

## **Preliminary investigations of inclusions in some topaz crystals from Volodarsk-Volynski Massif (Western Ukraine)**

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The aim of this paper is the gemmological and microthermometric studies of colour types of topazes (colourless, light pink and blue) from pegmatites of the Volodarsk-Volynski massif (Western Ukraine). These topaz crystals are characterized by the presence of numerous solid and fluid inclusions, mainly of a secondary origin as well as the abundance of micropores. The solid inclusions include mainly albite, tourmaline, Fe-bearing mineral phases and probably organic matter. Among the groups of fluid inclusions, secondary two-phase (liquid-vapour) inclusions distinctly dominate over sparse inclusions of a primary origin. The measured values of temperature homogenization (Th) for selected primary and secondary fluid inclusion assemblages range from 350-380°C and 322°C, respectively. Topaz from Volodarsk-Volynski Massif crystallized during hydrothermal stage in medium temperature conditions. The presence of different secondary and pseudosecondary fluid inclusions together with the traces of necking down processes, point that after the crystallization the topaz was also affected by mechanical, thermal and metasomatic processes.

## **Geodiversity in the Natural Park “Porțile de Fier”: cave mineralogy and mineral deposits**

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The Iron Gates (“Porțile de Fier”) Natural Park is located in South-Western Romania and extends along the Danube Gorges and the affluent valleys. The Park is one of the biggest in Romania, having a surface of 115665.8 hectares and including 18 Natural Reserves. The geodiversity of the Iron Gates Natural Park is given by the distribution of a large variety of magmatic, metamorphic and sedimentary rocks, and particularly of limestones of Jurassic and Cretaceous age, affected by a large number of karst phenomena: caves, swallow-holes, gorges, dolina, lapies, uvalas.

The most representative caves in the Park are those from Gura Ponicovei, Padina Matei and Gaura cu Muscă. All of them contain important deposits of fossil bat guano, with a large diversity of phosphate species, including apatite-(CaOH), taranakite, ardealite, brushite, monetite, francoanellite and leucophosphate. These mineral species generally occurs as crusts of yellow cream or reddish brown color deposited on the cave floor or on some speleothems, or, rarely, as earthy masses of white or white cream color. They were identified using a combination of X-ray powder diffraction, Fourier-transform infrared absorption and electron microscopy.

In the upper basin of Mraconia Valley, a system of galleries opened a tungsten-bearing skarn deposit, which develops at the very contact between crystalline limestones and a porphyric granodiorite of Mesozoic age. The skarn is mainly andraditic, but also contains plagioclase, potassic feldspar, ferroactinolite, magnetite, epidote, apatite, vesuvianite and wollastonite. Four stages of mineralization overprint the primary skarn: (1) a high temperature stage conducted to the deposition of scheelite in the mass of skarn; a parallel deposition of quartz and molybdenite on cracks affecting the granodiorite mass is likely; (2) a second hydrothermal stage conducted to deposition of pyrite, chalcopyrite and calcite on the cracks and of impregnations of pyrite and chalcopyrite in the skarn mass; (3) a third hydrothermal stage conducted to the massive deposits of chalcopyrite, pyrite, sphalerite, galena, scarce pyrrhotite and tertahedrite, as veins and lenses in the skarn mass; (4) a low temperature

hydrothermal stage yields the formation of bornite and covellite on chalcopyrite but also of hematite (specularite) on magnetite.

## **Use of the optical porosimetry for monitoring of deteriorative laboratory tests impacts on natural and agglomerated stone**

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Determination of the resistance against freezing water and salt crystallization are two important standard deteriorative tests of building or decorative stones. These tests partially simulate the influence of weather and polluted environment on rocks and check their durability. Impact of the tests on the pore structure of selected natural and agglomerated stone types have been studied by means of optical porosimetry. The optical porosimetry is a technique of a detailed study of porosity in discontinuous materials. Dried porous samples were fully saturated with blue coloured resin, and after hardening, thin cuts were prepared. Effective pores could be well recognized by the colour in thin cuts under microscope (visual analysis - VAO), but also in pictures taken by a digital camera, that were statistically analysed by the computer (digital analysis - DAO). Visual and digital analyses have been carried out before and after the frost resistance tests (25 cycles of freezing/thawing) and before and after the salt crystallisation tests (15 cycles of immersion into a salt solution and drying). Mineral composition, pore network, and selected physical properties have been studied on both, untreated samples and on samples after mentioned laboratory destructive tests. Changes in rock microstructure predominantly in the pore network due to laboratory weathering tests were identified and illustrated.

Seven types of sandstones from a territory of Slovakia, one type of rhyolite and of travertine, as well as one type of agglomerated stone VASPO simulative various types of natural stones (a Slovak product widely used as exterior and interior cladding stone) have been selected for the research.

Optical porosimetry analyses refer to both realised laboratory tests had destructive effects on studied stones. The degradation due to the salt crystallization was more intensive. The used salt was hydrate phase of sodium sulphate, mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ). According to VAO, micro-cracks were formed, predominantly near the samples surface, pore spaces were enlarged by chemical dissolution of some minerals reacting with the salt solution and existing fractures were opened. These visual signs of the stone decay and weakening were confirmed by changes of physical-mechanical properties after tests. Changes in values of total porosity, water absorption, velocity of ultrasonic pulses and uniaxial compressive strength were recorded.

Statistical parameters determined by DAO, i. e. total optical porosity, size-count parameters and erode-dilate parameters, confirmed changes in the rock pore networks after laboratory deteriorative tests.

In general, presented results of both, visual and digital porosity analyses after laboratory degradation tests demonstrate the applicability of the optical porosimetry method in a research of weathering of natural and agglomerated stones or building stone generally, under experimental or natural conditions, especially in cases when the effective (open) porosity of stones is higher than 5 %. More accentuated visual readable demonstrations require the realization a greater number of cycles of freezing/thawing than have been realized in our research.

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