

The occurrence of robertsite in a sedimentary phosphate ore from Thailand

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Abstract

During a mineralogical study of guano-derived sedimentary phosphate ore from the Lamphun area of northwest Thailand, robertsite [$\text{Ca}_6(\text{H}_2\text{O})_6\text{Mn}^{3+}_9\text{O}_6(\text{PO}_4)_9 \cdot 3\text{H}_2\text{O}$] was identified and concentrated to a level suitable for X-ray diffraction and chemical analysis. Robertsite has previously been described only in association with altered phosphatic pegmatites. This new occurrence in a phosphate deposit indicates that it may be found in a broad spectrum of sedimentary rocks.

KEYWORDS: robertsite, phosphate ore, Thailand

Introduction

MOORE (1974) first described robertsite [$\text{Ca}_3\text{Mn}_4(\text{PO}_4)_4(\text{OH})_6 \cdot 3\text{H}_2\text{O}$], jahnsite [$\text{CaMn}^{2+}\text{Mg}_2(\text{H}_2\text{O})_8\text{Fe}^{3+}_2(\text{OH})_2(\text{PO}_4)_4$], and segelerite [$\text{CaMg}(\text{H}_2\text{O})_4\text{Fe}^{3+}(\text{OH})(\text{PO}_4)_2$] in the Tip Top pegmatite near Custer, South Dakota. Moore also described mitridatite [$\text{Ca}_2\text{Fe}^{3+}_4(\text{OH})_6(\text{H}_2\text{O})_3(\text{PO}_4)_4$] from the same locality and proposed that robertsite and mitridatite belong to the same structural type based on their similar diffraction patterns. Mitridatite, widespread in occurrence, was considered to be the Fe^{3+} analogue of robertsite. Moore also noted the presence of small quantities of the robertsite in the nearby Linwood, White Elephant, and Gap Lode pegmatites. Robertsite has also been identified in altered pegmatites from southwest Africa (Keller, 1974) and in the Hagendorf pegmatite of Oberpfalz, Germany (Mücke, 1978). Nriagu (1984) revised the basic formula to $\text{Ca}_6(\text{H}_2\text{O})_6\text{Mn}_9\text{O}_6(\text{PO}_4)_9 \cdot 3\text{H}_2\text{O}$. While robertsite has been previously described in association with altered phosphatic pegmatites, to the authors' knowledge it has never been described in association with sedimentary phosphate ores nor has a chemical analysis been published.

General ore description

Robertsite occurs in the Khoa Rang Kai phosphate deposit in the Lamphun area, northwestern Thailand, near Chiang Mai. This phosphate deposit is classified as a guano type resulting from the phosphatization of pre-existing Permian lime-

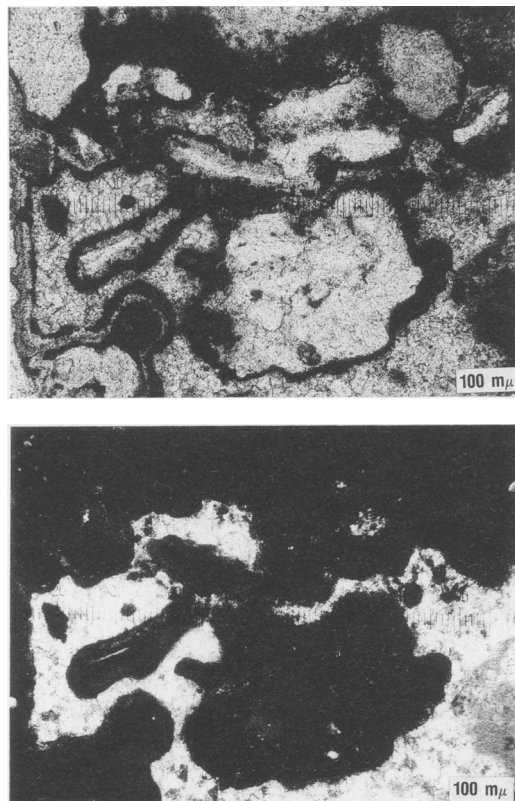
stones. Apparently the phosphatizing processes of the majority of the deposits in this area are cave-related, and the phosphatizing constituents were derived from bat guano (Sheldon, 1984). Phosphate ore occurs as blocks of altered limestone ranging in thickness from 9 to 24 metres. Ore textures vary from well-indurated phosphatized limestone to nodules, concretions, and highly weathered disaggregated material (Suwanich, 1980). The exact age of the phosphatization is unknown.

The material studied was a run-of-mine sample consisting of rock fragments varying in size from < 1 cm to 10 cm. A massive, porous, dark reddish-gray (10R 3/1)* to brown (7YR S/2) lithology was the most common rock type. A second lithology was characterized by a laminar texture. Layers of light gray (7YR S/10) and brown (7YR S/2) apatite, 1–3 mm in thickness, constituted the bulk of this textural type.

Robertsite occurs in many different modes in the sample (Figs. 1 and 2). Submicron size crystals may be disseminated within apatite. Most commonly, the mineral occurs as pore fillings and as distinct bands. These bands both coat phosphate particles and occur between bands of apatite. Multiple banding of the robertsite and apatite indicates a number of episodes of mineral deposition and changing environmental conditions.

Apatite constitutes approximately 70 wt. % of the

* Munsell Soil Color Charts, Munsell Corp., Baltimore, Maryland.



FIGS. 1 and 2. FIG. 1 (*top*). Plane-polarized light photomicrograph; multiple generations of robersite (dark mineral) coating and disseminated within apatite particles with pore-filling sparry calcite. FIG. 2 (*bottom*). Crossed nicols photomicrograph of Fig. 1.

bulk sample. X-ray diffraction (XRD) measurements and calculations of the unit-cell dimensions of the apatite ($a = 9.413 \pm 0.001 \text{ \AA}$ and $c = 6.889 \pm 0.001 \text{ \AA}$) indicate that the apatite is a carbonate-hydroxyapatite variety. Chemical analyses indicate that, although the apatite is fluorine deficient (1.1 wt. % F^{1-} , 34.3 wt. % P_2O_5 , bulk sample), it contains more than the minimum 1 wt. % fluorine level to be considered a carbonate fluorapatite (francolite) (Sandell *et al.*, 1939). Such fluorine-deficient carbonate apatites are commonly associated with guano-related phosphate deposits.

Calcite and dolomite collectively constitute approximately 11 wt. % of the bulk sample, and robersite forms approximately 10 wt. %. There are minor amounts of quartz (*c.* 2 wt. %), smectite and illite. Although no distinct XRD peaks indicating iron oxides or hydroxides were noted, the presence of goethite is suspected. Whitlockite could not be

identified microscopically, but its presence is suspected because of a minor diffraction peak.

Robersite

In order to confirm the presence of robersite and evaluate this component of the ore by chemical and XRD means, attempts were made to separate the mineral from the apatite, carbonate, and silicate components. The sample was lightly ground to minus 50-mesh (Tyler) in a mortar and pestle; then it was digested with warm 10% hydrochloric acid for 1 hour to remove carbonates and the apatite. Insoluble material accounted for approximately 18 wt. % of the original sample. The XRD and chemical analyses indicated that the concentrate contained approximately 85 wt. % robersite and 15 wt. % quartz and clays. Heavy-liquid separation was attempted and was successful in removing only a portion of the silica.

The XRD data (Table 1), gathered on the sample before further extraction, are in substantial agreement with the robersite data of Moore (1974). Interferences from quartz, illite, and smectite have been subtracted from the pattern. Because of the very fine particle size of the robersite ($< 3 \mu\text{m}$), extensive optical microscopy analysis was impossible. The robersite was highly birefringent and dark reddish brown (2.5YR 2 S/4) in colour. The average index of refraction ($N_D^{25} = 1.780$) is in agreement with the observations of Moore (1974).

In order to obtain a chemical analysis of the robersite in the mineral concentrate, the HCl-insoluble fraction was treated with hydrogen peroxide and digested with perchloric acid. The acid-insoluble residue of this treatment was a mixture of clays and quartz. The chemical analysis of the perchloric acid extract of the concentrate (Table 2) compares favourably with calculated values based on the revised robersite formula of Nriagu (1984). The combined water analysis was calculated from data obtained from the mineral concentrate. All of the evidence collected (chemical, optical, and XRD) indicates that the mineral is robersite.

Although the analyses of Fe_2O_3 (1.1 wt. %) and Al_2O_3 (2.4 wt. %) may indicate some contamination by goethite and/or aluminium compounds, it is possible that a portion of these elements may be substituting in the robersite structure. This speculation cannot be verified because there are no published analyses of robersite (Nriagu, 1984) and the diffraction patterns of robersite and mitridatite are very similar. The low CaO analysis and subsequent low ionic formula calculation suggests other divalent cations are substituting for Ca^{2+} .

Table 1. *Robertsite X-Ray Powder Data*^a

d (obs)	Moore (1974)			Thailand Sample	
	I/I ₀ ^b	d (calc)	hKL ^c	d (obs)	I/I ₀ ^d
8.63	10	8.63	200	8.681	100
5.61	5	5.63	002	5.635	35
4.32	2	4.32	400	4.335	10
4.14	1	4.13	331	-	-
3.48	2	3.52	431	3.478	2
3.27	4	3.25	213	3.287	9
3.17	2	3.20	160	3.179	12
3.03	1	3.04	260	3.084	3
2.937	1	2.952	233	2.945	2
2.876	3	2.877	600	2.882	30
2.807	1	2.809	004	2.804	7
2.749	6	2.758	204	2.752	53
2.590	4	2.504	362	2.596	30
2.465	2	2.459	602	2.471	8
2.223	2	2.249	740	2.222	2
2.160	3	2.158	800	2.163	18
2.112	2				
2.048	2				
1.899	3			1.877	3
1.745	2				
1.623	5			1.612	11
1.585	1			1.585	2
1.542	3			1.543	
1.464	1			1.454	11
1.412	2				
1.375	2				

a. Cu K α radiation with a graphite monochromometer.

b. Based on a scale of 1 to 10.

c. Joint Committee on Powder Diffraction Standards (JCPDS) Mineral Powder Diffraction File (1980).

d. Based on a scale of 1 to 100.

Table 2. *Robertsite Chemical Composition*

	Theoretical ^a Composition (wt.%)	Thailand Sample	Thailand Sample ^b Number of Ions in Formula	
P ₂ O ₅	34.53	33.28	P	9.14
Mn ₂ O ₃	38.45	36.31	Mn ³⁺	8.97
CaO	18.22	16.08	Ca	5.59
Fe ₂ O ₃		1.10		
Al ₂ O ₃		2.41		
K ₂ O		0.22		
SiO ₂		0.01		
TiO ₂		0.25		
BaO		0.08		
SrO		0.04		
H ₂ O	8.78			
H ₂ O ⁺		9.85 ^c	OH ⁻	21.32
	100.00	99.63		

a. Based on Ca₆(H₂O)₆Mn³⁺₉O₆(PO₄)₉·3H₂O (Nriagu, 1984).

b. Based on analyses of CaO, Mn₂O₃, P₂O₅, and H₂O⁺.

c. Calculated from loss-on-ignition of mineral concentrate.

Hopefully, future work and more chemical data for robertsite will clarify this point.

Summary

Although robertsite has been previously reported as an alteration product of pegmatitic deposits, this study indicates that the mineral may be a constituent of guano-derived phosphate ores. Petrologists are advised to suspect the presence of robertsite in phosphatized limestones exhibiting anomalous concentrations of manganese. Where the presence of manganese has been attributed only to such minerals and mineraloids as pyrolusite, psilomelane, wad, and other Mn-bearing phosphates, robertsite should be added to the list of potential Mn-bearing phases.

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