

Kellyite, A New Mn-Al Member of the Serpentine Group from Bald Knob, North Carolina, and New Data on Grovesite¹

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Abstract

Kellyite, $(\text{Mn}_{3.8}\text{Mg}_{0.8}\text{Fe}^{2+}_{0.2}\text{Al}_{1.7})(\text{Si}_{2.0}\text{Al}_{2.0})\text{O}_{30}(\text{OH})_8$, occurs as transparent, yellow, 1 mm-sized grains dispersed within manganese carbonates (principally kutnahorite) at the Bald Knob manganese mine, near Sparta, North Carolina. Associated minerals include galaxite, jacobsonite, Mn-chlorite, alleghanyite, and sonolite. X-ray diffraction shows that it is isostructural with members of the serpentine group and thus the manganese equivalent of amesite. Two polytypes have been recognized, a six-layer rhombohedral phase and a two-layer hexagonal phase. The latter has space group $P6_3$ and lattice parameters $a = 5.438 \pm 0.008 \text{ \AA}$ and $c = 14.04 \pm 0.01 \text{ \AA}$. The name is in honor of William C. Kelly, faculty member of the Department of Geology and Mineralogy, The University of Michigan.

A mineral which yields a powder pattern identical to that of grovesite occurs with the kellyite. It is shown to be a one-layer chlorite having space group $C\bar{1}$ or $C1$, with lattice parameters $a = 5.44 \text{ \AA}$, $b = 9.40 \text{ \AA}$, $c = 14.27 \text{ \AA}$, $\alpha = \gamma = 90.0^\circ$, and $\beta = 98^\circ 12'$. It is proposed that grovesite, formerly classed as a member of the serpentine group, is actually a manganese chlorite which is chemically similar to pennantite.

Introduction

The mineralogy of the manganese deposit at Bald Knob, near Sparta, North Carolina, was originally described by Ross and Kerr (1932), who reported two new minerals, alleghanyite and galaxite. We recently collected from the waste dump at this locality in order to obtain specimens of the alleghanyite and galaxite. In several of these samples we observed small grains (up to 1 mm in diameter) of a transparent, yellow micaceous mineral. Powder X-ray diffraction data indicated that it was a member of the serpentine group. Since the rocks in which it occurs are manganese-rich, we suspected that it might be a new manganese-rich member of the

serpentine group. Subsequent, detailed studies have confirmed this and shown it to be the Mn-equivalent of amesite. The name, kellyite, is in honor of Dr. William C. Kelly, a member of the faculty of the Department of Geology and Mineralogy at The University of Michigan and an active contributor to the science of mineral deposits. The mineral and the name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. Type material is present in the collections of the U. S. National Museum (Smithsonian Institution) and the Department of Geology and Mineralogy, The University of Michigan.

Associated Minerals

Ross and Kerr (1932) described a large number of Mn-rich phases from the Bald Knob deposit in addition to their descriptions of alleghanyite and

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galaxite. We have initiated a more extensive study of the general mineralogy using electron microprobe, optical, and X-ray diffraction techniques, which will be reported in detail elsewhere. Our results already indicate that there are two separate parageneses consisting of carbonate- and silica-rich rocks, respectively. The carbonate-rich rocks consist largely of coarse-grained Ca-Mn carbonates with lesser amounts of alleghanyite, tephroite, sonolite, and spinel-family minerals. The rocks have a distinctly banded appearance deriving from concentrations of one or another of these phases. X-ray diffraction and electron microprobe analyses indicate that (commonly) the carbonate is near ideal kutnahorite in composition, but a series of both Ca- and Mn-rich samples have been identified which appear to exhibit complete solid solution toward both the pure Ca and Mn end member. The spinels are of two types: a Mn-Fe³⁺ rich phase (jacobsite) and a Mn-Al rich phase (galaxite). These commonly occur together in intergrowths or as separate grains in the same specimens. The kellyite occurs exclusively in the carbonate-rich samples usually interstitial to the carbonate grains or replacing galaxite. It forms ir-

regular-to-platy yellow tablets and laths. It is widespread at Bald Knob; virtually every thin-section containing carbonates shows at least a few grains of light yellow kellyite. Other phases identified as accessories in carbonate-rich rocks are Ni-rich catierite, cobaltite, arsenopyrite, chalcopyrite, pyrophanite, zircon, rutile, apatite, alabandite, caryopilite, and Mn-chlorite.

The silica-rich samples consist primarily of quartz and spessartine-rich garnet. Rhodonite and the Mn-amphibole tirodite are also both common phases. These samples contain no kellyite. Another manganese sheet silicate, identified by powder and single-crystal X-ray diffraction as a member of the stilpnomelane group, is also present in these rocks. It generally occurs as dark brown foliated aggregates, usually in contact with quartz. In contrast, kellyite, like serpentine, appears to be unstable with excess quartz.

X-Ray Crystallography

Weissenberg and precession photographs of kellyite yield results similar to those reported for cronstedtite (Frondele, 1962; Steadman and Nuttall, 1963, 1964). A hexagonal subcell ($a = 3.16$, $c = 14.10$ Å) is defined by a set of intense and relatively sharp reflections. The superstructure reflections are relatively weak and diffuse. The diffuse streaks parallel to c^* indicate a high density of layer stacking faults. Two crystals with superstructure reflections sharp enough to define the supercell have been examined. One of these has superstructure reflections which are barely discernible, but which define a rhombohedral lattice with $a = 5.44$ Å and $c = 42.13$ Å. This is analogous to the 6-layer polytype of cronstedtite described by Steadman and Nuttall (1963). The second crystal yields superstructure reflections which are significantly sharper than those of the first. It is a 2-layer hexagonal polytype with $a = 5.44$ Å and $c = 14.04$ Å. Extinctions are consistent with space group $P6_3$, and this crystal is also analogous to a cronstedtite polytype described by Steadman and Nuttall (1964). Although we have so far distinguished the occurrence of only two polytypes of kellyite, it may be predicted by analogy with cronstedtite that well-ordered crystals having a variety of stacking sequences may exist. The name kellyite should be retained for all such polytypes.

Powder diffraction data, including both Debye-Scherrer and diffractometer data, are listed in Table 1 for kellyite, along with comparable data for caryo-

TABLE 1. Powder Diffraction Data for Kellyite, Caryopilite, and Grovesite

hkl	Kellyite*			Caryopilite**		Grovesite***	
	d _{calc}	d _{obs.}	I	d _{obs.}	I	d _{obs.}	I
002	7.0	7.0	90	7.2	90	14.3	40
004	3.51	3.51	100	3.64	80	12.6	5
111	2.67	2.67	40	2.78	70	7.1	100
112	2.54	2.53	60	2.49	100	4.75	30
113	2.35		40	2.35	10	3.57	80
006	2.34	2.34		2.08	50	2.85	20
114	2.15	2.15	10	1.954	30	2.70	40
115	1.954	1.954	30	1.724	10	2.60	10
116	1.774	1.768	10	1.617	20	2.43	80
008	1.755			1.578	10	2.30	20
117	1.614	1.612	10	1.362	5	2.10	5
300	1.570	1.570	30			2.03	40
302	1.532	1.533	5			1.908	15
118	1.475	1.477	10			1.683	30
304	1.433	1.434	5			1.585	20
00,10	1.404	1.403	10			1.574	30
308	1.170		5			1.537	20
00,12	1.170	1.169				1.440	5
00,14	1.003	1.003	5			1.428	5
						1.361	5
						1.335	10
						1.322	5
						1.300	5
						1.246	5
						1.150	10
						1.117	10
						1.059	15

* FeK α , Mn-filtered radiation; 114.6 mm diameter Debye-Scherrer camera.
 ** CuK α , Ni-filtered radiation; 114.6 mm diameter Debye-Scherrer camera.
 Specimen from Langban, Sweden; University of Chicago Collection.
 *** FeK α , filtered radiation; 114.6 mm diameter Debye-Scherrer camera;
 data taken from photograph of type material provided by Dr. Richard
 Davis, British Museum of Natural History.

pilite and grovesite. Caryopilite, the Mn-equivalent of serpentine, has a powder pattern similar to that of kellyite. The occurrence of essential Al in the octahedral layers of kellyite results in a significant contraction in the value of c as compared to that of caryopilite, and these phases can therefore be readily distinguished on the basis of the magnitudes of the interplanar spacings corresponding to (00 l) reflections. The lattice parameters for kellyite ($a = 5.438 \pm 0.008$ Å and $c = 14.04 \pm 0.01$ Å) were obtained by least-squares refinement of the Debye-Scherrer data.

Comparison with Grovesite

Grovesite, $(\text{Mn,Mg,Al})_3(\text{Si,Al})_2(\text{O,OH})_9$ was described by Bannister, Hey, and Smith (1955) as a new mineral from the Benallt mine, Rhiw, Carnarvonshire, North Wales. They concluded that this phase is "a member of the cronstedtite-berthierine-amesite group, with a structure based on the two-layer sheets of the kaolin family . . .," and that it is related to the Mn-chlorite, pennantite, as cronstedtite is to the Fe-chlorite chamosite. Their conclusions were based primarily on powder diffraction evidence, as they state that: "While X-ray powder photographs of pennantite closely resemble those of other chlorites, and especially the iron-rich members such as thuringite and chamosite, those of the new mineral closely resemble powder photographs of cronstedtite and berthierine." Although they published no complete powder diffraction data, they did note the presence of a line with a spacing of 14 Å, not previously recorded for cronstedtite or berthierine.

As our analysis of kellyite proceeded, it became clear that it might be analogous to grovesite. We therefore obtained a powder photograph of type grovesite, as kindly provided by Dr. Richard Davis of the British Museum of Natural History. The powder pattern of grovesite proved markedly different than that of kellyite (Table 1). The specimen of grovesite was apparently not entirely pure, as the weak reflection having $d \sim 12$ Å is characteristic of stilpnomelane-group minerals. Davis (written communication) has confirmed, using single-crystal methods, that grovesite is a layer silicate having $c \sim 14$ Å. In addition to the 001 reflection ($d = 14.3$ Å in the powder pattern), he also notes that 003 and 005 are moderately strong in Weissenberg photographs. The appearance of these reflections (00 l ; $l = 2n + 1$) shows that grovesite cannot be a simple two-layer member of the serpentine group. These re-

flections are diagnostic of chlorite-group minerals, however.

At this stage of our investigation, the status of grovesite was uncertain. However, we subsequently detected a small number of brown crystals embedded in kutnahorite and closely associated with kellyite from Bald Knob, which yielded a Debye-Scherrer pattern identical to that of grovesite. The similarity of the two patterns is rather striking, in view of the chemical complexity of these two phases. Single-crystal diffraction studies of one brown crystal confirmed it to be a chlorite ($C\bar{1}$ or $C1$; $a = 5.44$ Å, $b = 9.40$ Å, $c = 14.27$ Å, $\alpha = \gamma = 90.0^\circ$, $\beta = 97^\circ 12'$). These lattice parameters agree well with those obtained by Smith, Bannister, and Hey (1946) for the manganese chlorite pennantite (except that the value of c is one half that of pennantite). Since the chemical analyses for pennantite and grovesite are nearly identical, it seems clear that grovesite is closely related to pennantite. One unresolved question, however, involves the difference in powder patterns between grovesite and pennantite, as noted by Bannister *et al* (1955). The difference could be caused by differences between the X-rayed samples either in preferred orientation of crystallites or in the polytypic stacking sequences (the latter interpretation is preferred by Davis and Hey; written communication). Indeed, both grovesite (Bannister *et al*, 1955) and the chlorite from Bald Knob are one-layer polytypes, but pennantite is a two-layer structure (Smith *et al*, 1946).

The exact status of grovesite should be further determined using type materials. It is at least clear that it is not isostructural with members of the serpentine group. It is essential that this be established, since we are proposing that kellyite properly occupies the niche to which grovesite was heretofore ascribed. Furthermore, preliminary microprobe analyses of grovesite coexisting with kellyite from Bald Knob demonstrate that grovesite is significantly richer in Mn and Si than kellyite.

Chemical Analysis

Since sufficient kellyite could not be separated for a complete wet chemical analysis, electron probe microanalysis was undertaken instead. A Broken Hill rhodonite (supplied by the Department of Geophysics, ANU, Canberra, Australia) was used as a standard for Mn and Si, synthetic periclase for Mg, Binns ilmenite for Fe, and synthetic Al_2O_3 for Al. The analysis was conducted with 0.015 μA specimen

TABLE 2. Microprobe Analysis of Kellyite

Oxide	Wt %	Molar Ratio/10 Cations	
SiO ₂	17.60	Si	1.951
TiO ₂	<.05	Al ^{IV}	2.049
Al ₂ O ₃	28.55	Al ^{VI}	1.681
Fe ₂ O ₃	2.18	Fe ³⁺	0.182
MnO	38.84	Mn	3.646
MgO	2.97	Mg	0.490
H ₂ O	(10.82)*	O	13.907
Sum	(100.96)	H ₂ O	(4.000)*

*H₂O calculated assuming the presence of 8(OH) per 10 cations.

current and 15 kV excitation voltage. Drift, atomic number, fluorescence, and absorption corrections were applied to the raw data. The analysis, converted to a unit cell basis using the measured density, corresponds approximately to $(\text{Mn}_{3.6}\text{Mg}_{0.5}\text{Fe}^{3+}_{0.2}\text{Al}_{1.7})(\text{Si}_{2.0}\text{Al}_{2.0})\text{O}_{10}(\text{OH})_8$ with hydroxyl assumed present in stoichiometric quantities (Table 2). The iron is assumed to be present as Fe^{3+} since this is the valence of iron in associated minerals and since this valence is required for charge balance on the octahedral site. It is suggested that the name kellyite be applied to manganese-aluminum serpentines approaching the ideal formula $\text{Mn}_4\text{Al}_2\text{Si}_2\text{Al}_2\text{O}_{10}(\text{OH})_8$. Partial microprobe analyses of other grains of kellyite were undertaken to outline the compositional range of this mineral. Little variance was found from the formula given above.

Physical Properties

Kellyite generally occurs as irregularly shaped golden- to lemon-yellow grains that display a perfect {001} cleavage. The density of kellyite is 3.07 as determined by repeated measurements of 15 mg of material on a Berman balance. The calculated density is 3.11.

Optically the grains show a low birefringence and are similar to chlorite in appearance except for their brownish-yellow color and higher refractive index. Most grains show irregular extinction with mottled

and undulose areas, apparently due to a mosaic structure. Some grains show a vague indication of sector twinning. Areas of grains with relatively uniform extinction give sharp biaxial negative figures with moderate dispersion $r > v$. The optical properties of kellyite are as follows: $\alpha = 1.639 \pm 0.001$, $\beta = 1.646 \pm 0.001$, $\gamma = 1.646 \pm 0.001$; optic orientation is $X \perp (001)$; pleochroism is $X =$ colorless to greenish yellow, $Y = Z =$ pale yellow to reddish brown. Refractive indices were measured in sodium light and corrected for temperature to 20°C. $2V$ measurements were made on basal sections with a movable micrometer ocular by the method of Tobi (1956), and the measured values of $2V_x$ range from just over 30° to about 16°, but some grains gave offcenter figures which could not be measured that appeared to be as low as 5 or 6 degrees. The biaxial nature of kellyite may be due either to the presence of non-hexagonal polytypes or the presence of distortion and strain in the grains.

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