Minerals of the Varuträsk Pegmatite.

IX. X-Ray Studies on Triphylite, Varulite, and their Oxidation Products.

By

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In connection with an investigation started by P. Quensel on minerals recently discovered at Varuträsk in north Sweden one of the present authors (Westgren) has at the request of Professor Quensel taken some X-ray powder photographs of triphylite, ferri-sicklerite and heterosite. The patterns thus obtained covered the diffraction range 58—115°. They were reproduced in the report in which Quensel describes these substances, proving that each of them may be considered to be a special mineral.[1]

The X-ray investigation has now been carried on to the point where it can be shown that although the specimens may be looked upon as three different minerals, they are at the same time very similar in structure. This seemed already likely from an inspection of the powder photographs containing the least deviated interferences which resembled each other strikingly, and a closer examination of the complete set of powder photographs has proved it beyond doubt.

Triphylite has been investigated by B. Gossner and H. Strunz, who found that the number of atoms in its translation group is the same as that in olivine and monticellite while the dimensions of its unit cell agree closely with those of the said minerals.[2] They have therefore concluded that the atomic grouping of triphylite is analogous to that of olivine and monticellite. Its unit cell dimensions were determined to be a = 4.67, b = 10.34 and c = 6.00 Å. The interferences of our triphylite powder photographs were found to be in good accord with these lattice dimensions. As may be seen in Table 1, the $\sin^2 \theta$-values agree perfectly with those calculated on the assumption that the identity periods are a = 4.711, b = 10.374, and c = 6.038 Å. The mineral is thus orthorhombic with an axial ratio of 0.454 : 1 : 0.583.

[1] P. Quensel, Geol. Fören. Förhandl. **59**, 77. 1937.

[2] B. Gossner and H. Strunz, Zeitschr. f. Kristallogr. **83**, 415. 1932.

In the report mentioned QUENSEL stated that H. VON ECKERMANN, after having investigated twinned crystal of what was thought to be triphylite, concluded that its symmetry may be lower than orthorhombic. In order to test this, we have taken two Laue photographs of a minute sliver of the mineral, in each case with the primary X-ray beam parallel to one of the main axes. The diagrams do not support the conclusion of VON ECKERMANN, but are instead in complete accord with the orthorhombic cell stated above. Moreover, F. ZAMBONINI and F. MALOSSI have measured artificially produced, very well developed crystals of lithiophilite, $LiMnPO_4$, and found them to be orthorhombic with an axial ratio of 0.4522 : 1 : 0.5834, *i. e.* very nearly the same as that of triphylite.[1]

There is thus no reason to doubt the orthorhombic symmetry of triphylite. Further, the powder photographs of ferri-sicklerite and heterosite prove that these minerals crystallize orthorhombic too. Their unit cell dimensions have been determined for ferri-sicklerite to be a = 4.787, b = 10.086, c = 5.939 Å, and for heterosite to be a = 4.760, b = 9.680, c = 5.819 Å. In Tables 2 and 3 may be seen how well the $\sin^2 \theta$-values of the X-ray patterns agree with those calculated.

Although the lattice dimensions of the three minerals do not differ very much, a decrease may be noted from triphylite through ferri-sicklerite to heterosite. The unit cell volume is for triphylite 295, for ferri-sicklerite 287, and for heterosite 268 Å³. This successive shrinking of the lattice is evidently connected with the leaching of lithium, which according to QUENSEL accompanies the successive oxidation of the iron and the manganese. The formulae of the minerals may be written for triphylite $[Li(\overset{2+}{Mn}, \overset{2+}{Fe})] PO_4$, for ferri-sicklerite $[(LiMn) \overset{2+}{} \overset{3+}{Fe}] PO_4$ and for heterosite $[\overset{3+}{Mn}, \overset{3+}{Fe}] PO_4$. As there are evidently four formula units present in the unit cell in each of the minerals, the translation group of triphylite consists of 28 atoms, that of heterosite of 24 atoms, and that of ferri-sicklerite of an intermediate number.

As may be seen in Tables 1—3, the relative intensity of the X-ray interferences is practically the same for all three minerals. As already mentioned, they must consequently be similarly built up. Reflections h 0 l with h + l odd and 0 k l with k odd are missing in all the powder photographs, indicating that the minerals are all isomorphous to D_{2h}^{16}, the space group of olivine. Starting from the approximate parameter values of olivine given by W. L. BRAGG and G. B. BROWN,[2] it has been

[1] F. ZAMBONINI and F. MALOSSI, Zeitschr. f. Kristallogr. 80, 442. 1931.
[2] W. L. BRAGG and G. B. BROWN, Zeitschr. f. Kristallogr. 63, 538. 1926.

possible by systematic variation of them and comparison between calculated and observed intensities to find out a structure that must be approximately correct, *viz.*

$$4 \text{ Mn and Fe in } 4 \text{ (c)}; \quad 2\pi u_1 = -10°; \quad 2\pi v_1 = 100°;$$
$$4 \text{ P} \qquad\qquad \text{in } 4 \text{ (c)}; \quad 2\pi u_2 = 150°; \quad 2\pi v_2 = 35°;$$
$$4 \text{ O}_I \qquad\qquad \text{in } 4 \text{ (c)}; \quad 2\pi u_3 = 90°; \quad 2\pi v_3 = 20°;$$
$$4 \text{ O}_{II} \qquad\quad \text{in } 4 \text{ (c)}; \quad 2\pi u_4 = 90°; \quad 2\pi v_4 = 160°;$$
$$8 \text{ O}_{III} \qquad\quad \text{in } 8 \text{ (d)}; \quad 2\pi x = 70°; \quad 2\pi y = 60°; \quad 2\pi z = 10°.$$

As may be seen in Table 3, the agreement between the calculated and observed intensities is not quite perfect but the discrepancies are so insignificant that the structure may be taken as mainly correct. That it cannot be very much in error is also indicated by the fact that the parameter values are almost the same as those of monticellite, $MgCaSiO_4$, which have been determined by G. B. BROWN and J. WEST.[1]

The PO_4 lattice of heterosite is the same as the SiO_4 arrangement of monticellite, and the Mn and Fe atoms have the same position in the former mineral as the Ca atoms in the latter. As the atomic grouping in triphylite is evidently very similar to that of heterosite, their P, O, and heavier metal atoms must be arranged in the same way. The assumption of GOSSNER and STRUNZ, that the Mn and Fe atoms of triphylite are situated in a set of symmetry centres has thus not been verified. From the close analogy between triphylite and monticellite it may be concluded that the Li atoms in the former mineral are situated in 4 (a), *i. e.* on the points 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. In ferri-sicklerite this position is only partially occupied by Li atoms, and in heterosite all its points are unoccupied.

It is rather astonishing that the oxidation of the heavier metals and the loss of the lithium is not accompanied by a more radical change in structure than a mere elimination of the lithium atoms from the lattice of triphylite. It must be remembered that the difference in atomic size between tri- and bivalent manganese (or iron) is quite considerable. The structure found for heterosite is also strange in view of the fact reported by V. CAGLIOTI that $FePO_4$, has the same structure as α-quartz.[2] That in this case the atomic arrangement of triphylite is largely maintained may be due to the occurring of the chemical processes at such a low temperature that any change in structure is prevented. Heterosite might thus be an unstable product. To determine if this might be the case we have heated the mineral for a few minutes at about

[1] G. B. BROWN and J. WEST, Zeitschr. f. Kristallogr. **66**, 154. 1928.
[2] V. CAGLIOTI, Rend. Accad. Lincei (6) **22**, 146. 1935.

Table 1.

Powder Photographs of Triphylite.   Cr-K Radiation.

h k l	sin² θ obs.	sin² θ calc.	Iobs.	h k l	sin² θ obs.	sin² θ calc.	Iobs.
021	0.0852	0.0843	w	151	0.3986	0.3971	w
101	0.0958	0.0946	v w	222 }	0.4285	{ 0.4268	st
111 }	0.1074	{ 0.1067	st	240 }		0.4293	
120 }		0.1073		123 }		0.4295	
121 }	0.1449	{ 0.1431	st	060		0.4368	—
002 }		0.1432		241	0.4655	0.4653	m
130	0.1705	0.1680	w	061	0.4726	0.4724	m
022		0.1917	—	232		0.4876	—
131	0.2054	0.2035	st	133	0.4905	0.4899	m
040		0.1940	—	160		0.4956	—
112	0.2156	0.2141	m	152		0.5052	—
041	0.2316	0.2300	m	043	0.5163	0.5164	m
200	0.2339	0.2351	v w	161		0.5314	—
210		0.2473	—	250		0.5384	—
122	0.2509	0.2505	w	310	0.5416	0.5413	v w
140	0.2530	0.2530	st	301		0.5650	—
211 }	0.2839	{ 0.2832	st	213		0.5695	—
220 }		0.2836		242 }	0.5727	{ 0.5725	m
141		0.2886	—	004 }		0.5728	
132	0.3111	0.3109	w	311 }	0.5791	{ 0.5773	m
221	0.3199	0.3194	w	320 }		0.5777	
042	0.3372	0.3372	v w	062 }		0.5800	
230		0.3444	—	223		0.6059	—
150	0.3619	0.3620	v w	321	0.6143	0.6135	w
023		0.3707	—	024		0.6213	—
202 }	0.3792	{ 0.3783	w	330		0.6384	—
231 }		0.3798		114	0.6427	0.6437	v w
103		0.3810	—	331		0.6744	—
212 }	0.3927	{ 0.3905	m	143		0.6842	—
113 }		0.3931		312		0.6845	—
142		0.3960	—				

500° C. When the powder thus treated was investigated by means of X-rays, it was found that it had changed. The lines of its X-ray patterns were blurred and indistinct. When the mineral had been heat-treated in the same way for about a day, its powder photographs were completely changed. The lines of heterosite had disappeared and were replaced by a great multitude of new reflections showing that the mineral had been transformed into a product with a very complicated structure. The reflections were far too numerous to be explained by an atomic grouping of the α-quartz type.

We have also taken some X-ray powder photographs of the minerals varulite and Mn-alluaudite, which according to QUENSEL correspond to triphylite and ferri-sicklerite but contain Na instead of Li. Their X-ray patterns have somewhat diffuse lines, but they show distinctly that the minerals of the Na-series are not isomorphous to those contain-

Table 2.

Powder Photographs of Ferri-Sicklerite.   Cr-K Radiation.

h k l	sin² θ		I obs.	h k l	sin² θ		I obs.
	obs.	calc.			obs.	calc.	
021	0.0887	0.0883	w	151	0.4143	0.4148	m
101	0.0944	0.0940	v w	222	0.4275	0.4271	st
111 ⎱	0.1070	⎰ 0.1068 ⎱	st	240	0.4328	0.4330	w
120 ⎰		⎱ 0.1083 ⎰		123	0.4412	0.4413	m
121	0.1465	0.1453	v w	060	0.4618	0.4620	v w
002	0.1489	0.1480	st	241	0.4700	0.4700	m
130	0.1740	0.1725	w	232		0.4913	—
022		0.1993	—	061	0.4989	0.4990	st
040	0.2049	0.2050	v w	133	0.5054	0.5055	st
131	0.2103	0.2095	st	160		0.5190	—
112	0.2188	0.2178	m	310		0.5254	—
200	0.2285	0.2278	v w	152		0.5257	—
210		0.2406	—	043	0.5382	0.5382	m
041	0.2423	0.2422	m	250		0.5486	—
122	0.2565	0.2563	m	301		0.5496	—
140	0.2621	0.2622	m	161		0.5560	—
211 ⎱	0.2780	⎰ 0.2776 ⎱	m	311	0.5624	0.5624	m
220 ⎰		⎱ 0.2791 ⎰		320		0.5639	—
141		0.2992	—	213	0.5727	0.5726	w
221	0.3156	0.3161	w	242		0.5810	—
132	0.3203	0.3205	v w	004	0.5919	0.5920	st
230		0.3433	—	143		0.5952	—
042	0.3537	0.3532	w	321	0.6006	0.6009	w
023	0.3657	0.3643	v w	062	0.6104	0.6100	m
202	0.3758	0.3758	m	223		0.6121	—
150		0.3778	—	330		0.6281	—
231		0.3803	—	024	0.6431	0.6432	w
212	0.3893	0.3886	m	114	0.6620	0.6618	m
103		0.3900	—	331		0.6651	—
113	0.4029	0.4028	m	312		0.6734	—
142		0.4102	—				

ing Li. Varulite and Mn-alluaudite seem, however, to be related to each other in the same way as triphylite and ferri-sicklerite. Their X-ray patterns resemble each other closely, but the lines of Mn-alluaudite are somewhat displaced in the direction of larger diffraction angles showing that its lattice dimensions are smaller than those of varulite. The oxidation of the iron of varulite is accompanied by a corresponding leaching of sodium, and this evidently brings about a shrinkage of the lattice dimensions as in the case of the transformation of triphylite into ferri-sicklerite.

Having theoretically deduced a mineral, which he called Na-purpurite,[1] QUENSEL has now obtained specimens from Varuträsk that evidently consist of this substance and thus represent the end product formed by the complete oxidation of varulite or Mn-alluaudite. Their

[1] P. QUENSEL, loc. cit. p. 96.

Table 3.

Powder Photographs of Heterosite.   Cr-K Radiation.

h k l	sin² θ obs.	sin² θ calc.	I obs.	I calc.	h k l	sin² θ obs.	sin² θ calc.	I obs.	I calc.
021	0.0937	0.	w	0.8	222	0.4398	0.4403	m	3.3
101	0.0958	0.0961	v w	0.	151	0.4438	0.4443	w	1.5
111	0.1094	0.1100	st	25	240	0.4532	0.4532	w	1.5
120	0.1126	0.1133	w	3.3	123	0.4597	0.4602	m	0.7
121	0.1516	0.1518	v w	0.5	241	0.4915	0.4917	m	3.1
002	0.1540	0.1542	st	13	060	0.5015	0.5015	v w	0.6
130	0.1832	0.1832	w	1.5	232		0.5100	—	0.1
022		0.2099	—	0.05	133	0.5297	0.5299	m	3.5
131	0.2212	0.2215	st	13	310		0.5323	—	0.2
040		0.2229	—	0.1	061	0.5402	0.5400	w	2.4
112	0.2256	0.2257	m	5.0	301		0.5570	—	0.00
200	0.2303	0.2304	v w	0.2	160		0.5591	—	0.3
210	0.2439	0.2443	v w	0.5	152		0.5601	—	0.4
041	0.2608	0.2613	m	4.2	043 } 311 } 320 }	0.5698	{ 0.5697, 0.5708, 0.5741 }	m	{ 2.6, 2.0, 0.6 }
122	0.2670	0.2675	m	4.8	250		0.5787	—	0.5
140 } 211 }	0.2812	{ 0.2804, 0.2818 }	m	{ 2.9, 0.8 }	213	0.5919	0.5912	v w	0.8
220		0.2861	—	0.6	161		0.5976	—	0.01
141	0.3185	0.3189	w	3.6	242		0.6075	—	0.2
221	0.3246	0.3246	w	1.4	321	0.6119	0.6126	w	1.6
132	0.3372	0.3372	m	3.2	004	0.6167	0.6168	st	5.2
230	0.3558	0.3558	v w	0.1	143		0.6274	—	0.3
042	0.3763	0.3770	v w	1.4	223		0.6330	—	0.2
202	0.3846	0.3846	w	3.7	330		0.6438	—	1.1
231		0.3943	—	0.05	062	0.6555	0.6559	m	5.0
212	0.3986	0.3985	m	4.2	024	0.6723	0.6725	v w	0.6
023		0.4026	—	0.01	331 } 312 } 114 }	0.6871	{ 0.6823, 0.6865, 0.6873 }	m	{ 1.8, 0.01, 1.0 }
103		0.4045	—	0.002					
150		0.4059	—	0.09					
113	0.4181	0.4184	m	2.0					
142		0.4347	—	0.07					

X-ray powder photographs resemble neither those of varulite or Mn-alluaudite, nor those of heterosite. They contain a very large number of lines, proving that the structure of Na-purpurite is exceedingly complicated. When the manganese of Mn-alluaudite is oxidized its atomic grouping, because of the largeness of the removed Na-atoms, evidently can last no longer but changes into a new one.

The investigation of the varulite series of minerals has so far only been of an orientating character. It will be carried on with a view of determining the structure of varulite, which may be possible through the analysis of artificially produced $NaFePO_4$ or $NaCuPO_4$ crystals. A more complete determination of the triphylite-heterosite structures will also be attempted.