

## Crystal chemistry of two coexisting K-richterites from St. Marcel (Val d'Aosta, Italy)

ANNIBALE MOTTANA

Dipartimento di Scienze della Terra, Sezione Mineralogico-Cristallografica, Università di Roma "La Sapienza,"  
Città Universitaria, 00185 Roma, Italy

WILLIAM L. GRIFFIN

Mineralogisk-Geologisk Museum, Sars' Gate 1, N-0562 Oslo 5, Norway

### ABSTRACT

Two coexisting F-bearing K-richterites from the blueschist-facies metamorphic manganese ore deposit St. Marcel (Val d'Aosta, Italy) have been studied by combined EMPA and IR analytical techniques. Despite their different colors (pink and blue) and cell dimensions, these amphiboles have formulae summing up to near 16 cations pfu on the basis of  $22\text{O} + 2(\text{OH} + \text{F})$  and are chemically almost identical. The major differences are in the F/OH ratio and the Ca content, and significant minor differences occur in Fe and Ti.

The IR spectra in the OH-stretching region are notably different, probably as a result of the different F contents. However, both amphiboles have a prominent absorption peak at  $3731\text{ cm}^{-1}$ , typical of the K-OH-(MgMgMg) configuration, plus weak bands at  $3672$  and  $3653\text{ cm}^{-1}$ , typical of configurations having the A site empty. Moreover, pink K-richterite has a strong absorption band at  $3715\text{ cm}^{-1}$  that was assigned to the Sr-OH-(MgMgMg) configuration, balancing the A sites that are empty. Site assignments based on EMPA and IR compare well with those determined by crystal-structure refinement. However, they also allow detection of empty A sites in the structure.

### INTRODUCTION

Although amphiboles are widespread in the Earth's crust, K-richterite may be considered a rare mineral. Nevertheless, it has one of the widest experimentally determined *P,T* stability fields among the amphiboles (Kushiro and Erlank, 1970; Gilbert and Briggs, 1974; Hariya et al., 1974; Gilbert et al., 1982). These experimental data are consistent with the occurrence of K-richterite, which ranges from hyperpotassic volcanic or subvolcanic rocks (Carmichael, 1967; Velde, 1967; Thy, 1982) to the upper mantle. The most common occurrence of K-richterite is in ultramafic xenoliths from kimberlites (Erlank and Finger, 1970; Aoki, 1975; Dawson and Smith, 1977; Erlank and Rickard, 1977; Jones et al., 1982), where it is believed to have formed by infiltration metasomatism in the mantle, prior to entrainment of the xenoliths in the kimberlite.

K-F-richterite is even rarer and was defined as a natural species only recently, in contact-metamorphic ejecta from the Monte Somma volcano (Della Ventura et al., 1983), although F-bearing K-richterites have been known for some time (Olsen et al., 1973; Delaney et al., 1980; Jones et al., 1982). This apparent rarity may be due to a lack of F analyses.

Nothing is known about the mutual relationships between F- and OH-bearing K-richterites, nor between these and richterite. All four endmembers have been synthesized (Huebner and Papike, 1970), but the thermody-

namic properties of the solid solutions have not been studied completely.

F-poor and F-rich K-richterites occur in contact and in apparent equilibrium within the St. Marcel manganese deposit, Val d'Aosta, Italy. Only richterite was previously known from this deposit (Rondolino, 1936; Martin-Vernizzi, 1982); these K-bearing amphiboles are the products of blueschist-facies metamorphism and represent the first occurrence in such a geologic environment. However, more interesting is the apparent equilibrium relationship observed between the phases, as this implies the possibility of a compositional gap between phases differing solely in their volatile contents.

### PETROLOGIC SETTING

A description of the Praborna orebody in the St. Marcel valley has recently been presented (Griffin and Mottana, 1982). The present sample was collected from the dump; thus the geologic relationships are not known. The chip available for study ( $14 \times 10 \times 5\text{ mm}$ ) consists mostly of granular braunite intergrown with quartz, as well as a clear quartz zone containing a cluster of pink and blue prisms. The splinter is presumably a part of the main ore, crossed by one of the numerous quartz veins containing both high-*P* and low-*P* minerals (Griffin and Mottana, 1982; Martin-Vernizzi, 1982).

The individual prisms are pink next to quartz and blue

Table 1. Unit-cell parameters and physical properties of St. Marcel K-richterites

	VM-9 pink	VM-9 blue
$a$ (Å)	9.9951(3)	10.0220(4)
$b$ (Å)	17.9710(8)	17.9810(9)
$c$ (Å)	5.2715(1)	5.2750(2)
$\beta$ (°)	104.743(2)	104.690(3)
$V$ (Å <sup>3</sup> )	915.70(10)	919.51(13)
$D$ (g·cm <sup>-3</sup> )	3.040	3.024
$D_{\text{meas}}$	3.05(2)	3.03(2)
$\alpha$	1.606(3)	1.615(3)
$\beta$	1.623(3)	1.630(3)
$\gamma$	1.635(3)	1.640(3)
$2V_x$ (°)	80(3)	76(3)
$Z\Delta c$	18(2)	20(2)

Note: Unit-cell parameters from L. Ungaretti (pers. comm.). Values in parentheses refer to estimated standard deviation of the last digit.

in the center of the cluster. The blue phase is never observed in contact with quartz. The elongate crystals (1.0–1.5 × 0.5 mm) are in parallel alignment, with mutual contact occurring along prism faces. They are either pink or blue; no intermediate shades or zonations in color have been observed.

The aggregate is coarse but not tough; individual grains up to 0.5 mm in size can be extracted with gentle needle pressure.

#### X-RAY AND PHYSICAL DATA

The amphiboles were identified from their unit-cell parameters. Those listed in Table 1 were obtained by the LAT routine on an automated single-crystal diffractometer, a preparatory step toward the refinement of the crystal structure (courtesy of L. Ungaretti). Procedure and instrumentation are as described by Ungaretti et al. (1983).

Like other richterites, the St. Marcel amphiboles have particularly large  $a$  parameters (Cameron and Papike, 1979). The  $a$  parameter also shows the largest difference between the two grains, but the values for  $b$  and  $c$  agree within two standard deviations; the larger  $V$  of the blue variety is mainly a result of its larger  $a$  dimension.

When compared with synthetic F- and OH-K-richterite endmembers (Huebner and Papike, 1970; Cameron et al., 1983), these richterites show  $a$  and  $V$  intermediate between the two endmembers (Fig. 1), such that the F/(OH + F) ratio in the pink and blue variety would be >0.5 and <0.5, respectively, provided that no Na is present at the A site.

Optical data were obtained with the spindle stage, Carville liquids, and white light on grains different from those used for single-crystal X-ray and EMPA work, from the same batches used for IR spectroscopy. The refractive indices of blue richterites are systematically higher than those of pink richterite, as is the extinction angle, but  $2V_x$  is smaller (Table 1). Density was measured on the same grains using the floatation method in Clerici solution; the pink richterite is denser than the blue one (Table 1).

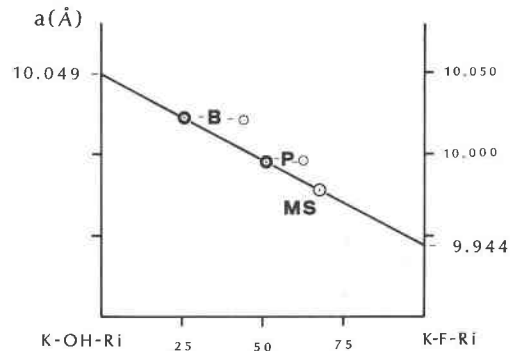


Fig. 1. Variation of the  $a$  unit-cell parameter in synthetic richterite endmembers (Huebner and Papike, 1970; Cameron et al., 1983) and in natural K-richterites from St. Marcel (P, pink; B, blue; present work) and Monte Somma (MS: Della Ventura et al., 1983). The lighter circles for B and P represent the F/(F + OH) contents derived from the chemical analyses.

#### CHEMICAL COMPOSITION

The same grains used for structure refinement were analyzed by EDS electron microprobe. Methods, standards, and precision are given in Griffin and Mottana (1982). In addition, K and Sr were analyzed, using orthoclase and celestite as standards. F was measured by wds microprobe, using a fluorapatite standard. The pink grain was lost prior to the quantitative determination of F. Another grain from the batch used for optics was analyzed using the blue amphibole as a secondary standard. The analyses are given in Table 2. If Mn and Fe are expressed as Mn<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, as is probably the case for minerals in equilibrium with braunite + quartz, and if the amount of H<sub>2</sub>O is calculated to balance the formulae, totals in the range 99.4–99.7 wt% are obtained.

Both analyses show high SiO<sub>2</sub> and MgO contents, but contain little Al<sub>2</sub>O<sub>3</sub> and MnO (despite their coming from a manganese ore) and only traces of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. The differences in Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, although apparently minor, are analytically significant, whereas the variations in SiO<sub>2</sub> and MgO are not (cf. Griffin and Mottana, 1982). Alkalis are present in nearly equal amounts; K<sub>2</sub>O always exceeds Na<sub>2</sub>O and is particularly high for an amphibole, although even higher values are known from amphiboles in potassic lavas (Carmichael, 1967). The original richterite from Långban, Sweden (Michaelson, 1883), also contained K<sub>2</sub>O in excess of Na<sub>2</sub>O.

Among richterites with measured F, the blue grain is the amphibole richest in K<sub>2</sub>O. Prider's (1939) "magnophortite," although reported by Deer et al. (1963) as a K-richterite with 1.29 wt% F, is in fact a K-fluor-magnesian-kataphorite according to the IMA classification (Leake, 1978).

The formulae calculated on the anhydrous basis of 23 oxygens (Robinson et al., 1982) give sums very close to 16 cations, with a slight excess for the blue grain (probably

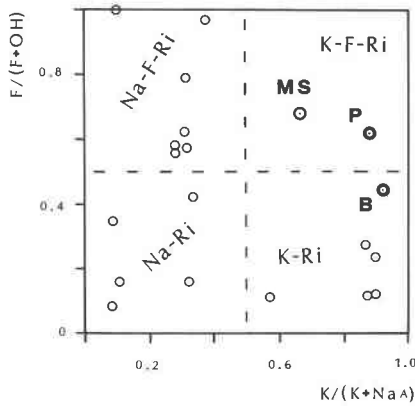


Fig. 2. Compositional variation of richterites with known F content (data after Charles, 1977; Delaney et al., 1980; Jones et al., 1982; and Della Ventura et al., 1983; MS); (P, pink; B, blue; present work)

due to overestimation of silica) and negligible deficiency for the pink one. We therefore normalized cations to 16, i.e., all sites filled. The deviations in stoichiometry are so small that we consider these richterites to have complete Si occupancy of the T position. This is in marked contrast to the richterites from upper-mantle rocks, in which deficiencies at the tetrahedral position are often so large as to remain unfilled even after allocation of all available Al and  $\text{Fe}^{3+}$  (Dawson and Smith, 1977; Jones et al., 1982).

In the St. Marcel richterites, the C group cations are almost entirely Mg, Mn being the second major cation present. Note, however, that minor Ca is required to fill

the five C sites, a procedure that, although unusual, is considered to be "reasonable" by Robinson et al. (1982) for alkali amphiboles. Allocation can continue by filling the B group almost equally with divalent (Ca, Sr) and monovalent (Na) cations, leaving only a little Na to enter the A site, together with the dominant K.

The blue grain has  $F/(OH + F) = 0.44$  and should therefore be considered an F-bearing K-richterite; the pink one has  $F/(OH + F) = 0.62$ , thus meeting the requirement for being classified a K-F-richterite (Fig. 2). As none of the kimberlitic K-richterites exceeds 0.5 in  $F/(OH + F)$  ratio, this is only the second known example of a K-F-richterite, after the Monte Somma type occurrence (Della Ventura et al., 1983), and the only known high-*P* occurrence.

All the allocations suggested so far have been made according to standard, "normal" or "reasonable" crystal-chemical considerations (Hawthorne, 1982a, p. 69; Robinson et al., 1982, p. 7), the only addition being that of combining Sr and Ca, as seems reasonable on the basis of valence and ionic radius. However, the formulae given in Table 2 do not consider the possibility that local vacancies may be present. Thus, although stoichiometrically correct, these formulae may be subject to changes in the case that other, independent methods of establishing site occupancy yield different values (Hawthorne, 1983b, 1983c).

#### INFRARED SPECTROSCOPY

In the decade 1965–1974, infrared spectroscopy found extensive application in studies aimed at assigning the various cations present in the amphibole formulae to sites

Table 2. Microprobe analyses and calculated formulae of St. Marcel K-richterites

	Analysis (wt%)		Atoms per formula unit				
	1	2	1*	2*	1**	2**	
$\text{SiO}_2$	56.74	57.14	Si	7.953	8.024	7.960	8.005
$\text{Al}_2\text{O}_3$	0.59	0.39	$\text{Al}^{\text{VI}}$	0.047	—	0.040	—
$\text{TiO}_2$	0.06	0.00	$\Sigma\text{T}$	8.000	8.024	8.000	8.005
$\text{Fe}_2\text{O}_3$	0.00	0.10	$\text{Al}^{\text{VI}}$	0.050	0.065	0.058	0.065
$\text{Mn}_2\text{O}_3$	0.67	0.53	Ti	0.006	0.000	0.006	0.000
MgO	22.89	23.03	Fe	0.000	0.011	0.000	0.011
CaO	6.94	5.31	Mn	0.071	0.057	0.071	0.057
SrO	0.63	0.93	Mg	4.779	4.818	4.783	4.806
$\text{Na}_2\text{O}$	4.10	4.65	$\text{Ca}^{\text{C}}$	0.094	0.025	0.082	0.056
$\text{K}_2\text{O}$	4.88	5.16	$\Sigma\text{C}$	5.000	4.976	5.000	4.995
F	1.40†	1.00	$\text{Ca}^{\text{B}}$	0.948	0.772	0.961	0.741
$\text{H}_2\text{O}$	(0.81)	(1.19)	Sr	0.051	0.076	0.051	0.075
Total	99.71	99.43	$\text{Na}^{\text{B}}$	1.001	1.152	0.988	1.184
			$\Sigma\text{B}$	2.000	2.000	2.000	2.000
			$\text{Na}^{\text{A}}$	0.113	0.110	0.127	0.078
			K	0.872	0.922	0.873	0.922
			$\Sigma\text{A}$	0.985	1.032	1.000	1.000
			$\Sigma\text{CAT}$	15.985	16.032	16.000	16.000
			F	0.620	0.444	0.620	0.444
			OH	(0.380)	(0.556)	(0.380)	(0.556)

Note: Samples are (1) VM-9 pink (four spots) and (2) VM-9 blue (three spots). Values in parentheses are calculated.

\* On 23-oxygen basis. \*\* On 16-cation basis. † WD-EMP analysis on a different grain (error  $\pm 0.20$ ).

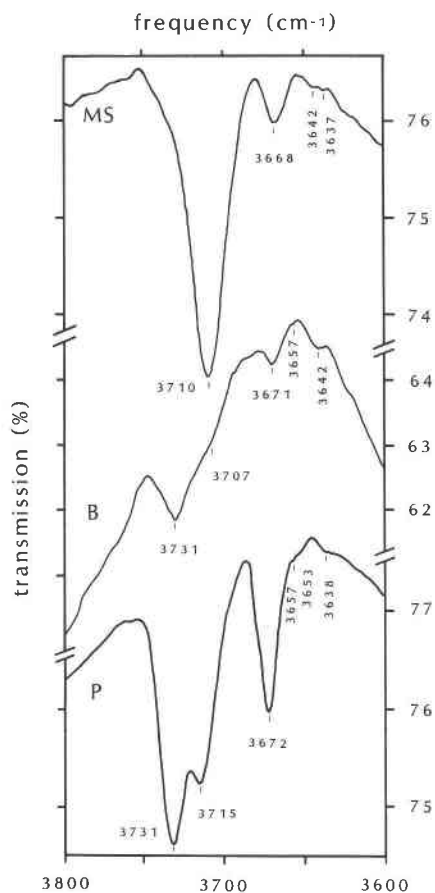


Fig. 3. The hydroxyl-stretching region of the St. Marcel K-richterites (P, pink; B, blue) and of the Monte Somma type sample (MS). Note the variation of the transmission scale for each sample.

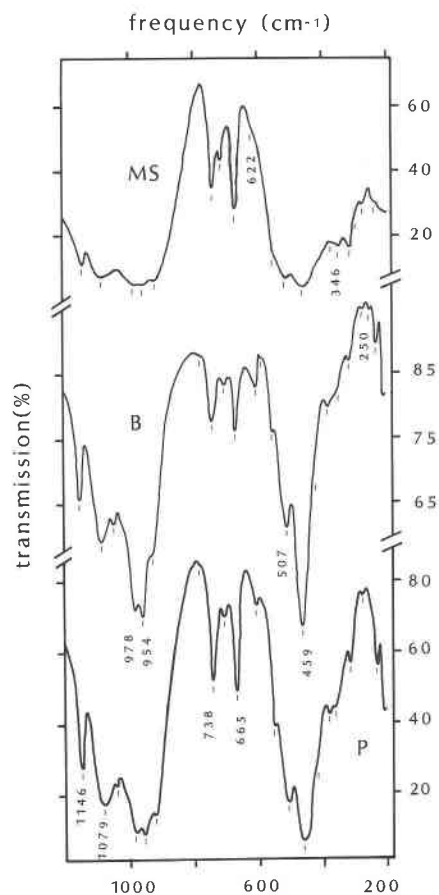


Fig. 4. The region of lattice vibrations for the Monte Somma type K-F-richterite (MS), the blue richterite (B), and the pink (P) richterite from St. Marcel. Note the changes in the transmission scale, but the similarity of the frequency position.

in the structure. However, after Strens' (1974) review, the method fell partly into neglect, because the many problems involved had become apparent. Nevertheless, the IR spectrum gives a variety of qualitative and semiquantitative information, so that the technique retains its usefulness (Hawthorne, 1982b).

The IR spectrum of amphibole consists of two main regions: a low-frequency region (1200–200  $\text{cm}^{-1}$ ) where the vibrations typical of the structure occur; and a high-frequency region (3800–3600  $\text{cm}^{-1}$ ), characteristic of the stretching (valence) vibrations of hydroxyl. The hydroxyl-bending region is less important as it is difficult to separate from the lattice vibrations; in addition, it also may overlap with the lattice vibrations of adsorbed water, which tenaciously adheres to the amphibole fibers (Strens, 1974). Therefore, efforts toward the quantitative determination of site populations have been concentrated essentially on the high-energy region.

The IR spectra of blue and pink richterites were recorded on a Perkin-Elmer model 983A grating spectrometer. They are given in Figures 3 and 4, together with a new spectrum of the K-fluorrichterite from the type locality, rerun on

the original disk supplied by Della Ventura et al. (1983). To avoid overcrowding of the figures, only a few of the observed peaks are indicated, but all are listed in Table 3.

#### The hydroxyl-stretching region

It is well known that in the amphibole structure  $\text{OH}^-$  is located at the O(3) site (Hawthorne, 1982a), where  $\text{F}^-$  (Warren, 1929) and presumably  $\text{Cl}^-$  (Leake, 1968) are also located (Fig. 3). The same site may also be occupied by  $\text{O}^{2-}$ , either competing with  $\text{OH}^-$ , as in oxy- and Ti-bearing amphiboles (Leake, 1968; Kitamura et al., 1975), or with  $\text{F}^-$  as in the amphiboles of meteorites (Olsen et al., 1973). The latter are particularly interesting, as they are (Na)-F-richterites.

The IR method is specific only for OH valence vibrations, those for F, Cl, and O being either Raman-active or occurring in the NIR region. However, the presence of competing anions is evident in the spectrum from the decreased intensity of the OH absorption bands (provided a constant amount of amphibole is used). The integrated areal intensities of bands in the 3800–3600- $\text{cm}^{-1}$  region are inversely proportional to the measured F contents and

Table 3. Observed infrared bands for K-richterites

St. Marcel		
VM-9 pink	VM-9 blue	Monte Somma
3731	3731	
3715		
	~3707s	3710
3672	3671	3668
3657	3657	
3653		
	3642	3642
3638		3637
1146	1146	1144
1079	1079	1084b
1043	1043	
~1015s	~1015s	
979	978	981
953	954	957
918	~920s	916
775s	~775s	
738	738	738
704	702	713
665	665	668
		~622
604	606	
~590s	590	
549	548	549
507	507	512
459	459	457
~420s	~420s	
381	380	
~355s	360	363s
		346
314	314	311
		~290s
		272
277	277	
250		
228	229	238s

Note: s = shoulder; b = broad.

thus roughly proportional to the H<sub>2</sub>O contents. Both EMP and IR analyses therefore indicate that the pink amphibole contains less OH than the blue one. The IR analysis does not give a quantitative estimate of OH, as the spectra were recorded in transmission mode rather than absorption mode, and the recording technique is nonproportional.

Pink richterite shows a sequence of bands which is much better defined than that of the blue richterite. As the grinding technique and pellet preparation were identical for both samples, such a difference is real and may be related to different clustering of the OH present in the samples.

Pink richterite shows three sharp transmission minima at 3731, 3715, and 3672 cm<sup>-1</sup>, plus two other weak shoulders on the lower-energy side of the 3672-cm<sup>-1</sup> band, at 3653–3657 and 3638 cm<sup>-1</sup>, respectively.

Blue richterite shows only two poor, broad minima at 3731 and 3671 cm<sup>-1</sup>, plus weak shoulders at 3705–3710, 3657, and 3642 cm<sup>-1</sup>. All of these bands are much broader than the corresponding bands in the pink richterite spectrum. Broadening of the OH valence bands suggests greater disorder in the arrangement of the OH in the blue richterite than in the pink one (decreasing segregation, in the sense of Law, 1976) with reference to the cations occupying the M(1) and M(3) sites coordinating the O(3) (Oh,F)-bearing site. Apparently, therefore, although the

pink richterite contains less OH, it is substantially more ordered with respect to the coordinating cations than the more OH-rich blue one.

Broadening of the OH-stretching bands is particularly evident in the Monte Somma richterite. The broad band at 3710 cm<sup>-1</sup> is most likely derived from the overlap of at least two bands. Such a broadening may be related to the disordered cation arrangement around OH as a result of the high temperature of formation of the sample (over 550°C according to Della Ventura et al., 1983, as compared with ca. 400°C for the St. Marcel material; see Griffin and Mottana, 1982).

In an amphibole with an empty A site, hydroxyl completes the octahedral coordination of the M(1) and M(3) sites by forming the apex of a flat pseudotrigonal pyramid, the base of which consists of two M(1) sites and one M(3) site. When all the cation sites are occupied by Mg, the cluster has the configuration (MgMgMg)-OH-□, and the IR spectrum consists of a single, strong and sharp peak at 3673 cm<sup>-1</sup> (peak A of Burns and Strens, 1966). When cations other than Mg occupy M(1) and/or M(3), a frequency shift takes place that depends upon the change in the energy of the OH-M bond, in turn affected by the electronegativity of the cation (Strens, 1974). Therefore the cluster having the configuration (Fe<sup>2+</sup>Fe<sup>2+</sup>Fe<sup>2+</sup>)-OH-□ has a characteristic frequency at 3625 cm<sup>-1</sup> (peak D of Burns and Strens, 1966), and it is not only shifted to lower energy but is also weaker than the 3673-cm<sup>-1</sup> peak because of the differences in bond strength. Other clusters, having different types of segregation such as (MgMgFe<sup>2+</sup>)-OH-□ and (MgFe<sup>2+</sup>Fe<sup>2+</sup>)-OH-□, generate independent peaks at 3660 and 3648 cm<sup>-1</sup> (C and D of Burns and Strens, 1966) as do those involving Fe<sup>3+</sup> (see Hawthorne, 1983b).

The undisputed assumption behind this interpretation is that frequency shifts occur in discrete steps, each configuration having a characteristic vibrational frequency. Thus, in chemically intermediate members of solid solutions, the configurations of the endmembers are all simultaneously present with their own characteristic frequency but with peak intensity proportional to the number of each configuration versus the total number of configurations. This model, developed mainly by Strens (1966) and by Burns and Strens (1966) and later improved by Burns and Greaves (1971), Nikitina et al. (1973), and Law (1976) with regard to various theoretical and fitting aspects, suffers severe drawbacks when accurate quantitative determinations of site occupancy are attempted (see, among others, Strens, 1974; Whittaker, 1979; Hawthorne, 1983a). However, it proves sufficiently accurate for simple solid solutions like the tremolite-ferroactinolite series, as well as for qualitative assignments in amphiboles of other series (Burns and Greaves, 1971), providing clustering does not occur (Whittaker, 1979).

In amphiboles with filled or partially occupied A sites, a new type of configuration is present. The hydroxyl no longer forms the apex of the triangular pyramid but bridges between the M(1)M(1)M(3) pseudotriangular base and the cation located at or near the center of the large, 12-fold

coordinated cavity formed by two back-to-back  $\text{Si}_6\text{O}_{24}$  rings of the tetrahedral chains (Hawthorne, 1982a). Configurations with a filled A site possess greater energies than those with empty ones, because the repulsion arising between the cation at A and the proton of the OH dipole projecting into the A-centered cavity leads to an increase in the stability of the O-H bond (Hanisch, 1966). Consequently, these configurations will show OH vibrations shifted to higher energy, i.e., they will display positive frequency shifts with respect to the  $3673\text{ cm}^{-1}$  frequency of the (MgMgMg)-OH-□ configuration. Rowbotham and Farmer (1973) found a strong peak at  $3734\text{ cm}^{-1}$  in a synthetic K-richterite and another at  $3728\text{ cm}^{-1}$  in a synthetic Na-richterite, which they assigned to the (MgMgMg)-OH-K and (MgMgMg)-OH-Na configurations, respectively. In addition, Maresch and Langer (1976) assigned to the (MgMgMg)-OH-Li configuration a vibration occurring at  $3708\text{ cm}^{-1}$  in a complex orthorhombic synthetic amphibole.

Although criticized by Hawthorne (1983b) with regard to the homogeneity of the amphiboles synthesized, Rowbotham and Farmer's assignment has not been disputed. Therefore our  $3731\text{-cm}^{-1}$  band can be also assigned to the configuration (MgMgMg)-OH-K present in both richterites. The intensity of this band shows that such a configuration is indeed the most significant in our samples.

Following Burns and Strens (1966) and Rowbotham and Farmer (1973), the band at  $3672\text{ cm}^{-1}$  is assigned to the (MgMgMg)-OH-□ configuration. We therefore accept that a number of A sites are empty in our pink richterite. Moreover, the shoulders at  $3653\text{--}3657$  and  $3638\text{--}3642\text{ cm}^{-1}$  can be assigned to configurations such as (MgMgMn)-OH-□ and (MgMnMn)-OH-□, respectively, on the basis of arguments originally suggested by Burns and Strens (1966). This is a further indication that a number of the A sites are vacant, at least among those close to the hydroxyls occupying the O(3) site in place of F.

The assignment of the sharp, well-defined peak at  $3615\text{ cm}^{-1}$  in the pink richterite still requires explanation. The position is such as to make it unlikely that it derives from configurations involving either Na or Li. Therefore we assign it to the (MgMgMg)-OH-Sr configuration, on the basis of the following reasoning.

In Strens' (1974) theoretical treatment, frequency shifts from the (MgMgMg)-OH-□ configuration, assumed to be the standard ( $3673\text{ cm}^{-1}$ ), are a function of the electronegativity of the intervening cation. They are negative in the case of substitutions at the M(1) and M(3) sites and positive when the A site is occupied. In addition, there is also a contribution due to the effective charge in such a case. Work on synthetic amphiboles has shown the following shifts:  $+62\text{ cm}^{-1}$  for  $\text{K}^+$  (electronegativity 0.8);  $+56$  for  $\text{Na}^+$  (0.9) and  $+35$  for  $\text{Li}^+$  (1.0), as listed above. In the present case, a  $+42\text{ cm}^{-1}$  shift has been observed in addition to the  $+59$  attributed to  $\text{K}^+$ . This shift cannot be attributed to any other alkali metal ion, the electronegativities of which are even lower than K (Rb 0.8; Cs 0.7), but it can be related to alkaline earths, the electro-

Table 4. Configurations in pink richterite

Configuration	Wavenumber ( $\text{cm}^{-1}$ )	Contribution (%)
MgMgMg-OH-K	3731	87.3
MgMgMg-OH-Sr	3715	5.1
MgMgMg-OH-□	3672	5.1
MgMgMn-OH-□	3653	
MgMnMn-OH-□	3638	
		97.5

negativities of which are in fact intermediate between those of Na and Li (Ca 1.0; Sr 1.0; Ba 0.9). As Ba is not present in our richterites (see Table 2), the choice is restricted to Ca and Sr.

Charge and electronegativity being equivalent, the probability for an ion to enter the A site is inversely proportional to size, as the larger the ion, the more stable the structure will be:  $\text{K} (1.64\text{ \AA}) > \text{Sr} (1.44) > \text{Na} (1.39) > \text{Ca} (1.34)$  for the 12-fold coordination (Shannon, 1976). Thus Sr is not only favored over Ca, but over Na as well, more so as the total local effective charge is increased.

This interpretation explains not only why the  $+56\text{ cm}^{-1}$  shift for Na is not detected in our spectrum, but also why configurations with empty A sites are observed. They are needed to balance the total charge at the A site because of the entry of a divalent cation.

From this chemical interpretation, and taking into account the analytical data of Table 2, we suggest the configurations given in Table 4 to be present in pink richterite.

The filling up of the A site requires a very minor contribution of another configuration, which may be MgMgMg-OH-Na or MgMgMg-OH-Ca. If they are present, these bands are mostly hidden below those of the dominant contributions, although there appears to be in the spectrum another very weak shoulder at  $3657\text{ cm}^{-1}$ . Alternatively, the balance of the A site is reached by assuming the presence of 0.006 Ti at M(1) (cf. Table 2); such a substitution is possible in amphiboles, but it has been shown to be unresolvable in the IR spectrum (Kitamura et al., 1975).

The contribution of the Mn segregation to the configurations involving the empty A site can be calculated from the intensity ratios of the C and D to the A peak (Burns and Strens, 1966; Nikitina et al., 1973). The amount of Mn at the OH-coordinating M(1) + M(3) sites is 0.003 atoms pfu at best, out of a total of 0.071 (Table 2). The rest is either in sites coordinated by F or enters the M(4) sites together with Na displaced by Sr entering the A site.

It should be stressed here that the assignments given above refer only to the 38% of the A sites adjacent to OH; nothing can be said for the 62% for which F occupies the O(3) position.

### The region of lattice vibrations

Despite their large number and strong intensity, the absorption bands in this region add very little to our insight of the amphibole crystal chemistry (Fig. 4). In fact the two examined richterites have spectra identical in all

details, in terms of their frequency, and also in perfect agreement in their intensity when minor variations in chemical composition are also taken into account. On the contrary, there is a striking difference between the St. Marcel richterite spectra and that of the Monte Somma sample. They have essentially identical frequencies, but differ in the sharpness and intensity of the bands. As a whole, the Monte Somma richterite spectrum seems to indicate a disordered structure in comparison with the highly ordered St. Marcel spectra. This may be the result of the different  $P, T$  conditions of formation. The Monte Somma amphibole formed rapidly in a high- $T$ , low- $P$  contact-metamorphic environment, whereas the St. Marcel amphiboles formed in a low- $T$ , high- $P$  regional metamorphic episode (over several million years?). However, this interpretation cannot be supported by other data, as there are no spectra of volcanic K-richterites available in the literature.

#### CAUSE OF THE COLOR

The type K-F-richterite from Monte Somma is colorless in grains about 0.5 mm in size, as are most richterites. The color of the two St. Marcel amphiboles may be related to their contents of transition metals. Although they have nearly equal amounts of Mn, they differ essentially in containing Ti (pink) and Fe (blue). It may be questioned whether these minor amounts are enough to produce the clear colors exhibited by 0.5-mm-thick grains. However, no other chromophores were detected at the EMPA level, and we are forced to attribute the different colors to the modifying effects of Ti and Fe on the prevailing Mn. Thus K-F-richterite presumably is pink owing to the effects of Ti and  $Mn^{3+}$ . This interpretation is supported by the color shown by other  $Mn^{3+}$ -bearing minerals present at St. Marcel (pyroxenes, epidotes and phengites) although these all show violet to red, rather than pink hues. The color of the blue K-(OH)-richterite probably is due to electron transfer between Mn and Fe, although this interpretation is admittedly tentative. There are at St. Marcel no other blue minerals to test it, nor are blue colors in minerals usually attributed to such a mechanism. In most cases it is related to  $Fe^{2+}-Ti^{4+}-Fe^{3+}-Ti^{3+}$  charge transfer (e.g., kyanite, sapphire), but in amphiboles it has been demonstrated to be due to the  $Fe^{2+}-Fe^{3+}-Fe^{3+}-Fe^{2+}$  charge transfer (cf. Smith and Strens, 1976). We have no optical spectra to support our suggestion of the possibility of a  $Mn^{2+}-Fe^{3+}-Mn^{3+}-Fe^{2+}$  charge transfer. However, Fe in the blue grain probably is too little to cause the color by itself, there is no Ti to allow a transfer similar to that in kyanite, and the properties of Mn and Fe are very similar. These points suggest that the proposed mechanism is likely.

#### CONCLUSIONS

The crystal chemical study of the pink and blue K-richterites of St. Marcel has produced no clue as to how minerals with such a small difference in cation composition, but with a large difference in anion substitution, can coexist in apparent chemical equilibrium. The cause of the color is apparently related to the presence of trace

amounts ( $<0.010$  atoms pfu) of Fe in the blue richterite and Ti in the pink one, in both cases in the presence of  $Mn^{3+}$ .

The IR study completes the knowledge of the crystal chemistry in a way unexpected and undetected either via a careful EMPA or XRD investigation. The presence of empty A sites is revealed by the occurrence of IR bands typical of tremolite-type amphiboles. As these cannot be detected by microprobe analysis and were not detected during crystal-structure refinement (L. Ungaretti, pers. comm.), we suggest that domains with empty A sites occur to balance locally the presence of Sr at the A site in place of a monovalent cation. In fact, in addition to the well-known  $3731\text{-cm}^{-1}$  band typical of the (MgMgMg)-OH-K clusters, the spectra show a band at  $3715\text{-cm}^{-1}$  that can be explained as due to the (MgMgMg)-OH-Sr configuration. This requires the simultaneous presence of empty A sites to maintain the local bond-valence requirements, as well as the overall neutrality of the crystal structure. Thus, IR spectroscopy, although still fraught with difficulties, is able to give *additional* information about aspects of crystal chemistry, even in the case of complex structures such as amphiboles. Some of this information is not apparent either in a conventional evaluation of the analysis nor in a structural refinement. This additional information does *not conflict* with that given by the above methods. IR spectroscopy can discriminate among unit-cells with empty vs. full A sites.

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