

On the occurrence of smolyaninovite in the Mount Cobalt deposit, in north-western Queensland, Australia

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SUMMARY. Smolyaninovite, $(\text{Co, Ni, Ca, Mg})_3(\text{Fe, Al})_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$, has recently been recognized in the mineralized region around Mount Cobalt, Queensland. It is a soft polycrystalline earthy yellow-brown material, is probably the weathering product of cobaltian arsenopyrite or alloclase, and shows para-magnetic properties.

OVER the last several years the Department of Chemical Engineering of Monash University has been studying the general problem of mineral beneficiation of cobalt minerals. As part of the investigation, samples were obtained from the cobalt-mineralized area around Mount Cobalt, which is situated some 110 km south of Cloncurry in north-west Queensland, Australia.

The geology of the area has been described by Rayner (1953), who reported the presence of two distinct cobalt-containing minerals, the primary sulpharsenide cobaltite and its weathering product erythrite. Mineral dressing studies in the laboratory showed that a third distinct cobalt-bearing mineral was present as well, with properties quite different from the two reported by Rayner.

The 'new' mineral occurs as a relatively soft polycrystalline earthy yellow-brown material in veinlets and is frequently, but not always, associated with erythrite. It is a weathering product and has probably resulted from the weathering of cobaltian arsenopyrite or alloclase $(\text{Co, Fe})\text{AsS}$, both of which have been detected by Croxford (1974) in a copper orebody in near-by Mount Isa but not as yet at Mount Cobalt.

Chemical analysis of the mineral showed it to be essentially a cobalt-iron-calcium arsenate. Mössbauer spectra indicated that the iron was present in the ferric state only. Electron-microprobe analyses and element mapping of individual grains confirmed that the constituent elements were uniformly distributed over the entire exposed grain surfaces and hence throughout the particles, and none was present as a gangue inclusion. These analyses showed further that the iron:cobalt ratio was constant from grain to grain within the accuracy of the techniques used.

The only hydrated iron (III) cobalt arsenate that has been reported is smolyaninovite, which was described by Yakhontova (1956, 1973). Smolyaninovite is an earthy oxidation product found at Bou-Azzer, Morocco, with a composition listed as: $(\text{Co, Ni, Ca, Mg})_4(\text{Fe, Al})_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$. The chemical analyses of the mineral isolated from the Mount Cobalt deposit and of one sample of smolyaninovite given by Yakhontova are shown in Table I. The new analysis was carried out by wet-chemical methods except for water, which was determined by a microgravimetric technique.

The major difference between the mineral described by Yakhontova and the one obtained from the Australian source is in the ratio of the divalent to trivalent cations. The ratio for the Mount Cobalt mineral approximates to 3:2 while the Russian author gives a value of 4:2,

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but with actual values quoted ranging from 4.9:2 to 4.0:2 (the variation is put down to small amounts of gangue inclusions). It is believed that the two minerals are the same, and that the composition should more correctly be: $(\text{Co}, \text{Ni}, \text{Ca}, \text{Mg})_3 (\text{Fe}, \text{Al})_2 (\text{AsO}_4)_4 \cdot 11 \text{H}_2\text{O}$, which composition allows all elements to exhibit normal valencies. Further evidence that the Mount Cobalt mineral is smolyaninovite is seen in Table I, in which the physical properties of the Mount Cobalt mineral are compared with those reported for smolyaninovite by Yakhontova.

TABLE I. *Chemical analyses and physical properties of the Mt. Cobalt mineral compared with those of smolyaninovite*

	1	2	3		1'	2'		1	2
SiO ₂	0.0	0.75	—	Ca ²⁺	0.93	0.74	H.	<2	2
CaO	5.10	3.69	3.72	Mg ²⁺	0.33	0.87	<i>n</i>	1.626-1.628	1.625 [±] 0.005
MgO	1.31	2.10	1.34	Σ	1.26	1.61	Extinction		
CoO	14.88	8.01	14.93	Co ²⁺	2.02	1.21	Elongation	+	+
NiO	0.42	8.18	—	Ni ²⁺	0.06	1.08	Birefringence	n.d.	ca.0.006-0.008
Fe ₂ O ₃	12.01	11.8	11.93	Σ	2.08	2.29	Colour	Yellow-brown*	Yellow, earthy
Al ₂ O ₃	2.36	1.5	2.54	Fe ³⁺	1.53	1.67	Sp.gr.	3.05†	2.43-2.49
As ₂ O ₅	43.96	41.88	45.80	Al ³⁺	0.47	0.33	Average grain size	100-200μm	n.d.
H ₂ O+	20.83	15.38	19.74	Σ	2.00	2.00	Magnetic	23.5-53.2	n.d.
H ₂ O—	—	6.41	—	AsO ₄ ³⁻	3.89	4.11	susceptibility	X 10 ⁻⁶ cm. ² g ⁻¹	
Sum	100.87	99.7	100.00	OH ⁻	1.01	1.47			

1. Mt.Cobalt mineral. 2. Bou-Azzer smolyaninovite (Yakhontova, 1956),

3. Theory for $(\text{Ca}, \text{Mg}) (\text{Co}, \text{Ni})_2 (\text{Fe}, \text{Al})_2 (\text{AsO}_4)_4 \cdot 11 \text{H}_2\text{O}$ with Ca:Mg = 2, no Ni, and Fe:Al = 3.

1', 2'. Ionic ratios to a basis of $\Sigma(\text{Fe}, \text{Al}) = 2$.

* Transparent; no pleochroism.

† Apparent sp.gr. 1.86, porosity 39%. Calculated sp.gr. for Z = 5 and the unit cell of Yakhontova *et. al.*, 3.055.

X-ray powder data were obtained using Co-K α radiation and are shown in Table II, together with data given by Yakhontova for smolyaninovite. The line indexing reported for the Mount Cobalt mineral is based on the unit cell dimensions given by Yakhontova, Sidorenko, Sergeeva, and Rybakova (1973), namely *a* 6.40 Å, *b* 11.72 Å, and *c* 21.9 Å. Laue techniques were used to show that each of the Mount Cobalt mineral grains was polycrystalline (it should be noted that all samples of the Mount Cobalt smolyaninovite used were obtained by hand picking individual grains under a low-powered microscope). The Mount Cobalt mineral seems to be significantly more crystalline than the Bou-Azzer materials.

As a final check on the properties of the Mount Cobalt smolyaninovite to differentiate it from a mixture of hematite and erythrite, a series of differential thermal analyses was carried out under both oxidizing and inert atmospheres. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) responses obtained for erythrite (fig. 1) and smolyaninovite (fig. 2) are quite different and there is no possibility that smolyaninovite is a composite mixture containing erythrite.

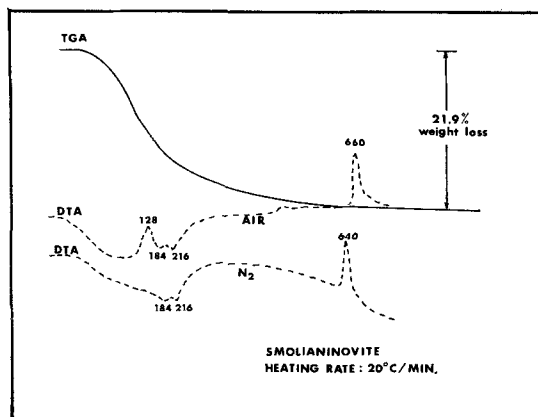
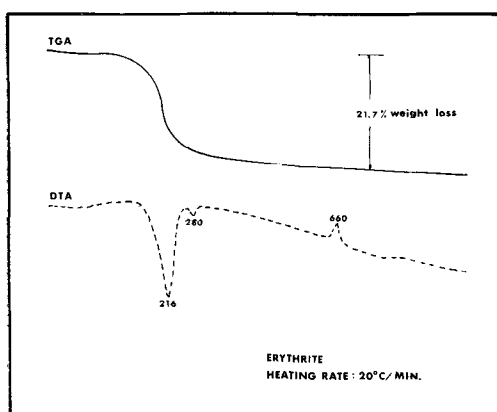
When the pink needle-like crystals of erythrite were heated under nitrogen and under air, there was no difference in the DTA-TGA traces obtained. The first and major endothermic peak occurred at 216 °C and was accompanied by a 21.7 % weight loss. This corresponds to

the removal of the water of crystallization (theoretical loss 24.0 %). No other chemical reaction occurs up to a temperature of 900 °C although two additional small peaks, one endothermic at 280 °C and one exothermic at 660 °C, were detected in the DTA trace.

The DTA-TGA responses for smolyaninovite when the material was heated under an inert atmosphere or under an oxidizing atmosphere were similar (fig. 2) except that a quite distinct exothermic peak appeared at 128 °C in the 'air-atmosphere' trace. The peak appears to be an

TABLE II. X-ray diffraction data for the Mt. Cobalt mineral compared with those of smolyaninovite

Mt. Cobalt mineral			Smolyaninovite			Mt. Cobalt mineral			Smolyaninovite		
<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>
23.08 Å	10	001	21.94 Å	10	001	2.97-2.89 Å	7b	212, 203, 040	2.92 Å	5	040
12.0-9.95	9b	010, 011, 002	11.58	8	010	2.78	3	220, 221	—	—	—
7.85	10	003	—	—	—	2.61	3	223, 044	2.59	1	—
6.85	5	100	—	—	—	2.50	3	230	—	—	—
4.48	5	113	—	—	—	2.39	3	233, 232	—	—	—
3.90	2	030	(3.51)	2	—	1.76	3	341, 340	—	—	—
3.25-3.15	8b	200, 201, 131	3.20	6	200	—	—	—	1.642	5	400
	b, broad and diffuse								1.486	2	080



FIGS. 1 and 2: FIG. 1 (left). DTA-TGA traces for erythrite heated under air and under nitrogen atmospheres. FIG. 2 (right). DTA-TGA traces for smolyaninovite heated under air and under nitrogen atmospheres.

oxidation peak but no explanation can be offered to explain it. Any trace impurities that might conceivably be present would not react at such a low temperature. Yakhontova and her colleagues (1973) also give a DTA trace of smolyaninovite that agrees closely with the one obtained under an inert atmosphere for the Mount Cobalt material. X-ray diffraction data taken of the smolyaninovite before heating and after heating to 150 °C showed only a very minor change: a single relatively strong line appeared at *d* 1.95; all other lines were in identical positions and at the same intensities as given in Table II.

The 'new' mineral was found to be present in about the same quantities as erythrite in several 50 kg samples from Mount Cobalt area examined. The recovery of this mineral would therefore be important in any cobalt treatment process of ores from such a mineralized deposit. Chemically smolyaninovite is similar to erythrite in that it is very soluble in mineral acids suggesting that an acid leach process for the recovery of cobalt and arsenic from oxidized mineral concentrates may be able to be devised provided that other acid soluble gangue constituents in the concentrates were minimal.

Since this work was completed, we have learnt from Miss E. E. Fejer of the British Museum (Natural History) that a specimen purchased by the Museum in 1927 (BM 1927, 61), from Schneeberg, Saxony, has been found to carry small amounts of smolyaninovite, constituting a third occurrence of the mineral. The X-ray powder data for this specimen show slightly longer spacings than those for the Mt. Cobalt mineral, perhaps due to a slightly different composition; unfortunately there is not enough material for an analysis.

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