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The behaviour of Ti in amphiboles :
I. Four- and six-coordinate Ti in richterite

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Abstract : The crystal structures and site-populations of 12 richterites have been refined to R indices of 1-2% using single-crystal Mo*K*α X-ray diffraction data. Potassium-fluor-richterites from lamproites are characterized by $^{[4]}$(Si+Al) sums less than 8.0 apfu (atoms per formula unit), suggesting the presence of other isomorphous tetrahedral substituents; richterites from other environments do not show this feature. The results of the structure refinements (mean bond lengths and mean atomic numbers) and crystal-chemical arguments show $^{[4]}Ti^{4+}$ to occur at the T(2) site in lamproitic richterites. Some richterites also show significant amounts of Ti^{4+} in octahedral coordination; combination of site occupancy refinement and stereochemical data show $^{[6]}Ti^{4+}$ to occur almost entirely at the M(1) site in these amphiboles, locally associated with the occurrence of O^{2-} at the adjacent O(3) site(s).

Key-words : Titanium, richterite, crystal-chemistry, amphibole.

1 - Introduction

Titanium is a ubiquitous minor component in amphiboles, and in some parageneses can attain the status of a major constituent. Despite its importance, the behaviour of Ti in amphiboles is not very well characterized, and as a consequence of this, is also not very well understood. Recognizing the distribution of Ti between the various sites able to host it is not a straightforward matter from an experimental point of view; the effects of Ti are usually obscured by the effects of other transition metals, specifically Fe^{2+} and Fe^{3+}. In most diffraction experiments, the scattering from Ti is overwhelmed by the scattering from Mg, Al and Fe, and even in optimum cases (such as neutron diffraction), there is usually not a unique solution to the problem solely from the measurement of the scattering power at each site. The results obtained for site-occupancies must therefore be integrated with complete crystal-chemical information (mean bond lengths (m.b.l.), shape and dimension of the thermal factors). For spectroscopic techniques, the problem is even more severe. Heteronuclear intervalence charge transfer usually prevents a unique interpretation of electronic absorption spectra in the chemically complex amphiboles. XANES may give some unique information, but cannot (as yet) distinguish between crystallographically distinct sites of similar coordination. The behaviour of Ti is the major area of ignorance in amphibole chemistry at the present time, and the optimum approach to its solution would seem to be a careful examination of specific amphibole compositions that are susceptible to a unique solution by crystallographic and/or spectroscopic methods.

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2 - Previous work

2.1 - Valence state

Titanium is usually assumed to be tetravalent in an oxide environment. However, this is not always the case. Spectroscopic methods have shown the presence of significant trivalent titanium in lunar and meteoric pyroxenes (Burns *et al.*, 1976 ; Dowty & Clark, 1973a,b ; Mao & Bell, 1974) and in melanite-schorlomite garnets (Burns, 1972 ; Huggins *et al.*, 1977 ; Schwartz *et al.*, 1980). In addition, $NaTi^{3+}Si_2O_6$ pyroxene has been synthesized by Prewitt *et al.* (1972). The similarity of the pyroxene and amphibole structure suggests the possibility that Ti may be (at least partially) in the trivalent state in amphiboles. However, until recently, any direct evidence on this point was lacking.

Schwartz & Irving (1978) examined three kaersutites using the approach of Burns (1972) ; they derived $Ti^{3+}/(Ti^{3+}+Ti^{4+})$ ratios of 0.04, 0.04 and 0.09 for these amphiboles, which had TiO_2 contents in the range 5.1-5.8 wt%. As indicated by the authors, these values are probably not significant in terms of the uncertainty of the method, indicating that Ti is dominantly to completely in the tetravalent state in these kaersutites.

Waychunas (1987) has examined the question of the valence of Ti in minerals using XANES spectroscopy. His results for a wide variety of minerals (including a kaersutite and a titanian 'barkevikite') are consistent with tetravalent Ti in all the terrestrial minerals examined. The same results have been obtained by Otten & Buseck (1987) by means of electron-energy-loss spectroscopy.

2.2 - Site-occupancy

Fig. 1 shows a projection of the crystal structure of *C2/m* amphiboles; the IMA standard amphibole chemical formula and site nomenclature (Leake, 1978) are used throughout the paper.

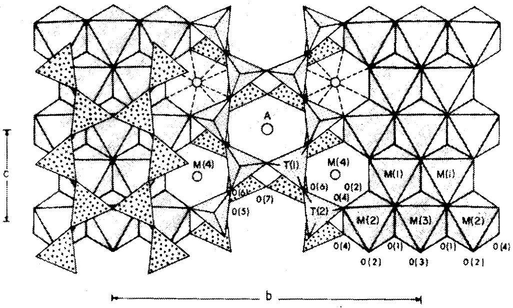

Fig. 1. (100) projection of the *C2/m* amphibole crystal structure (modified after Hawthorne, 1983).

Titanium is usually considered as an octahedral cation in most amphiboles. When present in small amounts [< 0.20 atoms per formula unit (apfu)], most structural studies (see Hawthorne, 1983) have assigned it to the M(2) site, which typically hosts highly-charged cations. However, there is no direct evidence for this, as the scattering from Ti is usually overwhelmed by the scattering from the more abundant Fe in X-ray diffraction work. Indeed, there is some chemical evidence to suggest that this may not be the case (Hawthorne, 1983, Fig. 62). For kaersutite, in which Ti is present in much larger amounts (up to ~ 1 apfu) and is usually associated with partial dehydroxylation at O(3), the situation is little clearer. A neutron structure refinement of an oxy kaersutite (Kitamura *et al.*, 1975) showed Ti to be strongly ordered at the M(1) site, presumably locally coordinating an O^{2-} anion occupying the O(3) site, with lower occupancy at M(3) and low occupancy at M(2). Recent accurate structure refinements of some oxy kaersutites at the CSCC (Pavia) detected a split M(1') position shifted towards O(3) ; this is a feature connected with the presence of Ti and the mechanism for obtaining local charge balance (Cannillo *et al.*, 1988). However, in the case of some very Ti-rich amphiboles [*e.g.* sadanagaites (Ti up to 0.50 apfu), Shimazaki *et al.*, 1984], which are not oxy-amphiboles, the behaviour of titanium is completely unknown.

Although in most amphiboles titanium is octahedrally coordinated, this does not always seem to be the case. Potassium-bearing richterites from lamproites (*e.g.* Wagner & Velde, 1986) often show T site sum deficiencies when only Si and Al are assigned to these sites. There are three possibilities here :

(1) there are significant vacancies at the T sites ;

(2) Ti occupies one or both of the T sites ;

(3) Fe occupies one or both of the T sites.

Possibility (1) is unlikely both because of bond valence considerations and because the octahedral cations in those samples is always > 5 apfu. Possibilities (2) and (3) seem reasonable from a chemical bond-valence viewpoint. It must be noted that in the first structure refinement of a K-richterite (from potassic volcanics), Papike *et al.* (1969), on the basis of the chemical analysis alone, attributed 0.21 Ti apfu to the tetrahedra in order to get complete tetrahedral occupancy. As far as spectroscopic techniques are concerned, Della Ventura *et al.* (1991) studied a series of synthetic Fe-free Ti-bearing richterites, and assigned specific bands in the infrared and Raman spectra to $^{[4]}$Ti-O vibrations. This has also been confirmed by EXAFS and XANES data on these amphiboles (Mottana *et al.*, 1990 ; Paris *et al.*, in prep.).

3 - The current study

This work will focus on a careful characterization by means of X-ray single-crystal structure refinement (XRef) of the crystal-chemical behaviour of Ti in amphiboles. The chemical compositions of the natural samples have been chosen so as to minimize the problems associated with interfering scattering species. This first paper will deal with the behaviour of Ti in richterites.

4 - Experimental

The provenance of the samples used in this work is indicated in Table 1. The sample set consists of a series of richterites for which $^{[4]}$(Si+Al) < 8 apfu, taken from lamproites (R(4)-R(12)), together with a smaller set of more typical richterites from other parageneses. Unfortunately, richterite crystals from lamproite parageneses are usually small and of poor quality, and we examined material from several parageneses without finding crystals sufficiently good to allow the collection of accurate diffraction data. Fortunately, a few localities gave crystals of adequate quality.

4.1 - X-ray data collection

Crystals were selected for crystallographic measurements and intensity data collection on the basis of optical clarity, freedom from inclusions and equant shape. All crystals were mounted on a Philips PW-1100 automated four-circle diffractometer and examined with graphite-monochromated Mo*K*α X-radiation ; crystal quality was assessed *via* the profiles and widths of Bragg diffraction peaks. Unit-cell dimensions were calculated from least-squares refinement of the *d* values obtained for 48 rows of the reciprocal lattice by measuring the center of gravity of each reflection and of its corresponding antireflection in the θ range between -35 and +35° ; values for the crystals used in the collection of the intensity data are given in Table 2.

Intensity data were collected for the monoclinic equivalent pairs *hkl* and *h-kl* in the Laue group 2/*m* in the θ range 3-35° using the step-scan profile technique of Lehman & Larsen (1974). Full details of the data collection procedure are given in Ungaretti (1980) and Ungaretti

Table 1. Provenance of richterite samples.

No.	Name	SEQ	Locality
R (1)	Fluor-richterite	359	Ontario, Canada
R (2)	Potassium-richterite	363	Val d'Aosta, Italy
R (3)	Potassium-fluor-richterite	354	M.Somma, Italy
R (4)	Potassium-fluor-richterite	481	Cancarix, Spain
R (5)	Potassium-fluor-richterite	537	Cancarix, Spain
R (6)	Potassium-fluor-richterite	538	Cancarix, Spain
R (7)	Potassium-fluor-rictherite	536	W. Kimberley, Australia
R (8)	Potassium-fluor-richterite	540	W. Kimberley, Australia
R (9)	Potassium-fluor-richterite	539	W. Kimberley, Australia
R(10)	Potassium-fluor-richterite	160	W. Kimberley, Australia*
R(11)	Potassium-fluor-richterite	161	W. Kimberley, Australia*
R(12)	Potassium-fluor-richterite	159	W. Kimberley, Australia*

* late-stage low-pressure phases

SEQ is the sequence number in the CSCC crystal-chemical data base for amphiboles.

Table 2. Unit-cell dimensions and miscellaneous structure refinement information for richterites ; maximum e.s.d. in unit-cell dimensions are < 3 on the last figure.

	R(1)	R(2)	R(3)	R(4)	R(5)	R(6)	R(7)	R(8)	R(9)	R(10)	R(11)	R(12)
a(Å)	9.884	9.998	9.970	9.950	9.948	9.950	10.020	10.022	10.025	10.017	10.025	10.028
b	18.005	17.976	17.985	18.022	18.025	18.035	18.026	18.029	18.034	18.021	18.039	18.039
c	5.274	5.273	5.273	5.280	5.281	5.284	5.282	5.284	5.286	5.279	5.286	5.289
β(°)	104.65	104.75	104.81	104.72	104.72	104.76	104.96	105.01	104.98	104.92	105.01	105.04
V(Å^3)	908.12	916.44	914.05	915.73	915.93	916.87	921.82	922.19	923.13	920.88	923.41	923.96
D_c	3.06	3.02	3.03	3.11	3.12	3.12	3.07	3.07	3.07	3.08	3.07	3.07
$\#_{all}$	1364	1147	1386	1385	1392	1391	1403	1397	1403	1399	1400	1399
$\#_{obs}$ I>5σ(I)	1152	950	1199	1081	926	866	1119	1180	1204	1095	1200	1114
R_{sym}	2.1	1.8	0.9	1.3	1.4	1.8	2.3	1.1	6.0	1.6	2.7	1.4
R_{obs}	1.9	1.5	1.4	1.4	1.4	1.5	1.6	1.4	2.8	1.6	1.9	1.7
R_{all}	2.6	2.1	1.9	2.4	3.0	3.7	2.3	1.9	3.2	2.3	2.3	2.3

et al. (1981). The intensity data were corrected for absorption by the method of North *et al.*, (1968), corrected for Lorentz and polarization effects, averaged and reduced to structure factors. A reflection has been considered as observed if its intensity exceeds that of five standard deviations based on counting statistics.

4.2 - Structure refinement

Fully ionized scattering factors were used for non-tetrahedral cations, whereas both neutral and ionized scattering factors were used for the tetrahedral cations and the oxygens (Ungaretti *et al.*, 1983). In all the Ti-richterites, the equivalent isotropic atomic displacement obtained at convergence for the O(3) oxygen was systematically and significantly lower than those obtained for the other oxygens and for the O(3) site in OH-amphiboles, suggesting the presence of F^- substituting for hydroxyl. This was further confirmed by the absence of the H peak in the difference Fourier maps. The scattering factors of O^{2-} and F^- were therefore used at O(3) in the last cycles of the structure refinement.

At the T(2) site, a significantly lower equivalent isotropic atomic displacement than that obtained at T(1) suggested for crystals R(4-12) the presence of some isomorphous species with higher atomic number; the scattering factor of Ti was therefore introduced, and its occupancy was refined against that of Si.

Concerning the A cations, the structural model used at the beginning of the refinement had (Na, K) only at the special position A (2*b*, with coordinates 0, 1/2, 0) ; the occupancy of the A(m) (4*i*) and A(2) (4*g*) positions were checked at convergence on the difference Fourier maps and then inserted in the model.

All the refinements were done in the space group *C*2/*m*, and converged to R factors of ~ 2% (Table 2) for observed reflections. As repeatedly observed in the course of the crystal-chemical study of a very large number of amphiboles (see also Ungaretti, 1980, pp. 44-46), full-matrix refinement of scale factor, secondary extinction coefficient, atomic positions, site occupancies

Table 3. Atomic fractional coordinates (x 10^4) and equivalent isotropic atomic displacements (Å^2) ; e.s.d. are on the last figure.

		R(1)	R(2)	R(3)	R(4)	R(5)	R(6)	R(7)	R(8)	R(9)	R(10)	R(11)	R(12)
O(1)	*x/a*	1111	1097	1106	1113	1112	1111	1103	1102	1103	1104	1103	1103
	y/b	853	866	853	856	862	864	854	854	854	854	853	853
	z/c	2187	2178	2191	2200	2203	2204	2199	2200	2202	2197	2203	2203
	B	0.51	0.46	0.47	0.55	0.57	0.56	0.51	0.50	0.53	0.46	0.54	0.51
O(2)	*x/a*	1190	1182	1177	1176	1175	1175	1172	1172	1171	1177	1170	1169
	y/b	1698	1702	1693	1686	1686	1686	1693	1694	1694	1693	1695	1695
	z/c	7262	7261	7263	7249	7240	7240	7258	7258	7258	7257	7255	7158
	B	0.55	0.53	0.56	0.66	0.67	0.63	0.63	0.64	0.67	0.59	0.70	0.66
O(3)	*x/a*	1053	1054	1029	1029	1041	1045	1023	1022	1021	1024	1020	1021
	z/c	7140	7143	7146	7126	7119	7127	7148	7148	7151	7146	7148	7152
	B	0.65	0.59	0.65	0.87	0.92	0.93	0.77	0.72	0.78	0.69	0.81	0.71
O(4)	*x/a*	3630	3620	3619	3607	3606	3606	3609	3610	3608	3608	3612	3611
	y/b	2487	2481	2485	2487	2486	2487	2484	2484	2485	2484	2484	2485
	z/c	7935	7980	7967	7978	7986	7984	7989	7993	7985	7989	7992	7990
	B	0.73	0.71	0.84	1.00	1.00	0.99	0.99	1.00	1.05	0.89	1.09	1.09
O(5)	*x/a*	3469	3436	3447	3455	3453	3451	3439	3439	3440	3437	3441	3441
	y/b	1326	1302	1306	1298	1295	1296	1299	1300	1300	1297	1302	1302
	z/c	970	948	974	947	940	941	992	997	1001	983	1006	1011
	B	0.80	0.66	0.79	0.84	0.87	0.89	0.90	0.89	0.94	0.78	0.99	0.97
O(6)	*x/a*	3436	3399	3412	3427	3430	3431	3407	3407	3408	3406	3407	3406
	y/b	1173	1172	1171	1181	1185	1185	1176	1175	1176	1176	1175	1175
	z/c	5933	5929	5940	5914	5907	5909	5950	5951	5955	5943	5955	5958
	B	0.73	0.64	0.76	0.84	0.85	0.85	0.89	0.88	0.94	0.76	0.98	0.96
O(7)	*x/a*	3393	3319	3348	3361	3353	3356	3335	3335	3332	3333	3334	3335
	z/c	2929	3008	3003	3035	3050	3058	3063	3068	3066	3060	3068	3070
	B	0.86	0.63	0.74	0.87	0.84	0.84	0.76	0.76	0.76	0.70	0.81	0.79
T(1)	*x/a*	2793	2749	2767	2781	2780	2782	2758	2758	2759	2757	2759	2759
	y/b	845	853	848	848	849	849	848	848	848	849	848	848
	z/c	2978	2987	3005	3004	3002	3007	3028	3030	3034	3022	3036	3038
	B	0.38	0.33	0.36	0.46	0.48	0.47	0.45	0.43	0.46	0.39	0.48	0.46
T(2)	*x/a*	2875	2847	2854	2857	2855	2855	2845	2845	2845	2845	2846	2845
	y/b	1714	1720	1716	1713	1714	1714	1718	1718	1718	1717	1718	1718
	z/c	8046	8042	8056	8049	8046	8049	8080	8083	8087	8074	8090	8093
	B	0.38	0.34	0.41	0.47	0.49	0.48	0.47	0.46	0.49	0.41	0.51	0.48
M(1)	*y/b*	886	892	892	856	836	830	886	886	886	889	886	885
	B	0.48	0.47	0.44	0.80	0.84	0.82	0.60	0.61	0.66	0.54	0.66	0.61
M(2)	*y/b*	1781	1795	1789	1797	1796	1795	1792	1792	1791	1795	1790	1789
	B	0.47	0.51	0.55	0.61	0.61	0.58	0.60	0.60	0.65	0.57	0.67	0.62
M(3)	B	0.45	0.39	0.46	0.54	0.57	0.51	0.49	0.49	0.55	0.45	0.58	0.49
M(4)	*y/b*	2774	2776	2780	2767	2766	2766	2778	2779	2780	2778	2781	2781
	B	0.89	0.86	0.87	0.97	0.98	0.91	0.97	0.97	1.01	0.94	1.01	0.95
M(42)	*y/b*	-	-	-	2542	2559	2512	-	-	-	-	-	-
	B	-	-	-	1.49	0.55	0.57	-	-	-	-	-	-
A	B	4.39	1.29	2.47	1.97	2.30	2.19	1.64	1.98	2.00	2.00	2.01	2.41
A(m)	*x/a*	368	328	326	352	369	357	284	300	283	307	303	269
	z/c	811	764	747	767	790	762	644	663	652	649	648	598
	B	3.02	0.83	1.63	2.11	1.71	2.17	1.48	1.57	1.53	1.57	1.64	2.50
A(2)	*y/b*	-	-	4706	4637	4670	4739	-	-	-	-	-	-
	B	-	-	4.80	0.91	2.51	2.17	-	-	-	-	-	-
H	*x/a*	1983	1904	-	-	-	-	-	-	-	-	-	-
	z/c	7911	7509	-	-	-	-	-	-	-	-	-	-
	B	0.40	2.05	-	-	-	-	-	-	-	-	-	-

and anisotropic atomic displacement parameters can be carried out without any problem of correlation between the varied parameters; the final results have been proved to be independent from the scheme used in varying the about 100 parameters to be refined. Atomic coordinates and equivalent isotropic atomic displacements are given in Table 3 ; selected interatomic distances are given in Table 4, and the mean atomic numbers for the structural sites are listed in Table 5. Tables with observed and calculated structure factors and with anisotropic atomic displacement parameters may be obtained on request from the authors.

4.3 - Electron microprobe analysis

Subsequent to the experimental crystallographic work, most of the crystals used in the collection of the intensity data were analyzed by electron microprobe (EMP) techniques. The crystals were mounted in piccolite in small holes in one-inch perspex discs; each disc also contained several crystals of tremolite (56) of Hawthorne

Table 4. Selected individual and mean bond distances (Å) in richterites; e.s.d. are < 1 on the last figure.

	R(1)	R(2)	R(3)	R(4)	R(5)	R(6)	R(7)	R(8)	R(9)	R(10)	R(11)	R(12)
T(1)-O(1)	1.609	1.597	1.601	1.606	1.605	1.608	1.602	1.603	1.604	1.600	1.604	1.604
-O(5)	1.636	1.630	1.630	1.630	1.628	1.629	1.631	1.632	1.632	1.629	1.635	1.634
-O(6)	1.637	1.627	1.624	1.622	1.623	1.622	1.623	1.623	1.624	1.622	1.622	1.623
-O(7)	1.636	1.635	1.632	1.632	1.631	1.633	1.634	1.633	1.632	1.633	1.633	1.633
<T(1)-O>	1.629	1.622	1.622	1.622	1.622	1.623	1.623	1.623	1.623	1.621	1.623	1.624
T(2)-O(2)	1.613	1.610	1.617	1.618	1.617	1.618	1.620	1.620	1.621	1.615	1.623	1.624
-O(4)	1.586	1.577	1.586	1.586	1.585	1.587	1.587	1.587	1.588	1.585	1.588	1.590
-O(5)	1.660	1.673	1.671	1.671	1.673	1.672	1.678	1.679	1.680	1.677	1.679	1.681
-O(6)	1.677	1.681	1.683	1.685	1.686	1.687	1.693	1.694	1.695	1.691	1.697	1.698
<T(2)-O>	1.634	1.635	1.639	1.640	1.640	1.641	1.644	1.645	1.646	1.642	1.647	1.648
M(1)-O(1)	2.058	2.062	2.061	2.060	2.059	2.059	2.064	2.064	2.064	2.064	2.064	2.065
-O(2)	2.058	2.055	2.040	2.077	2.100	2.108	2.048	2.049	2.051	2.046	2.050	2.051
-O(3)	2.076	2.087	2.077	2.025	2.002	1.998	2.072	2.071	2.072	2.074	2.071	2.071
<M(1)-O>	2.064	2.068	2.059	2.054	2.054	2.055	2.061	2.061	2.062	2.061	2.061	2.062
M(2)-O(1)	2.164	2.162	2.175	2.190	2.181	2.177	2.184	2.183	2.184	2.187	2.183	2.182
-O(2)	2.086	2.093	2.087	2.094	2.097	2.098	2.095	2.096	2.095	2.098	2.096	2.095
-O(4)	2.003	1.995	1.999	1.994	1.994	1.995	2.002	2.001	2.005	1.999	2.003	2.004
<M(2)-O>	2.084	2.083	2.087	2.092	2.091	2.090	2.094	2.093	2.095	2.095	2.094	2.094
M(3)-O(1)	2.063	2.074	2.063	2.075	2.083	2.086	2.068	2.068	2.069	2.068	2.069	2.069
-O(3)	2.038	2.047	2.027	2.035	2.047	2.047	2.029	2.030	2.028	2.030	2.029	2.029
<M(3)-O>	2.055	2.065	2.051	2.061	2.071	2.073	2.055	2.055	2.055	2.055	2.056	2.054
<A-O>	2.923	2.945	2.935	2.936	2.940	2.942	2.952	2.953	2.954	2.951	2.956	2.956
<A(m)-O>	2.863	2.885	2.878	2.936	2.872	2.875	2.901	2.900	2.903	2.898	2.904	2.910

(1983) to check for analytical accuracy and mount-to-mount compatibility. The discs were polished and subsequently carbon-coated.

Electron microprobe analyses were done on a fully automated Cameca SX-50 operating in the wavelength dispersive mode with the following conditions : excitation voltage : 15 kV ; specimen current : 20 nA ; peak count time : 20s ; background count time : 10 s. The following standards and crystals were used for $K\alpha$ X-ray lines : Al : Al_2O_3, TAP ; Fe : fayalite, LiF ; Si : diopside, PET ; Mg : MgO, TAP ; F : fluor-riebeckite, TAP ; Mn : tephroite, LiF ; Ti : titanite, LiF. Each grain was analysed at a minimum of 12 points (commonly twice this number, depending on the size of the exposed surface) to check for compositional zoning and to obtain a representative composition for the whole crystal used in the collection of the diffraction intensities. Data reduction was done with the $\varphi(\rho Z)$ method (Pouchou & Pichoir, 1984, 1985), and the resultant mean analysis for each grain is given in Table 6. H_2O values were obtained by calculation, taking into account the observed F values.

5 - Discussion

Cameron *et al.* (1983) reported refinements of the structure of synthetic fluor-richterite and potassium fluor-richterite; because they are strict end-member compositions, they are very useful for comparative purposes in the present study, and are shown as squares in the Figures. The refinement of a K-richterite by Papike *et al.* (1969) is also shown in the Figures (and marked with a diamond), in that its position in the plots is perfectly coherent with the hypothesis of 0.21 $^{[4]}Ti^{4+}$ apfu.

The general structural characteristics reported by Cameron *et al.* (1983) are also found in the natural richterites examined in the current work. Only the A site deserves comment. It is noteworthy that in the cases of the crystals for which only K was detected by EMP analysis (R(7), R(8), R(9) and R(12)), only the A and A(m) positions were found to be occupied; this confirms that K in amphiboles is ordered along the mirror plane, and does not occupy mainly the general (8*j*) position as suggested by Docka *et al.* (1987) on the basis of model energy calculations.

Table 5. Refined mean atomic numbers (electrons) in richterites ; e.s.d. are ~0.1 electrons. For reader's convenience, the final refined Ti occupancies (*vs.* Si) are also reported ; $^{[4]}$Ti (apfu) is equal to 4 x occ.

	R(1)	R(2)	R(3)	R(4)	R(5)	R(6)	R(7)	R(8)	R(9)	R(10)	R(11)	R(12)
M(1)	12.3	12.2	11.9	14.5	15.4	15.7	12.8	12.8	12.9	12.8	12.9	12.9
M(2)	13.3	12.3	12.1	14.3	14.0	13.8	13.5	13.5	13.6	13.9	13.6	13.6
M(3)	12.3	11.8	12.0	13.5	14.3	14.4	12.4	12.4	12.6	12.5	12.5	12.4
M(4)	17.6	15.7	15.9	15.3	15.3	15.3	16.0	16.2	16.3	15.9	16.5	16.4
M(42)	-	-	-	0.4	0.3	0.2	-	-	-	-	-	-
T(1)*	13.9	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
T(2)	14.0	14.0	14.0	14.2	14.2	14.2	14.3	14.4	14.4	14.3	14.5	14.5
Ti occ.	0.00	0.00	0.00	0.03	0.03	0.03	0.04	0.05	0.05	0.04	0.06	0.06
A	2.8	9.1	8.7	7.7	7.3	6.7	8.0	9.9	9.5	9.8	9.9	10.4
A(m)	3.8	3.8	3.4	4.5	4.7	5.1	5.6	4.7	4.7	4.8	4.8	4.5
A(2)	-	-	0.4	0.1	0.2	0.2	-	-	-	-	-	-
O(3)	8.6	8.2	8.8	8.7	8.9	8.3	8.8	8.8	8.8	8.8	8.9	8.8

* not varied during the refinement

5.1 - The tetrahedral sites

Stereochemical details for the T(1) and T(2) tetrahedra are shown in Table 4. The variation in chemistry (Table 6) is accompanied by some scatter in the corresponding sizes of the tetrahedra. The relative variation in tetrahedral size is shown in Fig. 2, which also shows the range of tetrahedral sizes found for the nearly 600 monoclinic amphiboles refined so far at the CSCC. It is immediately apparent from Fig. 2 that the <T(1)-O> distance shows a wide range in size (1.617 - 1.685 Å) that corresponds to variations in constituents $^{[4]}\mathrm{Al}^{3+}/^{[4]}\mathrm{Si}^{4+}$ content (Robinson *et al.*, 1973 ; Hawthorne & Grundy, 1973a ; Ungaretti, 1980). On the contrary, excluding richterites (a) and few other amphiboles [(b) and (c)], <T(2)-O> shows a rather limited range (1.626 - 1.634 Å, within the dashed lines), which can be explained by the influence of the composition of the other structural sites, with little or no substitution of $^{[4]}\mathrm{Al}^{3+}$ for $^{[4]}\mathrm{Si}^{4+}$. Two of the trends deviating from the general behaviour [(b) and (c)] have been proved by combined XRef and chemical information to be due to $^{[4]}\mathrm{Al}^{3+} \Leftrightarrow {}^{[4]}\mathrm{Si}^{4+}$ substitution at the T(2) site (Previde Massara *et al.*, 1989). The richterites refined in this work(a) are characterized by short <T(1)-O> distances, consistent with the low Al content, and by considerable variation in <T(2)-O> distances, suggesting other significant substitutions at the T(2) site, in full agreement with the site population refinement, as discussed in section 4.2.

Table 6 shows the range in tetrahedral site chemistry as indicated by the electron microprobe analyses. Except for samples R(1) and R(2), the Si content falls significantly below 8.0 apfu and the Al content is not enough to bring the assigned T cations to their ideal sum of 8 apfu. Tetrahedral vacancies are not expected on the basis of bond-valence arguments, and this possibility is discounted. On the other hand, the sum (Si+Al+Ti+Fe+Mg+Mn) is always ~ 13 apfu. Thus, with regard to the T sites, there are three questions to be considered:

(1) are the small amounts of Al tetrahedrally or octahedrally coordinated?

(2) which transition metal(s) occurs at the T sites?

(3) what is the relative cation ordering over the T sites?

Presuming that $^{[4]}\mathrm{Al}^{3+}$ will order at the T(1) site, any variation in <T(1)-O> should correlate with Al/Si occupancy if the Al^{3+} is [4]-coordinate. This point is examined in Fig. 3 ; note that the straight line in this figure is not a least-squares line through the data points, but represents the ideal (hard-sphere model) $^{[4]}\mathrm{Si}^{4+} \Leftrightarrow {}^{[4]}\mathrm{Al}^{3+}$ substitution passing through the mean of the <T(1)-O> values for synthetic stoichiometric Na- and K-fluor-richterites. The range in both Al and <T(1)-O> is very small in these richterites ; nevertheless, the slope of the trend is coherent with Al being 4-coordinate and ordered at the T(1) site.

Next there is the question of which transition metal is [4]-coordinate in these richterites. Previous work (Czamanske & Atkin, 1985 ; Wagner & Velde, 1986) has assumed that Ti occurs at the tetrahedrally coordinated sites. However, there was no direct evidence for this, and the possibility of tetrahedrally coordinated Fe^{3+} must be considered, as it is a common feature in volcanic pyroxenes (Virgo, 1972). Both Wagner & Velde (1986) and Table 6 give analyses of richterites

Table 6. Electron microprobe analyses of richterites ; chemical formulae were calculated on the basis of 24 (O^{2-}+ OH^-+ F^-). Analysis of R(2) has been taken from Mottana and Griffin (1986).

	R(1)	R(2)	R(3)	R(5)	R(6)	R(7)	R(8)	R(9)	R(12)
SiO_2	54.57	56.74	56.88	53.42	53.29	54.24	53.29	53.01	53.17
Al_2O_3	2.17	0.59	0.11	0.47	0.50	0.32	0.37	0.42	0.46
TiO_2	0.35	0.06	0.02	6.54	6.21	3.01	3.73	3.98	3.63
FeO	2.30	0.00	0.11	4.86	4.53	2.46	2.45	2.55	2.72
MgO	22.75	22.89	24.83	18.18	18.55	21.99	21.95	21.93	21.93
MnO	0.11	0.67	0.03	0.08	0.13	0.05	0.06	0.06	0.04
CaO	9.30	6.94	7.39	6.23	6.25	6.69	6.73	6.76	6.91
Na_2O	4.31	4.10	4.36	4.18	4.27	3.51	3.31	3.39	3.33
K_2O	1.49	4.88	4.09	4.18	4.20	5.46	5.51	5.50	5.34
SrO	-	0.63	-	-	-	-	-	-	-
F	2.63	1.40	2.88	1.47	1.60	3.09	3.21	3.16	n.d.
H_2O	(0.90)	(1.47)	(0.80)	(1.41)	(1.35)	(0.65)	(0.59)	(0.56)	(2.11)
O=F	-1.11	-0.59	-1.21	-0.62	-0.67	-1.30	-1.25	-1.35	-
Total	99.77	99.78	100.28	100.40	100.21	100.17	99.95	100.05	99.64
Chemical formulae:									
Si	7.629	7.951	7.887	7.578	7.572	7.677	7.580	7.542	7.565
Al	0.358	0.049	0.018	0.079	0.084	0.053	0.062	0.070	0.077
Ti	0.013	0.000	0.002	0.343	0.344	0.270	0.358	0.388	0.358
Sum T	8.000	8.000	7.907	8.000	8.000	8.000	8.000	8.000	8.000
Al	0.000	0.048	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ti	0.024	0.006	0.000	0.355	0.320	0.050	0.041	0.038	0.030
Fe	0.269	0.000	0.013	0.577	0.538	0.291	0.295	0.303	0.324
Mg	4.741	4.782	5.133	3.845	3.929	4.640	4.654	4.651	4.652
Mn	0.013	0.071	0.004	0.010	0.016	0.006	0.007	0.007	0.005
Sum C	5.047	4.907	5.150	4.787	4.803	4.987	4.997	4.999	5.011
C-5	0.047	Sr 0.051	0.150	0.000	0.000	0.000	0.000	0.000	0.011
Ca	1.393	1.042	1.098	0.947	0.951	1.014	1.026	1.030	1.053
Na	0.560	0.907	0.752	1.053	1.049	0.963	0.935	0.935	0.919
Sum B	2.000	2.000	2.000	2.000	2.000	1.977	1.961	1.965	1.923
Na	0.608	0.207	0.420	0.097	0.127	0.000	0.000	0.000	0.000
K	0.266	0.872	0.724	0.756	0.761	0.986	1.000	0.998	0.969
Sum A	0.864	1.079	1.144	0.853	0.888	0.986	1.000	0.998	0.969
F	1.163	0.620	1.263	0.664	0.719	1.383	1.444	1.467	-
OH	0.837	1.380	0.737	1.336	1.281	0.617	0.556	0.533	(2.000)

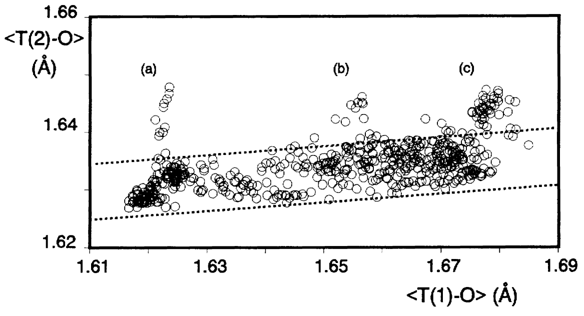

Fig. 2. Variation of <T(1)-O> and <T(2)-O> distances in the monoclinic amphibole data base at the CSCC. Dashed lines define the range of <T(2)-O> values which are not dependent on substitutions at the T(2) site.

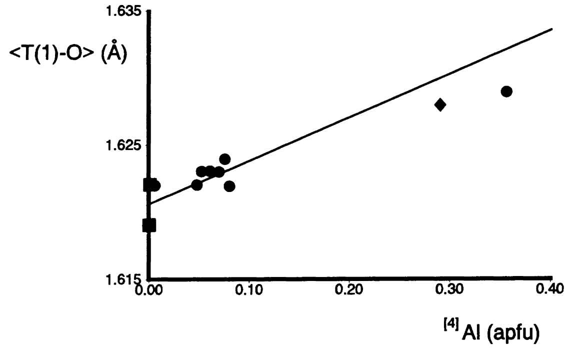

Fig. 3. Variation in <T(1)-O> distances as a function of analysed $^{[4]}Al$ content; the straight line represents an ideal hard-sphere model $^{[4]}Si^{4+} \Leftrightarrow {}^{[4]}Al^{3+}$ substitution. Here and in the following Figures, circles refer to the refinement obtained in this work, squares to those reported by Cameron *et al.* (1983) and diamond to that reported by Papike *et al.* (1969).

from West Kimberley, Australia, with insufficient Fe to bring the sum of the assigned T cations to their ideal sum of 8.0 apfu. More direct evidence for the presence of $^{[4]}Ti^{4+}$ comes from the synthesis and characterization studies of G. Della Ventura, J.-L. Robert and co-workers. Della Ventura *et al.* (1991) report the synthesis of amphiboles along the series $K(NaCa)Mg_5Si_8O_{22}(OH)_2$ - $K(NaCa)Mg_5(Si_7Ti)O_{22}(OH)_2$ in which Ti^{4+} is the only transition metal cation present. They give spectroscopic evidence to indicate that Ti^{4+} is [4]-coordinate, in agreement with the results obtained by Mottana *et al.* (1990) and Paris *et al.* (in prep.) by means of XANES spectroscopy.

We are now left with the question of the relative ordering of $^{[4]}Ti^{4+}$ over the T sites. Above we showed that the small amount of variation in <T(1)-O> is compatible with the analyzed variations in $^{[4]}Al^{3+}$ and therefore with the corresponding assignment of Al to the T(1) site. Concerning T(2), there is a significant increase in the <T(2)-O> distances (Table 4), which parallels the increase of the m.a.n.'s at T(2) (Table 5) ; this clearly indicates that $^{[4]}Ti^{4+}$ occurs at the T(2) site in richterites. The stereochemical details of this are examined in Fig. 4, which is based on the $^{[4]}Ti^{4+}$ contents calculated from the EMP analyses in Table 6 ; note that the line shown in Fig. 4 is not a least-squares line through the data, but is

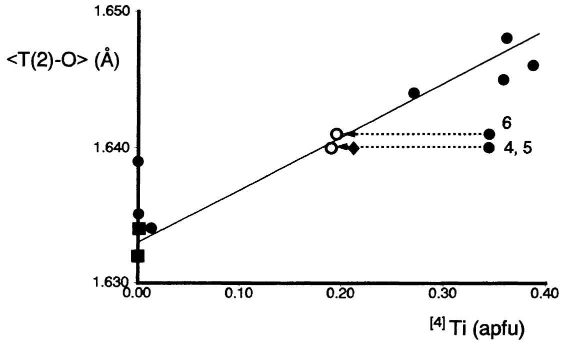

Fig. 4. Variation in <T(2)-O> distance as a function of $^{[4]}Ti^{4+}$ assigned on the basis of the formulae calculated from EMP analyses in Table 6 ; the line is drawn through the <<T(2)-O>> value for synthetic Na- and K-fluor-richterites (Cameron *et al.*, 1983), with a slope corresponding to a hard-sphere model for $^{[4]}Si^{4+} \Leftrightarrow {}^{[4]}Ti^{4+}$ substitution. Open circles refer to the $^{[4]}Ti^{4+}$ contents recalculated in Table 7. The Ti occupancies obtained from the structure refinement are in agreement with the EMP values for all the samples but R(5-6) ; for these latter, the refined occupancies support the recalculated $^{[4]}Ti$ values (open circles).

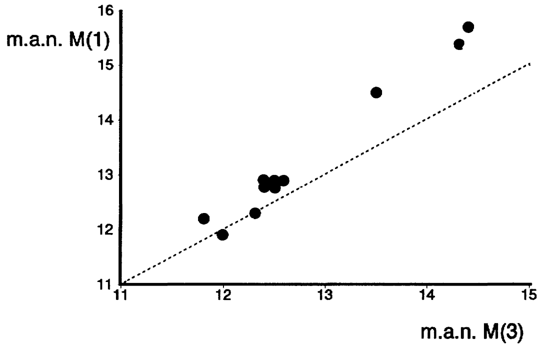

Fig. 5. The relative ordering of electrons over the M(1) and M(3) sites in richterites.

drawn through the mean of the <T(2)-O> values for synthetic end-member Na- and K-fluor-richterites with a slope corresponding to a hard-sphere model for substitution of $^{[4]}\mathrm{Ti}^{4+}$ for $^{[4]}\mathrm{Si}^{4+}$. The correspondence of the line and the observed data indicate that $^{[4]}\mathrm{Ti}^{4+}$ occurs at the T(2) site in richterites. The deviation observed for samples R(4), R(5) and R(6) will be explained in the next section.

Sample R(3) is a very special one. In this case, a small but significant lengthening of the <T(2)-O> distance (1.639 Å) couples with a virtual absence of Al, Ti and Fe. The EMP analysis (Table 6) gives (Si+Al+Ti) = 7.907 apfu and (Ca+Na+K) = 2.994 apfu, whereas Mg (5.133 apfu) exceeds the stoichiometric limit of 5.0 octahedral cations pfu. A model with Mg (r = 0.57 Å) + Si (r = 0.26 Å) at T(2) was tentatively refined but brought to some inconsistencies. On the other hand, EMP analyses performed on other grains show slightly different chemical compositions (Della Ventura *et al.*, 1983) ; other experimental work is therefore planned on this richterite sample.

5.2 - The octahedral sites

Inspection of Table 6 shows that there are usually three scattering species (Mg, Fe, Ti) to be distributed over the M(1), M(2) and M(3) sites; this is further complicated by the fact that Fe may be in the divalent and/or trivalent state. The refinement of octahedral site-occupancies gives the total number of electrons at the sites (Table 5), but there is no way of assigning three scattering species to these sites solely on scattering considerations. As a first approach to the problem, we will examine the relative ordering between the M(1) and M(3) sites; this is shown in Fig. 5 in terms of numbers of electrons. There seems to be a very regular distribution of electrons between the two sites, with a preference for the M(1) site. However, as we will see later, the situation is more complicated that this simple picture suggests.

In terms of cations, we must consider the distribution of Mg, Fe^{2+}, Fe^{3+} and Ti^{4+} over these sites. This can be done by using size considerations. This approach is further complicated by the fact that the anion occupancy of the O(3) site is variable (due to $OH^- \Leftrightarrow F^-$ substitution), a factor that is particularly important in richterites. The procedures described in Ungaretti *et al.* (1981) and Cannillo *et al.* (1986), which enable calculation of octahedral site populations from the results of the structure refinement, cannot be applied to these samples in a straightforward manner. The coordination of the M(1) and M(3) sites are similar [4 oxygens and 2 O(3) anions], and OH $\rightleftarrows$ F substitution at O(3) should affect the sizes of the two analogous octahedra in a similar fashion. The variations in size of the M(1) and M(3) octahedra are shown in Fig. 6. For most richterites, an increase in size of the M(1) octahedron is accompanied by a similar increase in size of the M(3) octahedron. These size increases are affected by :

(1) changes in anion occupancy of O(3) ;

(2) changes in cation occupancies of M(1) and M(3).

As indicated above, changes in anion occu-

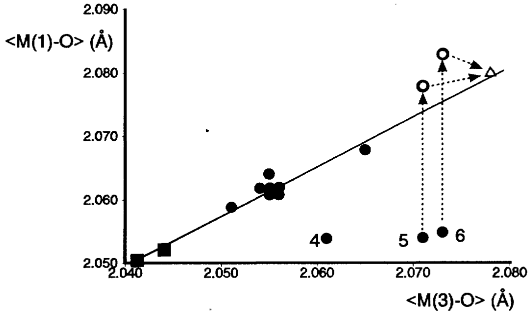

Fig. 6. Variations in <M(1)-O> and <M(3)-O> distances ; the numbered points denote richterites with significant $^{[6]}\mathrm{Ti}^{4+}$, the open circles refer to the positions calculated on the basis of complete $^{[6]}\mathrm{Ti}^{4+}$ ordering at M(1), whereas the triangle refers to that obtained taking into account small amounts of $^{[6]}\mathrm{Ti}^{4+}$ at M(3).

pancy of O(3) affect each octahedron similarly, and will shift the data points along a 1:1 line on Fig. 6. If the cations show a regular distribution over M(1) and M(3), then the sizes of the octahedra will change in a way that is dependent on the relative cation sizes and the values of K_d, the distribution coefficient. Such a relationship will give rise to an approximately linear variation over the limited compositional range of the amphiboles in Fig. 6. Thus the dominantly linear trend shown in Fig. 6 may be interpreted as resulting from a 'well-behaved' distribution of (two) cation species over the M(1) and M(3) sites.

It is notable that there are exceptions to the well-developed trend of Fig. 6 ; these are richterites R(4), R(5) and R(6) which lie well below the rest of the data. Inspection of Table 6 shows that the samples from Cancarix, (and only them) contain significant amounts of residual Ti^{4+} that had been assigned to the octahedrally coordinated C sites. The fact that the <M(1)-O> distances in these samples are much smaller than both the corresponding <M(3)-O> distances and the M(1) scattering powers would suggest, indicates that (at least most of) the octahedrally coordinated Ti^{4+} in these amphiboles occurs at the M(1) site. This conclusion is also supported by a close examination of the individual bond lengths of the M(1) octahedron (Table 4) ; in richterites with low $^{[6]}Ti^{4+}$, M(1)-O(3) ranges from 2.071 to 2.087 Å, whereas in $^{[6]}Ti^{4+}$-rich richterites, M(1)-O(3) ranges from 1.998 to 2.025 Å.

Table 7. Chemical formulae for samples from Cancarix recalculated by taking into account the kaersutitic substitution.

	R(5)	R(6)
Si	7.730	7.720
Al	0.080	0.085
Ti	0.190	0.195
	-----	-----
Sum T	8.000	8.000
Ti	0.522	0.482
Fe	0.588	0.549
Mg	3.921	4.006
Mn	0.010	0.016
	-----	-----
Sum C	5.041	5.053
C-5	0.041	0.053
Ca	0.966	0.970
Na	0.993	0.977
	-----	-----
Sum B	2.000	2.000
Na	0.180	0.223
K	0.772	0.777
	-----	-----
Sum A	0.952	1.000

Following the arguments of Hawthorne & Grundy (1973b) and Ungaretti (1980), the occurrence of $^{[6]}Ti^{4+}$ at M(1) and the short M(1)-O(3) distance suggest that some O^{2-} occurs at O(3), locally associated with $^{[6]}Ti^{4+}$ at M(1). The structure refinements of richterites R(4), R(5) and R(6) gave anomalously high equivalent isotropic atomic displacements at the M(1) site, indicative of the presence of some kaersutitic substitution $^{[6]}(Mg,Fe)^{2+} + 2\ (OH, F)^- \rightarrow {}^{[6]}Ti^{4+} + 2\ O^{2-}$; as already said, in order to achieve a better local charge-balance $^{[6]}Ti^{4+}$ probably moves towards the position of the O(3) site (Cannillo *et al.*, 1988).

There is another feature of the data presented here that also suggests this to be the case. As can be seen in Table 6, the C-group cation sums for R(5) and R(6) are 4.80 and 4.79 apfu respectively, considerably lower than the ideal value of 5 apfu. Although this estimate is very sensitive to analytical errors, we note that Wagner & Velde (1986) also obtained C-group sums of 4.89 and 4.78 apfu on richterite from the same locality, supporting our contention that this is a real observation (rather than an artifact of a bad analysis). If the $^{[6]}Ti^{4+}$ is associated with O^{2-} at O(3) in these amphiboles, this means that the calculation of the formula unit on the basis of 24 oxygens will lead to significant errors in the site sums (*c.f.* Hawthorne, 1983, Table 6). Table 7 shows the unit formulae for these amphiboles, recalculated assuming O^{2-} at O(3) in an amount ~ twice the $^{[6]}Ti^{4+}$ occupancy, *i.e.* corresponding to the $^{[6]}Ti^{4+} + 2\ O^{2-} \Leftrightarrow (Mg,Fe)^{2+} + 2\ OH^-$ substitution. The C-group cations sums are now > 5.0 apfu. Furthermore, the change in the calculated $^{[4]}Ti^{4+}$ content for these amphiboles brings them close to the ideal relationship shown in Fig. 4 (see the positions of the open circles). Thus it seems to be the case that the $^{[6]}Ti^{4+}$ is entering into the richterite structure *via* an 'oxy-type' substitution.

The question now arises as how much of the $^{[6]}Ti^{4+}$ occurs at M(1) ; does all of it occur there, or is there some small degree of disorder ? We may consider this question *via* the size effect of

Ti occurring at the M sites. If $^{[6]}Ti^{4+}$ (r = 0.605 Å) substitutes for $^{[6]}Mg$ (r = 0.720 Å) at M(1), we can calculate the effect on <M(1)-O> of all $^{[6]}Ti^{4+}$ occurring at M(1) ; for the richterites R(5) and R(6), the effects are 0.030 and 0.028 Å respectively. This brings them into closer correspondence with the rest of the richterites in Fig. 6 (open circles), but if all the $^{[6]}Ti^{4+}$is assigned to M(1), then the values for R(5) and R(6) lie above the general trend. This indicates that some of the $^{[6]}Ti^{4+}$ also occurs at M(3). The Ti occupancies of M(1) and (M3) can be calculated by adjusting the occupancies until the values for R(5) and R(6) lie on the general trend of Fig. 6 ; reasonable values are 0.46, 0.06 and 0.44, 0.04 apfu for M(1), M(3) in R(5) and R(6), respectively (triangle). The same kind of reasoning can be applied to R(4), for which the EMP analysis could not be done as the crystal plucked out during polishing.

Inspection of Table 7 shows that Ti-richterites from Cancarix [R(4), R(5) and R(6)] are the only ones in which Ti^{4+} shows a preference for octahedral coordination. The different crystal-chemical behaviour of titanium is very likely related to differences in the conditions of crystallization, primarily in the F composition of the magma. These samples have the lowest F contents, and if sufficient H is not available, the richterite structure can be stabilized by means of the kaersutitic substitution $^{[6]}(Mg,Fe)^{2+}$ + 2 $(OH,F)^{-} \rightarrow {}^{[6]}Ti^{4+} + 2\ O^{2-}$.

5.3 - A crystal-chemical model for $^{[4]}Ti^{4+}$ in richterites

The presence of $^{[4]}Ti^{4+}$ in synthetic silicates (richterites : Della Ventura *et al.*, 1991 ; garnets : Huggins *et al.*, 1977) has been shown using spectroscopic methods. In natural samples, small amounts of $^{[4]}Ti^{4+}$ have been suggested by XRef only for some clinopyroxenes from lamproites (Carbonin *et al.*, 1989 ; max = 0.036 apfu) and for some magmatic Ca garnets (Callegari *et al.*, 1991 ; max = 0.27 apfu). The only stable compound so far known containing $^{[4]}Ti^{4+}$ is synthetic Ba_2TiO_4 (Bland, 1961); synthetic metastable $Ni^{2+}_{2(1+x)}Ti^{4+}_{(1-x)}O_4$ ($0.16 \leq x \leq 1$) cation excess spinels have been also proved to contain $^{[4]}Ti^{4+}$ (Lager *et al.*, 1981) ; $^{[4]}Ti^{4+}$ should therefore be considered rather uncommon in nature.

Almost all of the richterite samples with significant $^{[4]}Ti^{4+}$ come from lamproites, and have crystallized from a primary K-, F-, Ti-rich peralkaline liquid at 800-1000° C and 1-2 kbar. Other coexisting phases show $^{[4]}(Si+Al)$ deficiencies ; these are slight (< 0.05 apfu) in clinopyroxenes but significant in phlogopites where Ti^{4+} is generally [6]-coordinated (Robert, 1991 ; Brigatti *et al.*, 1991). On the other hand, richterites do not show significant K, F, Ti, (Si+Al) partitioning with respect to phlogopites (Wagner & Velde, 1986). It seems that their composition simply reflects that of the liquid. The tetrahedral site-preference for Ti under these conditions is evident for all but the Cancarix samples (Tables 6 and 7). The question therefore is : what makes richterite so special with regard to the entrance of Ti into the tetrahedra?

Richterite is a peculiar amphibole end-member ; it never shows significant heterovalent octahedral substitutions. This implies some structural constraints due to the relative dimensions of the different parts of the structure. In particular, the K ⇔ Na substitution at the A site causes a further increase in the M(4) and octahedral strip dimensions, the latter already being the largest possible for an A-filled amphibole composition ; this prevents heterovalent volume-decreasing substitutions at the octahedral sites. It must also be noted that heterovalent octahedral substitutions occur principally at M(2) in amphiboles ; in richterite, M(2) is by far the largest octahedron, and is therefore less suitable for the entrance of smaller cations ; accordingly, $^{[6]}Ti^{4+}$ substitution in richterites never occurs at the M(2) site.

In this situation, tetrahedral substitution of cations with ionic radii larger that that of $^{[4]}Si^{4+}$ (0.26 Å) should be favoured in order to achieve a better fit with the other structural units. But what is the crystal-chemical constraint for $^{[4]}Al^{3+}$ (r = 0.39 Å)/$^{[4]}Ti^{4+}$ (r = 0.42 Å) ordering between T(1) and T(2) ? The two independent tetrahedra in the amphibole structure are significantly different from a stereochemical viewpoint. T(1) is a fairly regular tetrahedron, and is always smaller than T(2) (*e.g.* <T(1)-O> = 1.618 Å, <T(2)-O> = 1.628 Å in glaucophanes). On the other hand, T(2) is always a highly irregular tetrahedron: two of the oxygens, O(2) and O(4), are underbonded and two, O(5) and O(6), are overbonded in the case of an ideal polyhedron ; therefore, two of the observed bond distances are very short and two are very long in the T(2) tetrahedron. In particular, the underbonding on O(4), which is the only 3-coordinate oxygen in the amphibole structure, is so high that all the bonds in which it is involved are by far the shortest in all the coordinated polyhedra, which therefore become very irregular. In richterites, the nominal charge deficiency on O(4) is the highest observed in amphiboles, and a hypothetical heterovalent $^{[4]}Si^{4+} \rightarrow {}^{[4]}Al^{3+}$ substitution at T(2) would increase this underbonding. The $^{[4]}Al^{3+}$ substitution at T(2) is therefore not likely to be operative.

Conversely, $^{[4]}Ti^{4+}$ combines a larger ionic radius (r = 0.42 Å) with the same charge as Si. Moreover, its electronic configuration fits better with a distorted tetrahedral coordination. It must be noted that the Ti tetrahedron in Ba_2TiO_4 (Bland, 1961) shows exactly the same kind of distortion as the T(2) tetrahedron in richterite.

It is interesting to consider the effect of P,T conditions of crystallization on $^{[4]}Ti^{4+}$ substitution in richterites. Concerning temperature, Cameron *et al.* (1983) have shown that high-T (>800° C) conditions promote misfit between the tetrahedral double-chain (which has a far lower expansion coefficient) and the rest of the structure. This misfit is lowered by significant straightening of the silicate chains, as in the case when a suitable chemical substitution ($^{[4]}Al^{3+}$ at T(1) and $^{[4]}Ti^{4+}$ at T(2)) increases the sizes of the two independent tetrahedra. We can conclude that in lamproite, both the high K content of the magma and the high T of crystallization favour $^{[4]}Si^{4+} \rightarrow {}^{[4]}Ti^{4+}$ substitution in richterites. Concerning pressure, a comparison is useful with the coexisting K-richterites and K-phlogopites found by Aoki (1974 ; 1975) in ultrabasic xenoliths in kimberlitic magmas from South Africa. These show exactly the same partitioning trends for major elements observed in lamproites (Wagner & Velde, 1986), but have far lower (<0.2 apfu) Ti contents. The $^{[4]}(Si+Al)$ deficiencies are still present, although in lower amounts, and some $^{[4]}Ti^{4+}$ substitution can be inferred also for these richterites. On the other hand, Kushiro & Erlank (1970) demonstrated that synthesis at high P (30 kbar) with a starting material of composition similar to that of samples R(4-6) yields far lower titanium contents (~ 0.5 % TiO_2).

The fact that Ti^{4+} is preferentially 4-coordinate in richterites allows us to explain these observations. Increasing pressure prevents the larger $^{[4]}Ti^{4+}$ cation from entering T(2), and consequently from further expanding the unit-cell. In any case, it must also be noted that high-P conditions of crystallization generally favour an increase in the coordination number of the atomic species which enter different polyhedra.

6 - Conclusions

Stereochemical analysis and site-occupancy refinement of a series of richterites show that Ti behaves in the following manner in these amphiboles :

(1) Ti^{4+} preferentially enters the tetrahedral chain in richterites, and is fully ordered at the T(2) site ;

(2) the presence of $^{[4]}Ti^{4+}$ is related to the very high-T, low-P conditions of crystallization of lamproitic richterites ;

(3) octahedrally coordinated Ti^{4+} can also occur in some richterites, where it is strongly ordered at the M(1) site ;

(4) The entrance of Ti^{4+} at M(1) seems to be associated with the occurrence of O^{2-} at the O(3) sites ; the ordering of $^{[6]}Ti^{4+}$ is therefore related to local charge-balance requirements ;

(5) the amount of Ti^{4+} is inversely related to the P conditions of crystallization, whereas its site preference is most likely related to the (H_2O,F^-) contents of the liquid.

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