

Phosphate minerals from Reaphook Hill, Flinders Ranges, South Australia

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SUMMARY. Several uncommon phosphate minerals including *tarbuttite*, *parahopeite*, *scholzite*, and *collinsite* occur in near-surface gossans at the Reaphook Hill zinc prospect. Electron-probe microanalyses of the tarbuttite and scholzite compare well with published analyses of specimens of these minerals from the type localities in Zambia and Bavaria respectively. However, microanalyses of the parahopeite are significantly different from published analyses of parahopeite, and suggest that it may be one member of an isomorphous series in which six-coordinated Zn can be replaced by other cations, including Fe, Mg, and Mn. Furthermore, crystals of the Reaphook Hill parahopeite are compositionally zoned with their centres enriched in Fe and Mn relative to the margins, which are enriched in Mg.

Zincian collinsite occurs at Reaphook Hill as concentric crusts composed of very fine grained radially oriented plates. Electron-probe microanalyses of this material are significantly different from published analyses of collinsite from the type locality in British Columbia: Zn instead of Fe occupies the divalent cation sites; this material may be part of an isomorphous series that includes fairfieldite. Microanalyses also indicate that the Reaphook Hill collinsite crusts are compositionally zoned such that Zn:Mg ratios vary from the base to the outer edges of the crusts. This zoning is interpreted as the result of variation in the availability of Zn and Mg during growth. Zoning of similar type, but due to variation in the Fe:Mg ratio, was observed in concentric crusts of collinsite from the type locality in British Columbia.

In 1966, during geochemical exploration by the South Australian Geological Survey and Kennecott Explorations (Australia) Pty. Ltd., *scholzite* was discovered as prismatic needles in three discrete near-surface mineralized zones in unmetamorphosed sediments of the Lower Cambrian Parachilna Formation at Reaphook Hill, approximately 100 km north-east of Hawker in the Flinders Ranges, South Australia (Johns, 1972). The mineralized zones have resistant ferruginous and manganiferous cappings, which grade downwards into complexly fractured phosphatic pebble conglomerates, sandstones, and siltstones. They seem to have developed as a result of the action of groundwater causing near-surface enrichment of manganese, iron, zinc, and phosphorus in fractured and faulted zones in the Parachilna Formation.

Many other phosphate minerals, in addition to scholzite, have since been identified in the mineralized zones by X-ray powder diffraction. These include *tarbuttite*, *parahopeite*, *collinsite*, *switzerite*, and *phosphophyllite*. Hemimorphite pseudomorphs after smithsonite have also been noted. Manganese minerals are very common throughout the zones and include chalcophanite, cryptomelane, psilomelane, manganite, and

pyrolusite. The phosphate minerals, generally found lining voids in the mineralized zones, occur both as euhedral and as complexly intergrown anhedral crystals.

An investigation of the crystal structures of the Reaphook Hill phosphates has been undertaken by one of us (R. J. H.). A reinterpretation of the crystal structure of scholzite as published by Taxer (1970) has already been published (Hill *et al.*, 1973). An electron-microprobe examination of the material selected for structure analysis was a necessary adjunct to the crystallographic investigation; the results of this examination are reported here.

TABLE I. *Least-squares cell dimensions of Reaphook Hill phosphate minerals*

	Space group	a(Å)	b(Å)	c(Å)	α	β	γ	Volume (Å ³)
Reaphook Hill tarbuttite	P $\bar{1}$	8.130 (1)	12.896 (2)	7.754 (1)	90°9 (1)'	91°36 (2)'	107°44 (1)'	773.9 (2)
ASTM	P $\bar{1}$	8.113	12.93	7.703	89°34'	91°37'	107°47'	769.14
Reaphook Hill tarbuttite (unit cell orientation after Cocco <i>et al.</i>)	P $\bar{1}$	5.538 (1)	5.726 (2)	6.456 (2)	102°46 (2)'	102°35 (2)'	87°45 (2)'	194.87 (8)
Cocco <i>et al.</i>	P $\bar{1}$	5.499	5.654	6.465	102°51'	102°46'	86°50'	191.12
Reaphook Hill parahopeite	P $\bar{1}$	5.763 (1)	7.537 (2)	5.292 (1)	93°20 (2)'	91°21 (1)'	91°18 (1)'	229.33 (6)
ASTM	P $\bar{1}$	5.766	7.550	5.303	93°17.5'	91°55'	91°19'	230.27
Reaphook Hill scholzite	P ₂ /b	17.164 (6)	22.244 (8)	6.673 (2)	90°0(3)'	—	—	2547 (1)
Bavarian scholzite (Taxer, 1970)	P ₂ /c	17.149 (3)	22.236 (2)	6.667 (1)	—	90°	—	2542
ASTM	P ₂ /m	17.14	22.19	6.61	—	—	—	2514
Reaphook Hill collinsite	P $\bar{1}$	5.712 (3)	6.830 (3)	5.393 (2)	98°38 (3)'	106°50 (3)'	103°23 (2)'	190.5 (1)
ASTM	P $\bar{1}$	5.71	6.73	5.39	96°48.5'	107°16.5'	104°32'	187.22

Uncertainty in the final figure is indicated by parentheses.

Experimental techniques. Powdered specimens of the phosphates had to be carefully prepared for X-ray diffraction investigation as a too vigorous grinding resulted in unacceptably broad diffraction peaks.

X-ray data were obtained with a 19-cm camera using Co- $K\alpha$ radiation, or alternatively with a Philips X-ray powder diffractometer incorporating a focusing monochromator and using Cu- $K\alpha$ radiation. Indexing and least squares refinement of cell dimensions were carried out using the procedure of Evans *et al.* (1963).

The microanalyses were obtained on a Cambridge Instruments 'Geoscan' electron-probe microanalyser. Under normal conditions of analysis using a focused electron beam, significant systematic drifts in count rate with time have been observed for elements in many minerals, including phosphates. This effect is probably due to a combination of photochemical degradation (McConnell, 1969) and thermal decomposition of the minerals under the influence of the electron beam in the evacuated specimen chamber (Sweetman and Long, 1969). During the present study, the effect was minimized by analysing the phosphate minerals with the electron beam expanded to an area 50 μm in diameter. The accelerating voltage and beam current were maintained at 20 kV and 50 nA respectively.

Eight elements, selected on the basis of reconnaissance spectrometer scans, were determined in each mineral. Zn metal, Mn metal, and analysed specimens of apatite (Ca, P), barytes (Ba, S), and olivine (Fe, Mg, Si) were used as standards. Corrections to the raw data were made according to the method of Sweatman and Long (1969) using the procedure of Oertel (1971).

The major phosphate minerals

Tarbuttite, $Zn_2(PO_4)(OH)$, occurs in the Reaphook Hill mineralized zones mainly as compact aggregates of crystals up to 5 mm along their maximum dimension. Euhedral crystals lining voids are colourless and transparent with an equant to prismatic habit, and are deeply grooved (figs. 1 and 2). Many crystals appear to be pseudo-isometric, although the mineral has triclinic symmetry. In these respects the Reaphook Hill tarbuttite is very similar to the type material from the Broken Hill mines in Zambia (Spencer, 1908).

X-ray powder diffraction data for the Reaphook Hill tarbuttite (Tables I and II) agree well with both the ASTM data and with the data of Richmond (1938) for the Zambian material. Cocco *et al.* (1966) redetermined the lattice parameters using a different orientation of the elementary cell. One set of our refined cell dimensions also relate to a cell in this orientation.

Electron-probe microanalyses of selected tarbuttite euhedra gave the average composition presented in Table III. The structural formula of tarbuttite calculated from these data is close to the ideal formula.

Parahopeite, $Zn_2Zn(PO_4)_2 \cdot 4H_2O$, is present only as a minor phase in the mineralized zones at Reaphook Hill. It occurs as white to yellow-brown euhedral crystals with an equant to prismatic habit and a well-developed (001) cleavage (fig. 3). For the most part, the Reaphook Hill parahopeite is encrusted with chalcophanite, scholzite, gypsum, and hemimorphite.

X-ray powder diffraction data for the Reaphook Hill parahopeite (Tables I and II) are similar to ASTM data for parahopeite from the type locality in Zambia. However, electron-probe microanalyses indicate that euhedral crystals of the Reaphook Hill parahopeite are significantly different in composition from the type material, and are compositionally zoned. Random microanalyses of parahopeite crystal aggregates, and of the core and rim of an euhedral crystal are given, along with a calculated structural formula, in Table IV. On the basis of these data, the formula for the Reaphook Hill parahopeite can be expressed as $Zn_2X(PO_4)_2 \cdot 4H_2O$, where X represents Zn, Fe, Mn, and Mg. Zoned parahopeite euhedra are characterized by cores enriched in Fe and Mn and outer zones enriched in Mg. Zn appears to be uniformly distributed throughout the euhedra (figs. 4-8).

Scholzite, $CaZn_2(PO_4)_2 \cdot 2H_2O$, is the most common and conspicuous phosphate mineral in the mineralized zones at Reaphook Hill. It occurs in voids as sprays of radiating white to colourless prismatic needles up to 3 cm long (figs. 9 and 10), or as interpenetrating groups of white fibres. It was discovered in surface exposures of the mineralized zones by C. C. Brooks of Kennecott Explorations (Australia) Pty. Ltd. in 1966. The only other localities in which scholzite is known to occur are Hagendorf

TABLE 11. Observed and calculated X-ray powder diffraction data for Reaphook Hill phosphate minerals

Tarbuttite			Parahopeite			Scholzite†			Collinsite			
d_{obs}	d_{calc}	I^*	d_{obs}	d_{calc}	I^*	d_{obs}	d_{calc}	I/I_1	d_{obs}	d_{calc}	I^*	hkl
6.14	6.141	VS	7.53	7.522	VS	9.3	9.335	15	6.22	6.462	m	010
5.40	5.396	m	5.76	5.760	W	8.65	8.581	100	5.02	5.019	W	001
4.38	4.586	m	5.28	5.282	m	7.66	8.006	5	4.52	4.506	W	011
3.87	3.870	VW	4.63	4.627	VW	6.92	6.808	5	3.24	3.231	m	020
3.75	3.748	VW	4.52	4.521	VW	4.56	4.529	25	3.132	3.132	s	101
3.69	3.689	VS	4.45	4.447	s	4.29	4.290	40	3.041	3.061	s	021
3.26	3.260	s	4.21	4.208	m	4.16	4.146	5	2.713	2.714	m	210
3.07	3.070	VW	3.85	3.845	W	3.745	3.747	5	2.691	2.688	VVS	211
2.96	2.962	s	3.76	3.761	W	3.711	3.708	20	2.558	2.565	W	121
2.90	2.900	W	3.53	3.532	m	3.400	3.404	30	2.467	2.467	VW	021
2.87	2.869	s	3.34	3.345	W	3.335	3.336	5	2.404	2.403	VW	220
2.78	2.781	s	3.19	3.184	W	3.247	3.245	10	2.361	2.361	VWV	112
2.70	2.700	W	3.15	3.152	m	3.183	3.185	10	2.290	2.292	W	221
2.57	2.569	VW	2.98	2.982	VS	3.116	3.115	20	2.232	2.233	m	130
2.53	2.534	m	2.88	2.880	VS	3.027	3.032	5	2.155	2.154	VW	030
2.47	2.470	W	2.77	2.771	s	2.865	2.867	15	2.118	2.119	W	031
2.45	2.451	W	2.71	2.711	m	2.806	2.805	60	2.089	2.077	W	212
2.42	2.420	W	2.71	2.711	m	2.687	2.686	15	1.996	1.998	W	122
2.41	2.418	W	2.67	2.668	m	2.640	2.637	5	1.968	1.966	m	230
2.40	2.393	VW	2.64	2.641	m	2.633	2.633	10	1.923	1.924	VW	221
2.35	2.349	m	2.54	2.539	W	2.584	2.586	10	1.868	1.867	VW	222
2.33	2.330	VWV	2.51	2.507	W	2.482	2.481	20	1.831	1.831	W	031
2.27	2.271	VW	2.45	2.447	VW	2.398	2.394	5	1.802	1.798	W	222
2.22	2.228	VW	2.42	2.424	VW	2.390	2.392	5	1.783	1.783	W	113
2.09	2.090	W	2.38	2.378	VW	2.382	2.382	10	1.758	1.756	m	132
2.07	2.070	VW	2.34	2.340	VWV	2.327	2.327	25	1.696	1.692	W	203
2.05	2.051	s	2.31	2.310	W	2.266	2.266	30	1.666	1.673	s	003
2.01	2.012	VW	2.28	2.279	W	2.15	—	5	plus 10 lines to 1.144			
1.94	1.937	W	2.26	2.260	VW	2.08	—	10				
1.85	1.850	W	2.13	2.132	W	2.00	—	20				
1.82	1.820	VWV	2.12	2.121	W	1.84	—	5				
1.80	1.799	VW	2.10	2.104	W	1.81	—	15				
1.79	1.791	VWV	2.04	2.038	W	1.76	—	15				
1.74	1.738	m	1.97	1.971	W	1.72	—	5				
1.71	1.711	VW	1.92	1.920	W	1.66	—	20				
1.70	1.700	W	1.82	1.819	W	1.61	—	5				
1.69	1.692	VW	1.80	1.800	W	1.59	—	10				
1.60	1.602	VW	1.78	1.782	W	1.55	—	15				
1.59	1.590	W	1.76	1.761	VW	plus 11 lines to 1.17						
1.54	1.540	VW	1.69	1.692	VW							
1.49	1.489	VW	1.63	1.632	VW							
1.44	1.441	VW	1.59	1.590	VW							
1.39	1.390	VW	1.56	1.560	VW							
			1.54	1.540	VW							
			1.44	1.440	VW							

* Estimated from powder diffraction photograph
 † Reported as for an orthorhombic cell

Nord¹ and Sud, Bavaria (Strunz, 1948), Transbaikal, U.S.S.R., and Domažlice, Otov, south-west Bohemia. Reaphook Hill scholzite needles are generally pseudo-hexagonal in cross-section, although the mineral has monoclinic symmetry (Hill *et al.*, 1973, present a space-group with the *a*-axis as unique symmetry axis). Some crystals have a 'Roman sword' or linear-planar habit as a result of the dominance of (100) and (*h*31) planes (fig. 11).

X-ray powder diffraction data for the Reaphook Hill scholzite (Tables I and II) are in good agreement with the ASTM data for the type scholzite from Bavaria. Electron-probe microanalyses of several scholzite needles have been averaged to give the analysis in Table III. The analysis is consistent with the ideal formula.

TABLE III. *Electron-probe microanalyses of tarbuttite and scholzite from Reaphook Hill*

	T	S		T'	S'
ZnO	66.9	40.3	Zn	3.91	1.93
FeO	0.02	0.01	Fe	tr	tr
MnO	0.01	0.01	Mn	tr	tr
			Mg	tr	tr
CaO	0.04	14.7	Ca	tr	1.02
SO ₃	0.01	0.00	S	tr	0.00
P ₂ O ₅	30.3	36.7	P	2.03	2.02
SiO ₂	0.06	0.04	Si	tr	tr
MgO	0.03	0.01	H	1.4	3.6
H ₂ O*	2.6	8.2			

T, tarbuttite, mean of 10 spot analyses.

S, scholzite, mean of 6 spot analyses.

T', S', atomic ratios on an ignited basis of 9 oxygen atoms for tarbuttite, 8 for scholzite.

Analyses are given to within calculated counting error.

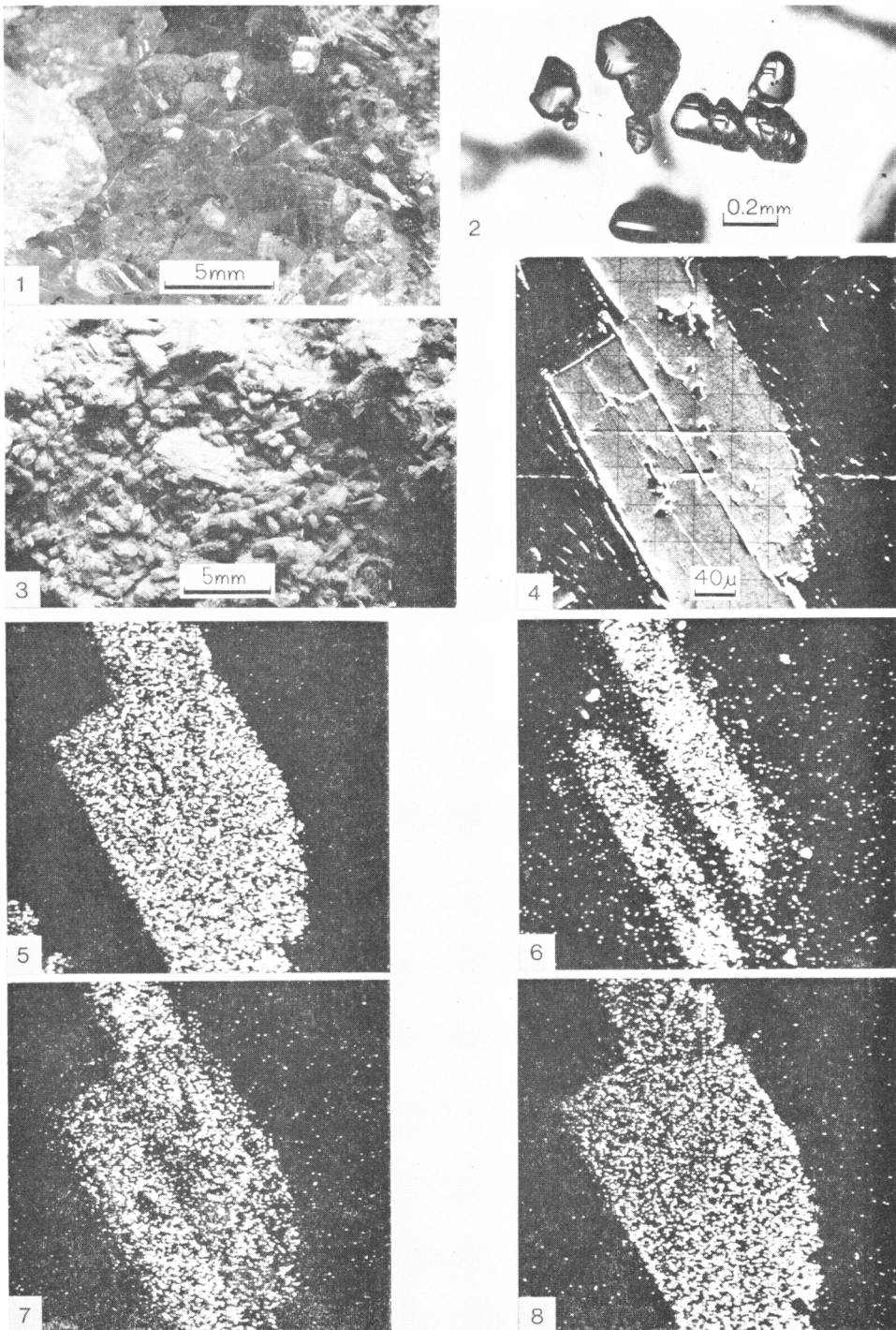
* By difference.

Zincian collinsite, Ca₂(Mg,Zn)(PO₄)₂·2H₂O, from Reaphook Hill was originally identified, on the basis of morphological and X-ray powder diffraction data, as collinsite. It occurs as greyish-blue or white concentric crusts with a radial platy habit (figs. 12 and 13). The crusts commonly occur on botryoidal cryptomelane or on goethite within voids. In this respect, the Reaphook Hill collinsite is similar to the type collinsite from François Lake, British Columbia. However, the Reaphook Hill collinsite also occurs as crystal overgrowths on parahopeite and scholzite.

The composition of the Reaphook Hill collinsite differs considerably from the composition of the type collinsite, Ca₂(Mg,Fe)(PO₄)₂·2H₂O (Poitevin, 1927; Wolfe, 1940), in that it contains Zn in place of Fe (Table V). On this basis, the ideal formula of the Reaphook Hill collinsite can be given as Ca₂(Mg,Zn)(PO₄)₂·2H₂O. Furthermore, the microanalyses indicate the crusts are compositionally zoned: the Zn:Mg ratio varies from about 0.6 near the base to about 1.4 at the outer edges. The collinsite is

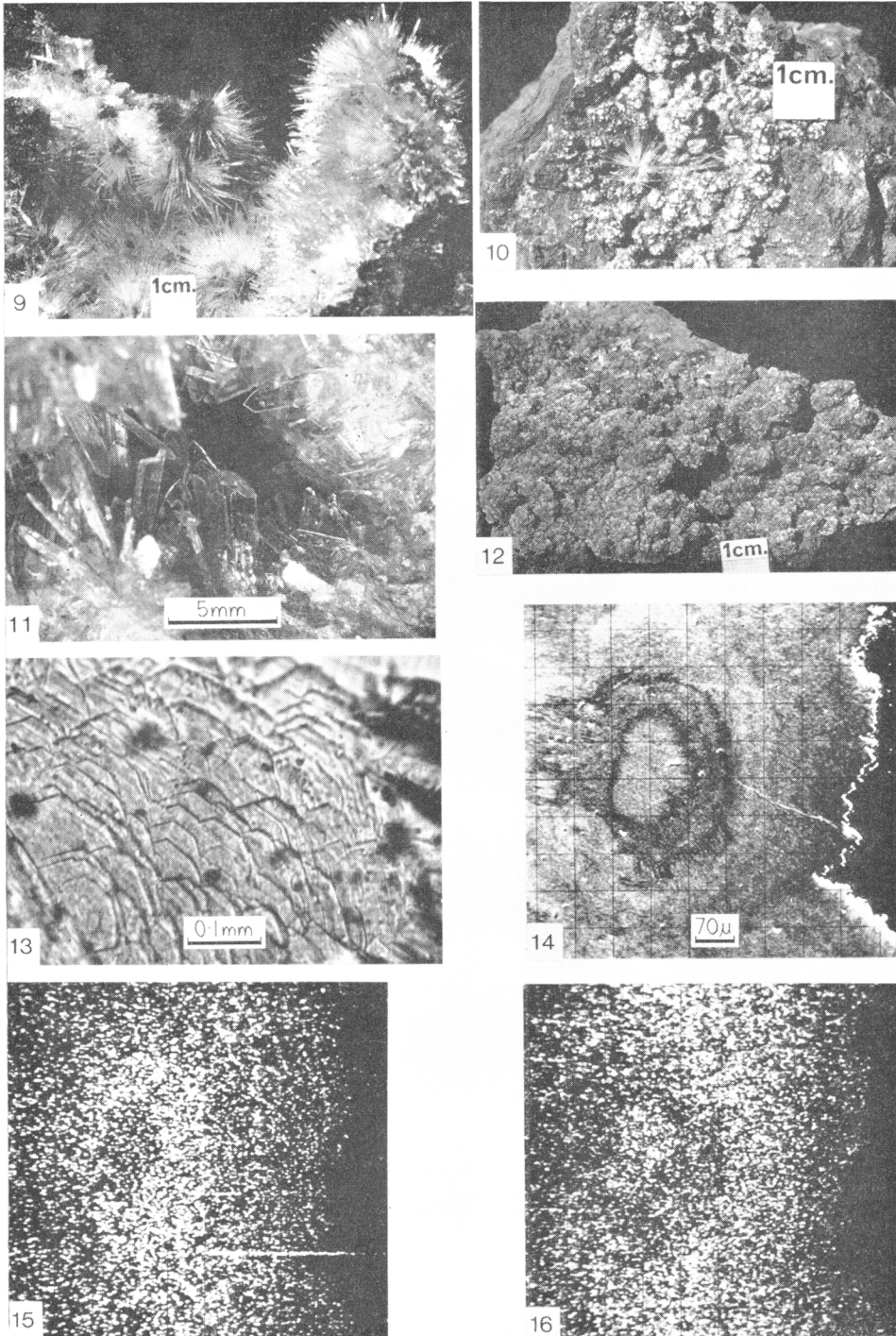
¹ Hagendorf Nord is no longer in production.

showing the distribution of Fe in the field of fig. 4. The cores of the crystals are rich in Fe, whereas their margins are almost free of Fe. FIG. 7 Scanning X-ray image showing the distribution of Mn in the field of fig. 4. An enrichment of Mn in the cores of the crystals relative to their margins can be discerned. FIG. 8 Scanning X-ray image showing the distribution of Mg in the field of fig. 4. An enrichment of Mg in the margins of the crystals relative to the cores can just be discerned.



FIGS. 1 to 8: FIG. 1 Euhedral tarbuttite crystals lining void. FIG. 2 Tarbuttite euhedra in polished thin section prepared for electron-probe microanalysis. Note equant habit and deeply grooved faces. FIG. 3 Euhedral parahopeite crystals lining void. FIG. 4 Scanning electron image of euhedral parahopeite crystals. FIG. 5 Scanning X-ray image showing the distribution of Zn in the field of fig. 4. The white areas, corresponding to the parahopeite crystals, are Zn-rich. FIG. 6 Scanning X-ray image

[Caption continues at bottom of preceding page.]



FIGS. 9 TO 16: FIG. 9 Rosettes of scholzite needles in void. FIG. 10 Radiating cluster of scholzite needles overgrowing very fine grained scholzite in void. FIG. 11 Roman sword habit of scholzite crystals in rosettes in void. FIG. 12 Collinsite crusts overgrowing cryptomelane and goethite in void. FIG. 13 Terminations of plates in collinsite crust fragment in polished thin section prepared for electron-probe microanalysis. FIG. 14 Scanning electron image of part of collinsite crust. Concentric

[Caption continues at bottom of following page.]

very fine grained and, to prevent its decomposition, was analysed with a 50 μm diameter beam in the electron microprobe. This condition for analysis was used for all the phosphates, but it precluded the analysis of single collinsite crystals. We therefore interpret the compositional variation as the result of growth banding of the crusts, and this is supported by the distribution of Mg and Zn seen in the scanning X-ray images in figs. 15 and 16. The possibility that the compositional variation is due to the

TABLE IV. *Electron-probe microanalyses of parahopeite from Reaphook Hill*

	<i>Random analyses</i>					core	rim 1	rim 2	Av.
	a	b	c	d	e				
ZnO	42.2	42.4	41.5	41.2	40.4	41.9	42.5	42.8	41.9
FeO	3.23	2.55	3.58	4.62	4.78	2.47	0.57	0.50	2.79
MnO	1.21	1.57	1.45	1.38	1.70	1.17	0.34	0.81	1.20
CaO	0.04	0.00	0.01	0.00	0.02	0.01	0.01	0.03	0.02
SO ₃	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.01
P ₂ O ₅	33.3	33.3	33.5	32.8	32.7	33.2	33.7	33.3	33.2
SiO ₂	0.01	0.04	0.03	0.00	0.07	0.10	0.06	0.04	0.04
MgO	3.5	3.0	3.1	3.0	3.0	4.5	6.3	4.6	3.9
H ₂ O†	16.5	17.1	16.8	17.0	17.3	16.6	16.5	17.9	17.0
<i>Structural formulae calculated on an ignited basis (8 oxygen atoms)</i>									
Ca	tr	0.00	tr	0.00	tr	tr	tr	tr	tr
Fe	0.19	0.16	0.22	0.28	0.29	0.15	0.03	0.03	0.17
Mn	0.07	0.10	0.09	0.09	0.11	0.07	0.02	0.05	0.07
Zn	2.26	2.28	2.22	2.23	2.19	2.23	2.22	2.30	2.24
Mg	0.37	0.32	0.33	0.33	0.33	0.48	0.66	0.50	0.42
S	0.00	0.00	0.00	0.00	0.00	tr	tr	0.00	tr
Si	tr	tr	tr	0.00	tr	0.01	tr	tr	tr
P	2.04	2.05	2.05	2.03	2.03	2.02	2.02	2.05	2.04
Zn	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Zn*+Fe+Mn+ +Ca+Mg	0.89	0.86	0.86	0.93	0.92	0.93	0.93	0.88	0.90
S+Si+P	2.04	2.05	2.05	2.03	2.03	2.03	2.02	2.05	2.04
H	8.0	8.3	8.1	8.3	8.5	8.0	7.8	8.7	7.2

* Excess Zn.

† By difference.

Suggested parahopeite structural formula: $\text{Zn}_2(\text{Zn,Fe,Mn,Mg})(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Analyses are given to within calculated counting error.

presence of more than one phosphate mineral in the crusts can be discounted on the basis of X-ray powder diffraction data (Table I and II), which agree closely with the ASTM data for collinsite from the type locality.

Electron-probe microanalyses of crusts of collinsite from the type locality¹ indicate

¹ A specimen of collinsite from François Lake, British Columbia, was obtained through the courtesy of the South Australian Museum.

growth banding can be discerned due to differences in electron density. FIG. 15 Scanning X-ray image showing distribution of Mg in field of fig. 14. An enrichment of Mg in the zone that appears dark (low electron density) in 14 can be seen. FIG. 16 Scanning X-ray image showing the distribution of Zn in the field of fig. 14. Zn is depleted in the Mg-rich zone shown in 15.

TABLE V. Electron-probe microanalyses of zincian collinsite from Reaphook Hill

	Reaphook Hill 'blue-grey' collinsite				Reaphook Hill 'white' collinsite									Av.
	1	2	3	4	1	2	3	4	5	6	7	8	9	
BaO	0.02	0.00	0.07	0.00	0.02	0.00	0.05	0.00	0.03	0.05	0.00	0.09	0.10	0.04
ZnO	9.3	10.4	9.3	11.1	10.0	12.0	13.5	12.4	11.8	11.1	12.1	11.6	11.4	11.9
FeO	0.03	0.00	0.03	0.20	0.07	0.03	0.00	0.02	0.02	0.00	0.04	0.00	0.05	0.02
CaO	32.6	33.1	33.7	32.5	33.0	32.6	32.1	32.4	32.6	32.1	32.5	32.0	32.4	32.3
SO ₃	0.51	0.18	0.20	0.35	0.31	0.68	0.48	0.35	0.86	0.49	0.89	0.75	0.65	0.63
P ₂ O ₅	40.6	41.0	41.1	40.8	40.9	40.5	40.9	40.6	39.8	40.3	40.2	40.6	40.1	40.4
SiO ₂	0.09	0.00	0.01	0.00	0.03	0.00	0.06	0.02	0.05	0.02	0.07	0.02	0.06	0.04
MgO	7.2	6.2	7.4	5.4	6.5	5.1	4.8	4.6	5.2	5.2	5.0	5.4	5.6	5.1
H ₂ O*	9.7	9.1	8.2	9.7	9.2	9.1	8.1	9.6	9.6	10.7	9.2	10.5	9.5	10.2
<i>Structural formulae calculated on the basis P = 2 atoms</i>														
Ca	2.03	2.04	2.07	2.01	2.04	2.04	1.99	2.02	2.07	2.01	2.04	1.99	2.00	2.02
Ba	tr	0.00	tr	0.00	tr	0.00	tr	0.00	tr	tr	0.00	tr	tr	tr
Fe	tr	0.00	tr	0.01	tr	tr	0.00	tr	tr	0.00	tr	0.00	tr	tr
Zn	0.40	0.44	0.39	0.47	0.43	0.51	0.58	0.53	0.52	0.48	0.52	0.46	0.50	0.51
Mg	0.62	0.53	0.63	0.46	0.56	0.44	0.41	0.40	0.46	0.46	0.44	0.47	0.48	0.44
(Fe+Zn+Mg)	1.02	0.97	1.02	0.94	0.99	0.95	0.99	0.93	0.98	0.94	0.96	0.93	0.98	0.95
S	0.04	0.01	0.01	0.03	0.02	0.05	0.04	0.02	0.06	0.04	0.07	0.06	0.04	0.05
Si	0.01	0.00	tr	0.00	tr	0.00	tr	tr	tr	tr	tr	tr	tr	tr
P	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
H	3.7	3.5	3.1	3.7	3.5	3.5	3.1	3.7	3.7	4.2	3.5	4.1	3.7	4.0

* By difference.

Analyses are given to within calculated counting error.

that these crusts are also compositionally zoned, but in this case the zoning is reflected in variable Fe:Mg ratios (Table VI). Only trace amounts of Zn were detected. For the reasons discussed in relation to the Reaphook Hill collinsite, the variation in composition within the collinsite crusts from British Columbia is also interpreted as the result of growth banding. The structural formula of this material closely approaches the ideal formula.

TABLE VI. *Electron-probe microanalysis of collinsite from François Lake, British Columbia*

	Core of clump					Edge	
	1	2	3	4	5	6	Av.
ZnO	0.05	0.04	0.08	0.04	0.04	0.03	0.05
FeO	4.00	8.52	6.66	6.32	5.60	4.36	5.91
MnO	0.20	0.26	0.27	0.25	0.32	0.31	0.27
CaO	33.8	33.4	33.3	33.3	33.4	33.8	33.5
SO ₃	0.08	0.01	0.07	0.11	0.00	0.13	0.07
P ₂ O ₅	42.5	40.6	41.9	41.8	41.9	42.6	41.9
SiO ₂	0.05	0.03	0.01	0.03	0.00	0.03	0.03
MgO	8.9	6.6	7.4	7.5	7.9	9.1	7.9
H ₂ O*	10.4	10.5	10.3	10.7	10.8	9.6	10.4
<i>Structural formulae calculated on an ignited basis (8 oxygen atoms)</i>							
Ca	2.02	2.06	2.02	2.02	2.03	2.01	2.03
Fe	0.19	0.41	0.32	0.30	0.27	0.20	0.28
Mn	0.01	0.01	0.01	0.01	0.02	0.01	0.01
Zn	tr	tr	tr	tr	tr	tr	tr
Mg	0.74	0.56	0.62	0.63	0.67	0.75	0.66
S	tr	tr	tr	tr	0.00	tr	tr
Si	tr	tr	tr	tr	0.00	tr	tr
P	2.01	1.98	2.01	2.01	2.01	2.00	2.00
Fe+Mn+Mg+Zn	0.94	0.98	0.95	0.94	0.96	0.96	0.96
S+Si+P	2.01	1.98	2.01	2.01	2.01	2.00	2.00
H	3.9	4.0	3.9	4.0	4.1	3.6	3.9

Analyses are quoted to within calculated counting error.

* By difference.

On the basis of X-ray powder diffraction data and chemical data, we conclude that both the Reaphook Hill and British Columbia collinsite crusts are composed of a single phase in which the divalent cations Zn and Mg, and Fe and Mg respectively are able to continuously substitute for each other. The observed compositional zoning was very likely controlled by the availability of Zn or Fe with respect to Mg during crystal growth of the crusts. The Reaphook Hill collinsite is isostructural with and has approximately the same cell dimensions as the British Columbia collinsite.

Aspects of the crystal chemistry of the major phosphate minerals

A crystal structure determination by Cocco *et al.* (1966) shows that tarbuttite has a framework structure with two formula units per unit cell. Two distinct sets of Zn²⁺

coordination polyhedra are held together by $(\text{PO}_4)^{3-}$ tetrahedra as stabilizing bridges, resulting in a relatively tight structure without any sixfold coordination sites. This may account for the observed lack of compositional variations.

Kumbasar and Finney (1968) have shown that the crystal structure of parahopeite is similar to that of phosphophyllite (Kleber *et al.*, 1961), and also to that of hopeite (Liebau, 1965), the dimorph of parahopeite. In fact, the chemical composition of the Reaphook Hill parahopeite bears some resemblance to that of phosphophyllite, $\text{Zn}_2(\text{Fe,Mn})(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. Parahopeite, hopeite, and phosphophyllite contain two crystallographically distinct Zn sites (one Zn and one Fe in phosphophyllite). One of these has sixfold coordination with oxygen atoms and water molecules, whereas the other has fourfold coordination with oxygen atoms. On the basis of radius ratio considerations, Fe, Mg, and Mn present in the Reaphook Hill parahopeite will be accommodated in the sixfold coordination sites, and any vacant sixfold sites may be filled with excess Zn from the fourfold sites.

The crystal structure of scholzite was determined by Taxer (1970) and has been re-refined by Hill *et al.* (1973). The most obvious feature of the scholzite structure is the chains of ZnO_4 tetrahedra parallel to the *c*-axis. The tetrahedra share corners with each other and with PO_4 tetrahedra to form sheets in the (100) plane. The Ca atoms are present at the centre of distorted oxygen and water octahedra, which serve to link the (100) sheets in the *a* axial direction. The structure shows severe stacking disorder parallel to [100]. The absence of variation in the composition of scholzite is thought to reflect the rather narrow range of conditions required for the formation of what could be interpreted as a delicately balanced structure.

Collinsite is a member of the fairfieldite group of phosphate minerals and according to Palache *et al.* (1951), may be isostructural with fairfieldite, $\text{Ca}_2(\text{Mn,Fe})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. A crystal structure determination by Mrose and Appleman (1960) has shown that fairfieldite consists of infinite chains of Mn octahedra parallel to the *c* axis. The chains are held together by Ca ions coordinated by six oxygen atoms and a water molecule. There are two crystallographically distinct cation sites in the structure, one occupied by Ca atoms and the other by Fe and Mn atoms. Only a limited amount of substitution would be expected to take place between them because of the appreciably greater ionic radius of Ca compared with Mn and Fe. Hence the variation in Zn:Mg ratio with constant Ca content observed in the Reaphook Hill collinsite.

Conclusions

On the basis of electron-probe microanalytical data, crystals of scholzite and tarbuttite from the Reaphook Hill zinc prospect have a chemical composition consistent with the ideal formulae. They are chemically homogeneous, and have therefore proved eminently suitable for X-ray structure investigation. Such an investigation has already been carried out for scholzite (Hill *et al.*, 1973). On the other hand, zincian collinsite and parahopeite from Reaphook Hill have chemical compositions that depart from the ideal formulae, and as they are in addition chemically zoned, are not suitable for single crystal X-ray crystallographic investigation.

The composition of the Reaphook Hill parahopeite is consistent with a structural

formula of the type $Zn_2X(PO_4)_2 \cdot 4H_2O$, where X represents Zn, Fe, Mn, and Mg. In fact, the composition of parahopeite is similar to that of phosphophyllite— $Zn_2(Fe, Mn)(PO_4)_2 \cdot 4H_2O$. The presence of two crystallographically distinct cation sites in both parahopeite and phosphophyllite is indicated from the crystal structures of these minerals. Therefore it seems likely that parahopeite with the ideal formula $Zn_2Zn^*(PO_4)_2 \cdot 4H_2O$ may be part of an isomorphous series in which the six-coordinated Zn^* atom can be replaced by other divalent cations including Fe, Mn, and Mg.

The Reaphook Hill zincian collinsite— $Ca_2(Mg, Zn)(PO_4)_2 \cdot 2H_2O$ —is quite different in chemical composition from the British Columbia François Lake collinsite— $Ca_2(Mg, Fe)(PO_4)_2 \cdot 2H_2O$. Furthermore, both types of collinsite exhibit differences in the amount of replacement of Mg by Zn or Fe due to growth zoning. Therefore collinsite may form an isomorphous series with a crystal structure of the type $Ca_2X(PO_4)_2 \cdot 2H_2O$, where X represents Mg, Fe, and Zn. The similarity between the structural formulae of collinsite and fairfieldite— $Ca_2(Mn, Fe)(PO_4)_2 \cdot 2H_2O$ —suggests that fairfieldite may also be part of this series.

The chemical inhomogeneity of the Reaphook Hill parahopeite and zincian collinsite is clearly not desirable in X-ray studies of crystal structure. However, hydrothermal syntheses of chemically homogeneous crystals of these minerals is possible, and may provide single crystals suitable for future X-ray crystallographic studies.

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