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Relationships between crystal data and crystal chemistry of carpholite-group minerals

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ABSTRACT - Multiple linear regression analyses have been conducted on minerals of the carpholite group, whose members have the general formula $A_{0\text{-}1}M1_2M2_2M3_2$ $[(OH,F)_4|Si_2O_6]_2$, to find the relations between unit cell parameters, mean polyhedral cation-oxygen distances, refractive indices and composition. For the regression, the mean ionic radii of atoms occupying the octahedral coordinated sites *M*1, *M*2 and *M*3 have been used as compositional parameters. The investigation is based on crystal structure of 9 samples, cell metrics of 35 samples and optical data of 13 samples all belonging to the carpholite group. The resulting regression equations enhance the prediction models of crystallographic parameters reported in the literature and they can be used for minerals with chemical compositions more complex than mere Fe-Mg-carpholites. Moreover, multiple linear correlation has been detected among the lattice parameters *a*, *b* and *c*.

RIASSUNTO - Analisi di regressione lineare multipla sono state eseguite su minerali del gruppo della carpholite, i cui membri hanno la formula generale $A_{0\text{-}1}M1_2M2_2M3_2$ $[(OH,F)_4|Si_2O_6]_2$, per trovare le relazioni tra parametri di cella, distanze medie poliedriche catione-ossigeno, indici di rifrazione e composizione. I raggi ionici medi degli atomi occupanti i siti a coordinazione ottaedrica *M*1, *M*2 and *M*3 sono stati usati come parametri composizionali per le analisi di regressione. L'indagine si basa sulla struttura cristallina di 9 campioni, sui lati di cella di 35 campioni e sui dati ottici di 13 campioni tutti appartenenti al gruppo della carpholite. Le equazioni di regressione ottenute migliorano i modelli di predizione di parametri cristallografici riportati in bibliografia e possono essere utilizzate per minerali con composizioni più complesse di semplici carpholiti a ferro e magnesio. Inoltre è stata trovata una correlazione lineare multipla tra i parametri di cella *a*, *b* e *c*.

KEY WORDS: *carpholite group; crystallographic properties; crystal chemistry; multiple linear regression analyses.*

INTRODUCTION

The carpholite group, whose members have the general formula $A_{0\text{-}1}M1_2M2_2M3_2$ $[(OH,F)_4|Si_2O_6]_2$, actually includes the mineral species balipholite, $Ba(Al_1Li_1)Al_2Mg_2[(OH)_2F_2|Si_2O_6]_2$, carpholite, $\square Mn_2Al_4[(OH)_4|Si_2O_6]_2$, ferrocarpholite, $\square(Fe,Mg)_2Al_4[(OH)_4|Si_2O_6]_2$, magnesiocarpholite, $\square(Mg,Fe)_2Al_4[(OH)_4|Si_2O_6]_2$ (Strunz and Nickel, 2001), together with the more recently described potassic-carpholite, $(K,\square)(Li,Mn^{2+})_2Al_4[(OH,F)_4$

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$|Si_2O_6]_2$, (Tait *et al*., 2004) and vanadiocarpholite, $\square Mn_2V^{3+}{}_2Al_2[(OH)_4|Si_2O_6]_2$ (Basso *et al*., 2005). Their structural model is described in the space group *Ccca*. A view along [001] of the polyhedral framework of carpholite group minerals is shown in Fig. 1. One cationic site in general position is tetrahedrically coordinated and usually fully occupied by Si atoms; the tetrahedra are linked to generate pyroxene-like single silicate chains running parallel to *c*. Three other cationic sites *M*1, *M*2 and *M*3, are octahedrally coordinated. Generally the $M1O_6$ octahedron is the largest, with mean cation-oxygen distance <*M*1-O> > 2.1 Å, whereas the $M3O_6$ octahedron is the smallest, with <*M*3-O> < 1.94 Å. The *M*1 site is mainly occupied by divalent cations such as Fe^{2+}, Mg^{2+} and Mn^{2+} like in the end-members ferrocarpholite, magnesiocarpholite and carpholite, respectively, or by Al and Li in a ratio 1:1 in balipholite (Peng *et al*., 1987). The *M*2 and *M*3 positions commonly host trivalent cations, i.e. Al^{3+}, but a replacement by V^{3+} ions takes place in vanadium-rich carpholites leading to an ideal composition with V^{3+} fully occupying the *M*2 site in vanadiocarpholite. Only in balipholite the *M*3 site is occupied by the divalent cation Mg^{2+}. Two different open channels parallel to *c* are recognizable in the structure (Ghose *et al*., 1989). One of them hosts the *A* site, with dodecahedral coordination, that may be empty or partially occupied by large cations such as K^+; in balipholite it is fully occupied by Ba^{2+}. Possible cationic substitution paths, derived from structural studies, involve: i) substitutions among R^{2+} divalent cations as Fe^{2+}, Mg^{2+} and Mn^{2+} in the *M*1 site; ii) a coupled substitution $\square_A + R^{2+}{}_{M1} \longleftrightarrow K^+{}_A + (Li^+, Na^+)_{M1}$, when a significant content of K^+ enters the *A* site as in potassic-carpholite; iii) $\square_A + 2Al^{3+}{}_{M3} \longleftrightarrow Ba^{2+}{}_A + 2Mg^{2+}{}_{M3}$ and $2R^{2+} \longleftrightarrow Al^{3+} + Li^+$ in the *M*1 site, as in balipholite; iv) $Al^{3+} \longleftrightarrow V^{3+}$, preferably in *M*2 but partially also in the *M*3 site, as in V-rich carpholite and in vanadiocarpholite, respectively (Basso *et al*., 2005).

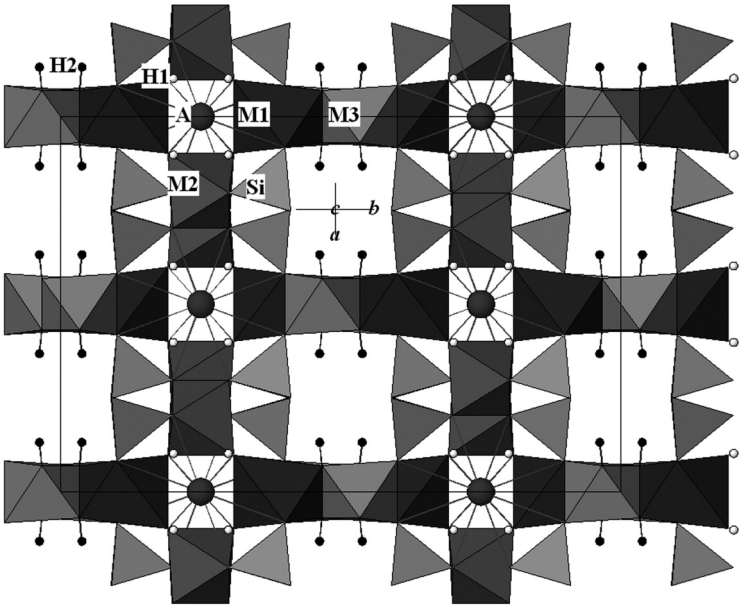

Fig. 1 - View along [001] of the polyhedral framework of carpholite group minerals.

The five crystallographically different oxygen atoms occupy general positions; two of them are generally pertaining to hydroxyl groups, but a replacement of one of the $(OH)^-$ groups by F^- is reported by Peng *et al.* (1987) in balipholite and by Ghose *et al.* (1989) in a nonstoichiometric carpholite. Partial and disordered $(OH)^-$ ‹—› F^- substitution for both the hydroxyl groups was found by Fuchs *et al.* (2001) in magnesiocarpholites.

Since 1951 structural, chemical and optical studies have been carried out on minerals belonging to the carpholite group. A variety of chemical compositions characterizes these minerals evidencing several possible substitutions involving the *A*, *M*1, *M*2, *M*3 and OH structural sites. The general formula unit $A_{0\text{-}1}\ M1_2\ M2_2\ M3_2\ [(OH,F)_4|Si_2\ O_6]_2$, where $A = \square$, Ba, K, Na, *M*1 = Mn^{2+}, Mg, Fe^{2+}, Al, Li, Na, Fe^{3+}, Ca, *M*2 = Al, V^{3+}, Fe^{3+}, Ti and *M*3 = Al, Mg, V^{3+}, Fe^{3+}, Ti, can represent the chemical composition of the group minerals.

The dependence of crystallographic parameters on chemical composition, reported in literature, has been studied for selected sets of Fe-Mg-carpholites, and described through simple linear equations involving the degree of substitution of Mg by Fe^{2+} as compositional parameter. In the present paper multiple linear regression equations relating observed crystallographic parameters, like unit cell edges and refractive indices, to the mean constituent cationic radii of the *M*1, *M*2 and *M*3 sites are proposed. Multiple linear regression equations have been obtained also to predict mean polyhedral cation-oxygen distances, because they are insufficiently reproduced by linear combination of cation and anion radii. Finally the internal multiple linear correlation of the unit cell edges *a*, *b* and *c* has been evidenced.

Relations among crystallographic parameters and chemical composition

Viswanathan and Seidel (1979) found two equations relating the lattice parameters *a* and *b* to the mole proportion $X = Fe^{2+}/(Mg+Fe^{2+})$, respectively, through simple linear regression analysis performed on a sample of 13 ferrocarpholites and magnesiocarpholites. They pointed out that the unit cell edge *c* remains almost constant in spite of the Mg-Fe-Mn substitution.

In this paper it was aimed finding correlations between unit cell parameters and the mean cation-oxygen distances and the ionic radii of relevant cations. Multiple linear regression analyses were performed on the cell edges and on the mean cation-oxygen distances of the carpholite-group minerals (Table 1), using as independent variables the mean ionic radii r(*A*), r(*M*1), r(*M*2), r(*M*3) (Shannon, 1976) and the ratio $F^-/(OH)^-$. The <Si-O> bond distances were not included in the regression analysis because they are nearly invariant. A preliminary check indicated that r(*A*) and $F^-/(OH)^-$ don't

Table 1

Selected minerals of the carpholite group with refined structure.

Sample	ICSD#	Formula	Name	Reference
1	34520	$\square\ Mn_2\ Al_4\ [(OH)_4|Si_2O_6]_2$	carpholite	Naumova *et al.* (1974)
2	68260	$Ba\ (Al_1\ Li_1)\ Al_2\ Mg_2\ [(OH)_2\ F_2|Si_2O_6]_2$	balipholite	Peng *et al.* (1987)
3	7289	$\square\ (Fe_{1.52}\ Mg_{0.48})\ Al_4\ [(OH)_4|Si_2O_6]_2$	ferrocarpholite	Ferraris *et al.* (1992)
4	100431	$\square\ (Mn_{1.94}\ Mg_{0.16}\ Fe^{2+}_{0.14})\ (Al_{3.80}\ Fe^{3+}_{0.02})\ [(OH)_4|Si_2O_6]_2$	carpholite	Lindemann *et al.* (1979)
5	100873	$\square\ (Mg_{1.6}\ Fe_{0.4})\ Al_4\ [(OH)_4|Si_2O_6]_2$	magnesiocarpholite	Viswanathan (1981)
6	158095	$K_{0.004}\ (Mg_{1.30}\ Fe^{2+}_{0.64}\ Fe^{3+}_{0.06})\ Al_{3.94}\ [(OH)_{3.95}\ F_{0.15}|Si_2\ O_{5.90}]_2$	magnesiocarpholite	Fuchs *et al.* (2001)
7	158096	$K_{0.004}\ (Mg_{1.30}\ Fe^{+2}_{0.68}\ Fe^{3+}_{0.02})\ Al_{3.96}\ [(OH)_{3.96}\ F_{0.12}|Si_2\ O_{5.92}]_2$	magnesiocarpholite	Fuchs *et al.* (2001)
8	172128	$K_{0.012}\ (Mn_{1.74}\ Mg_{0.26})\ (Al_{1.02}\ V^{3+}_{0.98})\ Al_2\ [(OH)_4|Si_2\ O_6]_2$	V-rich carpholite	Basso *et al.* (2005)
9	172129	$K_{0.168}\ (Mn_{1.84}\ Mg_{0.16})\ (V^{3+}_{1.68}\ Al_{0.32})\ (Al_{1.70}\ V^{3+}_{0.30})\ [(OH)_4|Si_2\ O_6]_2$	vanadiocarpholite	Basso *et al.* (2005)

significantly affect the unit cell edge values and the polyhedral sizes. Moreover, the independent variables statistically unrelated to the dependent one have been excluded from each regression analysis. Among the minerals with refined structure, reported in literature and also in the ICSD database (release 2010-1), the ferrocarpholite of MacGillavry *et al.* (1956) has been rejected, because the refinement results are not very accurate and the chemical composition is very near to that of the ferrocarpholite of Ferraris *et al.* (1992). Also the nonstoichiometric carpholite (Ghose *et al*., 1989) has been neglected because the central atoms of the $(Li,Mn)O_6$ octahedron occupy a split position leading to a non-univocal mean cation-oxygen distance. The linear equations obtained to predict the unit cell edge values are:

$$a = 1.2(3)r(M1) + 12.83(2)$$
$$R = 0.87, SE = 0.043$$

$$b = 1.8(5)r(M1) + 4.5(6)r(M2) + 1.2(4)r(M3) + 15.7(4)$$
$$R = 0.99, SE = 0.042$$

$$c = 0.16(7)r(M1) + 0.63(9)r(M2) + 0.27(6)r(M3) + 4.51(7)$$
$$R = 0.98, SE = 0.006$$

where R is the multiple correlation coefficient and SE the standard error of estimate.

The cell parameter *a* is affected only by the *M*1 cationic size, whereas the values of *b* and *c* increase with increasing size of all the three octahedral cations, depending more on the *M*2 cationic radius.

The equations for the mean cation-oxygen distances are:

$$\langle A\text{-O}\rangle = 0.12(5)r(M1) + 0.23(6)r(M2) - 0.11(4)r(M3) + 2.87(5)$$
$$R = 0.98, SE = 0.005$$

$$\langle M1\text{-O}\rangle = 0.89(6)r(M1) - 0.29(8)r(M2) + 0.43(5)r(M3) + 1.40(6)$$
$$R = 0.99, SE = 0.006$$

$$\langle M2\text{-O}\rangle = -0.08(4)r(M1) + 0.78(7)r(M2) + 1.56(4)$$
$$R = 0.98, SE = 0.006$$

$$\langle M3\text{-O}\rangle = 0.36(6)r(M2) + 1.71(3)$$
$$R = 0.92, SE = 0.005$$

From these equations it follows that the *M*2 cationic population plays a great role in the structure geometry affecting all the four cation-oxygen distances.

Furthermore, multiple linear regression analyses have been performed on the unit cell edges of 35 members of the carpholite group, belonging to a second and larger set of minerals obtained by adding to the above 9 minerals the first 26 (from sample 10 to 35) reported in Table 2. In this case only the two mean ionic radii r(*M*1) and r(*M*2, *M*3) have been used as independent variables, because the lack of structure refinement for the 26 added minerals prevent the experimental knowledge of the distribution of the cations occupying the *M*2 and *M*3 octahedral sites. The linear equations obtained are:

$$a = 1.42(6)r(M1) + 12.68(4$$
$$R = 0.98, SE = 0.012$$

$$b = 3.0(2)r(M1) + 4.1(4)r(M2, M3) + 15.6(3)$$
$$R = 0.94, SE = 0.045$$

$$c = 0.24(4)r(M1) + 0.71(7)r(M2, M3) + 4.54(6)$$
$$R = 0.88, SE = 0.008$$

The improvement of the prediction of the *a* value using the linear equation obtained from the second set is evident, in agreement with the fact that the *a* value turns out to have a high correlation only with the cationic population of the *M*1 site.

Finally, it may be pointed out that, using the extended set of 35 minerals, an internal dependence of *a*, *b* and *c* is detected. Viswanathan and Seidel (1979) showed a linear relationship between the

TABLE 2
Selected minerals of the carpholite group with non-refined structure.

Sample	Formula	Name	Reference
10	$\square\,(Mn_{1.30}\,Mg_{0.50}\,Fe^{2+}_{0.182})\,(Al_{3.86}\,Fe^{3+}_{0.13}\,Ti_{0.014})\,[(OH)_4|Si_2O_6]_2$	carpholite	1 - Mottana and Schreyer (1977)
11	$\square\,(Mn_{1.74}\,Fe^{2+}_{0.20})\,Al_{4.26}\,[(OH)_4|Si_2O_6]_2$	carpholite	2 - Mottana and Schreyer (1977)
12	$\square\,(Mn_{1.44}\,Mg_{0.60}\,Fe^{2+}_{0.32})\,Al_{4.12}\,[(OH)_4|Si_2O_6]_2$	carpholite	3 - Mottana and Schreyer (1977)
13	$(Na_{0.042}\,K_{0.012})\,(Mn_{1.70}\,Mg_{0.32}\,Fe^{2+}_{0.164})\,(Al_{3.94}\,Fe^{3+}_{0.062})\,[(OH)_4|Si_2O_6]_2$	carpholite	5 - Mottana and Schreyer (1977)
14	$(K_{0.006}\,Na_{0.004})\,(Mn_{1.62}\,Mg_{0.28}\,Fe^{2+}_{0.07})\,(Al_{3.82}\,Fe^{3+}_{0.18})\,[(OH)_4|Si_2O_6]_2$	carpholite	6 - Mottana and Schreyer (1977)
15	$\square\,(Mn_{1.70}\,Fe^{2+}_{0.24})\,(Al_{3.82}\,Fe^{3+}_{0.17})\,[(OH)_4|Si_2O_6]_2$	carpholite	8 - Mottana and Schreyer (1977)
16	$(Na_{0.030}\,K_{0.028})\,(Fe^{2+}_{1.76}\,Mg_{0.42}\,Ca_{0.016}\,Mn_{0.014})\,(Al_{3.98}\,Fe^{3+}_{0.106}\,Ti_{0.018})\;\;[(OH)_4|Si_2O_6]_2$	ferrocarpholite	18 - Mottana and Schreyer (1977)
17	$\square\,(Fe^{2+}_{1.04}\,Mg_{0.90}\,Mn_{0.03})\,(Al_{3.98}\,Fe^{3+}_{0.118}\,Ti_{0.012})\;\;[(OH)_4|Si_2O_6]_2$	ferrocarpholite	19 - Mottana and Schreyer (1977)
18	$\square\,(Fe^{2+}_{0.98}\,Mg_{0.94}\,Mn_{0.028})\,(Al_{3.98}\,Fe^{3+}_{0.102}\,Ti_{0.012})\;\;[(OH)_4|Si_2O_6]_2$	ferrocarpholite	20 - Mottana and Schreyer (1977)
19	$\square\,(Fe^{2+}_{1.26}\,Mg_{0.72}\,Mn_{0.04})\,(Al_{3.94}\,Fe^{3+}_{0.02}\,Ti_{0.02})\;\;[(OH)_4|Si_2O_6]_2$	ferrocarpholite	Steen and Bertrand (1977)
20	$\square\,(Mg_{1.570}\,Fe^{2+}_{0.402})\,Al_{4.04}\,[(OH)_4|Si_2O_6]_2$	magnesiocarpholite	A Chan 782 - Goffé (1980)
21	$(K_{0.024}\,Na_{0.018})\,(Mg_{1.424}\,Fe^{2+}_{0.534}\,Ca_{0.032})\,(Al_{3.582}\,Fe^{3+}_{0.228}\,Ti_{0.082})\;\;[(OH)_4|Si_2O_6]_2$	magnesiocarpholite	Van 73 - Goffé (1980)
22	$(Na_{0.012}\,K_{0.002})\,(Mg_{1.244}\,Fe^{2+}_{0.642}\,Ca_{0.016}\,Mn_{0.006})\,(Al_{3.870}\,Fe^{3+}_{0.078}\,Ti_{0.078})\;\;[(OH)_4|Si_2O_6]_2$	magnesiocarpholite	Chan 764 - Goffé (1980)
23	$\square\,(Fe^{2+}_{1.208}\,Mg_{0.724}\,Mn_{0.038})\,(Al_{3.952}\,Fe^{3+}_{0.036}\,Ti_{0.012})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	1 - Viswanathan and Seidel (1979)
24	$\square\,(Fe^{2+}_{1.178}\,Mg_{0.724}\,Mn_{0.024})\,(Al_{3.926}\,Fe^{3+}_{0.064}\,Ti_{0.016})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	2 - Viswanathan and Seidel (1979)
25	$\square\,(Fe^{2+}_{1.226}\,Mg_{0.712}\,Mn_{0.018})\,(Al_{3.946}\,Fe^{3+}_{0.048}\,Ti_{0.012})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	3 - Viswanathan and Seidel (1979)
26	$\square\,(Fe^{2+}_{1.092}\,Mg_{0.864}\,Mn_{0.024})\,(Al_{3.942}\,Fe^{3+}_{0.042}\,Ti_{0.016})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	4 - Viswanathan and Seidel (1979)
27	$\square\,(Fe^{2+}_{1.070}\,Mg_{0.870}\,Mn_{0.030})\,(Al_{3.924}\,Fe^{3+}_{0.054}\,Ti_{0.026})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	5 - Viswanathan and Seidel (1979)
28	$\square\,(Fe^{2+}_{1.168}\,Mg_{0.774}\,Mn_{0.044})\,(Al_{3.942}\,Fe^{3+}_{0.048}\,Ti_{0.012})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	6 - Viswanathan and Seidel (1979)
29	$\square\,(Fe^{2+}_{1.324}\,Mg_{0.620}\,Mn_{0.014})\,(Al_{3.948}\,Fe^{3+}_{0.044}\,Ti_{0.016})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	7 - Viswanathan and Seidel (1979)
30	$\square\,(Fe^{2+}_{1.142}\,Mg_{0.804}\,Mn_{0.034})\,(Al_{3.904}\,Fe^{3+}_{0.084}\,Ti_{0.016})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	8 - Viswanathan and Seidel (1979)
31	$\square\,(Fe^{2+}_{1.248}\,Mg_{0.702}\,Mn_{0.022})\,(Al_{3.890}\,Fe^{3+}_{0.106}\,Ti_{0.012})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	9 - Viswanathan and Seidel (1979)
32	$\square\,(Fe^{2+}_{1.236}\,Mg_{0.714}\,Mn_{0.026})\,(Al_{3.932}\,Fe^{3+}_{0.058}\,Ti_{0.014})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	10 - Viswanathan and Seidel (1979)
33	$\square\,(Mg_{1.594}\,Fe^{2+}_{0.406}\,Mn_{0.038})\,(Al_{3.970}\,Fe^{3+}_{0.012}\,Ti_{0.012})\,[(OH)_4|Si_2O_6]_2$	magnesiocarpholite	11 - Viswanathan and Seidel (1979)
34	$\square\,(Mg_{1.294}\,Fe^{2+}_{0.684}\,Mn_{0.004})\,(Al_{3.966}\,Fe^{3+}_{0.026}\,Ti_{0.012})\,[(OH)_4|Si_2O_6]_2$	magnesiocarpholite	12 - Viswanathan and Seidel (1979)
35	$\square\,(Mg_{1.92}\,Fe^{2+}_{0.10})\,(Al_{4.0})\,[(OH)_4|Si_2O_6]_2$	magnesiocarpholite	13 - Viswanathan and Seidel (1979)
36	$\square\,(Fe^{2+}_{1.22}\,Mg_{0.78}\,Mn_{0.024})\,(Al_{3.96}\,Fe^{3+}_{0.034})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	13 - Mottana and Schreyer (1977)
37	$\square\,(Fe^{2+}_{1.32}\,Mg_{0.62}\,Mn_{0.010})\,(Al_{3.92}\,Fe^{3+}_{0.086})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	14 - Mottana and Schreyer (1977)
38	$\square\,(Fe^{2+}_{1.52}\,Mg_{0.44}\,Mn_{0.028})\,(Al_{3.96}\,Fe^{3+}_{0.040})\,[(OH)_4|Si_2O_6]_2$	ferrocarpholite	15 - Mottana and Schreyer (1977)

TABLE 3
Observed unit cell edges (Å) and refractive indices. Mean ionic radii (Å) used for the regression analyses are also reported.

Sample	*a*	*b*	*c*	n_x	n_y	n_z	r(*M*1)	r(*M*2,*M*3)	r(*M*2)	r(*M*3)
1	13.831	20.296	5.121	-	-	-	0.825	0.535	0.535	0.535
2	13.587	20.164	5.144	-	-	-	0.647	0.627	0.535	0.720
3	13.797	20.200	5.116	1.627	1.639	1.645	0.766	0.535	0.535	0.535
4	13.718	20.216	5.132	1.612	1.627	1.633	0.819	0.539	0.542	0.535
5	13.714	20.079	5.105	-	-	-	0.732	0.535	0.535	0.535
6	13.716	20.084	5.110	-	-	-	0.737	0.535	0.535	0.535
7	13.726	20.099	5.112	-	-	-	0.740	0.535	0.535	0.535
8	13.840	20.452	5.143	-	-	-	0.816	0.561	0.586	0.535
9	13.830	20.681	5.188	1.684	1.691	1.700	0.821	0.587	0.623	0.551
10	13.785	20.242	5.108	-	-	-	0.798	0.539	-	-
11	13.831	20.296	5.121	1.611	1.628	1.630	0.825	0.535	-	-
12	13.816	20.252	5.118	-	-	-	0.795	0.535	-	-
13	13.849	20.306	5.130	1.616	1.633	1.639	0.811	0.537	-	-
14	13.827	20.267	5.118	1.621	1.633	1.637	0.813	0.540	-	-
15	13.845	20.318	5.126	1.624	1.629	1.638	0.824	0.540	-	-
16	13.760	20.194	5.111	1.628	1.644	1.647	0.771	0.538	-	-
17	13.730	20.140	5.109	-	-	-	0.753	0.538	-	-
18	13.747	20.123	5.110	1.625	1.634	1.638	0.752	0.538	-	-
19	13.763	20.162	5.115	1.614	1.630	1.635	0.760	0.536	-	-
20	13.705	20.085	5.111	-	-	-	0.732	0.535	-	-
21	13.714	20.081	5.110	-	-	-	0.741	0.572	-	-
22	13.723	20.075	5.108	-	-	-	0.743	0.538	-	-
23	13.760	20.156	5.112	-	-	-	0.759	0.536	-	-
24	13.753	20.137	5.111	-	-	-	0.757	0.538	-	-
25	13.748	20.159	5.110	-	-	-	0.759	0.537	-	-
26	13.752	20.150	5.112	-	-	-	0.754	0.536	-	-
27	13.754	20.146	5.111	-	-	-	0.754	0.537	-	-
28	13.758	20.165	5.110	-	-	-	0.758	0.537	-	-
29	13.761	20.176	5.112	-	-	-	0.761	0.537	-	-
30	13.763	20.161	5.112	-	-	-	0.756	0.538	-	-
31	13.765	20.164	5.114	-	-	-	0.759	0.538	-	-
32	13.755	20.140	5.112	-	-	-	0.759	0.537	-	-
33	13.714	20.079	5.105	-	-	-	0.732	0.536	-	-
34	13.737	20.104	5.109	-	-	-	0.741	0.536	-	-
35	13.694	20.040	5.108	-	-	-	0.723	0.535	-	-
36	-	-	-	1.617	1.633	1.638	0.757	0.536	-	-
37	-	-	-	1.621	1.636	1.640	0.761	0.537	-	-
38	-	-	-	1.624	1.639	1.643	0.767	0.536	-	-

lattice parameters *a* and *b* plotting the data relative to 13 ferrocarpholites and magnesiocarpholites, but the simple linear regression *a vs b* over the extended set reaches a value of 0.70 of the correlation index. Also Mottana and Schreyer (1977) reported an internal dependence of *a*, *b* and *c* plotting *a vs b* and *c vs b* for 19 samples of carpholites. Using the extended set the simple linear

regression *c* vs *b* has a R value of 0.87. The multiple regression analysis has a higher correlation index and leads to the following linear equation:

$$b = 1.09(8)a + 5.8(3)c - 24.4(15)$$
$$R = 0.98, SE = 0.024$$

In TABLE 3 the observed unit cell edges and the mean ionic radii used for the regression analyses are reported.

RELATIONS BETWEEN REFRACTIVE INDICES AND CHEMICAL COMPOSITION

Steen and Bertrand (1977) showed a linear increase of the indices of refraction with rising degree of substitution of Mg by Fe^{2+} in ferrocarpholites. In the present study multiple linear regression analyses have been performed on the subset of the 38 members (TABLES 1 and 2) of the carpholite group consisting of 13 minerals with well-determined refractive indices and composition given in TABLE 3. The derived equations are:

$$n_x = 0.98(6) - 0.12(5)r(M1) + 1.37(11)r(M2, M3)$$
$$R = 0.97, SE = 0.005$$

$$n_y = 1.07(5) - 0.13(5)r(M1) + 1.23(10)r(M2, M3)$$
$$R = 0.97, SE = 0.005$$

$$n_z = 1.03(5) - 0.12(5)r(M1) + 1.31(10)r(M2, M3)$$
$$R = 0.97, SE = 0.004$$

The results show good linear dependence of all the three refractive indices on both the radii. No meaningful correlation has been detected for 2V data.

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