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Mineralogia. — *The crystal structure of asbecasite* (*). Nota di ELIO CANNILLO, GIUSEPPE GIUSEPPETTI e CARLA TADINI, presentata (**) dal Socio G. CAROBBI.

RIASSUNTO. — L'asbecasite, silicato di formula $Ca_3(Ti, Sn)[(As_3SiBeO_{10})_2]$, è trigonale, con due unità stechiometriche nella cella elementare. Il gruppo spaziale è $P\bar{3}c1$ e le costanti reticolari sono: $a = 8{,}36$, $c = 15{,}30$ Å. La struttura cristallina è stata studiata utilizzando 695 effetti di diffrazione di raggi X registrati con la camera di Weissenberg. I parametri degli atomi sono stati ricavati con i consueti metodi di Patterson e di Fourier e raffinati col metodo dei minimi quadrati fino a un fattore di discordanza finale R = 0.054 per i riflessi osservati. Nella struttura sono presenti strati di poliedri paralleli a (0001) che si susseguono nell'ordine ...AABAAB... Lo strato A è costituito da tetraedri BeO_4, SiO_4 e da piramidi AsO_3; lo strato B da ottaedri $(Ti, Sn)O_6$ e antiprismi quadrati CaO_8. Le distanze di legame e l'equilibrio elettrostatico che ne risultano presentano qualche particolarità che viene discussa.

INTRODUCTION.

Two new minerals, asbecasite and cafarsite, were found by Graeser in the gneiss of the Monte Leone nappe in the southern part of the Binnatal (Switzerland).

The morphological, optical, physical and chemical properties of asbecasite were fully described by Graeser himself [1] and we shall report only those features that are necessary for the following discussion. The space group is $P\bar{3}c1$, the lattice parameters are: $a = 8.33$, $c = 15.29$ Å, $Z = 3$. The chemical formula reported by Graeser is:

$$Ca_2Si_{1.5}Be_{0.75}Ti_{0.5}Al_{0.2}Sn_{0.1}Tl_{0.03}(AsO_3)_5 .$$

More recently Strunz [2] suggested the following alternative formula ($Z = 2$), more consistent with the space group:

$$Ca_3(Ti,Sn)BeSi_2\,(O_3As_6O_{18}),$$

but it is noteworthy that the resulting balance of the valences is unsatisfactory.

EXPERIMENTAL.

A specimen of asbecasite, with spherical shape (radius 0.19 mm), was used to collect the X-rays diffraction data. A redetermination of the cell dimensions carried out by means of precession and Weissenberg photographs was in accordance with the previous results, and gave the following values:

$$a = 8.36 \pm 0.02 \text{ Å}$$
$$c = 15.30 \pm 0.03 \text{ Å}.$$

(*) This work was performed in the Sezione di Pavia del Centro Nazionale di Cristallografia del C.N.R., Istituto di Mineralogia dell'Università, via Bassi 4, 27100 Pavia (Italy).

(**) Nella seduta dell'8 marzo 1969.

Equi-inclinated Weissenberg photographs of the integrated reflections were taken by the multiple–film technique and CuKα radiation, *b* being the rotation axis and *k* ranging from 0 to 8. The intensities were measured by a Nonius microdensitometer and a total of 695 independent reflections out of about 800 present in the CuKα limiting sphere (87 %), were examined. It was found that 122 of them could not be detected and a value of half of the minimum observable intensity was assigned to them.

Corrections were made for the absorption (linear coefficient $\mu = 283 \text{ cm}^{-1}$ for CuKα) and for the incipient but incomplete α_1–α_2 separation.

Crystal structure determination and refinement.

With these data, a three–dimensional Patterson synthesis was calculated and the heavy atoms, arsenic and titanium were situated according to the equivalent points of the space group $P\bar{3}c1$. On this basis a three–dimensional electron density synthesis was successively obtained, on which new maxima appeared reasonably due to Ca atoms and to Si atoms, as well as possible positions for forty oxygens surrounding the heavy atoms. Finally some maxima located in a special position, with four–fold multiplicity, could reasonably be attributed to Be atoms. The above results do not agree with the chemical formula suggested by Strunz, which shows two Be atoms, instead of four, and forty-two oxygens instead of forty.

Yet, at this stage, we assumed that the structural model we had obtained could be taken as the starting point for the refinement. The refinement was carried out by means of some cycles of least squares (full matrix, isotropic temperature factors, equal weight for all the observed reflections). The structure factors were calculated by using the HFS scattering factors for neutral atoms published by Hanson, Herman, Lea and Skillman [3]. The scattering amplitudes for Ti take into account the presence of a 20 % Sn.

During the former cycles the temperature factors of three or four out of the nine independent atoms became always negative, although the R factor dropped from 0.17 to 0.08. An inspection of the Fo–Fc table revealed a conspicuous secondary extinction effect. In fact, the agreement between observed and calculated structure factors was improved by excluding from the refinement the most intense reflections. In such a way it was possible to reduce the number of negative temperature factors to only one.

In the meantime a new version of the least squares program became available. This permitted one to take into account the anomalous dispersion in the Fc calculation and to include the secondary extinction as a parameter in the refinement. Some further cycles of least squares allowed the complete elimination of the negative temperature factors, the reduction of the R factor to 0.054 for the observed reflections and to 0.066 for all the reflections, and the improvement of the standard deviations.

The final parameters are reported in Table I. In the final calculation of the Fc's, presented in Table II, the small contributions of the imaginary components of the anomalous dispersion are neglected. The real components are those given by Cromer [4]. In the formula of the secondary extinction, given by Zachariasen [5] and rearranged in order to apply the correction to the Fc's, the terms involving the absorption were neglected. The final value of "g", secondary extinction parameter, is $6.2 \cdot 10^{-6}$.

TABLE I.

Final atomic parameters and their standard deviations (in parentheses).

ATOMS	x/a	y/b	z/c	B
As	0.01840 (14)	0.29632 (14)	0.10361 (6)	0.35 (3)
(Ti, Sn)	0	0	1/4	0.66 (5)
Si	2/3	1/3	0.07320 (28)	0.20 (6)
Ca	0.59205 (31)	0.59205 (31)	3/4	0.38 (4)
O(1)	0.89326 (97)	0.77841 (97)	0.17534 (41)	0.54 (10)
O(2)	0.53703 (96)	0.72118 (96)	0.17392 (42)	0.56 (10)
O(3)	0.59836 (97)	0.46997 (97)	0.11721 (43)	0.78 (11)
O(4)	1/3	2/3	0.03008 (85)	1.06 (20)
Be	1/3	2/3	0.13011 (126)	0.22 (29)

TABLE II.

Structure factors of asbecasite.

Reflections marked with an asterisk were unobservably weak; in this case Fo derives from $0.5\ I_{min}$.

h	l	$10F_o$	$10F_c$	h	l	$10F_o$	$10F_c$	h	l	$10F_o$	$10F_c$	h	l	$10F_o$	$10F_c$
	h 0 l			2	—2	692	—739	3	14	1064	—1121	5	8	1363	1354
				2	4	784	824	3	—14	1034	—1075	5	—8*	153	—143
0	4	1992	—1840	2	—4	1678	1729	3	16	577	—623	5	10	990	—951
0	6	1987	—2007	2	6*	183	—156	3	—16*	87	85	5	—10	1333	—1356
0	8	1515	1599	2	—6	852	—846	3	18	286	339	5	12*	125	63
0	10	1292	1332	2	8	1375	1468	3	—18	302	—336	5	—12	900	928
0	12	1151	1250	2	—8*	190	196	4	0	1404	1460	5	14	365	—356
0	14	2224	—2439	2	10	883	—910	4	2*	121	—130	5	—14*	140	71
0	16*	95	127	2	—10	1210	—1261	4	—2*	121	131	5	16	875	933
0	18	495	600	2	12	288	265	4	4	1115	—1039	5	—16	406	393
1	2	390	—479	2	—12	367	339	4	—4	943	—953	6	0	768	689
1	—2	478	—641	2	14*	205	—209	4	6	819	—823	6	2	651	—610
1	4	518	517	2	—14*	121	—26	4	—6	1395	—1455	6	—2	1221	1149
1	—4	627	—567	2	16	635	687	4	8	858	858	6	4*	157	—123
1	6	439	—452	2	—16	598	673	4	—8	871	877	6	—4	175	—209
1	—6*	125	63	2	18	474	—528	4	10	548	512	6	6	231	—221
1	8	325	—266	2	—18	514	—618	4	—10	1511	1559	6	—6	918	—888
1	—8	639	652	3	0	2137	2076	4	12*	123	—36	6	8	400	363
1	10*	157	151	3	2	1474	1409	4	—12	558	574	6	—8	183	—174
1	—10	352	317	3	—2	558	—568	4	14	1027	—1108	6	10	208	169
1	12*	130	—11	3	4	1265	—1302	4	—14	1191	—1289	6	—10*	92	12
1	—12	586	607	3	—4*	169	147	4	16	293	—297	6	12	454	—456
1	14	641	—704	3	6	2166	—2152	4	—16	640	—708	6	—12	678	667
1	—14	416	—427	3	—6	2093	—2103	5	0	306	—261	6	14	153	—111
1	16*	119	122	3	8	1498	1548	5	2	1825	—1808	6	—14	130	106
1	—16	332	—371	3	—8	980	983	5	—2*	173	—196	7	0	1806	1719
1	18	313	334	3	10	582	526	5	4	1017	1006	7	2	344	—289
1	—18*	71	—50	3	—10	1125	1123	5	—4	1775	1832	7	—2	351	—290
2	0	325	—256	3	12	765	778	5	6*	128	30	7	4	498	—455
2	2	1411	—1487	3	—12	272	212	5	—6	821	—809	7	—4	980	—984

TABLE II (*continued*).

h	*l*	$10F_o$	$10F_c$
7	6	1353	—1319
7	—6	1434	—1389
7	8	1016	996
7	—8	1386	1386
7	10	571	561
7	—10	908	940
7	12	266	252
7	—12	578	603
8	0	366	310
8	2	1064	—1111
8	—2	344	348
8	4*	71	—56
8	—4	468	473
8	6*	71	6
8	—6	508	—470
8	8	824	848
8	—8*	71	—72
8	10	135	122
8	—10	439	—446
9	0	185	140
9	2	707	—761
9	—2	340	390
9	4*	43	—18
9	—4	837	868
	h 1 *l*		
1	0	472	—492
1	1	1025	—1045
1	2*	108	50
1	3	2147	—2043
1	4	984	1055
1	5	927	960
1	6	680	633
1	7	1344	1407
1	8	702	—704
1	9	1198	1177
1	10	1027	—1078
1	11	1524	—1572
1	12*	135	72
1	13	898	—941
1	14	872	916
1	15	259	224
1	16	460	513
1	17	1240	1390
1	18	520	—567
1	19	151	—123
2	0	506	—499
2	1	1019	—1109
2	—1	635	654
2	2	617	—649
2	—2	684	—737
2	3	352	—375
2	—3	874	914
2	4	416	477
2	—4	929	964
2	5	429	—386
2	—5	371	385
2	6	643	615
2	—6	279	—279
2	7	1294	1344
2	—7	1203	—1248
2	8*	139	167
2	—8*	139	86
2	9*	141	133
2	—9*	141	—70
2	10	1224	—1266
2	—10	323	271
2	11	675	—682
2	—11*	143	98
2	12*	138	—42
2	—12	456	446
2	13	720	—747
2	—13	833	844
2	14*	121	149
2	—14*	172	—192
2	15	580	607
2	—15*	109	—96
2	16	351	344
2	—16*	108	84

h	*l*	$10F_o$	$10F_c$
2	17	337	372
2	—17	451	—457
2	18*	67	26
2	—18	360	—405
3	0	612	681
3	1	520	537
3	—1	1542	—1517
3	2	442	413
3	—2*	118	—11
3	3*	173	153
3	—3	337	329
3	4	987	—976
3	—4	775	—781
3	5	1034	1060
3	—5	446	436
3	6	895	—927
3	—6	518	—545
3	7	783	—751
3	—7	809	828
3	8	836	835
3	—8	710	748
3	9	442	—434
3	—9	820	—799
3	10	1125	1105
3	—10	413	405
3	11	379	—367
3	—11*	138	—74
3	12*	186	200
3	—12	666	—667
3	13	1005	1041
3	—13	443	—457
3	14	527	—594
3	—14	602	—623
3	15	213	—184
3	—15	741	784
3	16	526	—557
3	—16*	88	39
3	17*	109	—67
3	—17*	75	—35
3	18	179	173
3	—18	536	595
4	0	432	400
4	1	669	—674
4	—1	727	744
4	2*	169	201
4	—2	265	—267
4	3	955	—954
4	—3	606	604
4	4	485	481
4	—4	419	422
4	5*	188	216
4	—5*	170	150
4	6	282	—174
4	—6*	156	76
4	7	1046	1001
4	—7	803	—788
4	8	352	—315
4	—8*	139	—132
4	9*	156	91
4	—9	465	—423
4	10	530	—521
4	—10	576	—575
4	11	551	—531
4	—11	473	448
4	12	369	350
4	—12*	116	95
4	13	625	—619
4	—13	601	608
4	14	329	311
4	—14	324	291
4	15	360	338
4	—15	207	—202
4	16	240	235
4	—16	419	438
4	17	511	583
4	—17	318	—344
5	0	1104	—1049
5	1	1198	—1154
5	—1	754	701
5	2	546	—511

h	*l*	$10F_o$	$10F_c$
5	—2*	161	—197
5	3	1177	—1092
5	—3	1466	1397
5	4	1135	1094
5	—4	547	527
5	5	636	586
5	—5*	155	—126
5	6	471	417
5	—6	370	331
5	7	953	898
5	—7	1015	—978
5	8*	197	—176
5	—8*	192	206
5	9	531	499
5	—9	867	—861
5	10	827	—802
5	—10	567	—558
5	11	859	—856
5	—11	734	730
5	12	500	—491
5	—12	251	221
5	13	783	—779
5	—13	1008	1055
5	14	391	390
5	—14	538	534
5	15	378	379
5	—15	195	—189
6	0*	130	118
6	1	339	—304
6	—1	890	—854
6	2*	173	93
6	—2*	136	—146
6	3*	147	122
6	—3	675	618
6	4*	160	—139
6	—4	249	—241
6	5	863	812
6	—5	236	221
6	6	564	—550
6	—6*	129	82
6	7	236	—176
6	—7	379	364
6	8	210	186
6	—8	337	337
6	9	287	—243
6	—9	550	—544
6	10	727	740
6	—10	184	—164
6	11	696	—687
6	—11	224	—219
6	12	325	315
6	—12	310	—302
6	13	548	574
6	—13*	82	—61
7	0	660	631
7	1	505	—455
7	—1	510	—473
7	2	547	523
7	—2	291	—240
7	3	611	575
7	—3	164	—160
7	4*	133	65
7	—4*	158	—137
7	5	306	284
7	—5	857	826
7	6	730	—725
7	—6	354	—325
7	7*	134	107
7	—7*	87	45
7	8*	125	—112
7	—8	353	324
7	9	655	—654
7	—9	319	—273
7	10*	61	15
7	—10*	77	—24
7	11*	65	2
7	—11	544	—550
8	0	546	—557
8	1	308	—267
8	—1	276	254

h	*l*	$10F_o$	$10F_c$
8	2	409	—467
8	—2	278	—270
8	3	1183	—1177
8	—3	1106	1068
8	4	521	537
8	—4	408	415
8	5	578	567
8	—5	351	—332
8	6	819	856
8	—6	486	492
8	7	593	571
8	—7	569	—546
	h 2 *l*		
2	0	362	—273
2	1*	130	171
2	2*	188	—196
2	3	1240	1363
2	4	1165	1244
2	5*	134	—108
2	6*	139	—51
2	7	1022	—1055
2	8	323	—255
2	9	667	—678
2	10	1055	—1083
2	11	922	955
2	12	297	294
2	13	509	501
2	14	630	645
2	15*	107	40
2	16	514	535
2	17	807	—851
2	18	634	—687
3	0	395	—337
3	1	595	619
3	—1	928	—383
3	2	600	—606
3	—2	1730	—1650
3	3	1303	1373
3	—3	1013	—1040
3	4	1743	1642
3	—4	937	969
3	5	246	—248
3	—5*	188	166
3	6*	136	48
3	—6	632	640
3	7	1132	—1125
3	—7	1118	1116
3	8	598	—561
3	—8	683	664
3	9	361	—343
3	—9	462	462
3	10	1325	—1323
3	—10	939	—933
3	11	680	679
3	—11	952	—948
3	12	728	722
3	—12	374	365
3	13	661	647
3	—13	575	—586
3	14*	102	71
3	—14*	143	—163
3	15*	131	—153
3	—15	420	397
3	16	508	518
3	—16	735	735
3	17	657	—717
3	—17	572	600
4	0	415	—383
4	1	757	—703
4	—1	1210	1202
4	2*	147	—23
4	—2	794	—774
4	3	670	—627
4	—3	753	716
4	4	347	332
4	—4	406	381
4	5	876	—841
4	—5	328	—323

TABLE II (*continued*).

h	l	$10F_o$	$10F_c$
4	6*	186	178
4	—6	785	759
4	7	1372	1247
4	—7	1482	—1457
4	8	397	—358
4	—8*	142	—111
4	9	439	428
4	—9	615	592
4	10*	131	38
4	—10	561	—535
4	11	332	—306
4	—11	572	591
4	12	688	694
4	—12	443	—414
4	13	850	—879
4	—13	562	558
4	14	197	131
4	—14*	121	—139
4	15	292	286
4	—15	676	—725
4	16	325	—348
4	—16	442	456
5	0	771	775
5	1	729	669
5	—1	282	235
5	2	536	—489
5	—2	483	—419
5	3	353	—286
5	—3	518	—474
5	4	951	897
5	—4	602	528
5	5	446	—436
5	—5	269	—210
5	6	588	—566
5	—6	447	—438
5	7*	128	—5
5	—7*	146	105
5	8*	140	55
5	—8	473	422
5	9	274	243
5	—9	310	242
5	10	779	—710
5	—10	906	—839
5	11	300	274
5	—11	213	184
5	12	596	564
5	—12	483	459
5	13	180	—138
5	—13	374	—336
5	14*	60	—28
5	—14	167	—133
6	0	791	—751
6	1*	126	114
6	—1	661	—627
6	2	212	194
6	—2	811	—774
6	3	1396	1323
6	—3	1170	—1164
6	4	801	779
6	—4	556	495
6	5*	130	83
6	—5	686	649
6	6	258	201
6	—6	338	317
6	7	892	—893
6	—7	867	897
6	8	245	—247
6	—8	349	340

h	l	$10F_o$	$10F_c$
6	9	879	—908
6	—9	300	282
6	10	853	—855
6	—10	239	—181
6	11	837	859
6	—11	943	—975
6	12*	60	66
6	—12	222	—218
7	0	219	—197
7	1*	88	31
7	—1	587	583
7	2*	164	101
7	—2	921	—852
7	3*	172	—161
7	—3	223	—206
7	4	548	511
7	—4	506	476
7	5	374	—376
7	—5	310	—311
7	6	465	—406
7	—6	331	324
7	7*	122	127
7	—7*	132	—113
7	8*	64	44
7	—8	500	479
7	9	252	280
7	—9	284	308
8	0	688	680
8	1*	86	27
8	—1	570	622
8	2	247	245
8	—2	641	—598
8	3	429	—467
8	—3	308	299
	h	3	*l*
3	0	1881	1752
3	1	512	544
3	2*	113	42
3	3	153	—94
3	4	865	—801
3	5	301	252
3	6	543	—469
3	7	545	—490
3	8*	167	93
3	9	205	178
3	10	473	423
3	11*	126	—113
3	12	393	353
3	13	417	406
3	14	676	—669
3	15	312	—292
4	0	1436	1347
4	1	610	537
4	—1	338	303
4	2	199	161
4	—2	405	—368
4	3	337	—300
4	—3*	169	—66
4	4	689	—642
4	—4	1012	—966
4	5	292	—267
4	—5	743	—713
4	6	994	—965
4	—6	913	—895
4	7	472	—430
4	—7	264	214

h	l	$10F_o$	$10F_c$
4	8	601	565
4	—8	1007	960
4	9	627	600
4	—9	199	186
4	10	675	638
4	—10	1033	1062
4	11	302	254
4	—11	401	376
4	12	222	169
4	—12	397	363
4	13	195	—137
4	—13	309	—253
4	14	1071	—1100
4	—14	1017	—1082
5	0*	140	—106
5	1	762	716
5	—1*	201	—216
5	2	1139	—1088
5	—2*	145	—95
5	3	501	483
5	—3	644	—621
5	4*	171	87
5	—4	1265	1211
5	5	472	—417
5	—5	390	—328
5	6	387	361
5	—6	370	—337
5	7	665	—646
5	—7	537	502
5	8	905	892
5	—7	441	—488
5	9*	97	64
5	—9	592	558
5	10	590	—522
5	—10	666	—623
5	11	511	499
5	—11	198	—172
5	12	153	74
5	—12	545	545
5	13	323	352
5	—13	543	—597
6	0	195	—124
6	1	547	501
6	—1	575	—534
6	2*	130	—95
6	—2	475	447
6	3	154	99
6	—3*	89	1
6	4*	89	—28
6	—4	609	580
6	5	282	250
6	—5	404	—329
6	6	248	202
6	—6	403	—371
6	7	704	—677
6	—7	692	643
6	8	192	176
6	—8	545	—541
6	9	235	195
6	—9	108	—108
6	10	455	—469
6	—10	153	—146
7	0	853	846
7	1	290	246
7	—1	406	426
7	2*	79	67
7	—2	483	—444
7	3	335	—339

h	l	$10F_o$	$10F_c$
7	—3*	75	—27
7	4*	58	—24
7	—4	358	—357
7	5	395	—411
7	—5	324	—314
	h	4	*l*
4	0	772	694
4	1	507	—551
4	2	387	361
4	3	207	189
4	4	426	—370
4	5	383	—327
4	6	503	—469
4	7	610	559
4	8*	102	34
4	9	326	—309
4	10	279	262
4	11	237	186
4	12*	67	35
4	13	425	—400
5	0	651	—637
5	1	360	—323
5	—1	203	152
5	2	796	—736
5	—2*	110	9
5	3	631	—572
5	—3	814	742
5	4	355	355
5	—4	1022	963
5	5*	103	12
5	—5*	103	—40
5	6	805	780
5	—6	413	—316
5	7	716	659
5	—7	632	—574
5	8	560	489
5	—8	416	—374
5	9	421	335
5	—9	237	—240
5	10	1099	—1020
5	—10*	67	—26
6	0	455	400
6	1	694	—689
6	—1	299	—264
6	2	312	—242
6	—2	185	140
6	3	115	98
6	—3	220	227
6	4	656	—639
6	—4	145	66
6	5	562	568
6	—5	833	779
6	6	180	—189
6	—6	439	—374
6	—7	297	—219
	h	5	*l*
5	0	412	453
5	1	471	—554
5	2	390	—400
5	3	557	—635
5	4	676	769
5	5	222	223
5	6	497	—558
5	7	402	541

CRYSTAL STRUCTURE DESCRIPTION AND DISCUSSION.

Fig. 1 shows a clinographic projection of the trigonal cell. As one can see the most prominent feature of the structure consists of layers of polyhedra parallel to (0001). Two kinds of layers are present: layer A, formed

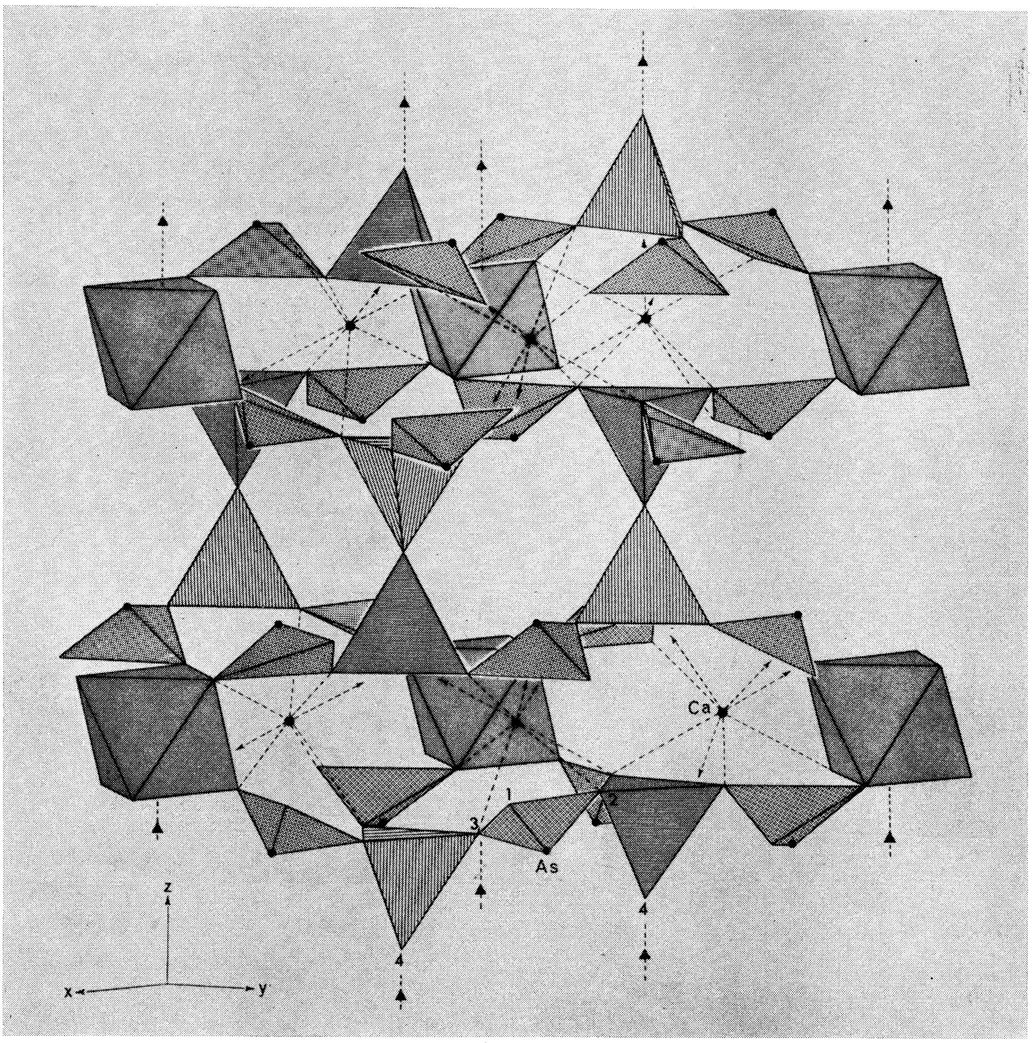

Fig. 1. – Clinographic projection of the trigonal cell (with a rotation angle ϑ of $18°16'$ about the triad axis and an elevation angle φ of the same axis of $6°20'$).

by BeO_4 tetrahedra, SiO_4 tetrahedra and AsO_3 pyramids, and layer B, formed by $(Ti, Sn)O_6$ octahedra and CaO_8 square antiprisms. Two A layers, placed upon each other, are inverted with respect to a symmetry centre, and they are connected by a common vertex of the BeO_4 and SiO_4 tetrahedra, so forming $(BeSiO_7)$ groups. Layer B acts as a bridge between pairs of these double A layers.

In order to explain better the structural model, the polyhedra contained in limited slabs of the unit cell, projected on a plane normal to the *c* axis are presented in fig. 2–3–4.

Fig. 2 shows the projection of the cell slab which includes the A layer of the BeO_4, SiO_4 and AsO_3 polyhedra. The two tetrahedra BeO_4 and SiO_4

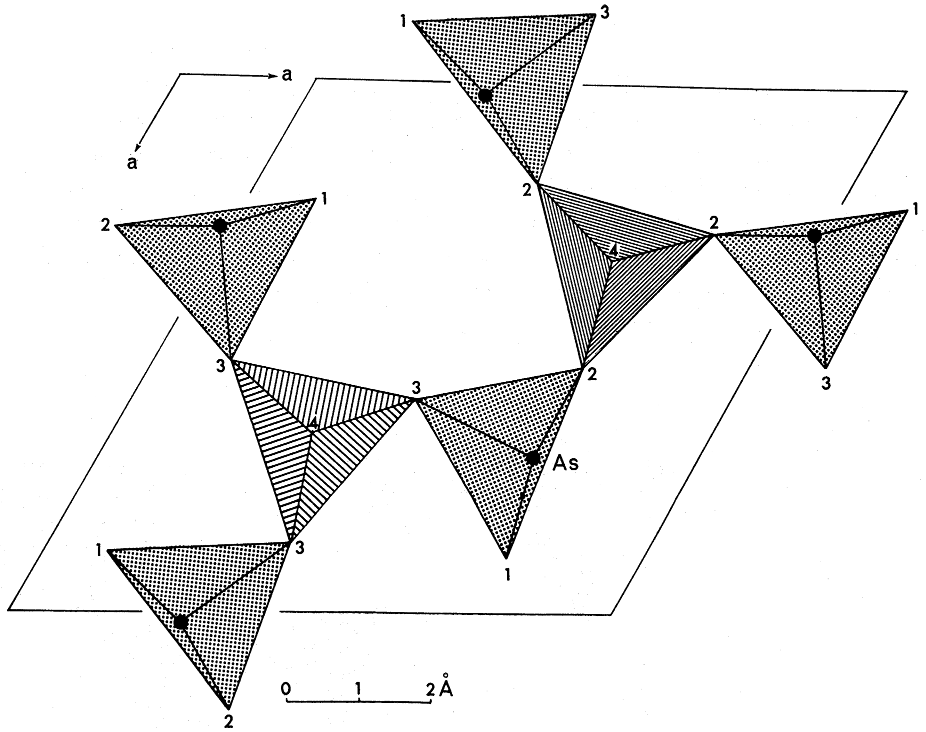

Fig. 2. – Projection of the cell slab with —0.03< z/c< 0.20, showing the A layer of polyhedra.

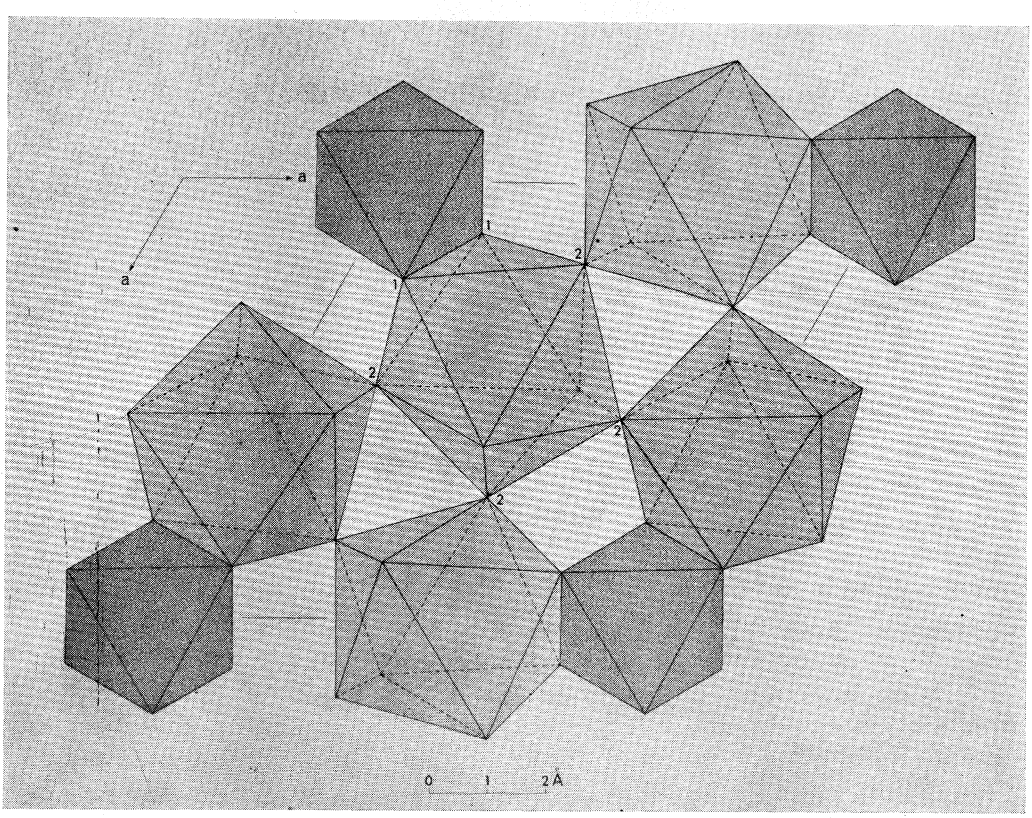

Fig. 3. – Projection of the cell slab with 0.11 < z/c < 0.38, showing the B layer of polyhedra.

have the beryllium and silicon atoms on a triad axis; owing to their position, three vertices of each tetrahedra are occupied by equivalent oxygens (O(2) for BeO_4 and O(3) for SiO_4); the fourth oxygen O(4), common to both tetrahedra, is aligned along the three-fold axis with the Be and Si atoms. The arsenic is situated on the vertex of a sort of trigonal pyramid and the remaining three vertices are occupied by independent oxygens (O(1), O(2), O(3)) belonging respectively to the titanium octahedron and, as said above, to the beryllium and silicon tetrahedra.

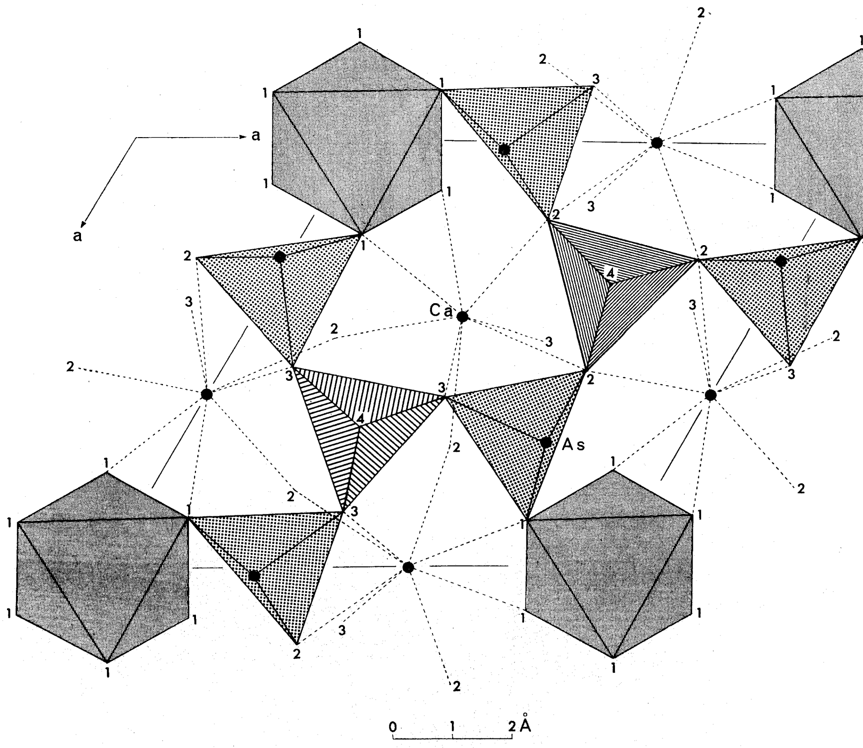

Fig. 4. – Projection of the cell slab with $-0.03 < z/c < 0.38$, showing the connections between the antiprism of calcium and the other polyhedra.

The B layer of the remaining groups of polyhedra is represented in fig. 3. The (Ti, Sn) atom, lying on $\bar{3}$, co-ordinates six equivalent oxygens O(1) in a nearly regular octahedron, whereas the Ca atom, which lies on a diad axis, is connected with eight oxygens and forms a coordination polyhedron that could be described as a square antiprism. Each CaO_8 polyhedron is always joined to four equivalent Ca polyhedra by means of four vertices occupied by O(2) and is also connected with a common edge to a (Ti, Sn) octahedron.

It is possible to understand more clearly the various connections between the antiprism of calcium and the other polyhedra from fig. 4, consisting of the overlying of fig. 2 and 3. The connections occur by edges as well as by vertices. In fact the CaO_8 antiprism, besides the edge O(1)—O(1) in common with the octahedra, has two more edges O(2)—O(2) in common with two BeO_4 tetrahedra, and also it shares two vertices O(3) with respectively a tetrahedron SiO_4 and a pyramid AsO_3.

From the structural arrangement of the atoms, the chemical formula results:

$$Ca_6As_{12}(Ti\,,Sn)_2\,Si_4Be_4O_{40}.$$

Owing to the presence of the anionic group ($SiBeO_7$) the formula could be modified as follows:

$$Ca_3As_6(Ti,Sn)[O_{13}\,SiBeO_7].$$

On the other hand, if one regards the layer arrangement of the polyhedra and by assigning an anionic character to the A layer, the previous formula could be written:

$$Ca_3(Ti\,,\,Sn)[(As_3SiBeO_{10})_2];$$

consequently two of these formula units are present in the unit cell. However only a new chemical analysis could definitively confirm the results of the structural study, but the amount of material at our disposal is not enough to permit a new analysis.

The bond lengths and angles.—The (Ti, Sn) octahedron is nearly regular; the Ti–O(1) distance between the cation and surrounding oxygens measures 1.970 Å.

The eight fold coordination polyhedron of Ca forms a very irregular square antiprism, whose bases have sides of different lengths ranging from 2.5 Å to 3.2 Å and the Ca—O distances from 2.433 to 2.560 Å.

The polyhedron of arsenic is not regular: in each «trigonal» pyramid the distance As—O(3) (1.846 Å) is somewhat longer than the two others (As–O(1) 1.787 Å and As–O(2) 1.757 Å). The same coordination of As^{3+} has been found in finnemanite [6].

Also beryllium and silicon tetrahedra are not perfectly regular: the two distances Be–O(2) and Si—O(3) are respectively 1.668 and 1.654 Å, but the O(4) forms distances noticeably shorter than the preceding ones, 1.530 Be–O(4) and 1.580 Å Si—O (4).

The bond angles are listed in Table III.

TABLE III.

Interatomic angles (°) and their standard deviations (in parentheses).

O(2)BeO(4)	113°42′ (50′)	O(1)AsO(2)	102°50′(20′)
O(2)BeO(2)′	104°56′(1°30′)	O(1)AsO(3)	94°55′(21′)
O(3)SiO(4)	114° 1′ (17′)	O(2)AsO(3)	90° 6′(21′)
O(3)SiO(3)′	104°34′ (49′)		
		O(1)TiO(1)′	178° 2′(38′)
SiO(3)As	127°38′ (24′)	O(1)TiO(1)″	91°39′(38′)
SiO(4)Be	180°	O(1)TiO(1)‴	89°45′(38′)
		O(1)TiO(1)⁗	88°52′(38′)

The balance of charges.—Some remarks can be made on the electrostatic equilibrium of the crystal structure. As it can be seen in Table IV, in which are reported the bond lengths, ordered according to their electrostatic polarity, the balance of the electrostatic charges on the oxygens atoms is not seemingly satisfied: the sum of the positive charges is 1.92 on O(1), 2.00 on O(2), 2.25 on O(3), and 1.50 on O(4).

TABLE IV.

Bond lengths (Å) ordered according to their electrostatic polarity (standard deviations in parentheses).

	Neutral oxygen atoms O(1) and O(2)	Overbonded oxygen atoms O(3)	Underbonded oxygen atoms O(4)
Ti	(6) TiO(1) 1.970 (6)		
Ca	(2) CaO(1) 2.433 (6)	(2) CaO(3) 2.471 (7)	
	(2) CaO(2) 2.560 (7)		
	(2) CaO(2)′ 2.435 (9)		
As	(1) AsO(1) 1.787 (7)	(1) AsO(3) 1.846 (7)	
	(1) AsO(2) 1.757 (8)		
Be	(3) BeO(2) 1.668(12)		(1) BeO(4) 1.530(23)
Si		(3) SiO(3) 1.654 (9)	(1) SiO(4) 1.580(13)

Actually a close relationship can be observed between the concentration of either positive or negative charge on the oxygen atoms, and the lengths of the cation–oxygen distances, that are respectively long or short; that is, the Pauling–Zachariasen [7] rule is well verified in this crystal structure.

The electronic mechanism that underlies such variable bond lengths can be different for the different cations, and, as Pant [8] observes, in a single cation–oxygen distance more than one mechanism could act for achieving the valency balance.

In the case of the SiO_4 system, the d–p π double bond theory put forward by Cruickshank [9] is consistent with the data presented here. In fact, the Si–O(4)–Be angle of 180°, imposed by a triad, favours a very good π–overlapping. On the other hand the O(3) atoms that connect silicon and arsenic can share their p–electrons with both the latter atoms, since also arsenic has d–orbitals available; then the double bond π–character of the Si–O(3) (As) bond is lower than the one of the Si–O(4) (Be). The Si–O(4) (Be) distance is very short (1.580 Å) whereas the Si–O(3) (As) is very long (1.654 Å); then, without excluding the possibility for other electronic mechanisms, the Cruickshank d–p π theory can be accepted as a work hypothesis for the SiO_4 system. Of course this mechanism cannot be put forward to explain the variability of the lengths of the BeO_4 system.

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