Nelenite, a manganese arsenosilicate of the friedelite group, polymorphous with schallerite, from Franklin, New Jersey

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ABSTRACT. Nelenite, $(Mn,Fe)_{16}Si_{12}O_{30}(OH)_{14}[As_3^{3+}O_6(OH)_3]$, is a polymorph of schallerite and a member of the friedelite group. X-ray diffraction patterns can be indexed on a supercell with $a = 13.418(5)$ and $c = 85.48(8)$ Å, space group $R\bar{3}m$, but by analogy with TEM results on mcGillite and friedelite, the structure is based on a one-layer monoclinic cell with $a = 23.240$, $b = 13.418$, $c = 7.382$ Å, $\beta = 105.21°$, and space group $C2/m$. Chemical analysis yields SiO_2 31.12, FeO 17.12, MgO 0.12, ZnO 3.63, MnO 29.22, As_2O_3 12.46, H_2O 6.42, sum = 100.09%. Analysis of a number of samples indicates that Fe substitutes for Mn up to 5.8 of the 16 octahedrally coordinated cations, but that the Si:As ratio is constant. The strongest lines in the X-ray powder diffraction pattern (d, I/Io) are: 2.552,*100*; 2.878,*70*; 1.677,*60*; 3.55,*60*; 1.723,*50*.

Nelenite is brown in colour with a vitreous luster and perfect {0001} cleavage, which easily distinguishes it from schallerite. The Mohs' hardness is approximately 5. The density is 3.45 g/cm³ (calc.) and 3.46 g/cm³ (obs.). Nelenite is uniaxial negative with $\varepsilon = 1.700$ and $\omega = 1.718$ (both ±0.004). Nelenite was formerly known as *ferroschallerite*, which is a misnomer. It was found in the Franklin Mine, Franklin, Sussex County, New Jersey, in the 1920s. It occurs in several parageneses, associated with actinolite, tirodite, albite, garnet, feldspars, and several members of the stilpnomelane group in coarse-grained assemblages with pegmatitic texture and a breccia likely derived from this rock. Nelenite is named in honour of Joseph A. Nelen, chemist at the Smithsonian Institution.

A SCHALLERITE-LIKE mineral was described by Bauer and Berman (1930) and named *ferroschallerite* in allusion to the high iron content, relative to manganese, and the chemical similarity to schallerite, $Mn_{16}Si_{12}O_{30}(OH)_{14}[As_3^{3+}O_6(OH)_3]$. It was re-examined by Frondel and Bauer (1953), who considered it to be a variety of friedelite, $Mn_8Si_6O_{15}(OH)_{10}$, considered at that time to be poly- typically related to schallerite. We have examined this material in light of current knowledge of the crystal chemistry of friedelite and schallerite and have found it to be a unique and valid species. The old name, *ferroschallerite*, is a misnomer in that this material is not the Fe-analogue of schallerite and does not have the schallerite structure. Hence, we have renamed it to avoid confusion.

We take pleasure in naming this new mineral nelenite in honour of Joseph A. Nelen, Chemist at the Smithsonian Insitution, in recognition of his contributions to the chemistry of minerals, in particular his analytical studies of the complex arsenosilicates of manganese which are found at Franklin and Sterling Hill. The name and the species were approved by the IMA Commission on New Minerals and Mineral Names, prior to publication. The holotype material is deposited in the Smithsonian Institution under catalog no. C6219. Cotype samples are in the Smithsonian Institution under catalog no. R7824 and at Harvard University under catalog no. H 92791-a. Additional specimens repose in the private collections of John Baum, John Kolic, and in the Spex–Gerstmann collection.

Designation of the holotype is non-ambiguous due to Lawson Bauer's habit of writing the chemical analysis directly on the unused portion of the analysed sample. We note here that the cotype samples R7824 and H-92791-a are identical in all details to the holotype, are extremely close in composition, and all three can be fitted together, indicating they were once a single sample. We retain the terms holotype and cotype, even though they may seem to be redundant because of the reconstruction, so as to indicate precisely which

fragment of this breccia was used for crystallographic and physical and optical measurements.

Physical and optical properties. Nelenite is light to medium brown in colour and transparent, with no apparent colour-zoning. The cleavage is perfect, parallel to $\{0001\}$, and is developed only with moderate difficulty. Cleavage plates are flat and highly lustrous, and it is this quality and appearance of the cleavage that immediately distinguishes nelenite from the other members of the friedelite group, which have cleavage fragments with slightly or grossly warped and curved surfaces. The streak is light brown. The hardness (Mohs) is approximately 5. The lustre of cleavage surfaces is vitreous; that of fracture surfaces is slightly resinous and decidedly duller than cleavage surface lustre. The density, determined using heavy liquid techniques, is 3.46 g/cm^3, in excellent agreement with the calculated value of 3.45 g/cm^3 and 3.44 g/cm^3 value obtained by Bauer and Berman (1930).

Optically, nelenite is uniaxial ($-$) with indices of refraction $\varepsilon = 1.700$ and $\omega = 1.718$ (± 0.004), measured in sodium light. It occasionally exhibits biaxial behaviour with 2V near 0° and is pleochroic with ε = colourless and ω = light brown. Nelenite is not discernibly fluorescent in ultraviolet radiation, nor is it phosphorescent.

X-ray crystallography. Single crystal photographs of nelenite were obtained using precession camera techniques. These photographs are nearly identical to those described by Dunn *et al.* (1981) for friedelite which, in turn, are nearly identical to those of mcGillite (Donnay *et al.*, 1980). The principal differences are that photographs of friedelite and nelenite exhibit diffuseness in reflections, which are spread out parallel to c^*, while mcGillite gives sharp reflections. The relations in diffraction patterns were noted by direct comparison of equivalent photographs obtained for the different species. The structures of nelenite and friedelite thus appear to be identical and, in turn, identical to that of mcGillite except that they are relatively disordered in stacking sequence. As the true symmetry of mcGillite and friedelite (and therefore nelenite) is a complex matter that is not unambiguously determinable by X-ray diffraction alone, we give here a discussion of the relations among these closely related phases.

Manganpyrosmalite, schallerite, and friedelite were until recently thought to be simple polytypes of $Mn_8Si_6O_{15}(OH)_{10}$ (with schallerite having some essential As) (Frondel and Bauer, 1953). All were thought to be hexagonal with $a \approx 13.4$ Å and with values of c that are multiples of 7.15 Å, the thickness of a single layer. Manganpyrosmalite, schallerite, and friedelite were interpreted to have one-, two-, and three-layer structures, respectively,

and mcGillite was shown (Donnay *et al.*, 1980) to be an apparent twelve-layer polytype with $c = 85.66$ Å (although it differs in composition in having 2Cl replacing 2(OH)). Dunn *et al.* (1981) showed that specimens of friedelite, which supposedly were three-layer polytypes, gave mcGillite-like diffraction patterns, and thus these phases differed only in composition in the anion sites, but not in the nature of their polytypic repeats, although diffuseness in the diffraction pattern of friedelite indicated disorder in the stacking sequence.

Iijima (1982a, b) has shown, using high-resolution TEM lattice imaging techniques in which the sequences of layers are directly imaged, that the mcGillite crystal structure is actually a complex stacking of several polytypes. The basic repeat unit consists of one of two kinds of layer, both of which have monoclinic geometry and which are designated $1M_1$ and $1M_2$. A third layer type, which is theoretically possible, was not observed. Iijima notes that the $1M_1$ layer (which has space group $C2/m$) is dominant and that it is repeated with regular occurrences of 120° rotation twinning on (001), giving rise to a variety of polytypes. This layer has dimensions $a = 23.279$, $b = 13.498$, $c = 7.390$ Å, and $\beta = 105.3°$. A critical point is that Iijima implies that the two-layer polytype has a structure that is not identical to that of schallerite; he notes that the relation between the three-layer polytype (which is trigonal) and friedelite (which is trigonal) remains to be investigated. The significant conclusion is that because nelenite is shown to be isostructural with friedelite, its structure must be based largely on the $1M_1$ layers. Such units are different from those of schallerite. The relation between schallerite and friedelite is therefore not a polytypic one, *sensu strictu.*

Ozawa *et al.* (1983) have observed similar relations for friedelite and mcGillite, obtaining dimensions for a one-layer monoclinic unit cell close to those of Iijima. They further note that friedelite is the disordered equivalent of mcGillite. The status of mcGillite, friedelite and, by analogy, nelenite thus appears to be well established.

Because the single-crystal X-ray diffraction patterns of nelenite, mcGillite, and friedelite are nearly identical, nelenite must also have a structure based on a one-layer unit. Donnay *et al.* (1980) interpreted the X-ray diffraction data for mcGillite as being due to a twelve-layer hexagonal polytype having a very pronounced substructure with $A = a/4$ and $C = c/4$. Because of that pseudosymmetry, indexing of powder diffraction data on the basis of the $1M_1$ unit cell parameters gives rise to multiple indices for most reflections, such that the parameters of the monoclinic cell cannot be refined by least-squares. The lattice parameters of nelenite

were therefore initially and tentatively assigned on the basis of the hexagonal supercell, and refined values were obtained through least-squares refinement of data from a Gandolfi powder pattern. The powder data are listed in Table I. They were obtained using a 114.6 mm diameter camera, Cu-$K\alpha$ X-radiation, Si as an internal standard, and polycrystalline sample. The refined parameters are $a = 13.418(5)$ and $c = 85.48$ Å. These cell parameters were then used to compute those for the $1M_1$ single-layer structure, resulting in the values $a = 23.24$ ($\sqrt{3} \times 13.418$), $b = 13.418$, $c = 7.382$ Å, and $\beta = 105.21°$, in good agreement with those of Iijima et al. (1982a, b) for mcGillite. The powder data of Table I have been indexed utilizing these

TABLE I. X-ray powder diffraction data for nelenite

d_{obs}	d_{calc}	hkl	I/Io*
7.10	7.12	001	40
3.55	3.56	002	60
2.878	2.879	80$\bar{1}$	70
	2.879	440	
2.552	2.552	80$\bar{2}$	100
	2.552	441	
2.402	2.403	801	40
	2.403	44$\bar{2}$	
	2.105	80$\bar{3}$	
2.104	2.105	442	40
	2.102	152	
	1.966	802	
1.962	1.966	44$\bar{3}$	10
	1.960	931	
	1.725	114	
	1.723	462	
1.723	1.721	443	50
	1.721	80$\bar{4}$	
	1.721	024	
	1.721	02$\bar{4}$	
	1.680	13$\bar{4}$	
1.677	1.677	12,4,$\bar{1}$	60
	1.677	080	
	1.616	10,0,$\bar{4}$	
1.616	1.615	803	10
	1.615	44$\bar{4}$	
1.518			10
1.449			5
1.429			5
1.401			10
1.373			20
1.202			5

* Intensities estimated visually.

unit cell parameters on the assumption that mcGillite and nelenite are structurally similar, and that nelenite has the space group $C2/m$ as reported by Iijima for mcGillite.

Nelenite was shown above to be isostructural with friedelite, $Mn_8Si_6O_{15}(OH)_{10}$, and mcGillite, $Mn_8Si_6O_{15}(OH)_8Cl_2$. It is the arsenic content which differentiates nelenite from these two species. Dunn et al. (1981) proposed that schallerite has the composition $Mn_{16}Si_{12}O_{30}(OH)_{14}[As_3^{3+}O_6 (OH)_3]$ although this substitution mechanism of the oxyhydroxyarsenite group for oxygen, hydroxyl, and vacancies of a friedelite-like formula was tentative and based on indirect evidence. It is in part by analogy to such results for schallerite that the formula for nelenite is based, in so far as the As anion group is concerned. Schallerite and nelenite are true polymorphs.

It is of further interest to note that Dunn et al. (1981) proposed that the apparently unique As content of schallerite, vis-à-vis friedelite and manganpyrosmalite, might somehow be the cause of its two-layer structure in contrast to those of friedelite and manganpyrosmalite. This proposal must be discarded, as the existence of nelenite shows that the As content is not restricted to a single-layer sequence. Indeed, assuming that the diffuse superstructure reflections are caused by the presence of many polytypes and stacking sequences as shown by Iijima (1982a, b), then the As content of nelenite must be associated with a similar variety of polytypes.

Chemistry. The holotype nelenite specimen was analysed using wet-chemical techniques by Bauer (in Bauer and Berman, 1930), and his analysis is presented in Table II, together with additional microprobe analyses we have obtained. The microprobe analyses were obtained using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, standardized on brass. The standards used were synthetic olivenite (As), synthetic ZnO (Zn), manganite (Mn), and hornblende (Si, Mg, Fe, Ca). The data were corrected using a modified version of the MAGIC-4 program. Analysed schallerites (NMNH C2873 and 95118) were employed as control standards (Dunn et al., 1981). Water was calculated by difference inasmuch as the calculated values are in excellent agreement with the determined value of Bauer and because our analytical data replicates his in other details. The oxidation state of As was determined to be 3+ by Bauer. We have accepted this determination inasmuch as Bauer was a superb analyst for arsenic and because our prior work on schallerite (Dunn et al., 1981) verified the determinations Bauer made for As^{3+} prior to his work on the phase described herein. Although Palache

Table II. Chemical analyses of nelenite

Analysis #	Sample #	SiO_2	FeO*	MgO	CaO	ZnO	MnO	As_2O_3	H_2O**	Total
1.	SG-954	32.3	3.7	0.5	0.3	1.8	43.8	12.1	6.6	101.1
2.	JK-449	32.1	3.7	0.5	0.3	1.9	43.1	11.5	6.6	99.7
3.	BAUM	31.9	5.9	0.7	0.2	2.2	40.2	12.5	6.6	100.2
4.	H89999	30.6	14.2	0.9	0.2	2.5	32.4	13.4	6.6	100.8
5.	H92791-b	31.9	14.8	0.9	0.2	2.7	32.0	12.6	6.6	101.7
6.	R6670	30.8	13.8	0.9	0.2	2.5	31.6	13.2	6.6	99.6
7.	H105542	30.9	14.3	0.9	0.2	2.7	31.4	12.9	6.6	99.9
8.	H92791-c	31.4	16.7	0.8	0.3	2.7	29.8	13.3	6.6	101.6
9.	H92791-a	31.7	17.5	0.7	0.3	3.2	29.3	12.5	6.6	101.8
10.	R7824	30.5	17.4	0.5	0.4	2.5	28.2	13.1	6.6	99.2
11.	C6219	30.8	17.8	0.5	0.4	2.6	28.1	13.2	6.6	100.0
12.	Bauer†	31.12	17.12	0.12	n.g.	3.63	29.22	12.46	6.42†	100.09
13.	Theory††	31.21	18.65				30.69	12.84	6.61	100.00
14.	Theory†††	31.29					49.22	12.87	6.62	100.00

*------Total Fe calculated as FeO.
**-----H_2O from theory except analysis # 12.
†------Analysis by Lawson Bauer in Bauer and Berman (1930).
††----Theoretical composition for $(Mn,Fe)_{16}Si_{12}O_{30}(OH)_{14}[As_3^{3+}O_6(OH)_3]$, with Mn:Fe = 10:6.
†††---Theoretical composition for $Mn_{16}Si_{12}O_{30}(OH)_{14}[As_3^{3+}O_6(OH)_3]$.
n.g.---Not given.

Sample numbers (analyses 1-3) = private collections
(analyses 4,5,7,8,9,)= Harvard U.
(analyses 6, 10, 11) = Smithsonian

Cl present only as traces in all samples.

Accuracy of data (analyses 1-11): ±3% of the amount present except As; As = ±5% of the amount present.

(1935) ascribed the As to As^{5+}, this is clearly a typographical error and does not represent a recalculation of Bauer's determination.

We noted a weak reaction for Fe^{3+} by microchemical test. Inasmuch as Dunn and Nelen (1980) had shown that Fe^{3+} appears to be an essential constituent of the structurally unrelated kraisslite and mcgovernite, and because Dunn et al. (1981) had shown that there was some Fe^{3+} in schallerite, we decided to investigate the amount of Fe^{3+} in nelenite, using wet-chemical methods, on the holotype sample.

Total iron was determined after dissolving a portion of the sample in a mixture of HF and H_2SO_4, and taking it to fumes of sulphuric acid, thus effectively removing all arsenic. Following standard procedures, total iron, given here as FeO, was determined to be 17.24 (±0.15) wt. %, in excellent agreement with Bauer's determination of 17.12%. For the determination of ferrous iron, portions of the sample were dissolved under non-oxidizing conditions, and the ferrous iron present was titrated with $K_2Cr_2O_7$. The possible interference of As^{3+} was investigated. The results indicated that even the addition of 50 wt. % As_2O_3 did not interfere significantly. The resultant FeO value of 16.98 (±0.15) wt. % indicates that the amount of Fe^{3+} in nelenite is exceedingly small. Accordingly,
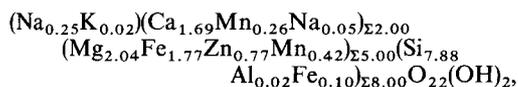
we have calculated total Fe as FeO in our microprobe analyses, presented in Table II.

Examination of the data in Table II indicates that the examined nelenite samples are relatively invariant in chemical composition, except for Mn and Fe. Calculation of a chemical formula, on the basis of Si = 12, by analogy with schallerite (Dunn et al., 1981), yields for Bauer's analysis (Table II, no. 12): $(Mn_{9.54}Fe_{5.51}Mg_{0.07}Zn_{1.04})_{\Sigma16.16}Si_{12.00}As_{2.92}^{3+}O_{36.28}(OH)_{16.52}$, and for analysis no. 11: $(Mn_{9.27}Fe_{5.80}Mg_{0.29}Ca_{0.17}Zn_{0.75})_{\Sigma16.28}Si_{12.00}As_{3.12}^{3+}O_{36.39}(OH)_{17.14}$. Both of these are in excellent agreement with the theoretical formula, $(Mn,Fe)_{16}Si_{12}O_{30}(OH)_{14}[As_3^{3+}O_6(OH)_3]$, supporting the polymorphic relationship of nelenite to schallerite. We note that substitution of Fe for Mn varies from 1.15 to 5.80 per 16 octahedrally coordinated cations. It is quite likely that there is solid solution between Fe and Mn to at least 5.8 Fe per 16 octahedral cations, but that it is not completely represented by the analyses presented.

Occurence and description. Nelenite, then known as ferroschallerite, was found in 1925 by George Stanton (Palache, 1935). It reportedly came from pillar 1597, about 50 feet south of the Trotter shaft, at the Franklin Mine, Franklin, Sussex County, New Jersey.

The holotype specimen consists of massive light

yellow willemite, which is rimmed by an impure stilpnomelane-like mineral, and which is adjacent to a firm breccia that composes most of the specimen. The breccia consists of fragments of nelenite up to 45 × 30 mm, which are in direct contact with a zincian, manganoan actinolite, and which are surrounded by discontinuous rims of the stilpnomelane-like mineral. The cementing medium of the breccia is white calcite, and very thin films of calcite permeate the incipient cleavage of some nelenite fragments. The actinolite in contact with this nelenite is of composition

$$(Na_{0.25}K_{0.02})(Ca_{1.69}Mn_{0.26}Na_{0.05})_{\Sigma2.00}$$
$$(Mg_{2.04}Fe_{1.77}Zn_{0.77}Mn_{0.42})_{\Sigma5.00}(Si_{7.88}$$
$$Al_{0.02}Fe_{0.10})_{\Sigma8.00}O_{22}(OH)_2,$$

calculated according to the amphibole nomenclature of Leake (1978), on the basis of 23 oxygens. Cotype samples NMNH R7824 and H-92791-a are of this paragenesis. Although Bauer and Berman (1930) indicated that tirodite (known to them as zinc-manganese-cummingtonite) was associated with nelenite (known to them as *ferroschallerite*) it is now clear that their statement applied not to the analysed holotype, but to other specimens described below.

The examination of additional samples in public and private collections indicates that there is considerable variance in the parageneses of nelenite, unlike schallerite (Dunn *et al.*, 1981), which is quite limited in its known occurrences.

The specimens represented by analyses 1–3 (Table II) are associated with zincian, manganoan amphiboles, and may represent a distinct paragenesis considering their very low iron content relative to other nelenites. The nelenites represented by analyses 4–7 are associated with a zincian tirodite containing approximately 10 wt. % ZnO and 13% FeO. Of these, nelenites H105542 and H92791-b are both associated with grey willemite and tirodite. By far the most complex of the assemblages is that of specimen H89999, which consists of nelenite in contact with rhodonite, willemite, apatite, and *lennilenapeite* (Dunn *et al.*, 1984). It appears that there are a number of diverse assemblages for nelenite, in addition to the holotype breccia, which was likely derived from the assemblage represented by H92791-c, consisting of massive microcline and actinolite, and which has Mn:Fe:Zn ratios similar to the holotype for both nelenite and the associated actinolite.

All of the samples are coarse-grained, with the major phases present in crystals exceeding several centimetres in diameter. Contacts are sharp and the texture is pegmatitic, except for the holotype breccia. Several unanalysed specimens appear to be from a sheared amphibole–nelenite assemblage and some of the nelenite is associated with, and altered to talc.

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