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MACEDONITE-LEAD TITANATE: A NEW MINERAL

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ABSTRACT

Macedonite, $PbTiO_3$, occurs as tiny grains and crystals in the amazonite quartz syenite veins in Crni Kamen near Prilep, Macedonia, Yugoslavia. It is tetragonal: *a* 3.889±0.024 Å; *c* 4.209±0.036 Å. The strongest X-ray powder diffraction lines are (Å): 2.843 (10), 2.728 (8), 2.284 (7), 1.954 (7), and 1.603 (9). Specific gravity is 7.82±0.06. Microhardness is 507±30 kg/mm^2 which corresponds to 5.5 on the Moh scale. Macedonite is soluble in warm HCl, HNO_3, and H_2SO_4. Chemical analysis: PbO 70.55%, Bi_2O_3 2.20%, TiO_2 25.07%, and FeO 2.69%. Macedonite is geneticaly related to the differentiation of an alkali syenitic magma and has been formed in the pegmatitic-pneumatolytic stage as an accessory mineral.

INTRODUCTION

Macedonite has been discovered as an accessory mineral in the amazonite-rich, quartz-syenite veins in Crni Kamen near Prilep, Macedonia, Yugoslavia on the western slopes of Selecka Mountain (Pelagonia province). A natural lead titanate had not been reported previously. On the other hand, $PbTiO_3$ has been produced synthetically, and, synthesized with $BaTiO_3$, has been used as a piezoelectric material.

The macedonite was discovered during detailed study of the mineral composition of quartz-syenite veins, and a concentrate of about 150 mg of pure mineral speared for the mineralogical and chemical investigations. A part of this concentrate has been preserved in the collection of the Institute for Nuclear Raw Materials in Belgrade, Yugoslavia. Determination of macedonite was a difficult task, particularly because of the easy misindentification as perovskite or other simple and complex titanium oxides.

It was named for the province of Macedonia, where the mineral was discovered. The name and mineral were approved by the commission on New Minerals, IMA.

OCCURRENCE

Crni Kamen is located on the western slopes of Selecka Mountain which is part of the Pelagonide tectonic unit within the Dinaric orogenic belt (Pavlović *et al.*, 1963). The area is composed of gneisses with mica schists and some amphibolites, that are intruded by granitic rocks in the form of small individual bodies. It is assumed that these bodies are interconnected in depth, representing parts of a single large granitic plutonic mass of the Pelagonides.

TABLE 1

granitic rocks	epidote sequence	epidote-sphene epidote-garnet type
	garnet sequence	garnet-epidote type garnet-sphene type

The granitic rocks are petrochemically highly differentiated, from leucogranite, through trondhjemite and granodiorite to quartz diorite.

The granites are represented by types containing biotite and two micas, but the muscovite-bearing types are less frequent. The granitic rocks may be divided into a number of types according to the most common accessory minerals (Markov, 1966). See Table 1.

The granitic magma has assimilated an appreciable amount of crystalline country-rocks and also has produced an intensive granitization and other types of alkali metasomatism.

The metamorphic rocks are cut by a large number of aplitic, pegmatitic quartz-feldspar, and quartz veins.

Macedonite was discovered at Crni Kamen where the rocks exposed are: alkali syenites, alkali quartz-syenite, gneisses, and pyroxene-amphibole schists (Protić *et al.*, 1959).

The alkali syenites occur as coarse- and fine-grained varieties. The coarse-grained variety is composed mainly of microcline, less aegirine-augite and alkaline amphibole, with very little quartz, albite, and muscovite. The fine-grained syenites are of similar mineralogical composition, but they have somewhat larger quantities of microcline and quartz.

Alkali quartz-syenite gnesiss has almost the same mineralogical composition as the alkali syenite, and the only difference is that the former contains a somewhat larger amount of microcline (mainly amazonite) and quartz, while the amount of femic minerals decreases. The same rock also is characterized by clearly visible orientation of the mineral constituents, *i.e.*, by a gneiss-type structure.

Pyroxene-amphibole schists are cut by a large number of alkali-quartz syenite veins, forming in this way injection-type gneisses. Macedonite occurs in some of these veins. The host rock is an amazonite quartz-syenite vein with essentially gneiss-type structure, locally showing pegmatoid character.

PROPERTIES OF MACEDONITE

Macedonite occurs in crystalline grains of irregular shape. The following forms were observed on the rare idiomorphic crystals: (100), (001),

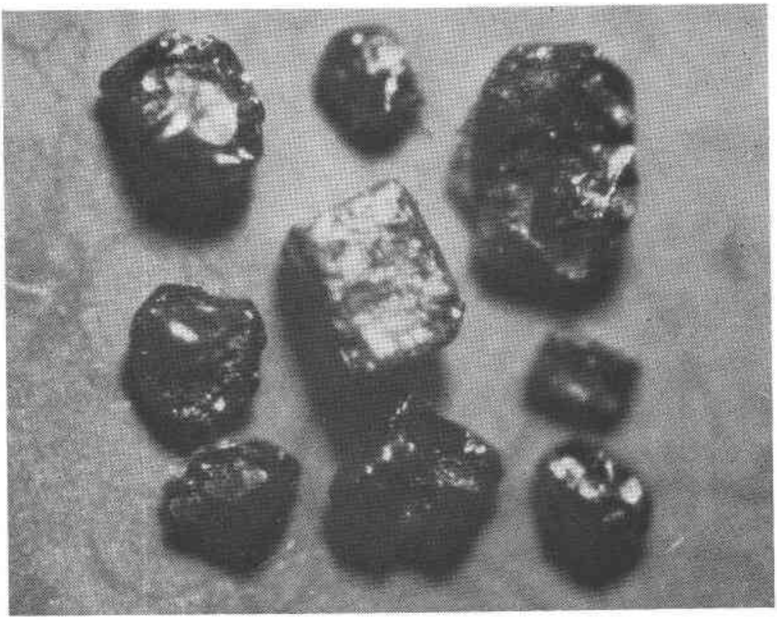

FIG. 1. Crystals of macedonite (100×).

(110), (101), and (111), the most common being crystals of prismatic shape. The grain-size is highly variable, ranging from a few tenths of a micron up to 0.2 mm; the most common sizes range from 80 to 100 μm.

The macedonite is opaque, except in extremely thin sections. Its reflected color is black, with a very weak brownish tint, and glassy lustre. Cleavage was not observed. The mineral is brown-yellow in thin section with a greenish tint. In reflected light it is grayish-white, similar to

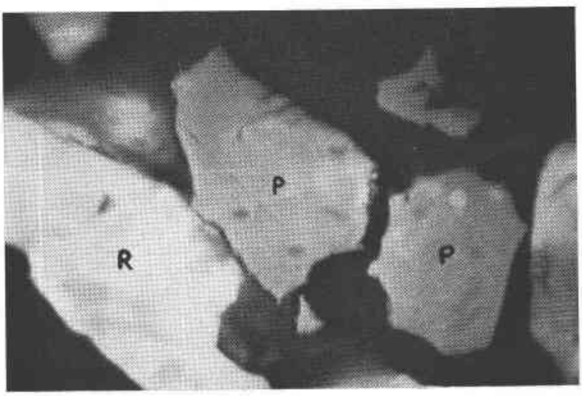

FIG. 2. Photomicrograph of macedonite (P) and rutile (R) (800×).

TABLE 2. X-RAY POWDER DATA OF MACEDONITE AND OF SYNTHETIC $PbTiO_3$

hkl	Macedonite		Synthetic[a] $PbTiO_3$	
	I^b	dÅ	I^c	dÅ
001	4	4.161	26	4.150
100	6	3.836	49	3.899
101	10	2.843	100	2.842
110	8	2.728	52	2.758
111	7	2.284	40	2.297
002	2d	2.104	15	3.076
200	7	1.954	32	1.950
102	2d	1.838	13	1.833
201	3	1.759	10	1.765
210	3	1.732	11	1.744
112	3d	1.669	19	1.658
211	9	1.603	42	1.607
202	4d	1.425	13	1.421
003	—	—	3	1.384
220	5	1.370	9	1.378
212	3d	1.334	7	1.335
221	2d	1.308	3	1.308
103	—	—	5	1.304
300	—	—	11	1.300
301	—	—	10	1.240
113	—	—	3	1.237
310	5d	1.230	7	1.233
311	4	1.177	10	1.181
222	3	1.147	5	1.148
203	—	—	3	1.128
302	—	—	2	1.101
213	—	—	7	1.084
320	—	—	3	1.081
312	4	1.060	9	1.060
321	5	1.044	8	1.046
004	—	—	1	1.038
104	—	—	2	1.003
223	—	—	3	0.976
114	—	—	1	0.971
322	—	—	3	0.959
401	—	—	2	0.949
303	—	—	2	0.948
410	—	—	4	0.945
411	4	0.920	6	0.922
314	4	0.804	—	—
	a—3.889±0.024 Å c—4.209±0.036 Å		a—3.899 Å c—4.1532 Å	

[a] xRDF Card 6-0452.
[b] Intensity 1–10 (estimated visually)
[c] Intensity 1–100.

rutile, but of lower reflectivity. The intensity of the reflected light is highly reduced in immersion oil. Internal yellow-brown to dark-brown-greenish reflections are always present, especially in immersion. Birefringence was not observed. In reflected light its anisotropy is very weak, so that macedonite behaves as an almost isotropic mineral.

Etch reaction on the polished surface using standard etch reagents were negative (HCl, HNO_3, H_2SO_4, KOH, KCN, etc.).

The mineral polishes well. The hardness is 507 ± 30 kg/mm^2 which corresponds to 5.5 on the Moh scale. The hardness is highly variable, but the microhardness along different crystallographic directions have not been measured because of the small size of crystals.

The measured specific gravity is 7.82; specific gravity calculated from X-ray data, assuming $PbTiO_3$, is 8.09.

The X-ray investigations have been performed by the powder-diffraction method. The results of X-ray powder diffraction studies are presented in Table 2. Macedonite is in the structural group of perovskite.

The mineral was studied by infrared spectrophotometry and the diagram is given in Figure 3 (analyst: G. Martinović). The part of the IR spectrum of macedonite over 750 cm^{-1} is not very characteristic but similar to that of several titanium minerals (perovskite, ilmenite, rutile, and brookite). Absorption maxima of macedonite are found at: 750, 560 and 400 cm^{-1} (the last is not determined with sufficient accuracy). Very similar spectra are known for perovskite (720, 570 and 450 cm^{-1}), and partially for ilmenite (690, 545, and 450 cm^{-1}).

Chemical properties. Macedonite is soluble in hot HCl, HNO_3, and H_2SO_4.

According to the chemical analysis summarized in Table 3, macedonite corresponds to the ABX_3 type of compound, *i.e.*, $PbTiO_3$.

Bismuth probably replaces lead, but the position of iron is not clear, so that the explanation of the nature of these impurities will need further crystallo-chemical investigation.

The trace-elements have been analyzed by a semiquantitative spectrochemical method and the results are given in Table 4. The trace-element content of pelagonite is similar to that of other accessory minerals from the same rock, particularly of rutile, and may be explained by the geochemical conditions prevailing during the formation of the alkaline syenite.

Paragenesis

Macedonite is found in a very interesting mineral paragenesis. Crni Kamen area is characterized by numerous pronounced radioactive and nonradioactive alkali quartz-syenite veins which intrude the pyroxene-amphibole schists. However, macedonite was found only in nonradioactive amazonite-quartz syenite veins. The above mentioned vein rocks

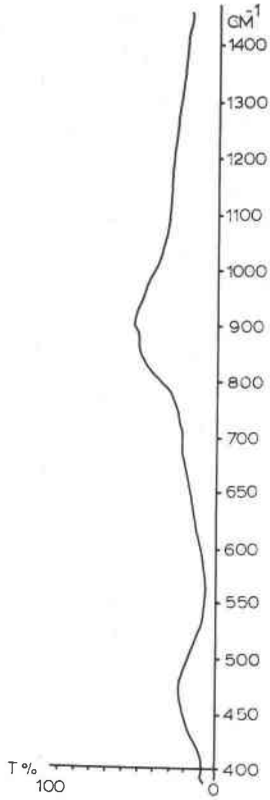

FIG. 3. Infrared spectrum of macedonite.

can be divided roughly into two groups, the first one showing more or less intense radioactivity and the second one showing very slight radioactivity. They are differentiated in respect to their essential mineral and geochemical characteristics as well.

TABLE 3. CHEMICAL ANALYSES OF MACEDONITE (ANALYST, D. NIKOLIĆ)

PbO	70.55%
Bi_2O_3	2.20
TiO_2	25.07
FeO	2.69
	100.51

The vein rocks of high radioactivity are composed of microcline, quartz, aegirine-augite, alkali amphibole, biotite, and muscovite as main constituents. Accessory minerals are: radioactive zircon, rutile, and sphene, which are all anomalously high in thorium and low in

TABLE 4. TRACE-ELEMENT CONTENT OF MACEDONITE (ANALYST M. ARSENIJEVIĆ)

Element	Concentration, ppm
Sn	65
Mn	50
Ga	10
Nb	1400
V	20
Cu	60
Ag	1
Ni	18
Co	6
Zr	2400
Cr	1000
La	2000
Ba	200
Sr	1500
Mg	550

uranium; and davidite (Vukasović *et al.* 1961) and brannerite (Vukasović *et al.* 1963) which contain uranium in appreciable amounts. The other accessory minerals are apatite, epidote, garnet, monazite, and scheelite.

The vein rocks of low radioactivity are characterized by an abundance of amazonite as well as by the presence of macedonite as an accessory constitutent. This rock represents a vein type of amazonite-quartz syenite and its mineral composition is given in Table 5.

The quantity of accessory minerals, particularly rutile, macedonite, zircon, and barite, is extremely variable within a single vein, even over

TABLE 5. MINERAL COMPOSITION OF AMAZONITE-QUARTZ SYENITE WITH MACEDONITE

Mineral	W %
Microcline (amazonite)	64.8
Albite	<0.1
Quartz	20.7
Aegirine-augite	12.8
Riebekite, arfvedsonite	1.0
Rutile	0.3
Macedonite	0.2
Zircon	0.1
Apatite	<0.1
Allarite	<0.1
Sphene	<0.1
Barite	<0.1
Epidote	<0.1
Garnet	traces
Pyrite	traces
Chalcopyrite (with covellite and malachite)	

very short distances. Macedonite and rutile are the main accessory minerals. They are mostly concentrated around the contacts of feldspars with pyroxene (aegirine-augite) and amphibole (mainly arfvedsonite and sometimes riebeckite). Locally, rutile and macedonite intergrow, as shown in Figure 2. Macedonite also occurs as inclusions in the alkali amphiboles and pyroxene, and very rarely in the feldspars. Among the accessory minerals, the most frequent is zircon, followed by apatite, barite and sphene.

Macedonite is genetically closely related with the formation of syenite. During the intrusion of the syenite magma, an intensive assimilation of the country rocks, particularly amphibolites, took place. The vein-type syenitic rocks were formed as the final result of intrusive processes. Based on mineralogical characteristics it was possible to identify two phases of syenitic vein rocks. The first phase, which was formed at elevated temperatures, is characterized by the presence of the radioactive minerals davidite, brannerite, monazite, allanite, and radioactive rutile, zircon, and sphene. The second phase, which corresponds to the aplito-pegmatitic-pneumatolytic mode of formation is characterized by the presence of large concentrations of feldspars (amazonite) and the development of macedonite.

The macedonite is genetically related to the differentiation of an alkali syenitic magma, and was formed in the pegmatitic-pneumatolytic stage, as an accessory mineral.

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REFERENCES

ARSENIJEVIĆ, M. (1965) Metalometric study of the uranium and thorium dispersion haloes (Crni Kamen). *Bull. Mus. Hist. Natur. Beograd, Ser. A*, 19/20.

MARKOV, C. (1966) *Mineralogical Characteristics of Granites from South Pelagonia Observed through their Accessory Minerals.* M. Sci. Dipl., Faculty of Mining and Geology, Beograd. [in Serbo-Croatian].

MEGAW, HELEN D. (1946) Crystal structure of double oxides of the perovskite type. *Proc. Phys. Soc. London*, **58**, 133–152.

PAVLOVIĆ, S., B. SIKOŠEK, AND M. RISTIĆ (1963) Geological, tectonic, and petrochemical study of some granites from Yugoslavia and their metallogeny. *Proc. II, Yugoslav-Polish Meeting Methods Uranium Prospecting, Herceg Novi.* [in Serbo-Croatian].

PROTIĆ, M., AND S. CVETIĆ (1959) Alkali syenites and related rocks at Crni Kamen, south of Prilep. *Ann. Geol. Peninsule Balkan.* **26**.

VUKASOVIĆ, M., AND A. DAMJANOVIĆ (1961) Davidite, a radioactive mineral from Crni Kamen in Macedonia. *Bull. Inst. Nucl. Raw Mater. Beograd*, **1**, [in Serbo-Croatian].

VUKASOVIĆ, M., AND N. MIHAJLOVIĆ–VLAJIĆ (1963) Branerite from Topolcane near Prilep. *Bull. Inst. Nucl. Raw Mater. Beograd*, **2**, [in Serbo-Croatian].

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