Ganomalite from Franklin, New Jersey, and Jakobsberg, Sweden: new chemical and crystallographic data

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ABSTRACT. Chemical analyses for ganomalite from Franklin, New Jersey, and Jakobsberg, Nordmark, Sweden, imply that Mn is an essential element and that the formula is $Pb_9Ca_5MnSi_9O_{33}$, with $Z = 1$ for the hexagonal unit cell. Preliminary crystal structure data confirm that Mn and Ca are ordered, as implied by the chemical analyses. Ganomalite is hexagonal, space group $P3$, with $a = 9.82$ and $c = 10.13$ Å. Occurrences of samples from both localities are described, together with analytical data for macedonite from Jakobsberg.

KEYWORDS: ganomalite, Franklin, New Jersey, USA, Jakobsberg, Sweden.

A PRELIMINARY description of ganomalite from Franklin, New Jersey (Dunn, 1979), contained a microprobe analysis which included 2.44 wt. % MnO. The similarity between the Mn content of this ganomalite and the Mn content of previously analysed specimens from Jakobsberg, Nordmark, Sweden, and Långban, Varmland, Sweden, implied that Mn is an essential and constant constituent. Because ganomalite had been generally accepted to be a Ca-Pb silicate ($Pb_6Ca_4Si_6O_{21}$ $(OH)_2$), this observation prompted a more detailed study of numerous samples from both Franklin and Jakobsberg.

Ganomalite was first described from Långban by Nordenskiöld (1876) and he later presented a more complete description (1877), which contained a chemical analysis by Lindström. This original analysis was incomplete and Nordenskiöld hoped later to present a better description. According to

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Flink (1917), Lindström himself considered the analysis to be of an impure mixture. That analysis, which gave a ratio of M^{2+} cations : silica of approximately 1 : 1, is not of ganomalite, and is not repeated here.

Ganomalite was found by Nordenskiöld at Jakobsberg, and Sjögren (1883) published a description of the material, together with two analyses by Wiborgh. However, the analyses were of impure material and there is no clear-cut designation of locality. These analyses were considered to be of little value by Flink (1917) and the present authors concur. A later analysis of Jakobsberg material was given by Lindström (1883) and is repeated herein, for comparison, in Table I. Flink (1917) reported that he separated, by heavy liquids and magnetic techniques, relatively pure material from both Långban and Jakobsberg, and he presented analyses of both materials by Naima Sahlbom; these are also given in Table I. X-ray powder diffraction data for ganomalite were given by Welin (1968) and all samples described herein have X-ray diffraction patterns in excellent agreement with his data.

Specimen descriptions. Ganomalite from Franklin, New Jersey, occurs in euhedral crystals which are enclosed in clinohedrite and occasionally encrust vugs in clinohedrite-willemite within andradite-franklinite assemblages. The crystals used in this study are from this latter assemblage. The paragenesis was described by Dunn (1979) and little remains to be added except to note that in thin section, ganomalite is seen as euhedral crystals in direct contact with nasonite, and both species are contained within clinohedrite.

We were unable to find ganomalite in specimens

so-labelled from Långban, in the collections of the Smithsonian Institution and the American Museum of Natural History in New York. Dana (1892) noted that ganomalite closely resembles tephroite, but all specimens fitting this description, with slightly greasy lustre, were tephroite. Given the fact that Flink (1917) had similar experience with similarly labelled specimens, it is possible that an incorrect description has been perpetuated through erroneous labelling of specimens. However, we have no doubt of the occurrence of ganomalite at Långban.

The Jakobsberg samples studied by us are of two types. The first of these (NMNH 93268) consists of an equigranular calcite–phlogopite–ganomalite groundmass. Ganomalite is abundant in the rock, and is anhedral for the most part; the few crystals were tabular like the Franklin material. Phlogopite is euhedral and contains approximately 2.3% MnO. Jacobsite is very sparse and of approximate composition $Mn(Fe^{3+}_{1.48}Mn^{3+}_{0.32}Mg_{0.09}Zn_{0.09}Al_{0.02})_{\Sigma2.00}O_4$ for several analysed crystals. The order of crystallization appears to be phlogopite, ganomalite, and calcite. Macedonite, $PbTiO_3$, occurs included within ganomalite; this is the third reported occurrence and an analysis of it is presented in Table I. Macedonite was reported from Långban by Burke and Kieft (1971) and its occurrence at Jakobsberg was predictable. Several unidentified phases are also present, but in very small amounts.

We tentatively assume the second assemblage to be from Jakobsberg, although the original label only stated 'Nordmark, Sweden' (NMNH C2642). The assemblage consists of phlogopite, celsian, and idocrase, with minor carbonate and macedonite. Both the celsian and phlogopite are Pb-free, but Pb is present in very minor amounts in idocrase. Celsian is surrounded by a reaction rim of flaky material which has the general formula $Pb_8Si_5Al_3O_{22}(OH)$, but is not a known mineral; an analysis of this material is given in Table I.

Chemistry. The samples studied herein were chemically analysed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a beam current of 0.025 μA, measured on brass. The standards used were PbO (Pb), ZnO (Zn), manganite (Mn), baryte (Ba), benitoite (Ti), and hornblende (Al,Fe,Mg,Ca, and Si). The data were corrected using a modified version of the *MAGIC-4* computer program.

Ganomalite had long been thought of as the (OH) analogue of nasonite, $Pb_6Ca_4Si_6O_{21}Cl_2$. The analogy was first proposed by Penfield and Warren (1899) and this resulted in perpetuation of this apparent relation in subsequent compendia. However, Engel (1972) showed that the symmetry (probable space group $P6$, and lattice parameters $a = 9.849$ and $c = 10.152$ Å) imply that ganomalite has a crystal structure which is intermediate between those of nasonite and pyromorphite. By analogy with synthetic compounds, Engel concluded that ganomalite had the probable formula $Pb_3Ca_2Si_3O_{11}$ ($Z = 3$), with some minor Mn in

Table I. Chemical analyses of ganomalite, macedonite, and an unknown.

Sample #	Species	Locality	SiO_2	TiO_2	Al_2O_3	CaO	PbO	MnO	BaO	FeO	MgO	Total
	Ganomalite	Theory*	18.65			9.67	69.24	2.44				100.00
Y-1	Ganomalite	Franklin	19.8	n.d.	0.0	11.5	66.5	2.1	0.0	0.0	0.0	99.9
Y-3	Ganomalite	Franklin	20.3	n.d.	0.0	11.9	67.4	2.1	0.0	0.0	0.0	101.7
C6227	Ganomalite	Franklin	19.7	n.d.	0.0	11.7	69.0	1.9	0.0	0.0	0.0	102.3
C6227	Ganomalite	Franklin	19.5	n.d.	0.0	11.1	68.4	2.4	0.0	0.0	0.0	101.4
93268	Ganomalite	Jacobsberg	19.7	n.d.	0.0	10.9	67.4	2.3	0.0	0.0	0.0	100.3
R18267	Ganomalite	Jacobsberg	19.6	n.d.	0.0	11.3	68.6	2.3	0.0	0.0	0.0	101.7
C2642	Ganomalite	Jacobsberg	19.6	n.d.	0.0	11.5	67.3	1.7	0.3	0.0	0.0	100.4
AM 26374	Ganomalite	Jacobsberg	19.9	n.d.	0.0	11.5	67.1	2.1	0.2	0.0	0.0	100.8
AM 32694	Ganomalite	Jacobsberg	20.0	n.d.	0.0	11.7	67.6	1.9	0.2	0.0	0.0	101.4
Lindström	Ganomalite	Jacobsberg	18.33	n.g.	0.07	9.34	68.80	2.29	n.g.	0.12	0.11	99.98+
Flink	Ganomalite	Jacobsberg	17.74	n.g.		10.42	66.53	2.88			0.45	99.11++
Flink	Ganomalite	Långban	17.21	n.g.		7.31	70.14	2.78			0.95	98.39+++
	Macedonite	Theory**		26.36			73.64					100.00
93268	Macedonite	Jacobsberg	0.3	25.1	0.0	0.2	72.5	n.d.	n.d.	1.0	0.2	99.1
C2642	Macedonite	Jacobsberg	0.4	22.7	0.0	0.2	74.8	n.d.	n.d.	1.4	0.2	99.7
C2642	Unknown	Jacobsberg	13.2	n.d.	7.0	1.4	75.2	tr.		0.4	1.2	97.4

* - Theoretical composition for $Pb_9Ca_5MnSi_9O_{33}$

** - theoretical composition for $PbTiO_3$

+ - Includes 0.24% Cl; 0.02% CuO; 0.04% P_2O_5;
    0.10% alkalies (mostly K_2O); 0.57% loss on ignition.

++ - Includes 0.26% CO_2; 0.60% H_2O; 0.17% K_2O; 0.06% Na_2O.

+++ - Includes 0.10% Cl.

n.g.- not given

n.d.- not determined.   tr. = trace.

Flink analysis from Flink (1917); Lindström analysis from Lindström (1883).

solid solution. The analyses given in Table I are consistent with that formula, with one exception; that is, Mn is present in relatively constant amounts, amounting to one Mn atom per 5 Ca. The data thus indicate that the apparent formula for ganomalite is $Pb_9Ca_5MnSi_9O_{33}$, with $Z = 1$.

X-ray diffraction analysis. Weissenberg and precession photographs confirmed that the apparent Laue symmetry is $6/m$, and that $a = 9.82(5)$ and $c = 10.13(5)$ Å. The space group was assumed to be $P\bar{6}$ because, as pointed out by Engel (1972), ganomalite is apparently isostructural with compounds which supposedly have that space group. Intensity data were obtained using a crystal fragment measuring approximately 0.1 mm mounted for rotation about the c-axis of a Weissenberg-geometry diffractometer. A total of 623 intensities, for which $h,k \geqslant 0$, were measured. Mo-$K\alpha$ radiation, monochromated with a flat graphite crystal and detected with a scintillation counter, was used with a Supper–Pace automated diffractometer system employing a scan across each reflection with background measured on each side. All intensities were corrected for Lorentz-polarization and absorption effects ($\mu = 422$ cm^{-1}), employing a modified version of the program ABSRP written by C. W. Burnham.

The refinement of the structure converged rapidly to an R-value of 8.5%, starting with parameters for the structure of $Pb_5Ge_3O_{11}$ (Newnham *et al.*, 1973). However, the final parameters were unsatisfactory for several reasons: (1) standard errors of atom coordinates are unusually high (e.g. $\sigma(x) = 0.004$–0.006 for oxygen atoms); (2) isotropic temperature factors and their standard errors are not sensible in general (e.g. B = 0.0 for O(4)); (3) refinement of occupancy values led to values which, although compatible with final site occupancies, had unusually large standard errors, and were incompatible with the chemical analysis; (4) some interatomic distances are not reasonable: in particular Si-O(5) = 1.47 Å. However, difference-Fourier syntheses were generally featureless.

At this stage of the refinement we became aware that the structure of $Pb_5Ge_3O_{11}$, which is isostructural with that of ganomalite, had been shown to have space group $P3$ at room temperature (Kay *et al.*, 1975; Iwata *et al.*, 1973) and $P\bar{6}$ at elevated temperatures. However, the original refinement of the structure of $Pb_5Ge_3O_{11}$ in space group $P\bar{6}$ (Newnham *et al.*, 1973) had terminated with the same kinds of problems (e.g. high standard errors, unusual temperature factors) that we encountered with ganomalite. These problems were solved with refinement in space group $P3$.

These data, therefore, strongly imply that ganomalite has space group $P3$. As the asymmetric unit for intensity data for this space group is twice the dimensions of that for space group $P\bar{6}$, we remeasured intensity data using the original crystal. However, the intensity data are exceedingly weak and imprecise, apparently reflecting some deterioration in the crystal, and could not be used for a structure analysis. Other crystals were also examined, but all had mosaic structures which cause data to be imprecise relative to the differences between reflections which are symmetry-equivalent in space group $P\bar{6}$.

We therefore briefly report these results of the structure analysis which are for the structure averaged over two asymmetric units of space group $P3$. These are of value for three reasons: (1) the overall geometry of the structure is confirmed, as the R-factor is a reasonable one and difference-Fourier syntheses display no significant features; (2) the space group is confirmed to be $P3$, with the structure at room temperature analogous to that of $Pb_5Ge_3O_{11}$; (3) the refinement confirms that the Mn is ordered and an essential component of ganomalite, which is the principal point of this presentation. Because the structure is an average one, we do not report the usual crystallographic data such as atom coordinates, interatomic distances, and structure factors. However, these are available from DRP on request.

Discussion of the crystal structure. Because of the problems described above, we give only a brief discussion of the results of the refinement. First, the refinement does verify that the average structure of ganomalite, as described by Engel (1972) is different than that of nasonite and intermediate to those of nasonite and pyromorphite. This structure, which has both single tetrahedra (Si(2)) and double tetrahedra (Si(1)) related by a mirror-plane passing through the bridging oxygen atom has been described elsewhere (Newnham *et al.*, 1973) and will not be discussed here.

The principal result of the refinement concerns the role played by Mn. First, Mn cannot proxy for Pb as the Pb–O bonds are dominated by lone-pair electrons, as demonstrated by the three-fold coordination of Pb(1) and the five-fold coordination of Pb(2) resulting in coordinations for Pb which are incompatible with Mn. There are four large cation sites which have octahedral coordination. These have average M–O distances of 2.40 for Ca(1), 2.45 for Ca(2), 2.41 for Ca(3), and 2.18 Å for Mn (the site labels were assigned after refinement). The average bond distances for sites Ca(1)–Ca(3) correspond to average Ca–O distances in other structures; that for Mn corresponds to well-defined Mn–O distances. Because the Mn site is of rank one, and because the chemical analytical data imply that there is approximately one Mn per cell, Ca and Mn must be

ordered. There is therefore a strong implication that Mn (or a cation of similar radius; perhaps Fe^{2+} or Mg) is essential to the stability of ganomalite. The formula should therefore be considered to be $Pb_9Ca_5MnSi_9O_{33}$.

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