



LA-ICP-MS study of fluorite from the Lukina Padina deposit, NW Bulgaria

LA-ICP-MS изследване на флуорит от нах. Лукина падина, СЗ България

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Introduction

Lukina Padina fluorite deposit is previously known as Chiprovtsi-East, the eastern section of the Ag-Pb Chiprovtsi deposit. During 1980–1990 in this section was exploited only Ag-Pb sulphide ore. The fluorite mining in the area began in 2009, aiming to achieve 50 000 tons annual fluorite extraction by the end of 2011. Fluorite or “fluorspar” is main source for production of hydrofluoric acid (HF), which has many uses, among them most strategic are aluminum and uranium processing. REE and trace element (Y, Rb, Sr, Na) incorporation in fluorite is characteristic for its formation (depositional mechanisms and conditions, ore-forming fluid sources). Impurities of REE and Y in fluorite determine also its color and luminescence pattern.

Materials and methods

Samples with fluorite were collected from four ore bodies cross-cut at three levels (495, 550 and 606 m) in the Lukina Padina fluorite mine. Major elements (Ca) were determined by wet chemical analysis. Trace and REE elements were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in the LA-ICP-MS Lab at Geological Institute (Bulgarian Academy of Sciences), Sofia, Bulgaria. The equipment consists of PerkinElmer ELAN DRC-e ICP-MS and New Wave UP193FX laser ablation system. The laser was run at a pulse frequency of 10 Hz and pulse energy of 1–2 mJ for 75 µm spot size. The NIST SRM 612 glass was used as external standard and was measured recurrently during the course of the analyses. Calcium content (wt.%) was used as internal standard in calculation of the 59 measured element concentrations using SILLS v.1.1.0 software (Guillong et al., 2008).

Geological setting

The Chiprovtsi Ag-Pb deposit is hosted in low-grade metamorphic rocks (marbles and schists) of the Diabase

Phyllitoid Complex (Precambrian–Early Ordovician age) (Carrigan et al., 2003). The formation of the main Ag-Pb metasomatic replacement mineralization is considered to be of Carboniferous age (Amov et al., 1981).

The fluorite mineralization occurs in zones of fracturing and displacement of the marble bodies, most intensively developed in the area between Velin Dol mine section and Zhelezna village, e.g. Lukina Padina mine section. Fluorite is brecciating and partially replacing the marble. Mineral composition of the fluorite bodies is presented by fluorite, quartz, calcite, ferrodolomite, barite, pyrite, and galena.

Results and conclusions

Eight spot LA-ICP-MS analyses were made on each sample. The ablation of fluorite is rough because of its perfect cleavage at {111}. Laser beam bursts the surface, no matter it is along or randomly across the cleavage, polished or not. This causes big mineral particles to enter simultaneously in the argon plasma and ionize, recording high intensities in the spectrum that decrease and become more stable in time. During ionization in the argon plasma, the ablated material (CaF₂) forms specific polyatomic interferences that occur at certain measured masses: ⁴⁰Ar¹⁹F⁺ at ⁵⁹Co, ²³Na³⁹K⁺ at ⁶²Ni and ³⁸Ar¹⁹F⁺ at ⁵⁷Fe, as reported by May and Wiedmeyer (1998). The presence of fluid inclusions in the ablated fluorite may cause formation of ¹³C¹⁸O⁺ or ¹²C¹⁸O¹H⁺ detected at ³¹P. A total of 59 elements were measured in the fluorite samples, however only 18 (REE, Rb, Sr, Y) exhibit concentrations above the detection limits (DL). Other 5 elements (Cs, Ba, Th, U and K) are randomly detected above the DL. The concentrations of 20 REE and trace elements (Na, Rb, Sr, Y, Th, U) for each sample are determined and plotted on a diagram shown on Fig. 1. They show some differences compared to those reported for Ce, Sm, Eu, Tb, Yb and Lu in previous studies (Zidarov, Zidarova, 1996; Zidarova et al., 2005), obtained by neutron-activation analysis on monomineral samples.

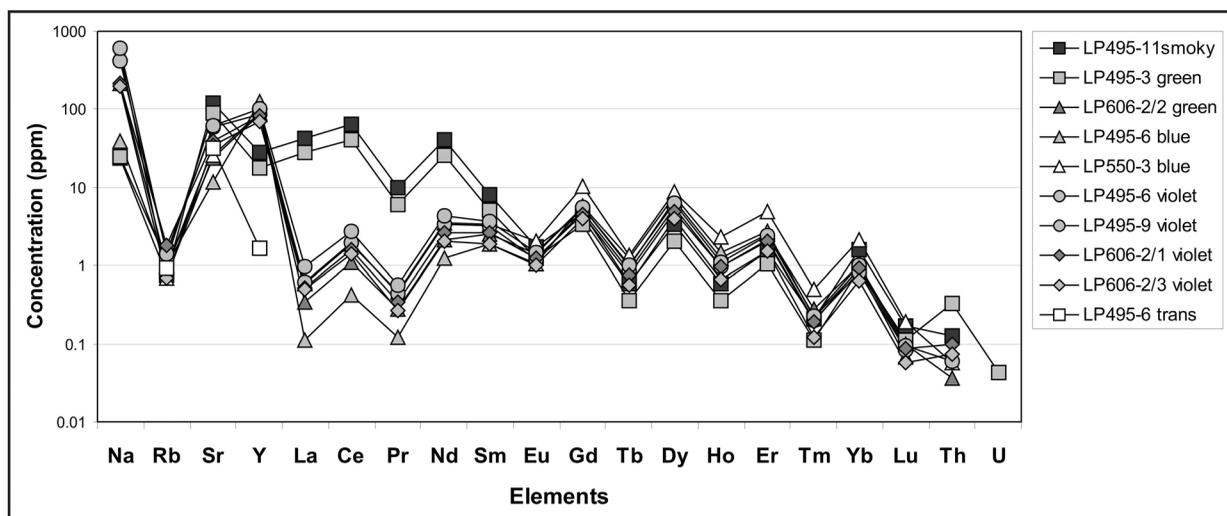


Fig. 1. Average concentrations of 20 REE and trace elements (Na, Rb, Sr, Y, Th, U) in fluorite samples from the Lukina Padina deposit

Two major distribution patterns of REE, Na, Sr and Y are formed: 1) enriched in LREE (La, Ce, Nd, Sm) and Sr, depleted in HREE with relatively low concentrations of Na and Y, observed in green- and “smoky”-colored fluorite; 2) enriched in HREE (Gd, Dy, Er), Na and Y and depleted in LREE and Sr, detected in blue- and violet-colored varieties of fluorite. This data suggest two relatively different fluorite forming fluids: early – enriched in LREE, which deposited the “smoky” and green-colored variety and late – enriched in Na, Y and HREE, which deposited the blue- and violet-colored variety. Transparent fluorite is probably latest deposited, because it is almost free of impurities. This sustains the idea of initial deposition of the green-colored variety suggested by Zidarov and Zidarova (1996), although it seems that the so-called “smoky”-colored variety contains the highest LREE

concentrations, and respectively earlier deposited. This data also suggest the following main substitutions in fluorite from the Lukina Padina deposit: 1) $2\text{Ca}^{2+}=(\text{Y}, \text{Ce}, \text{La})^{3+}+\text{Na}^{+}$; and 2) $2\text{Ca}^{2+}=(\text{Y}, \text{Gd}, \text{Dy})^{3+}+\text{Na}^{+}$; and less probable 3) $\text{Ca}^{2+}=\text{Sr}^{2+}$. It is also likely to occur $3\text{Ca}^{2+}=2\text{REE}^{3+}+\square$ and $\text{Ca}^{2+}=\text{REE}^{3+}+\text{F}^{-}$ according to Möller et al. (1998) and Schwinn and Markl (2005).

Comparison to the REE patterns of Sveti Nikola granite and the host rocks of DFC in the future could give some implications for the source of the fluorite-forming fluids. The Sm-Nd and Rb-Sr isotope studies (Zidarova et al., 2005) could not clearly unravel their origin.

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References

- Amov, B., V. Arnaudov, M. Pavlova, P. Dragov, Ts. Baldjieva, S. Evstatieva. 1981. Lead isotope data on the Paleozoic granitoids and ore mineralizations from the Western Balkan Mountains and the Tran district (West Bulgaria). I. Isotopic ratios and geochronology. – *Geologica Balc.*, 11, 2, 3–26.
- Carrigan, C. W., S. B. Mukasa, I. Haydoutov, K. Kolcheva. 2003. Ion microprobe U-Pb zircon ages of pre-Alpine rocks in the Balkan, Sredna Gora and Rhodope Terranes of Bulgaria: Constraints on Neoproterozoic and Variscan tectonic evolution. – *J. Czech. Geol. Soc.*, 48, 32–33.
- Guillong, M., D. L. Meier, M. M. Allan, C. A. Heinrich, B. W. D. Yardley. 2008. Appendix A6: SILLs: A MATLAB-based program for the reduction of laser ablation ICP-MS data of homogeneous materials and inclusions. – In: Sylvester, P. (Ed.). *Laser Ablation ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues*. Vancouver, B. C., Mineralogical Association of Canada, Short Course 40, 328–333.
- May, T. W., R. H. Wiedmeyer. 1998. A table of polyatomic interferences. – *Atom. Spectrosc.*, 19, 150–155.
- Möller, P., M. Bau, P. Dulski, V. Lüders. 1998. REE and Y fractionation in fluorite and their bearing on fluorite formation. – In: *Proceedings of the Ninth Quadrennial IAGOD Symposium*. Stuttgart, Schweizerbart, 575–592.
- Schwinn, G., G. Markl. 2005. REE systematics in hydrothermal fluorite. – *Chem. Geol.*, 216, 225–248.
- Zidarov, N., B. Zidarova. 1996. Fluorite mineralization in Chiprovtsi ore zone – peculiarities, development and morphogenic types. – *Rev. Bulg. Geol. Soc.*, 57, 3, 1–14 (in Bulgarian with an English abstract).
- Zidarova, B., I. Peytcheva, A. von Quadt, N. Zidarov. 2005. Geochemical and Nd-Sr characteristics of fluorite from “Chiprovtsi-East”. – In: Zidarov, N. et al. (Eds.). *Ten years Central Laboratory of Mineralogy and Crystallography Acad. I. Kostov*. Sofia, BAS, BAS press, 103–106 (in Bulgarian).