Uranium and REE enrichment of the phosphatite occurrence at Pécsely (Balaton Highland, Hungary)

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The study area is located in the Balaton Highland, in the southwestern part of the Transdanubian Range, which is composed mostly of Triassic formations. Earlier investigations have revealed radioactive anomaly in the vicinity of Pécsely, which was caused by a uranium-bearing sedimentary phosphatite indication (Kiss & Virágh, 1958). Though according to this study, the host rock of the phosphatite is the Megyehegy Dolomite Formation, according to latest results, it is hosted by the Vászoly Limestone Formation (Budai *et al.*, 1999). This formation is unconformably overlying the Anisian Tagyon Limestone Formation (platform carbonate), and has formed as a basinal carbonate with volcanic tuff intercalations in the Upper Anisian (Budai & Haas, 1997; Budai & Vörös, 2006).

The studied uranium-bearing layer is located in Triassic limestone while epigenetic fluorite veins are found in the older, underlying dolomite. The phosphatite is thought to have formed syngenetically with the limestone, during its deposition. The horizontal extension is large, but the small thickness (0.5-3 cm) of the mineralized layers makes the indication – from the practical point of view – rather unpromising. The main mineral found in the layers is carbonate-fluorapatite, but calcite, rare hematite, pyrite and zircon also occur. The phosphatite layers are finely banded, and contain desiccation cracks on their surfaces (Kiss & Virágh, 1958). By far the genesis of this layer and the veins are not well documented, so this work aims to contribute to our knowledge on the characteristics and origin of the mineralization.

Based on the petrographical observations, the carbonate-fluorapatite is located around the grains of the rock-forming calcite whereas the remaining space is filled by a later generation of calcite cement. Sometimes rock-forming dolomite is brecciated and has a phosphatitic cement. Fluorite found below the phosphatite layers is euhedral (0.1-2 mm) and is of dark purple colour. The fluorite crystals form veins and fill small cavities with minor amounts of calcite. Fluorite can also be found finely dispersed in the matrix of the host rock in which brecciated clasts of the phosphatite layers can be also found. The cathode luminescence pictures of the fluorite shows a fine zonation (Fig. 1.), which may be caused by the radioactivity of the phosphatite layers.

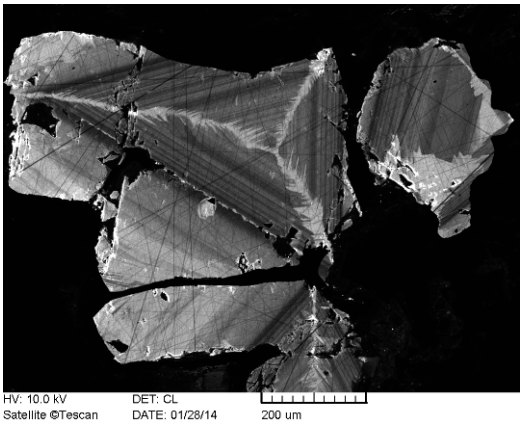

Fig. 1.: Cathode luminescence picture of the fluorite

Quantitative analyses (EPMA) of phosphatite grains showed, that they contain 5.9-7.855 mass% F, 41.621-53.759 mass% CaO, 25.169-36.993 mass% P_2O_5 and 1.013-1.762 mass% SO3.which does not match exactly the theoretical composition of carbonate-fluorapatite. Furthermore 0.013-0.3 mass% UO_2 and 0.029-11.982 mass% FeO, 0.066-0.104 mass% TiO_2, 0.043-0.104 mass% MgO, 0.024-4.625 mass% SiO_2, 0.02-0.028 mass% MnO, 0.04-0.073 mass% La_2O_3, 0.036-0.059 mass% Ce_2O_3, 0.032-0.104 mass% Nb_2O_5, 0.099-0.124 mass% Dy_2O_3, 0.147 mass% Sm_2O_3, 0.032-0.038 mass% Nd_2O_3, 0.051-0.098 mass% Tb_2O_3, 0.027-0.075 mass% Pr_2O_3, 0.181-0.242 mass% Ta_2O_5, 0.031-0.51 mass% Y_2O_3, 0.016-0.177 mass% Gd_2O_3 and 0.045-0.059 mass% Eu_2O_3 occur. The data analysis revealed that, the uranium and sulphur content and the uranium and calcium content correlate positively, while uranium and phosphorus show negative correlation. The fluorite contains 48.155-52.178 mass% F, 38.132-49.135 mass% Ca and 0.009-0.038 mass% P and may contain a small amount of Al (0.01 mass%), Ti (0.038-0.054 mass%), Mg (<0.016 mass%), Mn (0.022 mass%), S(0.014-0.028 mass%), Si (0.012-0.021 mass%), Nb (0.022-0.03 mass%), Dy (0.08 mass%), Sm (0.154 mass%), Gd (0.027 mass%), Eu (0.094 mass%) and U (~0.01 mass%). Elemental mapping prepared of the fluorite revealed, that its REE content is most likely related to submicron sized REE mineral inclusions.

Uranium appears as a trace element in the phosphatite grains and in the fluorite, no uranium minerals were identified. The source of the U was probably an older rock, e.g. the Permian alluvial sandstone, which can be found nearby, and its U content is already proven (Budai *et al.*, 1999). The relatively high phosphorous content may derive from the large amount of fishbones and other organic particles of the rock (Kiss & Virágh, 1958), but the concentrating role of a (hydrothermal) fluid has to be taken into consideration, too (see the euhedral carbonate-fluorapatite crystals in the cavities of the phosphatite layers). As brecciated phosphatite clasts occur also in the fluorite bearing rock, it is suggested that the fluorite formed later, than the phosphatite. The dark purple colour of the fluorite can be the result of its radioactive material content. Consequently, the fluorite of this locality may have formed by the leaching of the fluorine content of the carbonate-fluorapatite and the rare earth elements can also be derived from the phosphatite layers.

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