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### POTASSIUM-FLUORRICHTERITE FROM MONTE SOMMA (CAMPANIA) ITALY (\*\*)

ABSTRACT. - The potassium-fluorrichterite of a metamorphic ejectum from Monte Somma has been studied. The recalculated microprobe analyses gave the following crystal-chemical formula:  $(K_{0.67}, Na_{0.34})(Ca_{1.09}, Na_{0.91})(Mg_{4.975}, Fe_{0.018}, Mn_{0.002}, Ti_{0.007})(Si_{7.94}, Al_{0.05})O_{22}(F_{1.35}, OH_{0.65})$ . OH is inferred but supported by the I.R. analysis.

The unit-cell parameters are:  $a = 9.978 \pm 0.001$ ,  $b = 17.991 \pm 0.002$ ,  $c = 5.269 \pm 0.001$  Å,  $V = 914.2 \pm 0.3$  Å<sup>3</sup>,  $\beta(^{\circ}) = 104.90 \pm 0.02$ . The position of the Fe-O vibrational band is in accordance with the analytical data. The physical and chemical data give a further contribution to the isomorphous replacement of Na with K in the A site and of OH with F in the O3 site in natural sodic-calcic amphiboles as already experimentally verified by several authors.

The mineralogical assemblage coexisting with potassium-fluorrichterite from Monte Somma is: diopside and calcite, both analyzed and characterized. Inclusions of apatite are present in the amphibole.

RIASSUNTO. - È stata studiata una potassio-fluorrichterite di un proietto termo-metamorfico del Monte Somma. I dati microchimici possono essere sintetizzati nella seguente formula cristallografica:  $(K_{0.67}, Na_{0.34})(Ca_{1.09}, Na_{0.91})(Mg_{4.975}, Fe_{0.018}, Mn_{0.002}, Ti_{0.007})(Si_{7.94}, Al_{0.05})O_{22}(F_{1.35}, OH_{0.65})$ .

Il contenuto in OH è stato riportato per differenza dopo aver verificato attraverso analisi I.R. che la sua presenza tra i componenti volatili è appena apprezzabile.

I parametri della cella elementare sono:  $a = 9.978 \pm 0.001$ ,  $b = 17.991 \pm 0.002$ ,  $c = 5.269 \pm 0.001$  Å,  $V = 914.2 \pm 0.3$  Å<sup>3</sup>,  $\beta(^{\circ}) = 104.90 \pm 0.02$ . La posizione della banda di legame Fe-O è in accordo con i dati microanalitici. Questi risultati fisici e chimici rappresentano un ulteriore contributo alle possibilità di vicarianza tra K e Na nel sito A e tra F e OH nel sito O3 degli anfibioli sodico-calcici naturali, già riprodotti sperimentalmente da vari autori. La potassio-fluorrichterite del Monte Somma si trova in associazione con calcite e diopside, entrambi analizzati e caratterizzati. Inclusioni di apatite sono talora presenti nell'anfibolo.

KEY WORDS. - Potassium-fluorrichterite, amphibole, cell-dimensions, chemical composition, IR spectrum, Monte Somma (Campania), Italy.

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## INTRODUCTION

The presence of amphiboles in thermometamorphic ejecta of Monte Somma has been known since a long time. In 1825 Monticelli and Covelli described, besides the black or dark-green coloured common amphibole «orneblenda» and «attinoto», also «grammatite» (tremolite) (quoted in Zambonini, 1935). In the last century Breislak and Scacchi reported many occurrences of fibrous white-coloured crystals in calcareous skarns, all believed to be tremolite, but actually never analysed (Zambonini, 1935).

In this paper the study of an amphibole, found in an ejectum of Monte Somma (1), belonging to the sodic calcic amphibole group and particularly close to the end member richterite, is reported.

Richterites are monoclinic amphiboles (space group C2/m) with general formula:  $(K, Na)NaCa(Mg, Fe)_5Si_8O_{22}(OH, F, Cl)_2$ . The structure consists of infinite double chains of silicon-oxygen tetrahedra linked by cation sites containing (Na, K) in the 8-fold A site, (Na, Ca) in the 8-fold M4 site and (Mg, Fe) in the remaining octahedral M1, M2, M3 sites (Papike *et al.*, 1969). The possibility of a complete substitution between Na and K in the A site has been experimentally demonstrated by Huebner and Papike (1970), while the substitution between Fe and Mg has been studied by Cameron and Gibbs (1971) and by Charles (1975, 1977). The stability field of richterites was determined by Forbes (1971) and later refined by Charles (1975).

Richterites, thought to be uncommon and rare minerals, are found in both igneous and metamorphic environments: for example in alkaline lamprohyres (Prider, 1939; Velde, 1967); in omphacite nodules in kimberlite (Erlank and Finger, 1970) in metagranites (Bilgrami, 1955) in carbonatite complexes (Puustinen, 1972), in hornfelses (Reverdatto, 1967), in meteorites (Olsen, 1967), etc.

(1) At the beginning of the investigation this sample was wrongly indicated as coming from the Phlegrean Fields, but the information was later corrected and appropriately ascribed to Monte Somma region near S. Vito (M. Carati, pers. comm. 1983).

## DESCRIPTION OF THE EJECTUM

The richterite of Monte Somma was found in a calcareous thermometamorphic ejectum, the main mineralogical assemblage of which is calcite and clinopyroxene. The  $MgCO_3$  content of calcite, as determined by powder diffraction analysis (Hutchison, 1974) using the (104) reflection against the silicon (111) reflection, is 0.79 wt%.

The clinopyroxene was analysed both by X-ray diffraction and by microprobe. It is an almost pure diopside with the crystal-chemical formula:

$(Ca_{0.998}, Na_{0.003}, Ba_{0.001})(Mg_{0.974}, Fe_{0.004}, Mn_{0.001}, Cr_{0.002}, Ti_{0.001})(Si_{1.994}, Al_{0.005})O_6$  and the following cell parameters:  $a$  (Å) =  $9.768 \pm 0.002$ ,  $b$  =  $8.919 \pm 0.001$ ,  $c$  =  $5.257 \pm 0.001$ ,  $\beta$  (°) =  $105.98 \pm 0.02$ ,  $V$  (Å<sup>3</sup>) =  $440.3 \pm 0.1$ .

The amphibole, which is the subject of this paper, occurs as light-grey coloured euhedral prismatic crystals (max. linear dimension 0.5 cm) in the mass of the ejectum. It also occurs in thin veins dissecting the ejectum as small grains in association with calcite and diopside. Sometimes it contains extremely tiny inclusions of apatite that could be detected only by the microprobe.

## EXPERIMENTAL METHODS

Unit cell dimensions were determined by X-ray powder diffraction analysis (Philips PW 1050/25 diffractometer,  $CuK\alpha$  radiation, Ni filter,  $1/4^\circ 2\theta$  min<sup>-1</sup> goniometer speed and ASTM silicon as internal standard). The least square refinement of the powder data was performed, starting from preliminary single crystal unit-cell data, by the computer program of Appleman & Evans (1973).

The chemical analyses were performed by a Jeol 50A microprobe fitted with the Link EDS system. The used standards were natural minerals: diopside, albite, orthoclase, rutile, corundum, fayalite and tephroite. All the elements were measured by EDS except fluorine by WDS. Data were corrected by a ZAF program. All iron was calculated as FeO. The results obtained are the average of ten points over 3 grains.

The IR analyses were performed by a PE 580 spectrophotometer using a pellet disk with KBr matrix, with 10 mg of mineral and 200 mg of KBr.

TABLE I

*Chemical analysis of potassium-fluorrichterite from Monte Somma compared with analyses of natural potassium-richterites reported by Charles (1977).*

	Monte Somma	3	6	Charles (1977)		
				9	19	20
SiO <sub>2</sub>	57.13	50.58	54.30	55.02	53.43	56.03
TiO <sub>2</sub>	0.07	2.27	0.59	—	0.14	0.10
Al <sub>2</sub> O <sub>3</sub>	0.24	2.27	1.24	4.53	2.13	0.78
FeO	0.15	11.10	4.31	3.28	3.12	1.58
Fe <sub>2</sub> O <sub>3</sub>	—	3.24	—	1.04	7.78	5.68
Cr <sub>2</sub> O <sub>3</sub>	—	—	0.60	—	—	—
MnO	0.02	0.20	0.07	—	0.11	0.07
MgO	24.02	12.88	21.20	21.95	16.95	20.19
CaO	7.34	5.91	7.12	6.15	6.57	5.89
Na <sub>2</sub> O	4.63	4.65	3.26	5.15	5.07	4.87
K <sub>2</sub> O	3.75	4.68	4.72	1.80	1.58	2.62
F	2.86	—	—	—	—	—
H <sub>2</sub> O <sup>+</sup>	—	1.93	(2.10)	0.87	1.92	1.71
H <sub>2</sub> O <sup>-</sup>	—	0.30	—	—	0.04	0.05
Tot.	100.21	100.01	99.49	99.79	98.84	99.57
O ≡ F	1.24	—	—	—	—	—
	98.97	100.01	99.49	99.79	98.84	99.57

## UNIT-CELL CONTENTS CALCULATED ON THE BASIS OF 23(O)

Si	7.94	7.52	7.74	7.59	7.65	7.85
Ti	0.007	0.25	0.06	—	0.015	0.01
Al	0.05	0.40	0.21	0.72	0.36	0.13
Fe <sup>3+</sup>	—	0.36	—	0.11	0.84	0.60
Fe <sup>2+</sup>	0.018	1.38	0.51	0.33	0.374	0.18
Cr	—	—	—	0.07	—	—
Mn	0.002	0.02	0.008	—	0.01	0.008
Mg	4.975	2.85	4.50	4.48	3.62	4.22
Ca	1.09	0.94	1.09	0.91	1.01	0.88
Na	1.25	1.34	1.89	1.33	1.41	1.32
K	0.67	0.89	0.86	0.33	0.29	0.47

## CHEMICAL RESULTS

Chemical analysis is listed in Table I, and compared with the analyses of the potassium-rich natural richterites reported by Charles (1977). These are the only ones referred as such in geological records.

In the Monte Somma amphibole, the T site appears to be completely filled by Si being Al present in very small amounts. As the Fe and Ti contents are also very low, the octahedral sites M1, M2 and M3 are almost completely filled by Mg. The M4 site is occupied by Ca and Na in nearly equal amounts and the A site is dominantly filled by K over Na. As it will be pointed out later, the O3 sites appear to be mainly occupied by F, in a remarkable contrast to the other analyses of potassium-rich richterites reported in Table II.

End-member fluorine richterites have been synthesized by Huebner & Papike (1970), both with the A-site filled by Na (sodium richterite) and by K (potassium richterite).

The amphibole from Monte Somma is the first example of a natural potassium-fluorrichterite with a composition very near the end member. Like other fluorine-rich minerals (micas and amphiboles), our sample is extremely low in iron, a noticeable character pointed out previously by Petersen *et al.* (1982).

According to the recommended procedures (Leake, 1978) the amphibole of Monte Somma is to be considered a potassium richterite ( $K_A > 0.50$ ). According to Petersen *et al.* (1982), as F fills more than one half of the O3 site, this amphibole is also a fluorrichterite. Therefore we suggest to call it potassium-fluorrichterite.

Fig. 1 shows the classification diagram for sodic-calcic amphiboles approved by the I.M.A. (Leake, 1978). All the analyses of richterites reported by Charles (1977) are plotted there, after recalculating the formulae on the basis of 23 O.

The calculation of the standard formula for amphiboles has always been strongly debated (Hawthorne, 1983). As a matter of fact, the unit formulae calculated on the basis of 23 or 24 O are often different and problems arise when using either set of data for characterizing a phase. The formula based on 24 O is recommended only when the contents of all the volatile components are

TABLE II

X-ray powder diffraction data of potassium-fluorrichterite from Monte Somma compared with the data on a synthetic potassium-richterite (Huebner and Papike, 1970).

Potassium-fluorrichterite Monte Somma			Synth. potassium-richterite (Huebner and Papike, 1970)		
$d_{obs}(A)$	$I/I_0$	$d_{calc}(A)$	$hkl$	$d_{calc}(A)$	$I_{obs}$
8.490	95	8.499	1 1 0	8.548	21
			1 1 1	4.887	5
4.817	10	4.821	2 0 0	4.857	8
4.498	7	4.498	0 4 0	4.497	20
			1 1 1	4.000	9
			-1 3 1	3.875	13
3.379	8	3.378	1 3 1	3.386	100
3.288	80	3.289	2 4 0	3.299	108
3.166	100	3.164	3 1 0	3.187	109
			-3 1 1	3.071	11
2.950	7	2.950	2 2 1	2.961	85
2.931	4	2.935	-1 5 1	2.935	21
2.831	60	2.833	3 3 0	2.849	35
2.754	4	2.755	-3 3 1	2.766	55
2.701	9	2.701	1 5 1	2.705	126
2.583	3	2.583	0 6 1	2.584	54
2.536	3	2.536	-2 0 2	2.539	73
			-2 6 1	2.414	4
2.395	13	2.397	3 5 0	2.406	24
2.345	7	2.350	-4 2 1	2.362	69
		2.349	-3 5 1	2.356	
			-1 7 1	2.292	
			-3 1 2	2.291	51
			0 8 0	2.248	2
			-2 4 2	2.211	9
			2 6 1	2.167	74
2.164	4	2.163	1 3 2	2.166	
		2.162	-3 3 2	2.155	5
			-1 5 2	2.126	3
			2 0 2	2.051	19
			-4 0 2	2.037	15
			3 5 1	2.032	17
1.957	3	1.957	1 9 0	1.957	7
			-3 5 2	1.943	5
1.918	20	1.917	5 1 0	1.931	29
			-4 6 1	1.896	4
			-4 4 2	1.855	7
			5 3 0	1.848	3
1.840	6	1.839	-1 7 2	1.798	8
1.799	4	1.799	0 10 0	1.796	7
			1 9 1	1.796	7
			3 1 2	1.781	8
			-1 3 3	1.681	10
			4 6 1	1.665	42
		1.6601	-6 0 1		
1.659	5	1.6600	5 1 1		
		1.645	-2 10 1		
1.645	6	1.644	4 8 0	1.649	4

Potassium-fluorrichterite Monte Somma			Synth. potassium-richterite (Huebner and Papike, 1970)		
$d_{obs}(A)$	$I/I_0$	$d_{calc}(A)$	$hkl$	$d_{calc}(A)$	$I_{obs}$
1.633	15	1.632	-6 2 1		
			6 0 0	1.619	2
			1 11 0	1.612	9
			-1 5 1	1.574	14
			4 0 2	1.569	5
			-6 0 2	1.558	12
			5 5 1	1.521	2
			1 9 2	1.515	5
			-2 6 3	1.510	19
1.499	4	1.499	0 12 0	1.499	9
			4 4 2	1.481	3
1.452	4	1.452	-6 6 1	1.459	33
			5 1 2	3.380	8

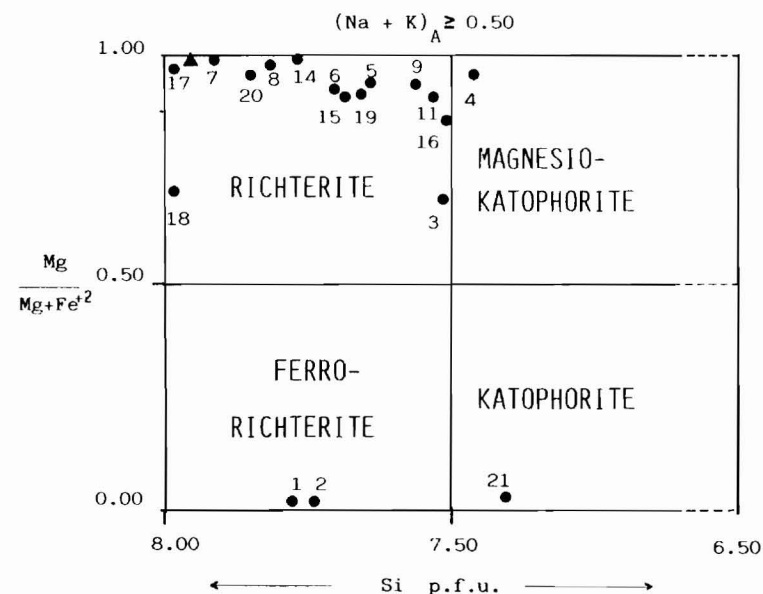


Fig. 1. - Richterite and katophorite fields of the classification diagram for sodic-calcic amphiboles with  $(Na + K)_A < 0.50$  (after Leake, 1978). ● analyses of richterites reported and numbered by Charles (1977) recalculated on the basis of 23(O). Samples 10, 12 and 13 fall in the winchite field. ▲ potassium-fluorrichterite from Monte Somma.

measured beyond doubt. In a microprobe analysis this cannot be performed because OH cannot be measured. Therefore, to classify the natural richterites reported by Charles' (1977), we recalculated

the chemical unit formulae on the basis of 23 O and of 16 cations (fig. 1). In both cases the results were very similar to those obtained on the basis of 24 O, except for samples 10, 12, 13 in Charles' (1977) list, which fall into the field of winchite, so that they could not be plotted in fig. 1. Among all the plotted richterites, the Monte Somma sample plots very close to the end member composition. Sample 17 and 7 of Charles (1977) plot just as close. However fig. 2 shows that they are Na-rich samples, while our is the only potassium-fluorrichterite where the boundary  $K/(Na + K) > 0.50$  is actually overtaken.

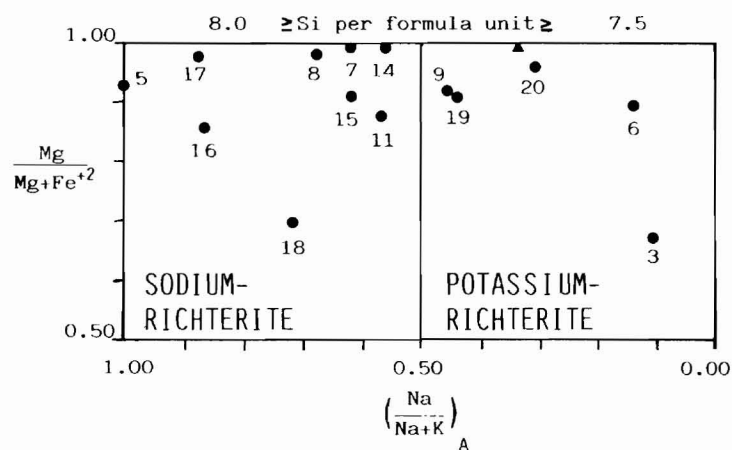


Fig. 2. - Classification diagram of sodium- and potassium-richterite (modified from Leake, 1978). The same richterites as in fig. 1 are plotted.

#### PHYSICAL DATA

The measured X-ray powder pattern is shown in Table II compared with the data of a synthetic potassic-richterite reported by Huebner and Papike (1970), as in J.C.P.D.S. data file no potassic-richterites are reported.

In Table III the cell dimensions of potassium-fluorrichterite from Monte Somma are listed, and the results of Huebner and Papike (1970), successively refined by Cameron *et al.* (1983) and Hawthorne (1983) are reported for comparison.

TABLE III

Unit cell parameters of potassium-fluorrichterite from Monte Somma (col. 1) compared with those of the potassium-fluor-richterite synthesized by Huebner and Papike (1970) as given by Cameron *et al.* (1983; col. 2) and Hawthorne (1983; col. 3), *e.s.d.* in parenthesis is referred to last digit.

	(1) Monte Somma	(2) synthetic	(3) synthetic
Space group	C2/m	C2/m	C2/m
<i>a</i> (Å)	9.978(1)	9.944	9.944(1)
<i>b</i>	17.991(2)	17.972	17.972(3)
<i>c</i>	5.269(1)	5.260	5.260(1)
$\beta$	104.90(2)	104.79	104.80(1)
<i>V</i> (Å <sup>3</sup> )	914.2(3)	908.9	908.9(2)

Huebner and Papike (1970) synthesized a complete solid solution series between sodium- and potassium-richterite, and showed that the *a* unit cell edge increases gradually with increasing K content in the A site, while *b* and *c* do not change significantly. They interpreted the variation as due to the large size of the K ion in comparison with the Na ion. Moreover they also pointed out that the substitution of F or OH in the O3 site has the opposite effect. There are no synthetic richterites with same  $K/(Na + K)$  ratio as found in the Monte Somma sample. However synthetic hydroxy-richterites with  $K/(Na + K) = 0.75$  have  $a = 10.01$  Å (Huebner and Papike, 1970). By correcting this value for fluorine, as suggested by Huebner and Papike, in the amount corresponding to a  $F/(OH + F)$  ratio = 0.65, i.e.  $0.08 \times 0.65 = 0.05$ , we should obtain  $a = 9.96$  Å in fair agreement with the measured value of 9.97 Å.

Huebner and Papike detected a change of the  $\beta$  angle from 104.23° to 104.80° in synthetic Na to K richterites. They interpreted the  $\beta$  increase as due to the slide of the chains along their length due to the substitution of Na by K. They did not detect significant changes due to the substitution of OH by F. The value

of the  $\beta$  angle of potassium-fluorrichterite from Monte Somma appears somewhat higher. Very likely the slight increase of the  $\beta$  angle is due to the small Ca excess over Na in the M4 site.

The IR spectrum is shown in fig. 3. Though the mineral/KBr ratio is very high (10/200) the OH presence is barely appreciable. In the inset of fig. 4 the spectrum in the OH region (3750-3600  $\text{cm}^{-1}$ ) magnified  $\times 25$  is shown, in order to reveal the OH bending vibrational band. Rowbotham and Farmer (1973) reported that the

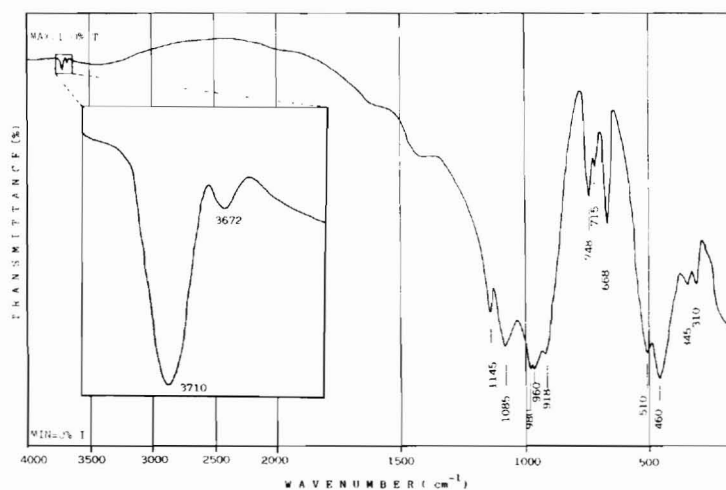


Fig. 3. - I.R. spectrum of potassium-fluorrichterite from Monte Somma. The OH region shown in the window is magnified  $\times 25$ .

bands in this region are due to the bonds OH-alkali cations in the A site. They found a shift of the 3750  $\text{cm}^{-1}$  band toward low frequencies with the increasing content of Na in the A site. In their materials the extreme measured values are 3734  $\text{cm}^{-1}$  for a Na-hydroxy-richterite and 3728  $\text{cm}^{-1}$  for a K-hydroxy-richterite. The position of corresponding band in our potassium-fluorrichterite from Monte Somma is in fact 3710  $\text{cm}^{-1}$ . This shift towards lower frequencies is probably due to the F content, which is also shown by the 345 and 310  $\text{cm}^{-1}$  bands, usually considered to be due to the presence of halogens (Farmer, 1974).

Another interesting feature arisen from the examination of the IR spectrum is related to the Fe/Mg ratio. Barabanov *et al.* (1974),

in the IR study of the cummingtonite-grunerite series, showed that the position of the 661  $\text{cm}^{-1}$  band is due to the Fe-O bond, and constructed a diagram relating the shift of this band against the Fe content (*in*: Hawthorne, 1983). The corresponding band is located in the potassium-fluorrichterite from Monte Somma at 668  $\text{cm}^{-1}$  so that an extrapolation of the diagram, proposed by Barabanov *et al.* (1974) (fig. 4) gives an extremely low FeO content, in good agreement with the analytical data. The lack of IR data on amphiboles of intermediate Fe content leads to a large uncertainty in such an extrapolation. We plan further studies on amphiboles of intermediate compositions.

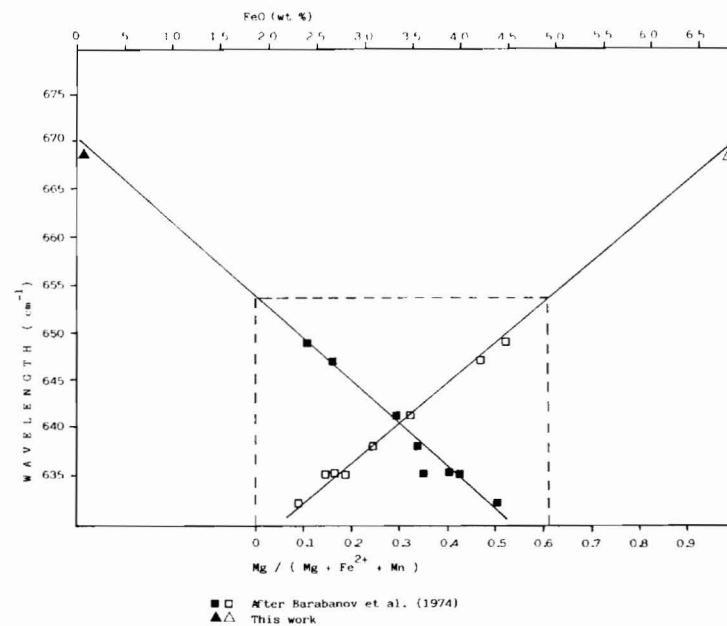


Fig. 4. - Extrapolation of Barabanov *et al.* (1974) diagram.

#### GENETICAL CONSIDERATIONS

Richterites are fairly rare in the mineralogical record, probably because they are imperfectly known and difficult to distinguish from other simple amphiboles. They have been described both in the igneous and metamorphic environments (see Charles, 1977, for a compilation).

Most of the metamorphic richterites are typically produced by the reaction of alkali-rich fluids with impure limestones or dolomitic host rocks (Charles, 1977). This appears to be the case of the potassium-fluorrichterite from Monte Somma, which probably grew from the interaction of silica- and K-rich fluids (typical of the volcanic activity of this region), reacting with the Triassic dolomitic series, which are believed to be present at low depth under the studied area (Rittmann, 1967).

Moreover the mineralogical composition of the ejectum is related to that of a skarn products.

The P-T conditions of formation are difficult to evaluate. We can only set a minimum P-T limit of 500°C at 1-2 Kb, suggested by the disappearance of the dolomite by the reaction  $\text{Do} + \text{SiO}_2 = \text{Di} + \text{CO}_2$ .

The thermal stability of richterites increases with Mg contents (Charles, 1975), while the high K content may reduced its stability somewhat (Charles, 1977).

#### CONCLUSIONS

The potassium-fluorrichterite of Monte Somma gives limiting data on the natural replacement of K and F in the structure of the amphiboles as already suggested experimentally on synthetic material by Huebner and Papike (1970).

Following the recommended procedures of the final report of the I.M.A. sub-committee for the amphiboles sub-groups (Leake, 1978), the Monte Somma amphibole is the potassium-end-member, extremely low in iron, of the richterite series. Moreover, following the suggestion of Petersen *et al.* (1982) we suggest to use for it the name potassium-fluorrichterite, since the F content exceeds 50% of the O3 is site so that this amphibole may be considered a distinct phase from hydroxyrichterite. The name potassium-fluorrichterite is now under attention of the I.M.A. commission on new minerals and mineral names.

Type material is deposited in Museo di Mineralogia dell'Università di Roma "La Sapienza" under specimen N° 24469/1.

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### NUCLEAR GAMMA RESONANCE CHARACTERIZATION OF COEXISTING CLINOPYROXENES AND GARNET IN SOME NORWEGIAN ECLOGITES (\*\*)

ABSTRACT. – A nuclear gamma resonance analysis of mineralogical phases coexisting in some eclogites of Norway is presented. Both ferric and ferrous ions occur in octahedral M1 site of inosilicates. The broadening of the Fe<sup>2+</sup> line suggests some variability in the pyroxene lattice. The garnet phase coexisting with inosilicates shows to be an almandine-like structure.

RIASSUNTO. – Vengono presentati gli spettri di risonanza gamma di alcune fasi mineralogiche presenti in alcune eclogiti norvegesi. Gli ioni Fe, ferrico e ferroso, occupano entrambi il sito M1 in coordinazione ottaedrica degli inosilicati. L'ampiezza delle righe relative allo ione Fe<sup>2+</sup> indica una certa variabilità del reticolo dei pirosseni. Il granato, coesistente agli inosilicati, presenta una struttura tipo almandino.

KEY WORDS. – Clinopyroxene, Garnet, Mössbauer spectrometry.

A nuclear gamma resonance analysis of was carried out in order to define the most meaningful crystal-chemical properties of mineralogical phases co-existing in some eclogites of Norway.

Analysis began on rock sample C 101 F. Fig. 1-a and 1-b exhibit the spectra, obtained respectively on the pyroxene component and on the garnet component with the ELSCINT (Haifa-Israel) Moessbauer equipment (10 mCi CO<sup>57</sup> in Rh; from 10<sup>6</sup> to 2 × 10<sup>6</sup> counts per channel).

The spectral lines of garnet are more solid and nearly symmetrical. A direct inspection shows that the positions of these lines correspond, the second to the far right line of the pyroxene spectrum, and the first to the slope variation on the left side of the same spectrum. Hence, the powder used for the pyroxene spec-

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