

## The chemical composition of gageite: an empirical formula

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### Abstract

Gageite from Franklin, New Jersey has been restudied analytically. Seven new analyses confirm the original analysis, and suggest that magnesium and zinc may be essential. The new data, together with a new density of 3.46 g/cm<sup>3</sup>, and a suggested trebling of the *c* axial dimension of previous work, lead to a new proposed formula for gageite of (Mn,Mg,Zn)<sub>40</sub>Si<sub>15</sub>O<sub>50</sub>(OH)<sub>40</sub>, with Mn:Mg:Zn about 28:10:2. Previous formulae are presumed to be incorrect.

### Introduction

Gageite was originally described by Phillips (1910) from Franklin, New Jersey, the only locality for the species to date. The original analysis was performed on a meagre portion of material and the mineral was subsequently re-analyzed by Bauer (in Palache, 1928), using a one-gram sample. This analysis, together with my results, is given in Table 1. Gageite has not been re-analyzed in the last 50 years, and little is known about the possible variation in its composition. The crystal chemistry of gageite was discussed by Moore (1968a,b), and he later (1969) presented a detailed exposition of the crystal structure.

Several of the gageite specimens examined were studied by X-ray powder diffractometry. Their patterns are all in excellent agreement with the powder data for gageite published by Moore (1968a) and with the powder pattern of the type gageite specimen in the Smithsonian Collection (NMNH #R6444). An excellent description of the physical appearance and characteristics of gageite was given by Moore (1968a) and need not be repeated here.

### Chemistry

The gageite specimens were analyzed with an ARL-SEMQ electron microprobe, using an operating voltage of 15 kV and a beam current of 0.15  $\mu$ A. The standards used were manganite for manganese, synthetic ZnO for zinc, and hornblende for iron, magnesium, calcium and silicon. The data were corrected using the MAGIC-4 computer program. A spectro-

graphic analysis indicated the absence of any light elements ( $1 < Z < 8$ ). There is inadequate gageite for the determination of water.

The analytical data (Table 1) show that the composition of gageite is fairly constant from sample to sample. The gageite specimens studied were quite different in matrix and associated species, and the varying nature and texture of the parageneses indicate that the specimens could not have come from one pocket. The specimens were acquired by the Smithsonian Institution over a period of 32 years and have no commonality. Therefore, the similarities in composition must have more than a chance significance. A further examination of the analytical data indicates:

- (1) The compositions of the specimens studied are in good agreement with the previous analysis by Bauer (Palache, 1928).
- (2) The consistency in relative amounts of the cations Mn, Mg, and Zn strongly suggests some ordering of these elements in the crystal structure.
- (3) The ratio of divalent cations to silicon is clearly 8:3 and not the value of 7:2 suggested in the crystal structure determination, which gave the formula  $M_7^{2+}(\text{O})(\text{OH})_8[\text{Si}_2\text{O}_6]$  (Moore, 1969).

### Discussion

The calculation of a formula from the average of the analyses suggests that the composition of gageite might be represented by the formula  $\text{Mn}_6\text{Mg}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$ . However, the consistency of

zinc and magnesium in the analytical data suggests that they may be essential to gageite, and a formula with more cations might be required.

The density of gageite determined by Palache (1928) was reported as 3.584 g/cm<sup>3</sup>. However, my repeated determinations failed to give values nearly that high. After dissolution of encrusting minerals in acid, and using heavy-liquid techniques, the density of sample NMNH #R11108 was determined to be 3.46(3) g/cm<sup>3</sup>, similar to that of the frequently associated chlorophoenicite.

The above formula cannot be completely reconciled with the crystal structure of Moore (1969), who gave  $a = 13.79(2)$ ,  $b = 13.68(2)$ , and  $c = 3.279(3)$ Å, for the orthorhombic subcell with space group  $Pnmm$ . These unit-cell parameters have been confirmed (D. Peacor, personal communication). Moore (1968a, 1969) noted the presence of streaks which require a trebling of the  $c$  axial dimension of 3.279Å. The presence of these streaks has been confirmed by single-crystal methods. If these reflections are significant, the cell volume then becomes 1855Å<sup>3</sup>, and can easily accommodate a larger formula.

A satisfactory formula for gageite, based on the newly determined density of 3.46 g/cm<sup>3</sup>, the tripled unit cell, and the average of seven analyses in Table 1, is  $(\text{Mn,Mg,Zn})_{40}\text{Si}_{15}\text{O}_{50}(\text{OH})_{40}$ , with Mn:Mg:Zn = about 28:10:2. This formula, with  $Z = 1$ , yields a calculated density of 3.41 g/cm<sup>3</sup>, in good agreement with the observed value of 3.46 g/cm<sup>3</sup>.

Using the unit cell with  $c$  trebled, the calculated density of 3.41 g/cm<sup>3</sup>, and the average of the seven microprobe analyses from Table 1, the calculation of cations per unit cell yields  $(\text{Mn}_{27.4}\text{Mg}_{10.7}\text{Zn}_{2.0}\text{Fe}_{0.1}\text{Ca}_{0.1})_{\Sigma 40.4}\text{Si}_{15.2}$ , in excellent agreement with the proposed formula, and giving a  $M^{2+}:\text{Si}$  ratio of 8:3.

In view of Moore's structure determination, there could be 42  $M^{2+}$  sites in gageite, but the discrepancy is clearly in the silicon content. The present analyses substantiate that of Bauer and indicate that there must be more silicon in gageite than the two atoms in Moore's proposed formula. Moore (1969) noted that "only the average arrangement of silicate tetrahedra can be ascertained in this structure analysis."  $Pnmm$  is apparently only an average space group for the substructure and the true superstructure space group

Table 1. Chemical analyses of gageite

NMNH #	SiO <sub>2</sub>	FeO	MgO	CaO	ZnO	MnO	H <sub>2</sub> O	Total
144078	23.75	0.21	10.31	0.14	4.66	51.11	n. d.	90.18
R6639	23.91	0.20	12.87	0.21	3.84	48.67	n. d.	89.70
R11108	23.66	0.23	11.30	0.22	5.22	50.41	n. d.	91.04
95563	24.05	0.21	10.12	0.16	4.91	52.01	n. d.	91.46
R6500	24.34	0.18	11.18	0.21	3.86	52.75	n. d.	92.52
C6803	24.08	0.18	10.65	0.16	3.50	53.37	n. d.	91.94
R6444	23.52	0.20	12.95	0.24	4.09	49.11	n. d.	90.11
Average*	23.90	0.20	11.34	0.19	4.30	51.06	n. d.	90.99
Bauer(1928)	<b>23.58</b>	<b>0.03</b>	<b>9.95</b>	n. d.	<b>3.96</b>	<b>53.74</b>	<b>8.24</b>	<b>99.65**</b>
Theory ***	23.65		10.57		4.27	52.09	9.42	100.00

\* Average of the preceding seven analyses.

\*\* includes 0.15 % Al<sub>2</sub>O<sub>3</sub>.

\*\*\* Theory for  $(\text{Mn,Mg,Zn})_{40}\text{Si}_{15}\text{O}_{50}(\text{OH})_{40}$  with Mn:Mg:Zn = 28:10:2.

Accuracy of data: ±3% of the amount present.

NMNH - National Museum of Natural History, Smithsonian Institution

n. d. - not determined.

(with  $c$  trebled) may still be unknown. The answer to this anomaly will likely lie with future crystal structure determinations.

Gladstone-Dale calculations, using the average analysis, the newly-determined density, and the constants of Mandarino (1976), yield  $K = 0.211$  from the chemical composition, and  $K = 0.211$  from the mean refractive index  $\bar{n}$  (Palache, 1928) of 1.731 and the density of 3.46 g/cm<sup>3</sup>. The formula proposed by Moore (with Mn:Mg:Zn = 28:10:2) and  $M^{2+} = 7$  atoms, yields  $K = 0.216$ , but this is regarded as fortuitous in view of the fact that this structural formula,  $M_7^{2+}(\text{O})(\text{OH})_8[\text{Si}_2\text{O}_6]$ , with the  $M^{2+}$  ratio noted above, requires SiO<sub>2</sub> 18.82, MnO 60.50, MgO 11.04, ZnO 4.46 and H<sub>2</sub>O 5.18 percent, in violation of the known composition of the mineral, according to all analyses.

In summary, the composition of gageite is shown to be nearly constant among various parageneses. This invariant composition is in good agreement with the original analysis, but not with the recent crystal structure determination. A tentative formula is proposed as  $(\text{Mn}, \text{Mg}, \text{Zn})_{40}\text{Si}_{15}\text{O}_{50}(\text{OH})_{40}$  with Mn:Mg:Zn = 28:10:2 and  $Z = 1$ . This requires a trebling of the  $c$ -axis translation to 9.837Å. The only way to effectively resolve the demonstrated ambiguity is by the solution of the superstructure, which will be extremely difficult and is beyond the scope of the present paper. I wish merely to point out that the formula of gageite must be other than that proposed by the crystal structure determination. The basic framework for the average substructure has been contributed by

Moore (1969), but it is improbable, given the nature of the crystals available, that the solution to this problem will be solved by X-ray techniques. The precise details of the atomic arrangement of gageite remain unknown, and will likely have to await examination by the lattice-imaging techniques of electron diffraction.

#### Acknowledgments

I am indebted to Drs. Donald Peacor, Joseph Mandarino, Sid Williams, and Daniel Appleman for critical readings of the manuscript, but this does not imply their agreement with the arguments presented herein. I thank Mr. Richard Johnson and Mr. Grover Moreland for the preparation of polished sections, and Mr. Charles Obermeyer for assistance with the microprobe. This research was supported, in part, by a grant from Mrs. E. Hadley Stuart, Jr.

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*Manuscript received, November 14, 1978;  
accepted for publication April 13, 1979.*