

CRYSTAL-CHEMISTRY OF SYNTHETIC AMPHIBOLES ALONG THE RICHTERITE-FERRO-RICHTERITE JOIN: A COMBINED SPECTROSCOPIC (FTIR, MÖSSBAUER), XRPD, AND MICROCHEMICAL STUDY

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ABSTRACT

In this paper we report a crystal-chemical study of amphiboles along the nominal join richterite [^ANa^B(NaCa)^CMg₅^TSi₈O₂₂^W(OH)₂] – ferro-richterite [^ANa^B(NaCa)^CFe²⁺₅^TSi₈O₂₂^W(OH)₂], ideally characterized by direct substitution of ^CMg with ^CFe²⁺. Six samples were synthesized by hydrothermal techniques: the three Fe-richer compositions at 500 °C and the three Mg-richer ones at 600 °C, 1 kbar *P*_(H₂O), and internally-buffered *f*_{O₂} conditions (Sergent *et al.* 1996). The experimental powders were studied using a combination of EMPA, FE-SEM, PXRD, and FTIR plus ⁵⁷Fe Mössbauer spectroscopy. Due to crystal-size limitations, only the Fe endmember could be analyzed by EMP-WDS, while two additional Fe-rich samples could be semi-quantitatively analyzed by FE-SEM-EDS. Rietveld refinement of X-ray powder diffraction patterns show that, although a linear trend in the amphibole cell-parameters is observed, there is a significant decrease in the amphibole yield counterbalanced by an increase in clinopyroxene (cpx), up to 27 wt.%, for the Fe endmember.

⁵⁷Fe Mössbauer spectra could be fitted on the basis of known spectral parameters of similar amphiboles in the literature and corrected for the spectral contribution of cpx. The results show that Fe³⁺ is completely ordered at *M*(2), while Fe²⁺ is disordered over all available *C* sites; no ferrous iron is resolved at *M*(4). The OH-stretching FTIR spectra show complex patterns for intermediate compositions with up to eight bands; these can be assigned to the various configurations involving Mg/Fe²⁺ at *M*(1,3), locally associated with both full and empty *A* sites.

Details of the crystal chemistry for all amphiboles in the series were obtained with the spectroscopic methods, and the resulting data were in reasonable agreement with those derived by WDS-EDS analyses for the three Fe-richer samples. For increasing Fe in the system, the amphibole composition deviates toward a sodic endmember following the exchange vector ^{M2}Fe²⁺ + ^{M4}Ca ↔ ^{M2}Fe³⁺ + ^{M4}Na₁, possibly due to the instability of endmember ferro-richterite for stereochemical reasons. Interestingly, along the studied series there is a general increase in the amphibole crystal size and an evolution of the crystal

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morphologies, from extremely acicular at the Mg endmember composition to prismatic and stubby for the Fe^{2+} -richer compositions.

Keywords: ferro-richterite, synthesis, cell parameters, EMP-WDS, SEM-EDS, FTIR and Mössbauer spectroscopy.

INTRODUCTION

Richterite, ideally $\text{Na}(\text{NaCa})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH},\text{F})_2$, is a relatively common sodium-calcium amphibole (Hawthorne *et al.* 2012). Richterite is almost invariably F-rich and is found in a wide variety of geological environments, such as alkaline to peralkaline igneous rocks, gneisses, and skarn-type metamorphic rocks (see Deer *et al.* 1997 for a compilation); occurrence from meteorites has been reported as well (Olsen 1967, Olsen *et al.* 1973). On the other hand, ferro-richterite is extremely rare and has only been reported from an alkali-rich lava (pantellerite) from Kenya (Nicholls & Carmichael 1969). Richterite has been the subject of a surprisingly large number of experimental studies, probably because of its extreme ease of synthesis, which commonly results in very high amphibole yields, and its ability to incorporate different cations and anions (Eitel 1954, Kohn & Comeforo 1955, Phillips & Rowbotham 1968, Huebner & Papike 1970, Forbes 1971, Robert *et al.* 1989, Della Ventura 1992, Della Ventura *et al.* 1997, Gottschalk & Andrut 1998, Senda *et al.* 2005, Iezzi *et al.* 2010, 2011a). By contrast, experimental studies of Fe^{2+} -rich compositions are relatively rare (Cameron & Gibbs 1971, Charles 1974, 1975, 1977, Redhammer & Roth 2002, Sergent *et al.* 1996). In particular, Charles (1974) gave a detailed description of the physical properties (optical properties and cell dimensions) of compositions obtained along the richterite–ferro-richterite join for different oxidizing conditions; however, the compositions and long range (LR) and short-range (SR) ordering patterns of these amphiboles were not constrained. Charles (1975) examined the phase relations at $P = 1$ kbar and showed that richterite decomposes at 1030 °C to give diopside + olivine + melt + vapor, whereas ferro-richterite decomposes at 715 °C to give hedenbergite + fayalite + melt + vapor at reducing (IW buffer) conditions. This indicates that the Mg–Fe substitution lowers the upper thermal limit of richterite by about 300 °C. At f_{O_2} conditions set by the QFM buffer, ferro-richterite is stable only up to 525 °C at the same pressure. Charles (1974, 1975) also showed that the oxygen fugacity, thus the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio during synthesis, plays a major role in the final composition of the mineral.

Redhammer & Roth (2002) provided a single-crystal structure refinement of two (nominally) potassic-ferro-richterites synthesized at $T = 600\text{--}700$ °C, $P = 4$ kbar, with redox conditions controlled using the tube-in-tube technique. Mössbauer spectroscopy showed their samples to contain significant Fe^{3+} at the $M(2)$ site, with a composition close to the limit between potassic-ferro-richterite and potassic-arfvedsonite (Redhammer & Roth 2002). The same samples were recently re-examined by Oberti *et al.* (2016), who provided new EMP and single-crystal X-ray refinements.

The extensive work of Iezzi *et al.* (2003a, 2003b, 2004, 2005) and Della Ventura *et al.* (2005a, 2005b) showed that in experimental studies involving iron-bearing amphiboles there is a need to characterize in detail the experimental products, which may depart significantly from the expected compositions. This problem is exacerbated by two main factors: (1) synthetic amphiboles are typically too small to be characterized by EMPA, and (2) lack of information regarding the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio hinders calculation of a reliable crystal-chemical formula by simple charge balancing, due to variable occupancy at the A site. In addition, for amphiboles it is necessary to characterize the short-range order (SRO) of cations and anions as well as the composition, since SRO is essential for developing accurate crystal-chemical and thermodynamic models (*e.g.*, Hawthorne & Della Ventura 2007, Della Ventura *et al.* 2014a). These difficulties prompted the need to develop alternative methods based mainly on spectroscopy, and indeed significant improvements have been made during recent years in this direction (*e.g.*, Hawthorne & Della Ventura 2007). An important outcome of these studies is the possibility to establish methods to characterize acicular or fibrous amphiboles for applications in environmental mineralogy (Iezzi *et al.* 2007, Della Ventura *et al.* 2014b).

In this paper, we present a multidisciplinary study of the amphiboles in the $\text{Na}_2\text{O}\text{--}\text{CaO}\text{--}\text{MgO}\text{--}\text{FeO}\text{--}\text{Fe}_2\text{O}_3\text{--}\text{SiO}_2\text{--}\text{H}_2\text{O}$ system, with ideal compositions along the richterite–ferro-richterite join, synthesized by Sergent *et al.* (1996). Characterization in terms of composition, but also LRO and SRO of the amphiboles, was done by combining microchemistry (EPMA

TABLE 1. SAMPLE LABELS AND EXPERIMENTAL CONDITIONS

Label	Nominal amphibole composition	<i>T</i> (°C)	<i>P</i> (Gpa)	Time (days)
NR1000	Na(NaCa)Mg ₅ Si ₈ O ₂₂ (OH) ₂	600	0.1	8
NR1002	Na(NaCa)(Mg ₄ Fe ²⁺ ₁)Si ₈ O ₂₂ (OH) ₂	600	0.1	8
NR1004	Na(NaCa)(Mg ₃ Fe ²⁺ ₂)Si ₈ O ₂₂ (OH) ₂	600	0.1	8
NR1006	Na(NaCa)(Mg ₂ Fe ²⁺ ₃)Si ₈ O ₂₂ (OH) ₂	500	0.1	8
NR1008	Na(NaCa)(Mg ₁ Fe ²⁺ ₄)Si ₈ O ₂₂ (OH) ₂	500	0.1	8
NR1010	Na(NaCa)Fe ²⁺ ₅ Si ₈ O ₂₂ (OH) ₂	500	0.1	8

and SEM), powder X-ray diffraction (PXRD), FTIR, and Mössbauer spectroscopies.

This paper is dedicated to Frank C. Hawthorne; we share with him a long-standing addiction to amphiboles, particularly synthetic amphiboles, and engaged in long discussions about the use of spectroscopic methods to derive crystal-chemical information for these complex silicates. We hope that this paper will provide a further piece of knowledge in this area that Frank pioneered, and we are proud to have shared part of this journey (besides our personal friendship) with him.

EXPERIMENTAL AND ANALYTICAL METHODS

The two starting endmember compositions were prepared as gels, following the method of Hamilton & Henderson (1968). Iron was added by mixing stoichiometric amounts of metallic Fe (Fe⁰) and Fe-nitrate (Fe³⁺) (Monier & Robert 1986, Iezzi *et al.* 2003a, 2003b). Intermediate compositions were prepared along the richterite [Na(NaCa)Mg₅Si₈O₂₂(OH)₂] – ferro-richterite [Na(NaCa)Fe²⁺₅Si₈O₂₂(OH)₂] join by mixing endmember gels in stoichiometric amounts considering their anhydrous molecular weights; powders were packed into gold tubes with 10 wt.% of deionized water. Sample labels and experimental conditions are given in Table 1.

Hydrothermal syntheses were done using externally heated Tuttle-type pressure vessels for a duration of 8 days at ISTO, Orléans (France). Redox conditions were imposed by the MW (magnetite–wüstite) solid buffer using the classical double-capsule method (Eugster 1957). However at 600 °C, and especially at 500 °C, the diffusion of H through Au is very sluggish, so the *f*_{O₂} within the capsule must be considered as internally buffered (Iezzi *et al.* 2003a, 2003b, 2004, 2005, Della Ventura *et al.* 2005a).

Samples were removed from the furnace at the end of the experiment and allowed to cool under pressure. The temperature was monitored by three sheathed type-K thermocouples placed around the hot spot, with a *T* gradient within ±5 °C. The pressure conditions

were continuously recorded with an Heise-Bourdon tube gauge; the estimated error is ±50 bar.

Experimental products were initially studied at the Istituto Nazionale di Geofisica e Vulcanologia (INGV, Rome) using a JEOL-JSM6500F Field Emission Gun-Scanning Electron Microscope (FESEM) and a JEOL-JXA8200 Electronic Probe Micro Analyzer (EPMA). Analytical protocols were as reported in Iezzi *et al.* (2011b) and Vetere *et al.* (2013). Samples were first prepared as loose powders dispersed on carbon tape to obtain 3D images of sizes and shapes of the synthetic crystals (Fig. 1). Then a few milligrams of each powder was embedded in epoxy, ground, and polished for quantitative micro-chemical analyses. Due to the extremely small size of the crystallites for the Mg-rich compositions (*e.g.*, Fig. 1a), we could only obtain WDS (wavelength dispersive) data for sample NR1010, while for samples NR1008 and NR1006 we were forced to use the FESEM-EDS (energy dispersive, at 10 kV accelerating voltage, 0.756 nA probe current, 10 s acquisition). From five to 10 analytical points with totals >95 wt.% were averaged; data points with lower totals were discarded. The reliability of the data obtained by EDS was checked by analyzing the same NR1010 mount with both methods: final differences in oxide contents were less than 10% relative. The conditions used in WDS mode were as follows: 15 kV accelerating voltage, 3.3 mA current, 0.5 µm beam diameter, acquisition time 10 s for peak and 5 s for background. The standards (element, crystal; all *Kα* lines) used were: anorthoclase (Na, TAP), augite (Ca, PET), and fayalite (Si, PETH; Fe LIFH). The crystals in experimental products NR1000, NR1002, and NR1004 (Table 1) were too small and acicular to be analyzed, even for the most reduced SEM beam size. Selected results (oxides wt.%) and calculated crystal-chemical formulae for the amphiboles and clinopyroxenes are given in Table 2 along with with nominal compositions of the starting materials. Amphibole formulae (*apfu*) were calculated on the basis of 13-CNK (Ca-Na-K) using the spreadsheet of Locock (2014); cpx formulae were calculated on the basis of 6 oxygen atoms, and Fe³⁺ was derived by electroneutrality.

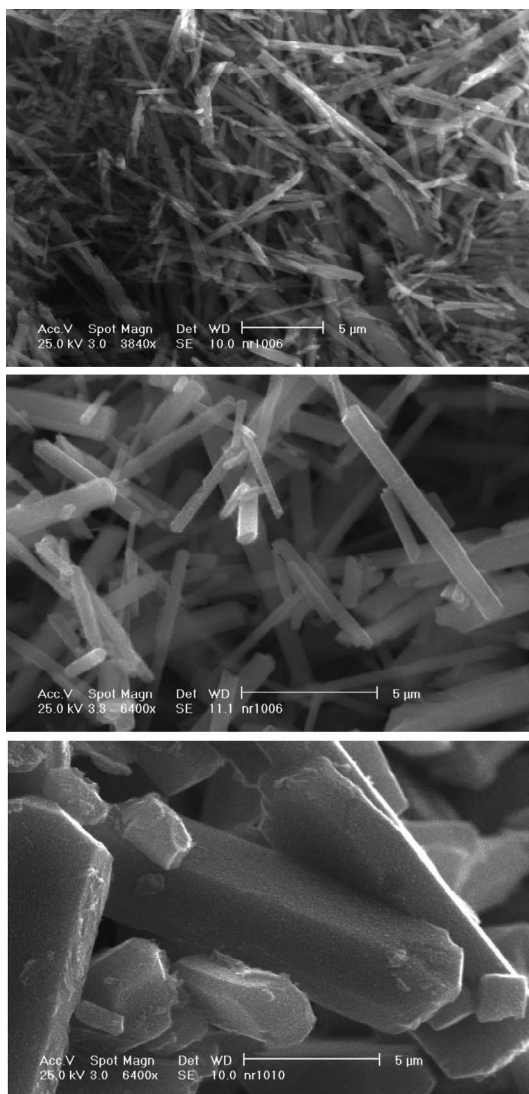


FIG. 1. SEM images of the amphiboles synthesized along the (nominal) richterite–ferro-richterite join; sample NR1000 (top), NR1006 (middle), NR1010 (bottom). For nominal compositions refer to Table 1.

Powder X-ray diffraction patterns (PXRD) were obtained using a Scintag X1 diffractometer operated in the vertical θ – θ configuration and equipped with Ni-filtered $\text{CuK}\alpha$ radiation and a $\text{Si}(\text{Li})$ solid-state detector. The patterns were recorded from 10–20 mg of each experimental product (after grinding for 10 min under alcohol) between 5 and $100^\circ 2\theta$, with a scan step of 0.05° and a counting time of 2 s/step. After identification of all crystalline phases in the PXRD patterns, the structural data for richterite (Senda *et al.*

2005), clinopyroxene (Redhammer *et al.* 2006), and quartz (Gualtieri 2000) were used as starting data for refinements. Metallic Si was added to the powder as an internal standard for the accurate determination of cell parameters. Diffraction patterns were first modeled with the software EXPGUI-GSAS (Larson & Von Dreele 1997, Toby 2001) using the Le Bail method (Le Bail 2005) in order to refine the cell parameters and the Lorentzian (Lx, Ly) and Gaussian contributions to the pseudo-Voigt function peak shapes (Finger *et al.* 1994); the background was described using the polynomial Chebyshev function with 10 coefficients. In a second step, the amount of each crystalline phase (wt.%) in each experimental product was determined using the Rietveld method, refining the amphibole preferred orientation on (001) and (110), as well as the isotropic thermal parameter (Walter *et al.* 2013), while leaving the structural parameters of all phases, except the cell dimensions, fixed. The site occupancies for the amphibole and cpx were first constrained with the data reported in Table 2, then further refined with the values provided by spectroscopy (see below).

Powder FTIR spectra were collected at room temperature with a Nicolet 760 spectrophotometer equipped with a DTGS detector and a KBr beamsplitter. Samples were prepared as KBr pellets using the procedure described by Robert *et al.* (1989). Ten mg of experimental powder was mixed with 200 mg of KBr and homogenized with an automatic mill for 30 min. Digitized spectra (average of 64 scans at 4 cm^{-1} nominal resolution) were fitted by interactive optimization followed by least-squares refinement. The background was modelled as linear and all peaks were defined as symmetric Gaussians (Della Ventura *et al.* 1996, 1997).

Transmission ^{57}Fe Mössbauer data were acquired at room temperature using an apparatus in a horizontal arrangement (^{57}Fe Co/Rh single-line thin source, constant acceleration mode with symmetric triangular velocity shape, multi-channel analyzer with 1024 channels, regular velocity calibration against metallic Fe). Data evaluation was done using the RECOIL program suite (Rancourt & Ping 1991, Rancourt *et al.* 1993, 1996). All spectra were corrected for thickness effects and then analyzed using the full static hyperfine interaction Hamiltonian analysis with Lorentzian-shaped doublets. Details for the sample preparation and data handling can be found in Redhammer & Roth (2002).

TEXTURES OF THE EXPERIMENTAL PRODUCTS AND MICROCHEMICAL DATA

Scanning electron microscope images showed three main phases in the experimental powders: amphibole,

TABLE 2. NOMINAL AND ANALYZED CHEMICAL DATA FOR AMPHIBOLES (AMPH) AND CLINOPYROXENES (CPX)

Sample	Phase	Analytical method	Oxide (wt.%)					Atoms per formula unit (<i>apfu</i>)					
			SiO ₂	FeO	MgO	CaO	Na ₂ O	Si	Fe ³⁺	Fe ²⁺	Mg	Ca	Na
NR1000	amph nominal	-	60.06	0.00	25.18	7.01	7.75	8	-	-	5	1	2
NR1002	amph nominal	-	57.79	8.64	19.38	6.74	7.45	8	-	1	4	1	2
NR1004	amph nominal	-	55.67	16.65	14.00	6.50	7.18	8	-	2	3	1	2
NR1006	amph nominal	-	53.71	24.09	9.01	6.27	6.93	8	-	3	2	1	2
NR1006	amph analyzed*	SEM	51.90	25.92	7.92	4.26	7.94	7.88	0.57	2.72	1.79	0.69	2.39
	cpx [#]	SEM	47.96	29.76	0.00	17.58	2.82	1.98	0.28	0.72	-	0.72	0.28
NR1008	amph nominal	-	51.88	31.02	4.35	6.05	6.69	8	-	4	1	1	2
NR1008	amph analyzed*	SEM	52.32	31.31	3.20	2.89	7.51	8.29	-	4.15	0.76	0.49	2.31
	cpx [#]	SEM	52.05	29.74	0.00	14.33	4.85	2.05	0.38	0.62	-	0.62	0.38
NR1010	amph nominal	-	50.17	37.50	0.00	5.85	6.47	8	-	5	-	1	2
NR1010	amph analyzed*	EPMA	48.88	38.11	0.00	2.96	7.57	7.93	0.52	4.65	-	0.52	2.38
	cpx [#]	EPMA	49.53	31.15	0.00	15.60	3.73	1.99	0.32	0.67	-	0.67	0.32

Amphibole formula calculated on the basis of 23 oxygen atoms: * using 13-CNK; [#] cpx calculated on the basis of 6 oxygen atoms; Fe³⁺ estimated by charge balance.

clinopyroxene, and quartz; in addition, trace amounts (undetected by PXRD) of olivine (fayalite, from EDS data) were observed on the Fe-rich side of the join. The amphibole amount decreases with increasing Fe in the systems, counterbalanced by increasing clinopyroxene in the assemblage (Fig. 2). Magnesium end-member richterite crystals are extremely acicular with a width between 0.5–1 μm and a length up to 10 μm (Fig. 1a). With increasing Fe, the amphibole crystals evolve toward more stubby morphologies (Fig. 1b); the Fe endmember amphiboles are characterized by a width : length ratio close to 1 : 2 (Fig. 1c). The clinopyroxene crystals are invariably smaller than the amphiboles.

The data in Table 2 show that the cpx synthesized on the Fe-rich side of the join (at 500 °C) are essentially Mg-free, as can be expected at this relatively low temperature, and with compositions along the hedenbergite ($\text{CaFe}^{2+}\text{Si}_2\text{O}_6$) – aegirine ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$) series; the compositions of those crystals synthesized along the Mg-rich part of the join, inferred on the basis of the XRD data (see below), plot instead within the hedenbergite–diopside series.

Examination of Table 2 shows that amphibole NR1006 can be classified as an intermediate (Mg,Fe) richterite with a composition deviating toward (Mg,Fe) arfvedsonite, whereas amphiboles NR1008 and NR1010 are on the compositional limit between ferro-richterite, defined as $^{\text{B}}\text{Ca} \geq 0.5 \text{ apfu}$ (Hawthorne *et al.* 2012), and arfvedsonite. It is worth noting that a similar deviation toward Na-rich compositions was also observed for synthetic potassic-ferro-richterite (Redhammer & Roth 2002, Oberti *et al.* 2016).

Figure 2, based on the data in Table 2, shows that all analyzed amphiboles are depleted in CaO and enriched in Na₂O with respect to the nominal stoichiometry, while the opposite is observed for cpx. The FeO and MgO contents of the amphiboles are relatively close to, or slightly lower, than the nominal ones. Considering that the NR1010, NR1008, and NR1006 cpx are MgO-free, a Mg-rich phase undetected due to its low amount, or, alternatively, minor amorphous quench material, should be present in the experimental product. For powders NR1002 and NR1004 the cpx composition could only be inferred based on the PXRD data (see below).

X-RAY POWDER DIFFRACTION

Powder XRD patterns show the presence of amphibole, clinopyroxene, and quartz in the experimental products; additional phases (*e.g.*, fayalite) observed by SEM or an undefined Mg-rich phase inferred by micro-chemical data (see above) were not detected, indicative of their extremely low abundances (possibly <1 wt.%). Relative amounts of the synthesized phases were obtained *via* quantitative phase-analysis from the Rietveld refinements (Table 3). A check for the reliability of the data is provided by mass-balance calculations: if the oxide contents of the amphiboles and clinopyroxenes from Table 2 are multiplied by their phase proportions (from Table 3) the bulk composition of the starting powder is closely reproduced, thus supporting the quality of both the Rietveld refinements and the microchemical analyses.

Table 3 shows that sample NR1000 consists of almost single-phase amphibole (99%) with traces of

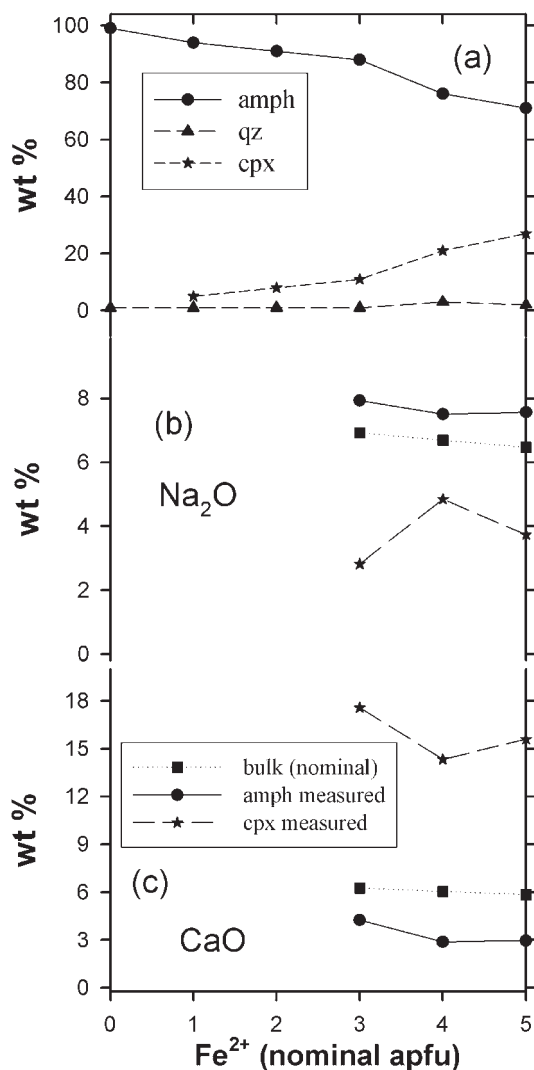


FIG. 2. (a) Rietveld refined phase abundances (wt.%), and comparisons between Na_2O (b) and CaO (c) (wt.%) in amphiboles and clinopyroxenes versus nominal Fe^{2+} (data from Table 2).

quartz (1%); therefore amphibole NR1000 can be inferred to be close to endmember richterite (Table 2), in line with extensive literature showing that this amphibole is very easily synthesized (*e.g.*, Della Ventura 1992, Hawthorne & Della Ventura 2007 and references therein). From samples NR1002 to NR1006, amphibole yields are close to or higher than ~90 wt.% and clinopyroxene amounts are low; this again suggests that departures of the amphiboles from nominal composition are limited, as confirmed by the microchemical data for experimental product NR1006

(Table 2). By contrast, experimental powders NR1008 and NR1010 are composed of 71 and 76 wt.%, respectively, of amphibole, with the remainder being essentially cpx, amounting to 27 and 21 wt.%, respectively (Table 3). Hence, increasing iron in the system induces the co-precipitation of cpx; its amount, however, does not increase linearly along the join, but there is massive crystallization of the single-chain silicate for higher FeO contents in the starting powder.

Figure 2 displays the phase abundances and the chemical data as a function of the evolving iron content in the system: at relatively low Fe^{2+} , the increase of cpx is moderate, whereas at higher Fe, between NR1006 and NR1008, the amount of cpx suddenly and significantly increases. The significant decrease of amphibole to 70/75 wt.% in the NR1008 and NR1010 experimental products is coupled to a nearly constant amount of Ca and Na in the double-chain phase (Fig. 2), while the FeO contents (see data for NR1006, NR1008, and NR1010, Table 2) are close to the nominal values. The plots of Figure 2 thus suggest that, under the experimental conditions used, Ca is preferentially partitioned into the cpx, whereas the double-chain structure deviates toward Na-rich stoichiometries (Fig. 2 and Table 2).

The compositional features described so far are mirrored by the cell dimension variation (Table 3) displayed in Figures 3 and 4. For the amphibole, all cell edges show an almost linear increase as a function of increasing Fe^{2+} in the system (Fig. 3a), except for the β angle, which decreases instead. The cell edges thus reflect a continuous increase in Fe^{2+} ($r = 0.780 \text{ \AA}$) substituting for Mg ($r = 0.720 \text{ \AA}$, all ionic data from Shannon 1976) in the structure. Figure 3b shows the evolution of the cell volume against the (nominal) cubed mean cation radius at the *M*-sites across the Ni ($r = 0.690 \text{ \AA}$) – Mg ($r = 0.720$) – Co ($r = 0.745$) – Fe^{2+} ($r = 0.780$) range. A well-developed linearity of the cell expansion is observed with a slight slope change at $\langle r_{\text{M123}}^3 \rangle = 0.720 \text{ \AA}$, corresponding to Mg. This behavior was previously observed and discussed by Della Ventura *et al.* (1997) in terms of a possible effect of the electronic configuration of *C*-site cations, besides their size dimension, on the cell dimension evolution.

However, on closer inspection (see in particular *a*, *b*, and β parameters), two linear trends can be interpreted to exist in Figure 3a, with a slight but appreciable change between Fe = 3 (NR1006) and 4 (NR1008) *apfu*, reflecting slight but significant deviations of the amphibole compositions from the nominal one for the Fe-richer compositions (Fig. 3a).

The evolution of the clinopyroxene cell-dimensions is displayed in Figure 4a, where the presence of two trends, one for the Mg-rich side (NR1000 to NR1006)

TABLE 3. MINERAL PHASES, RIETVELD-REFINED RELATIVE AMOUNTS (wt.%), AND CELL PARAMETERS

Label	Mineral phase	amount (wt.%)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
NR1000	amph	99	9.902	17.984	5.268	104.20	909.4
	qz	1	4.922	-	5.404	-	113.4
NR1002	amph	94	9.915	18.014	5.277	104.13	914.1
	cpx	5	9.773	8.939	5.257	105.74	442.0
NR1004	qz	1	4.923	-	5.405	-	113.5
	amph	91	9.934	18.065	5.285	104.08	919.9
	cpx	8	9.779	8.957	5.259	105.67	443.51
NR1006	qz	1	4.922	-	5.404	-	113.4
	amph	88	9.948	18.124	5.292	103.95	925.9
	cpx	11	9.788	8.973	5.261	105.59	445.02
NR1008	qz	1	4.922	-	5.405	-	113.4
	amph	76	9.944	18.127	5.303	103.76	928.5
	cpx	21	9.768	8.944	5.269	105.87	442.76
NR1010	qz	3	4.923	-	5.405	-	113.5
	amph	71	9.971	18.220	5.308	103.72	936.8
	cpx	27	9.779	8.956	5.269	105.75	444.16
	qz	2	4.922	-	5.405	-	113.5

Amph: amphibole, qz: quartz, and cpx: clinopyroxene; e.s.d. for cell parameters are ≤ 1 to the last digit.

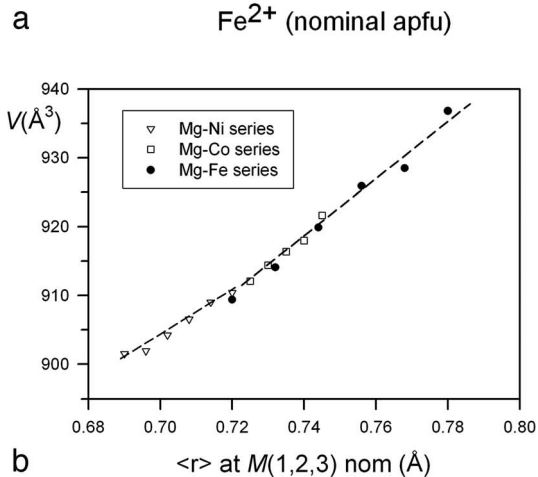
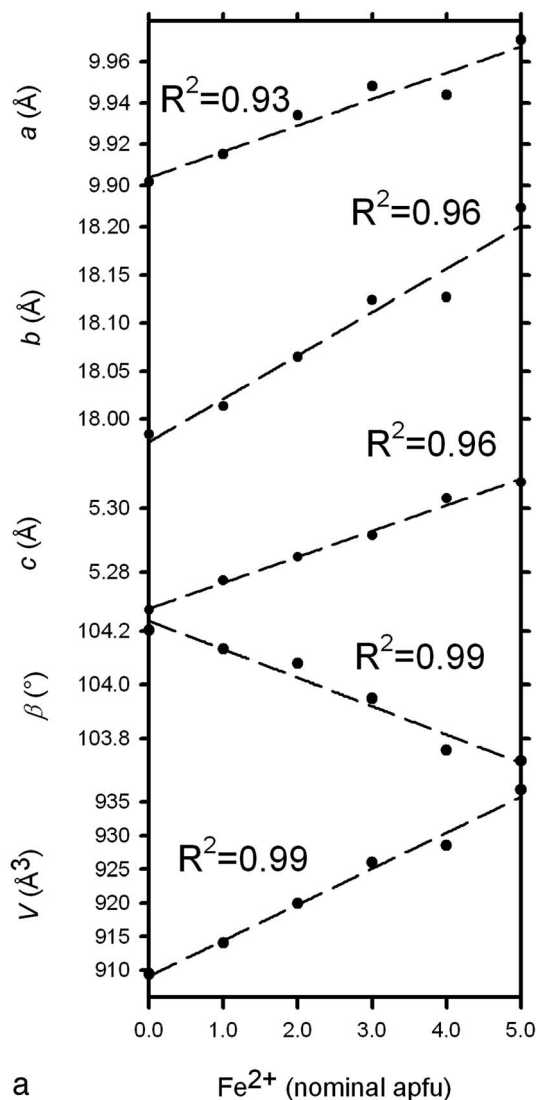
of the join, and a second for the Fe²⁺-rich (NR1008 and NR1010) side, is well evident. This feature is also visible in Figure 4b where the data from the present study are plotted in a *c* versus β diagram in comparison with available data from the literature for synthetic pyroxenes with similar compositions. Inspection of Figure 4b shows that while the cpx cell-dimensions for the two Fe²⁺-richest compositions NR1008 and NR1010 align along the hedenbergite-aegirine join (data from Redhammer *et al.* 2006), clinopyroxenes NR1002 to NR1006 define a perpendicular trend towards diopside, *i.e.*, towards stoichiometries with decreasing Na + Fe³⁺ and increasing Ca + Mg, in excellent agreement with the chemical data reported in Table 2.

In summary, combination of the chemical and X-ray data shows that the composition of the synthesized amphiboles progressively departs from the nominal one along the studied join toward Na-richer stoichiometries. The deviation is relatively small between samples NR1000 to NR1006, and increases markedly for the two Fe-richer amphiboles (NR1008 and NR1010).

POWDER INFRARED SPECTROSCOPY

The OH-stretching powder patterns and band nomenclature for the synthesized amphiboles along the studied join are given in Figure 5. As discussed above, some powders contain significant cpx that is anhydrous, thus the absorptions in the described

wavenumber range are due to the amphibole phase only. The spectrum of endmember richterite (sample NR1000, Fig. 5 top) shows an intense band at 3730 cm⁻¹ and a minor component at 3674 cm⁻¹. The higher wavenumber band is assigned to the vibration of the structural OH group in the local configuration ^{M(1)}Mg^{M(1)}Mg^{M(3)}Mg-OH-^ANa-^TSi; the minor component is due to the presence of vacant *A* sites in the structure (band A*, Fig. 5) (*e.g.*, Robert *et al.* 1989, Della Ventura 1992, Hawthorne *et al.* 1997, Gottschalk *et al.* 1999, Melzer *et al.* 2000, Senda *et al.* 2005, Iezzi *et al.* 2006, 2010), indicating a slight departure of the synthesized amphibole from the nominal composition toward tremolite. As expected (Della Ventura *et al.* 1996, 1997, Hawthorne *et al.* 1996, Reece *et al.* 2002, Iezzi *et al.* 2005), for all intermediate (Mg,Fe)-amphiboles along the join, both bands split into four components (Fig. 5), which are labelled A–D and A*–D*, respectively (Fig. 5). This feature, originally observed by Strens (1966) and Burns & Strens (1966) for actinolites, is related to the four local configurations resulting from the four possible combinations of two divalent cations (in the present case Mg and Fe²⁺) over the three hydroxyl-coordinated *M*(1,3) octahedra (*e.g.*, Hawthorne *et al.* 1996). The important issue here is that measurements of the relative intensities of the hyperfine components in the spectra in Figure 5 allow derivation of the Mg/Fe²⁺ content at *M*(1,3) with a high level of accuracy (Hawthorne *et al.* 1996, Della Ventura *et al.* 1996, 1997, 2003, Iezzi *et al.* 2005). In addition, from the



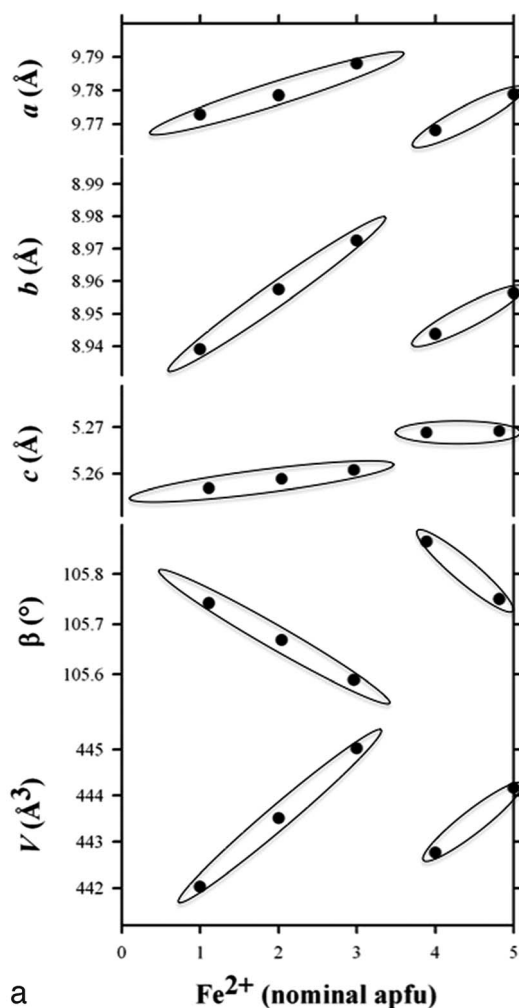
integrated band intensities (area %) of the A–D and A*–D* quadruplets, it is possible to calculate the number of empty *versus* occupied A sites in the sample (Hawthorne *et al.* 1997, Iezzi *et al.* 2007, Della Ventura *et al.* 2014b), another piece of information which is essential to deriving the final crystal-chemical formulae of the synthesized amphiboles. The digitized spectra of Figure 5 were fitted by interactive optimization followed by least-squares refinement (Della Ventura *et al.* 1999, Iezzi *et al.* 2005). The background was treated as linear and all bands were modeled as symmetric Gaussians (Strens 1974). The spectral parameters (position and width) of some strongly overlapping peaks were refined where these peaks are most prominent, and then fixed during the refinement of the other samples. This is clearly the case of the tremolite band at 3674 cm^{-1} (band A* in Fig. 5) that overlaps with the D band occurring at the same wavenumber. At convergence, the peak positions were released and only the widths were constrained to be roughly constant in all spectra. A typical example of a fitted spectrum is displayed in Figure 6. Refined band positions, widths, and relative intensities (I/I_{tot}) are given in Table 4, while final compositional data are summarized in Table 5. One final interesting point is that the FTIR spectrum of endmember ferro-richterite shows an overlapping but still well-defined additional component at around 3650 cm^{-1} (arrowed in Fig. 5) on the low-wavenumber side of the main band. The position of this component could be compatible with different local configurations, and will be discussed in more detail below.

MÖSSBAUER SPECTROSCOPY

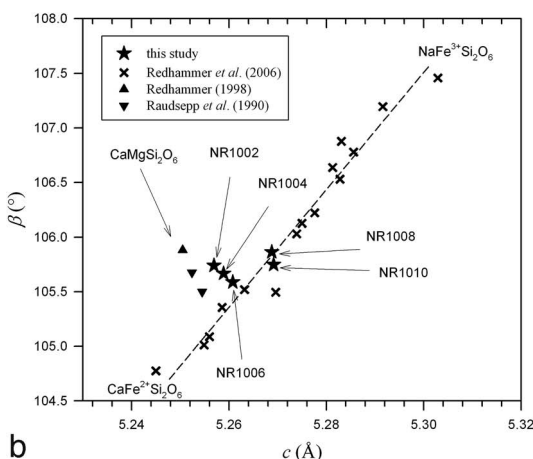
Considering that some samples contain significant amounts of Fe-bearing cpx (Table 3), it was necessary to also account for the contribution of this mineral in the Mössbauer spectra, especially those collected from the NR1008 and NR1010 experimental powders. A further element of complexity was the fact that the spectral contributions of cpx and amphibole closely overlap (Redhammer *et al.* 2006). However, because the composition of the Fe-rich clinopyroxene could be determined to lie along the hedenbergite–aegirine

FIG. 3. (a) Evolution of the unit-cell parameters for the amphiboles synthesized along the studied join as a function of nominal Fe^{2+} . Dashed lines are linear regressions to the data.

FIG. 3. (b) Relationship between cell volume and the mean octahedral radius at $M(1,2,3)$. Ni–Mg and Mg–Co series: data from Della Ventura *et al.* (1997); Mg–Fe: this work. Lines are only a guide for the eye.



a



b

join, with aegirine contents of 28–30 mol.% (Table 2), it was possible to model the contribution of this mineral using literature data given in Redhammer *et al.* (2006). During spectral fitting, isomer shift and quadrupole splitting values of the cpx resonance absorption contribution were kept constant, as was done with the amount of Fe^{3+} . Redhammer *et al.* (2006) showed that the ferric iron content in the cpx is controlled by the Na^+ to Ca^{2+} ratio, thus the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in cpx was fixed to scale with the Na/Ca ratio. The relative area fractions of the pyroxene Fe^{2+} contributions were estimated from literature data, while the total amount of clinopyroxene present in the samples was fixed at the value determined by Rietveld analysis (Table 3). Using this procedure, it was possible to extract reliable $\text{Fe}^{2+}/\text{Fe}^{3+}$ and ^{57}Fe Mössbauer parameters for the amphibole.

The ^{57}Fe Mössbauer spectra (Fig. 7) show iron in both valence states. The spectra are dominated by a broad, structured ferrous iron resonance absorption, which corresponds to Fe^{2+} at octahedral sites. Besides Fe^{2+} , the spectra also exhibit distinct amounts of ferric iron in octahedral coordination, revealed by a sharp and well-resolved resonance absorption line at $\approx +0.6$ mm/s; no evidence for ferric iron in tetrahedral coordination was found.

The spectrum of the Mg-free sample NR1010 (Fig. 7) was used to fashion a model for refinement. A strategy involving one Fe^{3+} and three Fe^{2+} doublets was chosen for the amphibole. Based on previous studies (*e.g.*, Hawthorne 1983, Redhammer & Roth 2002, Iezzi *et al.* 2003a) the ferric iron contribution was assigned to the $M(2)$ site, whereas the three other doublets were assigned to Fe^{2+} at the $M(1,2,3)$ sites. In particular, the outermost doublet with the largest quadrupole splitting ($\text{QS} \approx 2.90$ mm/s) was assigned to Fe^{2+} at $M(1)$, the doublet with intermediate quadrupole splitting (2.59 mm/s in NR1010) to Fe^{2+} at $M(3)$, and the one with the lowest quadrupole splitting to Fe^{2+} at $M(2)$. Data for the quadrupole splittings of Fe^{2+} at $M(2)$ in amphiboles compiled by Hawthorne (1983) range between 1.80–2.20 mm/s. Hawthorne (1983) and Redhammer & Roth (2002) observed that the quadrupole splitting of Fe^{2+} at $M(1)$

FIG. 4. (a) Evolution of the unit-cell parameters for the synthesized clinopyroxenes as a function of nominal Fe^{2+} . The indicated trends are just a guide for the eye.

FIG. 4. (b) Plot of c versus β for C2/c pyroxenes of this study (Table 3) in comparison with literature data for the hedenbergite–aegirine series (Redhammer *et al.* 2006), endmember diopside (arrowed) from Redhammer (1998), and data along the diopside–Ni-diopside join (Raudsepp *et al.* 1990).

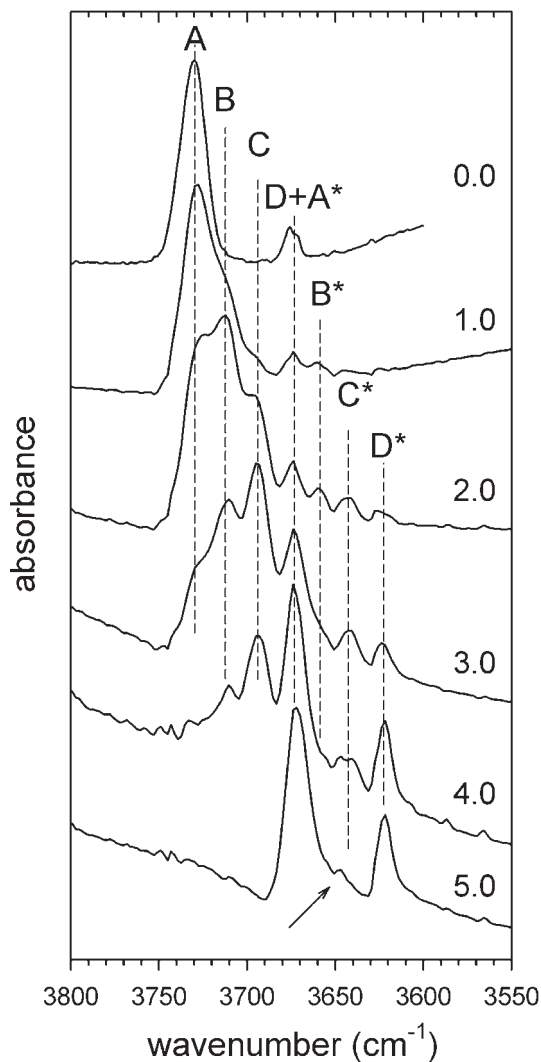


FIG. 5. FTIR spectra of synthetic amphiboles along the studied join as a function of increasing nominal Fe^{2+} (apfu), indicated on the right side.

and $M(3)$ is correlated with the average ionic radius of the $M(2)$ site. Using the graph constructed from literature data (Redhammer & Roth 2002), one has to expect quadrupole splitting values of $\approx 2.40\text{--}2.50$ mm/s for Fe^{2+} at $M(3)$ for average ionic radii above $0.72 \text{ \AA}$, which is the range of ionic radii found in the samples studied here. More recently, Iezzi *et al.* (2003a, 2004, 2005) and Della Ventura *et al.* (2005a, 2005b) showed that the quadrupole splitting of Fe^{2+} at $M(3)$ ranges between 2.45 and 2.65 mm/s in samples where the $M(2)$ site is occupied by trivalent cations. Thus the quadrupole splitting of the doublet with

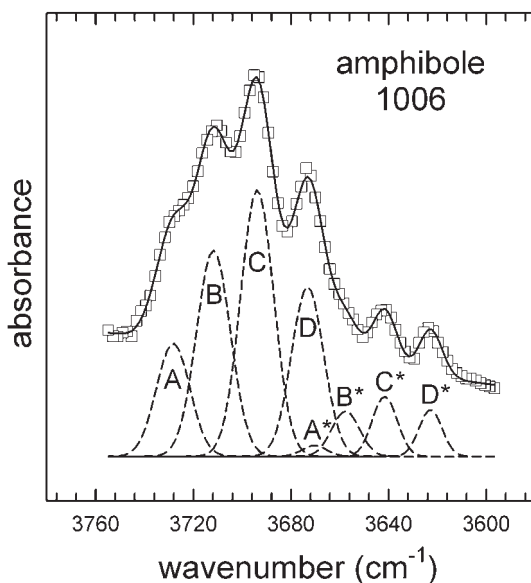


FIG. 6. Example of fitted spectrum: experimental data = empty boxes, fitted component bands = dashed lines, sum of the fitted components = black line.

intermediate values is well within the range of QS values for Fe^{2+} at the $M(3)$ site, whereas the one with the lowest QS is close to the range of data typically found for Fe^{2+} at $M(2)$. This model resulted in an excellent refinement with almost ideal $(\text{Fe}^{2+} + \text{Fe}^{3+})$ site populations of 2.00 : 1.00 : 2.00 apfu for the $M(1)$: $M(3)$: $M(2)$ sites, respectively (Table 6). It should be noted that for the amphiboles no constraints were used on any parameters. An innermost Fe^{2+} component, which is necessary to achieve convergence, corresponds to the cpx contribution, with Fe^{2+} occupying the $M(1)$ site having distinct line broadenings due to next nearest neighbor and charge transfer effects (see Redhammer *et al.* 2006 for more details).

Substitution of Fe^{2+} by Mg^{2+} does not alter the general appearance of the spectra, even if the shoulder at $\approx +2.20$ mm/s becomes more prominent, indicative of an increasing separation of the $M(1) + M(3)$ and the $M(2)$ Fe^{2+} resonance absorption contributions. This is most evident in the sample richest in Mg^{2+} (sample NR1002, Fig. 7). Within the studied series the isomer shift of all Fe^{2+} components tends to decrease with increasing Mg content (Fig. 8), meaning that the s-electron density at the probe nucleus increases. This can be related to an overall shortening of the $M\text{--O}$ bond lengths within the strip of $M(1)\text{--}M(3)$ octahedra as a result of the substitution of Fe^{2+} by the smaller Mg^{2+} cation. Thus ligand oxygen atoms are brought closer to the Fe^{2+} probe nuclei, thereby increasing the

TABLE 4. POSITIONS (cm^{-1}), WIDTHS (cm^{-1}), AND RELATIVE INTENSITIES FOR THE COMPONENT BANDS IN THE OH-SPECTRA OF SYNTHETIC AMPHIBOLES ALONG THE STUDIED JOIN

Band	Parameter	NR1000	NR1002	NR1004	NR1006	NR1008	NR1010
A	Position	3730	3730	3729	3728	3729	-
	Width	17.6	16.5	16.5	16.5	15.7	-
	Intensity	0.91	0.56	0.30	0.14	0.05	-
B	Position	-	3714	3712	3712	3711	-
	Width	-	16.8	16.8	15.6	15.2	-
	Intensity	-	0.30	0.34	0.23	0.13	-
C	Position	-	3697	3694	3694	3694	-
	Width	-	15.5	16.0	15.9	14.3	-
	Intensity	-	0.06	0.19	0.31	0.27	-
D	Position	-	3674	3674	3673	3673	3672
	Width	-	15.2	15.2	15.5	13.7	15.0
	Intensity	-	0.02	0.05	0.19	0.36	0.74
A*	Position	3675.2	3674	3674	3670	3674	-
	Width	10.8	8.5	11.2	12.0	10.8	-
	Intensity	0.09	0.03	0.03	0.01	0.01	-
B*	Position	-	3659	3659	3658	3657	-
	Width	-	11.0	11.0	13.4	11.3	-
	Intensity	-	0.02	0.04	0.04	0.03	-
C*	Position	-	3644	3643	3642	3642	-
	Width	-	9.1	11.5	11.5	11.1	-
	Intensity	-	0.00	0.04	0.05	0.05	-
D*	Position	-	3624	3624	3623	3622	3622
	Width	-	9.1	9.1	10.3	9.3	9.2
	Intensity	-	0.00	0.01	0.03	0.10	0.19
oxo	Position	-	-	-	-	-	3622
	Width	-	-	-	-	-	9.2
	Intensity	-	-	-	-	-	0.07

oxo: oxo component, see text for explanation.

local s-electron density. On the other hand, the isomer shift of Fe^{3+} remains constant within experimental errors.

Similar to the samples of the magnesio-riebeckite–clino-ferri-holmquistite series (Della Ventura *et al.* 2005b), the quadrupole splittings of the richterite

TABLE 5. Fe^{2+} SITE OCCUPANCIES AT THE HYDROXYL-COORDINATED $M(1,3)$ SITES FROM FTIR AND THE A-SITE OCCUPANCY DERIVED USING THE FTIR DATA (SEE TEXT FOR EXPLANATION)

Sample	Fe^{2+} at $M(1,3)$ FTIR (<i>apfu</i>)	A site FTIR
NR1000	0.00	0.05
NR1002	0.50	0.03
NR1004	1.02	0.06
NR1006	1.68	0.06
NR1008	2.18	0.10
NR1010	3.00	0.10

series also show some dependence on the chemical composition. Regarding Fe^{3+} , the QS on $M(2)$ increases with increasing Mg^{2+} content from 0.365 to 0.483 mm/s (Fig. 9a). Considering that, for Fe^{3+} , quadrupole splitting and geometric/electronic distortions from ideal octahedral symmetry are known to be positively correlated, this behavior can be interpreted as an increase of local distortions around $^{M(2)}\text{Fe}^{3+}$ with increasing Mg content. Also for the ferrous quadrupole splitting some systematic variations across the Fe–Mg series are observable (Fig. 9b): for the $M(2)$ and $M(3)$ sites, a slight decrease in Fe^{2+} QS is present, while for Fe^{2+} at $M(1)$ the QS remains almost constant, leading to an increasing separation of $M(1)$ to $M(3)$ components with increasing Mg^{2+} content (Fig. 7). It is well known that the QS of Fe^{2+} is inversely correlated with the geometric/electronic distortion of the octahedral site. Thus an increase in the quadrupole splitting is consistent with a decreasing electronic/geometric distortion of the local environment around the Fe^{2+} probe nucleus along the series, including decreasing

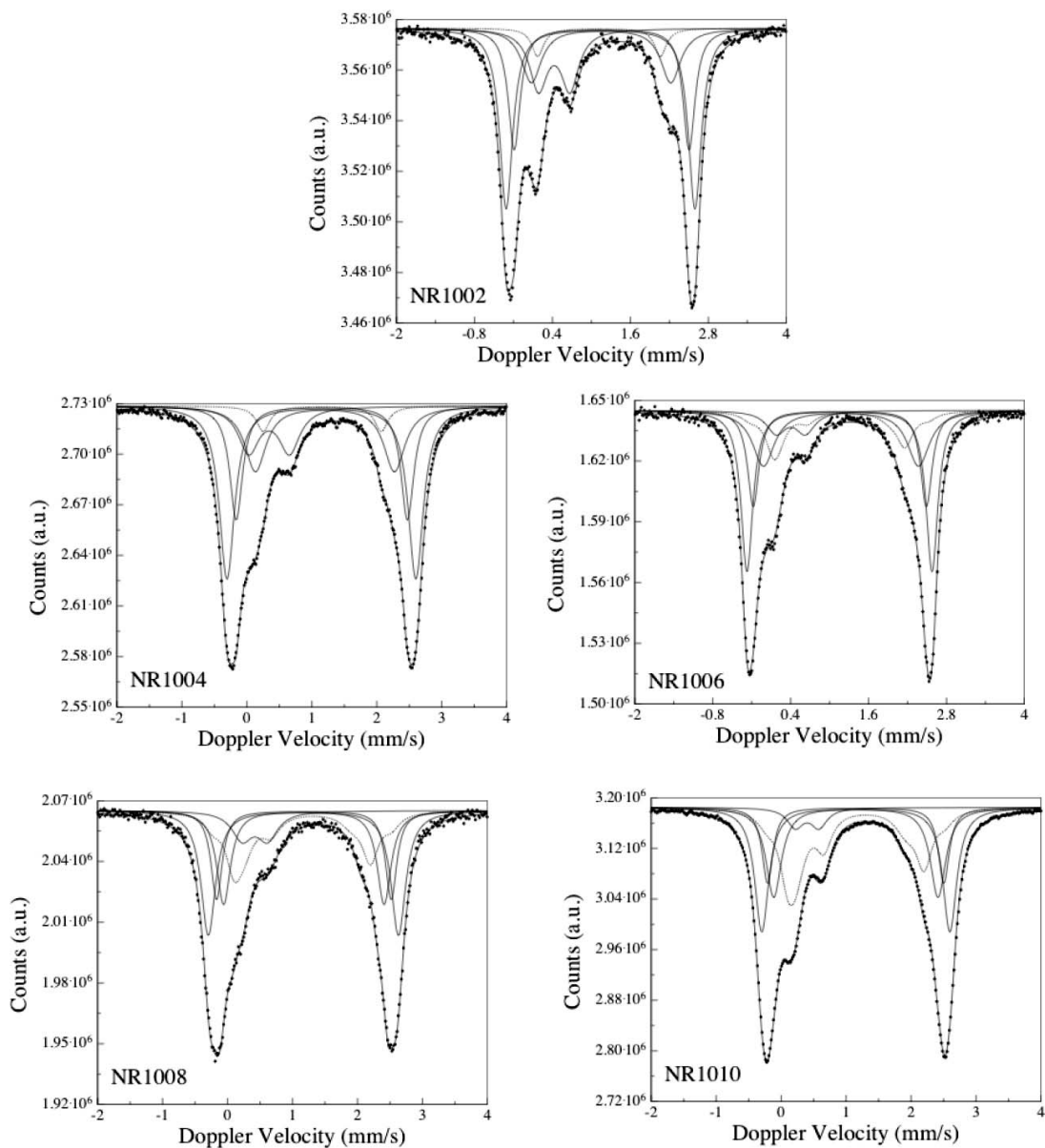


FIG. 7. ^{57}Fe Mössbauer spectra for the experimental powders along the studied join. For doublet assignments see text.

geometric distortion of the oxygen coordination octahedron; this seems to be the case for Fe^{2+} at $M(3)$, while the opposite is observed for Fe^{2+} at $M(2)$.

Below the $\text{Fe}^{2+}/\text{Fe}^{3+}$ site-occupancy data obtained from Mössbauer spectroscopy (Table 6) will be combined with the FTIR information (Table 5) to derive complete crystal-chemical formulae for the synthesized amphiboles.

THE COMPOSITION AND CRYSTAL CHEMISTRY OF THE SYNTHESIZED AMPHIBOLES

Synthetic amphiboles are typically very small and acicular, and this makes their microchemical analysis difficult. This issue is particularly critical in asbestos studies, and indeed several strategies or analytical protocols have been tested (*e.g.*, Meeker *et al.* 2003,

TABLE 6. ^{57}Fe MÖSSBAUER PARAMETERS FOR THE AMPHIBOLES OBTAINED ALONG THE STUDIED JOIN

Sample nom C-site	IS (mm/s)	QS (mm/s)	HWHM (mm/s)	Area (%) A_{abs}	Area (%) A_{rec}	
NR1010	0.403	0.365	0.161	4.9(9)	7.3	Fe^{3+} M(2)
Fe^{+2}_5	1.173	2.895	0.131	27.6(9)	40.8	Fe^{2+} M(1)
	1.178	2.713	0.100	13.1(8)	19.4	Fe^{2+} M(3)
	1.181	2.5284	0.144	22.0(9)	32.6	Fe^{2+} M(2)
	0.421	0.392	0.191	8.9(8)	11.9	Fe^{3+} M(2)
NR1008 $\text{Mg}_1\text{Fe}^{+2}_4$	1.167	2.926	0.136	29.1(6)	39.0	Fe^{2+} M(1)
	1.175	2.687	0.104	15.9(7)	21.3	Fe^{2+} M(3)
	1.174	2.470	0.129	20.7(8)	27.7	Fe^{2+} M(2)
	0.402	0.449	0.181	7.5(5)	9.0	Fe^{3+} M(2)
NR1006 $\text{Mg}_2\text{Fe}^{+2}_3$	1.152	2.851	0.110	34.1(6)	40.9	Fe^{2+} M(1)
	1.157	2.666	0.108	19.9(6)	23.9	Fe^{2+} M(3)
	1.166	2.387	0.205	21.9(5)	26.2	Fe^{2+} M(2)
	0.433	0.466	0.193	13.9(6)	14.6	Fe^{3+} M(2)
NR1004 $\text{Mg}_3\text{Fe}^{+2}_2$	1.147	2.906	0.143	39.0(7)	41.1	Fe^{2+} M(1)
	1.154	2.636	0.121	21.8(8)	22.9	Fe^{2+} M(3)
	1.153	2.239	0.199	20.4(8)	21.4	Fe^{2+} M(2)
	0.428	0.483	0.166	16.7(8)	17.6	Fe^{3+} M(2)
NR1002 $\text{Mg}_4\text{Fe}^{+2}_1$	1.140	2.906	0.122	37.8(8)	39.9	Fe^{2+} M(1)
	1.151	2.591	0.111	23.2(7)	24.5	Fe^{2+} M(3)
	1.150	2.145	0.184	17.1(8)	18.1	Fe^{2+} M(2)

The nominal C-site composition is indicated. Estimated standard deviations on isomer shift values = 0.01 mm/s, on quadrupole splitting 0.02 mm/s and half width at half maximum = 0.2 mm/s. Relative area fractions A_{abs} = obtained from refinements, A_{rec} = values recalculated on basis of 100% amphibole (see text for explanation).

Laskin & Cowin 2003, Paoletti *et al.* 2008, Iezzi *et al.* 2007, Della Ventura *et al.* 2014b). As extensively shown, see for example the reviews of Oberti *et al.* (2007) and Hawthorne & Della Ventura (2007), besides the usual EDS/WDS and X-ray diffraction methods, spectroscopic techniques and, when possible, TEM (transmission electron microscopy) techniques are extremely useful in amphibole studies, being able

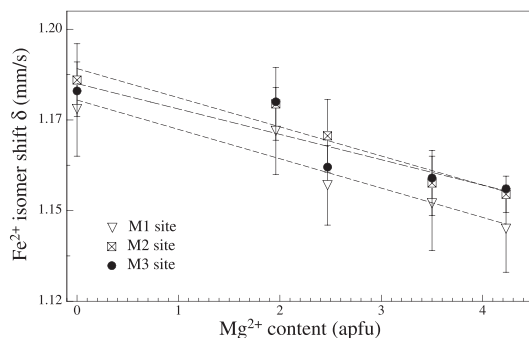


FIG. 8. Variation of the Fe^{2+} isomer shift for the amphiboles synthesized along the studied join as a function of varying nominal composition.

to provide, besides the phase identification, both LR and SR structural information. For the system studied here, we may consider the following constraints for deriving the stoichiometry of the synthesized amphiboles: (1) Mössbauer spectroscopy shows that in all of the amphiboles Fe^{3+} is completely ordered at M(2), whereas Fe^{2+} is disordered over all C sites and undetected at the B sites; in addition, there is no evidence of $^{[4]}\text{Fe}^{3+}$, thus the tetrahedral composition is $\text{Si} = 8 \text{ apfu}$ (Table 6); (2) infrared spectroscopy allows calculation of (see Hawthorne *et al.* 1997, Iezzi *et al.* 2007, Della Ventura *et al.* 2014b) the relative amounts of Mg and Fe^{2+} at M(1,3), as well as the A-site occupancy (Table 5); (3) the Ca/Na content at the B-sites can be obtained on the basis of electroneutrality requirements, assuming two OH molecules *apfu*. As we will see below, this is probably not strictly true for the Fe endmember composition, but the amount of the O(3) site that is deprotonated is minor and can be neglected for the general purposes of this study.

Considering the above points, we can combine the FTIR and Mössbauer data and derive the final crystal-chemical formulae for the synthesized amphiboles. The final results are given in Table 7 and can be compared with the EMP-WDS and FESEM-EDS

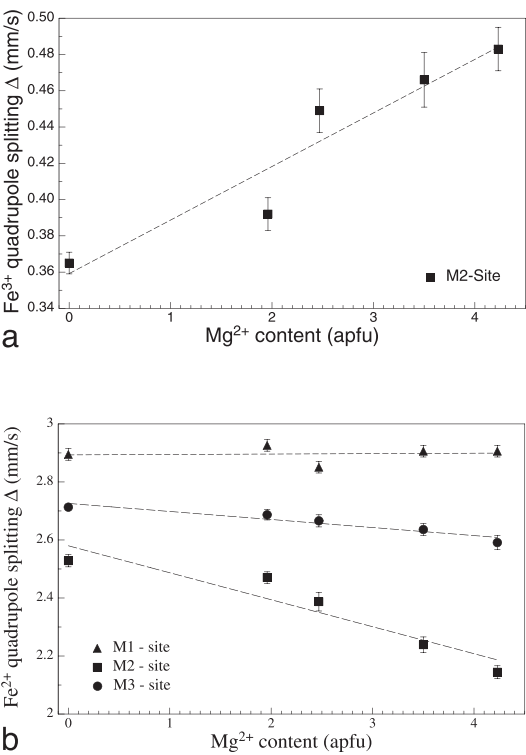


FIG. 9. Variation of the quadrupole splitting of (a) ferric iron and (b) ferrous iron in the amphibole samples along the studied join as a function of varying nominal composition.

analyses of Table 2 to check for consistency of the procedure.

The Fe endmember (sample NR1010)

According to Mössbauer spectroscopy (Table 6) the C-site composition of nominal endmember ferro-richterite (sample NR1010) is: $M^{(1)}(Fe^{2+}_{2.00})M^{(3)}(Fe^{2+}_{1.00})M^{(2)}(Fe^{2+}_{1.63}Fe^{3+}_{0.37})$, in reasonable agreement with the EMP data (Table 2). Considering that the tetrahedral double-chains have composition Sig₈, there are only three ways in which 0.37 apfu of

Fe³⁺ at M(2) can be balanced: (1) loss of ⁴Na with consequent departure toward ferro-actinolite; (2) Na → Ca substitution at M(4), i.e., departure of the amphibole composition toward arfvedsonite; (3) oxy-substitution at O(3), which can be represented as $M^{(1,3)}Fe^{2+} + OH^- \rightarrow M^{(1,3)}Fe^{3+} + O^{2-}$ and produces an oxo-amphibole. All these mechanisms can operate simultaneously. Infrared spectroscopy shows that mechanism (1) is active in the examined system; 0.10 apfu of vacant A sites can be estimated for amphibole NR1010 (Table 5), again in excellent agreement with the EMP data (Table 2). Based on electroneutrality constraints, the Na/Ca content at the B sites can finally be calculated; the result shows that mechanism (2) is responsible for the shift of the amphibole composition toward arfvedsonite. In addition, as discussed above, the FTIR spectrum of sample NR1010 (Fig. 4), besides showing the expected bands at 3672 and 3622 cm⁻¹, which are assigned to the FeFeFe–OH–Na and FeFeFe–OH–⁴□ configurations, respectively, exhibits a third evident peak at around 3650 cm⁻¹. This band is shifted 20 cm⁻¹ to lower wavenumbers with respect to the main band centered at 3672 cm⁻¹; given the controlled chemistry of the system, it could be compatible with different local configurations, for example with Fe²⁺ at M(4) (Iezzi *et al.* 2005), or Fe³⁺ at M(1,3) (Iezzi *et al.* 2003a, Hawthorne & Della Ventura 2007), or both. Unfortunately, the Mössbauer spectra do not provide enough resolution to differentiate minor amounts of Fe³⁺ at M(1,3), a possibility which, according to the known crystal-chemical models for amphiboles (e.g., Oberti *et al.* 2007), would imply deprotonation at the O(3) site. Iezzi *et al.* (2005) showed that the occurrence of ^BFe²⁺ in synthetic clino-ferri-holmquistites with variable (Mg,Fe²⁺) contents causes a downward shift of the main OH-band of 5 cm⁻¹, thus the 3650 cm⁻¹ band in the spectrum of sample NR1010 cannot be due to this effect. On the other hand, Della Ventura *et al.* (2007) showed that the occurrence of a deprotonated anionic site in the structure causes a downward shift of the main OH-band of 20 cm⁻¹, an effect already well known for OH–F substituted amphiboles (Robert *et al.*

TABLE 7. CRYSTAL-CHEMICAL DATA FOR THE AMPHIBOLES OF THIS WORK, OBTAINED BY COMBINING POWDER FTIR AND MÖSSBAUER SPECTROSCOPIES

Sample	⁴ Na IR	M(4) neutrality	M(1,3) IR	M(2) Möss + IR	Mg _{tot}	Mg _{nom}
NR1000	0.95	Na _{0.95} Ca _{1.05}	Mg ₃	Mg ₂	5.00	5.00
NR1002	0.95	(Na _{1.09} Ca _{0.91})	(Fe ²⁺ _{0.50} Mg _{2.50})	(Fe ³⁺ _{0.14} Fe ²⁺ _{0.14} Mg _{1.72})	4.22	4.00
NR1004	0.94	(Na _{1.17} Ca _{0.83})	(Fe ²⁺ _{1.02} Mg _{1.98})	(Fe ³⁺ _{0.23} Fe ²⁺ _{0.34} Mg _{1.43})	3.41	3.00
NR1006	0.94	(Na _{1.17} Ca _{0.83})	(Fe ²⁺ _{1.68} Mg _{1.32})	(Fe ³⁺ _{0.23} Fe ²⁺ _{0.68} Mg _{1.09})	2.41	2.00
NR1008	0.90	(Na _{1.33} Ca _{0.67})	(Fe ²⁺ _{2.18} Mg _{0.82})	(Fe ³⁺ _{0.43} Fe ²⁺ _{1.00} Mg _{0.57})	1.39	1.00
NR1010	0.90	(Na _{1.27} Ca _{0.73})	Fe ²⁺ _{3.00}	(Fe ³⁺ _{0.37} Fe ²⁺ _{1.63})	0.00	0.00

1989, Robert *et al.* 1999, 2000). On this basis, we assign the component at 3650 cm^{-1} in the spectrum of sample NR1010 to a minor deprotonation at the anionic $O(3)$ site, which is coupled with the presence of the corresponding amount of Fe^{3+} at $M(1,3)$. This interpretation is confirmed by recent single-crystal refinements of synthetic potassic-ferro-richterite (Oberti *et al.* 2016), and by recent HT-FTIR experiments on the same sample (Della Ventura *et al.*, unpublished data), which show clearly that increasing Fe oxidation at $M(1,3)$ is related to a significant increase in intensity of a band at this wavenumber. The final composition, from combination of the spectroscopic data, neglecting for simplicity the oxo-component, which can be estimated to be $<0.10\text{ apfu}$ from the intensity of the FTIR absorption, is given in Table 7. This formula is in good agreement with that obtained from the EMP analyses (Table 2): the calculated Fe^{3+} at $M(2)$ is 0.37 *versus* 0.52 *apfu*, while the total Fe^{2+} is 4.63 *versus* 4.65 *apfu*. A poorer, but still reasonable, agreement is obtained for ^BCa (0.73 *versus* 0.52 *apfu*) and for total Na (2.17 *versus* 2.38 *apfu*). It is, however, worth recalling that, while the EMP data represent a few analyzed points on a few larger crystals, the spectroscopic data reflect the average composition of thousands of crystallites.

The intermediate (Mg,Fe) samples along the join

The composition of the intermediate samples along the series can be derived by using the following procedure: the Fe^{2+} content at $M(1,3)$ is calculated from the IR spectra (Table 5), and the remainder of the $M(1,3)$ sites are filled with Mg. The Fe^{2+} value is used to scale the Mössbauer intensities to derive the $\text{Fe}^{2+}/\text{Fe}^{3+}$ contents at $M(2)$, the remainder of this site being filled with Mg. Next, based on the *A*-site occupancy from FTIR (Table 5) and the Fe^{3+} content at $M(2)$, the *B*-site population can be derived based on electro-neutrality constraints, considering that $\text{Na} = 1 + ({}^{M2}\text{Fe}^{3+} - {}^A\Box)$. The final results are given in Table 7. Comparison of Table 7 with Table 2 shows that the agreement between the formulae obtained from spectroscopy *versus* EDS microanalysis is, however, not as satisfactory as that observed for the WDS data, due to the difficulties discussed above. Considering also that the spectroscopic methods provide an average over the whole powder, we consider the results from the combination of FTIR and Mössbauer as the most reliable for constraining the crystal chemistry of the studied synthetic amphiboles.

CONCLUSIONS

Our work shows that although a linear evolution of the cell dimensions is observed for amphiboles along

the (nominal) richterite–ferro-richterite join, their compositions depart significantly from those expected. A similar problem has been faced in previous syntheses of Fe-bearing amphiboles (*e.g.*, Iezzi *et al.* 2004, 2005, Della Ventura *et al.* 2005a, 2005b). Regarding the system studied here, Oberti *et al.* (1992) showed that in richterite the dimension of the octahedral layer is the largest possible for an amphibole with its *A* site filled; therefore the substitution of Mg by the larger Fe^{2+} cation in the octahedral strip is highly unfavorable. The compositional data, and in particular the evolution of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, suggest that when Fe in the system increases beyond a certain threshold, the amphibole structure tends to adjust its geometrical stress by increasing its Fe^{3+} content. In other words, the geometrical misfit between the tetrahedral double chain and the octahedral layer is alleviated *via* the substitution of Fe^{3+} at $M(2)$, which must be balanced by the simultaneous substitution of Na for Ca at $M(4)$, following the exchange vector ${}^{M2}\text{Fe}^{2+}M^4\text{Ca}M^2\text{Fe}^{3+}{}_{-1}{}^{M4}\text{Na}_1$. This being the case, the availability of extra Ca in the system could be responsible for the enhanced crystallization of cpx observed in Figure 2. Therefore, besides the obvious adjustment of the amphibole chemistry due to the evolving system, there is also a stringent crystal-structural control on its final stoichiometry, leading to a possible instability of endmember ferro-richterite for stereochemical reasons; obviously, this inference holds true for the thermal and redox conditions of our work. Nonetheless, this observation could explain the rarity of this amphibole in nature. One implication of this hypothesis is that the role of crystal chemistry should be taken into account, in addition to thermodynamic and kinetic parameters, when the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of amphiboles are used to model f_{O_2} conditions during their crystallization (*e.g.*, Della Ventura *et al.* 2005a).

One interesting final aspect concerns the evolution of the crystal morphology along the studied join. The Mg endmember consists of extremely asbestiform crystals with average lengths of $10\text{ }\mu\text{m}$ and widths of $0.5\text{ }\mu\text{m}$ (Fig. 1), as previously observed for other Mg-rich compositions (*e.g.*, Iezzi *et al.* 2006, 2010). With increasing Fe in the system, the crystal shape progressively evolves toward stubby morphologies; the Fe endmember consists of prismatic crystals with average lengths of $>10\text{ }\mu\text{m}$ and widths of $5.0\text{ }\mu\text{m}$ (Fig. 1). The effect of the oxidation state of iron on the amphibole morphology is an important issue in asbestos mineralogy. Neglecting the role of the thermal conditions during crystal nucleation and growth, previous studies have shown that increasing Fe^{3+} in the amphibole correlates with more acicular morphologies (*e.g.*, Iezzi *et al.* 2004, Della Ventura *et*

al. 2005b), in agreement with the more pronounced asbestiform habit of riebeckite with respect to arfvedsonite. Along the studied join, however, although there is a slight increase in Fe^{3+} , the crystal morphologies tend to become prismatic and stubby. This further suggests that the Fe^{2+} content, the increase of which is more pronounced than that of ferric iron (Table 7), predominates in controlling the crystal shape.

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