Sulfides inclusions in minerals from volcanic rocks of the Panagurishte ore region, Bulgaria.

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Introduction

The Panagurishte ore region is a part of the Banat-Srednogorie belt characterized by upper Cretaceous Calk-alkaline to Shoshonitic magmatism and disposition of numerous copper, gold-copper and base metal deposits and ore occurrences. In the Panagurishte ore region are disposed several important ore deposits as Chelopech, Medet, Assarel, Radka, Elshitza, Tzar Assen, Krassen, and others. At present days in exploitation are only, Chelopech and Assarel.

The problem with the genetic relation between the upper Cretaceous magmatism and the ore processes is discussed from different point of views – time and space relations, geochemical similarities, favorable conditions and characteristics of the magmatism for the formation of the orthomagmatic hydrothermal system.

One of the important questions for the ore formation is the origin and the behavior of the sulfur needed for the formation of the huge amount of sulfide minerals in the deposits. The investigation of the sulfide inclusions in magmatic rock minerals could give some information in the approach of this important problem.

Geology

The geology of the Panagurishte ore region is characterized by Paleozoic basement and a Mesozoic to Tertiary cover. The basement is composed of by Paleozoic high grade metamorphic rocks (biotite and two mica gneisses, amfibolites, and schists) (Arnaoudov et al., 1989; Velichkova et al., 2001) intruded by variscan mainly granitoide plutons (Smilovene, Strelcha, Poibrene, Koprivshtitza)(Dabovski et al., 1965). The cover is composed of Triasic and Cretaceous (Karaguleva et al., 1974) sediments and magmatites. The Upper Cretaceous volcanic activity is localized in five subparallel volcanic stripes (VS) (from north to south - Chelopech VS, Assarel VS, Krassen-Petelovo VS, Pesovetz VS and Radka VS) with WNW direction (100-130^o). The last investigations explain the formation of the volcanic stripes as strike-slip basins formed in transtensional regime (Ivanov et al., 2001). In recent publications on the magmatism (Kamenov et al., 2003, 2004) it has been determined its subduction related character and it consecutive rejuvenation from north to south during a time span of 14 million years. The magmatic activity operated in several magmatic centers building volcanic or volcano-plutonic structures. The volcanism is subaerial producing predominantly volcaniclastic rocks and also effusive and subvolcanic magmatic bodies. The volcanic rocks in the four southern VS are presented by basalts (small amounts at Ovchepoltzi), basaltic andesites, andesites, latites, trachytes, dacites, rhyodacytes and rhyolytes (the last three rock types present mainly in the Radka VS). For the present study only volcanic rocks from the peripheries of the ore-magmatic centers, unaffected by hydrothermal alterations are investigated.

For some of the magmatic centers of the Panagurishte region magma mixing phenomena between more primitive basaltic in composition melt and more evolved intermediate to acid magma recipient were established. The petrological investigations of the magmatism from the Panagurishte region show that the parental magma was derived from a slightly enriched mantle and main magmatic processes are crystal fractionation, magma mixing and a slight crustal contamination (Kamenov et al., 2004, Nedialkov et al., 2006). The generated and the evolved magma are hydrous with water content up to 5-6% H_2O (Nedialkov et al., 2006).

Sulfide inclusions

In scientific geological publications, sulfide inclusions in magmatic rock forming minerals are interpreted as indicators for relatively high S fugacity and as indicators for fO_2 (often between the FQM and NNO buffers) of the magma during the crystallization (Hattori, 1993). With fO_2 increasing the sulfide blebs are destroyed and sulfur moves in the residual melt as SO_2. It is well known that the acid magma do not dissolve and do not carry sulfur enough for the formation of the ore deposits (Hattori, 1993; Hattori & Keith, 2001). Basaltic magmas have clearly higher S contents (up to 1000-2000 ppm, up to 3000 ppm in primitive magmas) and are estimated as the main supplier of S in the ore magmatic centers (Hattori & Keith, 2001; Maughan et al., 2002). The sulfide melt concentrates ore elements (Gorbachev, 1989; Halter et al., 2005). Recent investigations of Halter et al., (2002) demonstrate that the ratio Au/Cu from the sulfide melt inclusions is similar to that in the copper deposits emplaced in those magmatic rocks.

Results and interpretation

Sulfide melt inclusions are established in all the volcanic rock varieties from the four southern volcanic stripes of the Panagurishte ore region (form basalts to rhyolites). Sulfide inclusions are trapped in pyroxene and amphibole phenocrysts. Sulfide melt inclusions were not established in plagioclases, magnetites, biotites, quartz or the groundmass. They are predominantly spherical to oval with dimensions up to 35 microns but in rare cases such with complicated irregular shape or groups of inclusions are established (fig. 1). Those with complicated shape are disposed either in one surface (predestination from the crystal structure of the mineral host – fig. 1a) or irregularly in the volume of the mineral host (fig. 1b, c and e). The elongated shape of these inclusions is probably due to the gradual insertion of a relatively big sulfide melt bleb from the magma in the host mineral. The bigger part of the sulfide inclusions are pyrrhotites (determined under microscope and with microsond analyses – table 1) and also small occasional chalcopyrite melt inclusions were established (under the microscope).

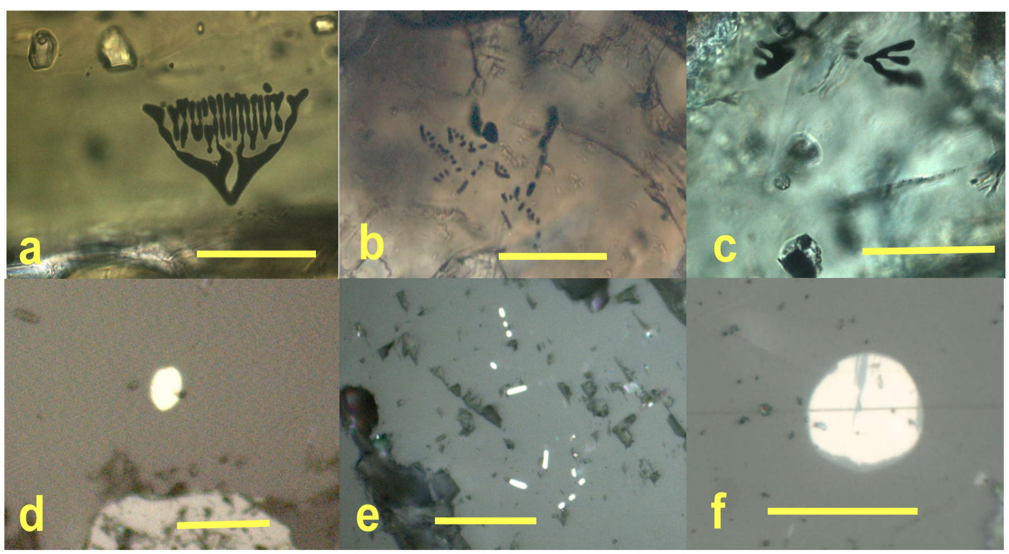

Fig. 1.Microphotographs of sulfide inclusions and group of inclusions in passing (a, b, c) and reflected (d, e, f) light in amphiboles and pyroxenes from volcanic rocks of the Panagurishte region. Scale bars – 50 microns.

The beginning of the crystallization for the observed mafic phenocrysts (pyroxenes and amphiboles) in the hydrous magma took place in intermediate magmatic chambers approximately at depth 15 to 25 km (pressures– 400-900 MPa - Nedialkov et al., 2006). The crystallization conditions in the hydrous magma at these depths are relatively reductive and the sulfur occurs as H_2S which favors the formation of the sulfide blebs. As mentioned above, sulfide blebs concentrate ore elements. The LA-ICP-MS analyses of sulfide (pyrrhotites) inclusions in amphiboles from volcanites of the Panagurishte region (fig. 2) show that they concentrate Cu, Ni, Au. The intensities for Au do not demonstrate a raised plateau but just irregularly dispersed pikes only in the melt inclusion. This could be related to the irregular distribution of Au in the sulfide melt inclusion as submicroscopic mineral segregations.

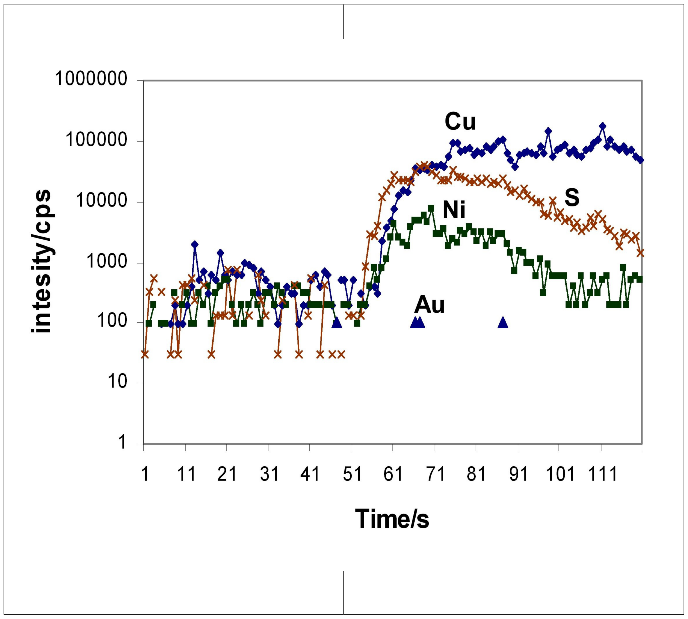

Fig. 2. Transient LA-ICP-MS signal of selected elements from sulfide melt inclusion in amphibole phenocryst in basaltic andesite.

sample	30	30	30	BKX	28	103
rock	Lat	Lat	Lat	Ban	Ban	Trach
Host min	Hb	Hb	Hb	Px	Hb	Px
Fe	61,01	61,15	62,09	57,79	57,39	62,88
S	38,32	39,23	35,78	38,26	41,65	36,14
Cu	0,55	0,00	2,45	3,55	0,37	0,14
Ni	0,00	0,00	0,20	0,37	0,33	0,44
Total	99,9	100,38	100,51	99,96	99,73	99,60
Fe	0,91	0,89	1,00	0,87	0,79	1,00
S	1,00	1,00	1,00	1,00	1,00	1,00
Cu	0,01	0,00	0,03	0,05	0,00	0,00
Ni	0,00	0,00	0,00	0,01	0,00	0,00

Table 1. Chemical composition of sulfide inclusions in mafic minerals from volcanites of the Panagurishte region. Abbreviations: Lat – latite; Ban – basaltic andesites; Trach – Trachyte; Hb – amphibole; CPx – Clinopyroxene;

Reduction conditions in the magma will preserve the existence of the sulfide segregates that leads to the inhibition of the ore bearing orthomagmatic fluids formation. Ore elements, trapped in the sulfide blebs could not be extracted with the exsolved from the magma fluids. The investigations on the Panagurishte volcanites show that oxygen fugacity increases with magmatic evolution (Nedialkov et al., 2006). Oxygen fugacity, with values more than 2 units above the NNO buffer, provoke the destruction of the sulfide blebs and the trapped ore elements move into the residual silicate melt. Thus they could be exsolved from the magma by aqueous fluids.

The presence of pyrrhotite inclusions, with determined composition, allows us to evaluate the S fugacity in the melts. Pyrrhotite composition was determined only from volcanites of the Assarel, Krasen-Petelovo and Pessovetz VS. Calculated fS_2 (after Toulmin & Barton, 1964) varies in a big interval from –9 to +6 probably due to the different conditions of magmatic evolution in the different VS and magmatic centers and to the influence of Cu and Ni concentrated in pyrrhotites. The estimated fO_2 in rhyolites from the Radka VS (after Spenser & Lindsley, 1981 – Ilm-Mt equilibrium) is 2,5 units below the Mt-Hm buffer at 770ºC. In such oxidation conditions sulfide blebs are destroyed and S and ore elements move in the residual silicate melt.

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Сулфидни включения в минерали от вулканските скали на Панагюрския руден район, България

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Панагюрския руден район вмества едни от най-значимите рудни находища на мед и злато, които са обект на всестранно изследване от много години. Един от по слабо изучените проблеми е за ролята и произхода на сярата в процеса на формирането на тези находища, където преобладават сулфидните минерали. Изхождайки от позицията на ортомагматичния характер на хидротермалните системи, в настоящата работа е обърнато внимание на поведението и формата на присъствието на сярата през магматичния период на съществуването на магматогенно-рудните системи. Установяването на сулфидни включения (пиротин и по-рядко халкопирит) във фемичните фенокристали на вулканитите от Панагюрския руден район са указание за относително високия потенциал на сярата и за относително редукционната обстановка при началото на кристализационния процес (при fO_2 между QMF и NNO буфери). Сулфидни включения с размери до 35 микрона са установени в практически всички скални разновидности. По морфология те са предимно сферични до яйцевидни, но се срещат и включения със сложна морфология. Сулфидните обособления се явяват концентратори на халкофилните рудни елементи през магматичния етап. При повишаването на фугитивността на кислорода при стойности повече от две единици над NNO буфер Сулфидните включения се разрушават и освобождават сярата и рудните компоненти в остатъчната силикатна топилка, от където те са в състояние да преминат в отделящите се от магмата надкритични водни разтвори.

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