

Article

FTIR Spectroscopy of the Regulated Asbestos Amphiboles

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Abstract: Vibrational spectroscopies (FTIR, Raman) are exceptionally valuable tools for the identification and crystal-chemical study of fibrous minerals, and asbestos amphiboles in particular. Raman spectroscopy has been widely applied in toxicological studies and thus a large corpus of reference data on regulated species is found in the literature. However, FTIR spectroscopy has been mostly used in crystal-chemical studies and very few data are found on asbestos amphiboles. This paper is intended to fill this gap; we report new FTIR data collected on a suite of well-characterized samples of the five regulated amphibole species: anthophyllite, amosite and crocidolite, provided by the Union for International Cancer Control (UICC) Organization, and tremolite and actinolite, from two well-known occurrences. The data from these reference samples have been augmented by results from additional specimens to clarify some aspects of their spectroscopic features. We show that the FTIR spectra in both the OH-stretching region and in the lattice modes region can be effective for rapid identification of the asbestos type.

Keywords: regulated asbestos amphiboles; FTIR spectroscopy, FEG-FESEM, TEM, SAED patterns

1. Introduction

The term "asbestos" is a misleading non-scientific commercial term [1], which commonly refers to silicate minerals with fibrous morphology [2]. From a legal perspective, six fibrous minerals are regulated as asbestos minerals: five species of the amphibole group, and chrysotile, which belongs to the serpentine group of the layer silicates [3-5]. From a mineralogical point of view, chrysotile has only limited variations from its ideal crystal-chemical composition described as $Mg_3(OH)_4Si_2O_5$ [6], whereas amphiboles exhibit extremely wide ranges in composition, even in samples from the same outcrop, in the same rock or within the same (zoned) crystal [7-10]. Such chemical variability results in significant challenges for identification and classification of amphiboles, implying difficulties for health and legal issues arising from exposure to the amphibole fibres [11-12]. Another critical aspect concerns the textural features describing "asbestiform", "fibrous" or "acicular" minerals [9,13-16]. According to the criteria of the World Health Organization (WHO), a regulated "fibre" is an elongated particles with a length $\geq 5 \mu m$, a width $\leq 3 \mu m$, and an aspect ratio (length:width) $\geq 3:1$. Needle-like crystals not fulfilling this criterion are more correctly termed "acicular"; we will use these definitions throughout this text.

Accurate and full characterisation of asbestos fibres and their host rocks requires a combination of several analytical techniques, most notably optical microscopy, scanning and transmission electron microscopy (SEM and TEM), X-ray diffraction (XRD) and vibrational spectroscopy (FTIR, Raman) [16]. Both FTIR and Raman spectroscopy have been applied for the

identification of fibres in environmental or biological/medical applications, where the identification of the sample was the main goal. However, a careful examination of the literature reveals that, although Raman spectra are available as reference data for the correct fibre identification, reference FTIR data for the regulated mineral species are lacking.

To fill this gap, we provide here FTIR data for well-characterized samples of the five regulated amphibole species: anthophyllite, amosite and crocidolite, provided by the Union for International Cancer Control (UICC) Organization, as well as tremolite and actinolite, which are from two well-known occurrences and were diffusively used in several previous studies. Where needed, the data from these reference samples have been augmented by, and compared with, results from additional specimens to clarify some of the spectroscopic features. All mineral samples used in this study have been examined by FEG-environmental SEM (FEG-ESEM) and TEM prior to their characterization by FTIR. The FTIR data presented shall serve as a reference data set when dealing with fibrous materials in environmental or toxicological studies.

2. Vibrational spectroscopy applied to the crystal chemistry of fibrous amphiboles

FTIR and Raman spectroscopy are frequently used for the characterisation of Earth and analogue materials [17-19]. Both methods have been used extensively for rapid identification of asbestosiform minerals and the characterization of their site occupancies [8, 20-23]. Vibrational spectra can be collected either on powders or on single crystals, requiring only a very small amount of material (mg), such as tiny crystals with sizes ranging from some μm to few tens of μm . The spatial resolution of conventional Raman spectroscopy is better than that of FTIR spectroscopy, but similar to that of an IR beam at a synchrotron source [24-25]. Commonly, FTIR data are collected on few mg of powdered asbestos samples dispersed in a salt matrix (e.g., KBr, NaCl) to form a pellet (see below). Asbestos materials can also be analysed by diffuse-reflectance IR spectroscopy (DRIFT), where the IR beam is scattered by the rough sample surface, collected by a mirror and then sent to the detector [26]. This technique is helpful when studying cement-asbestos, because the powder to be analysed can be easily scratched off a wall, a brick or a roof tile by using an abrasive paper, and subsequently placed onto the DRIFT sample holder without any further preparation.

The vibrational spectrum of an amphibole (as well as of all hydrous silicates) is conventionally divided into two ranges: the higher wavenumber region ($4000\text{-}3000\text{ cm}^{-1}$) where typical bands due to water/OH stretching are observed, and the lower wavenumber range ($< 1200\text{ cm}^{-1}$), where bands resulting from longer bonds, such as those of the tetrahedral skeleton, the cation-oxygen (\geq six-fold) polyhedra or the bending/libration modes, are found. The near-infrared (NIR) region, at wavenumbers $10,000\text{-}4,000\text{ cm}^{-1}$, although rarely used, is also of significant interest due to the possible applications in remote sensing [27].

Amphiboles may crystallize in several different space groups, but the $C2/m$ is by far the most common [28]. Their OH-stretching (3000 to 4000 cm^{-1}) FTIR and Raman spectra are very similar and show identical band multiplicity and band wavenumbers [25-26, 29]; by contrast, band intensities can be significantly different, a feature that has important consequences in quantitative analysis [30]. At low frequency, the lattice mode region ($< 1200\text{ cm}^{-1}$) can display a large number of peaks for a $C2/m$ amphibole [29]. Such complex spectra, typically consisting of many overlapping bands, prevent a reliable assignment of the observed modes to a single molecular motion. Moreover, in this low-frequency region, IR and Raman spectra are significantly different [26]. For mineral identification and crystal-chemical studies, however, the spectral results can be used by comparison with a relatively large dataset available in the literature, collected on samples spanning the complete compositional space of environmental/biological interest. Here, we focus on completing this set of reference data for FTIR, which are lacking or scattered throughout the literature.

In amphiboles, the OH group is directly bonded to three cations in six-fold coordination, labelled $M(1)$ and $M(3)$, forming the base of a nearly equilateral triangle around the OH group (Fig. 1a). The O-H distance is extremely short ($\sim 0.96\text{ \AA}$ [31]), and consequently, the OH-stretching modes occur at very high wavenumbers ($3750\text{-}3600\text{ cm}^{-1}$).

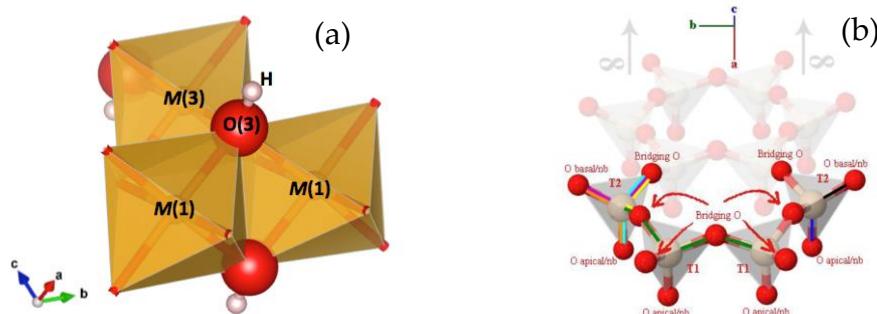


Fig. 1. (a) Local octahedral configuration around the OH group in amphiboles. (b) Schematic representation of the double-chain of tetrahedra in amphiboles, from [80].

This frequency range is almost invariably free from interferences by other absorptions, which represents a clear advantage of O-H stretching spectroscopy. The exact position (i.e., energy) of the principal OH-stretching band(s) scales with the relative strength of the O-H bond that is also depending on the degree of hydrogen bonding between the H atom and the surrounding O atoms. In other words, both the strength and the length of the O-H bond are extremely sensitive to any local arrangement of atoms around the OH group. This aspect makes IR and Raman spectroscopy very important tools for crystal-chemical studies of hydrous silicates. Details on how the exact position of the bands observed in the OH-stretching spectra of amphiboles can be used as a tool for their characterization can be found in a vast body of literature (see [21] and [32] for a complete list of references). Specifically, applications to the study of fibrous amphiboles can be found in [8, 26 and 33].

3. Materials and Methods

A list of the samples used for this investigation, including mineral formulae and information on their occurrence, is given in Table 1.

Table 1. Studied samples

Amphibole species	Provenance	Reference
Anthophyllite	UICC standard Anthophyllite from Paakkila, NB #4173-111-5	[36, 37]
Anthophyllite	AMNH34856, Talcville, New York State (USA)	[42]
Anthophyllite	MNHN 29_102	Della Ventura, unpublished
Amosite	UICC standard Amosite South African NB #4173-111-4	[36, 37]
Crocidolite	UICC standard Crocidolite South African NB #4173-111-3	[36, 65, 38]
Crocidolite	Madagascar	[61]
Tremolite	Val d'Ala, Turin (Italy)	[36, 64]
Actinolite	Valle Aurina (Bolzano, Italy)	[66]

Powder FTIR spectra were collected on KBr pellets, using 5:150 and 0.5:150 mg ratios for the 3000-4000 and <1200 cm^{-1} regions, respectively. Single-crystal FTIR spectra in the OH-stretching medium-infrared (MIR) and NIR regions (7000-4000 cm^{-1}) were collected with unpolarized light using a Bruker Hyperion 3000 microscope equipped with a MCT detector and a KBr beam splitter at Istituto Nazionale di Fisica Nucleare (INFN, Frascati, Rome).

For SEM analysis, the mineral powders were dispersed in 2-propanol and ground by hand, using an agate mortar for 3 min, resulting in a homogeneous suspension. A FEI Quanta 600 Field-Emission-Gun Mark II Environmental Scanning Electron Microscope (FEG-ESEM) was used to investigate the samples. Environmental SEM allows for observation of the sample without the need of a conductive coating, and thus, the 2-propanol suspensions containing the amphiboles were directly transferred onto a conductive carbon tape fixed onto a SEM stub (12.7 mm diameter). The instrument was set to environmental mode with a voltage of 15 kV and a chamber pressure of 0.53 Torr. Variable beam dimension was used to optimize imaging and semi-quantitative chemical analysis (in general, sizes 3 and 6, respectively). Chemical data obtained with the SEM through energy-dispersive X-ray (EDX) spectroscopy were used exclusively to confirm the identity of the studied specimen.

TEM analyses were conducted on a JEOL 2010F TEM and involved a combination of imaging and high-resolution (HRTEM) techniques together with selected area electron diffraction (SAED). The microscope was operated at 200 kV combining different sets of objective apertures, selected area apertures and camera lengths to optimize the observations. All examinations were performed on a minimum of 50 fibres.

4. Results

In the following paragraphs, we will discuss the general crystal-chemical features of the studied samples together with the FTIR data collected in the OH-stretching region. In the subsequent section, we will discuss the spectra obtained in the lower frequency (<1200 cm⁻¹) region.

4.1. UICC anthophyllite asbestos. Anthophyllite has the ideal end-member composition ${}^A\Box^B(Mg)_2{}^C(Mg)_5{}^TSi_8O_{22}W(OH)_2$. According to the most recent IMA classification, anthophyllite belongs to the magnesium-iron-manganese subgroup, defined by ${}^B(Ca + \Sigma M^{2+})/\Sigma B \geq 0.75$, $B\Sigma M^{2+}/\Sigma B > BCa/\Sigma B$. Amphiboles of this subgroup may be orthorhombic (space groups *Pnma* or *Pnmm*) or monoclinic (space groups *C2/m* or *P2₁/m*). End-member anthophyllite is orthorhombic, with a potential solid-solution toward ferro-anthophyllite ${}^A(\Box){}^B(Fe^{2+})_2{}^C(Fe^{2+})_5{}^TSi_8O_{22}W(OH)_2$. The monoclinic *P2₁/m* and Mg-rich polymorph of the series is named cummingtonite, where a low amount of Fe²⁺ at both B- and C-sites stabilizes the *C2/m* polytype [34].

Anthophyllite has a colour ranging between dull green to white; it typically occurs in metamorphic rocks of the lower to middle amphibolite facies and in serpentinized ultrabasic rocks [7], where it almost invariably grows as distinctly fibrous crystals. Anthophyllite was industrially employed in limited amounts, mainly for insulation products and construction materials; it frequently occurs as a contaminant in chrysotile asbestos, vermiculite and talc [7]. The main commercially exploited deposits are those in metamorphosed dunites and harzburgites of Eastern Finland (Paakkila and Maljasalmi), where anthophyllite was formed as a replacement of olivine and orthopyroxene during the serpentinization of the host rock. The UICC sample investigated here is from Paakkila (Tab. 1). Similar occurrences are known in the U.S., such as in Idaho, Georgia and North Carolina [35].

Table 2. XRD data for the studied reference amphiboles

sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	space group	Ref
Anthophyllite UICC	18.5770(8)	18.0353(22)	5.27285(9)	90	<i>Pnma</i>	[37]
Amosite UICC	9.5484(2)	18.3395(4)	5.3346(1)	101.825(2)	<i>C2/m</i>	[37]
Crocidolite UICC	9.73238(7)	18.0414(1)	5.32794(4)	103.515(1)	<i>C2/m</i>	[36]
Tremolite Ala	9.8424(1)	18.0712(2)	5.28354(7)	104.680(1)	<i>C2/m</i>	[64]
Actinolite Aurina	9.84896(4)	18.07748(8)	5.28860(2)	104.817(2)	<i>C2/m</i>	[66]

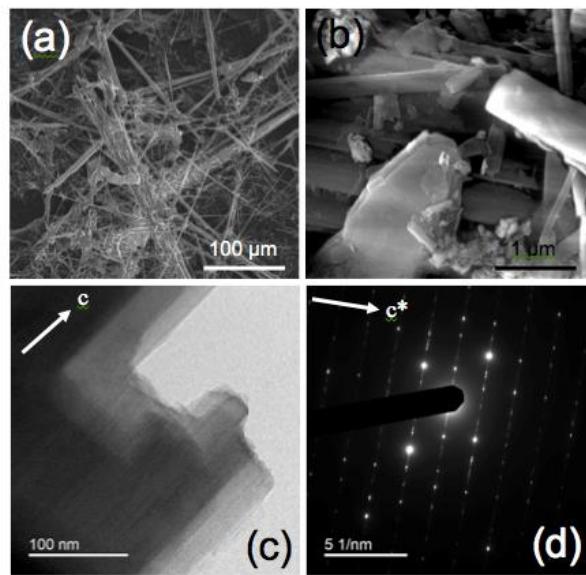


Figure 2. UICC standard anthophyllite Finnish NB #4173-111-5 sample (Tab. 1). Representative FEG-ESEM images at relatively low (a) and high (b) magnification, where a platy talc particle is visible. (c) High-resolution TEM image highlighting edge features of fibre viewed along the c axis, and (d) SAED pattern parallel to the c^* axis.

According to the X-ray powder diffraction (XRPD) analysis given in [36,37], the studied sample consists of amphibole with impurities of biotite, clinochlore/vermiculite and talc. The refined unit-cell data (Tab. 2) are in agreement with previous data for similar amphiboles [28].

FEG-ESEM images (Fig. 2a) show that the sample consists of asbestosiform to acicular crystals

Table 3. Microchemical data for the studied reference amphiboles. *Partition determined from Mössbauer spectroscopy[82].

Sample	Anthophyllite UICC	Amosite UICC	Crocidolite UICC	Tremolite	Actinolite
reference	[37]	[37]	[36]	[64]	[66]
SiO ₂	57.3(4)	49.8(2)	51.7(3)	57.8(1)	54.83(5)
TiO ₂	0.02(2)	0.04(2)	0.03(3)	0.02(2)	0.04(9)
Al ₂ O ₃	0.11(5)	0.04(2)	0.12(4)	0.11(7)	2.70(6)
FeO	9.9(7)	37.8(4)	17.3(9)*	2.4(4)*	6.76(5)
Fe ₂ O ₃	0.0	3.3(4)	18.7(9)*	0.3(4)*	1.01(5)
Cr ₂ O ₃	0.04(3)	0.01(1)	0.01(1)	0.02(2)	0.08(9)
NiO	0.04(4)	0.02(4)	0.01(2)	0.08(5)	0.18(2)
MnO	0.4(1)	0.42(6)	0.04(2)	0.15(5)	0.40(7)
MgO	28.5(2)	6.23(9)	2.3(4)	22.8(2)	18.21(3)
CaO	0.27(7)	0.09(1)	0.22(7)	12.9(1)	12.77(6)
Na ₂ O	0.02(1)	0.03(2)	6.7(2)	0.23(6)	0.48(6)
K ₂ O	0.02(1)	0.02(1)	0.05(4)	0.05(2)	0.13(3)
H ₂ O	2.30	1.94	2.18	2.02	2.47
Total	98.92	99.74	99.36	98.88	100.06

with dimensions averaging 1 μm in width and more than 100 μm in length. Larger bundles of acicular crystals, a few tens of μm in width, are also common. In agreement with the XRPD data, lamellar and platy particles of talc are recognizable in the FEG-FESEM images (Fig. 2b). The fibres show very straight edges and low amounts of amorphous material along the surfaces. Several stepped features can be detected at the apex and along the edges of the fibres (Fig. 2c).

The SAED patterns obtained by TEM display the typical amphibole streaking normal to the c axis (Fig. 2d), which results from diffuse chain-width errors (chain multiplicity faults: CMF). Published microchemical data (Table 3) show that the UICC anthophyllite contains appreciable amounts of iron; Mössbauer and XAS data indicate that Fe is present entirely as Fe^{2+} [38]. Additional components include Mn (0.04 apfu) and trace amounts of Ni, Cr, and Ca.

The FTIR spectrum in the OH-stretching region (Fig. 3) of the UICC sample displays a

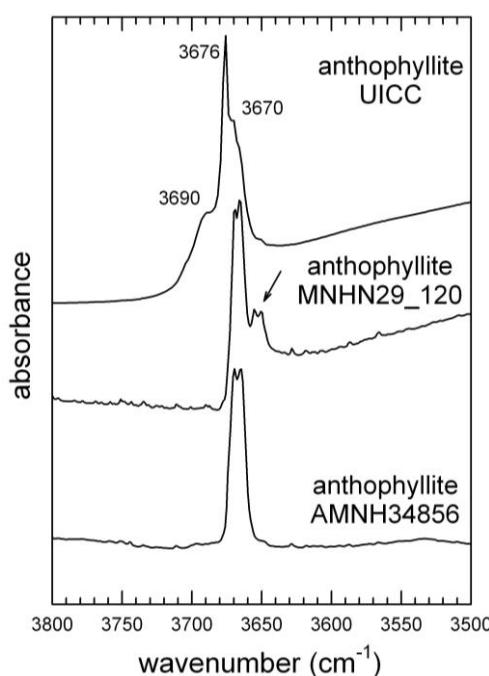


Figure 3. FTIR OH-stretching spectra of the studied UICC standard Anthophyllite Finnish NB #4173-111-5 compared to anthophyllite AMNH34856 (Welch et al., 2011) and sample MNHN29_102.

relatively broad absorption consisting of several overlapping bands at 3690, 3676 and 3670 cm^{-1} , with the 3676 cm^{-1} band being the sharpest and most intense. This type of pattern does not match the pattern expected by considering the local configuration of the OH group in amphiboles [21] with anthophyllite composition [39]; FTIR spectra of four ($\text{Mg}, \text{Fe}^{2+}$) anthophyllites published by [40] indeed show, in the OH-stretching region, four components, namely at 3666, 3654, 3639 and 3618 cm^{-1} , whose relative intensities are correlated with the Mg/Fe^{2+} ratio at M(1,3). Ishida and Hawthorne [41] later reported that anthophyllite shows considerable fine structure in the form of band splitting of the principal OH-stretching region, indicative of an orthorhombic symmetry with two very similar but crystallographically independent OH groups [28].

To further corroborate the FTIR data, we collected infrared spectra of two well-characterized anthophyllite-group minerals, for comparison (Table 1). For the amphibole from Norway (MNHN 29_102), we could collect a powder FTIR spectrum, whereas for that from Talcville (AMNH34856), we could collect only a single-crystal spectrum due to the scarcity of material. The anthophyllite from Norway shows (Fig. 3) a two-band pattern resulting from the presence of small amounts of Fe^{2+} at M(1,3) (Della Ventura, unpublished data), whereas the

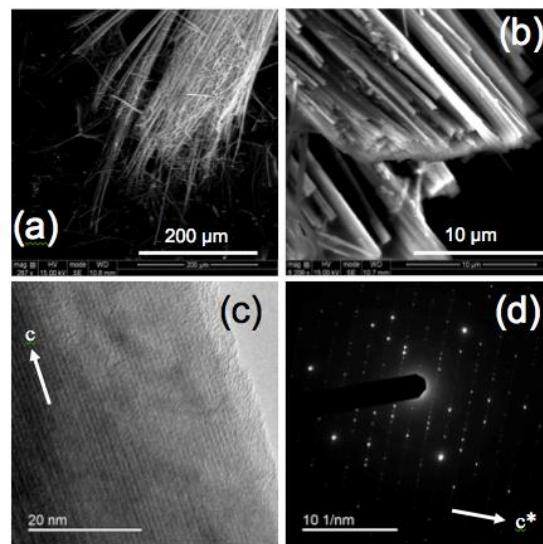


Figure 4. UICC amosite from South Africa NB #4173-111-4 (Tab. 1). Representative FEG-ESEM images at relatively low (a) and high (b) magnifications. (c) HR-TEM image documenting a limited-extent amorphous cover layer, and (d) SAED pattern parallel to the c^* axis.

anthophyllite from Talcville shows only one band (Fig. 3). This latter amphibole indeed represents a reference point for this species, because it exhibits nearly end-member composition; its complete crystal-chemical characterization [42], which included EMPA and XRPD data, returned the formula $^A\text{Na}_{0.01}^B(\text{Mg}_{1.30}\text{Mn}_{0.57}\text{Ca}_{0.09}\text{Na}_{0.04})^C(\text{Mg}_{4.95}\text{Fe}_{0.02}\text{Al}_{0.03})^T(\text{Si}_{8.00})\text{O}_{22}\text{W}(\text{OH})_2$, with significant Mn at $M(4)$ only. Therefore, only Mg is present at the OH-coordinated $M(1,3)$ -sites, besides trace amounts of Fe^{2+} and Al. In agreement with these results, only one band is present in the OH-stretching region. Inspection of Figure 3 shows, however, that the OH-stretching bands of both these samples are evidently split into two components at 3666 - 3671 cm^{-1} (splitting factor $\Delta = 5\text{ cm}^{-1}$), which are observed only at high resolution ($\leq 2\text{ cm}^{-1}$), both in powder and single-crystal spectra. The observed splitting is thus a direct evidence for the symmetry of the amphibole to be either $Pnma$ or $P2_1/m$. Based on the above discussion, in the FTIR spectrum of the UICC anthophyllite, the sharp peak at 3676 cm^{-1} is assigned to talc, whereas the broad absorption at 3690 cm^{-1} can be assigned to clinochlore/vermiculite impurities [39]. According to the Rietveld refinement results of [37], the UICC anthophyllite is orthorhombic $Pnma$, but the band splitting in the OH spectrum is not observable due to the overlap with the signals from the talc and clinochlore impurities. We also note that, although the sample contains significant Fe (Table 3), no absorptions due to local configurations, such as MgMgFe or MgFeFe , are observed in the spectrum. This is consistent with the fact that in the UICC anthophyllite, all ferrous iron is ordered at $M(4)$, whereas the $M(1,2,3)$ octahedra have a composition $\text{Mg} = 5.0$ apfu [37]. Anthophyllite MNHN 29_102 contains 13.0 wt% Fe, and the FTIR spectrum shows two split O-H absorptions (Fig. 3) again consistent with a $Pnma$ or $P2_1/m$ symmetry; however, the presence of the 3655 - 3650 cm^{-1} doublet (highlighted by the arrow in Fig. 3) indicates that Fe^{2+} is partially disordered at $M(1,3)$ in this sample.

4.2. UICC amosite (grunerite asbestos). The commercial material "amosite", an acronym for "Asbestos Mines of South Africa", is commonly referred to as "brown asbestos". It corresponds to the amphibole-group mineral grunerite, which is characterized by the ideal formula $^A(\square)^B(\text{Fe}^{2+})_2^C(\text{Fe}^{2+})_5^T(\text{Si})_8\text{O}_{22}\text{W}(\text{OH})_2$ and monoclinic $C2/m$ symmetry; the orthorhombic polymorph is instead labelled ferro-anthophyllite. Complete Fe^{2+} -Mg solid-solution may exist along the monoclinic grunerite-cummingtonite series, which is correlated to a symmetry adjustment from $P2_1/m$ to $C2/m$ [43,44]. Hence and in spite of the chemical simplicity involving the homovalent Mg - Fe^{2+} exchange, the amphiboles of the magnesium-iron-manganese subgroup can crystallise with different structures, a feature that is strongly correlated to the size of the B-site cations [45-48]. Notably, the Mg-end member anthophyllite is orthorhombic, the Mg-rich (or Fe-poor) cummingtonite is $P2_1/m$, whereas

the Fe-rich (or Mg-poor) grunerite is $C2/m$ [49-50].

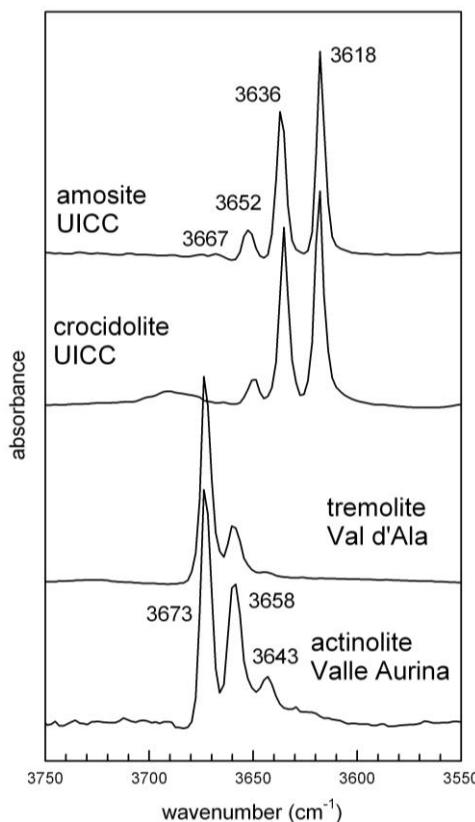


Figure 5. FTIR OH-stretching spectra of the studied amphiboles (Tab. 1): UICC amosite from South African NB #4173-111-4, UICC crocidolite NB#4173-111-3, tremolite from Val d'Ala, and actinolite from Valle Aurina.

The members of the cummingtonite-grunerite series are typically found in Ca-poor regionally and contact metamorphosed rocks; they are well known from metamorphosed banded iron formations (BIF). Amosite fibres, up to several cm long, occur interbedded within ironstones [51]. Mg-rich compositions are also reported from igneous environments [7]. Amosite was used most frequently in cement sheets and pipe insulation, insulating boards, ceiling tiles, and thermal insulation products. Although cummingtonite-grunerite amphiboles are relatively common, there is only one locality where these materials have been commercially exploited, i.e. the metamorphic iron formations of Eastern Transvaal (South Africa). We characterise here the standard UICC material, sourced from the Transvaal locality (Tab. 1). The same material was investigated with XRPD by [37], showing it to consist of amphibole with impurities of calcite, hematite and quartz. Rietveld refinement demonstrated that the sample is monoclinic $C2/m$, with the lattice parameters listed in Table 2, in agreement with previous data for similar amphiboles [28]. Specifically, the measured small β angle agrees well with monoclinic amphiboles hosting small divalent cations (Mg and/or Fe^{2+}) at the B-site. FEG-FESEM images of the studied UICC amosite (Fig. 4a and 4b) revealed that the sample consists of $\approx 1\ \mu m$ wide fibres, which are arranged in parallel fashion to form elongated bundles with lengths of several hundred μm . In addition, the amosite fibres exhibit crystal defects (CMF), which are visible in HRTEM images (Fig. 4c) and confirmed by streaking normal to the c^* direction, as observed in the SAED patterns (Fig. 4d). The SAED patterns display defined spots as well as disordered reflections, which exhibit less intense streaking than those in anthophyllite. Many fibres have an extended amorphous surface cover, with a thickness ranging between 1 and 5 nm (Fig. 4c). Inspection of the available chemical data for the UICC amosite reveals that this sample is close to the Fe-end member composition, but contains significant amounts of Mg (6.23 wt.% of MgO) and ferric iron (3.9 wt.% of Fe_2O_3). Trace elements include Ti, Cr, Ni, Mn, Ca and alkalis (Table 3). The FTIR spectrum of the UICC amosite in the OH-stretching region (Fig. 5) shows three well-resolved peaks at 3652, 3636 and

3618 cm^{-1} , as well as an additional, very weak peak at 3667 cm^{-1} . The spectrum is consistent with the distribution of Mg and Fe^{2+} at the C-sites, the observed bands being assigned to hydroxyl groups bonded to MgMgMg , MgMgFe^{2+} , $\text{MgFe}^{2+}\text{Fe}^{2+}$ and $\text{Fe}^{2+}\text{Fe}^{2+}\text{Fe}^{2+}$ octahedral clusters, from higher to lower frequency, respectively. Moreover, no bands due to the presence of Fe^{3+} are observed in this spectrum [52-53], demonstrating it to be fully ordered at the $M(2)$ -site. The peaks of UICC amosite are sharp, with a nearly Lorentzian shape and without any hyperfine splitting such as that observed for anthophyllite (Fig. 3). These features are indicative of a well-ordered $C2/m$ structure. It is known since the pioneering work of [54] and [55] that the relative intensities (peak area) of the four components observed in the OH-spectrum of amphiboles is correlated to the Fe^{2+}/Mg occupancy at the hydroxyl-coordinated $M(1,3)$ sites. This feature has been validated later with the analysis of several sets of synthetic solid-solution series with varying and controlled composition at the octahedral strip [56-60]. Deconvolution of the OH-spectrum of UICC amosite is relatively straightforward due to the peak sharpness and lack of band overlapping; following the method described in [26], a value of $M^{(1,3)}\text{Fe}^{2+} = 2.40$ apfu (atoms per formula unit) is obtained, in excellent agreement with the value derived from site-occupancy refinement via the Rietveld method from synchrotron-radiation XRD data [37].

4.3 UICC crocidolite (riebeckite asbestos). Crocidolite, the so-called "blue asbestos", is the most popular and commercially employed amphibole asbestos. Mineralogically, it corresponds to the end-member riebeckite, which has the nominal formula ${}^A(\square){}^B(\text{Na})_2{}^C(\text{Fe}^{2+}{}_3,\text{Fe}^{3+}{}_2){}^T(\text{Si})_8\text{O}_{22}\text{W}(\text{OH})_2$ and is classified in the sodic amphibole subgroup defined by ${}^B(\text{Na} + \text{Li})/\Sigma B \geq 0.75$, ${}^B\text{Na}/\Sigma B \geq {}^B\text{Li}/\Sigma B$ [34]; mineral species in this group invariably display the monoclinic $C2/m$ symmetry. The chemical composition of riebeckite can vary substantially, primarily due to two main substitutions at the C-sites, i.e. $\text{Fe}^{2+} \leftrightarrow \text{Mg}$ and $\text{Fe}^{3+} \leftrightarrow \text{Al}$ [53]. These amphiboles are typical constituents of acidic igneous rocks, such as granites and quartz syenites, as well as high-grade metamorphic rocks. The fibrous varieties are essentially found in meta-ironstones, where the blue asbestos occurs in columnar and slip-fibre veins, whose origin is connected with rock deformation coupled to intense activity of metamorphic/metasomatic fluids. This extensively exploited asbestos material was used massively for insulation of steam engines, but also for some spray-on coatings, pipe insulation, plastics and cement products. Notable occurrences of crocidolite are those of Bolivia, Western Australia (Hamersley Iron province) and South Africa (Transvaal and Cape Province). Here, we consider the UICC standard from South Africa (Tab. 1).

XRPD data for the amphibole studied here can be found in [36]; accordingly, the sample consists of amphibole plus very minor amounts of hematite, magnetite, quartz, talc and lizardite. The lattice dimensions of the amphibole are given in Table 2. A representative FEG-FESEM image (Fig. 6a) shows that the sample consists of parallelly arranged fibres with a width of 0.5-1.0 μm and a length of 50-100 μm . HRTEM and SAED (Fig. 6b-d) images document that the sample is the most defective and feature-rich of the studied amphiboles. CMFs are pervasive, together with a diffuse presence of Moiré fringes. The surface of many fibres is covered by an amorphous layer. As is the case for all investigated amphiboles, this surface layer, when present, can be identified as Si-rich amorphous material or as ferrihydrite; additional higher-resolution analytical techniques must be used to distinguish between the two materials without inducing beam-damage artefacts in the studied region that could lead to erroneous conclusions. Microchemical data of this studied UICC crocidolite (Table 3) show that the only significant departure of the amphibole from an end-member riebeckite composition is the presence of low, but significant amounts of Mg (0.52 apfu) at $M(1,3)$; the ferric iron content is also very close to the ideal value ($\text{Fe}^{3+} = 2.05$ apfu). Trace elements include Ti, Cr, Ni, Mn, and Ca.

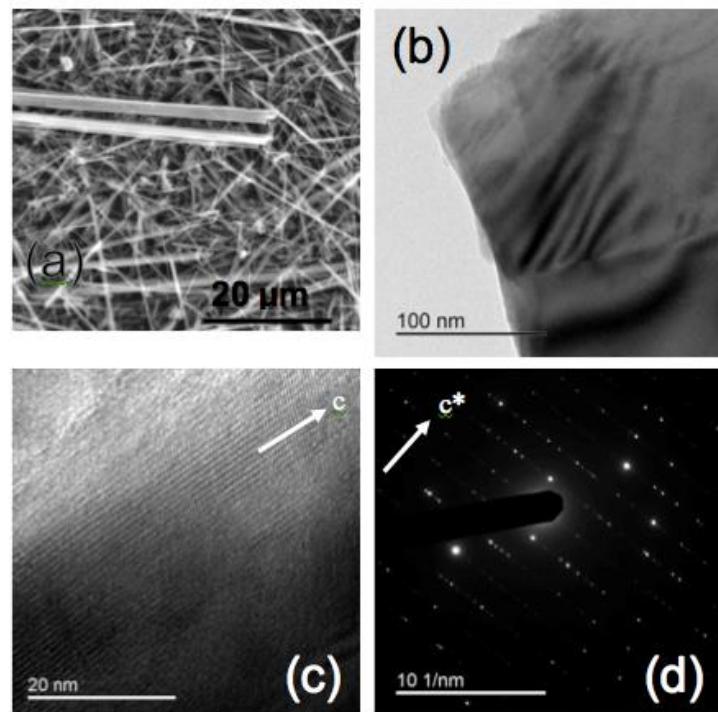


Fig. 6. UICC crocidolite NB#4173-111-3 (Tab. 1). Representative FEG-ESEM (a) image of the typical texture of the sample at high magnification. HRTEM image (b) with Moiré fringes; (c) HRTEM image showing a transition region from a highly crystalline area (streaking along c is clearly visible) to a nearly amorphous boundary; (d) Representative SAED pattern parallel to the c^* axis.

The FTIR spectrum of the UICC crocidolite in the OH-stretching region (Fig. 5) shows three well-resolved peaks at 3650, 3636 and 3618 cm^{-1} . This pattern is almost identical to that of a well-characterized sample from Madagascar published recently by [61] for the synthetic end-member riebeckite [46], and the UICC amosite (Figure 5). A broad absorption extending from 3710 to 3680 cm^{-1} can be assigned to small amounts of alkali cations at the A-site [46]. From the relative intensities of the component bands fitted to the spectrum of Figure 5, neglecting the broad absorption peak at 3690 cm^{-1} provides a Fe^{2+} content at $M(1,3) = 2.39$ apfu. Intriguingly, the high-temperature oxidation of crocidolite has been the object of a large number of studies during the 1960-1970, due to the increasing technological relevance of this material, whose widespread use was abandoned only once its carcinogenic effect was definitively recognized. A detailed study has been provided recently by [61] who showed that this process is far from being straightforward and may have significant implications for the surface availability of iron species.

4.4 Tremolite asbestos from Val D'Ala. Tremolitic amphiboles belong to the calcium-amphibole subgroup, defined by ${}^B(\text{Ca} + \Sigma \text{M}^{2+})/\Sigma \text{B} \geq 0.75$, ${}^B\text{Ca}/\Sigma \text{B} \geq {}^B\Sigma \text{M}^{2+}/\Sigma \text{B}$ [34]. Ideal tremolite has the formula ${}^A(\square){}^B(\text{Ca})_2{}^C(\text{Mg})_5{}^T(\text{Si})_8\text{O}_{22}{}^W(\text{OH})_2$, with a nominal solid-solution towards the end-member ferro-actinolite ${}^A(\square){}^B(\text{Ca})_2{}^C(\text{Fe}^{2+})_5{}^T(\text{Si})_8\text{O}_{22}{}^W(\text{OH})_2$; all compositions along this join have $C2/m$ symmetry [34]. Intermediate ${}^C(\text{Mg}, \text{Fe}^{2+})$ compositions are termed "actinolite".

Actinolites are essentially metamorphic minerals occurring in both contact and regionally metamorphosed rocks, whereby they are particularly common in the latter environment [7]. Actinolites are characteristic of greenschist-facies metabasites (ophiolitic sequences), whereas tremolite occurs in metacarbonates and metamorphosed ultrabasic rocks. Actinolites occur typically with extremely fibrous shapes, and their growth is in many cases connected to rock deformation, which is accompanied by fluid-rock interactions during the geological history of the parent rocks [62-63].

Mg-rich members are usually more fibrous than the Fe-rich ones, a feature that has been observed during synthesis of similar systems, such as along the richterite - ferro-richterite join [59], and they possess appreciable tensile strength [7]. Tremolite, as well as the other regulated amphibole of the calcium subgroup, i.e. actinolite, has not been commercially exploited, but it occurs in the

environment as contaminants in chrysotile asbestos, vermiculite and talc. In the absence of a UICC reference material, the sample described here is from a well-known occurrence of fibrous tremolite, namely from the serpentinites associated with the ultrabasic Massif of Lanzo outcropping at Ala di Stura (Val d'Ala), Piedmont, Italy [64-65].

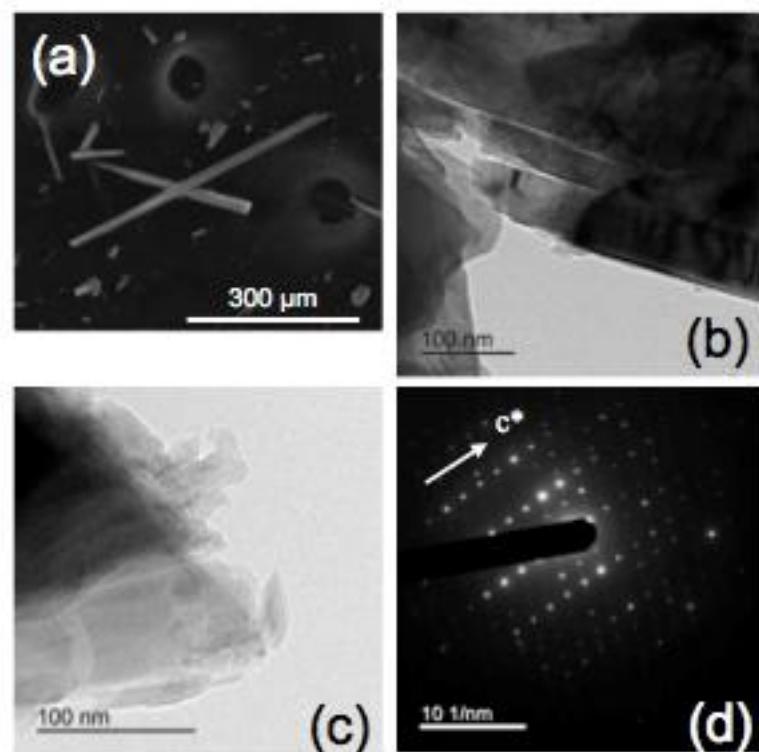


Fig. 7. (a) Representative FEG-ESEM images of the typical appearance of tremolite from Val d'Ala, Turin (Italy) (Tab. 1). (b) TEM medium high-resolution images displaying cleavage fragments that are detaching from the main fibre, with disoriented Moiré fringes. (c) HRTEM image showing highly irregular edge features. (d) Representative SAED pattern oriented parallel to the c^* axis.

Previous XRPD studies showed the studied sample to consist of tremolite with minor amounts of antigorite, clinochlore, hematite and quartz [36]. Refined unit-cell data (Tab. 2) match those measured in similar minerals [28]. In contrast to amosite, the measured β angle is close to 105°, in agreement with the presence of a large divalent cation (Ca) at the B-site (Tab. 2). The tremolite from Val d'Ala consists of asbestiform, bladed and acicular crystals, showing a tendency to split apart in fibres (mostly at the micro-scale) and/or cleavage fragments (down to the nano-scale) (Fig. 7a). TEM images of the Val d'Ala tremolite (e.g. Fig. 7b) document the separation of elongated fibre-like particles and/or cleavage fragments derived from the main fibres or from elongated bladed particles. The diffuse presence of Moiré fringes suggests a planar ((110) or (200)) rearrangement of crystal planes (Fig. 7b). The apex of the fibres shows evidence of dissolution and re-precipitation processes, with subsequent accumulation of probably Si-rich amorphous or re-crystallized material characterized by an irregular shape and multiple crystallographic orientations (Fig. 7c). The SAED (Fig. 7d) and HRTEM investigations did not provide evidence of structural defects. Microchemical data and the derived crystal-chemical formula of this sample from Val d'Ala, provided in [36] and [65], show that the amphibole is close to the tremolite end member, as it has a very low Fe^{2+} content (0.22 apfu) and only negligible amounts of Fe^{3+} (0.08 apfu). Trace elements include Ti, Cr, Ni, Mn and alkalis (Table 3).

The FTIR spectrum of the studied tremolite in the OH-stretching region (Figure 5) shows three well-resolved peaks at 3673, 3656 and 3643 cm^{-1} , which can be assigned to the different Mg/ Fe^{2+} configurations at M(1,3) [26, 59]. No peaks due to the OH-containing impurities, such as antigorite

and clinochlore, are observed in the spectrum, in agreement with their very low abundance determined by XRPD (see above). From the relative intensities of the component bands fitted to the spectrum of Figure 5, a Fe^{2+} content at $M(1,3)$ of 0.35 apfu is derived, in excellent agreement with the site occupancies refined via the Rietveld method by [64].

4.5 Actinolite asbestos from Valle Aurina. The sample described here is from a well-known occurrence of fibrous tremolite in Valle Aurina (northern Italy). It has been fully described in [66].

According to the high-resolution synchrotron radiation XRPD analysis, the studied sample consists of pure amphibole within the detection limit of the method. The refined unit-cell data (Table 2) are in agreement with previous data for similar amphiboles [28]. FEG-FESEM images [66] show that the sample consists of both fibrous and acicular crystals, and the HRTEM images and indexed electron diffraction spots provide evidence for a high degree of crystallinity of the amphibole and absence of dislocations [66]. Published EMPA data for actinolite from Valle Aurina (Table 3) show that the amphibole has an intermediate Fe^{2+} content (0.79 apfu), with minor Fe^{3+} (0.11 apfu) and traces of K, Na, Ni and Cr.

The FTIR spectrum of this actinolite in the OH-stretching region (Figure 5) shows three well-resolved peaks at 3673, 3658 and 3643 cm^{-1} , which can be assigned to the Mg/Fe^{2+} configurations at $M(1,3)$, similarly to what was discussed above for tremolite from Val d'Ala. The stronger intensity of the 3658 and 3643 cm^{-1} peaks in the OH-spectrum of actinolite compared to that of tremolite is in agreement with its higher Fe^{2+} content (Tabs. 3 and 4). From the relative intensities of the component bands fitted to the spectrum of Figure 5, a Fe^{2+} content at $M(1,3)$ of 0.91 apfu is derived, in excellent agreement with the site occupancies refined via the Rietveld method by [66].

5. FTIR spectra in the low-wavenumber region

As stated above, the interpretation of the vibrational spectra of amphiboles in the region $< 1200 \text{ cm}^{-1}$ and, in particular, at $< 650 \text{ cm}^{-1}$, is extremely challenging due to the complexity of the spectra and because in this range tetrahedral modes overlap with octahedral (M-O) modes and OH librations [26]. In addition, the internal vibrations of the T_4O_{11} double chain involve different types of T-O bonds, as a result of the occurrence of both bridging (O_b: O(5), O(6), O(7)) and non-bridging (O_{nb}: O(1), O(2)) oxygens (Figure 1b). [67-69] presented a factor group analysis of the vibrations that are IR-active for the T_4O_{11} unit of the amphiboles, but assignment of the many bands in this region is still done on an empirical basis [70-71]. Despite these difficulties, vibrational spectroscopy in the lattice region is extremely useful and widely applied for asbestos identification, particularly with micro-Raman spectroscopy [72-75]. The success of this method is essentially due to the fact that the Raman spectrum in the low-frequency region provides a reliable fingerprint for regulated asbestos species; the high-resolving power of Raman (beam dimension $< 1 \mu\text{m}^2$) also makes this technique suitable for biomedical/toxicological studies [76-77]. A comprehensive summary of Raman data for amphiboles in the region of framework phonon modes has been provided recently in [26]. FTIR data for the $< 1200 \text{ cm}^{-1}$ region are relatively scarce, however, and very few applications to asbestos minerals exist [78], although this technique might be extremely useful in environmental studies due to the ease of sample preparation and data acquisition/interpretation.

The few systematic FTIR studies performed on relatively well-constrained solid-solution series clearly show that the lattice-mode IR spectra are extremely sensitive to the chemical variations at the different structural sites. According to [70,71] the MIR range of amphiboles may be conveniently divided into three regions: (1) the 1200-800 cm^{-1} region, where seven to eight very intense to medium intense bands due to lattice Si-O-Si and O-Si-O antisymmetric stretching vibrations are observed. In particular, the highest wavenumber peaks in this range can be assigned to T(1)-O(1), which is a very short bond in the amphibole structure [79]. (2) The 800-600 cm^{-1} range, where four to six medium weak to very weak peaks resulting from Si-O-Si symmetric stretching or

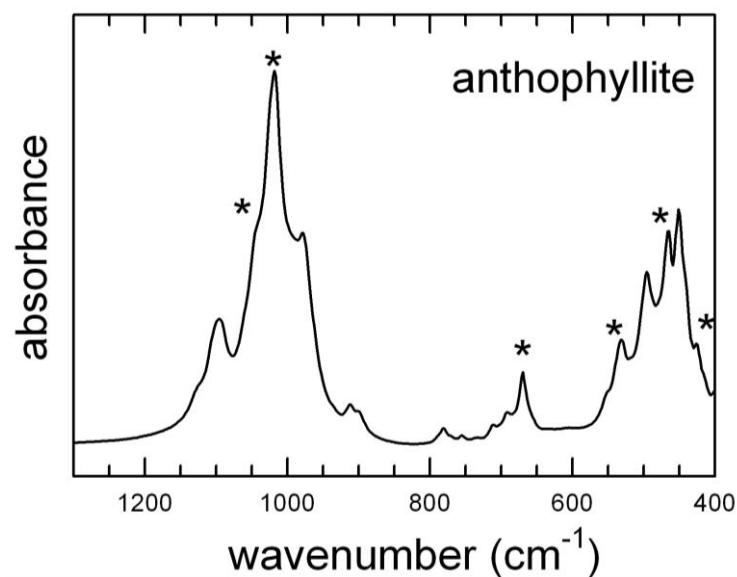


Figure 8. FTIR spectrum of UICC anthophyllite in the low-frequency (1300-400 cm^{-1}) region. The asterisks indicate the main bands of talc (Ishida, 1990b).

chain deformation modes occur; in this range two OH librational modes at around 700 and 690-640 cm^{-1} have been identified in ⁷Al-free amphiboles, *via* hydrothermal treatment with deuterium [39]. The most intense peak in the Raman spectrum of amphiboles occurs in this region, and it has been shown that the wavenumber value of this sharp peak provides a reliable identification of the species [20,76]. (3) At wavenumbers < 650 cm^{-1} , there is a mixture of T-O and M-O bending modes and OH librations [80]. For alkali amphiboles of the glaucophane - riebeckite series, Ishida et al. [70] reported linear shifts for most bands in this region, consistent with the strong influence of the chemical composition of the amphibole on the peak positions.

The spectra collected in the 1300-400 cm^{-1} range for the studied amphiboles are given in Figures 8 and 9. In particular, Figure 8 shows the spectrum collected for UICC anthophyllite, a sample that, as discussed above, contains significant impurities of hydrous silicates (talc and chlorite); the sharp peaks at 1041, 1091, 669, 531, 465 and 424 cm^{-1} , indicated with an asterisk in Figure 8, can be assigned to talc [39]. In Figure 9, the spectra of all other samples are displayed; relevant data and tentative band assignment from the literature are given in Table 4. Inspection of Figure 9 reveals that, in region 1, the patterns of tremolite and actinolite are almost identical, with the only chemical difference between these samples being the Mg-Fe²⁺ substitution at the C-sites. Five intense bands plus two shoulders are observed (Table 4). In the same region, however, the spectra of UICC anthophyllite, amosite and crocidolite are significantly different and show, as a peculiar characteristic, a major and sharp peak plus several medium intense bands and shoulders. Inspection of the literature data unveiled that the spectrum of anthophyllite MNHN29_102 is almost identical to those of anthophyllites published by [40], whereas the spectrum of UICC crocidolite is almost identical to that of riebeckites published by [70] and [81], suggesting that the IR patterns in this region are indeed characteristic of the species.

Following the work of [40], the positions of the medium strong peaks in region 2 are also characteristic of the amphibole species, being sensitive of both the A- and B-site occupants. In the present case, the A-site is empty for all samples, thus the observed differences are due to the B-site cation only: for Na (crocidolite) there is a single and relatively sharp peak at 778 cm^{-1} , for Mg (anthophyllite) a very weak single band at 780 cm^{-1} , for Fe^{2+} (amosite) a doublet at $797\text{-}775\text{ cm}^{-1}$, and for Ca (tremolite-actinolite) a medium intense peak at 757 cm^{-1} . The OH librations, identified through deuteration experiments, occur at 709 and 688 cm^{-1} for anthophyllite [40] and at 685 and 642 cm^{-1} (Table 4) for tremolite [71].

Significant differences are finally observed in region 3, and these are again related to the amphibole type: the Fe-Mg amphiboles anthophyllite and amosite show a medium-intensity peak around 530 cm^{-1} followed by an intense doublet around $480\text{-}500\text{ cm}^{-1}$. In the Na-amphibole crocidolite at the same wavenumbers there are two weak peaks, followed by a sharp and intense absorption at 450 cm^{-1} . The Ca-amphiboles tremolite and actinolite show two/three peaks with medium intensity at $500\text{-}550\text{ cm}^{-1}$ followed by an intense doublet at $445\text{-}465\text{ cm}^{-1}$.

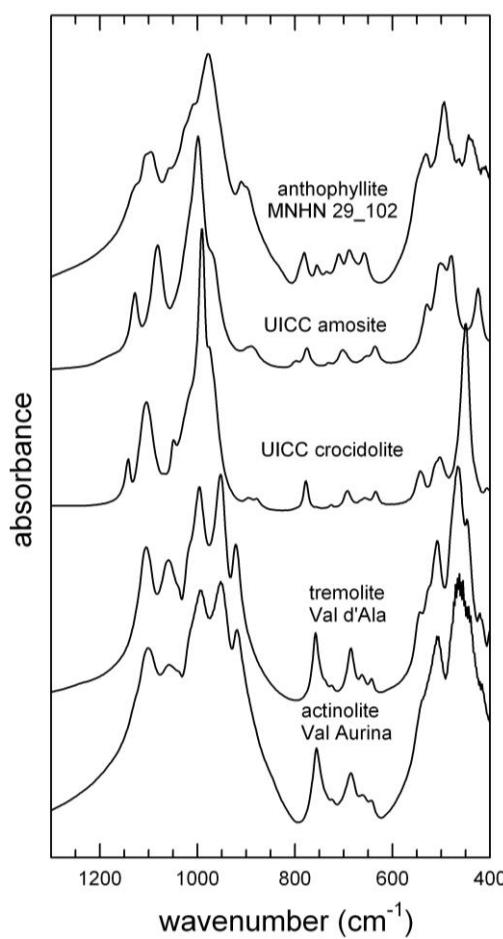


Fig. 9. Stacked FTIR spectra in the low-frequency ($1300\text{-}400\text{ cm}^{-1}$) region for the amphiboles investigated in this study (see Tab. 1).

6. Conclusions

This work is intended to fill a gap in vibrational spectroscopy of asbestos amphiboles, providing FTIR data for a suite of well-characterized regulated species, whose IR data are either scattered or not present in the literature. The data presented here can be used as reference spectra for environmental/toxicological studies where vibrational spectroscopy is used as an analytical tool. Our study shows that, based on a vast body of literature, mostly summarized in [21] and [26], the FTIR spectra in the OH-stretching region provide a relatively easy and rapid identification of the amphibole asbestos minerals; this task is eased by the fact that all asbestos amphiboles have a vacant

A-site, a feature that has a strong effect on the IR spectra [21], [30] and references therein. Considering that the exact wavenumbers of the OH-stretching bands are also sensitive, albeit weakly, to the next-nearest neighbours, i.e. the $M(4)$ and $M(2)$ cations [8, 46, 52], the calcic amphiboles tremolite-actinolite can be easily distinguished from the ferromagnesian amphiboles of the anthophyllite-grunerite type. For simple binary $M^{(1,3)}\text{Mg}-M^{(1,3)}\text{Fe}^{2+}$ solid-solutions, as is typically the case for asbestos amphiboles, the relative amount of these cations in the OH-bonded octahedra can be calculated with a high degree of confidence [26], and, provided that the Al and Fe_{tot} amounts are known from EMPA, the complete cation distribution at all octahedral sites can be derived.

The present work also shows that, although data from species spanning the complete chemical diversity of this large mineral supergroup are still lacking, the spectra in the mid-IR lattice modes region can be effective for rapid identification of the asbestos type.

Author Contributions: GDV and GI conceived the research and wrote the bulk of the manuscript; RV and RG did the FEG-FESEM and HRTM/SAED work and helped clarifying some aspect of the data; SP and AFG provided the samples and contributed to write the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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