

Mpororoite and anthoinite from the Kara mine, Tasmania

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ABSTRACT. The first occurrence of mpororoite and anthoinite outside the African Continent has been found in an altered skarn from the Kara mine, Tasmania, forming a white powdery mixture of the two minerals pseudomorphing scheelite. The wet chemical analysis of the mixture shows WO_3 , Al_2O_3 , and H_2O to be the essential constituents, proving the non-essential nature of Fe_2O_3 in mpororoite; the original mpororoite contained high Fe_2O_3 substituting for Al_2O_3 . The thermal treatment of the mixture at 100°C for 6 hours in air brings about the conversion of mpororoite into anthoinite, which re-hydrates into mpororoite, although the associated anthoinite does not. The source of Al is ascribed to the decomposition of aluminian andradite in the skarn.

IN 1980 the first author visited the Kara mine, Tasmania, as a member of Geological Survey Team of the National Science Museum, Japan, and collected some specimens of altered skarn from the trench and open pit of the ore deposit. The X-ray powder and chemical studies demonstrated the presence of mpororoite and anthoinite, forming a powdery mixture occasionally pseudomorphing scheelite which is the principal ore mineral of the deposit.

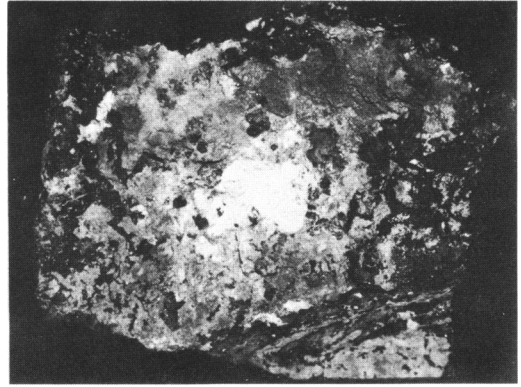
The present paper is the first report of their co-existence and occurrence in a contact metasomatic deposit. The chemical analysis of the mixture yields a formula $\text{WAlO}_3(\text{OH})_3 \cdot n\text{H}_2\text{O}$ with only a small amount of substitution of Fe_2O_3 for Al_2O_3 , proving the non-essential nature of Fe_2O_3 in mpororoite from the original locality. The thermal treatment of the mixture shows H_2O in mpororoite to be zeolitic; that is, artificially dehydrated mpororoite re-hydrates on treatment with H_2O under room temperature conditions.

Occurrence and description of the studied materials. The ore deposit of the Kara mine is located about 40 km SSW of Burnie, Northwestern Tasmania,

Australia. It is developed in contact metamorphosed late Ordovician or early Devonian sedimentary rocks belonging to June Group, intruded by a biotite granite of early Devonian to late Carboniferous age (Williams and Turner, 1973). The ore deposit is worked for tungsten and the principal and unique ore mineral is scheelite, which is dominantly formed in hedenbergite-actinolite-magnetite skarn forming a thin roof-pendant on the granite (Wolff, 1978).

The studied materials were from the wall of the old trench and the uppermost part of the open pit. In the former, the skarn minerals are completely altered to yellowish-green earthy montmorillonite, in which white to grey-white aggregates of powdery mpororoite and anthoinite, reaching a few centimetres across, are found (fig. 1). In the exposure the powder is mobilized downward along the fractures and exposure surface. No discrimination of the two was possible without X-ray powder diffraction work. A very small amount of scheelite is left unaltered as minute grains in the powdery aggregates. In the open pit materials the mixture of mpororoite and anthoinite contains varying amounts of scheelite and is found in a magnetite-rich skarn in which the constituent silicates are completely altered into light-brown earthy halloysite (fig. 2). In both places much unaltered scheelite is found in a magnetite skarn or in a garnet skarn closely associated with the magnetite skarn.

A comparison of the altered and unaltered skarn shows that the original skarn was rich in an aluminian andradite, comprising about 20 mole % of the grossular molecule, and the alteration could be the source of Al now contained in mpororoite and anthoinite. The alteration is a kind of decomposition accompanied by removal of Al. All the aggregates examined consisted of mpororoite



FIGS. 1 and 2. FIG. 1 (left). The mode of occurrence of the mixture of mpororoite and anthoinite (white) in altered skarn at the trench No. 1. Field view, approx. 50 × 35 cm. FIG. 2 (right). The mixture of mpororoite and anthoinite pseudomorphing scheelite (white in centre) in altered skarn. The specimen, approx. 10 × 7 cm.

and anthoinite, although the quantitative ratio changed from unity to anthoinite-rich, reaching an approximate ratio of 1:3, based on a direct comparison of the relative intensity of the strongest X-ray powder diffraction peaks. The present find is the first example of the co-existence of the two hydrous tungstates of aluminium and of their occurrence in a contact metasomatic scheelite deposit. Also, this is the first occurrence of these minerals outside the African Continent.

X-ray powder diffraction study. The separation of two minerals was impossible owing to their extremely fine grain size. Therefore, the X-ray powder study was made on the mixed specimens collected from the trench and open pit, and the pattern of the former (from trench No. 1, NSM FM-7799) is presented in Table I, together with those of mpororoite (von Knorring *et al.*, 1972) and anthoinite (Sahama *et al.*, 1970). No meaningful derivation of unit cell parameters was possible due to some overlapping diffraction peaks. The tabulated pattern is for the best crystallized material with a high ratio of mpororoite to anthoinite.

Although the proposed formulae of mpororoite and anthoinite are $(W,Al)(O,OH)_3 \cdot H_2O$ and $(W,Al)(O,OH)_3$ respectively, the present analysis indicates the ratio W/Al or $W/(Al + Fe)$ to be unity, corroborating the suggestion of Sahama (1981). That is, their ideal formulae, should be $WAlO_3(OH)_3 \cdot 2H_2O$ and $WAlO_3(OH)_3$, respectively, and their unit cells must be at least doubled to meet their unit cell contents.

The X-ray powder diffraction patterns of the inner and outer parts of aggregates from the open pit indicate that they consist mainly of anthoinite with small amounts of scheelite and mpororoite, and also the amount and crystallinity of mpororoite

increase outwards, whereas the amount of scheelite decreases. From this evidence scheelite is considered to have been altered firstly into anthoinite and subsequently into mpororoite.

The X-ray powder diffraction studies were also made on the dehydrated and re-hydrated materials. The former includes two samples prepared by heating the mixture at 100 °C for 2 and 6 hours. As

Table I. The X-ray powder data for mpororoite and anthoinite

1			2			3		
d	I	hkl	d	I	hkl	d	I	hkl
8.20	90	8.21	100	002	6.94	10	011	
6.96	2				6.11	10	110	
6.146	10	6.18	16	110	6.11	10	110	
5.654	100	5.69	18	102	5.63	100	002	
4.706	5	4.73	13	013				
4.320	15				4.33	35	02 $\bar{1}$,10 $\bar{3}$	
4.191	50	4.20	17	11 $\bar{3}$	4.19	85	12 $\bar{1}$	
4.130	30	4.09	19	004	4.12	35	200	
4.004	45				3.97	70	120,11 $\bar{3}$	
3.831	2	3.83	6	210				
3.782	5	3.75	9	20 $\bar{2}$,014				
3.735	5				3.65	25	02 $\bar{2}$	
3.654	10				3.48	20	022,121	
3.485	8				3.43	15	013	
3.422	5				3.21	8	104	
3.234	3				3.06	70b	030,30 $\bar{1}$	
3.070	85	3.084	90b	220,024	2.976	8	130	
2.894	5	2.911	9	124,130	2.716	11	124	
2.715	5				2.625	14	310	
2.623	10	2.647	9	30 $\bar{2}$	2.588	18	23 $\bar{1}$,13 $\bar{3}$	
2.590	5				2.537	6	215	
2.533	3				2.462	60	230,02 $\bar{4}$	
2.458	40	2.481	13	230,034	2.404	25	301	
2.394	8	2.395	7	23 $\bar{2}$	2.352	13	024	
2.355	15	2.357	15	026,134				
2.343	10	2.341	11	313	2.300	13	040	
2.302	7				2.250	17	414	
2.261	8				2.094	6	31 $\bar{6}$,24 $\bar{2}$	
2.098	5				2.051	9	400	
2.049	8				2.036	6	243	
2.003	6	2.016	6		1.971	6	32 $\bar{6}$	
1.932	15	1.943	7		1.936	20	41 $\bar{6}$	
					1.907	7	433	
1.871	20	1.872	7		1.863	25		
1.838	8				1.843	14		
1.792	10				1.791	16		

- Mixture of mpororoite and anthoinite. Kara mine, Tasmania. Cu/Ni rad. Diffractometer method. 13 reflections to 1.367
- Mpororoite. Mpororo mine, Uganda. Cu/Ni rad. Diffractometer method. After von Knorring *et al.* (1972). 1 reflection to 1.543
- Anthoinite. Nyamulilo mine, Uganda. Cu/Ni rad. Diffractometer method. After Sahama *et al.* (1970). 15 reflections to 1.369

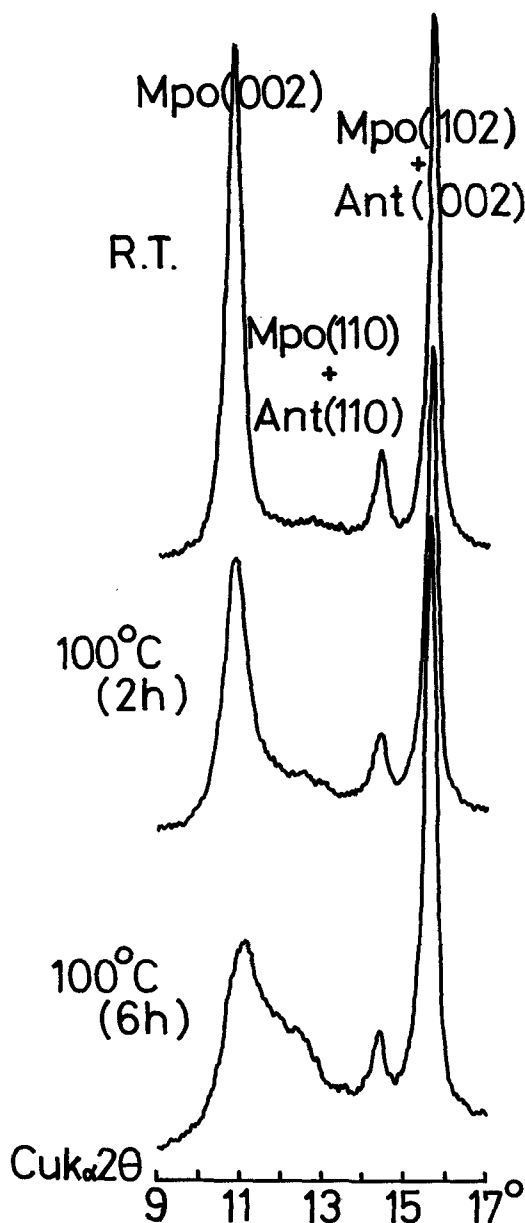


FIG. 3. Thermal change of X-ray diffraction diagrams for the mixture of mpororoite (Mpo) and anthoinite (Ant).

demonstrated in fig. 3, the diffraction lines of mpororoite decrease in sharpness and intensity and shift toward the higher angle side, and those of anthoinite increase in relative intensity. When the heated material is soaked in H_2O under room temperature conditions, the intensity of diffraction peaks of mpororoite tends to increase once again.

The size difference between their respective unit cells is principally seen in spacings with the contribution responsible for c^* , suggesting the presence of a layer structure perpendicular to c^* . This structure would allow the siting of interlayer water with a zeolitic nature in mpororoite, which may be responsible for the stronger (00 l) diffractions.

Chemical composition

The chemical analysis of the X-rayed material is given in Table II, where those of mpororoite from

Table II. Chemical analysis of the mixture of mpororoite and anthoinite (Analyst: Kozo Nagashima)

	1	2	3	4
WO ₃	65.92	66.90	72.90	74.84
SiO ₂	3.04	-	0.24	0.08
Al ₂ O ₃	13.90	8.22	15.82	16.03
Fe ₂ O ₃	1.34	9.78	1.74	0.07
CaO	tr	0.27	n.d.	n.d.
H ₂ O+	13.32	7.97	8.84	9.06
H ₂ O-	3.12	6.89	0.22	0.06
Total	100.64	100.03	99.76	100.14

1. Mixture of mpororoite and anthoinite including minor montmorillonite from Kara mine, Tasmania (The present study)
2. Mpororoite from Mpororo mine, Uganda (von Knorring *et al.*, 1972)
3. Anthoinite from Nyamulili mine, Uganda (Sahama *et al.*, 1970)
4. Anthoinite from Bugarama mine, Rwanda (Sahama *et al.*, 1970)

the Mpororo mine (von Knorring *et al.*, 1972) and of anthoinite from the Nyamulili mine, Uganda, and of Bugawara mine, Rwanda (Sahama *et al.*, 1970), are also given. In addition to the major elements, Mo, Ca, and Mg are found as minor constituents. Also, the present material contains a small amount of SiO₂, which can be ascribed to admixed montmorillonite. The empirical formula derived from the analysis is: $(W_{0.52}Al_{0.46}Fe_{0.02}^{3+})_{\Sigma 1.00}(O_{1.56}(OH)_{1.44})_{\Sigma 3.00} \cdot 0.59H_2O$ on the basis of $W + Al + Fe^{3+} = 1$ after the deduction of SiO₂ etc., as an iron-bearing montmorillonite with the estimated composition $SiO_2 \cdot 0.21Al_2O_3 \cdot 0.06Fe_2O_3 \cdot 0.45H_2O$. This corresponds to an intermediate composition between mpororoite and anthoinite with an approximate mole ratio 6:4.

The formation of mpororoite and anthoinite needs a supply of H₂O and Al₂O₃ and the leaching of a large quantity of calcium from scheelite and iron plus calcium from garnet. Such conditions are thought to have only rarely been attained, and

the occurrence of mpororoite and anthoinite is uncommon, despite the existence of numerous skarn-type scheelite deposits in the world.

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