Magnussonite: new chemical data, an occurrence at Sterling Hill, New Jersey, and new data on a related phase from the Brattfors mine, Sweden

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Abstract

New chemical analyses of magnussonite samples from Långban, Sweden, and Sterling Hill, New Jersey, support the original formula for this phase. Seven new microprobe analyses, including a water determination by TGA-EGA, support the Mn:As ratio determined in a recent structural study which proposed the formula $Mn_{18}^{2+}[Mn^{1+}As_6^{3+}O_{18}]_2Cl_2$ for magnussonite, but differ in two respects: (OH) > Cl; 4 (OH,Cl) per 12 As instead of two. Cu is present in all isometric magnussonite but its role is unclear. The new formula is $Mn_{10}As_6^{3+}O_{18}(OH,Cl)_2$ with Z = 16.

Additional analytical data are presented for a magnussonite-like phase from the Brattfors Mine, Nordmark, Sweden. These lead to a very tentative formula, $Mn_{10}As_6^{3+}O_{18}Cl(OH)$, with (OH) assumed for charge balance. This phase remains unnamed.

Introduction

Magnussonite was originally described from Långban, Sweden, by Gabrielson (1956). A second occurrence, at Sterling Hill in New Jersey, was described by Frondel (1961), who noted that there were some uncertainties with respect to the chemical analysis, but that the mineral was unambiguously magnussonite. Recently, Moore and Araki (1979) proposed a fluorite-derivative crystal structure for magnussonite, and gave the end-member formula $Mn_{18}^{2+}[As_6^{3+}Mn^{1+}O_{18}]_2Cl_2$. They verified that it has space group $Ia3d$ and unit cell parameter $a = 19.680(4)$Å, Z = 8. An interest in the chemistry of the Sterling Hill material prompted a re-investigation of the composition of magnussonite from there and Långban, and of a magnussonite-like mineral from the Brattfors Mine in Sweden, previously described as an unnamed tetragonal "magnussonite" by Moore (1970).

Sterling Hill occurrence

The original Sterling Hill occurrence, noted by Frondel (1961), was of a very small amount of green material associated with zincite and an impure selvage on a slickenside of willemite–franklinite–calcite ore (H-95036, NMNH 147730).

A new occurrence was recently found by John Kolic, a miner in the Sterling Hill Mine. Here it is associated with abundant zincite, minor kraisslite, and a light-brown microgranular mineral related to hematolite. The color varies from light brown to green, but examination of material of both colors revealed no significant variations in composition or X-ray powder diffraction patterns. In spite of the recovery of perhaps a dozen samples, magnussonite is present only in very small amounts and must be considered very rare at Sterling Hill.

Chemistry

The samples studied were chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA. The standards used were manganite (Mn), synthetic olivenite (As,Cu), synthetic ZnO (Zn), scapolite (Cl), fluorapatite (F), and hornblende for all other elements. The data were corrected using a modified version of the MAGIC-4 program. The samples are chemically homogeneous over 10 μm sample spots. The resultant data, presented in Table 1, are given "as-determined" but we note that the given weight percents are slightly high due to background effects. We have calculated total Cu as CuO, but have not determined the oxidation state of Cu.

Water was determined on one sample from Långban, (NMNH 96057), by TGA-EGA, resulting in a water loss of 1.5 wt.% (±0.2%) between 120 and 600°C. The samples studied herein were all identified as magnussonite or the Brattfors phase on the basis of X-ray powder diffraction patterns.

Table 1. Chemical analyses of magnussonite and a related phase

#	Sample #	FeO	MgO	CaO	CuO	ZnO	MnO+	As$_2$O$_3$	Cl	H$_2$O	O = Cl	Total	color	Locality
	Gabrielson (1956)		1.47		2.07		47.24	43.49	0.84	1.16	0.19	99.76*	green	Langban, Sweden
	Gabrielson (recalc.)		1.53		2.15		49.17	45.26	0.87	1.21	0.19	100.00	green	Langban, Sweden
	Mn$_{10}$As$_6^{3+}$O$_{18}$(OH)$_2$						53.71	44.93		1.36		100.00		(theoretical comp.)
1.	NMNH 96057	1.2	0.2	0.7	2.3	0.0	49.6	45.2	0.7	1.5	0.2	101.2	green	Langban, Sweden
2.	NMNH 138023	2.4	0.2	0.4	1.8	0.0	48.9	45.4	0.5		0.1	99.5	green	Langban, Sweden
3.	NMNH R9296	1.5	0.3	0.8	3.4	0.0	49.2	45.4	0.8		0.2	101.2	green	Langban, Sweden
4.	HU-95036	0.4	0.3	0.3	4.0	1.5	49.0	45.2	1.6		0.4	101.9	green	Sterling Hill, N.J.
5.	NMNH 147308	0.4	0.2	0.3	3.4	2.8	47.9	44.0	1.8		0.4	100.4	brown	Sterling Hill, N.J.
6.	NMNH 147308	0.5	0.2	0.3	3.3	2.4	48.7	44.1	1.7		0.4	100.8	green	Sterling Hill, N.J.
7.	NMNH 147370	0.4	0.3	0.4	3.9	2.4	48.0	44.2	1.7		0.4	100.9	green	Sterling Hill, N.J.
8.	NMNH R5757	0.5	0.8	1.4	0.7	0.0	49.5	45.2	3.0		0.7	100.4	brown	Brattfors Mine, Sweden
9.	NMNH B20580	0.4	0.9	1.3	0.6	0.0	49.8	44.5	2.9		0.7	99.7	brown	Brattfors Mine, Sweden
10.	NMNH 120060	0.4	0.9	1.3	0.6	0.0	50.6	45.0	2.8		0.6	101.0	brown	Brattfors Mine, Sweden
	Mn$_{10}$As$_6^{3+}$O$_{18}$Cl(OH)						52.97	44.31	2.65	0.67	0.6	100.00		(theoretical comp.)

+ -- Total Mn calculated as MnO.   * - sum includes 3.68% reported impurity.
Accuracy of data: ± 4 percent of the amount present for major constituents; fluorine present only as traces (analyses 1-10).
Analyses #1-7 are of magnussonites; analyses 8-10 are of the Brattfors phase.

Magnussonite composition

The original analysis by Blix *in* Gabrielson (1956) reported 3.68 weight percent barite impurity. We have recalculated Blix's analysis to 100% and present both the original and recalculated analyses in Table 1. The calculation of a chemical formula, on the basis of As = 6 atoms, yields: $(Mn_{9.09}Mg_{0.50}Cu_{0.34})_{\Sigma9.93}$ $As_{6.00}^{3+}$ $O_{17.89}$ $(OH_{1.76}Cl_{0.32})_{\Sigma2.08}$, or ideally, $Mn_{10}As_6^{3+}O_{18}(OH,Cl)_2$ in agreement with the interpretation of Gabrielson. Because Moore and Araki (1979) have proposed a formula with less (OH + Cl), we obtained a water analysis for our sample #96057 by TGA-EGA. The calculation of a chemical formula for this Långban sample, on the basis of As = 6, yields: $(Mn_{9.18}Cu_{0.38}Fe_{0.22}Ca_{0.16}Mg_{0.07})_{\Sigma10.01}As_{6.00}^{3+}O_{17.79}$ $(OH_{2.19}Cl_{0.26})_{\Sigma2.45}$, in agreement with the idealized formula given above.

Because the Sterling Hill material is identical in physical, optical, and X-ray characteristics with the Långban material, we assume that it also contains (OH), keeping in mind that we pointed out earlier in this paper that our determined weight percents are considered a bit high. Calculation of a chemical formula for Sterling Hill sample #147308, on the basis of As = 6, yields: $(Mn_{9.11}Cu_{0.58}Zn_{0.46}Fe_{0.08}Mg_{0.07}Ca_{0.07})_{\Sigma10.37}As_{6.00}^{3+}O_{18.37}(OH_{1.32}Cl_{0.68})_{\Sigma2.00}$, presuming H_2O to be present in an amount needed to sum (OH + Cl) to 2.00. We note that the previous analysis of Sterling Hill material by Lawson Bauer (in Frondel, 1961), performed on a very small amount of material, is in error. Our re-analysis of this sample (HU-95036) indicates that Bauer did not recover the Cu and Cl. However, he did find H_2O, in the amount of 0.58 wt.%, equivalent to $(OH)_{1.16}$.

The calculated formulae given for Blix's analysis and for sample #96057 yield calculated densities of 4.60 and 4.62 g/cm^3, respectively. Gabrielson (1956) gave a measured density of 4.3 g/cm^3 and this value was replicated by us for sample 96057, using a Berman balance and turbid fragments of green magnussonite. Sample R9296 provided a few flawless, emerald-green crystal fragments and their density was measured using Clerici's solution. The resultant value is >4.4 g/cm^3, approaching the limits of the technique. The discrepancy of 4% is tolerable, considering the quality of material available and the high density.

Moore and Araki (1979) have suggested the possibility of Mn^{1+} in magnussonite. We have obtained no evidence for the valence of Mn in either magnussonite or the Brattfors phase discussed below, but we note that there are adequate anions in magnussonite for all Mn to be present as Mn^{2+}. This matter, however, in addition to other points described below, remains unresolved.

Moore and Araki (1979) have proposed a crystal structure for magnussonite and have given the chemical formula as $Mn_{18}^{2+}[As_6^{3+}Mn^{1+}O_{18}]_2Cl_2$. We have chosen not to calculate our data in full accordance with this structural formula for the following reasons: (1) Both analyses of magnussonite for H_2O indicate that magnussonite has (OH) > Cl, and no isometric material approaches the 2 Cl given in the structural formula. (2) The analyses indicate that there are 4 (OH,Cl) per 12 As and not 2 as indicated by the structural formula. However, our study does support the basic structural framework proposed by Moore and Araki (1979) in that it verifies the Mn:As ratio, and the presence of Cl in this phase. The crystal chemistry of magnussonite is exceedingly complex, as evidenced by the presence of split atoms in the structure and the high *R* factor of the structure determination (Moore and Araki, 1979). Hence, it may be that there are some small variations on the structure scheme of Moore and Araki and the data presented herein may be of value in pointing the way toward resolution of some of the fine detail of the structure of magnussonite.

An additional observation to be drawn from the presented data is that all isometric magnussonites have Cu present, in amounts varying from 1.8 to 4.0 weight

percent CuO in material from both Långban and Sterling Hill. The role of this Cu is not clear. Araki and Moore (1981) have found a metallic cluster, $[As_4^{3+}Cu^{1+}]$ in dixenite, another Långban mineral, and we have noted the association of native copper, in very small amounts, with Sterling Hill material. However, Dr. Bengt Lindqvist (pers. comm.) has synthesized magnussonite without copper, thus indicating that it is not an essential constituent. The role of Cl is likewise unclear.

We present no final solution to the true nature of magnussonite. This study is a contribution toward a further understanding of this very complex mineral.

The Brattfors phase

As part of the present study, we included in our analyses some samples of a magnussonite-like mineral from the Brattfors Mine, Nordmark, Sweden, which had originally been described by Moore (1969) but not named. This phase occurs in a low-grade ore consisting of jacobsite, calcite, and manganoan clinohumite, together with several rare species such as katoptrite and manganhumite. Moore (1969) found this phase to be tetragonal, space group $I4_1/amd$, with $a = 19.58(2)$ and $c = 19.72(2)$Å, D (meas.) = 4.49 g/cm^3. Powder data were published by Moore (1969) and are not reprinted here.

Chemical analyses of this mineral are presented in Table 1 (analyses #8, 9, and 10), and were obtained using the same procedures used for magnussonite. The calculation of a chemical formula, based on As = 6, yields: $(Mn_{9.41}Ca_{0.31}Mg_{0.30}Cu_{0.10}Fe_{0.07})_{\Sigma 10.19}As_{6.00}^{3+}O_{18}Cl_{1.04}(OH)_{1.34}$, or ideally, $Mn_{10}As_6^{3+}O_{18}Cl(OH)$, with (OH) assumed to be present.

This chemical formula is provisional, pending a structural study. The formula given is presented in part by analogy to magnussonite, but many details of its nature remain obscure, in part due to paucity of material and the lack of pure samples free of admixture. The oxidation state of As is inferred from the analogy with magnussonite.

We presume that (OH) is present for charge balance, but the paucity of this material, which has abundant inclusions, precludes the determination of only 0.67 percent H$_2$O by direct methods. However, we note that Cl is constant among our analyzed specimens and, if (OH) is present for charge balance, this phase may be one with ordered (OH) and Cl. Copper is low in this material, as was noted by Moore (1969). We call attention to the presence of Ca in nearly constant amounts.

References

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