SEM-CL AND LA-ICP-MS ANALYSES OF VEIN QUARTZ FROM THE ELATSITE PORPHYRY CU-AU DEPOSITE, BULGARIA

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Introduction

Results from laboratory analyses of quartz from potassium feldspar-rich thin aplitic dykes from the Elatsite porphyry copper deposit are presented in this paper. Several studies have explored the aplitic dykes' formation in many of the world-class porphyry copper deposits (Heithersay, Walsh, 1995, etc.). The presence of the so-called "vein dykes" is assumed to be one of the most illustrative evidences for coeval processes of magmatism, hydrothermal activity and mineralization. Thin hydrothermal veinlets with prismatic quartz in the margins and a central infill of aplitic material, consisting of quartz and potassium feldspar are characteristic for those aplitic dykes.

The aim of this study is to present more detailed spatial and mineralogical description of aplitic veins in the Elatsite porphyry Cu-Au deposit. That includes unraveling the genesis of composite quartz-feldspar (q-fs) veins and their relationship with the main ore stages at Elatsite. Scanning electron microscope-cathodoluminescence (SEM-CL) study has been used to reconstruct the growth history of various generations of quartz and their relationship with the ore formation. SEM-CL is an efficient method for visualizing microtextures in minerals, which cannot be observed using optical microscopy. In environments with multiple quartz-precipitation events, these cryptic textures bring insight into timing and physical conditions of quartz growth. Based on CL pictures, LA-ICP-MS was used to analyze different quartz generations in order to quantify the distribution of 12 trace elements. With the data obtained, we were able to constrain the distribution of trace elements in quartz and its relation to SEM-CL response.

Geological setting

Elatsite porphyry Cu-Au deposit is located on the Etropole ridge of Western Balkan Mountains at the northern end of Panagyurishte ore district of Central Srednogorie zone (Bonchev, 1970).

The porphyry copper mineralization is associated with Late Cretaceous subvolcanic bodies and porphyry dykes intruded into the metamorphic rocks of Berkovitsa group (Haidoutov et al., 1979) and granodiorites of Vezhen pluton (Carboniferous age, 314±4.8 Ma - Kamenov et al., 2002). Elatsite area is built up by several dyke generations (Kamenov et al., 2002) grouped into two stages. The "ore-productive" stage includes quartz-monzodiorite porphyries, granodiorite porphyries and K-feldspar-rich thin aplitic dykes. The later dyke stage comprises mafic dykes (micro-diorites, micro-monzodiorites, diorite porphyries and their quartz-bearing varieties).

Methods and studied samples

Samples containing early stockwork and sheeted veins, potassium feldspar-rich thin aplitic veins and quartz-ore veinlets having different relationships were collected mainly from the north-eastern (levels 1165, 1180, 1195 and 1210) and southern (levels 1045, 1060) parts of the Elatsite deposit. Based on petrographic studies, three specimens were selected for investigation of their CL characteristics in order to identify different quartz generations. CL pictures are combined with back-scattered electron (BSE) images. BSE and CL images were taken immediately after each other under the same analytical conditions. The SEM-CL apparatus used (CamScan CS44LB instrument at the Electron microscopy Laboratory, ETH-Zurich) is not equipped to quantify the wavelengths and the intensities of the CL spectra but only records the CL signals as grayscale images. In the following discussion, the luminescence intensity is simply referred to as CL-dark, CL-grey and CL-bright.

Based on CL textures, twelve trace elements were measured by LA-ICP-MS using 60 μm and 75 μm laser beam diameter. Data are reported for Li, Na, Mg, Al, Si, P, K, Ti, Fe, Ga, Ge and Sn. Since there is only limited interstitial space in quartz' lattice and a strong configuration of the Si-O bonds, only few ions such as Al^{3+}, Ga^{3+}, Ge^{3+}, Ti^{4+} and P^{5+} are able to substitute for silicon atoms in the quartz structure. Some of those elements require charge compensation, satisfied by the incorporation of additional monovalent ions such as H^+, Li^+, Na^+, K^+, Cu^+, and Ag^+ in interstitial sites related to structural channels (Götze et al., 2001). Incorporation of trace impurities in quartz is considered a key factor controlling the cathodoluminescence of quartz (Götze et al., 2001). In addition, structural defects also play a role.

Results and discussion

SEM-CL reveals a complex multigenerational history of early stockwork or sheeted veins (vein I), comprised mainly of quartz and later quartz-feldspar veins (vein II), built up of symmetrical quartz in the salband and quartz + feldspar in the central part. Vein II crosscuts the earlier vein and causes the observed off-set. Both veins I and II are cut by several ore veinlets, build up mostly of quartz, chalcopyrite, and bornite with or without magnetite. Disseminated magnetite, bornite and chalcopyrite grains can be observed in q-fs vein (Fig. 1).

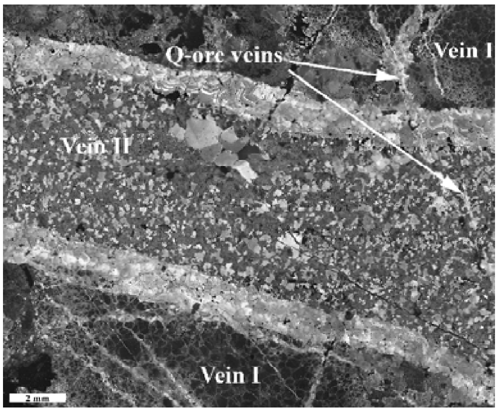
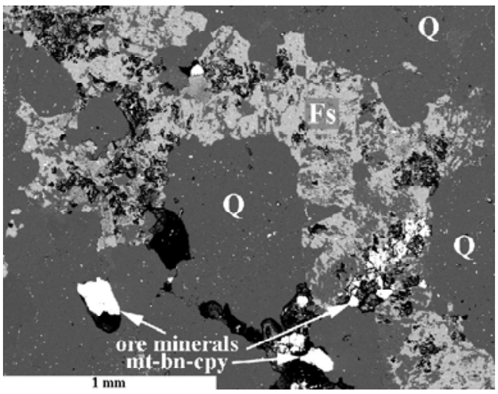


Fig 1. Vein I, II and Q-ore veins, SEM-CL image.

SEM-CL and BSE images of the same area of vein I containing quartz (Q), feldspar minerals (Fs), chlorite (Chl), calcite (Cal), magnetite (Mt), bornite (Bn) and chalcopyrite (Cpy) are shown in Figure 2. The SEM-CL image reveals two separate generations of quartz. CL-dark quartz cores are overgrown by CL-grey quartz. Cores and rims are optically continuous and no evidence for multiple hydrothermal fluids is present in BSE image. This texture is caused by precipitation of CL-dark quartz followed by second quartz generation (CL-grey quartz), formed together with minor Fs, Cal, Chl and ore minerals.

Two different textures of q-fs veins could be distinguished at Elatsite: aplitic (Fig. 1) and microporphyrytic (Fig. 3). SEM-CL images show textural and grey-intensity difference between quartz precipitated in the salband and quartz from the central part of vein II. The quartz from the salband typically has euhedral growth zones, indicating growth in an open space. It shows a distinct oscillatory zonality ranging in luminescence from CL-bright to CL-grey. Fracturing of this quartz is ubiquitous. CL-dark bands cut across zonal CL-grey to CL-bright quartz grains (Fig. 3). These cobweb-like networks of CL-dark quartz appear to be result from corrosion of quartz along microfractures, followed by precipitation of CL-dark quartz, rich in fluid inclusions.

Quartz from the central q-fs vein has a CL-grey luminescence, showing weak internal zoning (Fig. 1) but on some places quartz grains with euhedral zonal growth could be observed. CL-petrography of q-fs veins with microporphyrytic textures shows that these veins are build up of two generations of quartz. Many phenocrysts exhibit a CL-dark luminescent, rounded or globular core (first generation of quartz) overgrown by CL-gray luminescent quartz (second generation of quartz) (Fig. 3a).



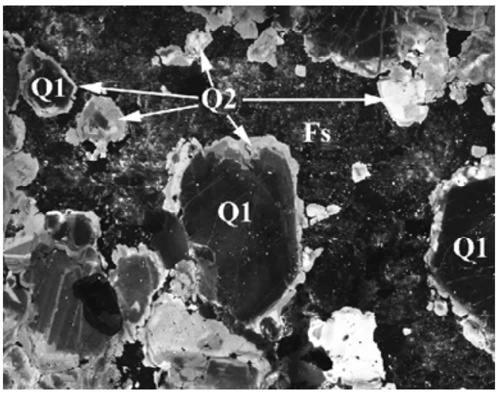


Fig. 2. Images of Vein I acquired by SEM-BSE (left) and SEM-CL (right)

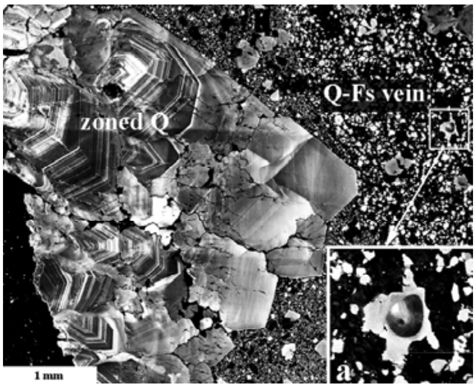


Fig. 3. SEM-CL image of vein II with zoned quartz in salband and quartz+feldspar in the central part; a – CL-dark core overgrown by CL-bright rim.

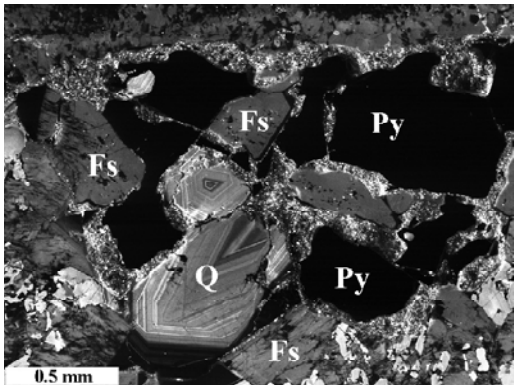


Fig. 4. SEM-CL image of quartz with pyrite in quartz-feldspar vein.

CL images of sample 3 show another quartz generation (Fig. 4), well developed in open space zones of the vein together with pyrite (Py) and calcite (Cal) and occurs as CL-grey to CL-bright luminescence with perfect oscillation.

Straight to irregular-walled quartz-ore veinlets not wider than 2 mm cut both veins I and II (Fig. 1). Quartz is CL-bright luminescent and often shows oscillatory zoning.

Twelve trace elements from three quartz generations – quartz from vein I, quartz from the salband and from the central part of the vein II, were measured by LA-ICP-MS. Since there are two generations of quartz in the analyzed quartz grains from vein I, the chemical analysis represents compositional data from both generations (CL-dark and CL-grey quartz). In vein II both zonal (CL-grey to CL-bright) and monochrome (CL-grey) quartz grains from the salband (Fig. 1) were probed. Higher concentrations of Al were obtained for CL-grey to CL-bright luminescent quartz (up to 477 ppm) in comparison to CL-grey quartz (up to 92 ppm). The most prominent substitutional ion of Si^{4+} is Al^{3+} that is charge-balanced dominantly by K $\left(Si^{4+}_{-1}Al^{3+}_{1}K^{+}_{1}\right)$ and Na $\left(Si^{4+}_{-1}Al^{3+}_{1}Na^{+}_{1}\right)$. The concentration of Ti in the vein I quartz is up to 141 ppm, in salband quartz – up to 182 ppm and in q-fs vein – up to 175 ppm. In most cases Ga and Fe content are under the limit of detection (LOD). Ge and Sn concentrations remain relatively uniform in all quartz generations.

Conclusions

SEM-CL textures of vein quartz from Elatsite demonstrate that the apparently simple picture of quartz veins visible in transmitted light belie a complex history of quartz fracturing, dissolution and reprecipitation. We use these textures to distinguish among multiple generations of quartz precipitated at different time in an individual vein and to relate this quartz to specific events.

Correlation between SEM-CL and LA-ICP-MS data is observed: quartz with brighter luminosity has higher concentration of trace elements.

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SEM-CL И LA-ICP-MS АНАЛИЗИ НА ЖИЛЕН КВАРЦ ОТ МЕДНО ПОРФИРНО НАХОДИЩЕ ЕЛАЦИТЕ, БЪЛГАРИЯ

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В настоящата работа са представени резултати от лабораторни изследвания на кварц от богати на калиев фелдшпат тънки аплитови дайки от Cu-Au порфирно находище Елаците. В редица публикации се разглежда въпросът за образуването на т. нар. жилни дайки в световно известни Cu-порфирни находища (напр. Heithersay, Walsh, 1995 и т. н.). Присъствието на жилните дайки се смята за едно от най-илюстративните доказателства за едновременното действие на магматични процеси, хидротермална дейност и орудяване. Характерно за тях е присъствието на тънки хидротермални ивици с призматичен кварц в залбанда и жентрална част, запълнена с аплитов материал.

Целта на настоящето изследване е да бъде определен генезиса на кварц-фелдшпатовите (Q-Fs) жили и връзката им с рудообразуването в находище Елаците. Използваните методи са SEM-CL в комбинация със SEM-BSE и LA-ICP-MS. SEM-CL е ефективен метод за разкриване на микроструктурните особености на кварц, които не могат да бъдат наблюдавани с петрографски микроскоп. Той е подходящ за изследване на обекти с многофазно отлагане на кварц и помага за определяне на времето и физичните условия на образуването на отделните генерации. На базата на получените от катодната луминесценция снимки, различни генерации от кварц са изследвани с LA-ICP-MS метод с цел да бъде определено разпределението на 12 елемента примеса и връзката между разпределението на елементите и луминесценцията на кварца.

Характеризирани са катодолуминесцентните свойства на три образеца, съдържащи ранна щокверкова жила (жила I) и по-късна Q-Fs жила (II), изградена симетрично от кварц в залбанда и Q+Fs в аксиалната част. Двете жили I и II са пресечени от множество по-късни кварц-рудни жилки, съставени предимно от кварц, халкопирит (Cpy), борнит (Bn) с или без магнетит (Mt).

Интензитетът на луминесценцията е определен като тъмен, сив и светъл. Получените от SEM-CL структури на кварца разкриват сложната история на напукване, разтваряне и преотлагане във видимо прости, наблюдавани с петрографски микроскоп, картини. Ние използваме тези структури за разграничаването на отделни генерации от кварц, отложени по различно време в една жила и привързваме този кварц към различни събития.

С помощта на LA-ICP-MS е измерено съдържанието на Li, Na, Mg, Al, Si, P, K, Ti Fe, Ga, Ge и Sn. Поради ограниченото интерстиционно пространство в решетката на кварца и здравата връзка между Si-O атоми само няколко йона като Al^{3+}, Ga^{3+}, Ge^{3+}, Ti^{4+} и P^{5+} могат да заместват силициевите атоми в структурата на кварца. Необходими са допълнителни едновалентни йони (H^+, Li^+, Na^+, K^+, Cu^+ и Ag^+), които да компенсират заряда на решетката. Според Götze et al. (2001) включването на елементи примеси е ключов фактор, контролиращ катодолуминесцентните свойства на кварца. Дефектите в структурата също оказват влияние. Резултатите от LA-ICP-MS на жилен кварц от находище Елаците показват, че Si^{4+} се замества предимно от Al^{3+}, а K^+ и Na^+ са главните йони, компенсиращи заряда на решетката.

Съпоставяйки данните от LA-ICP-MS и SEM-CL се забелязва следната зависимост: по-светло луминесциращия кварц има по-високи съдържания на елементи-примеси.