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The Crystal Structure of Fairfieldite*

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The mineral fairfieldite is triclinic, space group $P\bar{1}$; the cell dimensions, as determined from crystals from Foote Mine, North Carolina, are: $a=5{\cdot}79$, $b=6{\cdot}57$, $c=5{\cdot}51$ Å, $\alpha=102^\circ 16'$, $\beta=108^\circ 40'$, $\gamma=90^\circ 18'$. The cell content is $Ca_2Mn(PO_4)_2.2H_2O$. The crystal structure was solved from a three-dimensional Patterson function and refined first by successive Fourier syntheses and then by least-squares to an R value 0·075. The coordination around the Mn and P ions is octahedral and tetrahedral respectively: the average Mn–O and P–O distances are 2·20 and 1·55 Å. The Ca atom has the coordination number 7+1 with seven Ca–O bonds in the range 2·34 to 2·50 Å and one bond 2·72 Å long. The structure consists of infinite chains of Mn octahedra and P tetrahedra running along the c axes. Calcium ions occupy the vacant spaces between the chains connecting them in a three-dimensional network. The crystal structure of the fairfieldite mineral group is closely related to that of the kröhnkite mineral group. In both structures there is the same chain motif with a strictly similar connection of tetrahedra and octahedra inside the chain. Differences occur in the reciprocal array of the chains, which are shifted in the $\mathbf{c}$ direction by different amounts in the two mineral groups.

Introduction

The phosphate and arsenate minerals with the general formula $A_2B(XO_4)_2.2H_2O$, where A is Ca, B is Co, Fe, Mg, Mn, and X is As or P, may crystallize in the monoclinic or in the triclinic system. The monoclinic group comprises two minerals, brandtite and roselite, which are isostructural with the sulphate kröhnkite, $CuNa_2(SO_4)_2\ 2H_2O$. Members of the triclinic class are fairfieldite, neomesselite, collinsite and β-roselite.

The atomic arrangement in the monoclinic family was determined by Dahlman (1952) for kröhnkite and brandtite. Leone & Sgarlata (1954) redetermined the crystal structure of kröhnkite which was later refined by Rao (1961). In the present study the crystal structure of fairfieldite, which is a representative member of the triclinic group, was undertaken in an attempt to contribute to a better crystallochemical knowledge of phosphate minerals and to study its relationship with other compounds having a similar formula but belonging to the monoclinic system.

The mineral occurs as an accessory constituent in pegmatitic rocks, where it was first found by Brush

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& Dana (1879) at Branchville, Fairfield County (Connecticut). Wolfe (1940) gave the morphological elements of the crystals and the unit-cell dimensions, which were determined by the Weissenberg method.

On the basis of the chemical analysis, fairfieldite can be given the formula $Ca_2(Mn, Fe)(PO_4)_2.2H_2O$. There is a wide range of Mn/Fe atomic ratios: from 1·8:1 (Penfield, quoted in Brush & Dana) to 19·7:1 (Vassar, quoted in Landes, 1925).

For our investigation a small sample from Foote Mine, North Carolina, was used. The specimen consisted of white fairfieldite crystals with a pearly lustre, of short prismatic habit and associated with quartz.

Experimental

Fairfieldite is not supplied by Foote Mine with a chemical analysis. Because of the small amount of material, a complete chemical analysis was impossible. However, before the X-ray study, the Mn/Fe ratio in the sample under investigation was determined by a microchemical colorimetric method, which gave a value of 49·8:1. This value is higher than those reported in the literature for fairfieldite from other localities.

A transparent single crystal of fairfieldite was ground into a nearly perfect sphere, 0·57 mm in radius. The sphere obtained was mounted on an integrating precession apparatus. Intensity data were collected with Zr-filtered Mo radiation for two sets of layers, taken within the mechanical limits of the apparatus: *hkn* ($n=0$ to 2) and *nkl* ($n=0$ to 3). The lattice constants determined from precession photographs are:

$a=5{\cdot}79\pm0{\cdot}01$ Å $\quad \alpha=102°\ 16'\pm15'$
$b=6{\cdot}57\pm0{\cdot}01$ $\quad \beta=108°\ 40'\pm15'$
$c=5{\cdot}51\pm0{\cdot}01$ $\quad \gamma=\ 90°\ 18'\pm15'$

in agreement with the values given by Wolfe (1940). The calculated density for one formula unit in the cell is 3·095 $g.cm^{-3}$ which agrees with the value 3·08 – 3·11 $g.cm^{-3}$ found in the literature.

The space group $P\bar{1}$ was assumed at the first stage of the study and was confirmed by the crystal analysis.

Intensities were measured with a microdensitometer; Lorentz-polarization and absorption corrections ($\mu R=2{\cdot}07$) were made using a program written by Catani & Zanazzi (1965) for the IBM 1620 computer. The F^2 data were placed on the same relative scale by correlating the common reflexions on the films. 1089 non-equivalent diffraction effects were recorded, 185 of which were too weak to be observed.

Structure determination and refinement

The crystal structure was solved by the three-dimensional Patterson function, and the successive Fourier syntheses method. The refinement was carried out by means of the least-squares full-matrix program of Busing & Levy, adapted for the IBM 7090 computer by Stewart (1964).* Individual isotropic temperature factors were applied and the *R* index, defined as $\sum||F_o|-|F_c||/\sum|F_o|$, dropped from 0·25 to 0·075 in three cycles. Reflexions were given weights according to Hughes's (1941) scheme. Unobserved reflexions were excluded from calculations as well as some diffraction effects which seemed to be affected by extinction.

Anisotropic least-squares refinement did not yield an acceptable result because some thermal parameters shifted to give values without physical significance. A possible explanation for this fact may be an approximate absorption correction, the presence of secondary extinction or a slightly incorrect initial data rescaling. Isotropic temperature factors also assumed values lower than expected. Therefore, the refinement was stopped at this stage and no attempt was made to locate the hydrogen atoms.

The final atomic coordinates and individual isotropic thermal parameters are listed in Table 1 with their standard deviations. The observed and calculated structure factors are given in Table 2. The atomic scattering factors used in the calculations are those in *International Tables for X-ray Crystallography* (1962) for Ca^{2+}, P, Mn^{2+} and O. The scattering factor curve of Mn^{2+} was not corrected for the negligible Fe content.

Discussion of the structure

The crystal structure of fairfieldite projected along the *a* axis is shown in Fig. 1. Bond lengths and angles with their standard deviations are listed in Tables 3 and 4.

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* Calculations were performed with the IBM 7090 computer of the Centro Nazionale Universitario di Calcolo Elettronico of Pisa University.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

Standard deviations are given in parentheses.

	x	*y*	*z*	*B* (Å²)
Mn	0·0000	0·0000	0·0000	0·32 (3)
Ca	0·6020 (3)	0·2337 (2)	0·3332 (3)	0·22 (3)
P	0·2463 (3)	0·2325 (2)	0·6472 (3)	0·12 (3)
O(1)	0·0031 (11)	0·3264 (8)	0·6157 (11)	0·48 (7)
O(2)	0·4552 (11)	0·3995 (8)	0·6940 (10)	0·41 (7)
O(3)	0·2461 (11)	0·0699 (8)	0·3965 (10)	0·45 (7)
O(4)	0·3058 (10)	0·1177 (7)	0·8785 (10)	0·43 (7)
O(*W*)	−0·1543 (11)	0·3004 (8)	0·0663 (11)	0·58 (7)

In the structure the divalent manganese ion occupies the inversion centre at the origin of the cell. This cation coordinates octahedrally four oxygen atoms of different PO_4 tetrahedra and two water molecules. The distances are in the range 2·14–2·27 Å (average value 2·20 Å) in agreement with the values found in other phosphates containing manganese: in flinkite (Moore, 1967) the Mn–O average bond length is 2·19 Å, in retzian

Table 2. *Observed and calculated structure factors*

Unobserved reflexions are indicated with by *. Reflexions affected by extinction are marked with *E*.

H	K	L		10FO	10FC
0	-9	1	*	52	4
		2	*	49	-32
		3		124	142
0	-8	1	*	28	2
		2	*	28	18
		3		271	264
		4		65	-51
0	-7	1		296	286
		2		248	238
		3		68	-66
		4		235	230
		5		38	60
0	-6	1		300	282
		2		250	234
		3		132	-130
		4		196	200
		5		107	110
		6		167	-152
0	-5	1		112	106
		2		130	-114
		3		344	342
		4		145	138
		5	*	30	-12
		6		202	208
0	-4	1	*	28	16
		2		94	74
		3		455	484
		4	*	30	22
		5		120	118
		6		303	306
0	-3	1	*	26	10
		2		163	148
		3		225	220
		4	*	29	-32
		5		160	164
		6		129	128
0	-2	1	E	419	510
		2		103	-76
		3		283	-286
		4		343	346
		5		163	152
		6		89	-98
		7		291	286
0	-1	1		164	148
		2		294	296
		3		69	66
		4		141	136
		5		197	206
		6		59	48
		7		176	178
0	0	1		128	-146
		2	*	20	24
		3	E	549	670
		4		260	-256
		5	*	30	18
		6		250	260
		7		99	-84
0	1	0	E	207	296
		1		276	242
		2		197	180
		3		138	138
		4		70	-58
		5		73	64
		6		114	114
0	2	0		345	-372
		1		211	236
		2	E	487	584
		3		178	-176
		4		304	310
		5		178	174
		6		117	-132
0	3	0		243	210
		1		315	324
		2		306	312
		3	*	30	40
		4		283	286
		5		129	130
		6		144	-136
0	4	0		356	356
		1		60	-66
		2	*	30	30
		3		312	310
		4		46	-42
		5	*	26	22
0	5	0		220	178
		1		127	-120
		2	*	30	26
		3		220	222
		4		57	36
		5		67	48
0	6	0		194	-166
		1		232	218
		2		231	202
		3		120	-120
		4		227	208
0	7	0		115	-84
		1		244	232
		2		86	84
		3		121	-108
0	8	0		218	200
		1		51	48
		2		70	-50
0	9	0		172	244
1	-9	0		44	42
		1		202	176
		2	*	33	32
		3		104	90
		4		51	66
		5	*	28	-4
1	-8	0		113	-104
		-1		123	-118
		1		398	376
		-2		303	290
		2		160	-152
		3	*	34	32
		4		345	340
		5		132	-134
		6		43	56
1	-7	0		93	76
		-1		109	106
		1	*	35	8
		-2		45	-46
		2		173	160
		-3		106	110
		3		168	170
		-4		107	114
		4		104	96
		-5		29	-32
		5		133	122
		6		98	112
1	-6	0		354	346
		-1		186	172
		1		240	-218
		-2		85	-88
		2		215	204
		-3		307	296
		3		286	284
		-4		162	150
		4		200	-196
		-5		94	-102
		5		281	274
		-6		118	128
		6		98	104
1	-5	0	*	32	-10
		-1		115	102
		1		139	108
		-2		331	322
		2	*	32	22
		-3	*	34	18
		3	*	32	28
		-4		124	118
		4	*	33	12
		-5		216	204
		5		183	184
		-6		48	-58
		6		104	88
1	-4	0		57	60
		-1	*	31	-4
		1		353	352
		-2		378	372
		2		76	-72
		-3		49	-56
		3	*	30	28
		-4		43	-32
		4		347	342
		-5		268	252
		5	*	33	-36
		-6		102	-114
		6		94	88
		-7		49	36
1	-3	0		512	566
		-1		36	24
		1		332	338
		-2		301	286
		2		88	78
		-3		228	214
		3		139	144
		-4		98	-96
		4		146	150
		-5		81	72
		5	*	33	18
		-6		83	84
		6	*	34	16
		-7	*	32	4
1	-2	0	E	458	506
		-1	E	502	574
		1		285	-288
		-2		211	-206
		2	E	416	476
		-3		307	294
		3		167	168
		-4		261	244
		4		284	-296
		-5		115	-124
		5		223	224
		-6		242	230
		6		93	86
		-7		149	154
1	-1	0		303	294
		1		169	-138
		-2		281	-350
		2	E	437	502
		-3		183	228
		3		120	118
		-4		74	90
		4	*	29	16
		-5		37	44
		5		218	220
		-6		155	188
		6	*	34	28
		-7		92	116
1	0	0	*	14	-4
		-2		501	546
		2		299	298
		-3		110	-114
		3		84	70
		-4		123	-128
		4		376	392
		-5		506	470
		5	*	33	30
		-6		93	-100
		6	*	34	-36
		-7		54	-30
1	1	0		79	58
		1		412	452
		-2		348	348
		2		42	-40
		-3		229	200
		3		150	150
		-4		268	244
		4		343	344
		-5		172	198
		5		154	-158
		-6		85	84
		6		84	86
		-7		58	62
1	2	0	*	17	36
		-1		314	350
		1		243	-246
		-2		364	-344
		2		258	256
		-3		565	556
		3		74	62
		-4		328	294
		4		85	74
		-5		184	-172
		5		195	184
		-6		433	412
		6		101	86
		-7	*	41	50
1	3	0		183	160
		-1		432	468
		1		251	-248
		-2		155	-150
		2		400	402
		-3		245	222
		3		186	180
		-4		244	222
		4		96	-106
		-5		69	-68
		5		339	332
		-6		100	92
		6		138	128
		-7		54	56
1	4	0		84	56
		-1		172	156
		1		435	454
		-2		529	564
		2		115	-126
		-3	*	29	-6
		3		51	50
		-4		128	118
		4		229	214
		-5		235	220
		5		61	-62
		-6		129	-118
		6		93	88
		-7	*	34	42
1	5	0		113	-98
		-1		91	90
		1		436	424
		-2		460	458
		2		131	-128
		-3		51	-40
		3		93	-90
		-4		58	62
		4		292	278
		-5		268	240
		5		117	-122
		-6	*	34	22
		6		81	62
		-7	*	34	22
1	6	0		258	244
		-1		162	152
		1	*	34	-28
		-2		136	-122
		2		124	118
		-3		154	146
		3		189	170
		-4		109	106
		4	*	33	-32
		-5		155	-136
		5		74	68
		-6		192	184
		-7		158	142
1	7	0		248	226
		-1		200	184
		1	*	35	-8
		-2		83	-66
		2		213	204
		-3		130	122
		3		173	164
1	7	-4		137	134
		4		115	-120
		-5		137	-122
		-6		172	154
		-7		145	140
1	8	0	*	28	2
		-1		93	88
		1		125	124
		-2		168	164
		2		99	96
		-3		49	-40
		-4		125	122
		-5		235	216
		-6	*	32	-20
1	9	-1		184	-160
		-2		260	242
		-3	*	33	-22
		-4		50	-42
		-5		314	290
2	-10	5		76	-76
2	-9	1		83	64
		2	*	48	26
		3		145	154
		4		51	42
		5		45	68
		6		74	100
2	-8	0		97	-84
		-1		335	326
		1		70	-64
		-2	*	49	14
		2		242	246
		3		96	-90
		4	*	30	-26
		5		235	252
		6	*	29	-30
2	-7	0		73	74
		-1		93	86
		1		48	12
		-2		64	64
		2		128	130
		-3		105	110
		3		44	-30
		-4	*	31	8
		4		93	96
		-5		75	66
		5		196	204
		6	*	30	-40
2	-6	0		368	364
		-1		171	-158
		1		201	202
		-2		297	284
		2		86	-82
		-3		184	178
		3		236	244
		-4		250	-258
		4		46	58
		-5		118	230
		5		39	-26
		-6		42	40
		6		157	162
		-7		127	-142
2	-5	0		351	334
		-1		93	80
		1		154	142
		-2		136	122
		2		72	-58
		-3		187	168
		3		201	210
		-4		66	50
		4	*	28	28
		-5		59	52
		5		156	-150
		-6		96	90
		6		192	200
		-7		84	90
2	-4	0		97	-88
		-1		422	428
		1	*	25	6
		-2		171	-168
		2		426	490
		-3	*	26	10
		3		176	-182
		-4		271	274
		4		101	94
		-5		57	-64
		5		233	246
		-6		115	112
		6		118	-116
		-7		216	230
2	-3	0	*	28	34
		-1		348	370
		1		81	62
		-2		104	-96
		2	E	484	606
		-3		31	-24
		3		31	22
		-4		169	162
		4		73	74
		-5		68	64
		5		297	312
		-6		38	24
		6		112	-118
		-7		102	106
2	-2	0		344	316
		-1		179	-184
		1	E	296	478
		-2		353	340
		2		141	-136
		-3		332	338
		3		257	282
		-4		90	-92
		4		242	254
		-5		240	248
		5		141	-146
		-6		202	200
		6		124	124
		-7		132	-138
2	-1	0	*	21	2
		-1	*	26	-36
		1		141	132
		2		75	-88
		-3		308	344
		3		200	202
		-4		42	58
		4		212	212
		-5		201	220
		5		82	-98
		-6		231	226
		6		244	246
		-7		64	-68
2	0	0		36	24
		-1	E	394	464
		1		148	-126
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		3		152	154
		-4	E	288	424
		4		120	110
		-5		118	-124
		5		203	202
		-6		32	20
		6		121	120
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		2		291	328
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		4		137	140
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		2		26	-34
		-3		195	206
		3		54	32
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		4		69	60
		-5		200	184
		5	*	29	18
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		6		112	98
		-7		46	-66
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		-2		291	308
		2		280	-300
		-3		265	278
		3		340	362
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		4		97	88
		-5		204	206
		5		122	-138
		-6		173	176
		6		260	270
		-7		44	-50
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		-1		223	240
		1		249	266
		-2		202	188
		2		152	152
		-3		133	-136
		3		154	150
		-4		208	208
		4		34	24
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		5	*	30	42
		-6	*	26	-32
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		-7		234	244
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		-3		30	-32
		3		70	-82
		-4		427	446
		4	*	30	-6
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		5		186	186
		-6		36	36
		6		96	-110
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		-1		89	-90
		1		72	78
		-2		142	140
		2		102	102
		-3		94	98
		3		50	54
		-4		58	-46
		4		72	70
		-5		259	266
		5		157	148
		-6		128	120
		-7	*	30	6
2	7	0		231	234
		-1		216	-220
		1		130	136
		-2		198	208
		2		96	-106
		-3		140	148
		3		286	294
		-4		146	-148
		4		92	86
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		-7		101	-96
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		2	*	30	-2
		-3		203	204
		-4		89	92
		-5		35	38
		-6		89	100
		-7		37	44
2	9	-1		266	264
		-2	*	31	-8
		-3	*	31	24
		-4		248	250
		-5	*	30	16
		-6	*	31	-16
		-7		168	182
2	10	-7		66	70
3	-9	1		127	110
		2		121	100
		3	*	34	-20
		4	*	98	122
3	-8	0		308	314
		-1	*	52	16
		1	*	53	4
		-2	*	48	2
		2	*	48	-6
		-3	*	260	284
		3	*	138	168
		4	*	44	-42
		5		29	-32
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		1		104	-86
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		3	*	115	142
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		4	*	101	-104
		-5	*	22	26
		5		58	84
		6		131	148
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		-1		139	142
		1		225	204
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		2		229	200
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		3	*	36	20
		-4	*	131	136
		4	*	191	180
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		5		64	78
		6	*	23	-18
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		-1		194	202
		1		450	432
		-2		235	258
		2		210	192
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		3	*	142	-148
		-4	*	169	178
		4	*	391	350
		-5	*	147	154
		5	*	24	12
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		6		136	-142
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		-4	*	106	102
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		5		43	34
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		6		169	122
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		1		122	-126
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		2	*	35	-28
		3	*	473	426
		-4	*	19	-24
		4		26	-42
		-5	*	23	-12
		5		105	110
		-6		265	260
		6		257	288
		-7	*	24	-32
		-8	*	20	-8
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		1		216	324
		-2		339	398
		2		98	140
		4		121	134
		-5		100	104
		5		88	102
		-6		160	-172
		6		118	120
		-7		165	162
		-8		33	26
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		1		382	380
		-2	E	360	438
		2		49	50
		4		253	288
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		4		190	208
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		-5	*	24	14
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		-8		34	-12
3	6	0		248	218
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		3		154	168
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		-6		85	92
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		-8		70	74
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		2		61	60
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		2		110	126
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		3		124	-130
		-4		84	92
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		-5		45	-38
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		2		204	-186
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		2	*	38	-38
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		1		138	-126
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		1		211	212
		-2		213	204
		2		94	86
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		-2		190	-184
		2		196	198
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		-2	*	41	-28
		2		223	218
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		-1		144	128
		1		180	208
		-2		244	234
		2	*	47	30
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		-1	*	54	-28
		1		228	276
		-2		339	312
		2		102	-120
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		2		91	96
4	8	-2		227	-194
		2		180	228
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		2		125	-122
5	-8	-1		81	68
		1		100	82
		-2	*	47	52
		2	*	46	2
5	-7	0		109	-118
		-1		304	334
		1	*	52	40
		-2		59	76
		2		273	250
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		-1	*	53	68
		1	*	53	18
		-2		113	128
		2		68	40
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		-1		192	-204
		1		229	204
		-2		202	226
		2		190	-170
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		-1		100	102
		1		82	86
		-2		73	80
		2		65	74
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		1	*	51	10
		-2	*	41	-8
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		-1		163	164
		1		129	122
		-2		70	58
		2		312	298
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		-1		77	-82
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		1	*	50	-14
		-2	*	36	6
		2		213	196
5	2	0		99	-86
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		1		94	82
		-2	*	38	-12
		2		289	288
5	3	0		203	190
		-1		70	60
		1		142	142
		-2		260	252
		2	*	46	8
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		-1		116	-104
		1		113	116
5	4	-2		122	126
		2		170	-184
5	5	0	*	30	18
		-1		168	162
		1		124	142
		-2	*	45	-4
		2		112	116
5	6	0		91	-78
		-1		324	316
		1		64	74
		-2	*	47	26
		2		236	278
5	7	-1	*	51	-26
		-2		123	122
		2	*	43	-6
5	8	-1		164	-158
		-2		121	114
6	-9	2	*	37	-14
6	-8	-2		128	154
		2	*	43	28
6	-7	-1		64	54
		1		76	-74
		-2		77	-90
		2		102	82
6	-6	0		226	238
		-1	*	52	18
		1		56	-56
		-2	*	47	10
		2		96	90
6	-5	0		118	-118
		-1		98	106
		1		185	172
		-2		114	120
		2		112	132
6	-4	0		72	-64
		-1		94	78
		1		219	248
		-2		115	124
		2		158	132
6	-3	0		203	204
		-1		66	52
		1		69	-64
		-2	*	43	-6
		2		108	96
6	-2	0		225	224
		-1		69	66
		1		164	-174
		-2		110	-126
		2	*	45	30
6	-1	0		76	-74
		-1		207	192
		1		158	168
		-2		154	164
		2		99	126
6	0	0		86	-96
		-1		242	244
		1		264	280
		-2		311	336
		2		114	68
5	1	0		132	120
		-1		58	64
		1		148	132
		-2		94	94
		2		62	-58
6	2	0		264	260
		-1		110	96
		1		67	-68
		-2		150	-150
		2		133	126
6	3	0		185	170
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		1		81	86
		-2		68	74
		2		97	104
6	4	0		185	-178
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		1		258	318
		-2		339	342
		2	*	47	14
6	5	-1	*	53	32
		1		74	86
		-2		73	60
		2		51	56
6	6	-1	*	51	-38
		-2		58	-60
		2	*	42	42
6	7	-1		88	78
		-2		92	90
6	8	-1		88	102
		-2		148	154
7	-8	-2		93	-112
7	-7	1		138	158
		-2		94	128
7	-6	-1		76	-68
		1		171	170
		-2		173	198
7	-5	-1		96	96
		1	*	50	4
		-2	*	47	-28
7	-4	-1		300	316
		1		139	-136
		-2		133	-158
7	-3	0		115	114
		-1		106	98
		1		101	100
		-2		158	172
7	-2	0	*	30	12
		-1		89	-86
		1		309	332
		-2		357	392
7	-1	0		102	88
		-1		109	108
		1		76	92
		-2	*	44	-10
7	0	0		181	170
		-1		213	220
		1	*	53	-38
		-2		108	-118
7	1	0	*	29	22
		-1		144	124
		1		77	58
		-2		106	106
7	2	0		52	48
		-1		163	-172
		1		163	194
		-2		219	224
7	3	0		118	104
		-1		115	-102
		1		122	140
		-2		209	190
7	4	-1		234	232
		1		92	-112
		-2		68	-62
7	5	-1		178	168
		-2		45	-36
7	6	-1	*	43	-30
		-2		217	204
7	7	-2		178	176
7	8	-2		74	-70
8	-8	-2		66	72
	-7		*	40	-30
	-6			91	98
	-5			125	140
	-4			49	52
	-3			78	92
	-2		*	46	56
	-1			60	58
	0			91	90
	1			92	100
	2			61	56
	3		*	47	32
	4			124	130
	5		*	46	26
	6		*	43	-40
	7			67	60

(Moore, 1967) it is 2·18 Å, in allactite (Moore, 1968*a*) it is 2·22 Å, in laueite (Moore, 1965) it is 2·12 Å and in clorophoenicite (Moore, 1968*b*) it is 2·21 Å.

The coordination number of the calcium ion can be assumed to be 7+1, each ion being surrounded by seven oxygen atoms at an average distance of 2·45 Å, with values in the range 2·34–2·50 Å, while the next distance, Ca–O(3) (V), differs significantly from the others, with a value of 2·72 Å.

The PO_4 tetrahedra are nearly regular, with an average P–O bond length of 1·55 Å, a value in agreement with those found in metastrengite, 1·53 Å (Fanfani &

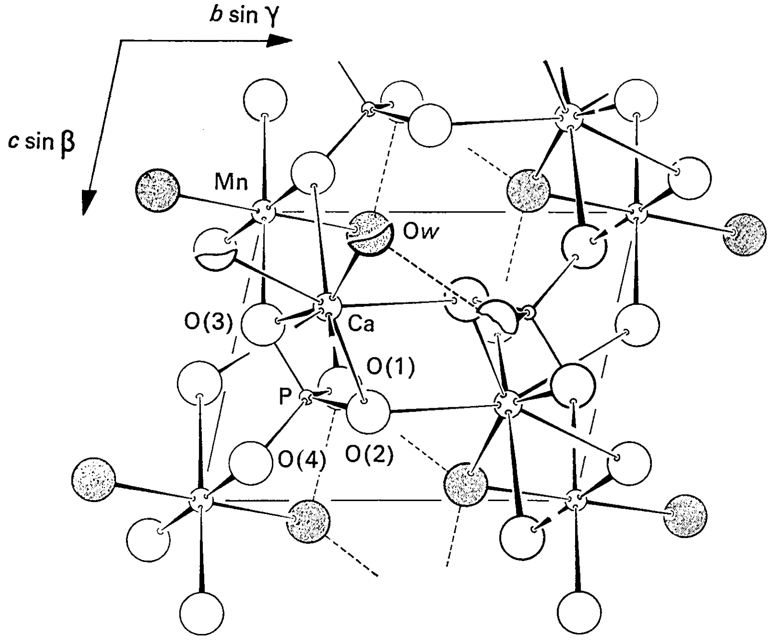


Fig. 1. Crystal structure of fairfieldite projected along the *a* axis. Shaded circles indicate water molecules, O(*W*).

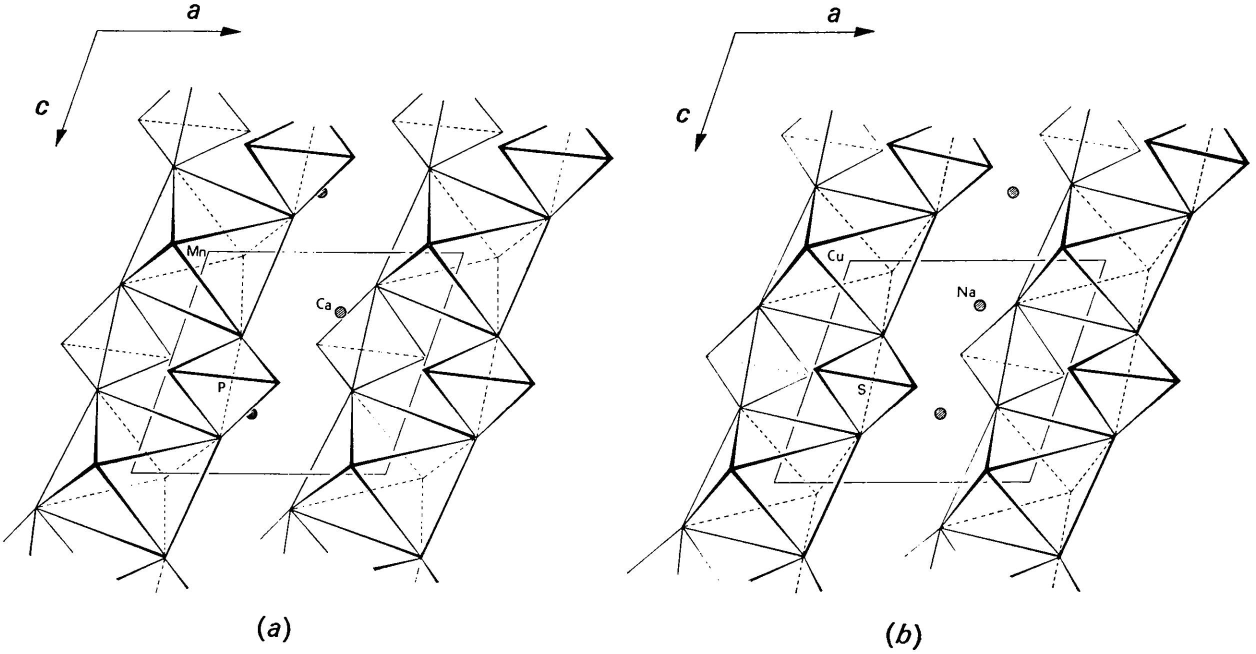


Fig. 2. A schematic view of the structures of fairfieldite (*a*) and kröhnkite (*b*) projected along the *b** axis. For kröhnkite a half cell is projected.

Table 3. *Bond lengths*

I	x	y	z	IV	$-x$	$1-y$	$1-z$
II	$1+x$	y	z	V	$1-x$	$-y$	$1-z$
III	x	y	$-1+z$	VI	$1-x$	$1-y$	$1-z$

Mn(1)–O(3) (I)	2·142±0·009 Å	×2
–O(4) (III)	2·269±0·007	×2
–O(*W*) (I)	2·180±0·007	×2
P(I)–O(1) (I)	1·514±0·007 Å	
–O(2) (I)	1·550±0·007	
–O(3) (I)	1·556±0·006	
–O(4) (I)	1·563±0·007	
Ca(I)–O(1) (II)	2·336±0·010 Å	
–O(2) (I)	2·456±0·008	
O(2) (VI)	2·465±0·008	
–O(3) (I)	2·475±0·008	
–O(4) (III)	2·495±0·011	
O(4) (V)	2·500±0·007	
O(*W*) (II)	2·438±0·007	
–O(3) (V)	2·724±0·009	
O(*W*) (I)–O(1) (IV)	2·650±0·012 Å	
–O(1) (III)	2·941±0·009	

Table 4. *Bond angles*

O(3) (I) —Mn(I)–O(4) (III)	87° 52′ ± 18′
–O(*W*) (I)	90 55 ±21
O(4) (III)–Mn(I)–O(*W*) (I)	95 42 ±16
O(1) (I)–P(I)–O(2) (I)	111 56 ±20
O(3) (I)	112 38 ±25
–O(4) (I)	109 15 ±22
O(2) (I)–P(I)–O(3) (I)	104 36 ±23
–O(4) (I)	110 45 ±22
O(3) (I)–P(I)–O(4) (I)	107 29 ±18
O(1) (II)—Ca(I)–O(2) (I)	88 59 ±19
–O(2) (VI)	90 37 ±20
–O(3) (I)	131 07 ±14
–O(3) (V)	70 50 ±17
–O(4) (III)	149 53 ±15
–O(4) (V)	94 19 ±21
–O(*W*) (I)	72 49 ±16
O(2) (I) —Ca(I)–O(2) (VI)	72 36 ±16
–O(3) (I)	59 47 ±17
–O(3) (V)	86 51 ±14
–O(4) (III)	119 41 ±15
–O(4) (V)	140 09 ±14
–O(*W*) (I)	143 11 ±13
O(2) (VI)–Ca(I)–O(3) (I)	111 18 ±16
–O(3) (V)	152 44 ±13
–O(4) (III)	89 38 ±20
–O(4) (V)	146 49 ±11
–O(*W*) (I)	75 49 ±16
O(3) (I) —Ca(I)–O(3) (V)	70 50 ±16
–O(4) (III)	76 04 ±17
–O(4) (V)	89 41 ±17
–O(*W*) (I)	153 02 ±13
O(3) (V)—Ca(I)–O(4) (III)	116 29 ±16
–O(4) (V)	57 23 ±13
–O(*W*) (I)	115 14 ±15
O(4) (III)–Ca(I)–O(4) (V)	70 09 ±19
–O(*W*) (I)	78 04 ±15
O(4) (V)—Ca(I)–O(*W*) (I)	74 25 ±15
O(1) (IV)–O(*W*) (I)–O(1) (III)	102 49 ±19

Zanazzi, 1966) and in beraunite, 1·54 Å (Fanfani & Zanazzi, 1967).

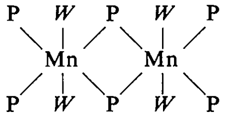
Two hydrogen bonds seem to occur between the water molecule and the oxygen atoms O(1) (IV) and O(1) (III); the distances are 2·65 and 2·94 Å, respectively; the angle between these bonds is 103°.

The charge balance according to Pauling's valence rule, assuming a completely ionic structure and taking into account the contribution of the hydrogen bonds, is as shown in Table 5.

Table 5. *Charge balance of oxygen atoms*

	Mn	P	Ca	–H··	··H–	Total
O(1)		$\frac{5}{4}$	$\frac{2}{7}$		$2\times\frac{1}{4}$	$2+\frac{3}{84}$
O(2)		$\frac{5}{4}$	$2\times\frac{2}{7}$			$2-\frac{15}{84}$
O(3)	$\frac{1}{3}$	$\frac{5}{4}$	$\frac{2}{7}$			$2-\frac{11}{84}$
O(4)	$\frac{1}{3}$	$\frac{5}{4}$	$2\times\frac{2}{7}$			$2+\frac{13}{84}$
O(*W*)	$\frac{1}{3}$		$\frac{2}{7}$	$2\times\frac{3}{4}$		$2+\frac{10}{84}$

The structure of fairfieldite consists of chains formed by Mn octahedra and PO_4 tetrahedra. The resulting motif of the chain is schematically as follows (*W* represents a water molecule):



The chains run along the *c* axis and are connected together in the **a** and **b** directions by the coordination polyhedra around the calcium ions and by the shorter hydrogen bonds.

This structural arrangement accounts for the good {010} cleavage, but it seems not to agree with the perfect {001} cleavage which was observed by Wolfe (1940). The wide discrepancy between the measured and calculated data suggests that a new morphological study of fairfieldite, impossible to us because of the small and poorly crystallized specimen, would be useful.

Relationship to the kröhnkite group

The crystal structure of the triclinic minerals with formula $A_2B(XO_4)_2.2H_2O$ can be related to the structure of the monoclinic minerals with the same general formula. The results of the present study on fairfieldite are compared with those given by Rao (1961) for kröhnkite, $CuNa_2(SO_4)_2.2H_2O$, this structure being generally assumed to be typical of the monoclinic family.

It is interesting to note that the unit-cell parameters are very similar in the two compounds; kröhnkite, space group $P2_1/c$, with cell constants: $a=5·80$, $b=12·67$, $c=5·52$ Å, $\beta=108°\ 36'$, shows nearly the same *a*, *c* and β lattice parameters as in fairfieldite, while the period along the *b* axis is nearly doubled. This feature can easily be explained by comparing the crystal structures of the two minerals: in both cases the atomic arrangement consists of chains of coordination octahedra and tetrahedra running along the *c* axes with a similar configuration. Calcium ions in fairfieldite and sodium ions in kröhnkite exhibit the same role: they occupy the interstices left vacant by the chains connecting them to form a three-dimensional framework and are each surrounded by six oxygen atoms and one water molecule. From Fig. 2, where the structure of fairfieldite and a part of the atomic arrangement occurring in kröhnkite are schematically projected along the b^* axis, the resemblance of the chain motif is evident and explains the good agreement between the lattice constants in the two minerals. In fact the **c** translation vector represents the period in the chain and $a \sin\beta$ the distance between two parallel chains in the *ac* plane.

The most remarkable difference in the two structures occurs in the reciprocal array of chains in the *bc* planes: in kröhnkite two parallel chains are shifted one half period along **c**, as is clear if one considers the presence of the glide plane at $\frac{1}{4}\,b$. This fact may account for the approximate doubling of the *b* parameter.

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Crystal Structure of an Orthorhombic Modification of Methyl Stearate

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A new orthorhombic modification of methyl stearate has been found. The cell parameters are $a=5{\cdot}61$, $b=7{\cdot}35$, $c=95{\cdot}15$ Å and the space group is *Pnab*; the unit-cell contains 8 molecules. The carbon chains are arranged in the orthorhombic packing $O\perp$. The molecules form the same double sheets as have been found in the monoclinic modification. However, chains in neighbouring sheets are inclined with respect to each other.

Introduction

During melting and freezing of methyl stearate, phenomena such as pre-melting and 'after-melting' (Smit, 1946; Simonelli & Higuchi, 1962) occur, which make the interpretation of melting curves and dilatometric measurements difficult. In order to study these phenomena, crystals of methyl stearate (purity > 99·8%) were grown from a CS_2 solution at $-15\,^{\circ}C$ to $-12\,^{\circ}C$ and from a melt at 37–38 °C. Two crystal forms were obtained from CS_2 solution:

(*a*) a monoclinic form M_1, described by Aleby & von Sydow (1960) with unit-cell parameters $a=5{\cdot}61$, $b=7{\cdot}33$, $c=106{\cdot}6$ Å, $\beta=116°47'$, $d_{001}=95{\cdot}2$ Å;

(*b*) an orthorhombic form, which will be described in this paper.

The crystals obtained from the melt were of poor quality. A second monoclinic form M_2 was found with the *a* and *b* dimensions about the same as those of the monoclinic and orthorhombic modifications from CS_2, but the *c* dimension was 47·9 Å. Some crystals from the melt appeared to be intergrowths of the orthorhombic form from the CS_2 solution and a twin of the monoclinic form from the melt. The form M_2 was not studied further in this investigation.

Experimental

The unit-cell parameters and space group were determined by taking rotation and Weissenberg photographs calibrated with Al lines using Cu $K\alpha$ radiation: