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MAGNESIUM-CHLOROPHOENICITE REDEFINED AND NEW DATA ON CHLOROPHOENICITE

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ABSTRACT

Magnesium-chlorophoenicite, originally defined as $10(Mg,Mn)O \cdot As_2O_5 \cdot 7H_2O$ on the basis of a faulty analysis, is redefined as $(Mg_{1.39}Mn_{1.18}Zn_{0.43})Zn_2(OH)_6[As_{0.42}H_{0.5}(O,OH)_3]_2$ or, ideally, $Mg_3Zn_2(OH)_6[As_{0.5}H_{0.5}(O,OH)_3]_2$. Magnesium-chlorophoenicite is the magnesium analogue of chlorophoenicite. Chlorophoenicite is re-analyzed and yields the empirical formula $(Mn_{2.65}Mg_{0.23}Zn_{0.12})Zn_2(OH)_6[As_{0.5}H_{0.5}(O,OH)_3]_2$, confirming the known structural formula. There is solid solution between magnesium-chlorophoenicite and chlorophoenicite, but it is not completely represented by available analyses.

Keywords: chlorophoenicite, magnesium-chlorophoenicite, Franklin, New Jersey, analytical data.

SOMMAIRE

La magnésio-chlorophoenicite, à laquelle on avait attribué la composition $10(Mg,Mn)O \cdot As_2O_5 \cdot 7H_2O$ sur la foi d'une analyse erronnée, est l'analogue magnésifère de la chlorophoenicite; sa formule empirique est $(Mg_{1.39}Mn_{1.18}Zn_{0.43})Zn_2(OH)_6[As_{0.42}H_{0.5}(O,OH)_3]_2$ ou, plus simplement, $Mg_3Zn_2(OH)_6[As_{0.5}H_{0.5}(O,OH)_3]_2$. Une nouvelle analyse donne, pour la chlorophoenicite, $(Mn_{2.65}Mg_{0.23}Zn_{0.12})Zn_2(OH)_6[As_{0.5}H_{0.5}(O,OH)_3]_2$, ce qui confirme la formule structurale admise. Ces deux espèces forment une solution solide incomplète, du moins sur le vu des échantillons analysés à ce jour.

(Traduit par la Rédaction)

Mots-clés: chlorophoenicite, magnésio-chlorophoenicite, Franklin, New Jersey, données analytiques.

INTRODUCTION

Chlorophoenicite was first described from Franklin, Sussex County, New Jersey, by Foshag & Gage (1924); it was given a more comprehensive treatment by Foshag *et al.* (1927), who proposed the formula $10(RO) \cdot As_2O_5 \cdot 7H_2O$, wherein R was essentially Mn and Zn with minor amounts of Ca, Mg and Fe. Additional data were given on the species by Bauer & Berman (1930); the crystal structure was solved by Moore (1968), who presented the structural formula $(Mn,Mg)_3Zn_2(OH)_6[As_{0.5}H_{0.5}(O,OH)_3]_2$.

Magnesium-chlorophoenicite was first described from the Franklin deposit by Palache (1935) in his now-famous monograph on the Franklin and Sterling Hill ore deposits. He proposed the formula $10(Mg,Mn)O \cdot As_2O_5 \cdot 7H_2O$ for this mineral, and noted that it was similar to chlorophoenicite except for the apparent substitution of magnesium for zinc. It was decided to investigate the compositions of magnesium-chlorophoenicite and chlorophoenicite because (1) neither species had been re-analyzed since the original descriptions and (2) the single analysis on the former mineral had been performed on admittedly impure material.

INTEGRITY OF THE TYPE SPECIMENS

The type (holotype) chlorophoenicite is well documented; it is sample number NMNH 94964 in the Smithsonian collection, and was clearly designated by catalog number in the description by Foshag *et al.* (1927).

Two type specimens exist for magnesium-chlorophoenicite. One, a matrix specimen in two pieces, is in the Harvard University collection, number HU 92803. The second type specimen, entered in the Smithsonian collection as NMNH number 96495, is accompanied by a letter from Harry Berman to William Foshag that states, in part: "this material occurred on only one specimen in our collection, of which most was taken for analysis. We saved about one-half of a radial group of which we are sending you a portion." It is clear from the correspondence that there was only one type specimen. However, the variance in chemical composition on the one specimen is rather large and makes this preliminary statement about the type specimens necessary.

All of the studied specimens are from the Franklin orebody. The non-type samples are associated with manganese silicates, chiefly either leucophoenicite, hodgkinsonite or gageite, together with willemite, zincite and calcite. Sterling Hill chlorophoenicite is much more widespread in occurrence; it accompanies pyrochroite assemblages, and is associated with many of the numerous arsenates discovered since 1972. Indeed, at Sterling Hill, chlorophoenicite is likely the most ubiquitous arsenate mineral. The X-ray powder-diffraction patterns of chlorophoenicite and magnesium-chlorophoenicite are very similar and in good agreement with data in the JCPDS file (PDF 25–1160).

ANALYTICAL METHODS

The samples were analyzed with an ARL–SEMQ electron microprobe using an operating voltage of 15 kV and a beam current of 0.15 μA. The standards used were synthetic ZnO for zinc, manganite for manganese, synthetic olivenite for arsenic, fluorapatite for phosphorus, and hornblende for iron, magnesium and calcium. A wavelength-dispersion microprobe scan of the type samples indicated the absence of any elements with atomic number greater than nine except those reported herein. The data were corrected with a modified version of the *MAGIC-4* computer program. The resultant analyses are given in Table 1. Iron and calcium are absent or present only as traces in all of the samples. Deficiencies of arsenic in some samples are likely due to the substitution of small amounts (up to 0.8%) of P_2O_5 or of carbonate for arsenate.

TABLE 1. ANALYSES OF MAGNESIUM-CHLOROPHOENICITE AND CHLOROPHOENICITE

Sample #	MgO	MnO	ZnO	FeO	CaO	As_2O_5	P_2O_5	H_2O	Total
Theory*	11.50	20.25	30.97	0.0	0.0	21.87	0.0	15.41	100.00
HU 92803	10.6	15.9	37.5	0.0	0.0	20.7	0.1	15.2Ψ	100.0
96495	7.6	18.7	37.2	0.0	0.1	20.8	0.1	15.5Ψ	100.0
96495	7.4	21.0	35.1	0.0	0.0	21.1	0.1	15.3Ψ	100.0
138029	2.7	33.8	29.6	0.0	0.0	20.7	0.1	13.1Ψ	100.0
C5912	2.4	35.7	29.2	0.0	0.0	19.8	0.1	12.8Ψ	100.0
94964	1.6	33.0	30.3	0.0	0.1	20.3	0.1	14.9†	100.3
95563	1.2	37.7	28.8	0.0	0.0	18.4	0.8	13.1Ψ	100.0
R5397	1.1	35.4	30.6	0.0	0.1	18.3	0.1	14.4Ψ	100.0
C6280-2	1.0	36.4	28.2	0.0	0.0	19.1	0.1	15.2Ψ	100.0
C3757	0.9	36.9	28.8	0.0	0.0	20.0	0.1	13.3Ψ	100.0
C3206	0.9	37.4	28.8	0.0	0.0	18.0	0.1	14.9Ψ	100.0
Theory**	0.0	37.24	28.48	0.0	0.0	20.11	0.0	14.17	100.00
Atomic Proportions									
Theory*	.285	.285	.380	.000	.000	.190	.000	1.712	
HU 92803	.263	.224	.461	.000	.000	.180	.001		
96495	.188	.264	.457	.000	.002	.181	.001		
96495	.184	.296	.431	.000	.000	.184	.001		
138029	.067	.476	.364	.000	.000	.180	.001		
C5912	.060	.503	.359	.000	.000	.172	.001		
94964	.040	.465	.372	.000	.002	.177	.001	1.655	
95563	.030	.531	.354	.000	.000	.160	.011		
R3597	.027	.499	.376	.000	.002	.159	.001		
C6280-2	.025	.513	.347	.000	.000	.166	.001		
C3757	.022	.520	.354	.000	.000	.174	.001		
C3206	.022	.527	.354	.000	.000	.157	.001		
Theory**	.000	.525	.350	.000	.000	.175	.001	1.574	

Accuracy of data: ±3% of the amount present.
* - Theoretical composition for midmember in the magnesium-chlorophoenicite--chlorophoenicite series with Mg:Mn = 1:1.
**- Theoretical composition for end-member chlorophoenicite.
† - Water determined by DTA-TGA.
Ψ - Water calculated by difference.
Sample numbers from U. S. National Museum of Natural History except HU-92803 from Harvard University.

Water was determined by DTA–TGA on the type chlorophoenicite only. The loss of 14.9% occurred between 38 and 587°C, with a partial pressure peak at 276°C. A small amount of carbonate was evolved as 0.2% CO_2 between 423 and 646°C.

RESULTS

Chlorophoenicite

An examination of the data given in Table 1 indicates that all chlorophoenicite samples contain some magnesium, and that the pure manganese end-member has not been found in nature. The CaO content of 3.36% reported by Foshag *et al.* (1927) is not confirmed. This high value was likely due to admixed calcite, which is abundant on the specimens. The compositions of the most manganese-rich samples conform to the structural formula of Moore (1968). The new analysis of the type sample, NMNH 94964, yields, on the basis of ΣM^{2+} atoms = 5, the formula $(Mn_{2.65}Mg_{0.23}Zn_{0.12})_{\Sigma 3.00}Zn_2(OH)_6[As_{0.5}H_{0.5}(O,OH)_3]_2$, in accordance with Moore's structural formula. This assumes limited substitution of magnesium and zinc for manganese.

Application of the Gladstone–Dale relationship using the constants of Mandarino (1976) yields the value of K_C = 0.199 for the chemical composition, and K_P = 0.195 for the physical properties using the newly measured density of 3.53 g/cm³ and the indices of refraction for this sample given by Foshag *et al.* (1927): α 1.682, β 1.690, γ 1.697. The compatibility of the data, using the relation $1-(K_P/K_C)$ of Mandarino (1979), is excellent.

Magnesium-chlorophoenicite

The three most magnesium-rich specimens analyzed, listed in Table 1, are of type magnesium-chlorophoenicite. Although both have claim to type status, only the Harvard University sample, HU 92803, has magnesium greater than manganese, and thus may be a legitimate magnesium-chlorophoenicite.

The new analysis of sample HU 92803 yields, on the basis of ΣM^{2+} atoms = 5, the formula $(Mg_{1.39}Mn_{1.18}Zn_{0.43})_{\Sigma 3.00}Zn_{2.00}(OH)_6[As_{0.42}H_{0.5}$

$(OH,O)_3]_2$, calculated in accordance with Moore's structural formula. The X-ray-diffraction powder pattern of type magnesium-chlorophoenicite is essentially identical to that of type chlorophoenicite, within error of measurement, and confirms that the phases are isostructural. Hence, in magnesium-chlorophoenicite, one must conclude that magnesium must likely occupy one of the sites normally occupied by manganese in chlorophoenicite. There is an excess of zinc over the two atoms required, and there is no apparent substitution of magnesium for zinc. The excess zinc indicates that there may be some substitution (up to 4–6 weight % ZnO) in the octahedral Mg/Mn sites in magnesium-chlorophoenicite.

The analysis by Gonyer (*in* Palache 1935) is clearly in error. Although there is some gross inhomogeneity in the type sample, it cannot account for the 29.95% MgO reported by Gonyer in his analysis of an admittedly impure sample weighing only 0.4 g. An attempt to explain the extremely high magnesium content prompted analyses of the associated minerals. However, the associated willemite contains only 2.5% MgO; the associated andradite and calcite, which might have been present as impurities, contain even less. Hence, no precise determination can resolve the disparity between the old analysis and the new data, which range from 7.6 to 10.6% MgO (Table 1). Although it may be fortuitous, it is interesting to note that if the MgO and ZnO figures of Gonyer are switched, they become 8.90% MgO and 29.95% ZnO, much closer to the composition of a magnesian chlorophoenicite. These reversed figures also give good agreement between the new and old data for MgO inasmuch as the reversed figure (8.90) is in good agreement with the mean of 9.1% MgO obtained for the holotype sample. However, this is conjecture; it does not account for the zinc content (still too low) and does not rigorously explain the matter. One is left with a poor analysis which cannot be explained satisfactorily.

Magnesium-chlorophoenicite is redefined as the magnesium analogue of chlorophoenicite. Re-analysis of the holotype specimen indicates that zinc is essential to magnesium-chlorophoenicite, and confirms the species relationship to chlorophoenicite.

Application of the Gladstone–Dale relationship, as previously cited, to magnesium-chlorophoenicite HU 92803 yields a K_P value of 0.195 based on a newly determined density of 3.45 g/cm^3 and the indices of refraction of Berman (*in* Palache 1935): α 1.669, β 1.672, γ 1.677. Using the results of the chemical analysis of this study and the constants of Mandarino (1976), one obtains a K_C value of 0.197. The resultant estimation of error $1-(K_P/K_C)$ of 0.010 indicates superior agreement of the data (Mandarino 1979).

Among collectors, there has long been the assumption that the stout prismatic crystals of this series are true chlorophoenicite and that the extremely acicular, radiating crystals are magnesium-chlorophoenicite. Based on examination and semiquantitative analyses of a large number of specimens from both Franklin and Sterling Hill, this former distinction is found to be invalid. The specimens examined have widely varying parageneses. There is no correlation between the Mg:Mn ratio and the acicular or stout habit of the species. The extremely acicular habit may be related to some compositional variations, however, inasmuch as some acicular crystals do contain up to 0.8 weight % P_2O_5, presumably in substitution for As_2O_5.

There are presently inadequate data to discredit magnesium-chlorophoenicite. The apparent ratio of octahedral cations clearly has Mg > Mn > Zn. The species should remain valid until a crystal-structure analysis of highly magnesian material can determine the actual site-populations of Mg and Mn, and validate or discredit the species. Magnesium-for-manganese substitution, although uncommon in most parageneses, is the rule and not the exception at Franklin and Sterling Hill; samples will likely be found in which Mg exceeds Mn.

The nomenclature used in this paper was approved by the I.M.A. Commission on New Minerals and Mineral Names.

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