

Ribbeite, a polymorph of alleghanyite and member of the leucophoenicite group from the Kombat mine, Namibia

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ABSTRACT

Ribbeite, $Mn_5(OH)_2(SiO_4)_2$, is a new mineral from the Kombat mine in Namibia. It is orthorhombic with space group $Pbnm$ or $Pbn2_1$, and with lattice parameters $a = 4.799(1)$, $b = 10.742(6)$, $c = 15.70(1)$ Å, $Z = 4$. Chemical analytical data are SiO_2 24.3, FeO 0.3, MgO 5.2, MnO 65.1, CaO 0.2, H_2O 4.9 (by difference), sum = 100.00%. Optical data include $\alpha = 1.780(3)$, $\beta = 1.792(3)$, $\gamma = 1.808(3)$, $2V_z$ (calc.) = 82.5; $X = b$, $Y = a$, $Z = c$; X , Y = colorless, Z = light pink; absorption $Z > X = Y$. It is inferred to be a member of the leucophoenicite group having octahedron sequence $(1,2^2)$ and is the unit-cell-twinned equivalent of alleghanyite. It occurs in Mn-rich silicate-carbonate units within lenses of manganese oxide ores as equigranular grains associated with alleghanyite, manganooan calcite, pyrochroite, chlorite, galaxite, jacobsite, and a mcgovernite-like mineral.

INTRODUCTION

During the course of mining at the Kombat mine in Namibia, several rare and interesting mineral species were encountered. At least four of these apparently are new minerals, and one was found to be related to the humite and leucophoenicite groups. Detailed investigation has confirmed that it is a new mineral, the unit-cell-twinned equivalent of alleghanyite. We have named this new species *ribbeite* in honor of Dr. Paul H. Ribbe in recognition of his many contributions to mineralogy, both to the science through his research, and to the society of mineralogists, in part through his editorship of the *Reviews in Mineralogy* series of the Mineralogical Society of America. It is particularly appropriate that ribbeite is closely related to the humite group, to which he has made major contributions. The new species and the name have been approved by the Commission on New Minerals and Mineral Names, I.M.A. Type material is deposited in the Smithsonian Institution under catalogue no. NMNH 163208.

X-RAY CRYSTALLOGRAPHY

Powder X-ray diffraction data (Table 1) were recorded with a 114.6-mm-diameter Gandolfi camera, Si as an in-

ternal standard, $FeK\alpha$ (Mn-filtered) radiation, and a powdered sample. The pattern has the general appearance of those of the Mn-humites and other members of the leucophoenicite group in the most intense lines, and especially in the grouping of intense reflections with d values near 2.8 Å. Although mixtures of such phases would therefore be difficult to characterize, patterns of pure ribbeite are easily identified as can be seen by comparison of the data of Table 1 with the powder-diffraction data for the Mn-humites as given by Winter et al. (1983).

Single-crystal Weissenberg and precession photographs showed that ribbeite is orthorhombic with space group $Pbnm$ or $Pbn2_1$. The unit-cell parameters [$a = 4.799(1)$, $b = 10.742(6)$, $c = 15.70(1)$ Å, $V = 809.2(5)$ Å³] were obtained by least-squares refinement of the powder-diffraction data; $Z = 4$ for this cell. The lattice parameters of ribbeite (r) are related to those of monoclinic alleghanyite (al), a member of the humite group, by the relations $a_r = a_{al}$, $b_r = b_{al}$, $c_r = 2c \sin \beta_{al}$. Because alleghanyite and ribbeite have the same composition, they are polymorphically related.

White and Hyde (1983) have shown that the structures of members of the leucophoenicite group are related to those of the humites. Each group has a characteristic pattern of sequences of edge-sharing octahedra, which they designated as $(3, 2^2)$ for humites and $(1, 2^2)$ for leucophoenicite group minerals. Yau and Peacor (1986) have

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Table 1. Powder X-ray diffraction data for ribbeite

hkl	d_{obs}	d_{calc}	hkl	hkl	d_{obs}
5	5.08	5.08	021	10	1.769
30	4.41	4.43	022	20	1.744
		4.38	110	10	1.720
2	4.23	4.22	111	10	1.695
1	3.93	3.93	004	20	1.661
30	3.83	3.83	112	5	1.618
5	3.53	3.54	103	2	1.587
5	3.49	3.49	121	5	1.569
10	3.362	3.359	113	30	1.554
5	3.256	3.256	122	10	1.490
70	2.925	2.923	114	20	1.460
80	2.873	2.870	130	1	1.441
70	2.821	2.823	131	5	1.415
60	2.695	2.695	132	20	1.378
80	2.552	2.552	115	20	1.304
40	2.515	2.516	133	1	1.277
2	2.398	2.400	200	2	1.2262
40	2.356	2.360	125	5	1.2034
		2.352	026	5	1.1894
				10	1.1810
5	2.315	2.318	141	10	1.1728
		2.317	134	1	1.1599
		2.316	211	1	1.1529
10	2.246	2.246	116	2	1.1437
		2.246	142	2	1.1210
		2.244	212	5	1.0996
2	2.216	2.216	044	20	1.0861
5	2.117	2.118	135	10	1.0695
1	1.996	2.011	214		
		1.996	117		
		1.993	230		
1	1.834	1.836	153		
100	1.796	1.797	225		
		1.791	118		
		1.790	060		
		1.789	240		

Note: Intensities visually estimated from Gandolfi photograph; d values calculated with lattice parameters $a = 4.799$, $b = 10.742$, and $c = 15.70$ Å.

further shown that the sequences for any two polymorphs, one of which is monoclinic and one orthorhombic, differ simply by addition of a unit-cell-twinning mechanism (this term is used in the sense defined by Ito, 1950) to the monoclinic phase; where the sequence of a humite is (3, 2^{*}), the sequence in the equivalent leucophoenicite group mineral is (1, 2⁺⁺¹). The lattice parameters of alleghanyite and ribbeite as compared above are consistent with such a relation. Ribbeite is thus inferred to have the octahedron sequence (1, 2²)² and is the unit-cell-twinning equivalent of alleghanyite, which has the sequence (3, 2). The second superscript in the ribbeite sequence shows that the basic repeat must be doubled in order to achieve translation periodicity.

PHYSICAL AND OPTICAL PROPERTIES

Ribbeite is transparent and pink and has a light pink streak. The luster is vitreous; cleavage was not observed; the hardness is approximately 5 (Mohs'). The density, measured using heavy liquid techniques, is 3.90 (5) g/cm³; $D_{calc} = 3.84$ g/cm³. Ribbeite forms fine-grained, anhedral granular aggregates of crystals approximately 0.5 mm in diameter with a typical granulitic texture. Optically, ribbeite is biaxial positive and weakly pleochroic. The op-

Table 2. Optical properties for ribbeite

Pleochroism	X, Y colorless Z light pink Absorption $Z > X = Y$
Optical orientation	$X = b, Y = a, Z = c$
Optic axial angle $2V_z$	$F(486 \text{ nm}): 80.1^\circ(2)$ $D(589 \text{ nm}): 81.3^\circ(2)$ $C(656 \text{ nm}): 81.8^\circ(3)$ $r > v$ moderate
Refractive indices (at 589 nm)	$\alpha = 1.780(3)$ $\beta = 1.792(3)$ $\gamma = 1.808(3)$ $2V_z(\text{calc.}) = 82.5^\circ$

Note: Standard errors are given in parentheses and refer to the last digit.

tical properties, which were measured on a single grain, are listed in Table 2.

CHEMICAL COMPOSITION

Ribbeite and the associated minerals were chemically analyzed using an ARL-SEM-Q electron microprobe with operating voltage 15 kV and sample current 0.025 μ A, measured on brass. A wavelength-dispersive microprobe scan failed to detect elements with atomic number greater than 9 except those reported here. Special care was used for F, but none was detected. Standards for the analysis of ribbeite and alleghanyite were synthetic tephroite (Mn, Si) and Kakanui hornblende (Fe, Mg, Ca). Standards for the analysis of associated spinels were magnetite (Fe), spinel (Mg, Al), manganite (Mn), and zincite (Zn). The associated chlorite was analyzed with the standards hornblende (Si, Al, Fe, Mg) and manganite (Mn). The data were corrected using standard Bence-Albee factors.

The analytical data for ribbeite are SiO₂ 24.3, FeO 0.3, MgO 5.2, MnO 65.1, CaO 0.2, with H₂O 4.9 (by difference), sum = 100.00 wt%. Calculation of the chemical formula on the basis of 10 oxygen atoms gives (Mn_{4.30}Mg_{0.60}Fe_{0.02}Ca_{0.02})_{4.94}Si_{1.90}H_{2.54}O₁₀. The ideal formula is inferred to be Mn₅(SiO₄)₂(OH)₂, identical to that of alleghanyite. These and other data given above confirm that ribbeite and alleghanyite are polymorphs.

OCCURRENCE

Ribbeite has been found only at the Kombat mine, 49 km south of Tsumeb, Namibia. The ore consists largely of copper and lead sulfides deposited in essentially unmetamorphosed dolomite (Innes and Chaplin, 1985). The dolomite contains lenses of iron and manganese oxides, the former dominated by magnetite and hematite and the latter by hausmannite, barite, alleghanyite, manganian calcite, and pyrochroite. The type specimen of ribbeite was found in one of the manganese-rich lenses in August, 1982, in the E15-11 South stope, 11-level, 1241-m elevation of the Asis West sector of the Kombat mine. Our description is restricted to the type sample.

Ribbeite occurs as pinkish lenses up to 5 cm thick and 20 cm long within a 20-m-wide zone of tectonically intercalated manganese and iron ores. Locally within the

stope environs, the complexly deformed manganese and iron ores assume the attitude of a vertically plunging cylindrical fold in which ribbeite has a preferential association with carbonate-silicate facies within the manganese ores. The lenses are derived by tectonic transposition and boudinaging of the original sedimentary protore layering. The area containing ribbeite measured only ca. 40 cm across as exposed on the stope back. Ribbeite can be regarded as a scarce mineral. The transposed layering is transgressed by an abundance of veinlets of a proposed new manganese hydroxy-carbonate that clearly postdate the major tectonism but are themselves slightly deformed. Of interest also is the occurrence of manganosite as a constituent (to 5% by volume) of some hausmannite-pyrochroite-barite-calcite layers within the Mn ores but not immediately associated with the ribbeite-alleganyite layers. The manganosite is altering to pyrochroite and hausmannite and occurs as ragged emerald-green relicts up to 2 cm in diameter. The textural evidence strongly suggests that manganosite was a syn-genetic precursor of the hausmannite ores.

All of the minerals intergrown with ribbeite occur as approximately 0.5-mm-diameter grains. There are four distinct bands in the type specimen that seem to have been inherited from a sedimentary protolith, each dominated by different minerals. The first is a 3-mm-wide band composed primarily of ribbeite and also having subhedral pyrochroite (containing 7.8% MgO), which is preferentially oriented with layers approximately parallel to the principal zoning, and a mcgovernite-like mineral. This grades moderately sharply into a 2-cm-wide band composed largely of ribbeite and chlorite, with minor spinels and calcite. The chlorite, which is not visible in hand specimen, consists of subhedral colorless laths in thin section. The composition is $(\text{Mg}_{4.20}\text{Mn}_{0.40}\text{Fe}_{0.05}\text{Al}_{1.34})_{5.99}(\text{Si}_{2.67}\text{Al}_{1.34})_{4.01}\text{O}_{10}(\text{OH})_8$. The laths have a preferred orientation, with (001) parallel to the mineral zoning. Two spinels occur, both as separate subhedral to euhedral grains or as irregular intergrowths. One is opaque, black, aluminian, manganean jacobsonite and the other is transparent, orange, zincian, magnesian galaxite. The compositions of two adjacent grains having the highest Zn content are $(\text{Mn}_{0.96}\text{Mg}_{0.04})(\text{Fe}_{1.28}\text{Mn}_{0.39}\text{Al}_{0.33})\text{O}_4$ and $(\text{Mn}_{0.46}\text{Zn}_{0.37}\text{Mg}_{0.17})(\text{Al}_{1.90}\text{Fe}_{0.06}\text{Mn}_{0.04})\text{O}_4$, respectively. There is no evidence for exsolution at optical-microscope levels of resolution. Manganoan calcite of composition $(\text{Ca}_{0.79}\text{Mn}_{0.19}\text{Mg}_{0.02})\text{CO}_3$ is intimately intergrown with ribbeite. The mcgovernite-like mineral occurs sparingly.

The band containing ribbeite grades continuously into a 2-mm-wide band of manganoan calcite with composition $(\text{Ca}_{0.82}\text{Mn}_{0.17}\text{Mg}_{0.01})\text{CO}_3$, nearly identical to that of the calcite associated with ribbeite. These data imply that this band is of primary metamorphic origin rather than being a late-stage vein. The calcite unit in turn grades into a band consisting almost entirely of equigranular alleganyite, but with some galaxite, jacobsonite, and calcite. The alleganyite may be differentiated from ribbeite only with difficulty in thin section. However, the alleganyite is fre-

quently twinned, some grains having several twin domains; it is then readily identified. The alleganyite has a composition identical within error to that of ribbeite, except that it contains 0.3% F; we therefore do not report it separately.

Although it was not possible to identify all grains as ribbeite in one area of the specimen, and all as alleganyite in the other, no exceptions were found to their occurring in separate domains in which identifications were made. The textural relations thus imply that large numbers of ribbeite grains separately formed in a prograde metamorphic environment only millimeters from the unit where alleganyite of the same composition formed.

Yau and Peacor (1986) showed that the orthorhombic polymorph of either the leucophoenicite or humite group could be derived by unit-cell twinning of the monoclinic form of the other group. Because the twin operation is associated with the (OH, F) ligands of octahedrally coordinated Mn, and because the Mn-bearing humites invariably contain F and the leucophoenicite group minerals do not, Yau and Peacor suggested that leucophoenicite-group minerals formed in the absence of F. There is indeed no detectable F (<0.1%) in ribbeite. However, there is an indication of only a minor amount of F (0.3%) in the associated alleganyite, implying that the relative activities of OH and F may not be the determining factors in stabilizing members of one group relative to another. Dunn (1985) has also pointed out that members of the leucophoenicite group are limited in their Mn contents, especially in that they usually contain measurable amounts of Ca, Zn, or Mg substituting for Mn. We have recently observed that for jerrygibbsite from the Kombat mine. Whether or not members of the leucophoenicite group are stabilized relative to humite-group minerals by the absence of F or the presence of cations other than Mn cannot now be determined.

Winter et al. (1983) showed that the occurrences of the various Mn-bearing humites and tephroite are principally controlled by the activities of SiO_2 and H_2O . They predicted that the Mn analogue of norbergite might be found in environments with relatively high $a_{\text{H}_2\text{O}}$ and in equilibrium with alleganyite or pyrochroite. Because ribbeite is polymorphic with alleganyite, the Mn analogue of norbergite might occur with ribbeite and pyrochroite. The leucophoenicite-group mineral grains occurring adjacent to the pyrochroite and within millimeters of ribbeite were therefore carefully studied using optical, powder XRD, and electron-microprobe analyses, but they were confirmed to be ribbeite. The absence in this paragenesis of the Mn analogue of norbergite or of a leucophoenicite-group polymorph of such a phase implies that they may not be stable phases, at least at the Mn/(Mn + Fe + Mg) ratios observed.

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