Minehillite, a new layer silicate from Franklin, New Jersey, related to reyerite and truscottite

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Abstract

Minehillite, a new zinc layer silicate mineral from Franklin, New Jersey, is hexagonal, space group $P6_3/mmc$, $P6_3/mc$ or $P6_2c$, with $a = 9.77(2)$ and $c = 33.01(7)$ Å. The strongest lines in the X-ray powder diffraction pattern are ($d$, $h$, $k$, $l$): 2.764, 100, 209, 216; 1.847, 905, 554, 349; 1.617, 70, 213, 1, 0, 10; 3.07, 70, 213, 1, 0, 10. Microprobe analysis with $H_2O$ by the Penfield method yielded: $SiO_2$ 50.4, $Al_2O_3$ 4.5, $FeO$ 0.2, $MgO$ 0.1, CaO 32.3, MnO 0.1, ZnO 8.4, $K_2O$ 2.0, $Na_2O$ 0.8, $H_2O$ 2.83, total = 101.3 wt.%. The tentative chemical formula, based on analogy to reyerite, is: $(K,Na)_{2-3} (Ca,Mn,Fe,Mg,Zn)_{528} [Zn=AlSiO_{12}, (OH)_4]_{324},$ with $Z = 1$.

Minehillite is colorless with perfect (0001) cleavage, hardness (Mohs) approximately 4, and density 2.93 (meas), 2.94 (calc) g/cm$^3$. The luster on cleavage surfaces is very pearly. Minehillite fluoresces in ultraviolet radiation with a medium violet fluorescence. Optically, minehillite is uniaxial (−) with $\omega = 1.607$ and $\epsilon = 1.604$ (both ±0.002). Minehillite occurs associated with diopside, calcite, grossular, vesuvianite, wollastonite, and microcline in a number of varied assemblages from the Franklin Mine. It apparently forms by low-temperature hydrothermal replacement of the associated minerals. Minehillite is named for Mine Hill, the hill upon which the Franklin deposit cropped out.

Minehillite is structurally related to reyerite, gyrolite, and truscottite. Type material is preserved at the Smithsonian Institution.

Introduction

During the detailed examination of the lead-silicate minerals from Franklin, New Jersey, a phase was encountered that bore some apparent similarity to margarosanite, but which lacked the latter’s characteristic fluorescence in ultraviolet radiation. Subsequent examination indicated that it is a new mineral species that is a member of the reyerite-truscottite-gyrolite group. All of these hydrated Ca-hydroxy-silicates have layered structures, and minehillite apparently represents a new variation on this structure scheme. The structure may also be related to that of jagoite.

We have named this species minehillite for Mine Hill, in Franklin, Sussex County, New Jersey. The Franklin deposit cropped out on Mine Hill and the mines that were later consolidated as the Franklin Mine were developed beneath Mine Hill. The mineral and the name were approved by the Commission on New Minerals and Mineral Names, I. M. A. The holotype specimen (NMNH # 150332) is preserved, together with a cotype (NMNH # C6412-1), in the Smithsonian Institution. Numerous spec-
imens repose in other public and private collections. Minehillite was locally abundant, as is discussed below.

**Physical and optical properties**

Minehillite is colorless but may appear white when it occurs as massive aggregates. Many samples, especially those associated with wollastonite, are gray to black in color due to abundant platelets of native lead dispersed throughout. The luster is vitreous on fracture surfaces and very pearly on cleavage surfaces. The [0001] cleavage is perfect and easily produced. The hardness (Mohs) is approximately 4. The density, determined using heavy liquid techniques, is 2.93 g/cm³, in excellent agreement with the calculated value of 2.94 g/cm³. Minehillite fluoresces in ultraviolet radiation; the response is much weaker than that of margarosanite with which it is often associated. Minehillite fluoresces medium dull violet in short wave-length and duller violet in long wave-length ultraviolet radiation. There is no discernible phosphorescence.

Optically, minehillite is uniaxial, negative, with indices of refraction \( n = 1.607 \) and \( e = 1.604 \) (both \( \pm 0.002 \)), determined in sodium light using a spindle stage.

**X-ray crystallography**

Cleavage fragments were studied using precession and Weissenberg X-ray diffraction techniques. Most of the material which was examined is highly imperfect, as shown by both ubiquitously curved cleavage surfaces and imperfect single-crystal reflections indicative of a complex mosaic structure. Such material displays three superimposed diffraction patterns which appear to be related in a twin-like fashion; that is, the patterns are related by rotation about a common c-axis. The relative rotation angles are not simple integers, but are the same in all three crystals studied. Relative rotation angles are: 0°, 7°30', and 32°50'. Undeformed crystals obtained from the type specimen showed no such features, however, and led simply and directly to a determination of the space group (P6₃/mmc, P6₃mc, or P62c) and unit cell parameters \( a = 9.77(2) \) and \( c = 33.01(7) \AA \). These parameters were determined by least-squares refinement of data from a Gandolfi powder pattern that was obtained using Si as an internal standard, CuKa X-radiation, and a polycrystalline sample. The powder diffraction data are presented in Table 1. Lattice parameters for reyerite and related phases are listed in Table 3. The relations between these parameters and those for minehillite clearly imply that these structures are closely related. Because the structure relations are significant relative to the definition of the chemical composition of minehillite, we discuss all of these data collectively in a later section.

**Chemical analyses**

Minehillite was chemically analyzed utilizing an ARL-SEMQ electron microprobe, using an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. The standards used were hornblende (Si, Al, Mg, Fe, K, Na), synthetic ZnO (Zn), and manganite (Mn). The data were corrected using standard Bence-Albee factors. A wavelength-dispersive microprobe scan indicated the absence of any elements with atomic number greater than 8, except those reported herein. Water was determined directly using the Penfield method; the two determinations are in very close agreement. Because the amount of zinc is slightly greater than predicted from structural considerations, we took pains to obtain additional analyses with other standards. These analyses confirmed the given ZnO compositions determined with ZnO as a standard, and yielded excellent results for other Zn-bearing species present as associated minerals. In addition, we analyzed the samples with very small beam spot techniques as a check on homogeneity. The very strong similarity of the analyses, coupled with their sums near 100%, suggests that they are reliable analyses of minehillite. The very small amount of variation in composition, particularly among the octahedral cations, shows that minehillite has very limited solid solution even though the parageneses are quite diverse. The chemical composition of minehillite is remarkably constant.

In addition, we obtained DTA-TGA analysis for H₂O inasmuch as the amount of H₂O, as opposed to (OH), in minehillite, could shed significant light on its interpretation. The analysis for H₂O was obtained using a Mettler TA-1 thermoanalyzer equipped with an IQ 200 quadrupole mass spectrometer. The analysis evolved 2.9(2) wt.% H₂O, as a single-step loss with a peak at 775°C,
suggesting that all the H$_2$O in minehillite is present as (OH). Inasmuch as this weight percent confirms those previously determined by the Penfield method, we have retained those closely-agreeing values in Table 2.

The resultant analyses are presented in Table 2. Calculation of unit cell contents, using the unit cell parameters and observed density, yielded the values given in the same table. The chemical formula is discussed in detail in the next section.

**Discussion**

The chemical analytical data of Table 2 further confirm the close relation between minehillite and the other members of the reyerite group (Table 3) that was indicated by the unit cell parameters and symmetry. Gard et al. (1975) have reviewed the relations among reyerite, truscottite, and Assarsson's "Z-phase". All of these phases, as well as the so-called "K-phase" (Gard et al., 1981) and fedorite (Sokolova, 1983) are hexagonal or pseudohexagonal with common $a$-values ($=9.75\text{Å}$), but different values of $c$. Clement and Ribbe (1973) suggested that the value of $a$ and the hexagonal symmetry implied, in part, that the structure has phyllosilicate-like sheets of six-rings parallel to (0001). Merlino (1972) determined the reyerite structure and confirmed this general feature. However, he showed that reyerite has a structure with a single sheet of composition Si$_8$O$_{20}$ and a double sheet of composition Si$_{14}$Al$_2$O$_{32}$, which alternate with octahedral layers of Ca-(OH) octahedra (Fig. 1). The ideal composition of reyerite, based on the structure analysis, is: (Na,K)$_2$Ca$_5$Si$_{12}$Al$_2$O$_{38}$ (OH)$_6$ $\cdot$ 6H$_2$O, with Al in tetrahedral coordination. The alkali atoms and H$_2$O occupy sites between the double tetrahedra layers with partial occupancies, and their proportions are therefore variable.

Gard et al. (1975) proposed structure models for gyrolite, truscottite, the "Z-phase", dehydrated equivalents of the "Z-phase" and gyrolite. The latter phases may re-expand reversibly if placed in an H$_2$O-enriched atmosphere. Gard et al. hypothesized structures for gyrolite and the "Z-phase" based on single tetrahedral sheets (of composition Si$_8$O$_{20}$) which alternate with octahedral Ca-layers. Such a scheme was confirmed by Eberhard and Rahman (1982) for gyrolite.

It is clear that the structure of minehillite must be some variation on the scheme of the reyerite group and that its complex composition must be interpreted on this basis in order to derive a formula. In particular, the formula of reyerite is closely related to the cell contents of minehillite (Table 3). For example, in reyerite, a single octahedral Ca-(OH,O) layer contains 7 Ca atoms. Because minehillite has approximately 28 Ca per unit cell, this implies that there are four octahedral layers. Reyerite has four such layers in the repeat distance $2 \times c = 38.08\text{Å}$, and it is therefore reasonable that the $c$-repeat unit of minehillite (33.01Å) could accommodate such units. In order that the number of octahedrally coordinated cations equal approximately 28, the small number of Fe, Mg, and

**Table 3. Chemical and crystal data for the reyerite group**

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>CHEMICAL FORMULA</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MINEHILLITE</td>
<td>$K_{2-3}Ca_{28}^{+}[Zn_{-4}Al_{14}^{3+}Si_{40}^{4+}O_{112}(OH)_{4}^{4-}]$</td>
<td>9.77</td>
<td>33.01</td>
<td></td>
<td>Present study</td>
</tr>
<tr>
<td>REYERITE</td>
<td>(Na,K)$<em>2$Ca$</em>{14}$Si$_{22}$Al$<em>2$O$</em>{50}$ (OH)$_8$ $\cdot$6H$_2$O</td>
<td>9.74</td>
<td>19.04</td>
<td></td>
<td>Merlino (1972)</td>
</tr>
<tr>
<td>TRUSCOTTITE</td>
<td>Ca$<em>{14}$(Si$</em>{14}$O$_{28}$)(OH)$_8$ $\cdot$2H$_2$O</td>
<td>9.73</td>
<td>18.84</td>
<td></td>
<td>Lachowski et al. (1979)</td>
</tr>
<tr>
<td>&quot;Z&quot;-PHASE</td>
<td>Ca$_4$Si$<em>5$O$</em>{18}$H$_2$O</td>
<td>9.65</td>
<td>15.30</td>
<td></td>
<td>Gard et al. (1975)</td>
</tr>
<tr>
<td>GYROLITE</td>
<td>Ca$<em>{14}$(Si$</em>{14}$O$_{28}$)(OH)$_8$ $\cdot$2H$_2$O</td>
<td>9.74</td>
<td>9.73</td>
<td>22.26</td>
<td>Eberhard and Rahman (1982)</td>
</tr>
<tr>
<td>FEDORITE</td>
<td>(K,Na)$<em>{2.40}$(Ca,Na)$</em>{7.6}$(Si$<em>{14}$O$</em>{28}$)(OH,F)$_2$ $\cdot$2H$_2$O</td>
<td>9.676</td>
<td>16.706</td>
<td>13.233</td>
<td>Sokolova et al. (1983)</td>
</tr>
<tr>
<td>&quot;K&quot;-PHASE</td>
<td>Ca$<em>{3}$(Si$</em>{14}$O$_{28}$)H$_2$O</td>
<td>9.70</td>
<td>9.70</td>
<td>12.25</td>
<td>Gard et al., (1981)</td>
</tr>
</tbody>
</table>
Mn must be included. When this is done, the numbers of such cations per unit cell are 28.05, 27.88, and 27.96 for the three analyses of Table 2, in remarkable agreement with the result predicted by the hypothetical structure relation.

As noted above, the structures of gyrolite and closely related phases are based on single or double tetrahedral sheets with compositions $Si_3O_{26}$ or $Ti_3O_{38}$. The different T:O ratios are due to vertex-sharing between sheets in the latter case, but the individual layers have 8 T per layer. Such layers reflect the hexagonal or pseudohexagonal nature of the structure, with $a = 9.74\AA$. We therefore suggest similar layers in minehillite.

If the structure of minehillite contained single and double layers of tetrahedra, as in reyerite, then there would be 48 tetrahedrally coordinated cations per unit cell. As the numbers of Si, Al, and Zn per unit cell are close to 40, 4, and 4, respectively, there is a strong implication of the existence of such units of structure in minehillite. We hypothesize that there must be double layers of tetrahedra because it is cavities in such layers that accommodate large cations in reyerite. The presence of approximately the same proportion of Na and K in minehillite implies a proportion of double tetrahedral layers that is the same as in reyerite.

Given that the minehillite unit cell accommodates four octahedral layers, 2 single tetrahedral layers, and 2 double tetrahedral layers, there must be 116 anions per cell which tetrahedrally coordinate to Si, Al, and Zn. In addition, the analytical data for hydrogen, combined with DTA-TGA data which shows that hydrogen is present as (OH), indicates that there are nearly 16 (OH) per unit cell. The formula may then contain $O_{116}(OH)_{16}$. However, this leads to a negative charge that is much too high, presumably due to the divalent character of the Zn, as compared to the $Si^{4+}$ of reyerite. At least one ligand bonded to a Zn may be (OH) in which case the anion content then becomes $[O_{112}(OH)](OH)_{12}$, in good agreement with the analysis, and consistent with reasonable assumptions about the structure. The full formula then becomes $K_{2.3}Ca_{28}[Si_{40}Al_{4}Zn_{4.9}O_{112}(OH)_{12}](OH)_{12}$. The non-stoichiometric number of alkalies (e.g.: $K + Na = 2.82$ for sample # 150332) per unit cell is consistent with the data of Merlino (1972) for reyerite, in which the alkalies have partial occupancies of sites in cavities within the double tetrahedral layers. These cavities also contain the H$_2$O and thus play a role similar to that played by large framework cavities in zeolites.

The assumption of tetrahedrally coordinated Zn in minehillite is supported by the common occurrence of Zn in tetrahedral coordination in other secondary minerals at Franklin, New Jersey. However, the sum of tetrahedrally coordinated cations per cell for the three analyses of Table 2 are 49.62, 48.57, and 49.59, respectively. The number of Zn atoms per cell is nearly 5. Such a number is not permitted by the possible space groups. The excess of tetrahedral cations per cell is in large part brought about by the excess of Zn over 4 atoms per cell. We have reanalyzed the samples using a different standard (zinian rhodonite) and obtain very similar results. The constancy of composition from sample to sample, coupled with analytical sums near 100%, also implies that the analytical data for minehillite in Table 2 are accurate. It is possible that some Zn may substitute for Ca in octahedrally coordinated sites, but this in turn causes the number of such cations to be too high. The apparent excess of Zn remains unaccounted for.

Given that minehillite and reyerite have common structural features, we are unable to determine the reason for the significant difference in the c-parameters. That is, $2 \times c$ of reyerite $= 38\AA$ and $c$ of minehillite is only 33.01\AA. The differences may be related to a unique role played by Zn, or to the assumed absence of molecular H$_2$O in minehillite. However, it is interesting to note that the structure of jagoite (Mellini and Merlino, 1981) also is hexagonal and has double and single layers of tetrahedra which alternate along c with layers of iron octahedra and lead polyhedra. Jagoite has $c = 33.33\AA$, a value very similar to that for minehillite, implying that such a structure topology (which is basically similar to that of reyerite) is possible for minehillite. However, the geometries of the tetrahedral layers in jagoite are different from those in reyerite, as shown by the value of $a$ (8.582\AA). This, and the major similarities in chemistry between reyerite and minehillite, and the large differences between jagoite and minehillite, are not compatible with a structural analogy between jagoite and minehillite. A definition of the detailed structure relations for minehillite and their relations to other members of the reyerite group must await a full crystal structure analysis.

**Occurrence**

Minehillite is known only from Franklin, Sussex County, New Jersey. All the specimens we studied are from...
mineral collections; the Franklin Mine was closed in 1954. The specimens were collected and retained primarily because they contained wollastonite, which has a bright orange fluorescence in short-wavelength ultraviolet radiation. Thus, serendipity played a major role in the preservation of substantial quantities of this new species. The location and geologic relationships of minehillite in the Franklin Mine are unknown, but the presence of margarosanite, Pb(Ca,Mn)₂Si₃O₈, suggests that minehillite came from the northern end of the west limb of the orebody. It was here that most of the lead silicate minerals were localized in a part of the mine known as the Palmer shaft pillar. The samples containing these lead silicates were first collected at the close of the last century, and were recovered in quantity in the mid-1950's when the Franklin Mine was being closed down. Minehillite appears to have been moderately abundant in that several dozen specimens are now known. It occurs in varied parageneses, unlike many of the minerals unique to Franklin, which have occurred in one-of-a-kind assemblages. This variety of parageneses suggests that minehillite was not restricted to a single occurrence but was distributed over some region of the deposit.

The holotype minehillite consists of 5-mm plates of colorless material, which appears white in the aggregate. These form a layer up to 1.0 cm thick and 5 cm wide encrusting gray microcline with grain size about 2 mm. There are 1–2 mm allanite crystals liberally distributed throughout the microcline. The minehillite layer is rounded on the surface, apparently due to handling over the years. Little can be said about the genesis of this specimen; the minehillite appears to have formed on a broad, flat fracture in microcline.

Other specimens, considered at first to be of separate assemblages, were found to be closely related. On one of these, minehillite forms at the contact between the above-described feldspar and a fine-grained, chalky-white mixture of wollastonite, grossular, and vesuvianite. In this occurrence, minehillite occurs as distorted aggregates a few mm in diameter. These aggregates have abundant inclusions of native lead, giving the minehillite a noticeable and characteristic grayish-black color, which aids in its recognition. In another assemblage, minehillite forms tight, distorted aggregates in a band 1 cm thick between broad-bladed margarosanite and pink calcite; the latter contains crystals of clinopyroxene of average composition: (Ca₀.₉₆Mn₀.₀₄)(Mg₀.₅₁Fe₀.₃₁Zn₀.₁₃Mn₀.₉₆)(Si₁.₉₈Al₀.₀₂)O₆. Observations of thin-sections show that this minehillite is replacing all the other phases.

All of the elements in minehillite can be derived from the precursor minerals as noted above, with the exception of zinc. There are no minerals with Zn as an essential constituent in these assemblages. Thus it may be that Zn was present as a now-replaced phase (willemite, most likely; zincite, a possibility) or that it was introduced in solution. The latter possibility is strong in that hydrothermally deposited willemite is ubiquitous at Franklin, and frequently occurs as late-stage vein-fillings and crack-fillers in fractured crystals. These observations and the textural relations described above imply that minehillite is a secondary, relatively low-temperature, hydrothermal, replacement mineral.

The occurrence of native lead included within minehillite suggests that components for formation of minehillite can originate from the breakdown of margarosanite and/or the other associated species mentioned above, in alkaline hydrothermal solutions. Preliminary calculations using data for 600°K at 1 atm (Robie et al., 1978) indicate that the fugacity of sulfur for the reaction Pb + S → PbS at equilibrium is about 10⁻⁰⁸ and the fugacity of oxygen for the reaction Pb + ½O₂ → PbO is about 10⁻¹⁴. The sulfur fugacity is several orders of magnitude below that calculated for the sulfide-bearing manganese deposit at Bald Knob, North Carolina (Winter et al., 1981), indicating an environment of extremely low sulfur fugacity. However, the oxygen fugacity, although numerically lower, is well within the stability range for magnetite and manganosite, both found in the orebody. Thus, the occurrence of native lead with minehillite does not prove that local conditions were more strongly reducing than those that prevailed in the orebody itself.

Acknowledgments
We are indebted to Mr. John Cianciulli for providing the only known specimen of undeformed crystals which permitted definitive resolution of the crystallographic properties of minehillite. We thank Mr. Richard Hauck and Mr. Richard Bostwick for the opportunity to study samples in their personal collections. The water determinations were performed by Mr. Joseph Nellen, to whom we express our gratitude. This study was supported, in part, by a grant from Mrs. E. Hadley Stuart, Jr. PJD acknowledges the continued assistance of the trustees of the Franklin Mineral Museum. Dr. Robert Hazen and Dr. Stefano Merlino reviewed the manuscript and contributed significantly to its improvement.

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Manuscript received, September 22, 1983; accepted for publication, July 24, 1984.