



More *x*-ray and phase studies will be required to obtain a better understanding of aenigmatite, a term that covers a wide variation in chemical composition. Such studies may show that new, accurate chemical analyses of very carefully selected samples are demanded. Perhaps when the remaining enigmatical characteristics of aenigmatite are cleared up the name aenigmatite will no longer be applicable.

#### ACKNOWLEDGMENTS

Michael Fleischer called my attention to the work of Bussen and Dudkin in which are recorded three new analyses of aenigmatites; they are illustrative of the wide range in their composition. I am also indebted to him for a stimulating discussion of the chemical aspects of the aenigmatite problem. I am deeply indebted to F. Chayes for critically reviewing the manuscript.

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#### EFFECTS OF MAGNESIUM ON THE FORMATION OF APATITE

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#### INTRODUCTION

Apatite, approximately  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  or the fluorine analog, is widely distributed in nature. It occurs as hard parts of organisms and in igneous, metamorphic, and sedimentary rocks. Magnesium likewise is common in

nature. Although the magnesium ion is somewhat smaller than that of calcium, its chemical behavior is quite similar and, therefore, magnesium might be expected to have a marked effect on the formation of apatite. A magnesium-apatite is unknown; however, chemical analysis of apatite commonly indicates the presence of some magnesium.

Phosphorite, of which apatite is the principal mineral, is commonly associated with limestone and dolomite. Phosphorites may be formed by (1) precipitation from waters, (2) interaction of pre-existing carbonate minerals with phosphate-bearing waters, (3) accumulation of phosphatic tests, or (4) some combination of these processes. Simpson (1964) and Ames (1959) have demonstrated the feasibility of the interaction mechanism for phosphatization of calcite. The occurrence of phosphatized fragments of shells as reported by Mansfield (1927) proves that interaction of calcium carbonate and solution has some role in the formation of phosphorite. Even though dolomite is commonly associated with limestone and although biogenic calcite may contain much magnesium in solid solution, interaction of calcium-magnesium carbonates and alkali phosphate solutions over long periods of time has not been previously reported.

#### EXPERIMENTS

Reactions were studied using dolomite from Cockeysville, Maryland, crushed to  $-100$  and  $+200$  mesh, and low alkali calcium carbonate (calcite) of reagent grade. Finely powdered calcite, dolomite, or mixtures of calcite and dolomite were put in a 0.3 molar sodium phosphate solution adjusted with sodium hydroxide to a pH of about 8.0. The mixture of solids and solution was agitated intermittently for ten months; and because of depletion of phosphate ions in the solution by reaction, the solution was frequently replaced. Table 1 gives the results of the experiments. Optical and  $x$ -ray examination show that dolomite failed to react to form a new product in the solution even after ten months; however, the calcite reacted completely to form apatite. Mixtures of dolomite and calcite reacted with the solution to form octacalcium phosphate (OCP) possibly with apatite. After the ten months, dolomite and calcite were absent in both samples which originally contained the minerals. Thus, under the conditions of the experiment, dolomite reacts to form a new product only in the presence of calcite; and the product of mixtures of calcite and dolomite is OCP in contrast to the product of calcite being apatite.

The experiment was repeated using the same solid materials but substituting a solution of potassium phosphate for the solution of sodium phosphate. In this experiment different products were formed (Table 1). Calcite and mixtures of calcite and dolomite formed apatite. Dolomite in

part reacted to form a potassium magnesium phosphate compound. Properties of this compound "A" are given in Table 2.

From these experiments it can be concluded that the formation of OCP is enhanced by the presence of sodium ions in the solution and calcium ions in excess of those of magnesium.

TABLE 1. REACTION OF CARBONATE MINERALS IN ALKALI PHOSPHATE SOLUTIONS

Initial Carbonate Minerals	Solution	Final pH of Solution	Product
(Reaction Time of 10 Months)			
Dolo	0.3 M Na-Phosphate	8.22	Dolo
1 Dolo+1 Ct	0.3 M Na-Phosphate	8.25	OCP+Ap(?)
1 Dolo+3 Ct	0.3 M Na-Phosphate	8.00	OCP+Ap(?)
Ct	0.3 M Na-Phosphate	8.05	Ap
Dolo	0.3 M K-Phosphate	8.92	Dolo+"A"
1 Dolo+1 Ct	0.3 M K-Phosphate	8.30	Ap
1 Dolo+3 Ct	0.3 M K-Phosphate	8.25	Ap
Ct	0.3 M K-Phosphate	8.30	Ap
(Reaction Time 1 Month)			
Spicules from <i>Plexaura</i> [(CaCO <sub>3</sub> ) <sub>86</sub> (MgCO <sub>3</sub> ) <sub>14</sub> ]	0.2 M Na-Phosphate	8.70	Ap
[(CaCO <sub>3</sub> ) <sub>86</sub> (MgCO <sub>3</sub> ) <sub>14</sub> ]	0.2 M K-Phosphate	8.84	Ap
OCP = octacalcium phosphate Ap = apatite "A" = compound "A", see Table 2 Ct = calcite Dolo = dolomite			

Magnesium is common in solid solution in biogenic calcite. To determine the effect of such solid solution on phosphatization processes, spicules from the gorgonian coral, *Plexaura*, were exposed to alkali phosphate solutions for one month. These spicules contain about 14 per cent MgCO<sub>3</sub>. Apatite formed from the spicules after one month in a 0.2 molar potassium phosphate solution at a pH of 8.84 and in a sodium phosphate solution at a pH of 8.70. Magnesium phosphate compounds and OCP

were not found. The absence of octacalcium phosphate may be a result of the high pH.

Sodium phosphate solution (0.2 M) containing 0.001 M magnesium ions react with calcite forming apatite if the pH is greater than 8.21. With solutions more acid than 7.61, OCP, brushite or monetite form. Euhedral crystals of brushite are forming after or probably at the expense of OCP. If 0.001 M chloride ions are added to the magnesium-bearing

TABLE 2. PROPERTIES OF COMPOUND "A"

X-ray		Optical
dÅ	I	Biaxial (-)
5.54	100	2V~50°
4.22	40	$\alpha = 1.484 \pm 0.002$
4.11	65	$\gamma = 1.488 \pm 0.002$
3.52	4	
3.43	4	
3.24	40	
3.16	11	
2.96	20	
2.77	72	
2.68	40	
2.64	8	
2.52	20	
2.37	8	
2.33	10	
2.24	4	
1.99	12	
1.96	4	
1.95	8	
1.93	8	

  

Thermal	
Temperature Range	Weight Loss
50°-135° C.	33%
135°-600° C.	10%

sodium phosphate solution, apatite will form at a pH as low as 7.09, and the addition of 0.001 M fluoride ions results in the formation of apatite of pH values as low as 6.51. Unfortunately, x-ray diffraction patterns of such low temperature apatite are diffuse and only an approximate  $c$  can be obtained from the 002 reflection. Values of  $c$  measured were from 6.84 to 6.87 Å.

The presence of fluoride and chloride ions permits the formation and persistence of apatite under more acid conditions than is possible in their absence. Furthermore, the effect is greater with fluoride than the chloride ions. The benefits of fluoridation in regard to dental health may, in part, be a result of this effect.

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## GREIGITE FROM THE LOJANE CHROMIUM DEPOSIT, MACEDONIA

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## INTRODUCTION

In 1956, during a study of the paragenesis of the sulfide mineralization in the Lojane ore deposit, the author discovered an unknown, highly magnetic, pink colored mineral which had formed during the same paragenetic stage as the stibnite. Although very fine-grained and intimately intergrown with stibnite, it was possible to concentrate a small fraction for mineralogical studies by magnetic means. A quantitative chemical analysis on the two hundred milligram quantity recovered was inconclusive; the sum of all analyzed components was only 95.04%.

From the data obtained the author could not identify the phase and it was believed the compound was a new mineral, provisionally called "mineral X" (Radusinovic, 1956).

In the recent papers by Polushkin and Sidorenko (1963) and by Skinner, Erd and Grimaldi (1964), a mineral has been described with general features identical to those of "mineral X." Polushkin and Sidorenko named the mineral melnikovite, Skinner *et al.* named it greigite. It is the opinion of the author that greigite should be considered as the correct name, because it represents an entirely new mineral species ( $\text{Fe}_3\text{S}_4$ ), while the name melnikovite was already accepted for a morphological variety of  $\text{FeS}_2$  (Doss, 1912 a, b).

According to the data published to date, greigite formed under typically sedimentary conditions. In Lojane, however, greigite is found in hydrothermal veins and in same paragenesis as the As and Sb sulfides.

## GEOLOGY OF THE LOJANE ORE DEPOSIT.

The Lojane chromium deposit is located about 40 km north of Skoplje, Macedonia, in southeast Yugoslavia. Mineral veins containing the sulfides of As and Sb, together with Ni, Co and U, were discovered during exploitation of the chromium deposit.