245.2(1) w, 228 m, 208.4(2) w	271(2) vw, 222.5(8) m, 199(3) w	270.7(5) w, 232.3(2) m, 216.6(3) w, 201.6(4) vw, 183.9(2) w	(Mg,Co)O ₆ and ^{<i>M</i>(4)} (Ca,Na)–O vibrations
181.1(6) vw, 173(2) vw	167.3(4) w	167 vw, 156.1(4) vw	^{<i>M</i>(1)} (Mg,Co)O ₆ vibrations
160.3(3) w	147.6(2) w	141.0(3) m	^{M(1)} (Mg,Co)O ₆ vibrations
107.6(5) w	100.9(4) m	97.4(2) m	$^{M(4)}$ Na–O and external modes of the silicate double chain

Note: s, m, w, and v stand for strong, medium, weak, and very to describe the linear intensity of the corresponding Raman signal.

crystallographic sites in the amphibole structure (Waeselmann *et al.* 2019). For samples within a simple solid-solution involving homovalent substitutions for $^{M(1,2,3)}$ Mg, for example along the tremolite–ferro-actinolite series, ω_{ring} monotonically decreases for increasing amounts of C Fe²⁺ replacing C Mg. Figure 10 compares the curve derived by Bersani *et al.* (2019) with the corresponding variation of band

position *versus* Co content in Na(NaCa)(Mg_{5-x}Co_x) Si₈O₂₂(OH)₂ richterites. We see a similar trend of decreasing frequency with increasing content of the divalent transition-metal ion. However, there is a difference in band frequency of 8–13 cm⁻¹ between the two sets of spectra for the compositional range of the tremolite data, and the effect of composition on phonon energy is significantly greater for tremolite



FIG. 9. Comparison between the Raman and FTIR spectra for Mg endmember richterite in the tetrahedral stretching modes region (1200–800 cm⁻¹). The vibrations of the ^{*T*(1)}Si–O1 and ^{*T*(2)}Si–O2 modes are indicated. A sketch of a fragment of the tetrahedral double chain showing the different tetrahedra is also given.

than for richterite. Presumably this difference is caused by the chemical and structural differences between the tremolite and richterite structures, *e.g.*, vacant *versus* filled *A* site and/or Ca *versus* Ca + Na at the M(4) site, rather than differences between Fe²⁺ and Co²⁺, as these ions have the same charge and similar mass.

Lattice dynamics calculations indicate that the moderate Raman peak near 740 cm⁻¹ in potassic-

magnesio-arfvedsonite arises from Si vibrations within the (**b**, **c**) plane. All (Mg,Co)-richterite samples exhibit a very weak Raman peak at 725 cm⁻¹, which we assign to the same type of vibration.

Figure 11 compares the FTIR and Raman spectra in the $800-550 \text{ cm}^{-1}$ range, where it is apparent that, due to selection rules, the symmetric ring-breathing mode is present only in the Raman pattern, while the IR spectrum shows a triplet of low-intensity bands at



FIG. 10. Variation in the position (energy) of the symmetric Si–O–Si bending mode in the region 665–685 cm⁻¹ for synthetic (Mg,Co)-richterites (red circles) and tremolite– actinolite (the dotted line is the relation for Fe²⁺-bearing tremolite (from Bersani *et al.* 2019)).

>600 cm⁻¹, plus a broad band at 600 cm⁻¹, that has been assigned to a OH-libration mode (Della Ventura *et al.* this volume). The corresponding Raman-active OH-libration mode generates a weak peak near 589 cm⁻¹ which decreases in intensity upon the addition of Co and can hardly be resolved for the sample with x =5. For increasing Co contents in the amphibole, only slight shifts occur in the FTIR spectra for the triplet at >600 cm⁻¹, while a new band whose assignment is not clear at the moment appears at 648 cm⁻¹.

The $<550 \text{ cm}^{-1}$ range: The M(1,2,3)–O and M(4)–O modes

The peaks in the lower-frequency <550 cm⁻¹ region are the most complicated to assign due to the overlapping of modes involving both the $M(1,2,3)O_6$ octahedra and M(4)-O vibrations as well as TO₄ bending and external modes. The lattice dynamics simulations reveal that the Mg–O and Fe²⁺–O partial spectra contribute in the range $150-550 \text{ cm}^{-1}$ and they are very similar to each other (Ivanov et al. 2018). The simulations also suggest that the M(1,2,3)-O modes should exhibit one-mode behavior (Chang & Mitra 1971), that is, a continuous shift in peak position as a function of the Mg/(Mg + Fe²⁺) ratio. The one-mode behavior has been experimentally confirmed for selected Raman-active MO₆ modes in this range by Waeselmann et al. (2019) and Bersani et al. (2019). Divalent cobalt has very similar chemical characteristics to divalent iron and, therefore, the MO₆ modes in (Mg,Co)-richterite should also show one-mode behavior, which indeed is observed for the majority of the peaks in the range 100–500 cm^{-1} (see Table 1 and Fig. 7).

The calculated partial Si–O spectrum also contributes to the range \sim 500–550 cm⁻¹, which is typical of O–Si–O and Si–O–Si bending modes in silicates, and therefore we assign the Raman peaks of (Mg,Co)richterite between 500–600 cm⁻¹ to mixed O–Si–O and Si–O–Si bending and (Mg,Co)–O stretching modes.

Our studies of K-rich deuterium-exchanged richterite indicate that the Raman scattering generated by a second OH-libration mode, allowed by group theory, is near 475 cm⁻¹ (Della Ventura *et al.* this volume). For all (Mg,Co)-richterites a very weak Raman scattering is indeed observed near 470 cm⁻¹ (marked with an arrow in Fig. 5). Interestingly, for x = 0 two Raman signals near 476 and 465 cm⁻¹ were resolved in this spectral range. Since there is no chemical variation at the M(1,3) sites, the two components may correspond to vacant and filled A sites or possible site-occupancy order of Na at the A(m) and A(2)positions. No matter the exact origin of this splitting, apparently the incorporation of Co into the structure smears out the energy difference between these two vibrational states.

The 430-300 cm⁻¹ range is dominated by (Mg,Co)O₆ vibrations. The weak Raman scattering near 300 cm⁻¹, which exhibits negligible dependence on the Co content, is assigned mainly to M(4) (Ca,Na)-O vibrations, which is consistent with the calculated Ca-O partial spectra by Ivanov et al. (2018); it is not exclusively attributed to Ca-O stretching because the experimental Raman spectra of sodium amphiboles also contains Raman scattering of similar intensity around this wavenumber (Waeselmann et al. 2019). Both the Ca-O and Na-O partial spectra contribute to the range 200-250 cm⁻¹, along with Mg-O and Fe²⁺-O modes (Ivanov et al. 2018), therefore we assign the Raman peaks of (Mg,Co)-richterite between 300-200 cm⁻¹ to combined $\overline{C}(Mg,Co)$ -O and $M^{(4)}(Ca,Na)$ -O vibrations.

X-ray diffraction and Mössbauer spectroscopic studies of the oxidation processes in riebeckite (Della Ventura *et al.* 2018) revealed that only M(1)-site Fe²⁺ transforms into Fe³⁺, while Raman spectroscopy shows that only the octahedral modes near 160–180 cm⁻¹ mirror the iron oxidation. These results enable us to attribute the Raman peaks in the 160–180 cm⁻¹ range of (Mg,Co)-richterite predominantly to M(1)(Mg,Co)–O vibrations.

Finally, the lowest-energy Raman peak near 100 cm^{-1} is attributed to external modes of the silicate double chain combined with $^{M(4)}$ Na–O vibrations based on two pieces of evidence: (1) the sensitivity of this peak to the amphibole symmetry and the



FIG. 11. Comparison between the Raman and FTIR spectra for Mg- and Co-endmember richterites in the 800-550 cm⁻¹ region.

occupancy of the M(4) site (Waeselmann *et al.* 2019), and (2) the fact that, according to the calculations of Ivanov *et al.* (2018), the partial Na–O spectrum also contributes to the scattering in this range.

CONCLUSIONS

Detailed assignment of the low-frequency (50–1200 cm⁻¹) region of Raman spectra of amphiboles has not been possible until recently, when the theoretical work of Ivanov *et al.* (2018) for potassic-magnesioarfvedsonite and the availability of extensive data for natural amphiboles (Apopei & Buzgar 2010, Leissner *et al.* 2015, Waeselmann *et al.* 2019, Bersani *et al.* 2019) became available. This work has significantly pushed forward our understanding of the vibrational spectra of the amphiboles and the assignment of the observed peaks to the different cation-anion modes in the structure. Here we have studied a series of synthetic richterites with compositions Na(NaCa) (Mg_{5-x}Co_x)Si₈O₂₂(OH)₂ (x = 1-5), where ^CMg is progressively substituted by ^CCo. We have shown that the Raman and FTIR spectra in the OH-stretching region are identical and both provide the possibility of deriving the relative amounts of the substituting cations at the OH-coordinated M(1,3) sites. Based on the previous work on amphiboles, we were also able to assign, with a high degree of confidence, the observed Raman peaks in the framework mode region <1200 cm⁻¹. We intend to continue to study additional synthetic solid-solution series in an effort to make, in the near future, Raman spectroscopy a robust quantitative technique for the microanalysis of amphiboles, particularly when high-resolution power is needed.

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