Identification of secondary Cu-phosphates at the libethenite type locality, Ľubietová, Slovakia

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The Ľubietová deposit, which is located in the north-eastern side of Slovenské Stredohorie Mts. and exploited since the Bronze Age, was one of the most important Cu-mines in Europe in the XV and XVI centuries. The deposit is also known for some very rare secondary minerals such as libethenite (type locality) and olivenite. Based only on the chemical composition, many secondary Cu phosphate minerals have been identified in the Ľubietová deposit. Due to their similar chemistry, Cu phosphate minerals are difficult to properly identify in the absence of X-ray diffraction data. It is thus of great interest to find an experimental technique that permits identification of the mineral species without long and costly preparation of the sample. Raman spectroscopy fits these criteria: it is a simple, non-destructive and rapid technique, and necessitates no sample preparation. It has been used successfully by a number of investigators in the study of Cu phosphate minerals (Frost et al., 2002).

The libethenite, pseudomalachite, cornetite, reichenbachite and ludjibaite have been characterized by using the Raman spectroscopy. The tetrahedral PO_4 molecule, which belongs to the T_d point group, is expected to show only four normal modes of vibration (i.e. $A_1 + E + 2F_2$) (Nakamoto, 1997). All four vibrations are Raman-active, whereas only ν_3 and ν_4 are infrared-active, where the trends ν_3 (F_2) > ν_1 (A_1) and ν_2 (E) > ν_4 (F_2) hold for the majority of the compounds. Because of intermolecular interactions, the symmetry of a molecule is generally lower in the crystalline state. Therefore, the vibrations of a molecule in the crystalline state are governed by a new selection rule derived from site symmetry. In the investigated minerals the symmetry of the tetrahedral PO_4 molecule is reduced to C_1 site symmetry. As a result, the selection rules are changed as A_1 into A (IR, R), E into $2A$ (IR, R) and the two F_2 into $6A$ (IR, R).

Raman spectra of libethenite reveals 17 bands, whereas those of pseudomalachite, cornetite, reichenbachite and ludjibaite show 12, 16, 13, and 11 modes of phosphate stretching and bending vibrations, respectively. Characteristic differences in the phosphate stretching and bending vibrations and in the hydroxyl vibrational regions are observed. The most characteristic phosphate stretching and bending vibrations of Cu phosphates occur in the ranges 1140–920 and 650–370 cm^{-1}.

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