LEONITE IN PRE-CARPATHIAN EVAPORITES AND ITS TRANSFORMATION UNDER INCREASED TEMPERATURES

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Leonite is a rare mineral in Precarpathian evaporites. It has been discovered as small admixture in the kainite and polymineral rocks and as fibrous streaks in the clayey saliferous breccia near and among potassium salt deposits.

Leonite is a light yellow, transparent, bitter-tasting mineral with high solubility in water. Its lustre is waxy to vitreous. The mineral is firm in dry air. Under the microscope leonite grains are colourless with low interferential colours (grey). Polysynthetic twins are sometimes visible. Some leonite grains have wavy extinction. The refractive indices of leonite are: $N_x=1.479$; $N_y=1.482$; $N_z=1.487$; $N_z=N_x=0.008$.

On the X-ray powder diffraction patterns of the fibrous leonite from Stebnyk potassium mine the following reflections appear: 6.1; 5.9; 5.25; 4.93; 4.77; 4.21; 3.97; 3.71; 3.52; 3.49; 3.42; 3.30; 3.04; 2.87; 2.75; 2.62; 2.50; 2.46; 2.38; 2.29; 2.21; 2.17 Å. They are similar to the reflections of the standard X-ray powder diffraction pattern (JCPDS \mathbb{N} 21-995).

The chemical composition of the studied leonite is $K_2O=25.30;$ MgO=11.01; SO₃=43.75; $H_2O=19.66;$ Na₂O=0.36; Cl=0.06 (wt%). Chlorine is connected with halite admixture. The crystallochemical formula of leonite (after subtraction of halite) is $K_{1.96}Na_{0.04}Mg_{1.00}[SO_4]_{2.00}$ • 4H₂O. The sodium in the formula may be connected to the presence of blödite (Na₂Mg(SO₄)₂ • 4H₂O), that is in close paragenetic association with leonite. Leonite and blödite are very similar because their refractive indices are close to each other. It is important to note that potassium may also substitute in blödite. Domain isomorphism (inclusions of blödite microlayers in the leonite structure and vice versa) is quite possible between them, too.

Based on the TG data, the loss of structural water of the studied leonite starts around 130°C. A bump on the dehydration curve around 200°C testifies some delay in the process. About 10% of water is lost under that temperature. Dehydration of the mineral is completed at about 240°C. The DTA curve shows two endothermic effects at 167 and 212 °C, respectively.

Experimental investigations were run to study the nature of these thermal reactions. Samples of the fibrous leonite from Stebnyk mine were heated in a regulated oven at temperatures of 100, 150, 200, 250, 300 and 400°C, respectively. Heating time was 30 minutes. Heating products were studied by X-ray powder diffraction.

On the X-ray powder diffraction patterns of leonite heated to 100 and 150°C all the reflections typical of natural leonite were present, but peak intensities became smaller.

At 200°C the crystal structure collapses. The new phase is most probably $K_2Mg[SO_4]_2 \cdot 2H_2O$ (d_{hkl}: 6.7; 5.6; 3.56; 3.36; 3.33; ... Å). That crystalline phase exists only in a narrow temperature range and we do not know it from nature. Some admixtures of langbeinite ($K_2Mg_2(SO_4)_3$; 3.15; 3.91; 2.67; 2.43; ... Å) and arcanite (K_2SO_4 ; 3.36; 3.01; 2.91; 2.87; ... Å) phases appear as well.

Further heating to 250°C leads to the complete loss of the structural water and to the formation of langbeinite (5.7; 4.05; 3.15; 3.01; 2.76; 2.66; 2.41; 2.28; 2.17; ... Å) and arcanite (5.0; 4.18; 3.76; 3.51; 3.39; 3.15; 3.01; 2.91 (100); 2.85; 2.66; 2.51; 2.43; ... Å). These two phases remain stable also at 300 and 400°C.

The transformation process of leonite can be represented with the help of the following equation:

$2K_2Mg[SO_4]_2 \cdot 4H_2O$	=	$K_2Mg_2[SO_4]_3$
733.37		419.99 56.59%
10070		0010770
$K_2[SO_4]$	+	$8H_2O$
174.25		144.13
23.76%		19.65%

Leonite admixtures in potassium salts are primary while its interlayers in the clayey saliferous breccia are secondary formations.

On the basis of these investigations we may assume that during catagenesis, under increasing pressure and temperature, leonite decomposes and transforms through an unstable, intermediate dihydrate phase into langbeinite and arcanite.

Considering also geological time, this process may take place in evaporites at temperatures even lower than the temperatures suggested by the above experiments.