

Hydrothermal amphiboles from Na–Ca and Na–Ca–K-silicate alterations: An example from Elatsite porphyry copper–gold deposit, Bulgaria

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Abstract: The progression of exploitation and new prospecting get to the discovery of Na–Ca and transitional Na–Ca–K-silicate alterations (transitional between Na–Ca and K-silicate alteration) in the deeper parts of the Elatsite porphyry copper–gold deposit (PCGD). The study of these new for the deposit alterations reveal the presence of different in morphology, distribution and chemistry hydrothermal amphiboles.

Introduction

The Elatsite PCGD is one of the biggest deposits of this type in Europe. It is operating since 1983–1984 and is the best studied in Bulgaria. Nevertheless, with the progressing exploitation and new prospecting drillings in deeper parts of the hydrothermal system are discovered new alteration types. Sodic–calcic (Na–Ca) alteration and the transition between Na–Ca and K-silicate alterations are characterised for the first time. These alterations are not frequently established in PCGDs and the information about them enrich the knowledge about the deposits and present the possibility to build up a more exhaustive model of the hydrothermal system of Elatsite PCGD.

Samples and methods of investigation

The studied alterations are established during several years of sampling and field observations on the constantly changing benches of the open pit mine and on some interesting drill cores samples conceded gentility by the mining company.

The petrography of the alterations is characterised under the microscope. The mineral chemistry is obtained with microprobe analyses (47 analyses) accomplished on JEOL JSM 35 CF at “Eurotest-Control” EAD, Sofia, Bulgaria (EDS analysis, 100 seconds for spectra acquisition, at 15 KEV acceleration voltage, using natural and synthetic standards, EDX – TRACOR NORTHERN TN-2000). Mineral trace elements (22 analyses) are made on LA-ICPMS at the Geological institute of the Bulgarian academy of sciences on a Perkin Elmer – ELAN DRC spectrometer with New Wave UP193FX

LA device. The internal standard (SiO_2) is from the microprobe analyses of the respective minerals. The laser system operated at constant 8 Hz pulse rate and laser energy 1.80–2.60 J/cm² on the sample surface for 25 to 35 μm spot size.

Geological setting

The Elatsite porphyry copper–gold deposit is situated at the most northern part of the Panagyurishte–Etropole ore region which is part of the Apuseni–Banat–Timok–Srednogorie Late Cretaceous copper belt (Popov 1996; Popov & Popov 2000; von Quadt et al. 2005). The magmatism of the belt is predominantly calc-alkaline to shoshonitic and it is subduction related (Kamenov et al. 2002, 2007).

The geology of the Elatsite deposit consists of a basement, intruded by the Late Cretaceous magmatic subvolcanic to hypabyssal complex, composed by dikes and dike-like, east-west elongated intrusive bodies. The main porphyritic rocks are presented by quartz-monzodiorites and granodiorites as well as quartz-diorites (von Quadt et al. 2002). The basement comprises low-grade Paleozoic variegated schists (anchymetamorphic to greenschist metamorphic degree) intruded by the Variscan Vezhen granitoid (mainly granodiorite) pluton (Kalaidziev et al. 1984; Kamenov et al. 2002). At the contact of the Vezhen pluton with the metamorphic rocks are formed sillimanite (observed in xenoliths in the magmatic rocks) and andalusite hornfelses, knotted schists with andalusite and/or rare biotite porphyroblasts and rare amphibole hornfelses.

The hydrothermal alteration products, related with the porphyritic magmatism, are represented by propylitic,

K-silicate, K-silicate-sericitic, sericitic (Kanazirski et al. 2002; Strashimirov et al. 2002; Georgiev 2005), phillitic–argillic (Tarkian et al. 2003), argillic (Kehayov 2005) and quartz–adularia–carbonate alterations (Ivanov et al. 2014). Indications for supposed mixed sodium–potassic alteration with summarized mineral association — richterite, paragonite (determined by X-ray spectroscopy) and pyroxene (diopside) were first reported in the PhD thesis of Georgiev 2005 (communication from Kanazirski).

Our recent studies ascertain the presence of Na–Ca alteration (rare in the deposit), the more common Na–Ca–K-silicate (transitional between Na–Ca and K-silicate alteration) and skarn formation (related with local disclosure of Ca alteration in the hornfelse sequence) affecting calc-schists.

Petrography

Na–Ca alteration is well preserved mainly in veins and veinlets and relatively rarely observed as affecting all the volume of the rock. The mineral composition of the Na–Ca alteration is represented dominantly by amphibole, epidote, plagioclase, albite, rarely clinopyroxene, rutile, magnetite, apatite, small amount of hematite and quartz. This type of alteration affects mostly the Late Cretaceous magmatic subvolcanic to hypabyssal porphyritic complex and less the granodiorites of the Vezhen pluton.

The amphibole veins with up to several tens of centimetres thickness are the most astonishing manifestations of the Na–Ca alteration (Fig. 1). They are hosted in



Fig. 1. Amphibole veins (black in colour) from Na–Ca alteration (1) in the granodiorites of the Vezhen pluton, with superimposed K-silicate alteration (2).

the granodiorites of the Vezhen pluton and are superimposed by the K-silicate alteration. The mineral assemblage includes dominantly amphibole (Hb-1) and small quantity of quartz and magnetite.

When Na–Ca alteration is disseminated uniformly in the volume of the host rocks, it is composed mainly of amphibole (Hb-2), rutile, apatite, magnetite and small quantity of quartz and clinopyroxene. Usually the magmatic texture is preserved, and the secondary amphiboles replace primary mafic minerals and form clusters or occurs in thin veinlets.

The transitional Na–Ca–K-silicate alteration is characteristic by the presence of amphibole, titanite, magnetite, apatite, secondary biotite and small amount of K-feldspar, quartz and rutile. Amphibole (Hb-3) has green colour and is typically replacing magmatic porphyroblasts, and/or occurs as veinlets and nests grown up with secondary biotite.

Discussion

Chemical composition of hydrothermal amphibole

The classification of the hydrothermal amphiboles was made using the equations of Locock et al. 2014 after Hawthorne et al. 2012.

The Hb-1 occurs as euhedral crystals up to few millimetres (rare 1 cm), black in colour. Hb-1 is determined as hornblende to actinolite, with $Mg^{\#}$ ratio ($Mg/(Mg+Fe)$) between 0.75–0.87 and high contents of Ti, Fe^{+3} , Mn and Cl (Fig. 2). The higher Cl values (0.11–0.42 wt. %) define Hb-1 as a Cl-rich amphibole (Kullerud 2000). Hb-1 has high concentration of Cr, Co, Ni, Cu, Pb and rare earth elements ($\Sigma REE=160.74$) compared to the other types of amphibole. It is showing deep Eu negative anomaly ($Eu/Eu^{*}=0.30$) on the chondrite normalized patterns and a relatively flat distribution of light and heavy REE with La/Yb ratio 0.25–0.63.

Hb-2 occurs as euhedral to anhedral, green coloured crystals (under the microscope), up to few tens of μm . It is characterised by two morphological types of reparation: in veinlets (Hb-2.1.) or uniformly distributed (Hb-2.2.) in the rocks. Hb-2.1. is determined as magnesio-hornblende while Hb-2.2. is defined as magnesio-hornblende to actinolite. Hb-2.1. has $Mg^{\#}=0.70$ –0.71 and higher values for Fe^{+2} , Al and Ti compared to Hb-2.2 ($Mg^{\#}=0.71$ –0.78; Fig.2).

Hb-3 is determined as magnesio-ferri-hornblende to actinolite, with $Mg^{\#}=0.72$ –0.83. Their chondrite-normalized patterns have the lowest content of REE

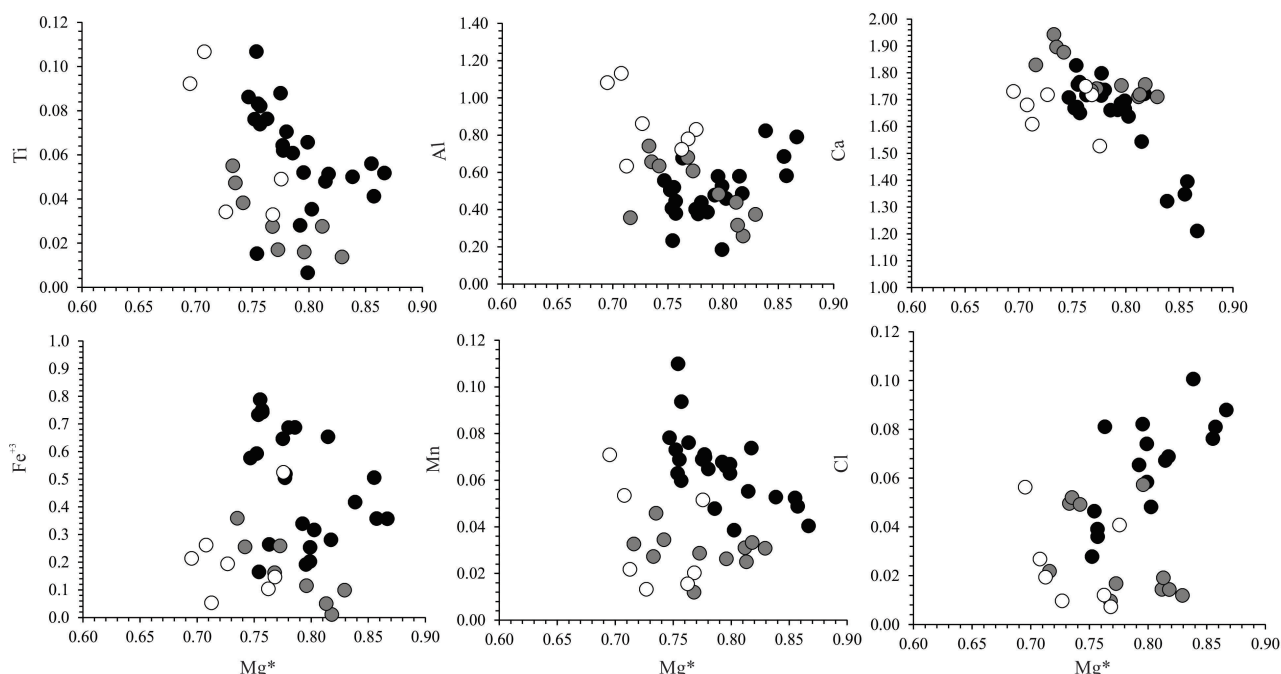


Fig. 2. Plots show compositional variations Mg^* ($Mg/(Mg+Fe)$ /element (apfu) in hydrothermal amphiboles: Hb-1 (with black); Hb-2 (with white) and Hb-3 (with grey).

($\sum REE=96.62$) and a deep negative Eu anomaly ($Eu/Eu^*=0.38$). In Hb-3 are determined the lowest contents of trace elements from the all amphiboles.

Pressure

The pressure of the hydrothermal amphiboles crystallization was determined after Mutch et al. 2016.

The estimated pressure for Hb-1 is between 0.59 to 1.18 kbar. For Hb-2.1., the results are 2.02–2.15 kbar, and for Hb-2.1., estimated pressure is around 1.11–1.52 kbar. For Hb-3 from the transitional alteration, estimated values are between 0.65–1.29 kbar. These results correlate with the pressure estimations of Stefanova (2009) obtained fluid inclusions associated with the K-silicate alteration (0.916 kbars).

Conclusions

During the transition of Na–Ca to Na–Ca–K-silicate alteration, the contents of Mg, Ti, Mn, Cl, trace and REE elements are decreasing. The Mg and Ti decrease (in Hb-3) is probably related to the appearance of secondary biotite.

The deep negative Eu anomaly of Hb-1 (indicating probably the presence of Eu^{+3}) and the high Fe^{+3} content in Hb-1 compared to Hb-2 and Hb-3 may indicate

a higher oxygen fugacity during their formation. The higher values of Cl in Hb-1 allows us to assume that in the early stage of Na–Ca alteration the fluid was Cl-rich. The decrease in rare and REE elements during the transition between Na–Ca to Na–Ca–K-silicate alteration is related to their preference to stay in the Cl-rich fluid.

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