Oxidation processes and thermal stability of actinolite

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Received: 20 May 2022 / Accepted: 24 October 2022 / Published online: 22 November 2022
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Abstract
Understanding the thermal behaviour of iron-containing amphiboles (AB2C5T8O22W2, C5 = M(1)2 M(2)2 M(3)) at atomic-level scale may have important implications in several fields, including metamorphic petrology, geophysics, and environmental sciences. Here, the thermally induced oxidation and decomposition of actinolite are studied by in situ high-temperature Raman spectroscopy and complementary thermogravimetric/mass-spectrometry analyses as well as X-ray diffraction of the products of amphibole decomposition. The effect of CFe2+ on dehydrogenation/dehydroxylation is followed by comparing the results on actinolite with those for tremolite. We show that mobile charge carriers, namely polarons (conduction electrons coupled to FeO6 phonons) and H+ cations, exist in actinolite at elevated temperatures ~ 1150–1250 K. The temperature-induced actinolite breakdown is a multistep process, involving (i) delocalization of e− from CFe2+ as well as of H+ from hydroxyl groups shared by Fe-containing M(1)M(1)M(3) species, which, however, remain in the crystal bulk; (ii) dehydrogenation and ejection of e− between 1250 and 1350 K, where actinolite can be considered as “oxo-actinolite”, as H+ also from hydroxyl groups next to M(1,3)(MgMgMg) configurations become delocalized and mostly remain in the crystal bulk; (iii) complete dehydroxylation and consequent structure collapse above 1350 K, forming an Fe3+-bearing defect-rich augitic pyroxene. The dehydrogenation of tremolite occurs at 1400 K, triggering immediately a disintegration of the silicate double-chain into single SiO4-chains and followed by a rearrangement of the amphibole octahedral strips and BCa2+ cations into pyroxene-type octahedral sheets at 1450 K. The result of tremolite decomposition is also a single-phase defect-rich clinopyroxene with an intermediate composition on the diopside–clinoenstatite join.

Keywords Actinolite · Tremolite · Raman spectroscopy · Oxidation · Decomposition · High temperature

Introduction

Amphiboles are among the most common rock-forming silicate minerals, constituting ~ 5 vol% of the Earth’s crust (Ronov and Yaroshevsky 1969). Their general formula is AB2C5T8O22W2, with the C-type cations dispersed over three different crystallographic sites, C5 = M(1)2 M(2)2 M(3), the T-type cations over two different crystallographic sites, T8 = T(1)4 T(2)4, and a large diversity of chemical elements at all cationic sites (Hawthorne et al. 2012). The amphibole structure consists of the so-called I-beams: strips of TO4-rings linked MO6 octahedra running along the crystallographic c axis (Fig. 1a). The tetrahedrally coordinated cationic sites T(1,2) are occupied by Si and Al. The majority of elements can enter the octahedrally coordinated M(1,2,3) sites, but the most common are Mg and Fe2+ (Hawthorne et al. 2012). The I-beams are interconnected via B-type cations, forming A-site cavities that can be filled or remain vacant. This structure type is extremely adaptive to variations in chemistry as well as to different temperatures and pressures, ensuring the occurrence of amphiboles in a wide range of geological settings (Hawthorne and Oberti 2007). This allows for using amphiboles as efficient chemical geothermobarometers (Schumacher 2007; Putirka 2016). Furthermore, most of the amphibole species carry hydroxyl...
groups at the W site (Hawthorne et al. 2012), making them critical suppliers of hydrous species during metamorphic processes in the upper mantle and thus, key contributors to the global water cycle (e.g. Kang et al. 2017). Amphiboles can release OH groups while they undergo a structure collapse at elevated temperatures, resulting in a formation of pyroxene (e.g. Johnson and Fegley 2003). However, for CFe2+-bearing amphiboles dehydrogenation may occur without necessity of structural breakdown, following the co-exchange $CFe^{2+} + W(OH)^{-} \rightarrow CFe^{3+} + W^{2-}$, which is triggered by the presence of external O2. That is, the stability field of amphibole may considerably vary, depending on the content of divalent iron as well as on the oxygen fugacity of the surrounding (Della Ventural et al. 2018, in press). Therefore, understanding the thermal behaviour and oxidation processes of iron-containing amphiboles at atomic-level scale is significant for petrology and geophysics, but also for material and environmental science, when studying the hazardous effects of asbestos amphibole (Bloise et al. 2017).

Our recent studies of iron-rich hydrous amphiboles (Mihailova et al. 2021) revealed another extremely important phenomenon occurring at lithospheric temperatures: formation of collectivized $FeO_{x}$-related polarons (conduction electrons coupled with polar phonons to carry a local structural distortion) and delocalized $H^{+}$ cations, meaning that at elevated temperatures iron-rich hydrous amphiboles are conductive. The formation of charge carriers was experimentally proven by polarized Raman spectroscopy and theoretically validated by density-functional-theory modelling (Mihailova et al. 2021). The results obtained on grunerite (nominally $A^{◻}Fe^{2+}_{2}^{2+}C^{5+}_{5}Fe^{2+}_{5}^{5+}Si_{8}O_{22}^{2-}W(OH)_{2}$, square symbol denotes vacancy) indicate that the formation of polarons begins at $T^{′} \approx 700$ and the process of activation of mobile polarons and delocalized H$^{+}$ is completed at $T^{″} \approx 850$ K. The activation temperatures may vary depending on the presence or absence of external oxygen and increase with the amount of CMg as a minor element in ferrous amphiboles (Mihailova et al. 2021). The direction-dependent occurrence of resonance Raman scattering revealed another interesting atomic-scale feature of ferrous hydrous amphiboles: the polaron dipoles are aligned along the I-beams, resulting in strongly anisotropic polaron mobility (Mihailova et al. 2021). The latter is in full accordance with impedance spectroscopy, showing that the conductivity along the c axis is about five times stronger than that in the perpendicular direction (Schmidbauer et al. 1996). Hence, polaron conductivity of minerals such as amphiboles as well as phyllosilicates (Wang and Karato 2013), rather than ionic conductivity of grain-boundary fluids, can be the major atomistic source of the well-known anisotropic lithospheric conductivity in subductions zones (e.g. Leibecker et al. 2002).

However, the conductivity of double-chain silicates decreases with the decreasing content of iron (Schmidbauer et al. 2000; Hu et al. 2018) and, therefore, it is necessary to study also amphiboles with Mg dominating over Fe$^{2+}$ at the octahedrally coordinated $M(1,2,3)$ sites, to check
whether delocalized $e^-$ and $H^+$ occur also in such minerals and if so, whether the excited electrons couple with polar phonons to form polarons with aligned dipoles. Here, we open this question by applying in situ temperature-dependent Raman spectroscopy to actinolite (ideally $\text{Ca}_{1.74}\text{Fe}_{2+}^3\text{Si}_8\text{O}_{22}\text{W}(\text{OH})_2$, with $0.5 < x \leq 2.5$). The thermal stability of actinolite is further compared to that of tremolite (nominally $\text{Ca}_{2}\text{Mg}_{5}\text{Si}_8\text{O}_{22}\text{W}(\text{OH})_2$) by Raman scattering and complementary thermogravimetric analysis.

**Materials and methods**

**Samples**

Both the actinolite and tremolite samples are from the collection of the Mineralogical Museum in Hamburg and their chemical compositions have been previously determined by wavelength-dispersive electron-microprobe analysis (Leissner et al. 2015). The studied actinolite sample (labelled S15 in Leissner et al. 2015) originates from low-grade metamorphic rocks from Zillertal, Austria. It is dark green in colour and its crystallochemical formula is $\text{Ca}_{1.74}\text{Fe}_{2+}^3\text{Si}_8\text{O}_{22}\text{W}(\text{OH})_2$. The studied tremolite sample (S10 in Leissner et al. 2015) originates from Nuristan Province, Afghanistan, appears whitish, and has a composition $\text{Ca}_{1.84}\text{Mg}_{0.12}\text{Fe}_{2+}^3\text{Si}_8\text{O}_{22}\text{W}(\text{OH})_2$. The thermal stability of actinolite is further compared to that of tremolite (nominally $\text{Ca}_{2}\text{Mg}_{5}\text{Si}_8\text{O}_{22}\text{W}(\text{OH})_2$) by Raman scattering and complementary thermogravimetric analysis.

**Raman spectroscopy**

Raman scattering experiments were conducted in back-scattering geometry with a Horiba Jobin–Yvon T64000 triple-monochromator spectrometer operating in a subtractive mode and equipped with an Olympus BX41 confocal microscope and Symphony liquid-N2-cooled charge-coupled device detector. The Raman experiments were excited with the green line of Coherent Innova 90C FreD Ar$^+$ laser (wavelength $\lambda = 514.532$ nm). The laser was focused on the sample surface through a $50 \times$ long-working distance objective, with a diameter of the laser spot on the sample surface of $\sim 2 \mu$m and laser power of $\sim 6.5$ mW. The spectral resolution and the accuracy of the peak position were $2$ cm$^{-1}$ and $0.35$ cm$^{-1}$, respectively. The spectrometer was calibrated to the Raman peak of Si at $520.5$ cm$^{-1}$. In situ temperature-dependent Raman experiments in N$_2$ atmosphere were conducted between 100 and 870 K, using a LINKAM THMS-E600 heating/cooling stage providing a temperature accuracy of 0.1 K. Three different temperature runs in air were conducted on three different actinolite specimens, whereby the highest temperature reached was 1300, 1350 and 1400 K. Tremolite (S10) was heated up to 1450 K. Parallel polarized spectra (polarization of the scattered light $\mathbf{E}_\parallel$ parallel to the polarization of the incident light $\mathbf{E}_\perp$) with the $c$ axis perpendicular to $\mathbf{E}_\parallel$ were collected in the above-described heating experiments. Additionally, parallel polarized spectra with the $c$ axis $\parallel \mathbf{E}_\parallel$ were collected from actinolite heated in air up to 1150 K. In the standard Porto’s notation (see e.g. Kuzmany 2009), the two scattering geometries are described as $\bar{\gamma}(xx)\bar{y}$ and $\bar{\gamma}(zz)\bar{y}$ with $x \perp y \perp z$ being the coordinate axes of the laboratory Cartesian coordinate system (see Fig. 1b), but to make the experimental geometry more transparent for readers not familiar with this notation, we will be referring to the corresponding polarized spectra as ($\mathbf{c} \perp \mathbf{E}_\parallel \parallel \mathbf{E}_\perp$) and ($\mathbf{c} \parallel \mathbf{E}_\parallel \parallel \mathbf{E}_\perp$), respectively.

Both types of polarized spectra are dominated by $A_g$ phonon modes, but different components on the Raman polarizability tensor $\alpha_{ij}$ are detected in the two scattering geometries: $\alpha_{xx}$ and $\alpha_{yy}$ in the ($\mathbf{c} \perp \mathbf{E}_\parallel \parallel \mathbf{E}_\perp$)-spectrum, and $\alpha_{zz}$ in the ($\mathbf{c} \parallel \mathbf{E}_\parallel \parallel \mathbf{E}_\perp$)-spectrum (Waeselmann et al. 2020). In the in situ high-temperature Raman spectra were collected from raw natural surfaces of single crystals. As the common cleavage planes of amphibole are parallel to (011) or (010) (e.g. Deer et al. 2013), the relative intensities in ($\mathbf{c} \perp \mathbf{E}_\parallel \parallel \mathbf{E}_\perp$)-spectrum may slightly vary from one specimen to another, depending on the orientation of the probed surface and consequently, on the relative contribution of the $\alpha_{xx}$ and $\alpha_{yy}$ components to the peak intensities. The heating/cooling rate in all experiments was 10 K/min and the stabilization time prior to collecting spectra at the desired temperature was 5 min. The total acquisition time to collect a spectrum in different runs varied between 10 and 20 min, depending on the quality of the signal. The exact temperature ramps are given in Table 1. At the highest temperature reached in each run, additional spectra after prolonged time (60 min in N$_2$, 30 min in air) were collected to verify the absence of extra spectral changes developed with time at that temperature.

The as-measured spectra were baseline-corrected, temperature-reduced for the Bose–Einstein population factor and fitted with pseudo-Voigt functions to derive the phonon wavenumbers $\omega$, full widths at a half maximum (FWHM), integrated intensities $I$, and weight coefficients of the Lorentzian contribution to the peak shape, as described in detail in the supplementary material of Mihaiova et al. (2021).

**Thermal analysis**

Thermogravimetric analysis (TGA) on actinolite and tremolite was performed on an SETSYS Evolution 2500 (SETERAM) apparatus. The experiments were carried out in air, using Al$_2$O$_3$ crucibles and heating from 300 up to
1470 K with a heating rate of 10 K/min. The mass of the actinolite powder subjected to TGA was 11.03 mg, whereas that of tremolite powder was 17.04 mg. A baseline correction of the TG curves was applied by subtracting the empty pan TG curve from the experimental sample curves. The first derivation curve of TG (dTG) was attached to determine more precisely the beginning, inflection point, and completion of the decomposition reactions. A simultaneous analysis of the evolved gases was performed via mass spectrometry (MS) using OmniStar apparatus and the intensity related to the m/z (mass-to-charge ratio) value of H2O (18) was examined. The temperature precision was ~0.1 K, while the precision in mass-loss determination was ~0.01%. Data were evaluated using CALISTO specialized thermal analytical software package.

**X-ray diffraction (XRD)**

After the temperature runs, the crystallinity of samples subjected to in situ high-temperature Raman spectroscopy was controlled by using a Nonius KappaCCD diffractometer with a CCD detector and graphite-monochromated MoKα radiation (λ = 0.71069 Å). The predominantly polycrystalline nature of the sample manifested itself by the presence of powder rings superimposed by some Bragg diffraction maxima. Simulated powder diffraction data were obtained by Gandolfi-type motion of the sample at a distance of 50 mm to the detector.

The powder XRD patterns of the samples subjected to a thermal analysis were collected with a STOE STADI-MP diffractometer equipped with an asymmetric germanium (111) monochromator, utilizing monochromatic MoKα radiation (λ = 0.70926 Å) in Bragg–Brentano geometry, in the 2θ-range 3°–50°, with a scanning step size of 0.01°. LeBail profile refinements and Rietveld structure refinements using these data were performed with JANA2006 (Petřiček et al. 2014).

### Results

**Effect of Fe^{2+} on the Raman spectra**

Figure 2 shows parallel polarized spectra of actinolite and tremolite measured at ambient conditions in two scattering geometries. As can be seen, both amphibole species exhibit nearly the same Raman spectra generated by the framework vibrations (15–1215 cm⁻¹) in either scattering geometry, as the small difference in the peak positions (see Table 2) is due to CFe^{2+} in actinolite (Waeselmann et al. 2020). The presence of octahedrally coordinated Fe^{2+} is also revealed by the additional Raman peaks in the range 3200–3800 cm⁻¹, arising from the OH-stretching modes, whose relative intensities directly probe the fraction of various A-M(1)M(1)M(3) chemical configurations (Leissner et al. 2005). The amount of A-M(1,3)Fe^{2+} in actinolite calculated from the OH-stretching intensities is 0.48 ± 0.07 apfu, which is the same within uncertainties as the total amount of CFe determined by EMPA, indicating that Fe^{2+} is preferably incorporated at the M(1) and M(3) sites.

**Phonon expandabilities**

Figure 3 shows representative \((c \perp E_i \parallel E_o)\)-spectra measured at different temperatures in N₂ as well as the calculated phonon expandabilities \(\alpha_o = \frac{V_{o2} - V_{o1}}{V_{o1}}\) derived from linear fits \(\omega(T) = \omega_o + \omega_o'T\) to data points in the temperature range 300–800 K, which could be measured in both air and N₂ atmosphere. The phonon expandabilities \(\alpha_o\) are representative of the response of atomic dynamics to a temperature change, that is, how the vibrational energy evolves with a temperature increase, similarly to the volume thermal expansion \(\alpha_v = \frac{1}{V_0} \frac{dV}{dT}\), representing how the volume develops with \(T\). In this temperature range, there
is no significant difference in the thermal behaviour between actinolite and tremolite, nor between air and N₂ for either mineral. The phonon expandability increases in following order: hydroxyl groups → silicate double chain → MO₆ octahedral strips, which is consistent with the decrease in the degree of covalency of O–H, Si–O, and M–O bond, respectively. It is worth noting that the OH stretching modes of hydroxyl groups next to a filled A site (peak near 3717 cm⁻¹) are softer to a temperature increase than that of hydroxyl groups next to a vacant A site (peaks within 3640–3680 cm⁻¹). This is most probably related to the fact that, due to the overall increase in the interatomic distances at elevated temperatures, the A⁺–H⁺ repulsion interactions decrease stronger than the O–H bond strength does, which leads to a larger change in the effective force constant for OH groups next to a filled A site than for OH groups next to a vacant A site. The phonon expandability of the TO₄-ring breathing mode (near 673 cm⁻¹) is smaller than α_0 of TO₄ stretching modes, indicating that the Si-O bridging bond contours, forming the SiO₄-rings, are more robust to a temperature increase than the Si-O non-bridging bonds.

**Oxidation of actinolite on heating in air**

Selected (ε ⊥ E_i || E_s)-spectra of actinolite heated in air up to 1300 K and 1350 K are shown in Fig. 4a, b, respectively. The overall spectrum profile is preserved in both cases, indicating that the amphibole structure remains stable up to 1350 K. There are, however, several significant spectral changes that occur on heating. At 1200 K, the MO₆ mode near 159 cm⁻¹ exhibits a minimum in wavenumber and a maximum in intensity (see Fig. 5a, b, respectively). Our previous studies on riebeckite and grunerite indicated that this mode is sensitive to M(1)Fe²⁺ → M(1)Fe³⁺ exchange, implying delocalized electrons e⁻ in the crystal bulk (Della Ventura et al. 2018; Mihailova et al. 2021). The slight but steady increase in the fractional intensity between RT and 1200 K is related to the enhancement of vibrational amplitude of Fe²⁺O₆ vibration just prior to the e⁻ delocalization and the subsequent decrease in intensity on further heating is due to the ongoing Fe oxidation in the octahedral strips (Della Ventura et al. 2018; Mihailova et al. 2021). The resulting shrinkage of the MO₆ octahedra is also manifested by the minimum of ω₁₅₉(T) at 1200 K (Fig. 5a). The SiO₄-ring
Table 2 Positions $\omega$ (in cm$^{-1}$) at room temperature for the pronounced Raman peaks for actinolite and tremolite and peak assignment to definite atomic vibrations (after Leissner et al. 2015; Ivanov et al. 2019; Waeselmann et al. 2020; Della Ventura et al. 2021; Ishida et al. 2008)

| Actinolite | Tremolite | Dominant type of vibration |
|------------|-----------|----------------------------|
| 119.4(1) w | 120.7(2) w | External modes of the silicate double chain |
| 141.9(6) vw, 159.5(1) m, 178.6 (1) m | 145.4(5) w, 161.5(1) m, 179.6(1) m | (Mg,Fe$^{2+}$)O$_6$ vibrations |
| n. r., 222.5(1) s, 232.7(1) s, 250.6(3) m, 260(1) w | 215.4(1) sh, 224.2(1) s, 233.8(1) s, 252.0(1) m, 264.9(5) w | (Mg,Fe$^{2+}$)O$_6$ and Mg$^{4+}$/Ca-O vibrations |
| 302.4(1) | 304.9(1) | $^{Mg^{4+}}$Ca-O vibrations |
| n. r., 333.7(3) w, n.r., 349(1) w, 371.8(3) s, n.r., 393.6(1) s, 416.9(2) s, 436.5(5) w | 312.3 (5) vw, 334.5(5) w, 344.3(3) sh, 353.7(2) w, 371.2(1) s, 376.2(1) sh, 395.8(1) s, 417.8(1) s, 437.3(1) w | (Mg,Fe$^{2+}$)O$_6$ and $^{Mg^{4+}}$Ca-O vibrations |
| 483(3) vw, 518(2) sh, 530(2) w, 580(2) vw | 491.(1) vw, 519(1) sh, 531.0(2) w, 585 (2) vw | T-O-T & O-T-O vibrations + (Mg,Fe$^{2+}$)-O stretching |
| 658 (1) sh | 653 (1) sh | OH-libration (Ishida 2008) |
| 673.0(1) vs | 675.2(1) vs | TO$_6$-ring Obridging breathing |
| 690(3) sh | 693.8(1) sh | OH-libration (Ishida 2008) |
| 744(1) w | 751.7(6) w | $^{T1}$Si motions within the (b,c) plane |
| 929.9(1) m, 943(1) w | 932.3(1) m, 949.4(4) w | $^{T2}$SiO$_4$ stretching |
| 1028.3(1) m, 1057.6(1) s, 1069 (1) m | 1029.8(1) m, 1061.7(1) s, 1076 (1) m | $^{T1}$SiO$_4$ stretching |
| 3644(3) w | – | OH stretching next to $^{M1,3}$Fe$^{2+}$Fe$^{2+}$Mg$^+$-A |
| 3959.2(5) m | – | OH stretching next to $^{M1,3}$Fe$^{2+}$Mg$^+$-A |
| 3673.3(1) s | 3674(1)s | OH stretching next to $^{M1,3}$MgMg$^+$-A |
| 3717(3) vw | – | OH stretching next to $^{M1,3}$Fe$^{2+}$Mg$^+$-A |

$w$, $m$, $s$, weak, medium, strong in intensity, $sh$ shoulder, $v$ very, n.r. not resolved

![Fig. 3](image-url) Fig. 3 Phonon expandabilities $\alpha_\omega$ for actinolite and tremolite derived from the $\omega(T)$ trends in the range 300–800 K as well as representative Raman spectra measured with $\mathbf{e} \perp \mathbf{E}_i || \mathbf{E}_s$ in $N_2$. For actinolite data from two different heating experiments in air are given to verify repeatability.
breathing mode near 673 cm$^{-1}$ exhibits a minimum of \( \omega(T) \) at 1250 K (Fig. 5c), indicating that at this temperature the ring geometry is slightly re-adjusted to adopt the smaller size of adjacent Fe$^{3+}$O$_6$ octahedra in the I-beams, thus making possible the already delocalized electrons to leave the crystal (Della Ventura et al. 2018; Mihailova et al. 2021). All these observations indirectly indicate that at least between 1200 and 1250 K, there are mobile electrons in the bulk of the actinolite grains that can hop from one octahedral site to another. On cooling to room temperature, the crystal-chemical and structural changes in the I-beams are quenched, as revealed by the increase in \( \omega_{673} \) with respect to the initial value (see Fig. 5c), which is consistent with the presence of MFe$^{3+}$ (Waeselmann et al. 2020), as well as by the increase in \( \omega_{159} \) (Fig. 5a) caused by the slight reduction of the average MO$_6$ volume. The decrease in the intensity of the (Mg,Fe$^{2+}$)O$_6$ peak near 159 cm$^{-1}$ (Figs. 4 and 5b) as well as the appearance of extra Raman scattering near 595 cm$^{-1}$ (Fig. 4), attributed to Fe$^{3+}$O$_6$ vibrations (Waeselmann et al. 2020; Mihailova et al. 2021), also indicates irreversible Fe oxidation after cooling down to room temperature from 1300 or 1350 cm$^{-1}$. The extra Raman peak 595 cm$^{-1}$ detected in the room-temperature spectra (e $\perp$ E$\parallel$, Li $\parallel$ E$_s$)-spectrum is considerably stronger after cooling from 1350 K than after 1300 K, reaching in intensity the SiO$_4$-ring mode near 673 cm$^{-1}$, indicating a resonance enhancement of a polar Fe$^{3+}$O$_6$ optical phonon even when e $\perp$ E$\parallel$. Given that for grunerite resonance Raman scattering was detected only when e $\parallel$ E$\parallel$ (Mihailova et al. 2021), this observation suggests that in actinolite there is a possible random orientation of polaronic dipoles at elevated temperatures.

Near 1200 K the OH-stretching peaks in the (e $\perp$ E$\parallel$ E$_s$)-spectra start reducing in intensity and completely vanish at 1300 K (see Figs. 4 and 5d). After cooling down to room temperature, the total intensity of the OH-stretching modes recovers to \approx 83% and 66% when heating to 1300 K and 1350 K, correspondingly, meaning that the total disappearance of these modes at elevated temperatures is chiefly due to the activated delocalization of H$^+$ cations, hopping from one W site to another in the crystal bulk, rather than to a complete dehydrogenation of actinolite. This is a clear indication that at high temperatures mobile H$^+$ cations coexist with mobile electronic polarons also in magnesian Fe-bearing amphiboles, as in the case of Fe-rich amphiboles.

A closer inspection of the Raman-intensity ratios of the OH-stretching modes associated with different M(1)M(1)M(3) configurations sharing W anions (see Fig. 6) reveals that the H$^+$ delocalised from hydroxyl groups attached to MgMgMg triads completely re-localise on cooling down to room temperature. However, the Raman...
scattering from OH groups attached to Fe$^{2+}$-containing $M(1)M(1)M(3)$ configurations changes: the (Fe$^{2+}$MgMg)-A peak disappears, the weak (Fe$^{2+}$MgMg)-A peak shifts from 3717 to 3693 cm$^{-1}$ and decreases in intensity (or cannot be resolved after cooling from 1350 K), and the peak near 3644 cm$^{-1}$, which is commonly generated by (Fe$^{2+}$Fe$^{2+}$Mg)-A, oddly increases in intensity. To understand these changes, one should examine possible temperature-induced ionic alterations of the local configurations schematically represented in Fig. 6b. Each $M(1)M(1)M(3)$ triad shares oxygen atoms from two WOH groups, one oriented up and one down to the octahedral strip (see Figs. 1a and 6b). If iron oxidation takes place in an Fe$^{2+}$MgMg configuration, one WOH$^-$ should transform into WO$_2^-$ to maintain a local charge balance (Fig. 6b). Therefore, if all Fe$^{2+}$MgMg triads in the actinolite structure become Fe$^{3+}$MgMg, the corresponding OH-stretching peak should shift to lower wavenumber, due to the increased $M(1,3)$-O force constant (Leissner et al. 2015), and halves its intensity, because (OH)$^-$-Fe$^{2+}$MgMg-(OH)$^-$ configurations will become (OH)$^-$-Fe$^{3+}$MgMg-O$^{2-}$. In the case of an Fe$^{2+}$Fe$^{2+}$Mg triad one or both Fe$^{2+}$ can transform into Fe$^{3+}$ and consequently, one or both W(OH)$^-$ will exchange to WO$_2^-$. Hence, if all Fe$^{2+}$Fe$^{2+}$Mg become Fe$^{3+}$Fe$^{2+}$Mg, the corresponding peak should shift to lower wavenumber and halves its intensity, because (OH)$^-$-Fe$^{2+}$Fe$^{2+}$Mg-(OH)$^-$ will become OH$^-$-Fe$^{3+}$Fe$^{3+}$Mg-O$^{2-}$, whereas if all Fe$^{2+}$Fe$^{2+}$Mg become Fe$^{3+}$Fe$^{3+}$Mg, the corresponding Raman OH-stretching peak should disappear because all (OH)$^-$-Fe$^{2+}$Fe$^{2+}$Mg-(OH)$^-$ will transform into O$^{2-}$-Fe$^{3+}$Fe$^{3+}$Mg-O$^{2-}$. Within the experimental uncertainty, the intensity ratio $I_{3644 cm^{-1}}/I_{MgMgMg}$ in the final spectrum, measured after cooling down from 1300 K as well as from 1350 K, is a half of the intensity ratio $I_{Fe^{3+}MgMg}/I_{MgMgMg}$ in the initial spectrum. This indicates that the Raman peak near 3644 cm$^{-1}$ in the final spectra is due to OH groups next to (Fe$^{3+}$MgMg)-A rather than next to (Fe$^{2+}$Fe$^{2+}$Mg)-A, revealing that the majority of (OH)$^-$-Fe$^{2+}$Fe$^{2+}$Mg-(OH)$^-$ chemical species have transformed into (OH)$^-$-Fe$^{3+}$Fe$^{3+}$Mg-O$^{2-}$. At the same time, as no extra peaks were detected below 3644 cm$^{-1}$, all (OH)$^-$-Fe$^{2+}$Fe$^{2+}$Mg-(OH)$^-$ chemical species should had transformed into O$^{2-}$-Fe$^{3+}$Fe$^{3+}$Mg-O$^{2-}$.

Next, we analysed the temperature evolution of the Raman scattering measured in the (c $\parallel$ E$_i$ $\parallel$ E$_s$) scattering geometry (see Fig. 7a). When c $\parallel$ E$_i$, the OH stretching peaks vanished at 1150 K and all three peaks reappeared on cooling down, but the relative intensity of the (Fe$^{2+}$MgMg)-OH-A peak was reduced with respect to the initial intensity. Another important feature was the appearance of weak and broad Raman scattering near 600 cm$^{-1}$, which on cooling became better pronounced and somewhat gained intensity (see Fig. 7b). This additional peak is assigned to the resonance Raman scattering (RRS) arising from a polar Fe$^{3+}$O$_6$ optical mode, similar to the extra Raman peak 595 cm$^{-1}$ detected in the room-temperature (c $\perp$ E$_i$ $\parallel$ E$_s$)-spectra of actinolite heated up to 1300 and 1350 K. Quite surprisingly, approximately 72 h after the heating–cooling ramp, the RRS signal considerably intensified and particularly in the (c $\parallel$ E$_i$ $\parallel$ E$_s$)-spectrum it became dominant (see Fig. 7a,
b), although the \((\text{Fe}^{2+}\text{MgMg})-\text{OH}^-\)peak was still clearly detected (see Fig. 7c) and exhibited a negligible change in intensity with respect to the spectrum measured immediately after cooling down. It should be, however, emphasized that the \((\text{Fe}^{2+}\text{MgMg})-\text{OH}^-\) peak has lost intensity after the heating–cooling ramp, while the peak near \(3644\ \text{cm}^{-1}\) has gained intensity, which indicates a co-existence of \((\text{OH})^-\text{Fe}^{3+}\text{MgMg}-\text{O}^{2-}\) and \((\text{OH})^-\text{Fe}^{2+}\text{MgMg}-(\text{OH})^-\) chemical configurations.

The change in time of the RRS intensity reveals that immediately after cooling, the crystal was in a metastable state at the superficial layer probed by Raman spectroscopy, which is commonly \(~2\ \mu \text{m}\) in thickness, and that a diffusion of \(e^-\) occurs overtime through the bulk. This implies the development of a chemical gradient between the bulk and the outermost rim of the crystal grain. To verify this assumption, we have embedded the actinolite grain heated up to \(1300\ \text{K}\) (run 1) in epoxy, polished it to remove approximately a half of its initial thickness, and collected Raman spectra from the centre of the crystal bulk as well as from periphery points across and along the prism axis. The results are shown in Fig. 8. It is clear that RRS is only subtle in the central part of the crystal, while it is well pronounced in the periphery, where also the OH-stretching peaks related to \(\text{Fe}^{2+}\)-containing \(\text{M}(1)\text{M}(1)\text{M}(3)\) configurations are weaker or vanished. This confirms the occurrence of a chemical gradient related to the thermally induced \(\text{CFe}^{2+} + \text{WO}^{2-} \rightarrow \text{CFe}^{3+} + \text{WO}^{2-}\) co-exchange. Moreover, the peripheral part of the crystal along the prism axis shows stronger RRS than the peripheral part across the prism.

**Fig. 6** OH-stretching Raman scattering of actinolite measured at room temperature with \(c \perp E_i, E_s\), prior and after heating up to \(1300\) and up to \(1350\ \text{K}\) (a). Sketch of possible temperature-induced changes in the W-M(1)M(1)M(3)-W chemical configurations in actinolite (b). The atomic configurations in (b) were plotted with VESTA (Momma and Izumi 2008)
axis. Besides, no (Fe$^{2+}$MgMg)-OH-$\square$ peak was detected in the periphery along the prism axis, while this peak is still resolved in the periphery across the prism axis. These observations are solid evidence that the hopping of electrons and consequently, $e^-$ ejection in the presence of external O$_2$, is preferably along the crystallographic c axis, i.e. along the octahedral strips, in full accordance with the stronger RRS signal detected in (c $\parallel$ E$_i$ $\parallel$ E$_s$) than in (c $\perp$ E$_i$ $\parallel$ E$_s$)-spectra. However, the existence of RRS in both scattering geometries indicates that the alignment of polaronic dipoles in actinolite is not complete as in Fe-rich amphiboles.

It is worth noting that in contrast to Fe-rich amphiboles (Mihailova et al. 2021), a complete suppression of the Raman peaks generated by silicate-anion or hydroxyl-group vibrations in (c $\parallel$ E$_i$ $\parallel$ E$_s$) scattering geometry due to the alteration of the selection rules is not observed for actinolite. This is consistent with the fact that Fe is a minor element in actinolite and, therefore, a change in its valence manifests only as a defect electron level coupled to a localized vibration, without affecting the activity of all crystal phonons.

Amphibole-to-pyroxene structural breakdown

The (c $\perp$ E$_i$ $\parallel$ E$_s$)-spectra of actinolite heated up to 1400 K as well as of tremolite heated up to 1450 K are shown in Fig. 9. Similar to the first two runs, in this experimental geometry the OH peaks of actinolite completely disappeared at 1300 K, but the Raman scattering from framework vibrations (below 1200 cm$^{-1}$) drastically changed only at 1400 K, where the SiO$_4$-ring mode near 673 cm$^{-1}$ weakened, while the $\tau(1)$SiO$_4$-stretching mode near 1000 cm$^{-1}$ intensified. Note that the $\tau(1)$SiO$_4$-stretching mode near 1000 cm$^{-1}$ of tremolite also increased in intensity, while the OH-stretching peak disappeared. Interestingly, the spectral pattern of tremolite below 400 cm$^{-1}$, generated mainly by M(1,2,3)O$_6$ and M(4)Ca-O vibrations, was still preserved at 1400 K and changed only at 1450 K, forming a spectral profile typical of proxenes (see Fig. 9). Note that according
to density-function-theory calculations, the Raman scattering of pyroxenes between 200 and 400 cm$^{-1}$ is generated by phonon modes in which octahedrally coordinated cations significantly participate (Prencipe et al. 2014; Strangarone et al. 2016). Therefore, our results reveal that if there is no Fe$^{2+}$ in the structure, the thermally induced dehydrogenation triggers the amphibole breakdown, as first the silicate double chains detach to form single chains of SiO$_4$ and then the non-silicon cations rearrange to adopt to the new silicate system. On a subsequent cooling down (from 1400 K for actinolite and from 1450 K for tremolite), the OH peaks in the Raman spectra of both minerals did not recover at all and the spectrum profiles resembled that of pyroxene. The samples were further examined using a single-crystal X-ray diffractometer. Initial short φ-scans showed rather homogeneous pyroxene powder diffraction rings with few superimposed Bragg maxima. To obtain an integrated powder diffraction exposure of all scattering maxima for arbitrary sample orientation, Gandolfi-type motion of the sample was used (Hooft 1997). The diffraction profile obtained from this measurement revealed a pyroxene structure, in full accordance with the Raman data. The final room-temperature Raman spectrum of heated tremolite reveals a single pyroxene phase, which matches best the spectrum of diopside, but the overall peak broadening reveals a considerable number of structural defects. The latter is consistent with XRD data, indicating a larger unit-cell volume than that of diopside. Moreover, the peak position of the Si-O$_{\text{bridging}}$-Si bending mode in the spectrum of decomposed tremolite appears between the corresponding peak positions for diopside and clinoenstatite, suggesting that the mineral phase resulting from the tremolite thermal breakdown is a pyroxene solid solution along the diopside-clinoenstatite join.

The final spectrum of actinolite heated to 1400 K is very similar to that of augite but having broader peaks related to structural defects, likewise thermally decomposed tremolite. Moreover, there is an extra Raman peak near 770 cm$^{-1}$ as well as a very broad and relatively weak band near 935 cm$^{-1}$. Comparison with reference spectra of various pyroxenes (measured by us and available online in RRUFF, Lafuente et al. 2015) indicates that the extra peak near 770 cm$^{-1}$ is consistent with the co-presence of octahedrally coordinated Fe$^{3+}$ and Ca in the pyroxene structure, as in the case of esseneite (nominally CaFe$^{3+}$AlSiO$_6$). For both esseneite and aegirine (nominally NaFe$^{3+}$Si$_2$O$_6$) the strong Raman peak generated by Si-O$_{\text{non-bridging}}$ bond stretching (near 1000 cm$^{-1}$) appears at lower wavenumbers in comparison to the corresponding peak in Fe$^{3+}$-free pyroxenes (e.g. augite, see Fig. 9). Therefore, the broad Raman scattering near 935 cm$^{-1}$ probably arises from stretching modes of SiO$_4$ tetrahedra in the vicinity of octahedrally coordinated Fe$^{3+}$. 

![Fig. 8 Room-temperature spectra of the actinolite sample heated up to 1300 K (run1) collected from different points after prolonged time after the heating–cooling ramp; red solid lines are the spectra measured with c $\parallel$ E$_i$ $\parallel$ E$_s$, whilst the blue dotted lines are the spectra c $\perp$ E$_i$. The sample was embedded in resin and thinned by polishing to approximately a half of the initial thickness (~ 0.5 mm) to expose the bulk of the crystal; the lateral dimensions of the crystal are ~ 1.5 and 0.5 mm along and perpendicular to the c axis, respectively.](image-url)
Thermogravitometric data show that the dehydroxylation of tremolite begins near 1250 K and it is complete near 1400 K (see Fig. 10a), in full accordance with the Raman data. The total H₂O mass loss is 2.11%, which perfectly matches the theoretical oxide fraction of H₂O = 2.21 mass % in tremolite. The TG(dTG) and MS curves of actinolite suggest three temperature steps of mass loss, between 620–775 K, 775–1200 K, and 1200–1400 K, respectively, the most pronounced corresponding to the dehydroxylation process. The dTG peak of actinolite is at 1300 K, i.e. 50 K lower than that of tremolite, which is in a full accordance with the Raman data, revealing that for actinolite the complete loss of OH groups and consequent collapse of the amphibole structure occurs 50 K below the corresponding process in tremolite. The weak mass loss of actinolite between 620 and 775 K is most probably related to unavoidable volatile impurities in the powdered sample; inspection of the dTG curve of tremolite shows a similar subtle mass loss in this temperature range. The mass loss of actinolite in the intermediate temperature range between 1050 and 1150 K can be attributed to the partial dehydrogenation related to the formation of (OH)⁻-Fe³⁺MgMg-O⁻² and O²⁻-Fe³⁺Fe³⁺Mg-O²⁻ arrangements, without a disruption of the amphibole structure. This is in a good accordance with the Raman data, showing a small decrease in the OH-stretching intensity even for the sample heated only up to 1150 K.

The Raman spectra collected from the powders subjected to thermal analyses are identical with those collected from the initially single crystals of tremolite and actinolite heated up to 1450 and 1400 K, respectively. Due to the intrinsically polycrystalline nature of the decomposed amphibole samples subjected to Raman spectroscopy, single-crystal XRD structure refinement of the run products was not possible. Therefore, the Rietveld refinements to powder XRD diffraction patterns have been performed. The XRD patterns of the heated powdered samples (see Fig. 11) also confirm that the major phase in the final product is pyroxene with a minor phase of cristobalite. The cristobalite weight fraction is less than 1% for the heated tremolite and approximately 5% for heated actinolite. Compared to the powder XRD profile of an untreated diopside (not shown), the Bragg peaks in the heated amphibole powders are significantly broader. As a consequence of the line broadening, individual Bragg peaks are hardly resolved at high 2θ-angles (Fig. 11). The overall large widths of the Bragg peaks may be primarily attributed to strain effects in the crystallite bulk, arising from structural defects.
Rietveld refinements to the powder XRD patterns obtained from heated tremolite and actinolite reveal a structural resemblance with a synthetic Mg-rich diopside with a composition Ca$_{0.59}$Mg$_{1.41}$Si$_2$O$_6$ (ICSD entry #151117, Tribaudino et al. 2005). Given the relatively low resolution of the powder XRD data, the obtained atomic coordinates are in reasonable agreement with those of the synthetic sample (see Table 3). However, both decomposed tremolite and actinolite have a slightly larger unit-cell volume than the reference Mg-rich diopside, which is consistent with the broadened Raman peaks, indicating a high degree of structural defects in the pyroxene structure.

**Discussion**

Commonly, the amphibole-pyroxene breakdown is described in terms of end-member mineral formulas. For example, the tremolite-to-diopside decomposition at high temperatures is given as $\mathbf{\Delta} \text{Ca}_2\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \rightarrow 2\text{C aMgSi}_2\text{O}_6 + \text{ Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (Deer et al. 2013) or $\mathbf{\Delta}$

---

**Fig. 10** Thermogravimetric (mass loss) and differential thermogravimetric (DTG) curves along with mass-spectroscopic signals (m/z, mass per charge) for tremolite (a) and actinolite (b)
\[ a_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 \rightarrow 2\text{CaMgSi}_2\text{O}_6 + 3\text{MgSiO}_3 + \text{SiO}_2 + \text{H}_2\text{O} \quad \text{(Johnson and Fegley 2000), depending on pressure and surrounding conditions. However, comparison of the XRD pattern of thermally decomposed tremolite with that of a mechanical mixture of two pyroxenes with end-member compositions as well as with the XRD pattern of a pyroxene solid solution excluded the co-formation of pure diopside and enstatite as a possible mechanism of tremolite breakdown at high temperatures (Johnson and Fegley 2003).}

Our experimental data clearly indicate that the chief product of the thermally induced tremolite decomposition is a single solid-solution pyroxene phase, namely a defect-rich diopside with a chemical composition close to the midpoint on the diopside-clinoenstatite join. Besides, only a negligible amount (less than 1%) of cristobalite is formed as an additional minor phase. The obtained results are consistent with the following equation:

\[ a_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 \rightarrow \text{H}_2\text{O} + (\text{Ca}_2\text{Mg}_2)(\text{Mg}_2\text{Si}_8\text{O}_{22}) \]

(1)

where the formation of a water molecule is realized via a structural O atom and does not require external O\text{2}, that is, as mentioned above, the thermally activated dehydroxylation of tremolite causes its decomposition, regardless of the environment. Since Ca usually occupies the larger M2 site of the pyroxene structure (e.g. Deer et al. 2013), we have put the whole amount of Ca at the M2 site of the pyroxene chemical formula in Eq. (1) and assumed cation deficiency at the smaller M1 site in the pyroxene structure to compensate for the oxygen vacancies, the existence of which is revealed by the Raman-peak broadening.

The absence of external oxygen suppresses the Fe\text{2+} \rightarrow Fe\text{3+} exchange in amphibole (Mihailova et al. 2021; Della Ventura et al. in press). Thus, in reducing conditions, the actinolite breakdown should be also a one-step process. For example, assuming one Fe\text{2+} apfu in the structure, one should expect the following reaction:

\[ a_2\text{Ca}_2\text{Mg}_4\text{Fe}_{2}\text{Si}_8\text{O}_{22}(\text{OH})_2 \rightarrow \text{H}_2\text{O} + (\text{Ca}_2\text{Mg}_2)(\text{Mg}_2\text{Fe}_{2}\text{Si}_8\text{O}_{22}) \]

or

\[ a_2\text{Ca}_2\text{Mg}_4\text{Fe}_{2}\text{Si}_8\text{O}_{22}(\text{OH})_2 \rightarrow \text{H}_2\text{O} + 4\text{M}^2_2(\text{Ca}_{0.5}\text{Mg}_{0.25}\text{Fe}_{2}\text{Si}_2\text{O}_{5.75}) \]

(2a)

(2b)

That is, the final products from 1 mol actinolite would be 1 molecule water + 4 mol defect-rich Fe\text{2+}-bearing augitic pyroxene. Likewise in the case of tremolite decomposition, all Ca\text{2+} cations are assumed to be at the pyroxene M2 site, while the cationic vacancies are at the M1 site; the Fe\text{2+} cations can enter either site (e.g. Deer et al. 2013).

Our in situ high-temperature Raman scattering data combined with thermogravitometric data revealed that in oxidizing conditions the actinolite-to-pyroxene breakdown is realized in three stages: (i) reversible dehydrogenation triggered by the \text{Fe}^2_+ + \text{wOH} \rightarrow \text{Fe}^3_+ - \text{wO}_2^- reaction
Table 3 Structural parameters of pyroxene (M2M1T2O6) obtained for thermally decomposed tremolite and actinolite samples by Rietveld analysis compared to the corresponding data for the synthetic Mg-rich diopside ICSD152227, Ca0.59Mg1.41Si2O6 (Tribaudino et al. 2005)

| Parameter          | Decomposed tremolite | Decomposed actinolite | ICSD152227 |
|--------------------|----------------------|-----------------------|-------------|
| \(a (\AA)\)       | 9.7557 (13)          | 9.7502 (18)           | 9.7110 (6)  |
| \(b (\AA)\)       | 8.9332 (12)          | 8.9119 (15)           | 8.8935 (6)  |
| \(c (\AA)\)       | 5.2627 (8)           | 5.2697 (9)            | 5.2452 (3)  |
| \(\beta (^\circ)\)| 107.321 (12)         | 107.098 (13)          | 107.278 (5) |
| \(V (\text{Å}^3)\)| 437.84 (12)          | 437.66 (13)           | 432.56 (7)  |
| \(M2\)            | 0.2763 (13)          | 0.2836 (14)           | 0.2839 (7)  |
| \(U_{	ext{iso}}\) | 0.029 (6)            | 0.050 (7)             | 0.017 (2)   |
| \(M2_{\text{occ}}\)| 0.29 (5)             | 0.60 (6)              | 0.59 Ca     |
| \(M1_{\text{y}}\) | 0.9003 (15)          | 0.9094 (18)           | 0.9068 (9)  |
| \(U_{	ext{iso}}\) | 0.010 (4)            | 0.025                 | 0.006       |
| \(T_x\)           | 0.2927 (9)           | 0.2865 (9)            | 0.2902 (4)  |
| \(T_y\)           | 0.0857 (8)           | 0.0895 (9)            | 0.0929 (4)  |
| \(T_z\)           | 0.2503 (18)          | 0.2351 (18)           | 0.2444 (8)  |
| \(U_{	ext{iso}}\) | 0.040 (3)            | 0.033 (3)             | 0.005       |
| \(O1_{x}\)        | 0.1164 (17)          | 0.1108 (17)           | 0.1168 (4)  |
| \(O1_{y}\)        | 0.089 (2)            | 0.077 (3)             | 0.0893 (8)  |
| \(O1_{z}\)        | 0.143 (4)            | 0.133 (4)             | 0.1445 (15) |
| \(U_{	ext{iso}}\) | 0.094 (7)            | 0.078 (9)             | 0.006       |
| \(O2_{x}\)        | 0.3706 (14)          | 0.3741 (13)           | 0.3665 (6)  |
| \(O2_{y}\)        | 0.2422 (15)          | 0.2442 (16)           | 0.2506 (6)  |
| \(O2_{z}\)        | 0.347 (3)            | 0.335 (3)             | 0.3301 (19) |
| \(U_{	ext{iso}}\) | 0.025 (5)            | 0.014 (6)             | 0.009 (2)   |
| \(O3_{x}\)        | 0.3445 (14)          | 0.3590 (17)           | 0.3514 (7)  |
| \(O3_{y}\)        | 0.0114 (15)          | 0.0126 (17)           | 0.0212 (2)  |
| \(O3_{z}\)        | 0.007 (3)            | -0.004 (4)            | 0.0077 (9)  |
| \(U_{	ext{iso}}\) | 0.025 (5)            | 0.077 (7)             | 0.008       |

Full Mg-occupancy was assumed for M1. \(U_{	ext{iso}}\) of M1 for decomposed actinolite was fixed to 0.025 to prevent it from becoming non-positive definite.

generating mobile charge carriers (\(H^+\) and \(e^-\)) in the crystal bulk, (ii) irreversible partial dehydrogenation caused by the ejection of \(e^-\) from crystal and \(1/2H_2\), but still without a structure collapse, and (iii) dehydroxylation in the presence of external \(O_2\), leading to the final formation of a pyroxene (see also the sketch in Fig. 12):

\[
\begin{align*}
\text{\(^{\Lambda}\)Ca}_2\text{Mg}_4\text{Fe}^{2+}\text{Si}_8\text{O}_{22}(\text{OH})_2 & \rightarrow \text{H}^+ + e^- + \text{\(^{\Lambda}\)Ca}_2\text{Mg}_4\text{Fe}^{3+}\text{Si}_8\text{O}_{22}[\text{O}^{2-}\text{OH}^-] \rightarrow \\
1/2\text{H}_2 + \text{\(^{\Lambda}\)Ca}_2\text{Mg}_4\text{Fe}^{3+}\text{Si}_8\text{O}_{22}[\text{O}^{2-}\text{OH}^-] & \rightarrow \\
1/2\text{H}_2 + 1/2\text{H}_2\text{O} + (\text{Ca}_2\text{Mg}_2)(\text{Mg}_2\text{Fe}^{3+}\square)\text{Si}_8(\text{O}_{23.5}\square_{0.5}) & \rightarrow \\
= \text{H}_2\text{O} \text{ (with 1/4O}^{2+}) + 4\text{M}^{11}(\text{Ca}_{0.5}\text{Mg}_{0.5})^{\text{M}^{11}}(\text{Mg}_{0.5}\text{Fe}^{3+}\square_{0.25}\square_{0.25})\text{Si}_2(\text{O}_{5.875}\square_{0.125})
\end{align*}
\]

In this case, the resulting products from 1 mol actinolite would be 1 molecule water + 4 mols defect-rich \(\text{Fe}^{3+}\)-bearing pyroxene of augitic type.

Although the exact temperatures separating the three steps towards actinolite-pyroxene breakdown should depend on the heating kinetics and crystalline-grain size, our data suggest that: (i) reversible delocalization of \(e^-\) from octahedrally coordinated Fe as well as of \(H^+\) from W sites next to Fe-containing \(M(1)M(1)M(3)\) species may take place up to 1250 K (marked by the minimum of the wavenumber of the \(\text{SiO}_4\)-ring mode near 673 cm\(^{-1}\)); (ii) irreversible dehydrogenation and ejection of \(e^-\) occurs between 1250 and 1350 K, where actinolite can be considered as “oxo-actinolite” because \(H^+\) from the W sites also next to \(M(1,3)\)(MgMgMg) configurations are entirely delocalized but at least partially still within the crystal bulk (as indicated by the reappearance of the \(M(1,3)\)(MgMgMg) OH-stretching peak on cooling); (iii) complete dehydroxylation and consequent structure collapse above 1350 K.

It is worth noting that stages (i) and (ii) may overlap, because the delocalization of \(e^-\) and \(H^+\) in the crystal bulk and their gradual ejection from the crystal surface may occur as simultaneously ongoing processes. Within both stages, actinolite is still stable and possesses mobile charge carriers in its bulk, but most probably ionic conductivity related to \(H^+\) detached from \(M(1,3)\)(MgMgMg) configurations is dominant in stage (ii). Another point to be made is that stage (iii) may consist of release of both molecular water and molecular hydrogen, without the necessity of involving external molecular oxygen, similar to the mechanism of thermal alteration proposed for minnesotaite (Lempart-Drozd et al. 2022). Therefore, external \(O_2\) is required for the most efficient release of water in the surrounding, after the amphibole breakdown and its transforms into a pyroxene.

Conclusions

The following conclusions can be derived from this study:

- In the temperature range 300–800 K, the phonon expandabilities of actinolite are the same in air and \(N_2\) atmosphere and their difference to the corresponding phonon expandabilities of tremolite is negligibly small. There-
fore, in this temperature interval, the presence of Fe$^{3+}$ as a minor element in Ca amphiboles is insignificant for the thermal behaviour of the mineral.

- Thermally activated delocalized $e^-$ and H$^+$ are also formed in Fe-bearing magnesian amphiboles, but at much higher temperatures than in ferrous (e.g. grunerite) and mixed-valence iron-rich amphiboles (e.g. riebeckite).
- Similar to Fe-rich amphiboles, the delocalized electrons in actinolite couple with polar FeO$_6$ phonons to form polarons with anisotropic mobility, being predominantly along the I-beams. However, the alignment of the polaronic dipoles in actinolite is not complete as in Fe-rich amphiboles, because iron cations are present in the actinolite structure as isolated octahedra or dimers of octahedra, while the majority of MO$_6$ octahedra in the strips are occupied by Mg.
- The final product of the thermally induced decomposition of both actinolite and tremolite is a single phase of monoclinic pyroxene with an intermediate chemical composition between diopside and clinoenstatite, having vacancies at the octahedral sites and, for actinolite, also Fe$^{3+}$. Crystobalite occurs only as a minor phase in amounts less than 1% and ~5% for tremolite and actinolite, respectively.
- The dehydroxylation of tremolite causes immediate collapse of the silicate double chain into SiO$_4$ single chains, which is followed up by a rearrangement of the amphibole B-type and C-type cations into pyroxene octahedral sheets.
- The actinolite-to-pyroxene breakdown is preceded by a state of “oxo-actinolite” in which all Fe$^{2+}$ are exchanged to Fe$^{3+}$, all W(OH)$^-$ groups next to Fe-containing $M(1)M(1)M(3)$ configurations are exchanged to $W$O$_2^-$, and all H$^+$, including those from W anions next to MgMgMg triads, are delocalized, but still in the bulk of the crystal grain.

Acknowledgements Financial support by the Deutsche Forschungsgemeinschaft (MI 1127/7-2) is gratefully acknowledged.

Author contributions CR and NW collected, evaluated, and analysed the Raman spectroscopic data. NP performed the thermogravimetric analyses. TM performed the XRD analyses. JS provided the samples and contributed to all analyses. BM contributed to all analyses, summarized the results, and wrote the paper. All authors reviewed the manuscript.

Funding Open Access funding enabled and organized by Projekt DEAL. This research has been financially supported by the Deutsche Forschungsgemeinschaft (Project MI 1127/7-2).

Data availability The datasets generated during the current study are available from the corresponding author upon request.

Declarations

Conflict of interest The authors declare that they have no conflict of financial or non-financial interests that are directly or indirectly related to the work submitted for publication.

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