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CACOXENITE AND BERAUNITE FROM FLORIDA

FRANK N. BLANCHARD AND STEPHEN A. DENAHAN,
Department of Geology, University of Florida, Gainesville, Florida.

INTRODUCTION

Weathering of certain phosphatic sediments from Florida has resulted in the formation of secondary phosphate minerals including meta-strengite (Hill, *et al.*, 1950), wavellite (Bergendahl, 1955, and Blanchard and Denahan, 1966b), crandallite (Altschuler, *et al.*, 1956), millisite (Owens, *et al.*, 1960), variscite (Blanchard and Denahan, 1966a) and vivianite (Watson and Gooch, 1918). This article reports the occurrence of beraunite ($\text{Fe}^{2+}\text{Fe}^{3+}_3(\text{PO}_4)_4(\text{OH})_5 \cdot 6\text{H}_2\text{O}$, Fanfani and Zanazzi, 1967) and cacoxenite ($\text{Fe}_3(\text{PO}_4)_3(\text{OH})_3 \cdot 12\text{H}_2\text{O}$, Palache, *et al.*, 1951), which have not previously been reported from Florida.

OCCURRENCE

Cacoxenite and beraunite were found in the overburden of unconsolidated sands of the Pliocene Bone Valley Formation at a phosphate mine, the Palmetto mine of the AGRICO Chemical Company, southwest of Bartow, Polk County, Florida. Both minerals occur in irregularly-shaped nodules which range in color from reddish-brown to pale greenish-blue to mottled combinations of red, brown, yellow, blue, green, and white, and which are composed of quartz grains tightly cemented by various combinations of limonite, beraunite, wavellite, and cacoxenite. Rarely, small crystals of vivianite are found in the nodules. The presence of wavellite indicates that the material in which these nodules were found is in what has been called the aluminum phosphate zone. According to Altschuler, *et al.* (1956), the aluminum phosphate zone contains secondary aluminum phosphate minerals formed during lateritic weathering of carbonate fluorapatite-bearing sediments. The development of aluminum phosphate minerals is typical in certain weathered parts of the Miocene Hawthorn Formation and the Pliocene Bone Valley Formation.

In a hand specimen, cacoxenite generally appears as small yellow specks, which, when magnified, can be seen to consist of spherulites of radiating acicular crystals lining the walls of small cavities, or of microcrystalline cement binding the quartz grains together. In addition to the tiny concentrations of cacoxenite, a magnified view of a freshly broken surface shows an abundance of delicate needle-like crystals of cacoxenite,

some in clusters and some separate, in random orientations and scattered over the broken surface of the nodule. In places the crystals are abundant and have a felted appearance. Recently cacoxenite has been reported from Arkansas (Fisher, 1966); from the description it is remarkably similar (except for the host rock) to what we find in Florida.

Individual crystals of beraunite are not easily seen in a hand specimen, partly because the deep blue color of beraunite does not stand out against the dark background, and partly because of the very small size of the crystals. Crystals of beraunite are generally of bladed habit and commonly are arranged in spherulitic aggregates. Much of the beraunite, however, is cryptocrystalline and imparts either greenish or bluish colors to the rock. These colors are particularly noticeable in nodules which contain little or no limonite.

IDENTIFICATION

Concentration. Beraunite and cacoxenite were first noted as rather abundant constituents of a thin section of a limonitic nodule. The two minerals were pre-concentrated by disaggregation with a magnetic stirrer, and wet sieved at 200 mesh. A cacoxenite concentrate (estimated to be 95 percent pure) was obtained from the -200 mesh fraction by gravity separation in a liquid of 2.50 specific gravity. A concentrate of beraunite containing almost no cacoxenite and no limonite was obtained from a greenish-blue nodule. Using thin sections and concentrates, cacoxenite was positively identified by its optical properties and was checked by X-ray diffraction, whereas beraunite could be identified only by X-ray diffraction, with optical properties and differential thermal analysis as supporting evidence.

Optical Properties.

1. Cacoxenite: Uniaxial positive; $\epsilon = 1.640 \pm .006$ $\omega = 1.575 \pm .003$; elongate parallel with c (length slow); pleochroic: E = yellow, O = colorless. These properties are very similar to those of Palache, *et al.* (1951) and are adequate for positive identification.

2. Beraunite (associated with cacoxenite and limonite):

Biaxial negative, $2V \approx 20^\circ$; $\alpha \approx 1.69 \pm 0.01$, $\beta \approx 1.73 \pm 0.01$, $\gamma \approx 1.73 \pm 0.01$; strong horizontal dispersion and strong axial dispersion ($r > v$); $B_{xo} = b$; length slow; tabular (100), elongate parallel with b (assuming $Y \wedge c$ at a small angle); pleochroic: X = blue, Y = green, Z = pale yellow to colorless; abnormal interference colors: blue, purple, and brown.

These optical properties of beraunite from Florida are not sufficient for identification. They are similar to those of beraunite from the

Palermo mine, N.H., but differ considerably from the usual optical properties of beraunite (Palache, *et al.*, 1951). Furthermore, beraunite from nodules containing little or no limonite varies in its indices, which are less than the lower limits recorded in standard references. Beraunite occurs in varying degrees of oxidation (Fanfani and Zanazzi, 1967), and the observed variations in optical properties may be related to variations in the oxidation state of iron.

X-Ray Analysis. The most concentrated beraunite (both from limonitic nodules and limonite-free nodules) yielded patterns showing quartz lines and all but the few weakest lines for beraunite given on ASTM card #17-472. The most concentrated cacoxenite showed most of the lines listed for cacoxenite on ASTM card #14-331. Quartz, wavellite, and goethite were also identified by X-ray analysis.

Differential Thermal Analysis. DTA curves were obtained from portions of all of the different concentrations of beraunite and cacoxenite, and from these we present curves which we believe show typical DTA reactions for the two minerals (Fig. 1). All analyses were made with a Fisher Differential Thermalizer, using alumina as an inert reference material, silica sample holders, platinel thermocouples, and a heating rate of 10° per minute from room temperature to 1100°C.

Beraunite shows endothermic reactions (dehydration and dehydroxylation) at about 190° (weak) and 330° (strong), an exothermic reaction at about 640° (probably due to crystallization of some form of iron phosphate) and perhaps a second exothermic reaction at 780°C. From a poor DTA pattern of beraunite, Frondel (1949) reported endothermic reactions at 220° and 340°, and an exothermic reaction at 625°C. Considering the possible effects of heating rate, crystal size, variations in degree of oxidation of the iron, and various factors of the experimental setup, the agreement is good.

Cacoxenite shows endothermic reactions at 130° and 265° (resulting from dehydration and dehydroxylation) and an exothermic reaction at 635°C (probably due to crystallization of some form of iron phosphate). Previous experience with other secondary phosphate minerals, especially, vivianite, variscite, and wavellite (Blanchard, in press), indicates that differential thermal analysis of mixtures of cacoxenite and beraunite with either wavellite or vivianite (which do occur in these rocks) or variscite (which could occur in rocks of this type) would yield complex patterns, with overlapping of peaks, difficult to interpret correctly.

THIN-SECTION DESCRIPTION

In thin section most of the cacoxenite appears as acicular crystals about 0.01 mm across and 0.1 mm in length. Generally these are arranged

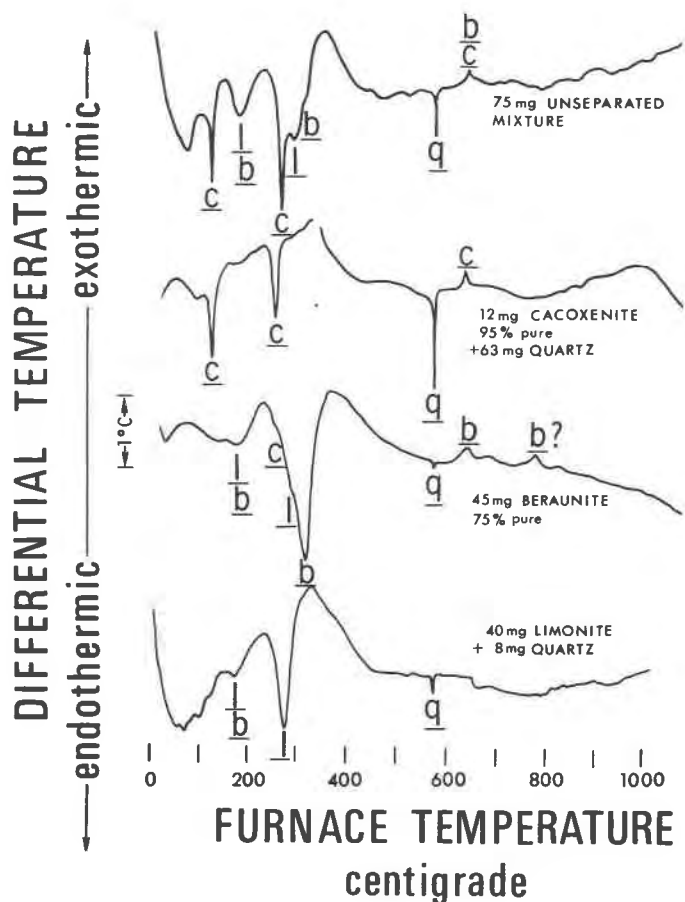


FIG. 1. DTA curves of minerals contained in limonite-cacoxenite-beraunite nodules. Thermal reactions for cacoxenite (c), beraunite (b), limonite (l), and quartz (q).

in radiating groups (Fig. 2) or in randomly oriented masses. Cacoxenite is also found in microcrystalline masses with pinpoint extinction. Beraunite occurs as clusters of roughly rectangular to elongate crystals (Fig. 2), the larger of which are about 0.1 mm square, and in irregular masses some of which are single crystals while others show aggregate extinction.

The limonite-beraunite-cacoxenite nodules consist essentially of quartz grains cemented by limonite, with the remaining spaces filled (partly to completely) with beraunite and cacoxenite. A small part of the beraunite and cacoxenite is found in micro-fractures in limonite grains, indicating that the iron phosphates have formed later than the

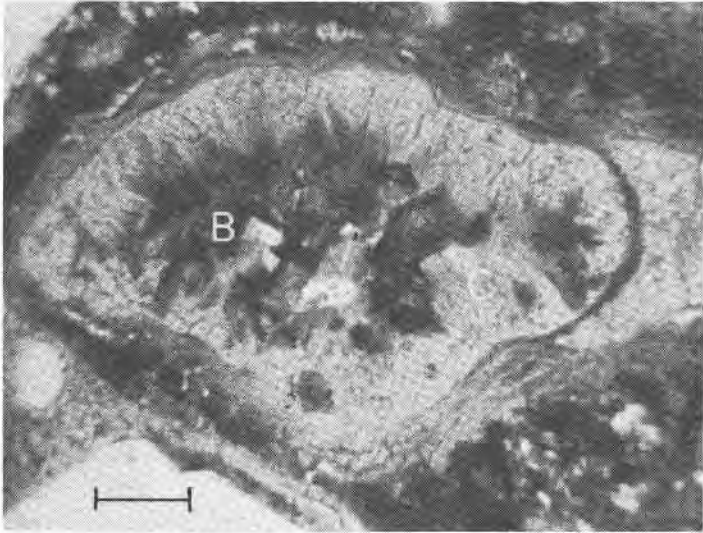


FIG. 2. Photomicrograph of limonite-beraunite-cacoxenite nodule. Beraunite (B) and cacoxenite (C). Ordinary light. Scale is 0.1 mm.

limonite. Most of the beraunite and cacoxenite has a sharp contact with the limonite, however, in a few places limonite and phosphate minerals are intimately mixed and because of this the limonite appears to be birefringent.

ACKNOWLEDGMENTS

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SYNTHESIS OF THE SCANDIUM ANALOGUE OF BERYL:
ERRATA

CLIFFORD FRONDEL AND JUN ITO,¹

*Department of Geological Sciences, Harvard University,
Cambridge, Massachusetts.*

page 945, line 26 in Table, formula should begin Be₃ not Be.

page 943, first line of abstract, comma missing before the formula
Be₃Al₂Si₆O₁₈.

page 943, line 3 from bottom, formula should begin Be₃ not Be.

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¹Present address. Inorganic Materials Division, National Bureau of Standards, Washington, D. C. 20234.