First reported sedimentary occurrence of berlinite (AlPO₄) in phosphate-bearing sediments from Cioclovina Cave, Romania—Comment

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ABSTRACT

In a recent work, Onac and White (2003) reported on berlinite, but also chlorellastadite and churchite, from the Bivouac Room, Cioclovina Cave, Romania. Our analyses of materials collected from this site failed to identify berlinite, chlorellastadite, or churchite. Due to the nature of the samples collected from the bat guano deposit at Cioclovina, many possible sources of confusion can occur. For example, separates from a mixture of taranakite, quartz, and minor illite could give the same analytical results as those reported by Onac and White (2003) for “berlinite”. For this reason, we consider that the occurrence of berlinite at Cioclovina, as well as the occurrence of other exotic species such as chlorellastadite or churchite, is not well enough substantiated and their report must be regarded with caution. Arguments to support this point of view are problems identified with the analytical techniques (EMP, XRD), the failure of the experimental synthesis of berlinite in “dry” conditions at atmospheric pressure, and the geochemical context from Cioclovina.

INTRODUCTION

Onac and White (2003) reported the finding of berlinite, a rare high-temperature aluminum orthophosphate, in the phosphate-bearing sediments from the Cioclovina Cave, Romania (hereafter referred to as Cioclovina). After careful studies of this deposit, and particularly of the Bivouac Room, from which the quoted authors collected the material analyzed, we must disagree with their conclusions. Unfortunately, Onac and White (2003) were unable to provide splits of the material analyzed by them for re-investigation.

Aluminum orthophosphate (AlPO₄) crystallizes in seven polymorphic forms, analogues of high- and low-temperatures forms of SiO₂, of which berlinite is isostructural with α-quartz (Strunz 1941; Muraoka and Kihara 1997), having a trigonal structure with space group P₃₁21. Occurrences of berlinite are sparse and restricted to high-temperature rocks such as felsic meta- or igneous rocks, pegmatites, and hydrothermally altered rocks (Onac and White 2003; Veksler et al. 2003 and references therein).

The occurrence of berlinite in a bat guano deposit is then surprising and the analytical data reported by Onac and White (2003) are subjected to re-consideration. Our experience and previous work on phosphate assemblages from the Cioclovina Cave were used to understand the possibilities of confusion that gave rise to the mention of berlinite, as well as of two other exotic mineral species, churchite and chlorellastadite. The aim of this discussion is to re-evaluate the results reported by Onac and White (2003) in the light of our findings.

Techniques and operating conditions used to acquire the supplementary electron microprobe (EMP), X-ray powder diffraction (XRD), and inductively coupled plasma-atomic emission spectrometry (ICP-AES) data needed for this discussion were essentially the same as described by Marincea et al. (2002), Marincea and Dumitraș (2003), and Dumitraș et al. (2004b). Supplementary XRD studies were carried out using a Philips PW 3710 diffractometer, under the following conditions: Mn-filtered FeKα radiation (λ = 1.9375 Å), 40 kV, 30 mA, step of 0.02°, 1 second per step counting time.

CHEMICAL COMPOSITION

Two different EMP analyses reported by Onac and White (2003) clearly gave results compatible with the presence of berlinite, i.e., Al:P ratios close to the ideal 1:1 for totals very close to 100 wt%.

The first problem arising from the report of Onac and White (2003) is that EMP analysis, and particularly the energy-dispersive method used by them, is not precise enough in the case of fine-grained and intergrown materials. As a rule, minerals from Cioclovina have very small dimensions: up to 7 µm were reported for taranakite (Marincea and Dumitraș 2003), up to 20 µm were mentioned for tinsleyite (Marincea et al. 2002), 1–10 µm were mentioned for brushite (Dumitraș et al. 2004b), etc. Although Onac and White (2003) did not mention the dimensions of the berlinite crystals, we suppose that they were in the range of those reported for the other phosphates. Because of the tiny crystals and the porous nature of the aggregates, microprobe results are expected to be poor; however, Onac and White (2003) reported surprisingly good analyses. In this particular case, the question is how a rastered or a defocused electron beam, which may be ideally used for analyzing phosphates in the bat-guano deposits, which are spongy and notoriously unstable under the electron beam, will avoid analytical interferences. If Onac and White