the synthetic material were more diffuse and no back reflection lines were recorded, indicating a difference in the degree of crystallinity of the two materials.

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RELATIONS OF THE MANGANESE-CALCIUM SILICATES, GAGEITE AND HARSTIGITE

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INTRODUCTION

A systematic study on the crystal chemistry of manganese silicates prompted further investigations on gageite and harstigite, two rare and poorly understood species. These studies indicate that the two minerals are structurally related but their unusual compositions are difficult to interpret without recourse to crystal structure analysis.

GAGEITE

Gageite was frequently found during mining at Franklin, Sussex County, New Jersey, its only reported locality, though it could hardly be called an abundant mineral. It is a late-stage low-temperature mineral, usually implanted upon other species in fissure fillings and solution cavities. Palache (1935) mentions its occurrence with pyrochroite, leucophoenicite, and calcite; and often with chlorophoenicite. The specimens used here included fibres from the vial of type material, kindly loaned by Professor Clifford Frondel, and a slightly warped prismatic crystal extracted from a solution cavity in zincite located in the Sjögren collection at the Swedish Natural History Museum in Stockholm.

Gageite was described as a new species by Phillips (1911) and a subsequent analysis on more plentiful material by Bauer (Palache, 1928) led to the composition $(Mn,Mg,Zn)_8(OH)_4(SiO_4)_3 \cdot \frac{3}{2} H_2O$, with Mn:Mg:Zn=0.72:0.23:0.05. Since the data on gageite were meager and not quite convincing, it was understandable that Strunz (1957) considered gageite synonymous with leucophoenicite to which gageite is chemically related.

TABLE 1. STRUCTURE CELL DATA FOR GAGEITE AND HARSTIGITE

	Gageite	Harstigite
a	13.79± .02 Å	13.90 Å
b	13.68± .02	13.62
c	3.279± .003[a]	9.68
ρ obs[b]	3.584	3.049
Z	2	4
formula	$H(_6Mn, Mg, Zn)_7Si_3O_{16}$ or $Mn_7(OH)_6(Si_3O_{10})$	$H_4(Ca, Mn, Mg)_7Al_2Si_6O_{24}$ or $Ca_7Al_2(OH)_4(Si_3O_{10})_2$
S.G.	*Pnn*2 or *Pnnm*	*Pcmn*
a:b:*c*	1.008:1:0.240	1.0206:1:0.7107[c]

[a] Very weak streaks on *c*-axis rotation photographs require *c* to be trebled.

[b] For gageite, Palache (1935); for harstigite, Flink (1886).

[c] Reorienting Flink's morphological a:b:c by (001/0$\bar{1}$0/100) gives 1.0150:1:0.7148, the transformed forms being {001}, {010}, {012}, {011}, {110}, and {221}.

Gageite can be easily confused with chlorophoenicite upon visual examination. It appears as colorless, pale brown, or pale pink laths and matted fibres and often occurs with the grayish-green to colorless laths of chlorophoenicite. However, unlike chlorophoenicite, gageite crystals display no terminal hemi-pyramidal faces, the termination usually being a simple basal pinacoid with rectangular cross-section. Upon microscopic examination, the gageite laths appear to be composites of single crystals in near parallel growth, often considerably warped so that Weissenberg photographs with the fibre as rotation axis show smeared spots which are difficult to interpret. Fortunately, one crystal on the Sjögren speci-

TABLE 2. POWDER DATA FOR GAGEITE AND HARSTIGITE
114.6 MM CAMERA DIAMETER; Fe/Mn RADIATION; STANDARDIZED FILM.

Gageite				Harstigite				Harstigite			
I/I_o	d_{obs}	d_{calc}	hkl	I/I_o	d_{obs}	d_{calc}	hkl	I/I_o	d_{obs}	d_{calc}	hkl
3	9.61	9.70	110	2	9.77	9.73	110	2	1.455		
10	6.87	6.89	200	4	4.35	4.35	221	1½	1.444		
		6.84	020			4.33	112	3 brd	1.372		
2	6.14	6.15	210	2	3.97	3.99	131	4 brd	1.331		
		6.12	120			3.97	022	1	1.323		
6	3.44	3.45	400			3.94	202	2	1.312		
		3.42	040			3.94	311	2	1.280		
4	3.34	3.32	140	2	3.83	3.81	122	1	1.266		
6	3.25	3.24	330	3	3.545	3.536	321	1	1.237		
4	3.08	3.08	420	4	3.222	3.219	312	1	1.223		
		3.06	240	2	3.127	3.129	411	1	1.205		
8	2.758	2.750	430	1	3.068	3.075	331	1	1.140		
		2.744	340			3.063	113	1	1.125		
8	2.707	2.704	510	3	2.885	2.915	421	1	1.121		
3	2.659	2.669	301			2.861	123	3	1.104		
5	2.614	2.614	131	5	2.817	2.823	042	1	1.093		
6	2.556	2.558	520	5	2.788	2.784	402	1 brd	1.085		
2	2.481	2.484	231	10	2.695	2.694	332	2 brd	1.056		
1	2.365	2.360	530	3	2.476	2.468	233	2 brd	1.046		
3	2.307	2.300	600	1	2.419	2.420	004	1½	1.033		
3	2.244	2.239	241	1	2.361	2.364	043	1	1.014		
3	2.176	2.178	620			2.359	441	2	1.012		
4	2.151	2.147	540	5	2.268	2.272	252	1	0.988		
3	2.103	2.101	051			2.270	600	1	0.981		
3	2.081	2.086	511	3	2.250	2.254	124	1	0.977		
1	2.056	2.053	630			2.253	061				
3	2.015	2.017	521			2.250	214				
3	1.952					2.246	522				
2	1.894			2½	2.127	2.129	352				
3	1.863			2½	2.091	2.089	062				
3	1.802			1	2.062	2.065	162				
6	1.6742			2	1.992						
2	1.6273			2½	1.946						
2	1.6172			1	1.925						
4	1.5869			2½	1.807						
3	1.5539			4	1.790						
6	1.5182			1	1.772						
About 15 more intensities, each less than 2				3	1.719						
				2	1.694						
				3	1.676						
				2½	1.628						
				2	1.589						
				1	1.575						
				1	1.510						
				1½	1.471						

men was found sufficiently 'single' for suitable photographs for structure cell determination. The dominant form is the unit prism.

The structure cell data were derived from a variety of oscillation, rotation, and Weissenberg photographs and are listed in Table 1. Table 2 presents powder data which were used to improve the cell translations.

The only reliable analysis (Bauer in Palache, 1928) is repeated in Table 3. This calculates to $(Mn_{10.15},Mg_{3.31},Zn_{.65},Fe_{.01})_{14.12}(OH)_{12.26}(Si_{5.26},Al_{.04})_{5.30}O_{18.59}$ in the structure cell. As the minimum equipoint rank number is 2 for the space groups, the ideal end-member composition for gageite is evidently $Mn_7(OH)_6(Si_3O_{10})$. Based on the X-ray data, there is no indication of any obvious relationship to leucophoenicite and gageite is apparently a valid species.

The composition as interpreted above bears a striking resemblance to that of leucophoenicite (Moore, 1967) which has the manganese humite formula $Mn_7(OH)_2(SiO_4)_3$. As the humites are olivine-related structures with insular silicate tetrahedra, there appears to be no structural relationship with gageite since some of the tetrahedra must be linked in that mineral—except if the formula is interpreted as $Mn_7(OH)_2(SiO_4)_3 \cdot 2H_2O$. As gageite appears to be structurally related to harstigite, discussion under that mineral suggests that the "linked silicate" formula should be adopted, at least for the present.

The Gladstone-Dale calculation using the specific refractive energies of Larsen (1921), the mean index of 1.731 (from Dana and Ford, 1932), and the analysis of Bauer affords a calculated density of 3.554, in very good agreement with the observed density of 3.584 cited in Palachec (1935).

The most remarkable feature of gageite is its very short axial translation parallel to the prism axis. Consequently, a *c*-rotation axis photograph was deliberately overexposed and the appearance of very faint streaks, requiring a trebling of that translation was noticed. Thus, for *hkl*, when $l=3n$ for the 3×3.279 Å translation, the layer lines are streaks. However, the streaks are so weak that they are effectively disregarded in this discussion. The only other example of a silicate displaying such a short translation is mentioned in a paper by Geiger (1948) who reports a 3.2 Å translation along the fibre axis for a sursassite from Val d'Err, Switzerland. Recent studies on the structure cell of sursassite by Freed (1964) indicate no such relation. It is possible that Geiger's material is in fact a gageite or gageite-related mineral, suspected since his material was collected from a low temperature manganese silicate-rich environment.

Since this translation of 3.3 Å suggests a structure composed of pyrochroite sheets, attempts were made to seek out a relationship, with one of the other axes projected on a sheet of manganese-centered octahedra, but met with failure. Also considered was a structure derivative of psilomelane (Wadsley, 1953) but the results were likewise inconclusive.

On the grounds of the structure cell formula for gageite, its crystal structure may lack a center of symmetry, since the sites of equipoint rank 2 for the centric group have symmetry $2/m$ and cannot accommodate silicate tetrahedra. Of course, it is assumed that there are no va-

Table 3. Analyses of Gageite and Harstigite

Gageite[a]					Harstigite[b]				
	Wt. %	Moles in cell	Ideal	k oxides		Wt. %	Moles in cell	Ideal	k oxides
SiO_2	23.58	5.26			SiO_2	38.94	22.07	24	0.0806
		5.30	6	0.0488	Al_2O_3	10.61	7.08 (Al)	8	0.0205
Al_2O_3	0.15	0.04 (Al)		0.0003					
					MnO	12.81	6.16		0.0245
MnO	53.74	10.15		0.1026	CaO	29.23	17.70 26.62	28	0.0658
MgO	9.95	3.31		0.0199	MgO	3.27	2.76		0.0065
		14.12	14						
ZnO	3.96	0.65		0.0061	K_2O	0.35	—		—
FeO	0.03	0.01		—	Na_2O	0.71	—		—
					H_2O	3.97	7.49 (OH)	8	0.0135
H_2O	8.24	12.26 (OH)	12	0.0280					
	99.65			0.2507		99.89			$0.211\times\frac{100}{98.83}=0.213$
	$\rho_{obs}=3.584$	$\Sigma 0=18.59$	20	$\rho_{calc}=3.554$		$\rho_{obs}=3.049$	$\Sigma 0=73.89^c$	80	$\rho_{calc}=3.19$

[a] Analysis of Bauer in Palache (1928).

[b] Analysis of Flink (1886).

[c] Does not include $(OH)^-$ already accounted for.

cancies or disordered tetrahedral groups in the structure, an assumption possibly questionable since very weak streaks were found on the rotation photograph requiring a larger translation.

HARSTIGITE

The mineral harstigite was originally described by Flink (1886) as a new species from the Harstigen manganese mine near Pajsberg, not far from Filipstad in Värmland, Sweden. This tiny manganese mine was once a prolific source of peculiar minerals, including such exotica as basic manganese arsenates, lead silicates, and what are reported to be the most beautiful rhodonite crystals in the world.

Harstigite is a rarity by any standard and the only specimen I have seen is the type material housed in the Swedish Natural History Museum—a fist-sized specimen of open fissure material in hausmannite and dolomite, upon which are implanted large reddish-orange andradites, manganoan humites, and prismatic barite crystals. The harstigite is implanted upon the garnets as small stout prismatic crystals almost indistinguishable from the barite except by its lack of cleavage; it is another credit to Flink's keen eye that this unspectacular mineral was looked upon with suspicion, studied in detail and found to be a unique species.

Flink presented one analysis of this mineral (Table 3) which, owing to its extreme rarity, was undertaken on only 304 mg of material. For the formula adopted in this paper, the structure cell contents are consistently low for each of the atomic species and, consequently, the density reported by Flink may be low. This wins further support from the computed density—3.19 gm/cc—based on the relationship of Gladstone and Dale using the specific refractive energies in Larsen (1921), the mean of the observed indices of refraction reported in Dana (1954), and the analysis of Flink. Increasing the cell contents of the atomic species so they are nearly integral multiples of 4 requires a density of 3.28. Using Flink's observed density of 3.049, the computed formula is $(Ca_{17.70}, Mn_{6.16}, Mg_{2.76})\ Al_{7.08}(OH)_{14.98}Si_{22.07}O_{73.89}$ and the end-member structure cell formula $4[Ca_7Al_2(OH)_4(Si_3O_{10})_2]$ is suggested.

The structure cell data, obtained from the usual oscillation, rotation, and Weissenberg procedures are given in Table 1 and the powder data in Table 2. Reorienting Flink's morphological cell in terms of the structure cell evidently requires the transformation $(001/0\bar{1}0/100)$.

DISCUSSION

Harstigite and gageite appear to be related crystallochemically, with $a_h \sim a_g$, $b_h \sim b_g$, $c_h \sim 3c_g$. The common formula unit is $[X_7(OH)_4(Si_3O_{10})]^{2+}$, where X is essentially Ca for harstigite and Mn for gageite. Certainly the assignment to both species of the $Si_3O_{10}^{8-}$ complex is not without ambiguities as the role of hydrogen is not known. For harstigite, even if all the hydrogens are bonded to water molecules, the silicate group cannot be composed strictly of insular tetrahedra. However, complications arise if some of the hydrogen atoms are directly attached to the oxygens associated with or in place of silicate tetrahedra, as in hydrogrossular or afwillite.

Hence, the assignment of the peculiar $Si_3O_{10}^{8-}$ group is only tentative. Though encountered in the prehnite structure as $AlSi_3O_{10}^{5-}$ groups, there does not appear to be any relationship to that mineral. In the prehnite structure, the $AlSi_3O_{10}^{5-}$ groups actually make up novel sheets (Preisinger, 1965) and though that group can be extracted from the harstigite formula, there are no available extra tetrahedrally coordinated ions in gageite to permit it. These two minerals may be prototypes of the prehnite structure or possibly even structures composed of the $Si:O=3:10$ triple groups of linked tetrahedra. Since the data do not permit any certain conclusions, the answer to these interesting questions must await a more detailed structure analysis presently being undertaken on gageite.

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