GUNNINGITE, A NEW ZINC SULPHATE FROM THE KENO HILL-GALENA HILL AREA, YUKON[1]

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ABSTRACT

Gunningite, $ZnSO_4.H_2O$, occurs as sparse white efflorescences on sphalerite in several mines in the Keno Hill area, Yukon. The new mineral is monoclinic and isostructural with the other members of the kieserite group. Synthetic gunningite has cell dimensions of $a = 7.566$, $b = 7.586$, $c = 6.954$ Å; $\beta = 115° 56'$; space group $C_{2h}^6 - A2/a$ (Pistorius, 1961). The unit cell contains four formula weights. Indexed *x*-ray powder data of synthetic and natural material are given. The strongest lines of the powder pattern are 3.40 (*s*), 4.78 (*ms*), 3.05 (*m*), 2.51 (*m*) Å.

Gunningite is very fine-grained, white in colour and streak, and has a hardness of about 2½. Specific gravity of synthetic material is 3.195 (pycnometer); 3.321 (calculated). Refractive indices are $\alpha' = 1.570$, $\gamma' = 1.630$. *X*-ray fluorescence analysis of a gunningite precipitate gave ZnO 40.8, MnO 3.1, CdO 1.0, FeO 0.6, total 45.5%, in good agreement with the theoretical value of 45.35% ZnO in gunningite.

The chemical relationships of gunningite with other members of the kieserite group were studied using synthetic material. Considerable quantities of magnesium, iron, and manganese may be substituted for zinc without effect on the configuration of the *x*-ray powder pattern. The association of other sulphates with gunningite in the Keno Hill area is briefly discussed.

INTRODUCTION

The Keno Hill–Galena Hill district is in Central Yukon, 35 miles northeast of Mayo and some 220 miles due north of Whitehorse. The district is noted for its silver-lead-zinc lodes which have been prolific producers since their initial development in 1913.

In 1953, one of the present writers (R. W. B.) commenced a detailed investigation of the deposits in the Keno Hill area, the results of which will be published in a forthcoming bulletin. Examination of the ores has revealed the presence of numerous supergene minerals derived from a relatively simple primary source. This paper describes a new hydrous zinc sulphate which has been found at several of the deposits, both on Keno Hill and Galena Hill. The new mineral, called gunningite, is named in honour of Dr. H. C. Gunning, a former member of the Geological Survey of Canada, and, until 1959, Head of the geology department at The University of British Columbia.

Gunningite was originally identified in the fall of 1960 as a barely megascopic white efflorescence on a specimen from the Comstock-Keno

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property (No. 23, Fig. 1). The sample consisted of brecciated vein quartz containing numerous thin, irregular veinlets of arsenopyrite. All surfaces of the rock were heavily coated with dark reddish-brown goethite and light yellow-green, fine-grained coatings of pharmacosiderite, scorodite, jarosites, and gypsum. Atop these minerals, and last to have formed, were white irregular patches of the mineral now called gunningite. Although *x*-ray powder photographs of the white sulphate showed it to be identical to synthetic $ZnSO_4.H_2O$, other zinc minerals were absent and insufficient pure material was available for a spectrographic analysis.

Some six months after this initial discovery, a thorough examination of over a thousand specimens from the Keno area was undertaken and small amounts of gunningite were found in samples from many additional properties: on Keno Hill, at the Gambler workings (22)[2], and in the No. 9 vein system; on Galena Hill, at the Galkeno mine (11), the 200 and 650 levels of the Calumet mine (8), the Cream (7), Silver King (1) and Leo 1–8 claims, the latter 4,000 feet northwest of the Silver King mine.

OCCURRENCE

The deposits of the Keno Hill–Galena Hill district are veins and lodes in faults that cut quartzites, phyllites, schists and greenstones (Fig. 1). The principal primary minerals are siderite, quartz, galena, sphalerite, chalcopyrite, pyrite, arsenopyrite and freibergite. These are altered in the zones of oxidation to limonite, various hydrous manganese oxides (wad), scorodite, jarosites, beudantite, bindheimite, cerussite, malachite, azurite, smithsonite, anglesite, and gypsum. In addition some native silver, pyrargyrite, and hawleyite occur in both the zones of oxidation and reduction.

The gunningite is generally found closely associated with incipiently oxidized sphalerite in the veins and lodes and on the old mine dumps. In the deposits the mineral is present in those parts that are relatively dry, and on the dumps the mineral appears on the oxidizing sphalerite after long periods of hot dry weather. In all occurrences the mineral appears as delicate efflorescences directly on the surface of sphalerite, or as efflorescences on limonite, scorodite, gypsum, and other supergene minerals closely associated with the zinc sulphide.

X-RAY AND CRYSTALLOGRAPHIC DATA

Gunningite, $ZnSO_4.H_2O$, is monoclinic and assumed to be isostructural with the other members of the kieserite group. The unit cell dimensions

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[2] Numbers in brackets refer to the mining properties shown in Figure 1.

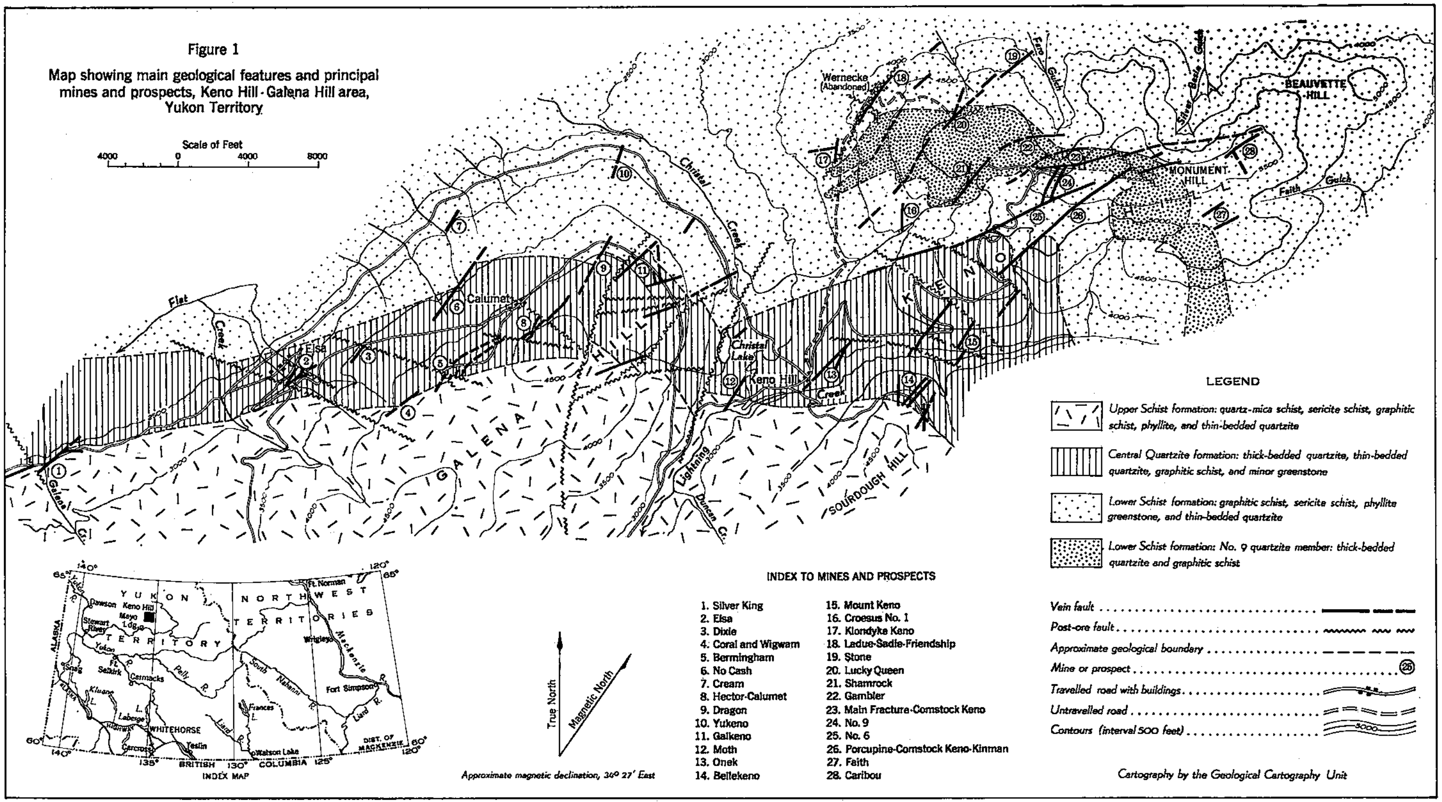

Figure 1

Map showing main geological features and principal mines and prospects, Keno Hill - Galena Hill area, Yukon Territory

Approximate magnetic declination, 34° 27′ East

INDEX TO MINES AND PROSPECTS

1. Silver King
2. Elsa
3. Dixie
4. Coral and Wigwam
5. Bermingham
6. No Cash
7. Cream
8. Hector-Calumet
9. Dragon
10. Yukeno
11. Galkeno
12. Moth
13. Onek
14. Bellekeno
15. Mount Keno
16. Croesus No. 1
17. Klondyke Keno
18. Ladue-Sadie-Friendship
19. Stone
20. Lucky Queen
21. Shamrock
22. Gambler
23. Main Fracture-Comstock Keno
24. No. 9
25. No. 6
26. Porcupine-Comstock Keno-Kinman
27. Faith
28. Caribou

LEGEND

Upper Schist formation: quartz-mica schist, sericite schist, graphitic schist, phyllite, and thin-bedded quartzite

Central Quartzite formation: thick-bedded quartzite, thin-bedded quartzite, graphitic schist, and minor greenstone

Lower Schist formation: graphitic schist, sericite schist, phyllite greenstone, and thin-bedded quartzite

Lower Schist formation: No. 9 quartzite member: thick-bedded quartzite and graphitic schist

Vein fault
Post-ore fault
Approximate geological boundary
Mine or prospect ㉕
Travelled road with buildings
Untravelled road
Contours (interval 500 feet)

Cartography by the Geological Cartography Unit

Geological Survey of Canada

FIG. 1.

and structure were calculated from the x-ray diffraction pattern by Pistorius (1961):

$$a = 7.566 \pm 0.008\ \text{Å};\ b = 7.586 \pm 0.008;\ c = 6.954 \pm 0.008$$
$$\beta = 115° 56';\ a{:}b{:}c = 0.9974{:}1{:}0.9167$$

the space group is $C_{2h}^6 - A2/a$. X-ray powder data for gunningite and its synthetic equivalent are listed in Table 1. The identification of the minerals of the kieserite group by x-ray powder method is made difficult by the similarity of the patterns of the various members. For purposes of identification in the present work, the group of reflections in the 2θ region shown in Figure 3 were found to be characteristic for the iron, manganese, and zinc members.

PHYSICAL AND OPTICAL PROPERTIES

The natural mineral in all cases is so fine-grained as to be virtually cryptocrystalline. Colour and streak are white, and the lustre vitreous. The hardness is about 2½. Synthetic $ZnSO_4 . H_2O$ has a specific gravity of 3.195 (pycnometer; Gmelin, 1956), in fair agreement with the calculated value of 3.321 assuming $Z = 4$. The mineral is rapidly soluble in cold water.

Refractive indices for the natural and artificial minerals are given below. The latter was prepared by dehydration of reagent grade heptahydrate at about 100° C. (see pyrolysis curve, Fig. 2).

Synthetic	$\alpha' = 1.570;\ 1.576$	$\gamma' = 1.630$
Calumet 200 level	$\alpha' = 1.577$	$\gamma' = 1.630$

maximum $\gamma' - \alpha' = 0.06$

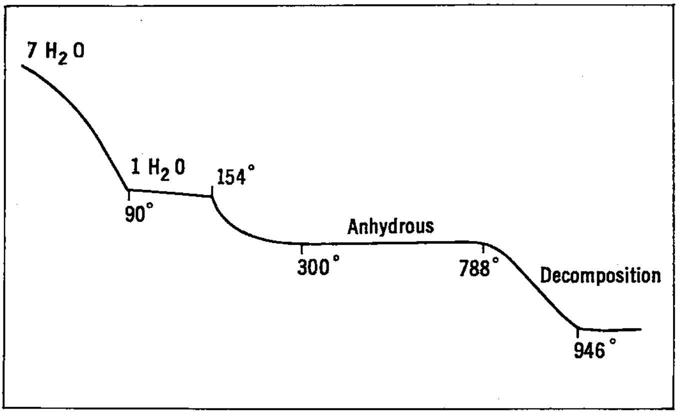

FIG. 2. Pyrolysis curve of zinc sulphate (Duval, 1953).

Comparison with the other members of the kieserite group shows that the true birefringence of gunningite is probably about 0.06. All other minerals in the group are biaxial positive.

TABLE 1. *X*-RAY POWDER DATA FOR GUNNINGITE

$ZnSO_4 \cdot H_2O$[a] (Pistorius, 1961)			$ZnSO_4 \cdot H_2O$[b] (synthetic, filtered copper radiation)		Comstock-Keno (filtered copper radiation)	Calumet 200 level (filtered iron radiation)	
I	*d*(calc.) Å	*hkl*	*I*(est.)	*d*(meas.)Å	*d*(meas.)Å	*I*(est.)	*d*(meas.)Å
40	4.825	011	*ms* (2)	4.78	4.80	7	4.77
53	4.768	$11\bar{1}$					
15	3.793	020	*w*	3.77	3.80	2	3.78
100	3.428, 3.402	111, 200	*s* (1)	3.40	3.41	10	3.40
23	3.367	$21\bar{1}$	*w*	3.33	3.36	3	3.32
27	3.313	120	*mw*	3.29	3.32	3	3.29
45	3.068	$20\bar{2}$	*m* (3)	3.05	3.06	6	3.05
15	2.563	$12\bar{2}$	*mw*	2.55	2.56	2	2.56
38	2.533	220	*m* (4)	2.51	2.52	4	2.51
3	2.422	211					
4	2.413	022	*vw*	2.40	—	1/2	2.41
3	2.386, 2.384	$31\bar{1}$, $22\bar{2}$					
10	2.344	031	*w*	2.33	2.34	2	2.33
5	2.338	$13\bar{1}$					
15	2.196	$11\bar{3}$	*m* (6)	2.19	2.19	3	2.19
3	2.179	$21\bar{3}$	*f*	—			
10	2.112	131	*mw*	2.10	2.10	2	2.10
6	2.098	$23\bar{1}$					
8	2.067	122	*mw*	2.05	2.06	2	2.05
12	1.973	$31\bar{3}$	*m* (7)	1.963	1.968	3	1.968
	1.896	040	*w*	1.898	1.902	2	1.898
4	1.878	$40\bar{2}$					
3	1.798	231	*mw*	1.807	1.815	2	1.810
	1.738	204	*vwb*	1.734	1.735	1/2	1.737
	1.701	400	*w*	1.698	1.705	1	1.699
10	1.683	422	*m* (5)	1.671	1.675	3	1.673
6	1.657	240	*w*	1.649	1.654	1	1.650
7	1.622	042	*mw*	1.617	1.621	2	1.619
5	1.589	$33\bar{3}$	*mw*	1.582	1.590	2	1.586
	1.552	420	*w*	1.555	1.557	1	1.557
2	1.532, 1.531	$40\bar{4}$, $32\bar{4}$	*f*	1.524	—	1/2	1.526
5	1.502	142	*mw*	1.499	1.505	2	1.500
4	1.479	213	*f*	1.468	—	1/2	1.469
2	1.474, 1.473	051, $15\bar{1}$					
4	1.455	340	*vw*	1.449	1.455	1	1.449
	1.435	$43\bar{3}$	*w*	1.435	1.440	1	1.437
3	1.411	151	*wb*	1.414	1.399	1/2	1.417
	1.407	$25\bar{1}$		1.405		1/2	1.407
	1.350	242	*f*	1.351	1.359	1/2	1.356
	1.320	$11\bar{5}$	*vw*	1.327	1.333	1/2	1.327
	1.310	124	*f*	1.312	—	1/2	1.311
	1.305	251	*f*	1.298	—	1/2	1.297
5	1.283, 1.281	$52\bar{4}$, $24\bar{4}$	*mw*	1.277	1.281	2	1.277
	1.280	431					
	1.266, 1.265	440, $15\bar{3}$	*mw*	1.261	1.266	2	1.261
	1.264, 1.263	060, $14\bar{4}$					
	1.263	313					

TABLE 1. X-RAY POWDER DATA FOR GUNNINGITE

$ZnSO_4.H_2O$[a] (Pistorius, 1961)			$ZnSO_4.H_2O$[b] (synthetic, filtered copper radiation)		Comstock-Keno (filtered copper radiation)	Calumet 200 level (filtered iron radiation)	
I	d(calc.)Å	hkl	I(est.)	d(meas.)Å	d(meas.)Å	I(est.)	d(meas.)Å
			vwb	1.244	1.251	1	1.243
			f	1.227	—	1/2	1.227
			f	1.216	—	1/2	—
			vw	1.198	1.203	1/2	1.197
			vw	1.180	—		
			vw	1.165	1.165		
			f	1.140	1.144		
			f	1.124	—		
			vw	1.099	1.104		
			f	1.087	1.089		
			w	1.052	1.056		
			f	—	—		
			f	1.019	1.021		
			vw	1.010	1.013		
			f	—	—		
			f	—	—		
			vw	0.9806	—		
			w	0.9723	—		

[a] Intensities obtained with Philips diffractometer on pure synthetic material by Pistorius (1961), whose unit cell dimensions were used to calculate the additional indices not accompanied by intensities.

[b] Baker's reagent grade $ZnSO_4.7H_2O$ dehydrated to the monohydrate. All films (columns 2, 3, 4) taken with 57.3 mm. dia. cameras; only $K\alpha_1$ lines recorded below $d = 1.40$. Intensities are visual estimations. Comstock-Keno gunningite (column 3) contains a small but undertermined quantity of manganese in substitution for zinc. The Calumet gunningite (column 4) is the first specimen shown in the table of spectrographic analyses.

CHEMICAL DATA

Insufficient gunningite was available for a chemical analysis. As the mineral is closely associated with sphalerite, considerable precaution was observed in preparing the samples used for the spectrographic analysis given in Table 2. Carbon electrodes were directly loaded with material carefully picked off the specimens with the blunted tip of a fine sewing needle. It was possible to obtain good samples in this manner as the

TABLE 2. SPECTROGRAPHIC ANALYSES OF GUNNINGITE

Description	Major	Minor	Trace	Faint Trace
Calumet 200 level	Zn		Si, Cu, Mn	Mg
Calumet 200 level	Zn			Mg, Cu, Si
Leo 1–8	Zn			Mg, Cu, Si
Synthetic[a]	Zn		Si, Cu	Mg

[a] Baker's reagent grade $ZnSO_4.7H_2O$ dehydrated to the monohydrate.

efflorescences do not cling to the rock surface, but are loosened at the slightest touch. Hand picking of the selected material was done under a 50× binocular microscope.

Two specimens of gunningite from the same locality in the Calumet mine 200 level were immersed in a beaker of distilled water for 30 seconds, a sufficient time to dissolve the sulphate from the rock surface. The solution was passed through fine filter paper (No. 42), gently evaporated, dehydrated to the monohydrate, and the metallic elements quantitatively determined by *x*-ray fluorescence analysis (Table 3). Discoloration of the precipitate indicated that some oxidation of iron had taken place. The coincidence of the theoretical and analytical values reported below is frankly regarded as being unusual for the *x*-ray method.

Table 3. *X*-ray Fluorescence Analysis of Gunningite Precipitate

$ZnSO_4.H_2O$		Calumet mine		
(theoretical)				
ZnO	45.35 ←	→ 45.5	ZnO	40.8
SO_3	44.61		MnO	3.1
H_2O	10.04		CdO	1.0
			FeO	0.6

X-ray fluorescence determination by G. R. Lachance. Spectrographic analysis shows additional Ca, Mg, Si (0.01–0.1%); Co, Ba, Cu, Al, Ag, Ni, Pb, B (<.01%).

Relationship of Gunningite to Other Members of the Kieserite Group

It is probable that considerable mutual substitution of cations takes place among kieserite ($MgSO_4.H_2O$), szomolnokite ($FeSO_4.H_2O$), and szmikite ($MnSO_4.H_2O$). The relationships of these minerals to gunningite were studied by means of synthetic preparations formed by dissolving in water weighed samples of the monohydrate sulphates, and evaporating the solutions at approximately 90–100 C°. While the chemical compounds encountered in these precipitates are not considered to be accurately representative of what may occur in nature, nevertheless some interesting relationships become apparent as the amount of substituting cation is increased (Table 4). The ratios shown below are expressed as weight ratios of the monohydrate sulphates, *i.e.*, 15 mg. of $FeSO_4.H_2O$ added to 30 mg. of $ZnSO_4.H_2O$ is shown as Fe:Zn = 1:2. The products were readily identified by their *x*-ray powder patterns as the transformation from one species to another is accompanied by an abrupt change in the characteristic reflections shown in Figure 3.

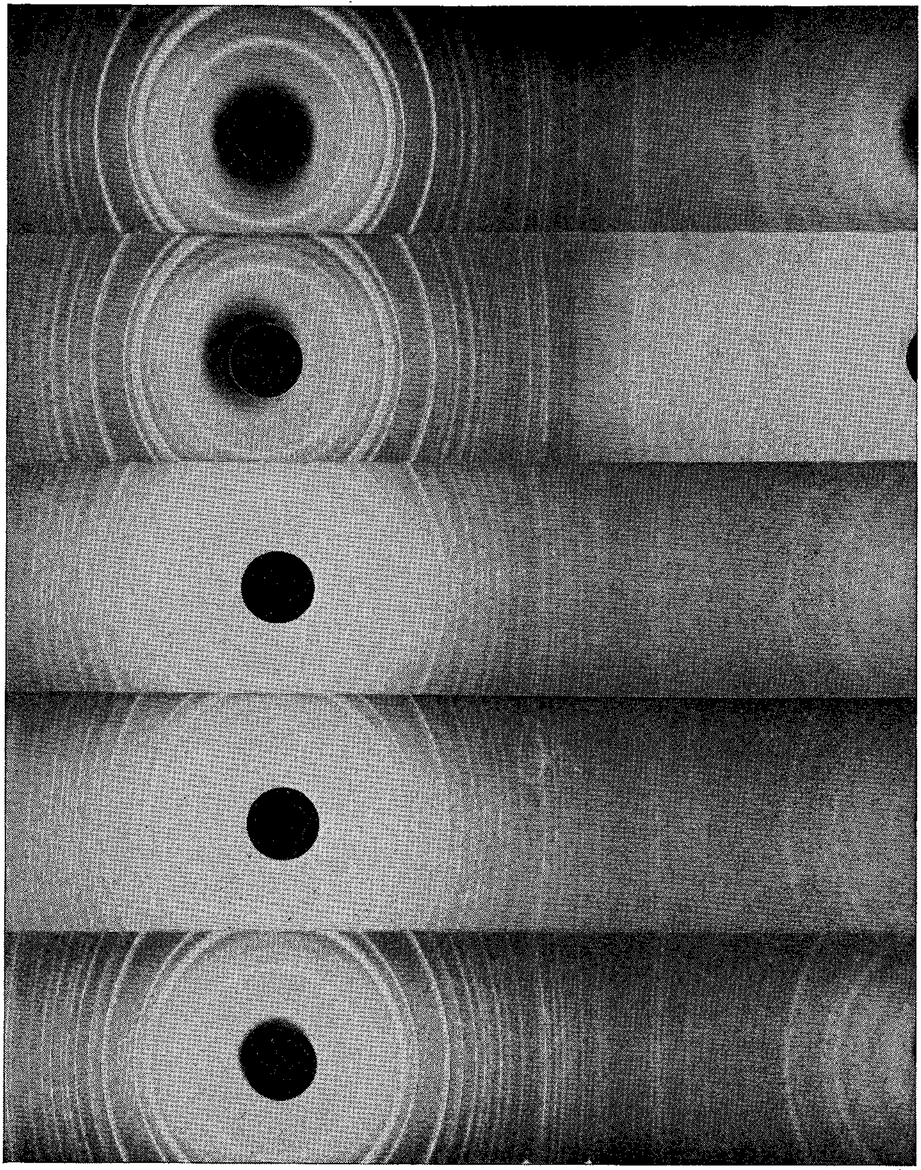

FIG. 3. *X*-ray powder patterns of the kieserite group minerals. (A) (*from top*) Szmikite, synthetic. (B) Szomolnokite, Tyrol. (C) Kieserite, Wathlingen, Germany. (D) Gunningite, Keno Hill. (E) Synthetic $ZnSO_4.H_2O$. All films taken with 57.3 mm. dia. cameras and manganese-filtered iron radiation. The group of reflections between two notches serve to distinguish szomolnokite and szmikite from each other, as well as from kieserite or gunningite.

TABLE 4. PRODUCTS FORMED BY EVAPORATION OF SULPHATE SOLUTIONS

Ratio			Product formed
		Mol. % $MnSO_4.H_2O$	
Zn:Mn	8:1	11	gunningite
Zn:Mn	4:1	19	gunningite
Zn:Mn	7:3	29	szmikite
Zn:Mn	3:2	39	szmikite
		Mol. % $FeSO_4.H_2O$	
Zn:Fe	2:1	32	gunningite
Zn:Fe	1:1	49	gunningite
Zn:Fe	1:2	65	szomolnokite
Zn:Fe	2:5	70	szomolnokite

Though not thoroughly investigated, magnesium is apparently capable of adopting a similar substitutional role.

Comparison of the *x*-ray powder photographs obtained from the above synthetic preparations leads to these conclusions: (1) considerable amounts of iron and manganese may be substituted for zinc in gunningite. (2) A continuous series apparently exists between $FeSO_4.H_2O$ and $MnSO_4.H_2O$ with $ZnSO_4.H_2O$. (3) The presence of a large quantity of iron in gunningite produces no change in cell edge and is not detectable by the film method. In marked contrast, significant increases in cell dimensions accompany the addition of manganese.

ASSOCIATED SULPHATES IN THE KENO HILL AREA

Additional members of the kieserite group occurring in the area are szomolnokite and szmikite, the former identified only from the 900 level of the Calumet mine. Relatively pure szmikite is sparingly distributed in several levels of the same mine.

Several grams of white and flesh-coloured efflorescences collected from specimens on the dump of the Silver King property are szmikites free of iron and unusually rich in zinc. The Silver King samples also contain admixed ilesite ($MnSO_4.4H_2O$) of similar composition.

Although the tetrahydrate sulphate of zinc ($ZnSO_4.4H_2O$) has not yet been identified from the Keno area, the mineral was found during the present study in association with bianchite ($ZnSO_4.6H_2O$) from Goslar, Germany. The *x*-ray powder pattern of the tetrahydrate is almost identical to that of $FeSO_4.4H_2O$, the minerals presumably being isostructural. It is likely that the zinc sulphate is much more common than is implied by the fact that the species has never been described as a new one.

Minerals containing additional water molecules beyond the tetrahydrate have not been reported *in situ* from the Keno Hill area, but microscopic examination indicates that the most abundant and widely distributed sulphate, rozenite ($FeSO_4.4H_2O$), was formed by dehydration of a higher hydrate, presumably melanterite.[3]

ORIGIN

Gunningite is derived directly from the oxidation of sphalerite which is known to have the composition (Zn,Fe,Cd,Mn)S in the Keno Hill deposits. Surface and ground waters carrying dissolved oxygen attack the sphalerite, yielding soluble sulphates of zinc, manganese, iron, and cadmium according to the following simple equations:

$$ZnS \text{ (zinc component) } + 2O_2 \rightarrow ZnSO_4$$
$$MnS \text{ (manganese component) } + 2O_2 \rightarrow MnSO_4$$
$$FeS \text{ (iron component) } + 2O_2 \rightarrow FeSO_4$$
$$CdS \text{ (cadmium component) } + 2O_2 \rightarrow CdSO_4$$

In the presence of abundant water all of the soluble salts are removed. If, however, the conditions are such that the supply of water is restricted or evaporation takes place, the metal-bearing solutions become supersaturated with the consequent precipitation of a number of hydrates of zinc, manganese, and iron of which gunningite, $ZnSO_4.H_2O$, is one.

ACKNOWLEDGMENTS

The writers are pleased to acknowledge that the spectrographic analyses are the contribution of G. Pattenden and W. F. White. In addition to the quantitative *x*-ray fluorescence analysis of gunningite, G. R. Lachance kindly made many related determinations. The writers are indebted to R. J. Traill for his generous assistance and careful review of the manuscript. Valuable service in various aspects of the problem was also rendered by R. Delabio, R. Brown, and T. Roach.

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[3] Rozenite is believed to be a species distinct from the pentahydrate, siderotil (manuscript in preparation; J. L. J.).