

Ganophyllite from Franklin, New Jersey; Pajsberg, Sweden; and Wales: new chemical data

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ABSTRACT. Ganophyllite from Franklin, New Jersey, Pajsberg, Sweden, and the Benallt Mine, Wales, has been chemically reinvestigated. Twelve new analyses confirm the general structure of Kato (1980) and yield the tentative formula $(K,Na,Ca)_2Mn_8(Si,Al)_{12}(O,OH)_{32}(OH)_4 \cdot 8H_2O$. There is little solid solution among octahedral cations, and the Si:Al ratio is nearly constant at 10:2. Ca and (Na + K) are apparently differentiated, but all examined ganophyllites are K-rich. Much of the water content is loosely bound and the upper limit of water content is not well defined. Ganophyllite is relatively invariant in chemical composition from locality to locality.

GANOPHYLLITE was first described from Pajsberg, Sweden, by Hamberg (1890) and subsequent occurrences were noted from Franklin, New Jersey (Palache, 1910; Larsen and Shannon, 1922, 1924; and Smith and Frondel, 1968), and from the Benallt mine in Wales (Smith and Bannister, 1948). Smith and Frondel (1968) provided unit cell data for Franklin ganophyllite and proved that some of the material formerly called ganophyllite (Foshag, 1936) was a separate species, now known as bannisterite. Recently, Jefferson (1978) found a triclinic polytype of ganophyllite. The average structure (substructure) has been solved by Kato (1980), who proposed the structural formula $(K,Na,Ca)_xMn_8(Si,Al)_{12}(O,OH)_{32}(OH)_4 \cdot nH_2O$ with $x = 1-1.5$ and $n \geq 4$. The present study was undertaken to establish the composition of Franklin ganophyllites from several parageneses, to ascertain the degree of variance among Ca/Na/K, M^{2+} , and Si/Al at different localities, to determine the

approximate degree of hydration, and to present as precise a chemical formula as possible.

Sample descriptions. The samples studied herein are from three localities. In addition to chemical analytical examination, all were characterized by X-ray powder diffraction techniques and found to be ganophyllite. The powder data are in good agreement with those of Smith and Frondel (1968).

The Benallt mine sample is part of one in the British Museum (NH) (BM 1949, 164) and occurs admixed with calcite in a vein assemblage. The sample from the Harstig Mine, Pajsberg, Sweden, occurs with calcite and rhodonite and is the same sample from which Kato (1980) obtained his crystals. The Franklin specimens are from two separate assemblages. Analyses 1-5 (Table I) are of ganophyllite with a pseudo-hexagonal habit, associated with clinohedrite, datolite, willemite, roebingite, and charlesite; a detailed discussion of this paragenesis is given by Dunn *et al.* (1983). Analyses 6-10 are of elongate, prismatic ganophyllite, which occurs on euhedral manganaxinite and rhodonite crystals. This is the assemblage studied by Larsen and Shannon (1922, 1924).

Crystals from Pajsberg and Franklin yielded identical densities of 2.77 g/cm^3 , measured using heavy liquid flotation techniques. The densities of crystals from both localities were measured under both moist and dry conditions; the densities varied only slightly and within error of measurement ($\pm 0.04 \text{ g/cm}^3$).

Analytical procedures. The samples were analysed

TABLE I. Analyses of ganophyllite

No.	Sample no.	SiO ₂	Al ₂ O ₃	FeO*	MgO	ZnO	MnO	CaO	BaO	K ₂ O	Na ₂ O	H ₂ O†	Total	Locality
1.	JEM 1158	40.4	8.3	0.2	0.1	0.7	35.3	1.4	0.1	2.8	1.3	9.4	100.0	Franklin
2.	JEM 1153	39.8	8.0	0.3	0.1	0.6	32.9	1.7	0.1	2.6	1.4	12.5‡	100.0	Franklin
3.	JEM 1149	39.6	8.1	0.3	0.1	0.7	33.8	1.6	0.1	2.8	1.2	11.7	100.0	Franklin
4.	JEM 1150	40.0	8.3	0.2	0.1	0.6	34.3	1.7	0.1	3.0	1.3	10.4	100.0	Franklin
5.	97499	40.4	7.7	0.3	0.2	0.9	33.5	1.6	0.4	2.2	1.2	11.6	100.0	Franklin
6.	95339	40.7	7.7	0.3	0.2	0.4	34.5	1.3	0.6	2.6	1.2	10.5	100.0	Franklin
7.	95564	40.8	7.6	0.5	0.5	0.5	34.1	1.3	0.3	2.5	1.0	10.9	100.0	Franklin
8.	R6609	40.5	7.8	0.4	0.5	0.4	34.7	1.3	0.3	2.3	1.0	10.8	100.0	Franklin
9.	C3313	40.6	7.6	0.3	0.2	0.4	34.5	1.5	0.5	2.5	1.0	10.9	100.0	Franklin
10.	138441	40.9	7.6	0.3	0.2	0.5	33.8	1.6	0.3	2.4	0.8	11.6	100.0	Franklin
(1-10 average)		40.4	7.9	0.3	0.2	0.6	34.1	1.5	0.3	2.6	1.1	11.0	100.0	Franklin
11.	106570	40.3	8.2	0.2	0.1	0.2	34.6	1.7	1.6	1.4	1.0	10.7	100.0	Wales
12.	B17240	40.0	7.9	0.4	0.5	0.2	34.0	1.0	0.6	3.2	1.3	10.9	100.0	Pajsberg
13.	B17240§	40.35	8.59	0.42	0.24	n.g.	35.90	0.76	n.g.	2.95	1.03	8.0§	98.3§	Pajsberg

* Total iron calculated as FeO for analyses nos. 1-12.

† Water by difference unless noted otherwise.

‡ DTA-TGA yielded 10.8 wt. % H₂O for this sample.

§ Analysis by Minami and Tanabe in Kato (1980); includes 0.06 wt. % TiO₂.

Accuracy of data: ±4% of the amount present, exclusive of H₂O.

SrO less than 0.1 wt. % in analyses nos. 1-12.

n.g. = not given.

using an ARL-SEM-Q electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μ A, standardized on brass. The standards used were manganite (Mn); synthetic ZnO (Zn); hornblende (Si, Al, Fe, Mg, Ca, K, Na); and baryte (Ba). The data were corrected using standard Bence-Albee factors. A large beam ($\approx 50 \mu$) was employed to minimize boil-off of volatiles, after first ascertaining the homogeneity of the samples with small beam procedures. The absence of any other elements with atomic number greater than 8 was verified by means of a wavelength-dispersive scan of selected samples. The absence of any light elements, except O and H, was confirmed by a spectrographic analysis with particular attention given to B, Be, and Li, all of which are absent in detectable quantities, with a sensitivity of 0.1-0.2 wt. %.

Water was determined, using the Penfield method, on a portion of Harstig sample B17240 that was impure, having abundant acmite inclusions. The resultant values were 7.96, 8.33 and 8.29, averaging 8.19 wt. %, in good agreement with the value of 8.00% obtained by Tanabe (in Kato, 1980). Because acmite, NaFe³⁺SiO₆, is anhydrous, and because it is the only inclusion we found, utilizing microprobe and X-ray diffraction procedures, we tentatively adopt 8.19% H₂O as the *minimum* amount of H₂O in ganophyllite. However, as we show below, ganophyllite undoubtedly contains much more water.

Because the sum for the analysis of Minami and Tanabe (in Kato, 1980; 8.00% H₂O) is 98.3%, and the oxide sum of our analysis of the same specimen (with 8.19% H₂O) is 97.3%, we suspected that additional loosely-bound H₂O might be present in

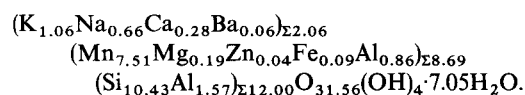
ganophyllite. The absence of light elements coupled with the fact that the closely related bannisterite (Dunn *et al.*, 1981) lost 3.9% H₂O at 20 °C under vacuum, suggests that ganophyllite might well have very loosely bound H₂O also. We note here that Hamberg (1890) found that type ganophyllite lost water readily upon heating and that if the sample was left long enough in moist air, it regained most of the lost water, thus behaving somewhat like a zeolite, in his opinion.

Accordingly, we took additional portions of sample B17240 and weighed them after 48 hours in a saturated humidity chamber and then again after 96 hours in a dry chamber utilizing H₂SO₄ as the air-dessicant. We found that the water content of this sample varied up to 2.2 wt. % in the moist and dry environments. Given the fact that the sample has abundant included acmite, this 2.2 wt. % variance is also a *minimal* figure. The sum of our determined water on this sample is 10.4 wt. % and we note that this agrees well with the 10.9 wt. % water by difference for our analysis of this sample. In addition, we obtained DTA-TGA determinations on a sample from Franklin which indicated that ganophyllite lost 5.3 (± 1.0) wt. % H₂O in vacuum at 21 °C after exposure of 140 hours at room temperature and 100% relative humidity, and experienced a total weight loss of 10.8 wt. %, in quite reasonable agreement with the value we obtained for Pajsberg material and the 11.0 average wt. % we infer by difference based on our microprobe analyses of Franklin samples. We emphasize here that the amount of water in ganophyllite remains ambiguous and may not be constant. The analytical data are presented in Table I.

Ganophyllite lost a total of 7.5 wt. % water at

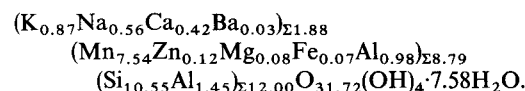
room temperature and continuously up to 190 °C. This is similar to the results reported by Eggleton (1972) for stilpnomelane which as a structure closely related to that of ganophyllite. Eggleton reported that water is present in interlayer positions in stilpnomelane. Threadgold (1979) showed that in the closely related mineral bannisterite H₂O is co-ordinated to Ca in interlayer sites between tetrahedral sheets. Thus in these phases, and likely in ganophyllite also, H₂O behaves in part as it does in some zeolites and smectites; that is, it is loosely bound to large cations in cavities between tetrahedral units, and can be added or lost depending on relative temperature and humidity.

Discussion. Calculation of unit cell contents for the Pajsberg sample (B17240, analysis 12), using the newly determined density of 2.77 g/cm³ and the unit cell parameters of Kato (1980), determined on this same sample ($a = 16.60$, $b = 27.13$, $c = 50.18$ Å, $\beta = 93.96^\circ$) yields the following formula with $Z = 24$ and $\Sigma(\text{Si,Al}) = 12$ atoms:



This formula is calculated to conform to the structural model of Kato (1980) who noted that most of the Al is in the tetrahedral sites and that a small part of the Al is in octahedral sites.

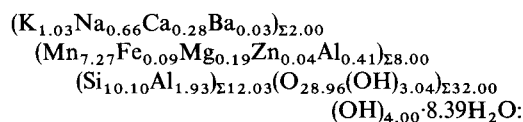
Calculation of unit cell contents for the average of 10 Franklin analyses (Table I), using the newly determined density of 2.77 g/cm³ and the unit cell parameters of Smith and Frondel (1968) ($a = 16.59$, $b = 27.08$, $c = 50.36$ Å, $\beta = 94^\circ 10'$) yields the following formula with $Z = 24$ and $\Sigma(\text{Si,Al}) = 12$ atoms, with water by difference:



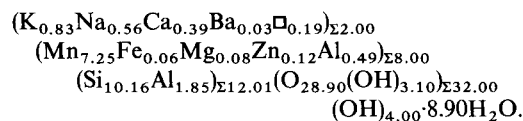
Although both formulae are reasonably close to an ideal composition of $(\text{K,Na,Ca})_2\text{Mn}_8(\text{Si,Al})_{12}\text{O}_{32}(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, and in agreement with Kato (1980) for the structure of the subcell, there are significant differences. The most significant difference between this formula and that of Kato (1980) is the excess of octahedrally co-ordinated cations (0.79 for Pajsberg material and 0.69 for Franklin material). The octahedrally co-ordinated cations make up a pyrochroite-like layer in ganophyllite. Because the excess of calculated cations far exceeds the vacancies calculated for the large-cation sites, they cannot be accommodated in that manner. We also note with interest that an even larger excess of octahedrally coordinated cations was calculated for the isostructural mineral, eggletonite (Peacor *et al.*, in press).

Because ganophyllite has a complex superstructure and because Kato (1980) has determined the structure only of the substructure, it is natural to consider if an explanation for the excess cations can be found in the deviations of the superstructure from the average substructure. However, because all octahedrally co-ordinated sites are occupied in the substructure and because no additional sites exist, variation in octahedral cations which relate to a superstructure can only be caused by vacancies. The presence of the superstructure therefore does not provide an explanation for the excess of octahedrally co-ordinated cations.

Because the calculation for our analyses on the basis of 36 anions (O,OH), and the recalculation of prior microprobe analyses (Kato, 1980) yield very similar results, and because the likely immediate volatilization of some of the water in the microprobe beam under vacuum would serve to raise the determined total oxide wt. %, we conclude that the unit cell parameters and newly determined densities are perhaps more reliable than the determined wt. %. Accordingly, we have recalculated these wt. % by a factor (0.9620 for Franklin; 0.9667 for Pajsberg) which sums octahedral and tetrahedral cations to 20.0, as required by the known crystal structure relations. The newly calculated formula for the sample B17240 from Pajsberg is:



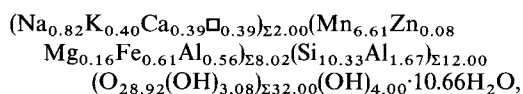
and for the average of ten Franklin analyses:



We have presented the analytical data 'as-determined' in Table I. We recognize that this interpretation of the analyses requires that (OH) substitute for some oxygen co-ordinated to Si or Al as was also suggested by Kato (1980). Although this is generally unacceptable, we have no explanation for this analytical problem beyond the possibility that some Fe and Mn may be in higher valence states, thus requiring that no (OH) substitutes for tetrahedral oxygens. The interpretation of the analyses that required > 20 octahedral plus tetrahedral cations did indeed not require the substitution of significant (OH) for oxygen to maintain charge balance, but we prefer the interpretation of $\Sigma(\text{octahedral} + \text{tetrahedral cations}) = 20.0$ for the reasons outlined above. At this time we have no further explanation for this dilemma, such that

both methods of calculation result in a formula with a small deviation from accepted crystal-chemical relations. Because both methods of calculation yield generally similar results, this does not affect the major features of the chemical formula.

The cell contents normalized to 20 octahedral and tetrahedral cations prompt further discussion of the crystal-chemical relations for ganophyllite as interpreted for the substructure determined by Kato (1980). We first note that the analyses are remarkably similar for the three localities studied. There are also no significant differences between the different assemblages from Franklin. In order to determine trends, if any, in the analyses, we must also consider the composition of the isostructural mineral eggletonite (Peacor *et al.*, in press) for which the composition was determined to be:



after similar normalization to twenty octahedral and tetrahedral cations. The following three points can be made, based on a comparison of the analyses presented here for ganophyllite and the above cited formula for eggletonite:

There is very little variation in the contents of the octahedrally co-ordinated sites. Mn constitutes approximately 7 of the 8 available sites, with very little Mg or Fe present. This is in marked contrast to the closely related mineral bannisterite in which there is substantial solid solution among these cations (Dunn *et al.*, 1981). Kato (1980) has shown how the misfit between the octahedral pyrochroite-like sheet, which is curved like a sine-wave, and the layers of the triple tetrahedral chains, is relieved by the combination of sheet curvature and geometry of the tetrahedral chains. We propose that this dimensional specialization is possible only with the relatively large Mn ions in the octahedral layer and that significant substitution of Mg or Fe would result in the structure being unstable. The restriction in composition of the octahedral sites is thus a requirement of the peculiar structure relations.

Ca and the sum of (K + Na) are relatively constant in all analyses. Threadgold (1979) has shown for bannisterite, which has a complex superstructure like ganophyllite, that Ca and (Na + K) are ordered between 5, 6, and 7-fold rings of tetrahedra, akin to the K-sites of muscovite. This apparent ordering of large cations was supported by the analytical studies of Dunn *et al.*, (1981). The superstructure

symmetry requires that the single large cation equipoint of the substructure be equivalent to more than one equipoint. Ordering of large cations, as suggested by Kato for ganophyllite, is thus shown by our analyses to be very probable, with Ca and (Na + K) differentiated as in bannisterite.

Substitution of Al in tetrahedral sites is confirmed to not exceed the approximate 10:2 Si:Al ratio as noted by Kato (1980). Whether or not this apparent limit is related to equipoint ranks cannot be ascertained until the full superstructure has been determined. In the substructure there is partial substitution of Al for Si over the three sites, but partial solid solution on a substructure site may correspond to full occupancy of superstructure sites. The limited substitution of Al on octahedral sites (0.5 per 8 cations) is probably limited by the requirements of relatively large Mn ions on those sites, as noted above. As solid solution of Al on the tetrahedral and octahedral sites is coupled, in part, in order to maintain charge balance, cation radius requirements for octahedral sites must restrict the total Al content.

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