

## Infrared spectroscopy of ardealite from the “type locality” Cioclovina Uscata Cave, Sureanu Mountains, Romania

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Ardealite, a rather rare hydrated calcium acid phosphate sulfate [ideally  $\text{Ca}_2(\text{HPO}_4)(\text{SO}_4)\cdot 4\text{H}_2\text{O}$ ] was first described and named by Schadler (1932) from the fossil bat-guano deposit in the “dry” Cioclovina Cave (Șureanu Mountains, Romania).

The “dry” Cioclovina Cave, hereafter referred to as Cioclovina, is located in the southern part of the Șureanu Mountains (Southern Carpathians), at about 16 km east-southeast of Hațeg, on Luncanilor Valley. It represents the upper fossil level of the Ponorici - Cioclovina cu Apă karst system (7890 m in length). The cave is developed in Tithonic - Neocomian algal micritic limestones with calcarenite levels.

The infrared absorption spectra obtained for four representative samples of ardealite from Cioclovina, which can be obtained by request from the first author, were recorded in the frequency range between 250 and 4000  $\text{cm}^{-1}$ .

The main remarks concerning the IR spectra are as follows: (1) There are only three bands clearly recognizable in the OH-stretching region between 3000 and 4000  $\text{cm}^{-1}$ , although the structure determination by Sakae *et al.* (1978) show that in synthetic  $\text{Ca}_2(\text{HPO}_4)(\text{SO}_4)\cdot 4\text{H}_2\text{O}$  there are four hydrogen bonds implying the water molecules in the structure. Two of the bands due to the stretching vibrations of molecular water consequently overlap. (2) As well as in brushite, a fifth hydrogen bond seem to be established between OH groups pertaining to the protonated phosphate groups, which could explain the presence, in our spectra, of the shoulder at  $\sim 2960 \text{ cm}^{-1}$ . (3) The different structural positions of the four water molecules in the structure of ardealite explain the pronounced splitting of the bending motions of molecular water: the didentate bending at  $\sim 1718 \text{ cm}^{-1}$  and the broad complex composed of six bands, centered at  $\sim 1640 \text{ cm}^{-1}$ . (4) As shown by Marincea *et al.* (2004). The bands due to the  $(\text{SO}_4)^{2-}$  and  $(\text{HPO}_4)^{2-}$   $\nu_1$  and  $\nu_3$  fundamentals overlap, whereas  $\nu_2$  and  $\nu_4$  are presumably distinct. (5) Even attempted, assumptions in the low-range wavenumber of the spectra are very hypothetical because there is difficult, if not impossible, to ascertain a band in the spectral range between 650 and 250  $\text{cm}^{-1}$ , where lattice modes, phosphate bendings and P-O-H librations largely overlap.

### References:

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Schadler, J. (1932), Zentralblatt für Mineralogie, A, 40–41.