# Florencite-(Ce,La,Nd) from the advanced argillic alterations in the Chelopech high-sulphidation epithermal Cu-Au deposit, Bulgaria

# Флоренсит-(Ce,La,Nd) от интензивно аргилизитовите изменения на високосулфидизираното епитермално Cu-Au находище Челопеч, България

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## Introduction

Florencite – $(Ce,La,Nd)Al_3(PO_4)_2(OH)_6$ is a mineral of the alunite supergroup, that contains more than 40 species with the formula $DG_3(TO_4)_2(OH,H_2O,F)_6$, where *D* is a large cation ($K^+$, $Na^+$, $NH_4^+$, $H_3O^+$, $Ag^+$, $Pb^{2+}$, $Hg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $Rb^+$, $Tl^+$, $Bi^{3+}$, $REE^{3+}$), *G* site is occupied by $Al^{3+}$, $Fe^{3+}$, $Cu^{2+}$, $Zn^{2+}$, $Sn^{2+}$, $V^{3+}$, $Cr^{3+}$, $Ga^{3+}$, $Mg^{2+}$, and ($TO_4$) position is dominated by $P^{5+}$, $S^{6+}$ and $As^{5+}$ (Jambor, 1999; Dill, 2001; Bayliss et al., 2010). Florencite has a trigonal symmetry with a space group $R\bar{3}m$ and generally is present as pseudocubic rhombohedra. The mineral forms during hypogene as well as supergene processes. As a part of aluminium phosphate-sulphate (APS) group it is typical for the advanced argillic alteration (AAA) zone from the high-sulphidation epithermal systems. In Bulgaria florencite-(Ce) of hydrothermal-metasomatic genetic type is known in Srednogorie zone (Dyuni and Sveta Agalina occurrences) (Kunov, 1999). Florencite-svanbergite s.s. is documented in the Asarel porphyry copper deposit (Hikov et al., 2010). Recently, florencite-(Ce,La,Nd) was established in the AAA zone of the Chelopech high-sulphidation Cu-Au deposit. The aim of this study is to describe the chemistry and specificity of the mineral.

The Chelopech deposit is located within the northern part of the Panagyurishte ore region that belongs to the Banat-Srednogorie metallogenic belt. It is hosted by an Upper Cretaceous volcanic and volcano-sedimentary complex. The volcanic rock assemblage is composed of dacite-andesitic lavas, breccias with volcanic elements and various tuffs (Popov et al., 2012). Part of these rocks has been intensively altered to an advanced argillic style and hosts the Cu-Au ore bodies of the deposit.

## Results

Florencite-(Ce,La,Nd) from the Chelopech deposit is found in the AAA zone, where the alteration assemblage consists of quartz, dickite, kaolinite, nacrite, pyrite, aluminium phosphate-sulphate (APS) minerals and anatase. At deeper levels of the system, the mineral assemblage is changed (Georgieva et al., 2002) and florencite-(Ce,La,Nd) occurs together with APS, dickite, kaolinite, quartz, diaspore, pyrophyllite, alunite and zunyite. The mineral is analyzed only chemically by electron microprobe analyser (EMPA) due to the limited amounts and the small grain sizes. Florencite-(Ce,La,Nd) occurs as bright, mostly euhedral, hemihedral or randomly shaped 5–40 μm core of the APS zonal aggregates associating mainly with kaolinite, dickite and quartz (Fig. 1). The chemical

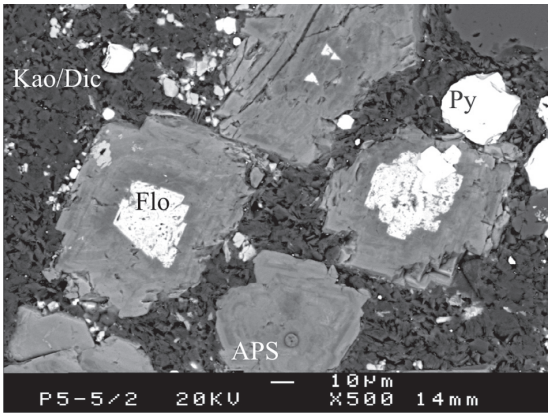


**Fig. 1**. BSE image of zonal APS crystals from the advanced argillic zone of alteration. The white cores represent florencite-(Ce,La,Nd) – Flo; Kao/Dic – kaolinite/dickite; Py – pyrite

composition of florencite-(Ce,La,Nd) is variable with Ce predominating over La and Nd. $Ce_2O_3$ content reaches up to 13.39 wt.%, or 0.43 atoms per formulae unit (*apfu*), whereas $La_2O_3$ is up to 6.81 wt.% or 0.22 *apfu* and $Nd_2O_3$ is up to 5.90 wt.% or 0.18 *apfu*, which allows us to determine the mineral as an end-member of the alunite supergroup. Some quantities of Ca (up to 0.33 *apfu*), Sr (0.20 *apfu*), K (0.10 *apfu*), Na (0.03 *apfu*), Ba (0.02 *apfu*) and F (0.06 *apfu*) were detected (Fig. 2). The content of P in the ($TO_4$) position is from 1.46 *apfu* to 1.91 *apfu* whereas S is up to 0.49 *apfu.* The increased content of S is connected with the increase of Ca and Sr. This probably represents solid solutions between florencite-(Ce,La,Nd) and other APS species. The mineral accommodate LREE and determine their immobility during the hydrothermal processes. According to Ripp et al. (1998), APS minerals are formed in conditions of high activity of $PO_4^{3-}$ ions, high oxygen potential and a large pH interval (3–8) of the fluid. The presence of alunite (pH 0.8–5.3) in the mineral assemblage suggests formation of the AAA zone in the Chelopech deposit in pH interval of 3–5. Sulphur is abundant in the hydrothermal solutions of epithermal systems whereas phosphorus is subordinate. According to Stoffregen and Alpers (1987), apatite from the initial rocks is dissolved in acid conditions providing additional $PO_4^{3-}$ for the formation of APS minerals. It is supposed that florencite-(Ce,La,Nd) from the Chelopech deposit is formed under the same conditions. The existence of APS s.s. with various chemistry (Ca, Sr, Ba, Ce, La, Nd, K, Na, $PO_4^{3-}$, $SO_4^{2-}$) and the formation of zonal crystals presume frequent changes of the fluid composition during the hydrothermal processes. Florencite and varieties of APS s.s. are considered as indicative for the advanced argillic type of alterations. This increases their genetic importance regarding the physicochemical condition of ore formation and particularly in ore prospecting.

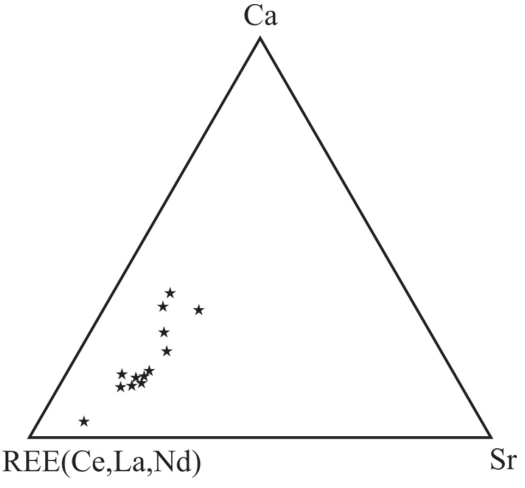


**Fig. 2**. *D* position diagram of APS minerals

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