# Rietveld structure refinement of synthetic strontium-rich potassium-richterites

## JEAN-LOUIS ROBERT<sup>1</sup>, GIANCARLO DELLA VENTURA<sup>2\*</sup>, MATI RAUDSEPP<sup>2</sup> and Frank C. HAWTHORNE<sup>2</sup>

<sup>1</sup>CRSCM-CNRS, 1A, rue de la Férollerie, F-45071 Orléans Cedex 2, France <sup>2</sup>Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

**Abstract:** Complete substitution of Ca by Sr has been experimentally obtained at 750°C, 1 kbar in hydroxyl potassium-richterite. The refinement of the site occupancies by the whole-powder-pattern refinement method (Rietveld method) shows Sr to be completely ordered at the M(4) site. Cell parameters vary as a function of the Sr  $\rightarrow$  Ca substitution in a strongly anisotropic way: *a* and *b* increase whereas *c* remains constant. There is also a major increase in the  $\beta$  angle. The variation of <M(4)-O> distance is linear. The structure refinements are good in the space group C2/*m* with the usual amphibole unit cell; in addition, there is no evidence for the existence of a supercell. Thus Ca and Sr show no evidence of any long-range ordering.

Key-words: synthesis, potassium-richterites, strontium, Rietveld structure refinement, cell parameters, order/disorder.

## Introduction

Amphiboles are among the most complex rock-forming minerals and exhibit wide chemical variation and a wide variety of parageneses. There are several crystallographically unique cation sites in the amphibole structure; these sites can accommodate cations of formal charge from +1 to +4 and ionic radius from 0.25 to 1.6 Å (Hawthorne, 1983). The standard formula of amphiboles is:  $A_{(0-1)}B_2C_5T_8O_{22}(W)_2$ . The T-group cations occupy the T(1) and T(2) sites of the tetrahedral double-chain. These sites typically accommodate Si and Al, and  $Ti^{4+}$  can enter T(2) in some sodic-calcic amphiboles (Della Ventura et al., 1991; Oberti et al., 1992; Della Ventura et al., 1993a). The C-group cations occupy the M(1), M(2) and M(3) sites of the octahedral strip; these sites can accommodate a wide variety of

divalent and trivalent cations (Mg, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Ti<sup>4+</sup>, Ni, Co, Zn, etc.). The B-group cations occupy the M(4) site; only a limited number of cation species is found at this site: Na and Ca for the most common amphiboles and Fe<sup>2+</sup>, Mn<sup>2+</sup>, Mg and Li for the ferromagnesian amphiboles. The A-cavity typically accommodates large monovalent alkali elements such as Na and K, but synthesis experiments on richterites show that Rb may substitute for K (Robert & Della Ventura, unpublished data). Owing to their close crystal-chemical properties, Ca, Sr and Ba can replace each other in several rock-forming minerals (feldspars, epidotes, micas, carbonates), but natural Sr- or Ba-rich amphiboles have never been reported. Recently a potassium-richterite containing some Sr has been described from the St. Marcel manganese deposit (Mottana & Griffin, 1986).

<sup>\*</sup> Permanent address: Dipartimento di Scienze della Terra, Sezione Mineralogico-Cristallografica, Università "La Sapienza", P. Aldo Moro 5, I-00185 Roma, Italy.

Richterites are C2/m amphiboles with a general formula (Na,K)(NaCa)Mg5Si8O22(OH,F)2 where the M(4) site is occupied by Na and Ca in the ratio 1:1. Experimental work shows that richterites are rather flexible with respect to cationic and/or anionic subtitutions (Huebner & Papike, 1970; Robert et al., 1989; Raudsepp et al., 1991; Della Ventura et al., 1993b). Recently, Della Ventura & Robert (1990) reported the synthesis of strontium-richterites A(NaSr)Mg<sub>5</sub>Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub> with A = Na or K. They showed that replacement of Ca by Sr is possible in these amphiboles. In principle, there are two feasible ordering patterns (and possibly a combination of these) in amphiboles of this sort: (i) A = (Na,K), M(4) = (NaSr);(ii) A = Sr,  $M(4) = (Na_2)$  or (NaK). In the last few years, the development of whole-powderpattern refinement techniques (Rietveld method) has greatly extended the possibility of deriving information on amphibole crystal-chemistry. Here we have synthesized potassium-richterites containing different amounts of Sr and have refined their structures by this method in order to derive the cation ordering patterns in these amphiboles, and to see if the structure is the normal C2/m type or alternatively a subgroup derivative of this, caused by Na/Sr ordering.

### **Experimental details**

*Synthesis*: Hydrothermal syntheses were done in cold-sealed, externally heated Tuttle-type vessels at  $T = 750^{\circ}C$  and  $P(H_2O) = 1$  kbar. Starting materials were prepared as silicate gels according to the method of Hamilton & Henderson (1968). Sr was added as SrCO<sub>3</sub> and transformed to nitrate by reaction with HNO<sub>3</sub>. About 10 wt.% H<sub>2</sub>O was added to the charge.

X-ray data collection: Details on the sample preparation and the equipment used may be found in Della Ventura *et al.* (1993a). Diffraction patterns were recorded under CuK $\alpha$ , Ni-filtered radiation, using a step interval of 0.10° 2 $\Theta$  and a step counting time of 5 s. As discussed by Hill & Madsen (1986), these are approximately the optimum conditions for reducing serial correlation without adversely affecting the accuracy of the results. Information pertinent to data collection is given in Table 1, where the data for the Sr-free sample are from Della Ventura *et al.* (1993b).

Rietveld structure refinement: The structures were refined with the program LHPM1 (DBW

3.2, originally written by Wiles & Young, 1981; modified by Hill & Howard, 1986); full details on the refinement procedures may be found in Della Ventura et al. (1993b). Initial structural parameters were taken from the single-crystal study of potassium-fluor-richterite (Cameron et al., 1983). Isotropic displacement factors were fixed at values approximately correct for amphiboles. K at the A site was allowed to disorder along the mirror plane (special position 4i). Information pertinent to the structure refinements is given in Table 1. Final convergence was assumed when the parameter shifts in the final cycle were less than 30% of their respective standard deviations. Typical observed, calculated and difference patterns for the end-member Srrich potassium-richterite may be obtained upon request from the senior author or through E.J.M. Editorial Office

#### **Experimental results**

#### **Run products**

Two samples were synthesized, one by replacing half the Ca with Sr, and the other by replac-

Table	1.	Data	collec	ction	and	structure	refinement	details	3:
stront	iur	n-ricł	1 pota	ssiur	n-rio	chterites			

	KSr <sub>0</sub>	KSr50	KSr100
$2\theta$ scan range (°)	9-100	9-100	9-100
Step interval (°2 $\theta$ )	0.10	0.10	0.10
Integration time/step (s)	5	5	5
$Maximum \ step \ intensity \ (counts)$	2705	3872	4563
No. of unique reflections	526	530	533
No. of structure parameters	35	36	36
No. of experimental parameters	13	13	13
N - P	863	862	862
$R_p$	9.0	8.8	7.6
$R_{wp}$	11.9	11.2	10.2
$R_B$	4.0	3.9	3.9
Durbin-Watson d-statistic	1.77	1.72	1.32
E.s.d.'s to be multiplied by:†	1.54	1.41	1.34
U	0.018	0.330	0.088
$V_{-}$	0.064	-0.144	-0.076
н.	0.030	0.051	0.042
<b>γ</b> 1	0.467	0.567	0.512
γ2	0.001	-0.001	0.002

Note: N - P = no. of observations (steps) - no. of leastsquares parameters.

<sup>†</sup>Correction for local correlations (Bérar & Lelann, 1991).



Fig. 1. SEM picture of Sr-bearing richterite.

ing all Ca with Sr. Nominal compositions are:  $KSr_{50} = K(NaCa_{0.5}Sr_{0.5})Mg_5Si_8O_{22}(OH)_2$ , and  $KSr_{100}$   $= K(NaSr)Mg_5Si_8O_{22}(OH)_2$ . In addition, the label  $KSr_0$  used throughout the text denotes the end-member, Sr-free, richterite composition  $K(NaCa)Mg_5Si_8O_{22}(OH)_2$ . However, it must be stressed that according to the approved nomenclature of amphiboles (Leake, 1978), the  $KSr_{100}$ sample should not be classified as richterite, since no Ca is present in the formula. The reason to call it richterite rests on the assumption that Sr is proxy for Ca.

For all samples, the run product was optically a single-phase amphibole; no additional phase was detected either by X-ray powder diffraction or by analytical SEM. Fig. 1 shows the typical morphology of the Sr-potassium-richterite.

## **Cell dimensions**

The unit-cell data of the synthesized amphiboles are given in Table 2. The increase in cell volume (Fig. 2) shows a linear trend as a function of the cube of the mean cation radius at M(4), indicating the accuracy of both the refined cell dimensions and the site occupancies. A strong anisotropic variation is observed for the individual cell parameters (Fig. 3) in response to the substitution of Sr (ionic radius = 1.26 Å) for Ca (ionic radius = 1.12 Å, in eight fold coordi-



Fig. 2. Variation of the unit cell volumes for Sr-bearing potassium-richterites as a function of the cubed mean cation radius at M(4). Data for Sr-free richterite are from Della Ventura *et al.* (1993b). Note that error bars are smaller than the data points.

nation, values from Shannon, 1976). There is a monotonic increase of 0.10-0.12 Å in the *a* and *b* dimensions with substitution of Sr for Ca, whereas the *c* parameter is essentially constant across the series. The  $\beta$  angle is most affected by the substitution and shows an increase of 0.60°.

The effect of the mean cation size at M(4) on  $\beta$  has long since been known (Whittaker, 1960) and the plot of  $asin\beta$  versus  $\beta$  has been used to classify the amphiboles into major groups. Fig. 4 shows  $\beta$  as a function of the mean radius of the constituent cations at M(4), including the data of our synthetic phases, synthetic tremolite (Jenkins, 1987) and some well-characterized ferromagnesian and alkali amphiboles (Hawthorne, 1983). There is a well-developed linear trend for  $<\mathbf{r}>$  at M(4) in the range 1.22 Å (NaSr, this work) down to 0.77 Å (cummingtonite and grunerite). It is notable that the alkali-amphiboles plot well off the trend defined by synthetic calcic and natural ferromagnesian amphiboles.

#### Site occupancies

The Rietveld method provides accurate site-occupancies and bulk compositions if reasonable

Table 2. Cell dimensions : synthetic strontium-rich potassium richterites

	a (A)	b (Å)	c (Å)	Э (°)	V (Å <sup>3</sup> )
KSro	10.0547(8)	17.997(1)	5.2746(4)	104.832(5)	922.66
$\mathrm{KSr}_{50}$	10.1063(8)	18.056(1)	5.2717(4)	105.168(5)	928.46
$KSr_{100}$	10.1534(5)	18.115(1)	5.2723(4)	105.421(3)	934.82



Fig. 3. Variation of the unit cell parameters for the Sr-bearing potassium-richterites as a function of the mean cation radius at M(4). Data for Sr-free richterite are from Della Ventura *et al.* (1993b). Note that error bars are smaller than the data points.

starting values for isotropic displacement factors are used (Raudsepp et al., 1990; Della Ventura et al., 1993a,b). For the KSr<sub>50</sub> sample, at least three atomic species (Na, Ca, Sr) distribute over the M(4) site. The site occupancies for this sample were refined fixing one of them at the nominal value and leaving the other two unconstrained, i.e. (i) Sr/Ca variable with Na fixed, and (ii) Sr/Na variable with Ca fixed, while leaving the occupancy for K at the A-site always unconstrained. For the KSr<sub>100</sub> sample the Sr/Na ratio at M(4) and the occupancy for K at A were refined simultaneously unconstrained. For all refinements, occupancies equal to the nominal ones (within  $3\sigma$ ) were obtained. The possibility of Sr at A was not included in the refinement cycles. but it can be disregarded considering that, if there was significant Sr at the A-site, the A occupancy, in terms of scattering, should have been notably different from the nominal one, since the scattering factors of K and Sr are significantly different. On the basis of these results we conclude that Sr directly substitutes for Ca and is completely



Fig. 4. Plot of the  $\beta$  angle as a function of the mean cation radius at M(4). Full dots, this work (dot representing end-member potassium-richterite is from Della Ventura *et al.*, 1993b); full square, synthetic tremolite (Jenkins, 1987); open square, cummingtonite (sample 21), grunerite (sample 22) and tirodite (sample 41) from Hawthorne (1983); full diamonds, alkali-amphiboles samples 64 to 69 from Hawthorne (1983). A = sample KSr<sub>0</sub>; B = sample KSr<sub>50</sub>; C = sample KSr<sub>100</sub>.

ordered at M(4). This result is also confirmed by the IR data given in Della Ventura & Robert

Table 3. Atomic positions : strontium-rich potassium-rich-terites

		$KSr_0$	KSr <sub>50</sub>	KSr <sub>100</sub>
O(1)	x	0.1079(17)	0.1026(15)	0.1025(13
	y	0.0880(8)	0.0888(9)	0.0876(7)
	z	0.2149(32)	0.2143(31)	0.2185(26)
O(2)	x	0.1136(20)	0.1150(18)	0.1172(15
	v	0.1716(8)	0.1705(10)	0.1696(9)
	z	0.7176(35)	0.7215(32)	0.7268(27
O(3)	x	0.1078(21)	0.1061(20)	0.1085(42
	y y	0	0	0
	z	0.7236(51)	0.7291(49)	0.7188(44
0(4)	x	0.3542(19)	0.3538(18)	0.3557(15
- ( - )	n	0.2486(8)	0.2479(8)	0.2468(7)
	z	0.7854(46)	0.8008(42)	0.8013(35
0(5)	T	0.3345(20)	0.3381(26)	0.3372(15
,	-	0.1300(8)	0.1298(8)	0.1282(7)
	5 2	0.0945(40)	0.0999(42)	0.1054(33
വരാ	r	0.3399(19)	0.3346(18)	0.3351(15
0(0)		0.1159(8)	0.1137(8)	0.1136(7)
	9	0.6030(39)	0.5963(38)	0.6052(32
	~	0.0000(00)	0.0000(00)	0.0032(32
O(7)	x	0.3271(23)	0.3275(23)	0.3275(19
	y	0	0	0.0100/40
	z	0.3072(60)	0.2998(51)	0.3100(42
T(1)	$\boldsymbol{x}$	0.2761(9)	0.2735(8)	0.2717(8)
	y	0.0859(4)	0.0854(4)	0.0848(4)
	z	0.3013(20)	0.3046(19)	0.3071(16
$\Gamma(2)$	x	0.2843(10)	0.2842(10)	0.2840(8)
	y	0.1710(4)	0.1708(4)	0.1709(4)
	z	0.8024(20)	0.8042(20)	0.8115(16
		0	0	0
M(1)	r	0 0805(7)	0.0000(%)	0.0808(7)
	9 2	0.0695(7)	0.0900(8)	0.0838(7)
	2	0.0	0.0	0.0
M(2)	x	0	0 1000(0)	0 1700(7)
	y	0.1798(7)	0.1808(8)	0.1799(7)
	2	0	0	0
M(3)	x	0	0	0
	y	0	0	0
	î	0	0	0
M(4)	x	0	0	0
	y	0.2761(6)	0.2778(4)	0.2804(3)
	z	0.5	0.5	0.5
A	x	0.0213(26)	0.0183(32)	0.0127(40
	y	0.5	0.5	0.5
	г	0.0270(80)	0.0304(82)	0.0228(92)

$$\begin{split} &=O(3)=O(4)=0.8;\,O(5)=O(6)=1.1;\,O(7)=1.2;\\ &T(1)=T(2)=0.4;\,M(1)=M(2)=M(3)=0.6;\,M(4)\\ &=0.90;\,A=2.3 \end{split}$$

(1990) which exclude any presence of a divalent cation at the A-site for both sodium and potassium strontium-rich richterites.

## **Bond lengths**

Atomic positions and selected bond lengths for the synthesized richterites are given in Tables 3 and 4, where data for Sr-free richterite (Della Ventura *et al.*, 1993b) are also given for comparison.

The  $\langle T1-O \rangle$  and  $\langle T2-O \rangle$  distances are in close agreement with single-crystal data for non <sup>[4]</sup>Al amphiboles (Hawthorne, 1983) and do not show any significant variation across the series. Amphiboles have prominent pseudosymmetry (pseudo-c-glides  $\_b$ ), and the resultant high cor-

Table 4. Interatomic distances  $(\text{\AA})$  : synthetic strontium-rich potassium-richterites

	KSr <sub>0</sub>	KSr50	KSr100
T(1)-O(1)	1.635(14)	1.668(13)	1.657(11)
T(1)-O(5)	1.578(17)	1.614(17)	1.602(14)
T(1)-O(6)	1.647(21)	1.585(20)	1.619(18)
T(1)-O(7)	1.627(8)	1.637(8)	1.635(7)
$\langle T(1)-O \rangle$	1.622(8)	1.626(8)	1.628(7)
T(2)-O(2)	1.658(16)	1.650(15)	1.632(12)
T(2)-O(4)	1.576(14)	1.562(14)	1.563(12)
$T(2) \sim O(5)$	1.666(21)	1.682(21)	1.687(17)
T(2)-O(6)	1.645(18)	1.678(17)	1.682(15)
$\langle T(2)-O \rangle$	1.636(9)	1.643(8)	1.641(7)
M(1)-O(1) $\times 2$	2.068(15)	2.040(14)	2.027(12)
M(1)-O(2) $\times 2$	2.033(20)	2.028(21)	2.045(18)
M(1)–O(3) $\times 2$	2.123(15)	2.139(15)	2.120(13)
$\langle M(1)-O \rangle$	2.075(7)	2.069(7)	2.064(6)
$\mathrm{M}(2)\text{-}\mathrm{O}(1)~\times 2$	2.137(16)	2.120(16)	2.137(14)
$M(2)-O(2) \times 2$	2.102(18)	2.106(17)	2.107(14)
M(2)–O(4) $\times 2$	$\underline{2.059(18)}$	$\frac{2.033(18)}{2.033(18)}$	2.048(17)
$\langle M(2)-O \rangle$	2.099(7)	2.086(7)	2.097(6)
M(3)–O(1) $\times 4$	2.083(15)	2.076(16)	2.072(13)
M(3)–O(3) $\times 2$	2.027(23)	1.997(22)	2.062(20)
(M(3)-O)	2.064(7)	2.050(7)	2.069(6)
M(4)-O(2) ×2	2.343(19)	2.400(19)	2.472(16)
M(4)~O(4) $\times 2$	2.397(21)	2.478(20)	2.480(16)
M(4)-O(5) $\times 2$	2.895(21)	2.846(20)	2.823(17)
M(4)–O(6) $\times 2$	$\frac{2.668(18)}{}$	$\underline{2.708(17)}$	$\underline{2.700(13)}$
(M(4)-O)	2.576(7)	2.608(6)	$\underbrace{2.619(5)}$



Fig. 5. Variation in  $\langle M(4) - O \rangle$  as a function of the mean cation radius at M(4) for the synthetized amphiboles. Vertical bars are proportional to the e.s.d. Data for Sr-free richterite are from Della Ventura *et al.* (1993b).

relations between some positional parameters during Rietveld structure refinement can lead to inaccuracy in pseudosymmetrically related bond lengths. Nevertheless, the mean M-O bond lengths are less affected by this problem, and the grand <M-O> bond lengths are in reasonable agreement with the general trend established for amphiboles (Hawthorne, 1983; Della Ventura *et al.*, 1993b). For Sr-richterites, the grand <M-O> distances do not show any systematic variation. On the other hand, a satisfactory linear trend is shown by the <M(4)-O> distances as a function of the mean cation radius at M(4) (Fig. 5). This is consistent with the site-scattering refinement results that Sr directly substitutes for Ca at the M(4) site in these amphiboles.

#### Space group symmetry

In the C2/m amphibole structure, there is a single crystallographically distinct M(4) site. In the Sr-bearing amphiboles refined here, the M(4) site is occupied by (Na<sub>0.5</sub>Ca<sub>0.25</sub>Sr<sub>0.25</sub>) and (Na<sub>0.5</sub>Sr<sub>0.5</sub>) respectively. Na and Sr are significantly different in both size and charge; this raises the possibility of Na/Sr ordering, particularly for the (NaSr) composition. This would require either (i) doubling of one or more cell dimensions, or (ii) a change in space group. Hawthorne (1983) has considered in detail possible subgroups of the C2/m amphibole structure. Most of these subgroups are primitive and



Fig. 6. Observed and calculated X-ray diffraction patterns over the region  $2\theta = 10-25^{\circ}$  for the Sr-bearing potassium-richterites and end-member potassium-richterite (the latter from Raudsepp *et al.*, 1992).

the resulting diffraction patterns would violate the usual C-centered criterion; other space groups  $(Cm, C2, C\overline{1})$  are not primitive, and these would not lead to additional reflections in the diffraction pattern. The observed patterns of our two Sr-rich amphiboles do not show any obvious additional reflections. Violating reflections from cell doubling or a  $C \rightarrow P$  lattice change would be most apparent at low  $2\theta$  angles. Fig. 6 shows an enlargement of the X-ray diffraction patterns of both amphiboles synthesized here and of Sr-free potassium-richterite (Raudsepp et al., 1992). The patterns of the Sr-bearing and Sr-free samples show significant differences in this region: in particular, the patterns of the Sr-bearing richterites show some distinct reflections (e.g. 220, 021, 001, 130) that are absent in the pattern of the Sr-free amphibole. However, these reflections can be indexed on the usual C2/m amphibole cell, and their assignement to these indices is shown to be correct by the fact that they have the correct intensities calculated from the refined C2/mstructure. Thus there is no diffraction evidence that the C2/m symmetry (with the usual cell) is violated.

It is possible that there may be some undetected long-range ordering if the structure changed to the Cm, C2 or  $C\overline{1}$  symmetries. However, we regard such a possibility as unlikely; Nature seems to prefer centrosymmetric space groups in topologically centrosymmetric arrangements.

#### Conclusions

The main conclusions of the present work may be summarized as follows:

(1) In synthetic potassium-richterite, there is complete substitution between Ca and Sr at the M(4) site. This means that Sr could be regarded as an uncommon but possible major constituent of amphiboles. The question which arises at this point is: why are Sr-rich amphiboles so rarely found in nature? Three factors should be considered: (i) the control of bulk rock chemistry on the composition of the amphibole; (ii) the competition for Sr between the amphibole and other coexisting phases; (iii) the order of crystallization of the phases able to incorporate Sr, which could affect the availability of Sr when amphibole starts to crystallize. These questions are difficult to answer because of the lack of information. The potassium-richterite described from St. Marcel

occurs in rocks in which epidotes extremely enriched in Sr occur (piemontites with SrO contents up to 15 wt%, Perseil, 1987); however the amphibole itself contains less than 1.0 wt% SrO (Mottana & Griffin, 1986). In addition, a large number of analyses of amphiboles from the St. Marcel mine may be found in literature (Martin-Vernizzi, 1982; Martin & Kienast, 1987) but none of them are reported as containing Sr. We suggest that amphiboles occurring in rocks of suitable composition should be re-analyzed for Sr. (2) The Sr-Ca substitution affects anisotropically the cell dimensions of potassium-richterite. The most sensitive parameter is  $\beta$ , which increases considerably across the series. A plot of  $\beta$  as a function of the average radius of the cations located at M(4) shows a linear trend connecting sodic-calcic, calcic and ferromagnesian amphiboles, whereas the alkali amphiboles depart significantly from this trend. This opens another question: is it possible to substitute Ca with Sr in calcic amphiboles? Fig. 4 suggests that in principle this should be possible, but will the structure be elastic enough to compensate for the strain induced by such a substitution? Experimental work to test this point is currently under way. (3) The Rietveld method is a valuable technique for the characterization of site occupancies in synthetic amphiboles. The data collection and refinement procedures for amphiboles are still capable of improvement, and this method is likely to have a major impact for the charac-

Acknowledgements: Part of this work was done during the stay of G.D.V. at the Department of Geological Science, University of Manitoba, Winnipeg, supported by an International Council for Canadian Studies grant. Financial assistance was provided by a C.N.R. "Bilaterale" grant to G.D.V. and by the Natural Sciences and Engineering Research Council of Canada Operating, Infrastructure and Major Equipment grants to F.C.H.

terization of synthetic materials in the future.

#### References

- Berar, J.-F. & Lelann, P. (1991): E.S.D.'s and estimated probable error obtained in Rietveld refinements with local correlations. J. Appl. Cryst., 24, 1-5.
- Cameron, M., Sueno, S., Papike, J.J., Prewitt, C.T. (1983): High temperature crystal chemistry of K and Na fluor-richterites. *Am. Mineral.*, 68, 924-943.

- Della Ventura, G. & Robert, J.-L. (1990): Synthesis, XRD and FTIR studies of strontium richterites. *Eur. J. Mineral.*, 2, 171-175.
- Della Ventura, G., Robert, J.-L., Beny, J.-M. (1991): Tetrahedrally coordinated Ti<sup>4+</sup> in synthetic Ti-rich potassic richterites: evidences from XRD, FTIR and Raman studies. *Am. Mineral.*, **76**, 1134-1140.
- Della Ventura, G., Robert, J.-L., Beny, J.-M., Raudsepp, M., Hawthorne, F.C. (1993a): The OH-F substitution in Ti-rich potassium-richterites: Rietveld structure refinement and FTIR and Raman spectroscopic studies of synthetic amphiboles in the system K<sub>2</sub>O-Na<sub>2</sub>O-CaO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O-HF. *Am. Mineral.*, in press.
- Della Ventura, G., Robert, J.-L., Raudsepp, M., Hawthorne, F.C. (1993b): Quantitative characterization of site occupancies in synthetic monoclinic amphiboles. Rietveld structure refinement (Ni-Mg-Co)-potassium-richterites. Am. Mineral., in press.
- Hamilton, D.L. & Henderson, C.M.B. (1968): The preparation of silicate compositions by a gelling method. *Mineral. Mag.*, 36, 832-838.
- Hawthorne, F.C. (1983): The crystal chemistry of the amphiboles. *Can. Mineral.*, **21**, 173-480.
- Hill, R.J. & Howard, C.J. (1986): A computer program for Rietveld analysis of fixed-wavelength X-ray and neutron diffraction pattern. Report no. M112, Australian Atomic Energy Commission (now ANSTO), Lucas Heights Research Laboratories, Menai, New South Wales, Australia.
- Hill, R.J. & Madsen, H.D. (1986): The effect of profile step-width on the determination of crystal structure parameters by X-ray Rietveld analysis. J. Appl. Cryst., 19, 10-18.
- Huebner, J.S. & Papike, J.J. (1970): Synthesis and crystal chemistry of sodium-potassium richterites (Na,K)NaCaMg<sub>5</sub>Si<sub>8</sub>O<sub>22</sub>(OH,F)<sub>2</sub>: a model for amphiboles. *Am. Mineral.*, **55**, 1973-1992.
- Jenkins, D.M. (1987): Synthesis and characterization of tremolite in the system H<sub>2</sub>O-CaO-MgO-SiO<sub>2</sub>. Am. Mineral., 72, 707-715.
- Leake, B.E. (1978): Nomenclature of amphiboles. *Can. Mineral.*, **16**, 501-520.
- Martin-Vernizzi, S. (1982): La mine de Praborna (Val d'Aoste, Italie): une serie manganésifère métamorphisée dans le facies éclogite. Ph.D. Thesis, Paris.

- Martin, S. & Kienast, J.-R. (1987): The HP-LT manganiferous quartzites of Praborna, Piemonte ophiolite nappe, Italian Western Alps. Schweiz. Mineral. Petrogr. Mitt., 67, 339-360.
- Mottana, A. & Griffin. W.L. (1986): Crystal-chemistry of two coexisting K-richterites from St. Marcel (Val d'Aosta, Italy). Am. Mineral., 71, 1426-1433.
- Oberti, R., Ungaretti, L., Cannillo, E., Hawthorne, F.C. (1992): The behaviuor of Ti in amphiboles. I. Fourand six-coordinate Ti in richterite. *Eur. J. Mineral.*, 4, 425-439.
- Perseil, E-A. (1987): Particularités des piémontites de Saint-Marcel-Praborna (Italie): spectres I.R. Actes du 112<sup>e</sup> Congrès National des Sociétés Savantes, Lyon, 1987, Ed. du CTHS, Paris.
- Raudsepp, M., Hawthorne, F.C., Turnock, A.C. (1990): Crystal-chemistry of synthetic pyroxenes on the join CaNiSi<sub>2</sub>O<sub>6</sub>-CaMgSi<sub>2</sub>O<sub>6</sub> (diopside): a Rietveld structure refinement study. *Am. Mineral.*, **75**, 1274-1281.
- Raudsepp, M., Turnock, A.C., Hawthorne, F.C. (1991): Amphibole synthesis at low pressure: what grows and what doesn't. *Eur. J. Mineral.*, 3, 983-1004.
- Raudsepp, M., Della Ventura, G., Hawthorne, F.C., Robert, J.-L. (1992): Powder diffraction data for synthetic potassium-richterite, nikel-potassiumrichterite, and cobalt-potassium-richterite. *Powder Diffraction*, 7, 52-55.
- Robert, J.-L., Della Ventura, G., Thauvin, J.-L. (1989): The infrared OH-stretching region of synthetic richterites in the system Na<sub>2</sub>O-K<sub>2</sub>O-CaO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O-HF. *Eur. J. Mineral.*, 1, 203-211.
- Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, A32, 751-767.
- Whittaker, E.J.W. (1960): The crystal chemistry of the amphiboles. *Acta Cryst.*, **13**, 291-298.
- Wiles, D.B. & Young, R.A. (1981): A new computer program for Rietveld analysis of X-ray powder diffraction patterns. J. Appl. Cryst., 14, 149-151.

Received 3 February 1992 Accepted 20 November 1992