Koninckite from the Suwa Mine, Chino City, Nagano Prefecture, Japan

By

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Abstract   Koninckite from the Suwa mine occurs as aggregates of globules in a limonitic goethite ore and in a jarosite ore.   Ores are the products of hydrothermal precipitation from an acidic hot spring on andesitic lavas and pyroclastics belonging to Yatsugatake volcanic rocks.   The microprobe analysis of an aluminum-richer band in a globule of the former occurrence gives Fe_2O_3 35.73, Al_2O_3 2.52, P_2O_5 35.16, H_2O (by difference) 26.59, yielding the empirical formula $(Fe_{0.90}Al_{0.10})_{\Sigma 1.00}P_{1.00}O_{4.00} \cdot 2.98H_2O$. The associated jarosite is phosphatian with P_2O_5 up to 4.54 wt.%.   X-ray powder diffraction pattern is indexed on a tetragonal cell with $a=11.977(2)$, $c=14.625(2)$Å, $Z=16$, validating the previous results.   The refractive index n$=1.669(2)$ with very low birefringence is slightly higher than the average of the material from the original locality.

Introduction

Koninckite is a rare hydrous phosphate of ferric iron firstly reported by Cesáro (1884) from Richelle, near Vise, Belgium as nodules in a sedimentary rock, secondly by Beus (1950) from Kyrk-Bulak, Turkestan Range as an alteration product of triphylite in a pegmatite, and thirdly by Kizaki (1983) from Oni-Ana, Fukushima Prefecture, Japan as a constituent of a cave deposit.   Among them Beus (1950) used the name mankankoninckite to indicate his material.   But Mn_2O_3 content is too low to creat a new mineral and it should be referred to as manganian koninckite.   The present material is found as a constituent of a limonitic goethite ore and a jarosite ore of hydrothermal precipitation origin due to hot spring activities, that is, a new mode of occurrence to koninckite.

The crystallographic data for koninckite are given by van Tassel (1968), who obtained a tetragonal cell with $a=11.95$, $c=14.52$Å, $Z=16(FePO_4 \cdot 3H_2O)$.   As to the chemical composition, the original material contains Al_2O_3 4.6 wt.% (Cesáro, 1884), and the second one does Mn_2O_3 2.72 wt.% (Beus, 1950).   Although both authors have designated the ideal formula $FePO_4 \cdot 3H_2O$, more complex composition has been suggested as seen in the footnote of JCPDS Card No. 22–339.

The present study supported above crystallographic data with better X-ray powder diffraction pattern.   Also the formula $FePO_4 \cdot 3H_2O$ is strongly suggested after the microprobe analysis.   But the refractive index is slightly higher than that of the original material.

Occurrence

The Suwa mine is located about 7 km SSW of Mt. Tateshina, Nagano Prefecture (Fig. 1).   The ore deposits consist of more than 30 discrete limonite orebodies concentrated in Tateshina highland, where many acidic hot springs containing higher concentration of Fe^{3+} and SO_4^{2-} are still active.   Orebodies are formed as hot spring precipitates on andesitic lavas and pyroclastic rocks, belonging to Yatugatake volcanic rocks, and still some of the hot springs are currently producing limonitic precipitates (SAKAMOTO & TADAUCHI, 1959).   The mining activities have already ceased about 20 years ago, and the studied materials were all collected from the dump of Midoriyama orebody located near the center of the area covering all the orebodies excavated to date.

There are two modes of occurrence of koninckite.   One is tiny (up to 2 millimeters across) cauliflower-like aggregates of globules in interstices of a limonitic goethite ore, and the other is the discrete or aggregated globules or masses embedded in a jarosite ore.   In the former, the globules are semitranslucent white in colour with a pinkish tint.   The limonitic ore is rich in interstices partially filled with jarosite.   In the jarosite ore, koninckite globules are less translucent than the previous case, forming mass or lens-like body exceeding 20 centimeters across.   In such a larger body, globular features are lacking in the highly concentrated parts, where jarosite is an interstitial material to koninckite.

The chemical, X-ray powder and optical studies were made on materials in the limonitic goethite ore, although no significant differences are found in the X-ray powder diffraction patterns of koninckite of two modes of occurrence, suggesting the compositional similarity between them.

Fig. 1.   Index map of the Suwa mine.

Chemical Compositions of Koninckite and Jarosite

After the employment of Link Systems energy-dispersive X-ray spectrometer, the chemical compositions of koninckite and the associated jarosite were determined. As seen in the back-scattered electron microphotograph (Fig. 2), there are a few
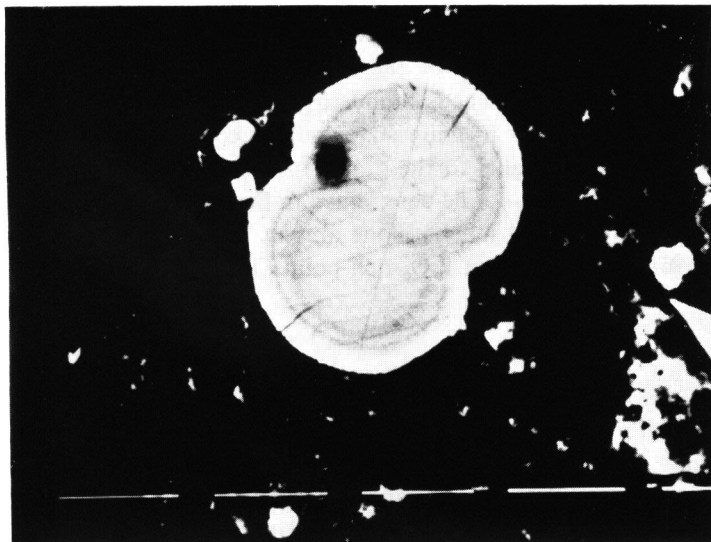

Fig. 2.   Globules of koninckite with aluminum-rich bands (dark).   The darkest band and the core were analysed.   A bar indicates 10 μ.

Table 1.   Chemical analyses of koninckite

	1.	1a.	2.	2a.	3.	4.
Fe_2O_3	35.73	0.90	37.25	0.94	34.4	38.98
Al_2O_3	2.52	0.10	1.64	0.07	4.6	
P_2O_5	35.16	1.00	34.60	0.99	34.8	34.64
SO_3			0.30	0.01		
H_2O	26.59*	5.96	26.21*	5.88	26.2*	26.38
total	100.00		100.00		100.0	100.00

1.   Koninckite. Suwa mine, Chino City, Nagano Prefecture, Japan. A band in a globule. Al_2O_3-rich analysis. (* by difference)

1a.   Number of atoms in chemical analysis 1. (basis: O=4 in the anhydrous part)

2.   Koninckite. Ditto. Core of the globule. (* by difference)

2a.   Number of atoms in chemical analysis 2. (basis: O=4 in the anhydrous part)

3.   Koninckite. Richelle, near Visé, Belgium. Average of two analyses. (* by difference) After CESÁRO (1884).

4.   Theoretical $FePO_4 \cdot 3H_2O$.

Empirical formulae:

1. $(Fe_{0.90}Al_{0.10})_{\Sigma 1.00}P_{1.00}O_{4.00} \cdot 2.98H_2O$

2. $(Fe_{0.94}Al_{0.07})_{\Sigma 1.01}(P_{0.99}S_{0.01})_{\Sigma 1.00}O_{4.00} \cdot 2.94H_2O$

darker bands concentrically developed in the globule of koninckite, and one of them was subjected to the chemical analysis (Table 1). If all the rest of analysis is ascribed to H_2O, the empirical formula is very close to the theoretical composition, $FePO_4 \cdot 3H_2O$. In the figure the core is less dark than the band and the periphery of globule is brightest. The chemical analysis of the core is poorer in Al_2O_3 content than in the band, it being 1.64 wt.%, with Fe:Al mole ratio 94:6 (Table 1). The bands are compositionally discontinuous to the adjacent portions in the globules.

The compositional variations of the associated jarosite include those of P_2O_5 and K_2O contents, and the former is found to be proxy for SO_3. The aggregates of jarosite are somewhat coarser in grain size, and the compositional variations have a zoned texture developed parallel to the grain surface forming the wall of interstices. Since the H_2O contents could not be determined in the analyses, no specification of the vicarious member to K could not be made among H, H_3O, and □. The tabulated analysis of jarosite is for the most P_2O_5-rich point (Table 2). It is rather low in K_2O content.

X-ray Power Study

A few globules in the limonitic goethite ore were subjected to X-ray powder diffraction study using Co/Fe radiation and diffractometer. The obtained pattern is essentially identical with that of the material from the original locality (van Tassel, 1968), but many weak subsidiary diffractions were found in addition and indexed on a tetragonal cell with $a=11.977(2)$ and $c=14.625(2)$Å (Table 3). Some of the diffractions have overlapped indices, making it meaning-less to derive any possible space group from the extinction rule, except for the possibility that $00l$ with $l=2n+1$ is forbidden.

Table 2.　Chemical analyses of jarosite

	1.	1a.	2.	2a.
Fe_2O_3	47.37	2.87	46.02	2.90
Al_2O_3	0.63	0.06	0.98	0.10
K_2O	7.53	0.79	8.15	0.87
SO_3	27.30	1.68	28.66	1.80
P_2O_5	4.54	0.32	2.77	0.20
H_2O	13.57*	7.44	13.42*	7.51
	100.00		100.00	

1. Jarosite. Suwa mine, Chino City, Nagano Prefecture, Japan. P_2O_5-rich analysis. (* by difference)
1a. Number of atoms in the analysis 1. (basis: S+P=2)
2. Jarosite. Ditto. P_2O_5-poorer analysis. (* by difference)
2a. Number of atoms in chemical analysis 2. (basis: S+P=2)

Empirical formulae:
1. $(K_{0.79}(H_3O)_{0.21})_{\Sigma 1.00}(Fe_{2.87}Al_{0.06})_{\Sigma 2.93}[(SO_4)_{1.68}(PO_4)_{0.32}]_{\Sigma 2.00}((OH)_{5.47}(H_2O)_{0.67})_{\Sigma 6.14}$
2. $(K_{0.87}(H_3O)_{0.13})_{\Sigma 1.00}(Fe_{2.90}Al_{0.10})_{\Sigma 3.00}[(SO_4)_{1.80}(PO_4)_{0.20}]_{\Sigma 2.00}((OH)_{5.80}(H_2O)_{0.66})_{\Sigma 6.46}$

Table 3.   X-ray powder patterns of koninckite

	1.				2.		
I	$d_{obs.}$	hkl		I	$d_{obs.}$	$d_{cal.}$	hkl
				1/2	9.27	9.28	101
100	8.42	110		100	8.47	8.48	110
				1/2	7.33	7.33	111
						7.31	002
8	5.99	200		10	6.00	5.99	200
2	5.50	112		6	5.54	5.54	201
						5.54	112
1	5.01	211		4	5.04	5.03	211
4	4.48	103		8	4.52	4.51	103
1	4.30	212		3	4.33	4.32	212
				2	4.229	4.233	220
						4.226	113
10	3.85	301		22	3.851	3.852	301
28	3.77	310		28	3.790	3.788	310
						3.780	203
4	3.64	311		9	3.656	3.666	311
						3.664	222
						3.656	004
				1	3.504	3.504	302
				1	3.497	3.496	104
2	3.33	312		11	3.358	3.363	312
						3.358	114
				2	3.237	3.239	321
2	3.19	223		2	3.196	3.196	223
18	2.98	400		22	2.993	2.995	400
						2.991	313
9	2.83	330		22	2.844	2.849	411
						2.841	105
				4	2.768	2.771	331
						2.765	115
1	2.747	323		1/2	2.749	2.745	323
1	2.614	332		3	2.630	2.633	332
						2.631	314
						2.628	205
2	2.564	215		3	2.566	2.567	215
2	2.489	413		3	2.496	2.495	413
				1/2	2.457	2.459	324
				1/2	2.388	2.388	106
				4	2.362	2.364	501
2	2.343	423		1	2.344	2.347	423
						2.343	116
				3	2.316	2.319	511
						2.317	404
						2.315	315
1	2.260	502		2	2.277	2.276	502
						2.274	414

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Table 3.   (Continued).

	1.			2.		
I	$d_{obs.}$	hkl	I	$d_{obs.}$	$d_{cal.}$	hkl
2	2.215	520				
			1	2.197	2.198	521
					2.195	325
1	2.151	424	3	2.149	2.150	503
			1/2	2.126	2.128	522
			1	2.116	2.117	440
					2.116	513
					2.112	226
1	2.095	441				
2	2.050	530	2	2.057	2.058	107
2	1.965	610	3	1.970	1.969	610
			1	1.951	1.951	611
1	1.918	602	1	1.925	1.926	602
			1/2	1.897	1.900	524
					1.894	620
			1/2	1.872	1.874	227
					1.871	540
			2	1.853	1.855	541
					1.853	505
					1.851	307
1	1.842	603				
			1/2	1.828	1.829	317
					1.829	008
					1.826	613
			1/2	1.808	1.807	108
1	1.798	426				
			3	1.772	1.772	631
2	1.762	623	3	1.770	1.769	327
1	1.740	543	2	1.745	1.746	543
1	1.705	700	1/2	1.707	1.708	506
			1	1.700	1.699	701
			2	1.695	1.696	417
					1.694	550
			2	1.682	1.682	624
					1.682	551
					1.681	535
1	1.672	633				
			4	1.649	1.650	641
2	1.640	720	4	1.646	1.646	318
					1.645	720
			1/2	1.608	1.610	109
1	1.600	722				
1	1.566	643	1	1.571	1.572	643
					1.571	536
			2	1.536	1.538	732
					1.537	554

Table 3. (Continued).

	1.			2.		
I	$d_{obs.}$	hkl	I	$d_{obs.}$	$d_{cal.}$	hkl
2	1.528	650				
			1/2	1.524	1.525	651
					1.524	635
					1.523	527
2	1.477	811	2	1.477	1.478	811
					1.477	705
			1/2	1.466	1.467	802
					1.466	555
					1.465	537
1	1.412	654	1	1.418	1.418	419
			1/2	1.373	1.373	3.0.10
					1.373	646
			1/2	1.301	1.302	912
					1.301	825
					1.301	754
1	1.290	921	1/2	1.292	1.293	727

1. Koninckite. Richelle, Belgium. CuKα-radiation. Camera method. After van Tassel (1968). $a = 11.95(5)$, $c = 14.52(8)$Å.

2. Koninckite. Suwa mine, Nagano Prefecture, Japan. Co/Fe radiation. Diffractometer method.   The present study. $a = 11.977(2)$, $c = 14.625(2)$Å.

Optical Properties

The globules were found to be composed of very fine moss-like aggregate of koninckite, but in the core of globules a slightly elongated form is seen.   The extinction is parallel to the outline and the sign of elongation is negative.   The refractive index measured by the immersion method is $n = 1.669(2)$ with very low birefringence covered within the error of measurement.   This is not coincident with the existing data: nE$ = 1.645$, nO$ = 1.655$; $n = 1.58$; $n = 1.660$ (Fleischer *et al.*, 1984), but closer to that of manganian koninckite, $\beta = 1.68 \sim 1.70$ (Beus, 1950).

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References

Beus, A. A., 1950. Magniophilite and mankoninckite, new minerals from pegmatites of the Turkestan Range. *Doklady Akad. Nauk SSSR*, **73**: 1267–1269. (In Russian.)

Cesáro, G., 1884. Sur la koninckite, noveau phosphate ferrique hydrate. *Ann. soc. géol. Belg. Mém.*, **11**: 247–157.

Fleischer, M., R. E. Wilcox & J. J. Matzko, 1984.   Microscopic determination of the nonopaque minerals.   *U. S. Geol. Surv. Bull.*, 1627, 37, 41, 105.

Kizaki, H., 1983.   New cave minerals, vashegyite and koninckite from Oni-Ana.   *Japan Caving*, **14**: 28–30. (In Japanese.)

Sakamoto, K. & T. Tadauchi, 1959.   Suwa mine.   In Unused Iron Resources.   No. 7, The Ministry of International Trade and Industry. 186–192. (In Japanese.)

van Tassel, R., 1968.   Donées cristallographiques sur la koninckite.   *Bull. soc. franç. minér. crist.*, **91**: 487–489.