Holdawayite, a new manganese hydroxyl-carbonate from the Kombat mine, Namibia

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ABSTRACT

Holdawayite is a new mineral occurring at the Kombat mine, Namibia. The chemical analysis is MgO 4.4, MnO 64.6, CaO 0.5, FeO 0.2, B_2O_3 1.2, CO_2 14.2, H_2O 11.47, Cl 4.4, less O $\equiv$ Cl 1.0, sum 100.1 wt%, corresponding to the ideal formula $Mn_6(CO_3)_2(OH)_7(Cl,OH)$. Holdawayite is monoclinic, space group $C2/m$, with $a = 23.437(5)$, $b = 3.3137(3)$, $c = 16.618(6)$ Å, $\beta = 111.15(2)°$, $Z = 4$. The most intense powder X-ray diffraction lines are $(d(Å), I, hkl)$ 10.93(100) $(\bar{2}01,200)$, 5.459(80) $(400,202)$, 3.879(70) $(\bar{6}02,004)$, 1.789(70) $(\bar{1}\bar{1}.1.3,117)$, 2.690(60) $(\bar{5}11,113,\bar{5}12,312)$, 2.589(50) $(\bar{6}06,\bar{5}13,006,\bar{3}14)$, 7.77(40) $(\bar{2}02,002)$, 2.926(40) $(\bar{8}02,602)$, 2.792(40) $(\bar{3}13)$, and 1.657(40) (020). It occurs principally as subhedral grains in manganese ores and rarely as fibrous, silky aggregates. It is pink and translucent and has a vitreous luster. The observed and calculated densities are 3.19(4) and 3.24(3) g/cm^3, respectively. Optical properties include biaxial $(-)$; $2V = 12(3)°$ (meas.), 18° (calc.); $\alpha = 1.644(1)$, $\beta = 1.719(1)$, $\gamma = 1.721(1)$; moderate dispersion, $r < v$; $X = b$, $Z \wedge c = 45(3)°$.

Holdawayite forms coarse veins cutting silicate-facies Mn-bearing rocks with assemblages including humite- and/or leucophoenicite-group minerals. Idealized Cl-free holdawayite, $Mn_3(CO_3)(OH)_4$, may form by hydration of rhodochrosite and in turn may oxidize to higher oxides and hydroxides of Mn. It has been named in honor of Dr. Michael J. Holdaway, professor of petrology at Southern Methodist University.

INTRODUCTION

A locally abundant pink carbonate was found in the Kombat mine in Namibia in 1982 but could not be identified as a known mineral. The hypothesis that it might be a new species has been borne out by subsequent investigations, and its characterization is presented herein. We have named this new mineral *holdawayite* in honor of Dr. Michael J. Holdaway, professor of petrology at Southern Methodist University, in recognition of his many research contributions to mineralogy and petrology, and especially for his efforts on behalf of the society of mineralogists as editor of the *American Mineralogist*. It is particularly appropriate that this mineral occurs as a major rock-forming mineral of petrologic significance. The species and the name were approved by the Commission on New Minerals and Mineral Names, IMA, prior to publication. Type material is deposited at the Smithsonian Institution under catalogue no. 163209 and at the National Museun of Natural History, Ottawa, under NMNS no. 51510.

OCCURRENCE

Holdawayite occurs at the Kombat mine, 37 km east of Otavi and 49 km south of Tsumeb, Namibia. The geology of the mine was described by Innes and Chaplin (1986). All known samples of holdawayite were collected between the 1238- and 1241-m elevations in the E15-11 South stope on 11 level of the Asis West sector of the mine. The original samples were collected on August 2, 1982, and the exposure was accessible until early in September, 1982. Holdawayite was restricted in occurrences to the footwall zone of a complexly deformed body of tectonically intercalated manganese and iron ores, which are locally dominated by carbonate- and silicate-facies rocks rather than by the more usual hausmannite ores. Holdawayite occurred typically as an anastomosing mesh

of veinlets, 1 to 8 mm in thickness, mainly in a hematite-carbonate matrix and also as patches and blebs 1 to 4 cm in diameter. It locally formed up to 40 vol% of the ore. It is estimated that ca. 200–300 metric tons of holdawayite-bearing material was removed from this stope during the course of mining.

The mineral was not encountered elsewhere within this manganese orebody nor within the other lenses in the Kombat mining field. However, it is noteworthy that at lower elevations in the E15-11 S body, the related mineral defernite (Sarp et al., 1980) is abundant within hausmannite-barite ores.

Occasionally, the veins of holdawayite mimic the ore foliation and the tectonically transposed mineral protore layering. The veins clearly postdate the major foliation event but are also deformed. There is an abundance of curvilamellar cleavages developed in the holdawayite crystal grains. In one instance, a crudely encrusted vein of coarsely crystalline magnesian siderite carrying blebby pyrite and chalcopyrite was clearly observed to crosscut the ore foliation in a 15-m-thick zone of tectonically intercalated feldspathic sandstone, calcitic dolostone, black argillite, and layered iron and manganese ores. Where this 10-cm-thick vein cuts the zone of manganese ores, holdawayite was the only vein mineral present. Only hematite and carbonates (siderite, dolomite) have been noted in immediate association with holdawayite. Lenses of silicate-facies manganese ores within a hematite + holdawayite matrix contain the assemblages ribbeite + pyrochroite + calcite + mcgovernite-like mineral (Peacor et al., 1987a), ribbeite + clinochlore + jacobsite + galaxite + calcite + mcgovernite-like mineral, alleghanyite + galaxite + jacobsite + calcite, and alleghanyite + jacobsite + kutnahorite + galena + hydroxylapatite. Although it is difficult to infer the relationship between holdawayite and any of these assemblages, there is little evidence of replacement or reaction with the matrix minerals at the edges of the holdawayite veins and patches. Layers of oxide-facies ore contain the assemblage hausmannite + barite + calcite + pyrochroite + manganosite, but holdawayite was not noted in immediate association with these phases.

The holdawayite veins are composed of monomineralic granular aggregates of the mineral, with grains 1 to 5 mm in size and usually showing marked elongation and subparallel alignment of cleavage surfaces. Rocks broken along the veins expose faces up to 30 cm square composed of virtually pure holdawayite that, when freshly exposed, is of a deep red-pink color and transparent to translucent in thick cleavage fragments.

Many holdawayite samples appear to have been leached by hydrothermal solutions with the resultant formation of a pink, fibrous mineral with a silky luster that appears to be in parallel growth with, and to grade into, massive holdawayite. This material was found by single-crystal X-ray diffraction methods to be holdawayite elongated parallel to [010]. Electron-microprobe analysis confirmed this identification and showed that the fibrous material has more Mg than other analyzed holdawayite, but still has Mn $\gg$ Mg. The fibrous holdawayite occurs only with the ribbeite + galaxite assemblage described above.

PHYSICAL AND OPTICAL PROPERTIES

Holdawayite occurs as subhedral crystals approximately 2 cm in diameter in the holotype sample. It is translucent and light to bright pink in color with a vitreous luster; fresh, glassy material resembles some rhodonite. It gradually changes to a brown color on exposure and in some cases has developed a thin black sooty coating that masks the true color. In an unusual occurrence, fibrous holdawayite with a silky luster occurs as a coating on massive material. The streak is light pink, and there is no discernible fluorescence in ultraviolet radiation. The hardness (Mohs) is approximately 3, and the mineral is moderately brittle. Cleavage is perfect on {100}, and there is an irregular fracture. The density is 3.19(4) g/cm³, measured with a Berman balance, compared with the calculated value of 3.24 g/cm³. Holdawayite effervesces weakly in dilute HCl. It is stained light pink with an alizarin-red–dilute HCl mixture.

Optically, holdawayite is biaxial negative, with $2V = 12(3)°$ (meas.), 18° (calc.), and $\alpha = 1.644(1)$, $\beta = 1.719(1)$, and $\gamma = 1.721(1)$, measured in Na light. Dispersion is moderate $r < v$. No pleochroism or color was observed in thin section. The orientation is $X = b$, $Z \wedge c = 45(3)°$ in the obtuse angle of beta.

X-RAY CRYSTALLOGRAPHY

Weissenberg and precession photographs obtained using cleavage fragments showed that holdawayite is monoclinic, with extinctions consistent with space groups $C2$, Cm or $C2/m$. A determination of the crystal structure (Peacor and Rouse, 1988) shows $C2/m$ to be the correct choice. Lattice parameters as determined by least-squares refinement of powder X-ray diffraction data are $a = 23.437(5)$, $b = 3.3137(3)$, $c = 16.618(6)$ Å, $\beta = 111.15(2)°$, $V = 1203.7(8)$ Å³, $Z = 4$. The powder X-ray diffraction pattern was obtained using a 114.6-mm-diameter Gandolfi camera, FeKα (Mn filter) radiation, Si as an internal standard, and a multicrystal mount. The data are listed in Table 1.

Defernite was originally described by Sarp et al. (1980) as having the composition $Ca_6(CO_3)_2(OH,Cl)_8 \cdot nH_2O$ and as being orthorhombic with space group $Pna2_1$ or $Pnam$ and with lattice parameters $a = 17.860(5)$, $b = 22.775(6)$, and $c = 3.658(1)$ Å. This unit cell has features that are very similar to those of holdawayite, especially in the equivalence of the small value of c as compared to b of holdawayite, and the large values of the other two translations; i.e., both cells have unusual, tabular shapes. Liebich and Sarp (1985) determined the crystal structure of defernite, but their determination appears to be unsatisfactory in that the apparent formula derived from the structure is $Ca_6(CO_3)_2(OH,Cl)_7 \cdot nH_2O$, which is not charge-balanced. Nevertheless, it is closely related to that of holdawayite, $Mn_6(CO_3)_2(OH)_7(Cl,OH)$. The relationship

TABLE 1. Powder X-ray diffraction data for holdawayite

I_{obs}	d_{obs}	d_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	hkl
100	10.93	10.99	$\bar{2}01$	5	2.117	2.117	$\bar{7}15$
		10.93	200	2	2.079	2.084	$\bar{1}16$
40	7.77	7.78	$\bar{2}02$			2.077	$\bar{4}08$
		7.75	002			2.043	$\bar{6}08$
80	5.459	5.465	400	20	2.040	2.041	712
		5.460	202			2.039	$\bar{9}13$
5	4.680	4.693	$\bar{4}03$			2.038	$\bar{2}08$
		4.654	401	20	2.019	2.027	605
70	3.879	3.880	$\bar{6}02$			2.018	$\bar{9}11$
		3.875	004	2	1.959	1.959	910
10	3.640	3.643	600	1	1.890	1.890	$\overline{12}.0.1$
10	3.302	3.297	204	5	1.847	1.847	$\bar{7}17$
1	3.077	3.078	$\bar{1}12$			1.823	515
40	2.926	2.929	$\bar{8}02$	10	1.820	1.822	12.0.0
		2.917	602			1.820	606
30	2.879	2.883	$\bar{8}03$	70	1.789	1.792	$\overline{11}.1.3$
		2.881	311			1.790	117
		2.874	$\bar{8}01$	2	1.752	1.754	$\overline{11}.1.1$
5	2.838	2.837	$\bar{1}13$			1.750	$\overline{12}.0.7$
40	2.792	2.793	$\bar{3}13$	5	1.739	1.740	917
30	2.749	2.750	$\bar{4}06$			1.738	12.0.1
		2.748	$\bar{8}04$	2b	1.710	1.713	$\bar{7}18$
		2.745	$\bar{2}06$			1.709	$\bar{1}18$
60b	2.690	2.703	511	20b	1.678	1.682	$\overline{11}.1.6$
		2.702	113			1.677	913
		2.685	$\bar{5}12$			1.673	516
		2.679	312			1.670	317
20	2.637	2.641	510	40	1.657	1.657	020
50b	2.589	2.595	$\bar{6}06$	20	1.616	1.618	$\bar{2}.0.10$
		2.591	$\bar{5}13$			1.613	$\overline{11}.1.7$
		2.583	006			1.612	$\bar{5}19$
		2.574	$\bar{3}14$	10	1.602	1.602	$\bar{3}19$
5	2.443	2.450	313	10	1.588		
		2.444	$\bar{5}14$	5	1.573		
10	2.343	2.344	$\bar{3}15$	2	1.540		
		2.339	$\overline{10}.0.3$	1	1.526		
5	2.295	2.295	607	2	1.473		
5	2.277	2.281	$\overline{10}.0.1$	2	1.460		
		2.276	604	1b	1.446		
2	2.190	2.193	115	5	1.419		
		2.186	10.0.0	1	1.408		
30	2.166	2.168	711	2	1.396		

Note: The d_{calc} values are based on the unit-cell parameters $a = 23.437(5)$, $b = 3.3137(3)$, $c = 16.618(6)$ Å, $\beta = 111.15(2)°$. Reflections were indexed with the aid of the structure-factor data (Peacor and Rouse, 1988). The symbol "b" indicates a broadened line.

between defernite and holdawayite has been confirmed by the solution of the holdawayite structure and comparison of the structure with that of defernite. Each structure has atoms in layers with coordinates in adjacent layers differing by 0.5 in the narrow slab direction, with units consisting of edge-sharing Ca or Mn octahedra knit together by CO_3 groups, and separated by large zeolite-like voids.

CHEMICAL COMPOSITION

Holdawayite was chemically analyzed using a combination of procedures. The elements Mn, Mg, Ca, Fe, and Cl were obtained by microprobe analysis, employing an ARL-SEMQ electron microprobe utilizing a 15-kV operating voltage and a 0.025-μA sample current measured on brass. The standards used were manganite (Mn), hornblende (Ca, Fe, Mg), and chlorapatite (Cl). The data were corrected using a modified version of the MAGIC-4 program. The coexisting minerals were analyzed with a CA-

MECA Camebax electron microprobe with a 15-kV operating voltage and a 0.01-μA beam current. Tests for F, Al, Ti, Zn, and As yielded none at the detection limits of 0.1 wt%.

Water was determined using the Penfield method. In this procedure, the sample, mixed with flux to aid decomposition, is placed in a bulb at the end of a borosilicate glass tube. The tube itself is wrapped with a piece of wet cloth, and the water condenses as the bulb is heated. At the end of the heating period, the bulb is cut off using a torch while at the same time the tube is sealed at the end. The total water collected is determined by weighing the tube before and after drying.

The C was analyzed with a Leco low-C analyzer. In this determination, the sample is heated under a stream of oxygen in a induction furnace. The CO_2 is adsorbed on a molecular sieve material in a trap while the oxygen passes through. At the end of the burning cycle, the trap is heated, and the CO_2 flushed out with He. The conduc-

tivity of the helium-CO_2 mixture is measured against pure He; a calibrated digital voltmeter serves to indicate the total micrograms of C produced.

For the B analysis, the sample was fused with potassium carbonate, the B extracted and separated from interfering elements and CO_2. After careful neutralization of the solutions, the B was titrated with NaOH in the presence of mannitol. The B content of holdawayite may be due to contamination by the borate mineral sussexite (see below).

These analyses yielded the values MgO 4.4, MnO 64.6, CaO 0.5, FeO 0.2, B_2O_3 1.2, CO_2 14.2, H_2O 11.47, Cl 4.4, less O $\equiv$ Cl 1.0, total 100.1 wt%. The empirical formula, based on (O + OH + Cl) = 8 is $[Mn_{2.62}Mg_{0.31}Ca_{0.03}Fe_{0.01}]_{\Sigma2.97}$ $[(CO_3)_{0.93}(BO_3)_{0.10}]_{\Sigma1.03}$ $[(OH)_{3.67}Cl_{0.37}]_{\Sigma4.04}$. The crystal-structure analysis shows that Cl is ordered in a single site, giving rise to the idealized formula $Mn_6(CO_3)_2(OH)_7(Cl,OH)$, for which Z = 4.

PETROGRAPHY

The sample containing holotype holdawayite and its matrix, from level 11 in the Kombat mine, was selected for detailed petrologic study. A polished thin section was examined optically, with backscattered-electron imaging and with quantitative electron-microprobe analysis. A matrix of fine-grained kutnahorite hosts polysynthetically twinned porphyroblasts of a humite-like silicate mineral. Microprobe analysis of the silicate gives $(Mn_{4.56}Mg_{0.30}Zn_{0.00}Ca_{0.02})Si_2O_8(OH_{1.98}F_{0.02})$, which corresponds to the composition of ribbeite or alleghanyite. The observation of macroscopic twinning suggests that this mineral is monoclinic alleghanyite rather than orthorhombic ribbeite. Indeed, powder X-ray diffraction of a different spot on this sample confirms the presence of alleghanyite. The rock is studded by small euhedral manganian jacobsite $[(Mn^{2+}_{0.82}Mg_{0.18})(Fe^{3+}_{1.23}Mn^{3+}_{0.50}Al_{0.27})O_4]$ and fine subhedral galena with rare specks of native copper and a copper sulfide. Small euhedral grains of hydroxylapatite $[(Ca_{0.98}Mn_{0.02})_5(PO_4)_3(OH)_{0.56}F_{0.44}]$ are scattered through the matrix carbonate. Larger anhedral kutnahorite $[(Ca_{0.51}Mn_{0.46}Mg_{0.03})CO_3]$ occasionally contains tablets of calcian rhodochrosite $[(Ca_{0.21}Mn_{0.79})CO_3]$, and the two may collectively represent the two limbs of a solvus (Peacor et al., 1987b). Energy-dispersive analysis of clusters of a phase having a high atomic number reveals major Ce and minor Ca, Pb, and Th; it is presumed tentatively to be bastnäsite.

Several generations of veins are evident in the sample. Early veins of coarse holdawayite irregularly traverse the sample apparently accompanied by replacement of the matrix by patchy holdawayite. Kutnahorite, apatite, leucophoenicite, and jacobsite are preserved within and immediately adjacent to the holdawayite vein without evidence of reaction. Veins and patches of barite and, more rarely, witherite cut the host rock. Late veins of a transparent, light-brown, fibrous Mn mineral commonly traverse the matrix and replace the holdawayite veins along grain boundaries. Debye-Scherrer X-ray diffraction photographs of a small amount of this phase extracted from

the thin section reveals that it is sussexite, and microprobe analyses are consistent with the formula $(Mn_{0.81}Mg_{0.19})BO_2(OH)$ with traces of Ca and no detectable F, Na, Al, Si, Cl, Ti, Fe, Zn, or As. This phase commonly coats and replaces the holdawayite and may be the source of the B reported in the bulk analysis of holdawayite. The sussexite and holdawayite veins also contain small amounts of an opaque, anisotropic Mn mineral. Microprobe analysis yields 71 wt% MnO and 6 wt% MgO. The opacity of this mineral suggests that it has Mn^{3+} and/or Mn^{4+}; the low totals of the chemical analysis imply that it contains Mn^{4+} and/or H_2O. Unfortunately, the small amount of this phase precludes further characterization by X-ray diffraction.

DISCUSSION

If ideal holdawayite is considered to be $Mn_3CO_3(OH)_4$, several simple reactions relate it to other Mn minerals. Holdawayite may form from rhodochrosite or pyrochroite by the reactions

$$3MnCO_3 + 2H_2O = Mn_3CO_3(OH)_4 + 2CO_2;$$
$$3Mn(OH)_2 + CO_2 = Mn_3CO_3(OH)_4 + H_2O.$$
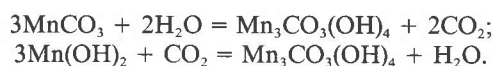
Some evidence for the first reaction is provided by observations of holdawayite veins and patches in the rock with a matrix of manganese carbonates. If ideal holdawayite has a stability field in the system $MnO-CO_2-H_2O$, topological constraints require that its stability field will intervene between those of pyrochroite and rhodochrosite. Although pyrochroite has been reported from the Kombat mine (Peacor et al., 1987a), its textural relations to holdawayite have not yet been observed.

Holdawayite may also become oxidized to higher oxides of Mn, for instance, hausmannite (Mn_3O_4) or manganite (MnOOH), by reactions such as

$$2Mn_3CO_3(OH)_4 + O_2 = 2Mn_3O_4 + 4H_2O + 2CO_2;$$
$$4Mn_3CO_3(OH)_4 + 3O_2 = 12MnOOH + 2H_2O + 4CO_2.$$
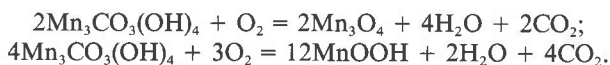
Oxidation of holdawayite to form higher oxides of Mn is supported by direct observations of its alteration to the opaque oxide in the rock. More complex reactions involving various Mn silicates may also be written but remain speculative without direct observation or through calculation with an adequate thermodynamic data base involving ideal holdawayite. Nevertheless, if ideal Cl-free holdawayite has a stability field, it would dominate other manganese oxides, carbonates, and oxyhydroxides at low temperatures, at relatively reducing conditions, and at moderate pressures of CO_2 and H_2O. The presence of Cl in holdawayite will affect the idealized reactions by the production of HCl at the expense of some H_2O, e.g.,

$$3Mn_7(CO_3)_2(OH)_7Cl + 9O_2 = 7Mn_3O_4 + HCl + 3H_2O + 6CO_2.$$
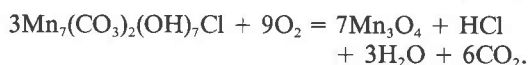
The resultant stability of Cl-bearing holdawayite is thus controlled by the relative fugacities of four fluid species. If Cl is indeed essential to the structure of holdawayite,

then its stability field will be extended by the increase in fugacity of HCl relative to H_2O and CO_2.

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