



## First find of florencite-(Ce,La,Nd) in advanced argillic altered rocks from the Asarel porphyry copper deposit, Central Srednogie

### Първа находка на флоренсит-(Ce,La,Nd) в интензивно аргилизираните скали от меднопорфирното находище Асарел, Централно Средногорие

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#### Introduction

Florencite –  $(\text{Ce,La,Nd})\text{Al}_3(\text{PO}_4)_2(\text{OH})_6$  is a mineral of the plumbogummite group which is part of the alunite supergroup (Jambor, 1999; Bayliss et al., 2010) with general formula  $DG_3(\text{TO}_4)_2(\text{OH,H}_2\text{O})_6$ , where  $D$  are large cations (K, Na, Ag, Tl,  $\text{NH}_4$ ,  $\text{H}_3\text{O}$ , Ca, Sr, Ba, Pb, Bi, La, Ce, Nd, Th) with coordination number larger or equal to 9.  $G$  site is occupied by cations in octahedral coordination (Al, Fe, Cu, Zn, V, Ga, Sn), and  $T$  site – by S, P, As in tetrahedral coordination. Most of these minerals are also known as aluminium phosphate-sulphate (APS) minerals (Stoffregen, Alpers, 1987) and have been object of increasing interest in the last 40 years. These minerals are widespread in the zones of advanced argillic alteration (AAA) in Bulgaria but florencite-(Ce) was established only in Dyuni and Sveta Agalina localities (Eastern Srednogie zone) (Kunov, 1999) and florencite-(Ce,La,Nd) in the AAA zone of the Chelopech high-sulphidation Cu-Au deposit (Georgieva, Velinova, 2014). Till now only florencite-svanbergite solid solution (s.s.) is documented in the Asarel porphyry copper deposit (Hikov et al., 2010). This study presents new data for florencite-(Ce,La,Nd) and other APS minerals in AAA rocks from the Asarel deposit. The analyses are made by SEM JEOL JSM-6610LV at the University of Belgrade, Serbia by EDS system with acceleration voltage 15–20 keV and current beam 2–6 nA.

The Asarel porphyry copper deposit is located in Panagyurishte ore region, part of the Upper Cretaceous Apuseni-Banat-Timok-Srednogie magmatic and metallogenic belt. The Asarel magmatic

center is a volcano-plutonic edifice emplaced in Paleozoic metamorphic and plutonic basement. Several volcanic (andesites to latites, basaltic andesites, andesites to dacites) and comagmatic porphyritic rocks (quartz diorite, quartz monzonite to granodiorite and granite porphyries) are distinguished (Nedialkov et al., 2007). Propylite, argillic, sericite, paragonite and advanced argillic alteration types are described in the deposit (Kanazirski, 2011; Hikov, 2013). Advanced argillic alteration consists of alunite, pyrophyllite, dickite, kaolinite and diaspore bearing rocks and the most intensively altered monoquartz (silicic) rocks.

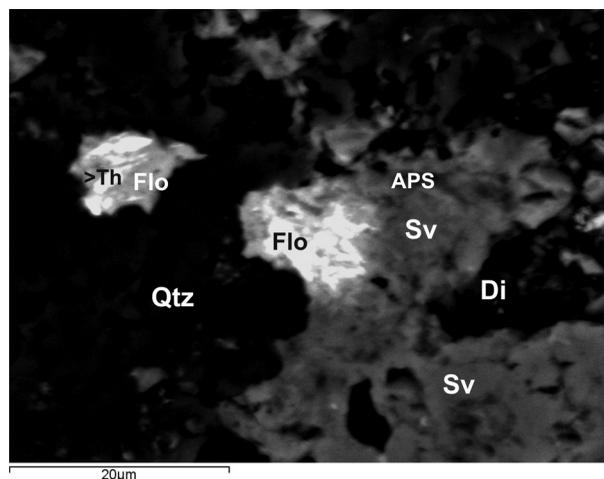
#### Results

Florencite-(Ce,La,Nd) was established in advanced argillic altered probably volcanic rocks with completely changed primary structure, texture and mineral composition. The altered rocks consist of non-equilibrium mineral association of quartz, sericite, diaspore, dickite, pyrophyllite, corundum, APS minerals, rutile, zircon and pyrite, as well as mixed intermediate phases rich in Th and Ba. The texture relationships suggest earlier formation of diaspore, corundum (microscopic elongated crystals up to 3  $\mu\text{m}$  in diaspore), APS minerals, rutile  $\pm$  pyrophyllite and later formation of sericite, dickite, pyrophyllite and pyrite while zircon is the only primary mineral preserved. Florencite-(Ce,La,Nd) grains are part of xenomorphic mineral aggregates of APS minerals from 10 to 50  $\mu\text{m}$  in size and variable composition ranging from florencite-(Ce,La,Nd) to

svanbergite and to APS minerals with svanbergite-woodhouseite composition. Cases without typical zonation predominate but sometimes florencite cores in svanbergite can be seen and in other cases mixed intermediate phases rich in Th form cores in florencite (Fig. 1). Cerium predominates over other REE in the chemical composition of florencite – from 0.27 to 0.42 *apfu* (9.36–14.98 wt% Ce<sub>2</sub>O<sub>3</sub>), La is from 0.19 to 0.28 *apfu* (6.68–9.95 wt% La<sub>2</sub>O<sub>3</sub>), while Nd is from 0.05 to 0.13 *apfu* (1.82–4.82 wt% Nd<sub>2</sub>O<sub>3</sub>). Thorium is also often present from 0.01 to 0.02 *apfu* (0.61–2.33 wt% ThO<sub>2</sub>). The total LREE+Th are from 0.52 to 0.66 *apfu*. Calcium up to 0.19 *apfu* (2.40 wt% CaO), Sr to 0.25 *apfu* (5.22 wt% SrO) and Ba to 0.03 *apfu* (0.82 wt% BaO) are constantly present while sodium (to 0.08 *apfu*) and Pb (0.01 *apfu*) are rare. Phosphorus is from 1.52 to 1.65 *apfu* (21.29–25.60 wt% P<sub>2</sub>O<sub>5</sub>) and sulphur is from 0.35 to 0.48 *apfu* (6.23–8.26 wt% SO<sub>3</sub>). The concentration of Al is relatively low from 2.40 to 2.60 *apfu*. Tungsten (2.78 wt% of WO<sub>3</sub>) and Zr (1.66 wt% of ZrO<sub>2</sub>) were established in some analyzed points. Svanbergite is with high Sr content from 0.76 to 0.97 *apfu* (17.51–22.82 wt% SrO), Ca is from 0.07 to 0.19 *apfu* (0.88–2.41 wt% CaO), Ba, Pb, Ce and Nd are established to 0.01 *apfu*, while K, Na and Th are not detected. Phosphorus (1.12–1.23 *apfu*) predominates over sulphur. APS minerals are svanbergite-woodhouseite solid solutions with Sr from 0.34 to 0.45 *apfu* (8.17–10.40 wt% SrO) and Ca from 0.22 to 0.49 *apfu* (2.91–6.11 wt% CaO). The concentration of other elements varies widely and a grain with high content of LREE and Th is also found: Ce 0.14 *apfu* (5.41 wt% Ce<sub>2</sub>O<sub>3</sub>), La 0.08 *apfu* (2.88 wt% La<sub>2</sub>O<sub>3</sub>), Nd 0.05 *apfu* (2.03 wt% Nd<sub>2</sub>O<sub>3</sub>) and Th 0.01 *apfu* (0.37 wt% ThO<sub>2</sub>). The analyzed transitional phases rich in Th are with non-stoichiometric composition but some of them are close to florencite-(Ce,La,Nd) while Ba-rich phases are probably mixtures between barite and APS minerals. One LA-ICP-MS analysis of REE-bearing APS solid solution shows presence of Na<sub>2</sub>O (0.28 wt%), P<sub>2</sub>O<sub>5</sub> (7.80 wt%) and trace elements as follows (ppm): Sr (9736.78), Ba (847.20), La (16 954.21), Ce (30 127.23), Pr (2402.46), Nd (6699.84), Sm (187.94), Eu (32.90), Gd (109.99), Ta (10.63), Pb (117.38), Th (3019.76), U (14.85).

## Discussion and conclusions

The studied florencite-(Ce,La,Nd) forms rare individual crystals as cores in svanbergite being mostly part of complex APS solid solutions varying from florencite-(Ce,La,Nd) to svanbergite and APS minerals with svanbergite-woodhouseite composition. Probably the formation of these minerals was very fast evidenced also by the presence in the neighbor-



**Fig. 1.** BSE image of florencite (Flo), svanbergite (Sv) and svanbergite-woodhouseite (APS) solid solution between quartz (Qtz) and diaspore (Di). Th-rich phase (>Th) in florencite is seen on the left side.

hood of mixed intermediate phases rich in Th (as a result of alteration of thorite) and Ba (probably mixture of barite and APS minerals). Florencite-(Ce,La,Nd) and other APS minerals are in association with corundum and diaspore which formation temperature is  $\geq 394$  °C while the absence of alunite show comparatively low activity of SO<sub>4</sub><sup>2-</sup> (Kanazirski, 2011). APS minerals form in various geological environments under high activity of PO<sub>4</sub><sup>3-</sup> and broad interval of temperature (15–500 °C) and pH (3–8) (Stoffregen, Alpers, 1987; Ripp et al., 1998; Schwab et al., 2005; Chakraborty et al., 2014). Their formation is related to the dissolution of magmatic apatite by acid fluids causing AAA (Stoffregen, Alpers, 1987). For the formation of florencite-(Ce,La,Nd) more activity of PO<sub>4</sub><sup>3-</sup> and higher pH (7–7.5) is needed compared to svanbergite (Ripp et al., 1998). The elements necessary for their formation such as LREE, Th and Sr are not added with hydrothermal fluids but are redistributed because they have inert behavior or concentrate during AAA in Asarel deposit (Hikov, 2013). The next hydrothermal event forms together sericite, dickite and pyrophyllite and indicates formation temperature of 273 °C (Kanazirski, 2011). All these mineral associations are free of alunite indicating for low activity of SO<sub>4</sub><sup>2-</sup> in the hydrothermal fluids (Kanazirski, 2011). Probably this is the reason for the preservation of magmatic zircon (Kovalenko, Ryzhenko, 2009) which is dissolved in the most of AAA zones in Asarel (Hikov, 2013) and, on the other hand, this probably prevents from dissolution the newly formed florencite. According to Gaboreau et al. (2005) the stability of svanbergite and florencite is highly sensitive to pH

and  $f(\text{O}_2)$ . Svanbergite is the stable APS end-member at low pH and relatively oxidizing conditions (*i.e.*, at  $f(\text{O}_2)=10^{-30}$  atm). More reducing conditions in the system (*i.e.*, at  $f(\text{O}_2)=10^{-38}$  atm) will strongly narrow the stability of svanbergite toward still more acidic conditions and hence promote the stability of florencite at lower  $\text{Sr}^{2+}/\text{Ce}^{3+}$  ratio.

Florencite-(Ce,La,Nd) is rare APS mineral in the Asarel porphyry copper deposit and is established in mineral assemblages not containing alunite or acid-chloride advanced argillic alteration (Kanazirski, 2011). Florencite formation depends on the total amount LREE, activity of  $\text{PO}_4^{3-}$  and is controlled by pH. It can be assumed that the formation and preservation of florencite in the zones of alunite-bearing or acid-sulphate advances argillic alteration is more difficult and its finding in these zones is an exception.

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