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The crystal structure of coquimbite

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Mineralogia. — *The crystal structure of coquimbite.* Nota (*) di CARMELO GIACOVAZZO, SILVIO MENCHETTI e FERNANDO SCORDARI (**), presentata dal Socio G. CAROBBI.

RIASSUNTO. — La coquimbite, $(Fe^{III}, Al)_2(SO_4)_3 \cdot 9\,H_2O$, cristallizza nel sistema trigonale, gruppo spaziale $P\bar{3}\,1c$, con quattro unità stechiometriche nella cella elementare. Le costanti reticolari sono: $a = 10{,}916$ $c = 17{,}06$ Å.

I cristalli utilizzati nella presente ricerca provengono da Dexter Mine, Utah; l'analisi chimica fornisce per questo campione un rapporto in atomi Al : Fe = 1 : 5,35. Sono stati registrati fotograficamente, mediante una camera Weissenberg, 956 riflessi indipendenti. La struttura è stata risolta mediante metodi diretti e mediante la funzione tridimensionale di Patterson. I parametri atomici e termici sono stati raffinati fino ad un valore dell'indice R di 0,072 relativo a tutti i riflessi osservati.

I poliedri di coordinazione del ferro sono costituiti da ottaedri quasi regolari; le distanze Fe—O variano da un minimo di 1,893 Å (nell'ottaedro dove il ferro è prevalentemente sostituito dall'alluminio) ad un massimo di 2,010. Le distanze S—O rientrano nella norma.

La struttura è costituita da ottaedri di coordinazione del ferro isolati e da gruppi, con composizione $Fe_3(H_2O)_6(SO_4)_6$, dovuti alla connessione di tre ottaedri e sei gruppi SO_4. I collegamenti fra ottaedri isolati e i gruppi di ottaedri e tetraedri sono assicurati da legami di idrogeno.

Una delle tre molecole indipendenti di acqua non è coordinata dallo ione ferrico.

INTRODUCTION

The structural investigation of coquimbite was undertaken as a part of a series of studies on ferric iron sulfates.

Coquimbite, dimorphous with paracoquimbite, is a hydrated sulfate of ferric iron with chemical formula $Fe_2(SO_4)_3 \cdot 9\,H_2O$. According to some analyses quoted in Dana's System of Mineralogy [10], Al substitutes for Fe^{3+} up to at least Al : Fe = 1 : 1.35.

Morphological and X-ray studies, carried out by Ungemach [15] and by Hocart [8] did not univocally establish the point group symmetry (3 m, 32 or $\bar{3}$ m). Recently Cesbron [1] confirmed lattice parameters previously measured and assigned coquimbite to the space group $P\bar{3}\,1c$ (as the most probable) on the basis of the extinction rules and lack of piezoeletric effect.

Thermal data have been published by Scharizer [11] [12], Cocco [2], Cesbron [1] etc.

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(**) Pervenuta all'Accademia il 19 luglio 1970.

EXPERIMENTAL

Crystals from Dexter mine, Utah, showing short prismatic habit and pale violet color, were kindly supplied by Dr. V. de Michele of the "Museo Civico di Storia Naturale, Milano".

Chemical Data.

As has been shown before, Al can substitute for Fe^{3+}. A preliminary X–ray spectrographic examination on crystals from Dexter mine, showed no more elements than Fe, S and perhaps Al. The Al presence was doubtful, but it is well known the analytical weakness of X–ray spectrography for such a light element.

Owing to the little amount of the available substance, only the colorimetric determination of Fe_2O_3 and Al_2O_3 was carried out; on the other hand SO_3 and H_2O percentage determination was unnecessary for the purpose of this work. The following values were obtained:

$$Fe_2O_3 = 24.3\ \% \qquad Al_2O_3 = 2.9\ \%$$

that is an atomic ratio Al : Fe = 1 : 5.35.

Crystal Data.

The lattice parameters were refined by Weissenberg photographs calibrated with a small quartz crystal (see Table I).

TABLE I.

chemical formula: $(Fe, Al)_2(SO_4)_3 \cdot 9\,H_2O$

trigonal: $a = 10.916 + 0.005$ Å $\quad c = 17.06 + 0.01$ $\quad V = 1760.5$ Å^3

$D_m = 2.11$ g cm^{-3} (*) $\quad Z = 4 \quad D_x = 2.09$ g cm^{-3}

space group: $P\bar{3}\,1\,c$

absorption coefficient for X–rays (λ CuKα = 1.5418 Å):

$\mu = 159.6$ cm^{-1} $\quad \mu R = 1.6$

(*) The measured density value 2.11 g cm^{-3} is given in Dana's System of Mineralogy.

A suitable crystal elongated [0001] with a roughly cylindrical shape (mean radius 0.01 cm) was chosen for the collection of intensity data. Diffraction effects from hki0 to hki13 were recorded with the equi-inclination Weissenberg method, using the multiple film exposure. A total of 956 independent reflections were collected; of these 331 were too weak to be evaluated. The

intensities of the integrated spots were measured with the help of a microdensitometer; Lorentz-polarization and absorption corrections were applied.

The F_0^2's values were converted to a common absolute scale by Wilson's method.

A statistical test was then carried out, as a further check of centrosymmetry. The test confirmed the space group previously determined. The solution of the structure gave no elements in favour of the acentric group.

STRUCTURE DETERMINATION AND REFINEMENT

A three-dimensional Patterson synthesis was computed from the complete set of observed reflections. In $P\bar{3}1c$ an atom in general position occupies an equipoint of rank 12; thus the Fe atoms (eight atoms in the unit cell) must lie in special positions (point symmetry: 2, $\bar{1}$, 3, 32 or $\bar{3}$).

TABLE II.

Atomic coordinates, their standard deviations (in parentheses) and equivalent isotropic thermal parameters according to Hamilton [7].

ATOM	*x/a*	*y/b*	*z/c*	B_H
(Fe, Al) (1)	0.0	0.0	0.0	2.77
Fe (2)	1/3	2/3	1/4	1.04
Fe (3)	1/3	2/3	0.5027 (1)	1.34
S	0.1700 (2)	0.7553 (2)	0.3767 (1)	1.16
O (1)	0.2765 (7)	0.7828 (7)	0.4412 (4)	1.76
O (2)	0.1808 (7)	0.6644 (8)	0.3158 (4)	1.88
O (3)	0.0270 (8)	0.6818 (7)	0.4101 (4)	1.90
O (4)	0.2022 (7)	0.8918 (7)	0.3453 (4)	1.76
O_w (1)	0.1667 (7)	0.0971 (7)	0.0609 (4)	1.62
O_w (2)	0.1591 (8)	0.5914 (8)	0.5698 (4)	2.35
O_w (3)	0.8835 (8)	0.3340 (8)	0.2912 (5)	2.53

Patterson map analysis showed that the Fe atoms lie on 3-fold axes; thus 6 h and 6 g Wyckoff positions must be excluded, but too many arrangements were still possible.

Then a statistical test for attributing the signs to the structure factors, according to Sayre's method, was carried out using the 344 strongest *E*

values. A three-dimensional E–Fourier synthesis computed using the signs so determined, confirmed the indications from the Patterson analysis and allowed the location of all the Fe atoms. Some maxima surrounding these positions, at distances characteristic of oxygen in octahedral coordination with the Fe atom, were also evident in the maps.

TABLE III.

Analysis of the anisotropic thermal parameters.

(root mean square thermal vibrations along the ellipsoid axes (Å), magnitude of the principal axes (Å^2) and angles (°) between the crystallographic axes and the principal axes of the vibration ellipsoids).

ATOM	r.m.s.	B	α	β	γ
Fe(1)	0.19	2.75			
	0.19	2.75			
	0.19	2.74			
Fe(2)	0.10	0.78			
	0.14	1.57	90	90	0
	0.10	0.78			
Fe(3)	0.14	1.55			
	0.14	1.55			
	0.11	0.91	90	90	0
S	0.12	1.26	112	31	59
	0.13	1.45	58	120	37
	0.10	0.77	41	83	107
O(1)	0.14	1.56	141	89	116
	0.17	2.35	125	11	80
	0.13	1.36	106	101	29
O(2)	0.16	1.98	89	151	87
	0.20	3.22	107	80	17
	0.07	0.43	17	116	73
O(3)	0.16	1.97	102	18	88
	0.18	2.76	25	107	68
	0.11	0.96	111	85	22
O(4)	0.16	2.01	82	103	13
	0.17	2.37	84	37	80
	0.11	0.89	10	124	99
$O_w(1)$	0.14	1.64	60	120	145
	0.17	2.28	89	36	109
	0.11	0.94	29	108	62
$O_w(2)$	0.16	1.96	54	153	65
	0.22	4.03	37	93	116
	0.11	1.06	82	63	38
$O_w(3)$	0.18	2.56	80	43	71
	0.20	3.08	26	117	115
	0.16	1.93	66	121	32

TABLE IV.

Structure factors of coquimbite.

Reflexions marked with an asterisk were unobservably weak. In this case F_0 derives from 0.5 I_{min}.

h	k	10FO	10FC	10AC	10BC
		h k 0			
2	0	1092	1190	-1187	-77
3	0	478	479	423	224
4	0	772	692	-688	-75
5	0	282	243	-231	-73
6	0	1185	1227	1210	201
7	0*	179	123	-102	-69
8	0	571	517	-513	-67
9	0	636	588	564	169
10	0*	160	129	-112	-61
11	0	301	319	-314	-57
12	0	1056	977	968	133
1	1	1338	1394	1375	230
2	1	733	733	729	-77
3	1	361	302	-292	-76
4	1	829	905	880	214
5	1	692	613	-608	-72
6	1	434	388	-382	-70
7	1	742	749	726	185
8	1	474	434	-429	-65
9	1*	171	180	169	-62
10	1	424	395	366	150
11	1	187	167	-157	-55
2	2	441	497	445	221
3	2	599	513	-507	-75
5	2	1072	1099	1080	199
6	2*	181	149	132	-69
7	2	437	399	-394	-66
8	2	339	296	245	167
9	2*	155	158	146	-60
10	2	340	308	-303	-57
3	3	1636	1741	1728	208
4	3*	167	140	-120	-71
5	3*	179	119	-97	-69
6	3	1206	1160	1145	181
7	3	459	433	-428	-64
8	3*	164	157	-145	-61
9	3	291	258	212	147
10	3*	88	86	67	-54
4	4	978	949	930	192
5	4*	184	83	-49	-67
6	4*	183	73	35	-65
7	4	502	465	436	161
8	4*	141	104	-86	-59
9	4	385	306	-300	-55
5	5	657	595	570	173
6	5	382	383	-378	-62
7	5	262	187	177	-59
8	5	597	538	520	140
7	6	357	323	-318	-56
		h k 1			
2	0	609	696	-694	57
3	0	1134	1088	1088	00
4	0	408	363	359	-56
5	0*	97	95	78	55
6	0	203	166	-166	00
7	0	559	614	-612	-52
8	0	329	370	367	50
9	0	387	351	-351	00
10	0	184	150	143	-47
12	0*	47	74	-74	00
2	1	1228	1126	-1124	-57
3	1	314	318	313	56
3	-1*	69	61	23	-57
4	1	517	466	466	00
4	-1	159	149	138	56
5	1	227	238	-232	-54
5	-1	136	124	-124	00
6	1*	112	145	136	53
6	-1	158	174	-165	-54
7	1	469	479	-479	00
7	-1	746	740	739	53
8	1	270	267	-262	-49
8	-1	570	585	585	00
9	1	229	202	196	47
9	-1*	118	59	-31	-49
10	1	282	290	290	00
10	-1	267	281	-277	47
11	1	449	431	-428	-43
11	-1*	92	81	-80	00
12	-1*	65	215	-210	-43
3	2	251	281	-275	-55
4	2	272	248	242	54
5	2	440	537	-537	00
6	2*	116	134	-124	-52
6	-2	601	660	658	54
7	2	555	580	578	50
7	-2	420	453	453	00
8	2*	114	96	-96	00
8	-2	756	822	-820	-52
9	2	187	154	-146	-46
9	-2*	119	118	107	50
10	2	189	163	157	44
10	-2*	114	138	-138	00
11	-2	286	273	269	-46
12	-2*	77	118	-109	44
4	3	275	285	-280	-53
5	3	211	195	188	52
6	3*	119	22	-22	00
7	3	419	469	-467	49
8	3*	105	71	-54	47
8	-3	346	381	-378	52
9	3	478	468	468	00
9	-3*	119	133	133	00
10	3*	56	76	62	-43
10	-3	305	312	-309	-49
11	-3*	105	129	121	47
12	-3	255	256	256	00
13	-3	191	216	-212	-43
5	4*	119	75	55	-50
6	4*	117	105	-92	49
7	4	207	170	170	00
8	4*	91	135	-127	-45
9	4*	65	78	64	43
9	-4	475	486	484	-51
10	-4	738	768	766	49
11	-4	345	348	-348	00
12	-4*	91	156	-149	-45
13	-4*	65	56	36	43
6	5*	110	136	128	-47
7	5	315	317	314	46
8	5	276	267	-267	00
12	-5	273	273	269	46
13	-5	187	147	147	00
7	6	252	241	-237	-44
		h k 2			
2	0*	70	139	139	-9
3	0	529	558	551	88
4	0	264	219	219	-9
5	0	339	279	279	-8
6	0*	124	134	112	73
7	0*	133	97	97	-7
8	0*	137	20	19	-7
9	0*	132	77	-56	53
10	0*	117	13	12	-5
11	0*	91	5	2	-4
2	1	188	213	212	-9
2	-1	1265	1667	1664	92
3	1	336	308	308	-9
3	-1	444	359	-359	-9
4	-1	547	502	-502	-9
5	1	519	453	-453	-8
5	-1	249	276	263	81
6	1	551	513	-513	-8
6	-1	737	696	696	-8
7	1	313	247	239	63
7	-1	627	569	569	-8
8	1	670	584	584	-6
8	-1*	136	66	-19	63
9	1	190	140	140	-6
9	-1	445	373	-373	-6
10	1*	104	144	-138	42
10	-1	268	210	-210	-6
11	1*	74	30	29	-4
11	-1	655	573	572	42
12	-1*	74	78	78	-4
2	2	533	509	502	87
3	2	487	442	-442	-9
4	2	360	358	358	-8
5	2	1072	996	993	72
6	2*	134	178	178	-7
6	-2	298	260	-260	-8
7	2	269	218	-218	-7
7	-2	219	186	172	72
8	2	322	291	-286	51
8	-2	289	262	-261	-7
9	2*	114	52	52	-5
9	-2	399	334	334	-7
10	2*	87	59	59	-4
10	-2	749	670	668	52
11	-2*	114	81	-81	-5
12	-2*	87	49	-49	-4
3	3	1392	1392	1390	78
4	3	404	382	382	-8
5	3*	133	49	-48	-7
6	3	451	426	422	60
7	3	362	364	-364	-6
7	-3	445	393	-393	-8
8	3	200	141	141	-5
8	-3*	133	158	158	-7
9	3*	97	123	116	40
9	-3	523	469	465	60
10	3*	63	20	-19	-4
10	-3*	133	204	204	-6
11	-3	266	244	-244	-5
12	-3	345	332	330	40
13	-3*	63	20	-20	-4
4	4*	132	90	-59	67
5	4*	137	11	-8	-7
6	4	425	393	393	-6
7	4	326	280	275	48
8	4*	103	62	-62	-5
8	-4	1569	1600	1599	67
9	4	199	190	-190	-4
9	-4	310	263	263	-7
10	-4	247	194	-194	-6
11	-4	124	103	-91	48
12	-4*	103	64	-63	-5
13	-4	213	180	180	-4
5	5	828	765	763	55
6	5	318	290	-290	-6
7	5*	107	71	71	-5
8	5*	80	40	-16	36
10	-5	535	449	-446	55
11	-5	380	317	317	-6
12	-5*	107	15	14	-5
13	-5*	58	51	36	36
7	6	288	248	248	-4
8	6*	34	39	-39	-3
13	-6	222	178	-177	-4
		h k 3			
2	0	1396	1494	-1492	-64
3	0	1779	1861	1861	00
4	0*	94	71	-33	63
5	0*	106	97	-75	-61
6	0	205	156	-156	00
7	0*	125	101	82	58
8	0	276	237	-231	-56
9	0	440	373	-373	00
10	0	232	226	220	51
11	0	160	139	-131	-49
2	1	1429	1427	1425	64
3	1	849	802	-800	-63
3	-1	257	283	-276	64
4	1*	102	81	-81	00
4	-1	655	581	578	-63
5	1	658	642	640	60
5	-1	1218	1143	1143	00
6	1*	122	128	-113	-59
6	-1	447	465	461	60
7	1*	127	105	105	00
7	-1	702	657	-654	-59
8	1	203	165	156	55
8	-1	560	528	-528	-00
9	1	411	494	-491	-52
9	-1*	127	112	97	55
10	1	138	136	136	00
10	-1*	116	133	122	-52
11	1	174	156	148	48
11	-1*	96	116	116	00
12	-1*	67	68	-48	47
3	2	310	343	337	62
4	2	276	247	240	-61
5	2*	119	104	-104	00
6	2*	126	77	-51	58
6	-2	371	395	-391	-61
7	2	193	190	-182	-56
7	-2*	119	23	-23	00
8	2*	121	27	27	-00
8	-2	546	511	507	58
9	2	493	506	504	51
9	-2*	128	115	100	-56
10	2	399	371	-367	-49
10	-2*	121	74	-74	00
11	-2*	105	59	27	51
12	-2	205	166	-158	-49
4	3	381	417	413	60
5	3	789	796	-794	-58
6	3	289	292	-292	00
7	3*	124	55	8	54
7	-3	283	315	310	60
8	3	218	199	-192	-52
8	-3	337	309	-303	-58
9	3	510	526	526	00
9	-3	227	224	224	00
10	3*	56	56	-30	47
10	-3*	124	130	-119	54
11	-3	319	320	-316	-52
12	-3	376	362	362	00
13	-3*	56	131	123	47
5	4	242	213	205	56
6	4	553	535	532	-54
7	4	218	198	-198	00
8	4	136	118	107	50
9	4*	67	64	-42	-48
9	-4	302	294	289	56
10	-4	296	286	-281	-54
11	-4*	114	161	161	00
12	-4	246	206	200	50
13	-4*	67	102	91	-47
6	5	374	350	346	52
7	5	212	159	-150	-50
8	5*	73	96	96	00
11	-5	396	380	376	52
12	-5*	98	54	-20	-50
13	-5	73	83	-83	00
7	6	478	458	455	48
		h k 4			
2	0	438	463	457	-76
3	0	1403	1444	1427	220
4	0	302	248	-237	-74
5	0	881	858	-855	-73
6	0	967	1069	1051	197
7	0	495	469	-464	-68
8	0*	133	83	-66	52
9	0	700	688	668	165
10	0*	112	136	-122	-60
11	0*	85	71	43	-56
12	0*	36	174	-115	130
1	1	1659	1334	1315	225
2	1	1049	1033	-1030	-76
3	1	368	276	-265	-75
3	-1	733	813	-809	-76
4	1	1708	1636	1622	209
4	-1	368	271	-260	-75
5	1*	120	118	94	-72
5	-1	969	1011	989	209
6	1*	130	73	-23	-69
6	-1	363	298	-290	-72
7	1	255	220	125	182
7	-1	268	199	-186	-69
8	1*	133	75	-38	-64
8	-1	1002	1048	1032	182
9	1	548	553	-552	-61
9	-1*	133	82	51	-64
10	1	509	474	450	147
10	-1	538	512	-509	-61
11	1*	66	67	-39	-55
11	-1	702	635	617	147
12	-1*	67	59	21	-55
2	2	1859	1927	1915	217
3	2	200	183	-167	-74
4	2	559	537	-532	-72
5	2	935	955	953	195
5	-2	379	406	399	-74
6	2	324	305	-298	-68
6	-2*	117	148	-129	-72
7	2*	135	76	-38	-65
7	-2	983	1063	1045	195
8	2	707	659	638	163
8	-2	643	629	-625	-68
9	2	497	484	-480	-59
9	-2	286	236	227	-65
10	2*	81	69	41	-56
10	-2	543	558	533	163
11	-2	291	276	-270	-59
12	-2*	81	101	84	-56
3	3	824	885	861	204
4	3	303	279	-270	-71
5	3*	132	117	-95	-68
7	3*	130	112	93	-63
7	-3*	125	168	-152	-71
8	3*	115	156	-143	-60
8	-3	281	285	-276	-68
9	3	631	618	600	144
9	-3	588	579	551	177
10	3	314	324	-320	-54
10	-3*	130	134	118	-63
11	-3*	115	63	-18	-60
12	-3	616	545	525	144
4	4	909	999	981	188
5	4*	135	131	-113	-66
6	4	304	275	-267	-64
7	4	547	533	509	158
8	4	272	296	-290	-58
8	-4	1568	1684	1674	188
9	4*	67	55	-4	-55
9	-4	474	501	-496	-66
10	-4	350	303	-296	-64
11	-4	271	265	213	158
12	-4*	97	151	-140	-58
13	-4*	67	58	20	-55
5	5	822	824	806	169
6	5*	120	77	-47	-61
7	5	367	387	-382	-58
8	5	456	366	339	138
10	-5	658	693	672	169
11	-5*	121	120	103	-61
12	-5	447	430	-426	-58
13	-5	348	304	271	138
6	6	857	795	781	149
12	-6	431	423	396	149
13	-6	192	180	-171	-55
		h k 5			
2	0	1359	1290	1289	47
3	0	733	645	645	00
4	0	435	479	-477	-46
5	0*	109	99	88	46
6	0*	119	64	64	00
7	0	238	240	-236	-44
8	0	203	215	-211	43
10	0	339	333	-331	-40
11	0*	77	68	-56	38
2	1	418	364	-361	-47
3	1	870	878	877	47
4	1	492	481	481	00
4	-1	358	376	-374	47
5	1	325	329	326	-45
5	-1	1181	1186	1186	00
6	1	708	748	747	44
6	-1*	115	74	59	-45
7	1	226	187	-187	00
7	-1*	123	58	-38	44
8	1	175	178	-173	-42
8	-1	907	937	-937	00
9	1*	111	70	56	41
9	-1*	124	132	-125	-42
10	1*	90	77	-77	00
10	-1	176	215	211	40
11	-1*	90	111	111	00
12	-1*	58	105	98	-37
3	2	154	138	-130	-46
4	2	309	310	306	45
5	2*	121	8	8	00
6	2	481	476	-474	-43
6	-2*	112	54	28	45
7	2*	126	46	-18	42
7	-2	235	230	-230	00
8	2	212	200	200	00
8	-2	458	500	499	-43
9	2	193	199	-196	-40
9	-2	211	164	158	42
10	2	299	281	278	38
10	-2*	117	144	144	00
11	-2	319	322	-320	-40
12	-2	200	198	194	38
4	3*	120	71	56	-45
5	3*	126	56	35	44
6	3*	127	126	-126	00
7	3*	121	45	17	-41
7	-3	689	733	-732	-45
8	3	320	339	337	40
8	-3	459	495	493	44
9	3*	82	118	-118	00
9	-3*	127	238	-238	00
10	-3*	121	66	-52	-41
11	-3*	105	171	166	40
12	-3*	82	93	-93	00
5	4	231	209	205	-43
7	4*	109	7	-7	00
8	4*	88	81	-71	-39
9	4	253	279	276	37
9	-4	705	771	-770	-43
10	-4	305	283	-279	42
11	-4	539	561	561	00
12	-4*	88	62	-48	-39
13	-4	168	206	203	37
6	5	284	307	-305	-41
7	5*	92	60	46	39
13	-6	215	243	-240	-38
		h k 6			
2	0	329	262	-261	-10
3	0	319	315	303	86
4	0*	90	110	110	00
5	0	202	159	-159	00
6	0	501	501	496	71
7	0*	115	136	-136	-8
8	0*	114	61	61	-8
9	0	293	337	333	51
10	0	169	138	138	-6
11	0*	65	40	40	-5
1	1	1322	1166	1162	89
2	1	302	274	-274	-10
3	1	243	234	-234	-10
4	1	582	626	621	79
4	-1	507	541	541	-10
5	1	534	547	547	-9
5	-1	830	876	872	79
6	1	296	330	330	-9
6	-1	539	537	-537	-9
7	1	258	272	265	61
7	-1	266	258	-257	-9
8	1	332	421	-421	-7
8	-1	679	741	738	61
9	1*	98	62	61	-6
9	-1	232	217	217	-7
10	1	249	230	227	41
10	-1*	98	166	166	-6
11	-1*	77	80	-69	41
12	-1*	46	79	-79	-4
2	2	1880	1743	1741	84
3	2	850	823	823	-10
4	2	293	264	-264	-9
5	2*	111	150	133	70
5	-2	287	268	-268	-10
6	2*	175	177	-177	-8
6	-2*	103	126	126	-9
7	2*	113	152	152	-7
7	-2	557	618	614	70
8	2*	104	120	109	50
8	-2	268	291	291	-8
9	2*	86	51	-51	-6
9	-2	291	300	-300	-7
10	2*	61	68	-67	-5
10	-2	268	290	285	50
11	-2*	86	67	67	-6
12	-2*	61	5	-2	-5
3	3	704	736	-732	76
4	3*	110	79	-79	-9
5	3*	115	84	-84	-8
6	3*	115	59	-4	59
7	3	419	456	456	-7
7	-3*	110	106	105	-9
8	3*	92	6	-1	-6
8	-3	297	294	294	-8
9	3*	70	119	-112	39
9	-3*	115	66	30	59
10	-3	209	239	-239	-7
11	-3*	92	90	90	-6
12	-3	180	204	200	39
4	4	588	645	642	65
5	4*	115	37	-36	-8
6	4	276	319	-319	-7
7	4	154	132	124	47
8	4	147	142	142	-5
8	-4	879	929	-927	65
9	4	250	290	290	-4
9	-4*	115	20	18	-8
10	-4	205	226	226	-7
11	-4	497	533	530	47
12	-4*	76	115	114	-5
13	-4	156	214	-214	-4
5	5*	110	153	143	54
6	5	271	253	253	-6
7	5*	80	97	-97	-6
8	5	298	330	328	35
10	-5*	110	143	133	54
11	-5	178	189	-189	-6
12	-5*	80	68	-68	-6
13	-5*	53	93	86	35
6	6	556	636	635	42
12	-6*	81	140	-133	42
13	-6	187	202	202	-5
		h k 7			
2	0	201	198	186	-69
3	0	383	319	-319	00
4	0	758	748	745	67
5	0	181	191	-179	-65
6	0*	115	36	-30	00
7	0	270	234	226	61
8	0*	118	145	-133	-59
9	0	240	234	234	00
10	0*	89	70	44	54
11	0	220	248	-242	-51
2	1	597	537	533	68
3	1	346	346	-339	-67
3	-1*	79	93	63	68
4	1	1099	1092	1092	00
4	-1	574	554	-550	-67
5	1*	112	66	13	64
5	-1*	103	61	-61	00
6	1	350	311	-305	-62
6	-1	359	297	-290	64
7	1	427	465	-465	00
8	1	294	266	259	58
8	-1*	120	36	-36	00
9	1*	98	55	5	-55
9	-1*	113	67	-31	58
10	1*	76	46	-46	00
10	-1	490	462	-458	-55
11	-1*	76	101	101	00
3	2	630	643	639	66
4	2	790	780	-777	-65
5	2*	117	103	103	00
6	2	586	585	582	61
6	-2	255	214	-204	-64
7	2	477	494	-491	-59
7	-2	303	341	-341	00
8	2*	105	33	-33	00
8	-2*	120	160	-148	61
9	2*	85	56	-15	53
9	-2	355	400	-395	-59
10	-2*	105	83	83	00
11	-2	249	281	276	53
12	-2	181	205	198	-51
4	3	189	180	-169	63
5	3	373	358	353	-61
6	3	279	248	248	00
7	3	278	271	265	57
7	-3	542	585	582	63
8	3*	92	113	-99	-54
8	-3	258	232	-223	-61
9	3	298	295	-295	00
10	-3	470	499	495	57
11	-3*	92	107	-93	-54
12	-3*	68	31	-31	00
5	4	182	192	182	60
6	4	566	574	-570	-57
7	4	364	343	343	00
8	4	247	262	257	52

Continued: TABLE IV.

h	k	10FO	10FC	10AC	10BC
9	-4	254	290	284	60
10	-4	224	226	-219	-57
11	-4*	96	93	93	00
12	-4*	74	83	65	52
6	5*	98	75	51	55
7	5	163	155	-146	-53
8	5*	48	10	10	00
11	-5*	98	93	75	55
12	-5*	78	110	-96	-52
13	-5*	48	138	138	00
7	6	153	144	-135	50

h k 8

h	k	10FO	10FC	10AC	10BC
1	0	238	209	-195	-75
2	0	833	735	-731	-74
3	0	1312	1253	1236	207
5	0	429	433	427	-70
6	0	364	362	311	186
7	0	220	170	156	-66
8	0*	103	91	-66	-63
9	0	473	469	442	156
10	0	258	256	-250	-57
11	0	174	218	-211	-54
1	1	996	915	890	213
2	1	463	451	445	-73
3	1	637	642	-638	-72
3	-1	122	133	-111	-73
4	1	1302	1328	1313	198
4	-1	483	443	-437	-72
5	1	268	301	-293	-69
5	-1	1223	1191	1175	198
6	1	198	212	-201	-67
6	-1	206	196	-183	-69
7	1	874	921	905	171
7	-1	222	196	-185	-67
8	1	304	274	-266	-62
8	-1	745	768	749	171
9	1	154	147	135	-59
9	-1	355	374	-369	-62
10	1	340	319	288	139
10	-1	242	210	202	-59
11	-1	258	285	248	139
2	2	1487	1488	1473	205
3	2	609	614	-610	-71
4	2	236	231	-220	-70
5	2	184	187	31	184
6	2	208	153	139	-65
7	2	240	293	-286	-63
7	-2	627	660	634	184
8	2	631	657	638	154
8	-2*	106	134	-117	-65
9	2*	71	96	78	-57
9	-2	472	504	-500	-63
10	2	195	213	-206	-54
10	-2	710	744	728	154
11	-2	195	166	156	-57
12	-2	314	350	-346	-54
3	3	1481	1485	1472	193
4	3*	104	117	-95	-68
5	3	326	369	-363	-66
6	3	649	668	647	167
7	3	419	433	-429	-61
7	-3	235	266	-258	-68
8	3	276	312	-307	-58
8	-3	252	236	-227	-66
9	3	287	270	233	136
9	-3	730	772	754	167
10	-3	296	287	-281	-61
11	-3	165	156	-145	-58
12	-3	341	295	261	136
4	4	193	190	66	178
5	4	293	287	-280	-64
6	4	208	205	-196	-61
7	4	764	793	779	149
8	4*	61	79	-57	-55
8	-4	383	355	-308	178
9	-4*	104	127	-110	-64
10	-4*	96	114	-96	-61
11	-4	586	613	594	149
12	-4*	61	65	-35	-55
5	5	501	553	530	160
6	5*	83	125	-110	-59
7	5*	64	123	109	-56
10	-5	501	503	477	160
11	-5	401	395	-391	-59
12	-5*	64	82	60	-56
6	6	240	269	230	141

h k 9

h	k	10FO	10FC	10AC	10BC
1	0	608	569	-568	-36
2	0	412	410	-408	36
3	0*	73	50	50	00
4	0*	84	47	31	-35
5	0	306	312	310	35
6	0*	97	78	-78	00
7	0	208	170	167	-34
8	0	203	224	222	33
9	0	152	176	-176	00
10	0*	63	64	55	-32
2	1	557	654	-653	-36
3	1*	80	62	-51	36
3	-1	361	427	426	-36
4	1*	89	58	58	00
4	-1	479	434	432	36
5	1	268	230	227	-35
5	-1	833	829	-829	00
6	1	356	331	-329	34
6	-1	185	218	-215	-35
8	1*	86	60	-50	-33
8	-1	443	448	448	00
9	1	177	173	170	32
9	-1	188	186	-183	-33
10	1*	51	58	-58	00
10	-1*	72	57	-47	32
11	-1	107	133	133	00
3	2	523	532	-531	-35
4	2*	93	101	-95	35
5	2	334	380	380	00
6	2*	97	74	-65	-34
6	-2	578	601	600	35
7	2	160	177	174	33
7	-2	250	320	-320	00
8	2	143	158	-158	00
8	-2	412	437	-436	-34
9	2	132	137	-133	-32
9	-2*	90	98	92	33
10	-2*	78	6	6	00
11	-2*	60	41	26	-32
4	3	268	249	-247	-35
5	3	349	329	327	34
6	3	182	179	179	00
7	3*	82	47	-34	-33
7	-3	197	148	144	-35
8	3*	66	46	-34	32
8	-3*	97	106	100	34
9	3*	43	36	-36	00
9	-3*	93	61	-61	00
10	-3	250	234	-231	-33
11	-3	219	216	213	32
12	-3	244	285	285	00
5	4	543	551	-550	-34
6	4*	84	69	60	33
8	4*	50	35	-15	-31
9	-4	192	161	157	-34
10	-4	475	479	478	33
11	-4	460	469	-469	00
12	-4	123	141	-137	-31
6	5*	72	47	34	-32
7	5	104	115	111	31
11	-5*	72	76	-69	-32
12	-5*	53	75	-68	31

h k 10

h	k	10FO	10FC	10AC	10BC
1	0	349	314	-314	00
2	0	194	188	187	-12
3	0	953	896	893	80
4	0*	93	65	-64	-12
5	0	145	102	101	-11
6	0	560	575	572	67
7	0*	103	79	78	-10
8	0*	96	14	-11	-9
9	0	277	315	311	49
10	0	160	170	-170	-7
1	1	204	226	210	84
2	1*	78	67	66	-12
2	-1	105	176	155	84
3	1	301	304	304	-12
3	-1	165	209	209	-12
4	1	1026	989	986	74
4	-1	232	219	-219	-12
5	1	420	432	-432	-11
5	-1	191	177	161	74
6	1	435	456	-456	-10
6	-1	352	342	342	-11
7	1	609	661	658	58
7	-1	313	331	330	-10
8	1	225	239	239	-9
8	-1*	100	66	-32	58
9	1*	71	60	59	-8
9	-1	154	142	-142	-9
10	1*	46	55	-38	39
10	-1*	71	18	-17	-8
11	-1*	46	89	80	39
2	2	147	154	-132	79
3	2	395	408	-407	-12
4	2	365	373	373	-11
5	2	151	145	129	66
6	2	164	143	143	-10
7	2	197	190	-190	-9
7	-2	270	275	-267	66
8	2	160	170	163	48
8	-2*	102	141	-141	-10
9	2	124	147	147	-7
9	-2	303	304	304	-9
10	-2	252	269	265	48
11	-2*	58	7	2	-7
3	3*	102	153	136	71
4	3*	105	134	134	-11
5	3*	103	21	18	-10
6	3	209	270	264	55
8	3	188	195	195	-7
8	-3	289	310	-310	-10
9	-3	161	166	156	55
10	-3	251	273	273	-8
11	-3*	64	124	-124	-7
4	4	644	702	-700	62
5	4*	98	68	67	-9
6	4	164	157	157	-8
7	4	250	264	262	44
8	4*	44	13	-11	-7
8	-4	483	510	507	62
9	-4*	98	134	-134	-9
10	-4	236	240	-240	-8
11	-4*	69	51	-24	45
12	-4*	44	24	-23	-7
5	5	179	184	177	51
7	5*	49	41	41	-7
10	-5	316	348	344	51
11	-5	244	210	210	-8
6	6	192	130	124	40
11	-6	246	210	210	-8
12	-6	668	500	497	40

h k 11

h	k	10FO	10FC	10AC	10BC
1	0	136	150	132	71
2	0	412	380	-374	-70
3	0*	93	13	-13	00
4	0	364	372	366	68
5	0	429	409	-403	-66
6	0*	113	47	47	00
7	0*	109	65	21	62
8	0	210	196	-187	-60
9	0	199	165	-165	00
10	0	405	377	373	54
2	1	365	347	340	-70
3	1	353	380	-374	-69
3	-1	329	377	370	70
4	1	901	889	-889	00
4	-1	586	562	-558	-69
5	1	285	295	287	65
5	-1	486	457	-457	00
6	1	317	313	-306	-63
6	-1	715	724	721	65
7	1	631	655	655	00
7	-1	396	345	-340	-63
8	-1*	104	43	43	00
9	1	373	379	-374	-55
9	-1	405	387	382	58
10	-1*	70	57	-13	-55
3	2	358	289	-281	67
4	2	382	400	395	-66
5	2	272	297	297	00
6	2*	108	92	-68	62
6	-2	423	416	-410	-66
7	2*	96	108	90	-59
7	-2*	113	16	16	00
8	2*	78	10	-10	00
8	-2*	108	71	36	62
9	2	253	254	248	54
9	-2*	96	89	66	-59
10	-2*	78	26	26	00
11	-2*	53	76	54	54
4	3	497	475	471	64
5	3	677	692	-689	-62
6	3*	100	37	37	00
7	3*	84	138	126	57
7	-3*	113	65	-9	64
8	3*	62	69	-43	-54
8	-3*	109	91	-67	-62
10	-3*	84	82	58	57
11	-3	291	261	-255	-54
5	4	432	414	410	60
6	4*	87	65	30	-58
7	4	446	426	-426	00
9	-4*	101	126	111	60
10	-4	225	246	-240	-58
11	-4	137	134	-134	00
6	5*	70	154	143	55

h k 12

h	k	10FO	10FC	10AC	10BC
1	0	136	127	-106	-70
2	0*	85	70	-7	-70
3	0	1347	1313	1300	189
4	0	275	280	-272	-68
5	0	452	440	-435	-66
6	0	1001	968	953	169
7	0	321	341	-335	-62
8	0	215	227	-219	-59
9	0	493	543	524	142
10	0*	47	54	6	-54
1	1	566	513	475	193
2	1	720	714	-710	-69
2	-1	1065	1288	1283	193
3	1	411	380	374	-68
3	-1	671	772	-768	-69
4	1	237	250	173	180
4	-1*	107	69	11	-68
5	1*	117	82	-50	-65
5	-1	503	502	469	180
6	1*	113	97	-74	-63
6	-1*	117	96	-70	-65
7	1	393	397	365	156
7	-1*	113	131	-115	-63
8	1*	86	92	72	-58
8	-1	351	350	314	156
9	1	229	230	-224	-55
9	-1*	86	91	70	-58
10	-1	327	305	-300	-55
2	2	343	348	294	186
3	2*	113	139	121	-67
4	2	218	217	-207	-66
5	2	996	973	959	167
6	2	324	335	-329	-61
6	-2	350	321	-315	-66
7	2*	92	98	-78	-59
7	-2	616	566	541	167
8	2	449	423	399	140
8	-2*	232	206	-197	-61
9	-2*	92	60	13	-59
10	-2	272	258	216	140
3	3*	255	323	271	175
4	3	453	482	-477	-64
5	3*	109	153	-140	-62
6	3	576	563	542	152
7	3*	79	64	29	-57
7	-3	278	239	-230	-64
8	3*	53	62	30	-54
8	-3	229	221	-212	-62
9	-3	328	308	267	152
10	-3*	79	59	15	-57
11	-3	115	168	-159	-54
4	4	785	802	786	162
5	4*	99	152	-140	-60
6	4*	82	169	-159	-57
7	4	262	268	232	136
8	-4	771	706	687	162
9	-4*	99	116	-100	-60
10	-4	206	232	-225	-57
11	-4	483	434	412	136
5	5	347	292	253	145
6	5*	63	144	-133	-55
10	-5	441	393	365	145
11	-5*	63	91	73	-55

h k 13

h	k	10FO	10FC	10AC	10BC
1	0*	55	28	-14	-24
2	0	286	254	253	24
3	0	823	751	-751	00
4	0	337	371	-370	-24
5	0	165	92	89	24
6	0*	97	77	77	00
7	0*	88	54	-49	-24
8	0	122	95	92	24
9	0	208	201	201	00
2	1	328	304	303	-24
3	1	227	233	232	24
4	1	391	437	-437	00
4	-1*	94	56	50	24
5	1	523	556	-555	-24
5	-1*	99	109	109	00
6	1	224	191	190	24
6	-1*	98	42	-34	-24
7	1	273	304	304	00
7	-1	187	218	217	24
8	1*	66	87	-84	-24
8	-1	136	112	-112	00
9	1*	42	25	-8	23
9	-1*	66	45	-38	-24
10	-1	534	474	474	23
3	2	432	425	425	-24
4	2	179	184	182	24
5	2*	95	79	-79	00
6	2*	86	35	-26	-24
6	-2	324	358	-357	24
7	2*	72	74	-70	24
7	-2*	95	134	134	00
8	-2	296	289	288	-24
9	-2*	72	24	-1	24
10	-2*	33	31	31	00
1	-3	369	304	303	-24
4	3*	96	55	49	-24
5	3*	88	35	26	24
6	3*	76	82	82	00
7	3*	59	27	13	-23
7	-3	320	338	-337	-24
8	-3*	88	114	112	24
9	-3*	76	62	62	00
10	-3*	59	44	-37	-23
5	4*	78	54	-49	-24
6	4	197	302	201	23
7	4	242	264	-264	00
9	-4	257	276	-275	-24
10	-4	221	221	-220	23
11	-4	329	313	313	00
6	5	205	223	-222	-23

By means of subsequent Fourier and by steric considerations, all the nonhydrogen atoms were located. R index value was, at this stage, 0.18.

The refinement of the structure was carried out by the least-squares method (full-matrix) using the Busing and Levy program on a 360/65 I.B.M. computer.

In the first stage a statistical distribution of Al and Fe was assumed: the scattering factors curves of (Fe^{3+}, Al^{3+}), S and O were prepared from the values given by Cromer and Waber [3]. The scale factors, the atomic coordinates and the isotropic thermal parameters were refined; anomalous dispersion correction for iron ($\Delta f'$ and $\Delta f''$ given in The International Tables) was taken into account in structure factor calculation. R index dropped in few cycles to 0.091.

At this stage, on the basis of an accurate analysis of the cation-anion distances, it seemed very likely that the alluminium substitute for Fe^{3+} only in the position labelled Fe(1). The inspection of this hypothesis allowed a substantial improvement of R index (from 0.091 to 0.080) and a more reliable temperature factor for the atom (Al , Fe) (1).

Individual anisotropic thermal parameters were taken into account in the next run. The final R value is 0.072 for 625 observed reflections and 0.102 including the non observed ones.

Table II shows the atomic coordinates and the isotropic equivalents of the final anisotropic temperature factors computed according to Hamilton [7]. The analysis of the anisotropic thermal parameters is given in Table III; their significance is lessened by the scaling procedure (level by level) adopted in the isotropic refinement, and by the approximative absorption correction applied to the intensities.

The observed and calculated structure factors are listed in Table IV.

For typografic clearness the cation (Al , Fe) (1) is afterwards indicated as Fe (1); the oxygen atoms belonging to water molecules are labelled O_w.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Fig. 1 shows the general arrangement of the atoms in coquimbite. In Tables V and VI the interatomic distances and angles are given.

The Fe atoms show octahedral coordination; half of the oxygen atoms surrounding iron belong to water molecules:

– Fe(1) at the origin of the cell, binds only oxygens of water molecules, with a distance of 1.893 Å;

– Fe(2) coordinates only oxygens belonging to sulfate groups with a distance of 1.998 Å;

– Fe(3) binds three oxygens (of sulfate groups) and three oxygens of water molecules, located on the opposite sides of the octahedron; distances are Fe—O 1.969 Å, Fe—O_w 2.010 Å.

Cation-anion distances in Fe(2) and Fe(3) polyhedra are in good agreement with those found in similar compounds: roemerite [4] Fe—O 1.939, Fe—O_w 2.033 Å; krausite [6] Fe—O 1.989, Fe—O_w 2.029 Å; amarantite [5] [14] (in this structure isolated Fe octahedra are not present) Fe—O 1.991, Fe—O_w 2.050 Å.

Fe(1)—O_w distance value, 1.893 Å, seems to be unusually low. The shortening of this distance must be related to the presence of Al atoms which substitutes for Fe in this position. The average Al—O distance given in The International Tables [9] in exactly 1.89 Å.

The sulfate group shows the well known tetrahedral shape with a mean S—O distance of 1.479 Å in good agreement with the values quoted in literature. The lengthening of S—O distances, observed by Fanfani, Nunzi and Zanazzi [4] when the oxygen atom is linked to a trivalent iron ion,

TABLE V.

Interatomic distances in coquimbite; standard deviations are in parentheses.

Fe(1)—O_w(1)	1.893 (7) Å	(×6)	O_w(1) —O (3)	2.688 (10)	
Fe(2)—O (2)	1.998 (7)	(×6)	O $(4)_1$	2.657 (10)	
Fe(3)—O (1)	1.969 (7)	(×3)			
O_w(2)	2.010 (8)	(×3)	$O_w(2)_3$—O (3)	2.661 (11)	
			O_w(3)	2.622 (11)	
S—O (1)	1.518 (8)				
O (2)	1.481 (8)		O_w(3) —O $(4)_2$	2.751 (10)	
O (3)	1.467 (8)		$O_w(3)_1$	2.759 (11)	
O (4)	1.451 (8)		$O_w(3)_2$	2.741 (11)	

TABLE VI.

Interatomic angles in coquimbite.

O_w(1) —Fe(1)—$O_w(1)_1$	92.8 (3)°	(×6)	O(1)—S—O(2)	109.4 (4)°	
$O_w(1)_2$	87.2	(×6)	O(3)	109.0	
$O_w(1)_1$—Fe(1)—$O_w(1)_2$	180.0	(×3)	O(4)	107.2	
			O(2)—S—O(3)	108.9	
O (2) —Fe(2)—O $(2)_1$	91.5	(×4)	O(4)	111.7	
O $(2)_2$	87.6	(×4)	O(3)—S—O(4)	110.5	
O $(2)_3$	180.0	(×3)			
O $(2)_1$—Fe(2)—O $(2)_2$	89.3	(×4)	O (3) —$O_w(1)_3$—O $(4)_1$	118.3 (5)°	
			O (3) —$O_w(2)_3$—O_w(3)	94.4	
O (1) —Fe(3)—O $(1)_1$	94.3	(×3)	$O_w(2)_3$—O_w(3) —O $(4)_2$	91.8	
O_w(2)	91.6	(×3)	$O_w(3)_1$	121.2	
$O_w(2)_1$	173.9	(×3)	$O_w(3)_2$	97.0	
O $(1)_1$—Fe(3)—O_w(2)	83.5	(×3)	O $(4)_2$—O_w(3) —$O_w(3)_1$	121.0	
O_w(2) —Fe(3)—$O_w(2)_1$	90.8	(×3)	$O_w(3)_2$	129.4	
			$O_w(3)_1$—O_w(3) —$O_w(3)_2$	96.2	

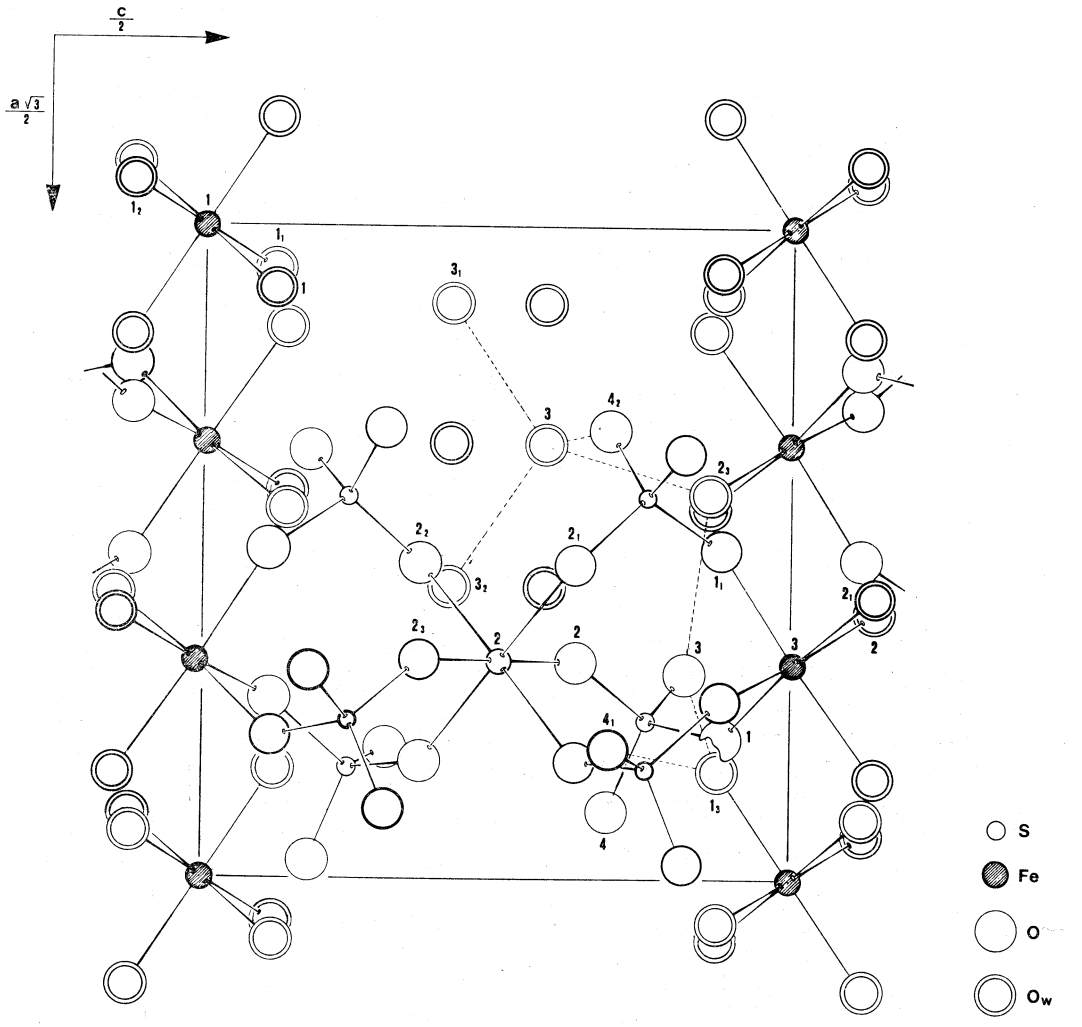

Fig. 1. – The crystal structure of coquimbite projected along the *b* axis. Postulated hydrogen bonds (one for each kind) are shown by dashed lines.

seems to be confirmed also in coquimbite. The average S—O bond length is 1.499 Å for oxygen atoms linked to iron and 1.459 for the unlinked ones.

The structure of coquimbite consists of isolated Fe(1) octahedra and groups with composition $Fe_3(H_2O)_6(SO_4)_6$, given by 3 Fe octahedra and 6 SO_4 tetrahedra connected to each other according to the scheme drawn in fig. 2. These groups and the isolated octahedra are connected together by hydrogen bonds (see below).

One water molecule, among the three independent ones, $H_2O(3)$, is not linked to any Fe^{3+} ion.

As to the crystal-chemical behaviour of the ferric iron it seems interesting to note that this ion shows a lower tendency than the bivalent transition metals to form $Me(H_2O)_6$ polyedra. Really in coquimbite half of the oxygen

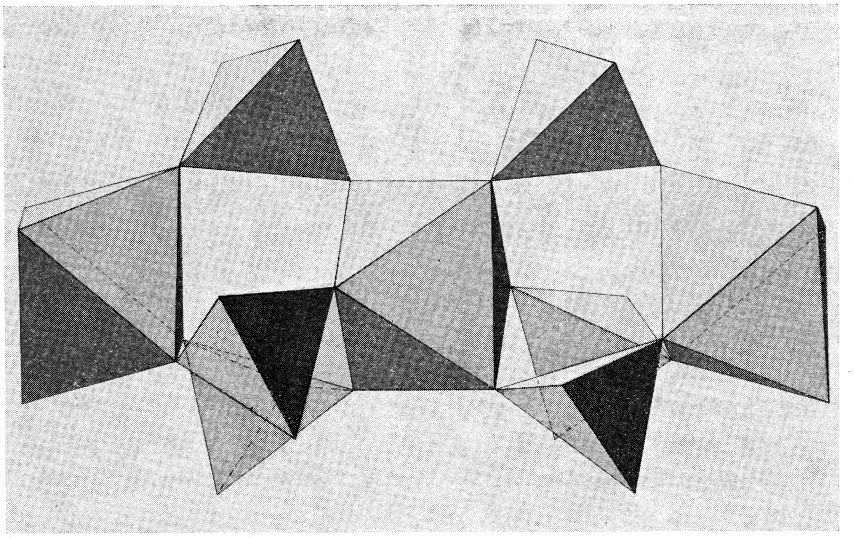

Fig. 2. – Group of octahedra and tetrahedra with composition $Fe_3(H_2O)_6(SO_4)_6$,

atoms surrounding Fe^{3+} belong to the sulfate group. Something analogous happens in amarantite and botryogen. In the first mineral, $Fe_2^{III}(SO_4)_2O \cdot 7\,H_2O$, the two independent Fe atoms bind: 1 water molecule + 5 sulfate-oxygen atoms and 3 water molecules + 3 sulfate-oxygen atoms respectively. In botryogen [13], $Fe^{III}(Fe^{II}, Zn, Mn, Mg)(SO_4)_2OH \cdot 7\,H_2O$, $Me^{3+}(1)$ is coordinated to 4 sulfate-oxygen atoms + 2 hydroxyl, $M^{3+}(2)$ binds 2 sulfate-

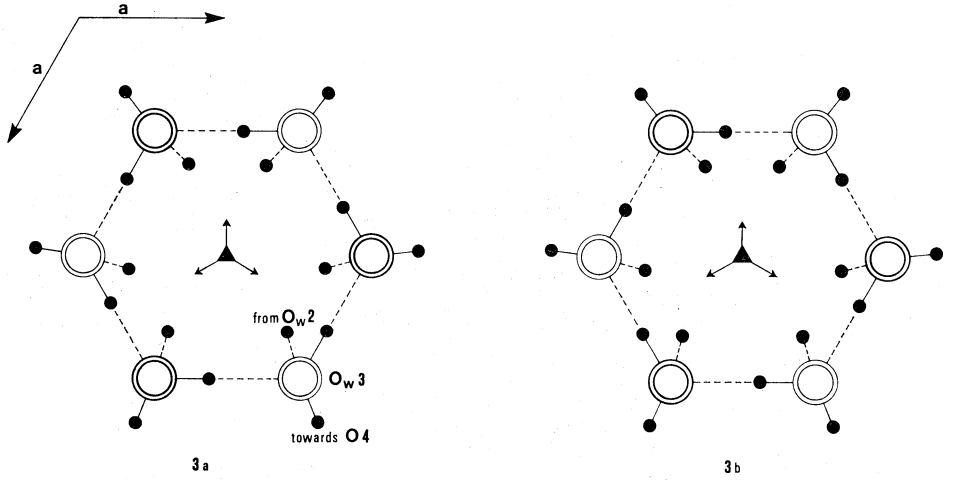

Fig. 3. – Scheme of the probable hydrogen bonds involving $O_w(3)$.

oxygen atoms + 2 hydroxyl + 2 water molecules, while Me^{2+} links 1 sulfate-oxygen atom + 5 water molecules. In roemerite [4] $Fe^{II}F_2^{III}(SO_4)_4 \cdot 14H_2O$, only the ferrous iron is completely surrounded by oxygen atoms belonging to water molecules.

It may be also interesting to note that, in coquimbite crystals studied in this work, Fe(1) $(H_2O)_6$ octahedra are actually $(Fe_{0.37}, Al_{0.63})(H_2O)_6$. In the more aluminian coquimbites quoted in literature [10], it seems not unlikely that true $Al(H_2O)_6$ octahedra are present.

According to the chemical formula, in coquimbite 6 hydrogen atoms per asymmetric unit are present. O—O distance analysis shows seven values in the range 2.62—2.75 Å.

$O_w(2)$ makes H bonds with O(3) and $O_w(3)$; $O_w(1)$ makes H bonds with O(3) and $O(4)_1$. Both $O_w(1)$ and $O_w(2)$ exibit only the function of proton donors.

$O_w(3)$, the free molecule, is surrounded approximately tetrahedrally by four oxygen atoms ($O_w(2)_3$, $O(4)_2$, $O_w(3)_1$ and $O_w(3)_2$) with O—O distances all in the range of H bonds; likely $O_w(3)$ accepts one hydrogen bond from $O_w(2)_3$ and donates one hydrogen bond to $O(4)_2$. Not so plain the arrangement of H bonds among $O_w(3)$ and its symmetry related. Fig. 3 shows six such atoms related by 3-fold and 2-fold axes. It is interesting to remark that $O_w(3)$—$O_w(3)_1$ and $O_w(3)$—$O_w(3)_2$ distances have the same value within the standard deviation. Now the position of H atoms can be intermediate by resonance between two oxygen atoms (on the 2-fold axes) or there may occur a statistical distribution of $O_w(3)$—H···$O_w(3)_1$ and $O_w(3)$···H—$O_w(3)_1$ configurations, as shown in fig. 3 *a* and 3 *b*. In the first hypothesis the O—O distance value seems too high for a symmetric hydrogen bond. However no conclusive evidence is provided by X-ray data; in fact the attempt of a direct location of H atoms on Fourier-difference maps was not successful.

TABLE VII.

Charge balance of oxygen atoms.

	Fe	S	–H····	····H–	Total
O (1)	1/2	3/2			2.
O (2)	1/2	3/2			2.
O (3)		3/2		2× 1/4	2.
O (4)		3/2		2× 1/4	2.
$O_w(1)$	1/2		2× 3/4		2.
$O_w(2)$	1/2		2× 3/4		2.
$O_w(3)$			2× 3/4	2× 1/4	2.

Under the assumption of an entirely ionic structure, a scheme of the electrostatic valence for the oxygen atoms can be developed as shown in Table VII; distributing each hydrogen contribution as 3/4 to the linked oxygen atom and 1/4 to the unlinked one, the balance is quite satisfactory.

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