

Janggunitite, a new manganese hydroxide mineral from the Janggung mine, Bonghwa, Korea

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SUMMARY. Janggunitite occurs as radiating groups of flakes, flower-like aggregates, colloform bands, dendritic or arborescent masses in the cementation zone of the supergene manganese oxide deposits. The flakes average 0.05 mm. Colour black, lustre dull, streak brownish black to dark brown. Cleavage one direction perfect. $H = 2-3$, very fragile. $D_{\text{meas}} = 3.59$, $D_{\text{calc}} = 3.58$. Under reflected light anisotropic and birefractant. No internal reflections. Etching reactions: positive - HCl , HNO_3 , SnCl_2 , H_2O_2 , $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$. Chemical formula, $\text{Mn}_{4.85}^{2+}(\text{Mn}_{0.90}^{2+}\text{Fe}_{0.30}^{3+})\text{O}_{8.09}(\text{OH})_{5.91}$, on the basis of $\text{O} = 14$, or ideally $\text{Mn}_{3-x}^{2+}(\text{Mn}^{2+}, \text{Fe}^{3+})_{1+x}\text{O}_8(\text{OH})_6(x = 0.2)$. The mineral has an orthorhombic unit cell with a 9.324, b 14.05, c 7.956 Å, $Z = 4$, $a:b:c = 0.663:1:0.566$. Important diffraction lines are 9.34(s), 7.09(s), 4.62(m), 4.17(m), 3.547(s), 3.101(s), 2.597(w), 2.469(m), 1.863(w), 1.664(w), 1.525(m), 1.405(m). D.T.A. curve shows the endothermic peaks at 250-370 °C and 955 °C. Infra-red absorption spectral curve shows vibrations at 515 cm^{-1} , 545 cm^{-1} , 1025 cm^{-1} , and 3225 cm^{-1} . The mineral and name have been approved before publication by the Commission on New Minerals and Mineral Names, I.M.A.

IN the course of an investigation of the manganese oxide minerals of the supergene oxidation zone from the Janggung mine, Korea, the author noted a mineral with very interesting occurrence and optical properties under the reflecting microscope. The X-ray powder pattern of this mineral does not quite match that of any known mineral, so the mineral was reported as mineral X (Kim, 1974). Subsequent investigation by electron-probe microanalysis and wet-chemical analysis, further X-ray analysis, D.T.A., and infra-red absorption spectral analysis, has verified that the mineral is indeed a new species, and the author has named it janggunitite for the Janggung mine, the first locality.

Occurrence. The geology of the Janggung mining area where the janggunitite was found consists of crystalline limestone, dolostone, and rhodochrostone (Kim, 1975), mica schists, and quartzite of Palaeozoic age (fig. 1). The janggunitite is found in the cementation zone below the highly porous or concretionary zone in the supergene manganese oxide deposits, which were formed by oxidation of the manganese carbonate rocks such as rhodochrostone and manganese dolostone in the Janggung Limestone. The occurrence of janggunitite is confined to the Nam ore deposit. The frequency of appearance of this mineral is about 5% in the cementation zone.

The mineral occurs as very fine-grained aggregates in dendritic or arborescent masses or radiating groups of flaky crystals (figs. 4 and 5), in cavities of nsutite or todorokite, or as nearly isotropic colloform bands. The size of the janggunitite flakes is 0.13 mm for the largest and 0.05 mm on average. Some of the radiating groups of janggunitite have a flower-like appearance (fig. 2). The flakes are elongated parallel to the cleavage and flattened probably on (010). The mineral is associated with nsutite, todorokite, and calcite.

The *janggunitite-bearing manganese oxide ores* are generally less porous and more compact than other types of ores, and have large or small brownish irregular spots of calcite in the black

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manganese oxide matrix. Some parts of such ores, however, are slightly porous. The janggunite-bearing ores show rough and diffuse or distinct bands in some places. In polished sections or fragments, the janggunite-bearing parts are easily discernible with the naked eye by their low reflectance, dull lustre, and compact fabric. Under the microscope, such parts are occasionally characterized by the presence of secondary rhodochrosite grains in calcite matrix. This rhodochrosite is partly oxidized along the margin of the grains.

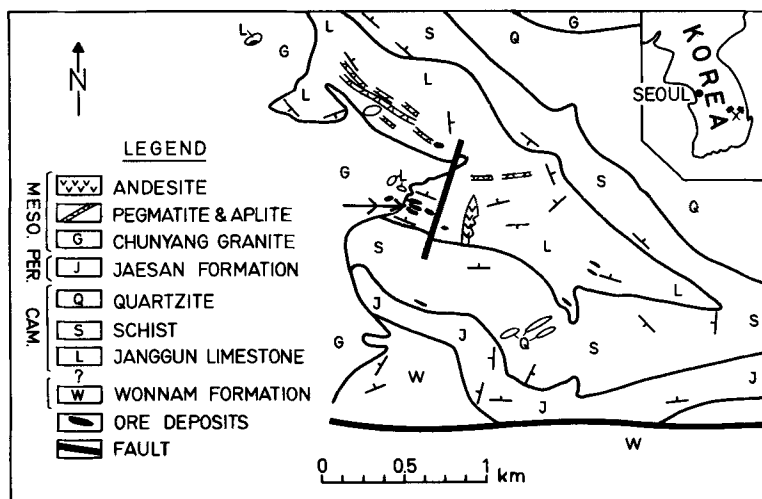


FIG. 1. Geological map of the Janggun mining area, Korea. Arrow indicates the Nam ore deposit where the janggunite is found.

Other parts, deficient in janggunite, have high reflectance, shining lustre, and compact fabric in polished section or fragments. Calcite grains in these parts are more coarse-grained than those in the janggunite-bearing part, and coloured distinctly brownish. Manganese oxides of such parts consist of nsutite, todorokite, or both. In the boundary between these two parts, however, janggunite is present together with nsutite or todorokite. Distinct colloform bands of janggunite and nsutite are occasionally found.

The *physical properties* of janggunite are summarized in Table I, where they are compared with those of psilomelane and bixbyite. Its optical properties are somewhat similar to those of todorokite or cryptomelane, but do not match exactly.

Microchemical reactions. Etch tests were made on the polished surface of the janggunite grains under the microscope. Positive reactions take place for HCl (conc.)—grey tarnishing; SnCl₂ (sat.)—grey tarnishing; HNO₃ (conc.)—grey colouration; H₂O₂—tarnishing with effervescence; H₂SO₄ + H₂O₂—grey tarnishing. It is unaffected by H₂SO₄ (conc.), KOH, and FeCl₃.

Chemical composition. A chemical analysis of janggunite was carried out using the electron-microprobe in the Institute for Mineralogy, Heidelberg University, and by wet-chemical analysis. Available oxygen, determined by the oxalate titration method, is allotted to MnO₂ from the total Mn, and the remaining Mn is calculated as MnO. Traces of Ba, Ca, Mg, K, Cu, Zn, and Al were detected. Li and Na were not detected from spectroscopic analysis. H₂O (+) is present as (OH) groups as verified from the infra-red absorption spectra. MnO₂ 74.91, MnO 11.33, Fe₂O₃ 4.19, PbO 0.03, H₂O + 9.46, total 99.92% (Fe and Pb by microprobe, MnO₂, MnO, and H₂O by wet-chemical techniques). This gives empirical unit-cell contents:

TABLE I. Comparison of janggunite, psilomelane, and bixbyite

	Janggunite	Psilomelane	Bixbyite
	Orthorhombic	Orthorhombic	Cubic
<i>a</i>	9.324 Å	9.1 Å	9.37 Å (Ramdohr, 1956, 1969)
<i>b</i>	14.05	13.70	
<i>c</i>	7.956	2.86 (Vaux, 1937)	
<i>Z</i>	4	2	16
Habit:	Flakes, radiated, colloform	Massive, fine-grained, colloform	Cubic crystals
Colour:	Black	Iron black to black	Black
Streak:	Brownish-black to dark brown	Brownish-black to black	Black with red-brown tint
Lustre:	Dull	Submetallic	Submetallic to metallic
H	2-3	5-6	6-6½
ρ	3.59 g cm ⁻³	4.71 g cm ⁻³	4.95 g cm ⁻³
Microscopic characters in polished section:			
Colour:	Air: greyish-white to grey Oil: much darker	Bluish-grey to greyish-white	Grey with creamy or yellow tint
Reflection pleochroism:	Air: distinct Oil: strong; [001] whitish; \perp [001] light grey	Strong; [001] almost white; \perp [001] dull grey or bluish-grey	Usually absent; sometimes very weak
Anisotropy:	Air: strong, yellowish-brown with bluish tint to grey Oil: very strong; yellowish-brown, bluish-brown, grey	Strong; white to grey	Weak to distinct
Extinction:	Parallel; occasionally undulatory	Straight	Undulatory
Internal reflection:	Not present	Brown	Not present
Reflectance	13-15%	15-20%	23%
Etch reactions:			
HCl (conc.)	+	+	-
HNO ₃ (conc.)	+	-	-
H ₂ SO ₄ (conc.)	-	+	+
H ₂ SO ₄ + H ₂ O ₂	+	-	+
SnCl ₂ (sat.)	+	+	+
H ₂ O ₂	+	+	-
FeCl ₃	-	-	-
KCN	-	-	-
Formula:	Mn _{5-x} (Mn ²⁺ , F ³⁺) _{1+x} O ₈ (OH) ₆ (<i>x</i> approx. 0.2)	(Ba, H ₂ O) ₂ Mn ₅ O ₁₀	(Mn, Fe) ₂ O ₃

Mn⁴⁺ 19.42, Mn²⁺ 3.60, Fe³⁺ 1.18, OH⁻ 23.67, O²⁻ 32.37, or ideally Mn_{5-x}⁴⁺(Mn²⁺, Fe³⁺)_{1+x}O₈(OH)₆, with *x* about 0.2.

X-ray diffraction data. X-ray powder diffraction patterns were taken with a 57.3 mm Debye-Scherrer camera using Fe-K α radiation filtered with Mn. Numerous X-ray photographs were taken for the janggunite of various habits. Powder data of janggunite are given in Table II. Some of the X-ray powder patterns resemble somewhat those of todorokite, but many discrepancies are found. The powder patterns of janggunite were indexed on an orthorhombic unit cell with *a* 9.324 Å, *b* 14.05 Å, *c* 7.956 Å; axial ratio *a*:*b*:*c* = 0.663:1:0.566. The volume of the unit cell is 1042.25 × 10⁻²⁴ cm³. *Z* = 4. Unit-cell edges *a* and *b* of janggunite are very close to those of psilomelane, but that of *c* is quite different (Table I).

Infra-red absorption spectral analysis was made by the potassium bromide pressed-pellet technique. Approximately 2 mg of sample (about - 300 mesh) was mixed and reground with about 600 mg of reagent-grade potassium bromide and the mixture was pressed under vacuum in a tool-steel die at roughly 1200 kg/cm².

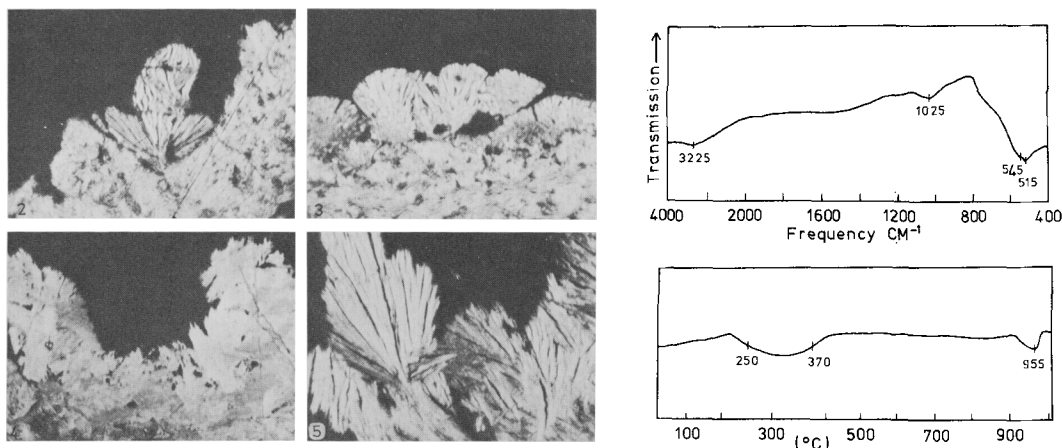
TABLE II. X-ray powder data for janggunitite (Mn-filtered Fe-K α radiation)

<i>I</i>	<i>d</i> _{obs}	<i>Q</i> _{obs}	<i>Q</i> _{calc}	<i>hkl</i>	<i>d</i> _{calc}	<i>I</i>	<i>d</i> _{obs}	<i>Q</i> _{obs}	<i>Q</i> _{calc}	<i>hkl</i>	<i>d</i> _{calc}
s	9.34 Å	0.0115	0.0115	100	9.33 Å	m	2.469	0.1640	0.1649	331	2.463
s	7.09	0.0199	0.0203	020	7.02	vw	2.214	0.2040	0.2043	420	2.212
m	4.62	0.0469	{0.0460 0.0476}	{200 121}	{4.66 4.58}	vw	2.098	0.2272	0.2284	260	2.092
m	4.17	0.0575	0.0571	130	4.19	w	1.863	0.2881	0.2876	500	1.865
s	3.547	0.0795	0.0798	112	3.540	w	1.664	0.3612	0.3614	314	1.663
vw	3.212	0.0969	0.0969	041	3.212	vw	1.554	0.4141	0.4141	600	1.554
s	3.101	0.1040	0.1035	300	3.108	m	1.525	0.4300	0.4299	601	1.525
w	2.597	0.1483	0.1473	013	2.606	m	1.405	0.5066	0.5066	0.10.0	1.406

The infra-red absorption spectra (fig. 6) show Mn-O stretching vibrations at 515 cm⁻¹ and 545 cm⁻¹, O-H bending vibrations at 1025 cm⁻¹, and O-H stretching vibration at 3225 cm⁻¹. Infra-red spectra indicate that H₂O(+) in the analysis of janggunitite is present as (OH) groups in the structure.

Thermal study. Differential thermal analysis (D.T.A.) of janggunitite was made at a running rate of 10 °C/min; the curve shows endothermic peaks at 250–370 °C and 955 °C (fig. 7). The first peak indicates dehydration and oxidation of janggunitite to (Mn, Fe)₂O₃ (cubic; *a* 9.417 Å), and the second indicates the formation of a hausmannite-type oxide (Mn, Fe)₃O₄ (tetragonal; *a* 5.76 Å, *c* 9.51 Å).

Formation of janggunitite. Janggunitite is closely associated with todorokite, nsutite, and calcite. Flower-like or radiating groups of janggunitite flakes in cavities indicate that it was formed by crystallization from solution, whereas nearly isotropic colloform bands indicate that it was formed by colloidal precipitation. Some of the dendritic or arborescent masses consist of fine-grained aggregates or nearly isotropic masses of janggunitite. Textural relations indicate that janggunitite was formed at almost the last stage of oxide ore formation and in a highly oxidizing condition in the supergene environment.



FIGS. 2-7: FIGS. 2-5 (left). Various habits of janggunitite in polished sections. Note the strong anisotropism in janggunitite. Black parts are calcite. Nicols crossed. $\times 525$ for figs. 2-4 and $\times 640$ for fig. 5. FIG. 6 (top right). Infra-red absorption spectral curve of janggunitite from the Janggung mine, Korea. FIG. 7 (bottom right). D.T.A. curve of janggunitite from the Janggung mine, Korea.

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