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ALESSANDRO CODA, ALBERTO DAL NEGRO, GIUSEPPE ROSSI

The crystal structure of krauskopfite

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Mineralogia. — *The crystal structure of krauskopfite* [*]. Nota di ALESSANDRO CODA, ALBERTO DAL NEGRO e GIUSEPPE ROSSI, presentata [**] dal Socio G. CAROBBI.

RIASSUNTO. — La krauskopfite, minerale con formula $BaSi_2O_5 \cdot 3H_2O$, è monoclina, con quattro unità stechiometriche nella cella elementare; il gruppo spaziale è $P2_1/c$ e le costanti reticolari sono $a = 7{,}837$, $b = 10{,}622$, $c = 8{,}460$ Å, $\beta = 94°32'$. La struttura cristallina è stata studiata con i raggi X, utilizzando circa 1000 riflessioni indipendenti, registrate con la camera di Weissenberg. Le coordinate degli atomi di bario sono state ricavate analizzando le sintesi di Patterson bidimensionali, e la risoluzione della struttura cristallina è avvenuta attraverso l'esame delle sintesi di Fourier tridimensionali ottenute con le fasi relative ai soli atomi di bario.

Il raffinamento delle coordinate e dei parametri termici anisotropi è stato effettuato con il metodo dei minimi quadrati (matrice completa). Il fattore di discordanza finale è $R = 0{,}047$, se si considerano le sole riflessioni osservate.

La krauskopfite è un inosilicato; ogni atomo di silicio è direttamente legato a un ossidrile, per cui la formula chimica si può scrivere come $Ba[Si_2O_4(OH)_2] \cdot 2H_2O$. Ogni atomo d'idrogeno forma un legame idrogenico; un'ipotesi sul sistema di ponti a idrogeno è stata costruita attraverso considerazioni sulle valenze elettrostatiche. Gli atomi di bario hanno coordinazione nove, e sono collegati in strati.

INTRODUCTION.

Krauskopfite is a hydrous barium silicate, with formula $BaSi_2O_5 \cdot 3H_2O$, recently found—for the first time—in Eastern Fresno County, California [1]. It is described as a typical vein-forming mineral occurring within or closely associated with sanbornite-quartz rock. Its appearance and properties are fully described by Alfors et al. [1]; we shall report here only those features that are necessary for the subsequent discussion.

The space group is $P2_1/c$, and the lattice parameters are:

$$a = 7.837 \pm 0.004 \text{ Å}$$
$$b = 10.622 \pm 0.006 \text{ Å}$$
$$c = 8.460 \pm 0.005 \text{ Å}$$
$$\beta = 94° \, 32' \pm 8'.$$

Each unit cell contains four stoichiometric units:

$$Z = 4 \, [BaSi_2O_5 \cdot 3H_2O].$$

The mineral occurs in fragments elongated following [001].

The cleavages are: {010} perfect, {100} perfect. The density is 3.14 ± 0.02 g/cm³.

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

(**) Nella seduta del 21 giugno 1967.

This investigation, concerning the crystal structure of krauskopfite, was undertaken to establish its position in the crystallochemical classification of the silicates.

EXPERIMENTAL.

The specimen.—No chemical analysis nor redetermination of the unit cell parameters were undertaken on the sample used for this investigation. The crystal chosen for the structure determination belonged to a specimen from Rush Creek locality, Fresno County. It was a colorless prismatic fragment elongated following [001]; its section cut normally to c, in the portion bathed by the X–rays, was a rectangle whose sides, approximately parallel to the a and b directions, were respectively 0.072 and 0.024 mm long.

Recording and measurement of the intensities.—The crystal was rotated about the c axis, and Weissenberg equi-inclination integrating photographs were obtained for reciprocal lattice levels from $l = 0$ to $l = 8$, using nickel-filtered copper radiation and the multiple-film technique. The X–ray beam did not bathe the full length of the crystal. The integration range was adjusted to correct for the spot contraction at the higher levels; the very few reflections elongated rather than contracted on the side of the " contraction effect " were discarded.

A total of 1413 reflections out of about 1630 present in the CuKα limiting sphere (87 %) were inspected; 1086 of them were measured with a Nonius microdensitometer, the remaining ones were too weak to be observed.

Precession pictures of the reflections $0\,k\,l$ were also recorded with the MoKα radiation for use in the preliminary work.

Correction and scaling of the intensities.—The intensities were corrected for the Lorentz-polarization and absorption factors, and for the incipient but incomplete $\alpha_1 — \alpha_2$ spot doubling.

The absorption correction factors were obtained through an exact integration over the whole diffracting volume—considered as continuous—of the crystal; the formulas used are those given by Cannillo and Mazzi (1967) [2]. The linear absorption coefficient of krauskopfite is $\mu = 481\ \text{cm}^{-1}$ for CuKα, and the transmission factors, on a relative scale, varied from 1 to 8.

The correction applied for the $\alpha_1 — \alpha_2$ splitting-effect is consistent with the application of the integration technique, that complicates the splitting-effect for its diagonal direction with respect to the sides of the film.

A secondary extinction correction was also applied at an advanced stage of the refinement.

The intensities for the different levels were put approximately on the absolute scale by the Wilson method; after each structure factor calculation the scale factor was improved by the criterion $\Sigma F_o = \Sigma F_c$, applied separately to each level.

THE STRUCTURE ANALYSIS.

Patterson projections along [100] and [001] were first computed; they gave full information on the coordinates of the barium atoms. The electron-density projections calculated by attributing the signs of the barium contributions to the experimental moduli $|F_o|$ of the $0kl$ and $hk0$ structure factors gave unexpectedly no further consistent information.

However a F_o three-dimensional Fourier synthesis carried out with the signs of the barium contributions supplied the structure map straightforward. Some unfavorable superpositions explained the failure of the preceding attempt.

The coordinates were improved by a Fourier synthesis carried out with the phases given by the bulk of the atoms. A structure factor calculation with the coordinates so obtained gave an overall disagreement index of 14 %.

THE REFINEMENT STAGE.

The least-squares method was used in order to refine the positional parameters and the individual temperature factors. At first five isotropic cycles were accomplished on an Olivetti ELEA 6001 computer, using a full-matrix program by Sgarlata [3]. Then the last two cycles were carried out using the Busing and Levi program for IBM 7040 and taking into account anisotropic thermal parameters.

The progress in the refinement is indicated by the steps that follow (some discussion on particular items is assembled below); R_{tot} is the disagreement index referred to the whole of the structure factors, and R_{obs} refers only to the observed ones:

Starting point: $R_{tot} = 0.140$; $R_{obs} = 0.118$

(1) 1st cycle: non-ionic scattering factors; isotropic temperature factors; hydrogen atoms excluded; no weighting scheme: $R_{tot} = 0.101$; $R_{obs} = 0.075$;

(2) 2nd cycle: the unobservably weak reflections are excluded: $R_{obs} = 0.066$;

(3) 3rd cycle: same conditions as for the 2nd cycle: $R_{obs} = 0.065$;

(4) the scattering factors for Ba^{++} and the hydrogen parameters are included in the structure factor calculation: $R_{obs} = 0.065$;

(5) a secondary extinction correction is applied: $R_{obs} = 0.061$;

(6) the anomalous dispersion correction for barium is applied: $R_{obs} = 0.058$;

(7) 4th cycle: 27 reflections with the highest $F_o — F_c$ values are excluded (starting $R_{obs} = 0.050$) : $R_{obs} = 0.046$;

(8) 5th cycle: conditions as for the 4th cycle: $R_{obs} = 0.046$;

(9) 6th cycle: barium, silicon and oxygen are considered as fully ionized (Ba^{++}, Si^{4+}, O^{--}); thermal anisotropic parameters are considered and refined; a weighting scheme is adopted: $R_{obs} = 0.042$;

(10) 7th cycle: conditions as for the 6th cycle: $R_{obs} = 0.043$.

TABLE I. – *Structure factors of krauskopfite.*

Reflections marked with a dot were unobservably weak; in this case F_o derives from 0.5 I_{min}.
The sign ″ marks the reflections excluded during the least-squares refinement.

h±	k	$10F_o$	$10F_c$
h k 0			
2	0	1275	-1345
3	0	1497	-1554
4	0	1182	1220
5	0	573	557
6	0	702	700
7	0	857	-864
8	0	327	-297
9	0	339	335
2	1	996	-1023
3	1	795	819
4	1	1096	1130
5	1	220	-191
6	1	1058	-1000
7	1	239	-206
8	1	675	663
9	1"	331	406
1	2.	53	-8
0	2	1049	-1089
2	2	1098	1157
3	2	243	230
4	2.	124	-27
5	2.	108	-40
6	2.	135	-40
7	2.	113	13
8	2	399	367
9	2.	92	-81
1	3	1021	-1082
2	3	351	-365
3	3	258	225
4	3	344	326
5	3.	140	-84
6	3	326	288
7	3	396	-362
8	3	174	161
9	3	223	220
0	4	1758	-1948
1	4	383	-394
2	4	989	1048
3	4	1015	1051
4	4	502	-498
5	4	961	-995
6	4.	179	-165
7	4	1077	1070
8	4.	96	39
9	4	351	-336
1	5	1678	1814
2	5	717	696
3	5	1008	-1033
4	5	746	-751
5	5	240	205
6	5	578	550
7	5	543	509
8	5	431	-425
9	5	608	-664
0	6	837	856
1	6	249	237
2	6	953	-943
3	6	927	-890
4	6	288	233
5	6	980	968
6	6.	149	-41
7	6	751	-759
8	6	315	-310
1	7	658	-653
2	7	188	165
3	7	529	500
4	7.	146	-9
5	7.	179	-88
6	7.	185	-167
7	7	200	-159
8	7.	76	52
0	8	1029	1053
1	8	331	-323
2	8	549	-511
3	8	365	-293
4	8	308	327
5	8.	188	-138
6	8.	167	156
7	8	333	-346
1	9	630	-637
2	9	623	-621
3	9	338	301
4	9	863	872
5	9.	190	-169
6	9	530	-534
7	9	238	-230
0	10	1085	-1066
1	10	271	-271
2	10	1169	1089
3	10	253	184
4	10	385	-392
5	10	623	-662
6	10.	92	-36
1	11	561	539
2	11	434	397
3	11	372	-375
4	11	549	-596
5	11.	96	26
0	12.	154	-25
1	12	194	202
2	12	409	-415
3	12	205	214
1	13	218	243
2	13.	126	67
h k 1			
1	1	536	-484
1-	1	778	762
2	1	913	-382
2-	1	194	-189
3	1.	132	115
3-	1	405	-389
4	1	799	836
4-	1	342	-330
5	1	492	477
5-	1	730	723
6	1	351	-343
6-	1	760	717
7	1	552	-537
7-	1	312	-283
8	1	.103	64
8-	1	556	-493
9	1	354	353
9-	1.	84	-46
1	2"	2278	-2053
1-	2	371	417
2	2	1052	1002
2-	2	2155	1977
3	2	2110	2136
3-	2	208	-187
4	2	868	882
4-	2	992	-1018
5	2	1560	-1579
5-	2	624	-600
6	2	478	-458
6-	2	1023	1047
7	2.	141	141
7-	2	748	722
8	2	868	905
8-	2.	181	-58
9	2.	82	51
9-	2	846	-842
0	3	1198	-1224
1	3	718	690
1-	3	955	-947
2	3	1551	1528
2-	3	488	492
3	3.	97	18
3-	3	1157	1206
4	3	1052	-1048
4-	3	572	536
5	3	703	-674
5-	3	856	-896
6	3	678	676
6-	3	1104	-1072
7	3	757	733
7-	3	567	541
8	3.	98	-79
8-	3	830	749
9	3	611	-608
9-	3	188	165
0	4	691	693
1	4	1455	1447
1-	4.	79	-10
2	4	278	-251
2-	4	726	-742
3	4	825	-828
3-	4.	100	19
4	4	275	-271
4-	4	691	682
5	4	805	819
5-	4	414	411
6	4	483	467
6-	4	264	-247
7	4	106	-70
7-	4	492	-474
8	4	346	-348
8-	4	242	210
9	4.	73	-75
9-	4	399	389
0	5.	76	-46
1	5	462	456
1-	5	293	262
2	5.	91	13
2-	5	492	-464
3	5	181	-162
3-	5.	140	-100
4	5.	131	-54
4-	5	317	-292
5	5	239	-249
5-	5	292	283
6	5.	131	27
6-	5	218	-209
7	5.	112	-33
7-	5	234	213
8	5	207	182
8-	5.	127	104
0	6	176	168
1	6	1142	1142
1-	6.	86	-5
2	6	290	-246
2-	6	1077	-1130
3	6	726	-669
3-	6	576	514
4	6	407	-360
4-	6	650	658
5	6	921	939
5-	6	592	559
6	6	225	199
6-	6	737	-710
7	6.	97	-39
7-	6	260	-252
8	6	493	-517
8-	6.	113	-83
0	7	902	908
1	7	859	-872
1-	7	687	673
2	7	1249	-1239
2-	7.	140	-117
3	7.	124	-13
4	7	987	961
4-	7	382	-365
5	7	627	585
5-	7	523	493
6	7	512	-521
6-	7	782	738
7	7	624	-606
7-	7	495	-463
8	7.	63	-26
8-	7	664	-649
0	8	901	-874
1	8	733	-711
1-	8	833	826
2	8	269	-248
2-	8	850	813
3	8	1245	1236
3-	8	237	219
4	8.	127	37
4-	8	1159	-1113
5	8	565	-531
5-	8	504	-445
6	8	643	-649
6-	8	478	445
7	8	418	426
7-	8	705	678
0	9	597	-580
1	9	245	203
1-	9	545	-517
2	9	687	650
2-	9.	127	90
3	9.	136	36
3-	9	491	469
4	9	601	-585
4-	9.	193	166
5	9.	177	-184
5-	9	378	-360
6	9	258	259
6-	9	298	-294
7	9	270	271
7-	9.	68	51
0	10.	128	44
1	10	317	-291
1-	10	260	-214
2	10.	134	163
2-	10.	134	117
3	10.	137	48
3-	10"	303	-236
4	10.	136	72
4-	10.	136	23
5	10	299	-304
5-	10.	117	-5
0	11	359	-324
1	11	291	251
1-	11	429	-405
2	11	435	406
2-	11.	129	114
3	11.	128	22
3-	11	369	367
4	11	343	-340
4-	11	231	222
5	11	293	-271
5-	11	365	-371
0	12	447	424
1	12	620	630
1-	12	496	-483
2	12.	160	-102
2-	12	626	-623
3	12"	766	-815
3-	12.	115	-97
4	12	174	-139
4-	12	622	591
0	13	451	433
1	13	214	-206
1-	13	533	558
2	13	594	-582
2-	13.	136	-118
h k 2			
1	0	1063	-1046
2	0	1963	-1820
2-	0	378	-328
3	0	1763	1768
3-	0	793	-821
4	0	774	809
4-	0	1624	-1720
5	0.	145	-107
5-	0	416	418
6	0	1852	-1922
6-	0	1259	1318
7	0	129	120
7-	0	381	365
8	0	463	450
8-	0	926	-971
9	0	619	639
9-	0	373	-387
0	1"	1529	-1388
1	1	134	89
1-	1	811	-754
2	1	421	425
2-	1	1764	1752
3	1	923	928
3-	1	1662	1663
4	1	147	-118
4-	1	840	-837
5	1	707	-732
5-	1	1057	-1042
6	1	310	-291
6-	1	182	162
7	1	673	716
7-	1	390	361
8	1	505	505
8-	1	487	485
9	1	389	-396
9-	1	219	-216
0	2	619	-550
1	2	517	506
1-	2	182	175
2	2	245	210
2-	2	334	-351
3	2	560	-530
3-	2	190	190
4	2	730	-739
4-	2.	140	63
5	2	351	333
5-	2	223	190
6	2	393	385
6-	2	664	-667
7	2.	142	-78
7-	2.	107	-66
8	2	192	-186
8-	2	346	347
9	2.	73	-92
9-	2	239	212
0	3	649	650
1	3	435	-408
1-	3.	56	-56
2	3	565	542
2-	3	643	628
3	3	490	460
3-	3	183	187
4	3	366	-370
4-	3	308	294
5	3	479	-435
5-	3	603	-623
6	3	334	327
6-	3.	117	31
7	3	340	336
7-	3	400	372
8	3.	87	26
8-	3	445	434
9	3.	92	74
9-	3	335	-343
0	4	173	140
1	4	1163	1184
1-	4	1955	1971
2	4	546	514
2-	4	449	-431
3	4	646	-612
3-	4	1039	1039
4	4	579	-600
4-	4	1278	1358
5	4	286	-246
5-	4	678	-704
6	4	1038	1066
6-	4	595	-606
7	4	336	322
7-	4	244	-203
8	4	585	-591
8-	4	440	432
9	4	582	-556
9-	4	157	167
0	5	949	1001
1	5	801	786
1-	5	552	534
2	5	844	-821
2-	5	851	-876
3	5	1125	-1081
3-	5	979	-963
4	5	722	710
4-	5	482	485
5	5	1237	1258
5-	5	1230	1286
6	5.	164	-152
6-	5	262	236
7	5	679	-690
7-	5	810	-838
8	5	257	-287
8-	5	473	-479
9-	5	588	556
0	6	228	-230
1	6	987	-988
1-	6	1219	1230
2	6	230	-218
2-	6	820	817
3	6	469	441
3-	6	899	910
4	6	800	782
4-	6	735	768
5	6.	133	157
5-	6	433	437
6	6	672	-670
6-	6	639	664
7	6	416	415
7-	6.	91	8
8	6	599	577
8-	6	273	-270
0	7	421	-421
1	7	390	-355
1-	7	163	151
2	7	418	399
2-	7	86	23
3	7	624	587
3-	7	258	231
4	7	243	-212
4-	7.	127	86
5	7	341	-344
5-	7	259	-244
6	7.	115	73
6-	7.	173	-142
7	7	177	177
7-	7	385	406
8	7.	50	-34
8-	7.	75	27
0	8	258	250
1	8	176	-128
1-	8	661	667
2	8	617	-606
2-	8	255	-245
3	8	585	568
3-	8.	155	142
4	8	245	235
4-	8	547	-551
5	8.	137	12
5-	8.	147	82
6	8	488	-467
6-	8	308	291
7	8	230	239
7-	8	251	252
8-	8	338	-356
0	9	642	-611
1	9.	106	-51
1-	9	648	-651
2	9	514	488
2-	9	918	911
3	9	313	325
3-	9	559	526
4	9	229	-212
4-	9	522	-538
5	9	590	-613
5-	9	671	-699
6	9	201	-187
6-	9	177	176
7	9	511	513
7-	9	304	283
0	10	307	-273
1	10	1011	982
1-	10	705	-706
2	10	632	627
2-	10	454	-458
3	10	426	-405
3-	10	465	457
4	10"	863	-940
4-	10	712	731
5	10	260	273
5-	10.	98	26
6	10	609	585
6-	10	778	-758
0	11	664	643
1	11.	98	-85
1-	11	251	237
2	11	560	-536
2-	11	591	-590
3	11	349	-344
3-	11	523	-538
4	11.	93	67
4-	11	473	489
5	11	527	501
5-	11	322	298
0	12	226	214
1	12	312	-293
1-	12.	143	-89
2	12.	161	-136
2-	12	248	263
3	12.	145	-70
3-	12.	105	-65
4	12	414	425
4-	12.	118	-98
0	13	172	158
1	13	165	135
1-	13.	98	-41
2	13.	106	-118
2-	13.	73	-69
h k 3			
0	1	1221	-1255
1	1	1344	-1362
1-	1	301	250
2	1	256	248
2-	1	812	854
3	1	547	566
3-	1.	104	65
4	1	166	146
4-	1	760	-773
5	1	385	-363
5-	1	525	-495
6	1	564	-561
6-	1	245	223
7	1.	95	87
7-	1	461	446
8	1	400	393
8-	1	241	-219
9	1.	64	12
9-	1	386	-371
0	2	1656	-1636
1	2	791	772
1-	2	1532	-1629
2	2	1243	1282
2-	2	508	512
3	2	590	595
3-	2	1680	1771
4	2	1382	-1411
4-	2.	177	-113
5	2	449	-437
5-	2	709	-720
6	2	395	348
6-	2	628	-641
7	2	967	907
7-	2	438	424
8	2	299	-276
8-	2	640	634
9	2	580	-541
9-	2	165	140
0	3	1426	1533
1	3	1372	1417
1-	3	907	-1006
2	3	657	-617
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4-	1	648	-693
5	1	202	220
5-	1	472	459
6	1	657	-731
6-	1	531	514
7-	1.	63	12
0	2	340	-338
1	2	404	-353
1-	2	281	273
2	2.	208	195
2-	2.	89	65
3	2	317	290
3-	2.	139	131
4	2	241	-235
4-	2.	127	-67
5	2	195	-220
5-	2	259	-240
6	2	117	132
6-	2	249	-214
7-	2	298	289
0	3	211	176
1	3.	97	-76
1-	3	547	561
2	3	433	-399
2-	3"	307	-238
3	3	414	390
3-	3.	114	51
4	3.	160	173
4-	3	412	-381
5	3.	121	-130
5-	3.	159	-116
6-	3	238	201
7-	3	341	378
0	4	606	-564
1	4	202	-145
1-	4	197	-183
2	4	349	315
2-	4	650	582
3	4	516	487
3-	4"	712	615
4	4.	102	-134
4-	4"	605	-496
5	4"	320	-460
5-	4	585	-589
6-	4	206	171
0	5	283	-237
1	5	766	760
1-	5	827	-836
2	5	668	702
2-	5.	95	-95
3	5	453	-516
3-	5	589	496
4	5	640	-708
4-	5	790	707
5	5	171	228
5-	5.	92	-94
6-	5	607	-645
0	6	573	555
1	6.	180	176
1-	6	341	301
2	6	286	-343
2-	6	656	-587
3	6	298	-359
3-	6	516	-463
4	6.	71	36
4-	6	472	429
5-	6	552	555
0	7	304	271
1	7	309	-325
1-	7.	107	-12
2	7.	167	-226
2-	7.	127	95
3	7.	126	158
3-	7.	125	-36
4-	7.	92	27
5-	7	175	-177
0	8.	154	204
1	8	210	268
1-	8.	149	-150
2	8.	103	-167
2-	8.	103	-3
0	9.	124	-139
1	9	289	-339
1-	9	616	678
2-	9	201	205

The last variations in the parameters were ten times (or less) lower than the standard deviations; so, at this point, the refinement was stopped.

After the reintroduction of the reflections excluded at (7) and a new rescaling, the final unweighted R–factors were:

$$R_{tot} = 0.070 \qquad R_{obs} = 0.047$$

The final observed and calculated structure factors are compared in Table I.

The atoms were considered as fully ionized following a discussion by Verhoogen [4].

The secondary extinction correction was applied because a plot of $\ln I_o/I_c$ for the 143 most intense reflections showed a secondary extinction effect that was not negligible. A linear relation between $\ln I_o/I_c$ and I_c was assumed and a least-squares secondary extinction coefficient derived. This was applied to all the F_o's by means of the formula:

$$(F_o)_{corr} = (F_o)_{ext} \cdot \exp\left(\frac{1}{2}\,\varepsilon I_c\right)$$

where $\varepsilon = 2.77 \cdot 10^{-6}$.

The anomalous dispersion correction for Ba^{++} was carried out by the method proposed by Patterson [5]; $\Delta f'$ and $\Delta f''$ are given by Cromer [6].

TABLE II.

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

	x/a	*y/b*	*z/c*
Ba	0.20617 (6)	0.14932 (5)	0.12217 (6)
Si(I)	0.49067 (29)	0.38317 (22)	0.27346 (31)
Si(II)	0.70113 (29)	0.24619 (23)	0.53086 (29)
O(1)	0.5351 (9)	0.2885 (6)	0.1273 (8)
O(2)	0.5205 (9)	0.5275 (6)	0.2182 (8)
O(3)	0.3071 (8)	0.3494 (6)	0.3190 (9)
O(4)	0.6407 (8)	0.3676 (6)	0.4175 (9)
O(5)	0.7659 (9)	0.1299 (6)	0.4325 (9)
O(6)	0.8566 (8)	0.2926 (6)	0.6594 (8)
O(7)	0.1253 (9)	0.1183 (7)	0.4587 (9)
O(8)	0.9930 (9)	0.4335 (7)	0.3292 (9)

Table III.

Hydrogen atom parameters postulated for the calculation of the final structure factors.

	x/a	y/b	z/c	B (Å^2)
H(1)	0.1182	0.4001	0.3248	2.5
H(2)	0.9442	0.3533	0.2682	2.5
H(3)	0.9915	0.1220	0.4494	2.5
H(4)	0.1653	0.0275	0.4984	2.5
H(5)	0.8197	0.1761	0.2695	2.5
H(6)	0.5901	0,0663	0.3403	2.5

Table IV.

Final anisotropic thermal parameters ($\times 10^4$) *and their standard deviations (in parentheses).*

The anisotropic temperature factors are in the form:

$$\exp\left[-\left(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2\,hk\,\beta_{12} + 2\,hl\,\beta_{13} + 2\,kl\,\beta_{23}\right)\right]$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	54 (1)	29 (1)	42 (1)	—1 (0)	2 (1)	0 (0)
Si(I)	41 (3)	20 (2)	37 (4)	0 (2)	1 (3)	2 (2)
Si(II)	44 (3)	25 (2)	30 (3)	0 (2)	3 (2)	4 (2)
O(1)	88 (10)	34 (6)	40 (10)	0 (6)	8 (8)	0 (6)
O(2)	84 (11)	32 (6)	67 (12)	5 (6)	—12 (8)	6 (6)
O(3)	63 (10)	35 (5)	57 (11)	5 (6)	13 (8)	6 (6)
O(4)	73 (11)	23 (5)	61 (11)	2 (6)	2 (8)	8 (5)
O(5)	97 (12)	37 (6)	53 (11)	8 (6)	16 (8)	5 (6)
O(6)	70 (10)	40 (6)	32 (9)	4 (6)	11 (7)	11 (6)
O(7)	93 (11)	53 (6)	65 (12)	—9 (7)	3 (9)	4 (7)
O(8)	85 (11)	44 (6)	78 (12)	2 (7)	5 (8)	—2 (7)

The weighting scheme used in the last two cycles was:

$$\sqrt{w} = \frac{1}{F_o} \qquad \text{if} \quad F_o > 4\,F_{o,\min}$$

$$\sqrt{w} = \frac{1}{\sqrt{4 \cdot F_{o,\min} \cdot F_o}} \qquad \text{if} \quad F_o \leq 4\,F_{o,\min}\,.$$

The positions of the hydrogen atoms were given choosing the bonds O—H on the basis of the hydrogen-bonding picture given below, and assuming a length of 1 Å for them.

The atomic and thermal parameters and their standard deviations are listed in the Tables II, III and IV. The analysis of the anisotropic thermal parameters is shown in Table V; of course the significance of the latter values is lessened by the criterion used in the scaling of the intensities ($\Sigma F_o = \Sigma F_c$, level by level).

TABLE V.

Analysis of the anisotropic thermal parameters.

(root mean square thermal vibrations along the ellipsoid axes (Å), magnitudes of the principal axes (Å²) and angles (°) between the crystallographic axes and the principal axes of the vibration ellipsoids).

Atom	r.m.s.	B	α	β	γ
Ba	0.13	1.30	63	34	111
	0.13	1.35	33	122	103
	0.12	1.18	72	78	25
Si(I)	0.11	0.99	31	67	74
	0.12	1.11	118	74	29
	0.10	0.87	103	28	113
Si(II)	0.12	1.07	4	89	91
	0.12	1.19	93	23	67
	0.10	0.79	93	113	23
O(1)	0.14	1.53	88	3	92
	0.17	2.15	7	92	88
	0.12	1.12	97	88	3
O(2)	0.15	1.75	61	50	57
	0.18	2.50	39	91	133
	0.12	1.22	113	40	119
O(3)	0.13	1.40	117	35	108
	0.16	1.96	60	56	51
	0.13	1.34	138	97	44
O(4)	0.15	1.75	37	74	61
	0.15	1.89	127	77	36
	0.11	0.93	95	21	110
O(5)	0.14	1.60	114	28	75
	0.18	2.53	27	71	76
	0.13	1.38	102	109	21
O(6)	0.14	1.62	29	119	94
	0.16	2.03	63	35	71
	0.10	0.75	100	108	19
O(7)	0.16	2.03	39	54	81
	0.18	2.68	128	40	77
	0.15	1.81	94	106	16
O(8)	0.16	2.08	32	72	68
	0.17	2.26	110	109	25
	0.16	1.94	114	26	79

DISCUSSION.

The interatomic distances and the bond angles are presented in Table VI as well as their standard deviations.

Silicon.—Krauskopfite appears to be a chain-silicate. In its structure there are two non-equivalent silicon atoms, Si(I) and Si(II), that connect

TABLE VI.

Interatomic distances (Å), *angles* (°) *and their standard deviations* (*in parentheses*).

An asterisk is used to distinguish equivalent atoms.

Atoms	Bond lengths	Atoms	Bond angles
Si(I)—O(1)	1.633 (7)	O(1)—Si(I)—O(2)	109° 6′ (22′)
Si(I)—O(2)	1.625 (7)	O(1)—Si(I)—O(3)	104° 49′ (22′)
Si(I)—O(3)	1.560 (7)	O(1)—Si(I)—O(4)	110° 31′ (22′)
Si(I)—O(4)	1.634 (7)	O(2)—Si(I)—O(3)	116° 22′ (22′)
		O(2)—Si(I)—O(4)	101° 28′ (22′)
		O(3)—Si(I)—O(4)	114° 36′ (22′)
Si(II)—O(1)	1.631 (7)	O(1)—Si(II)—O(4)	105° 14′ (22′)
Si(II)—O(4)	1.654 (7)	O(1)—Si(II)—O(5)	112° 39′ (22′)
Si(II)—O(5)	1.595 (7)	O(1)—Si(II)—O(6)	108° 25′ (22)′
Si(II)—O(6)	1.644 (7)	O(4)—Si(II)—O(5)	112° 56′ (22′)
		O(4)—Si(II)—O(6)	108° 14′ (22′)
		O(5)—Si(II)—O(6)	109° 9′ (22′)
		Si(I)—O(1)—Si(II)	138° 5′ (24′)
		Si(I)—O(4)—Si(II)	131° 53′ (24′)
Ba—O(3)	2.743 (7)		
Ba—O(2)	2.763 (7)		
Ba—O(3)*	2.776 (7)		
Ba—O(8)	2.821 (7)		
Ba—O(6)	2.849 (6)		
Ba—O(7)	2.876 (7)		
Ba—O(1)	2.969 (7)		
Ba—O(7)*	2.983 (8)		
Ba—O(8)*	3.010 (7)		

themselves by the oxygens O(1) and O(4) in an alternative way, giving rise to the following chain: ...—Si(I)—O(4)—Si(II)—O(1)—... A single chain is composed of units of four tetrahedra that repeat for simple translation along *c*; each unit is composed of two enantiomorphous sub-units equivalent by application of a glide *b* parallel to (010). A sub-unit contains the two non-equivalent tetrahedra mentioned above.

Two chains run in a single unit cell, equivalent by inversion but not enantiomorphous; their shape and mutual development are shown in the figures 1 and 2.

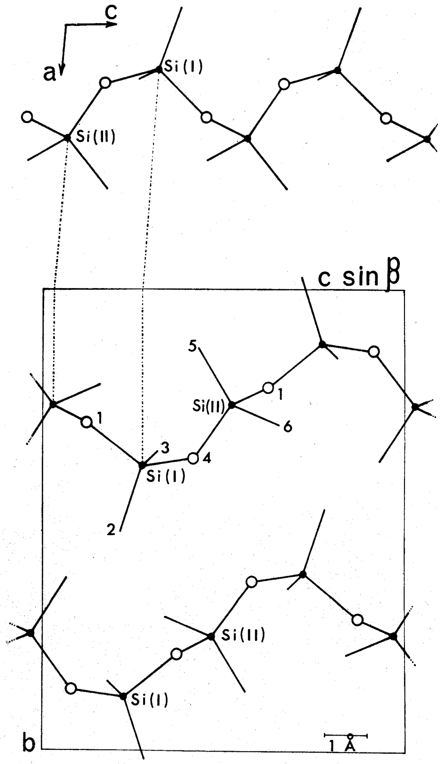


Fig. 1. – Shape and mutual development of the silicon chains.
The numbers refer to the oxygen atoms.

There are no evident similarities between the crystal structures of krauskopfite and sanbornite, $BaSi_2O_5$; the latter, studied by Douglass [7], is a layer-silicate.

Barium.—All the barium atoms are equivalent by symmetry. The nine shortest barium-oxygen distances are shown in Table VI, the next one, Ba—O(4), is 3.252 Å long and does not correspond to a contact between the atoms involved; therefore the barium coordination number can be settled as nine. The barium coordination polyhedron is very irregular and cannot be referred to a standard type. Pairs of enantiomorphous polyhedra are present in the structure.

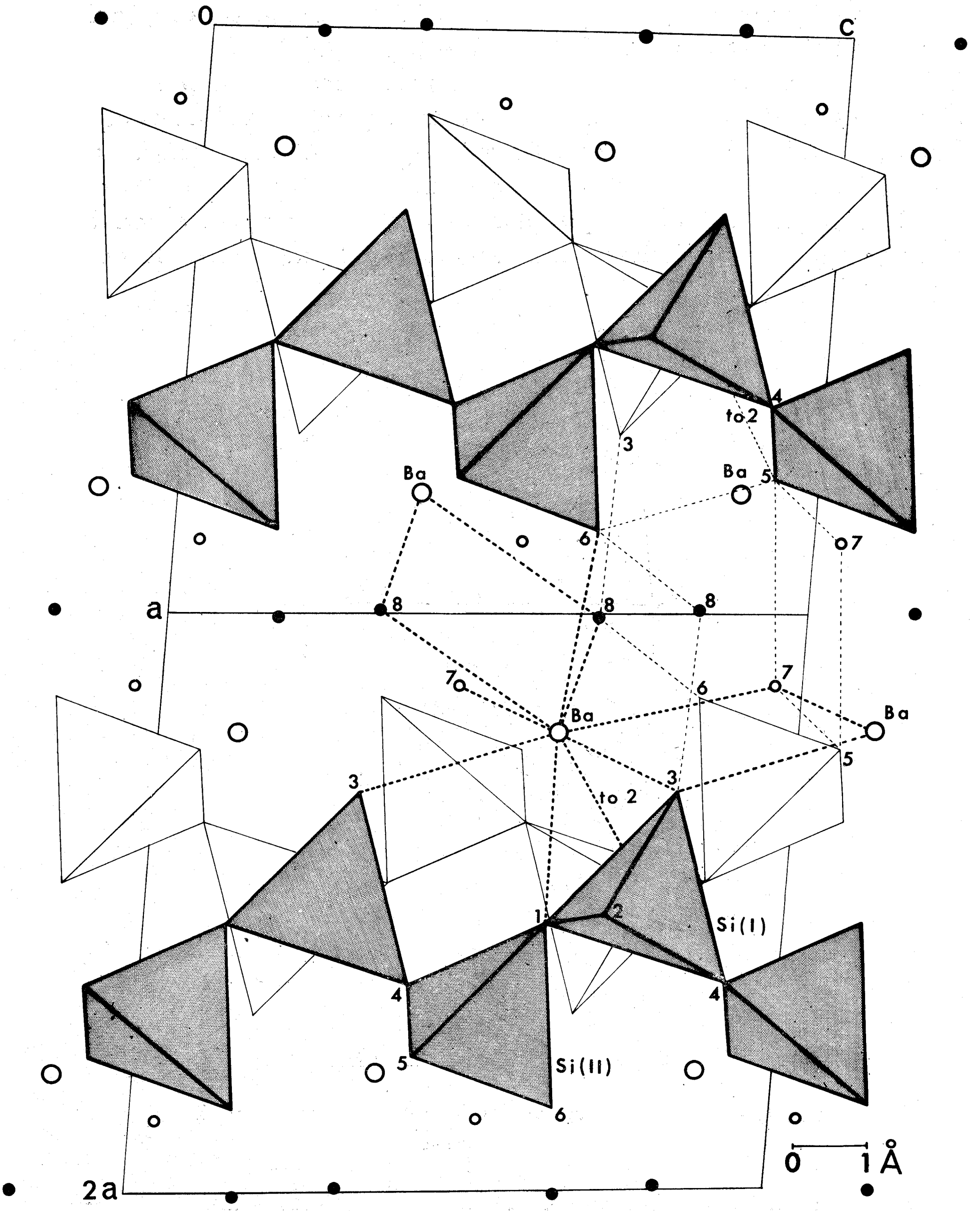


Fig. 2. – Projection along [010] of a double cell of krauskopfite.

The heavy dashes refer to the bonds Ba—O, the light ones to the H-bonds.
The numbers refer to the oxygen atoms.

Each barium polyhedron is connected to three similar polyhedra by sharing one edge with each of them: two edges O(3)—O(7) of each polyhedron, equivalent by symmetry, are shared in this way, resulting in a chain running approximately parallel to *c*; furthermore, these chains are interconnected by the sharing of a third edge, O(8)—O(8)*, between each polyhedron and its centrosymmetric one (here and elsewhere an asterisk is used to indicate an equivalence by an unspecified symmetry element). A sort of layer so arises, composed of six-membered rings of barium polyhedra (fig. 3); no oxygen connects two different layers, whose least distance covers an entire unit cell.

The layers are not planar; the mean plane that runs among the barium atoms coincides with the plane *bc*, whose cartesian equation is $x = 0$; the distance of each barium from this plane is 1.61 Å long (fig. 2).

Connections between the Si *and* Ba *atoms.*—Along the direction *a*, Ba-layers and Si–chain slabs are found alternately (fig. 2). Each barium atom is connected to three chains; O(3), O(1) and O(3)* provide the connections with a chain of a slab, O(2) with a second chain of the same slab, O(6) with a chain of a different slab; the remaining oxygens linked to Ba, O(7), O(7)*, O(8), O(8)*, do not belong to the Si-tetrahedra. An edge O(1)—O(3) (3.38 Å) covers two Si-tetrahedra, another edge O(1)—O(3)* (2.59 Å) is shared with a single tetrahedron; the edges O(1)—O(2) (3.11 Å) and O(3)—O(2) (3.70 Å) connect different chains.

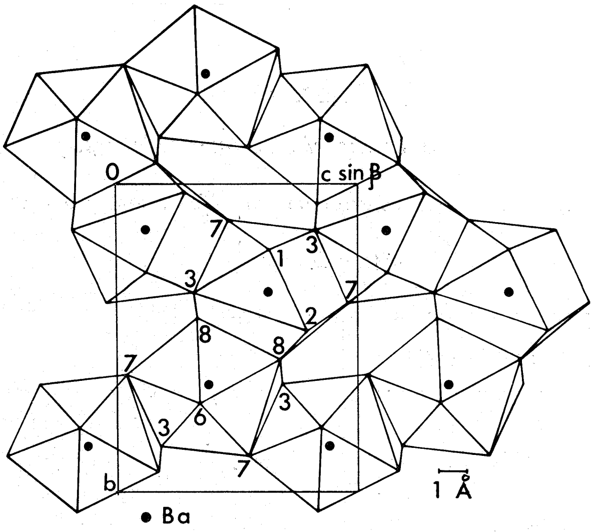


Fig. 3. – A portion of a layer of barium polyhedra.

The numbers refer to the oxygen atoms.

The hydrogen-bonding system.—In the crystal structure of krauskopfite six hydrogen atoms per asymmetric unit are present and six oxygen-oxygen distances shorter than 3 Å are found (of course excluding distances between oxygens of the same coordination polyhedron); they are collected in Table VII. It is reasonable to assume them to be hydrogen bonds and to try the identification of the oxygens directly linked to the hydrogens on the basis of the electrostatic valence Pauling's rule. In fig. 2 a part of the system of hydrogen bonds is shown.

TABLE VII.

Distances and angles related to the probable hydrogen bonds.

Standard deviations in parentheses.

O(7)—O(5)	2.810 Å (10)
O(7)—O(5)*	2.898 Å (10)
O(8)—O(3)	2.626 Å (10)
O(8)—O(6)	2.956 Å (10)
O(2)—O(5)	2.719 Å (10)
O(6)—O(5)	2.603 Å (10)
O(5)—O(7)—O(5)*	109° 27′ (20′)
O(3)—O(8)—O(6)	90° 44′ (20′)

TABLE VIII.

Balance of the electrostatic valences.

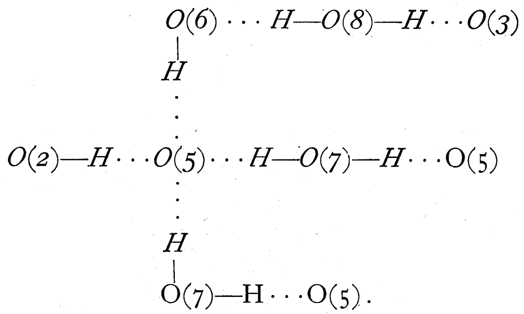
Each asterisk denotes a hydrogen contribution of $\frac{3}{4}+$, and each comma a hydrogen contribution of $\frac{1}{4}+$.

Oxygen	Linked atoms	I	II	III
O(1)	Ba, Si(I), Si(II)	$2+\frac{2}{9}$	$2+\frac{2}{9}$	$2+\frac{2}{9}$
O(2)	Ba, Si(I)	$1+\frac{2}{9}$	* $2-\frac{1}{36}$	$2-\frac{1}{36}$
O(3)	Ba, Ba, Si(I)	$1+\frac{4}{9}$	$1+\frac{4}{9}$	, $2-\frac{11}{36}$
O(4)	Si(I), Si(II)	2	2	2
O(5)	Si(II)	1	, , , , 2	2
O(6)	Ba, Si(II)	$1+\frac{2}{9}$	* $2-\frac{1}{36}$	, $2+\frac{2}{9}$
O(7)	Ba, Ba	$\frac{4}{9}$	** $2-\frac{1}{18}$	$2-\frac{1}{18}$
O(8)	Ba, Ba	$\frac{4}{9}$	$\frac{4}{9}$	** $2-\frac{1}{18}$

The first column of Table VIII gives the electrostatic valences of the oxygen atoms excluding the hydrogen contributions. As O(5) participates in four different hydrogen bonds (Table VII) and lacks only one electronic positive charge (1+), each contribution from the hydrogens cannot overcome 1/4+; so O(5) cannot be directly linked to the hydrogen atoms and four hydrogens linked respectively to O(7), O(7)*, O(2), O(6) are to be postulated. Distributing each hydrogen contribution among two oxygen atoms as 3/4+ for the linked one and 1/4+ for the unlinked atom, the second column of Table VIII is obtained.

To improve the figure given for O(8) in this Table, two hypotheses can be put forward: two hydrogens are directly linked to O(8), or only one of them is directly linked to it. The first hypothesis gives the overall best figures for the three oxygens O(3), O(6), O(8), as shown in the third column.

The hydrogen-bonding system that derives from the above considerations is made clear by the following scheme (the italics refer to the atoms pertaining to an asymmetric sector of the unit cell):



From this discussion two water molecules result, O(7) and O(8), and two hydroxyls, O(2) and O(6), that belong respectively to the tetrahedra Si(I) and Si(II).

This picture is consistent, because the supposed water molecules do not belong to the silicon tetrahedra, but are only linked to the Ba–atoms; moreover O(1) and O(4), that connect the Si–tetrahedra, do not belong to the system of hydrogen bridges. To complete this picture, each tetrahedron has one hydroxyl (as seen above) and a fourth oxygen involved in forming at least one hydrogen bridge (respectively O(3) and O(5); the latter is unique in forming four hydrogen bridges).

Of course the possibility of a statistical distribution of some hydrogens between two oxygens cannot be excluded on the preceding grounds; for example, this could happen for O(5) without seriously disturbing the electrostatic balance.

A difference synthesis computed with the final phases did not give any clear evidence about the hydrogen positions.

During the least-squares refinement the following test was carried out: each hydrogen atom was formally split in two half-hydrogens separately linked to the different oxygens of each hydrogen bond, and a thermal parameter of 2.5 Å^2 was given to them. A cycle of least-squares carried out with only the low-angle reflections resulted in rejecting some half-hydrogens (high thermal parameters) and strengthening others (low thermal parameters). This test was fully consistent with the assumptions made for the hydrogen bonds O(7)—O(5), O(8)—O(3), O(8)—O(6), O(6)—O(5), but was unfavorable for the bond O(2)—O(5); in the remaining case, O(7)—O(5)*, the thermal parameters moved in the same direction for the two halves and the test did not allow any conclusion (Table IX).

TABLE IX.

Isotropic thermal factors (Å^2) of the formal half-hydrogens, $H^{1/2}$, after the least-squares refinement of the low-angle F_o's (starting B for each $H^{1/2}$: 2.5 Å^2). Each B refers to the $H^{1/2}$ linked to the oxygen written at the side.

B	Bond	B
2.0	O(7)—O(5)	16.0
19.2	O(7)—O(5)*	10.5
— 5.6	O(8)—O(3)	12.7
— 5.9	O(8)—O(6)	3.5
21.2	O(2)—O(5)	— 12.2
—26.9	O(6)—O(5)	41.3

The bond lengths and angles.—The angles between the hydrogen bonds that meet in O(7) and O(8) are consistent with the assumption that the latter are water molecules; these angles are 109° 27′ and 90° 44′ respectively.

The bond lengths and angles within the silicon tetrahedra are regular. The four bonds between Si(I), Si(II) and O(1), O(4), that form the Si–chains, are long, as was expected (the figures range between 1.63 and 1.65 Å). The bonds Si(I)—O(2) and Si(II)—O(6) are again long (1.62 and 1.64Å respectively), which is consistent with the assumption that O(2) and O(6) are hydroxyls. The unshared oxygens O(3) and O(5) form shorter distances than the preceding ones, 1.56 and 1.60 Å respectively. There is a small difference between the latter distances; however attention has to be paid to the fact that O(3) forms only one hydrogen bridge, while O(5) is involved in four of them.

In Table VI the barium-oxygen bond lengths are divided in three groups: short (mean Ba—O distance: 2.76 Å), regular (mean: 2.85 Å) and long (mean: 2.99Å); this classification seems reasonable if attention is paid to the distribution of the distance figures. The sum of the ionic radii of Ba^{++} and O^{--}, corrected for 9–coordination [8] is 2.86 Å: only the second group of distances conforms fully to this value; the first group comprises distances noticeably shorter.

but they are very common among the barium compounds. Also the distances of the third group occur commonly in literature. If the oxygens of the third group—whose ionic interaction with barium is low—are excluded from the Ba–coordination polyhedron, a distorted octahedron is obtained. The exclusion of the electrostatic interaction Ba—O from the Table VIII for the oxygens of this group does not make the electrostatic balance worse; on the contrary, an improvement is registered for O(1) and O(3).

Cleavage.—Fig. 2 gives an explanation of the perfect cleavages {010} and {100}; they run parallel to the Si–chains and do not cut them.

Chemical formula.—After the crystal structure determination the chemical formula of krauskopfite can be written as: $Ba[Si_2O_4(OH)_2] \cdot 2\,H_2O$ or $[Ba(2\,H_2O)][Si_2O_4(OH)_2]$.

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