FLUID–SALT–MELT EVOLUTION AND SOURCES OF FLUIDS AT THE BANSKA ŠTIAVNICA EPITHERMAL ORE–FORMING SYSTEM, CENTRAL SLOVAKIA

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Abstract: To investigate the possible genetic link between magmatic and hydrothermal activity in the Banska Štiavnica epithermal ore-forming system, paragenetically constrained melt, salt and fluid inclusions in magmatic quartz and vein minerals were studied using microthermometric, electron microprobe and stable isotope techniques.

Key words: fluid-salt-melt inclusions, ore-forming system, Banska Štiavnica, stable isotopes, epithermal

Introduction

It has long accepted that epithermal ore-forming systems are formed at shallow levels by circulation hydrothermal solutions, and are genetically related to magmatic rocks. Intrusive magmatic bodies are generally regarded as providing heat to drive convecting hydrothermal cell (Berger, Bethke, 1985). However, despite the fact that most epithermal deposits demonstrate close spatial and temporal associations with magmatic rocks, the sources of fluids in hydrothermal solutions remain controversial.

This contribution presents the results of detailed study of primary melt, and primary and secondary fluid inclusions, and stable isotope in magmatic and hydrothermal minerals from Banska Štiavnica. These data provide further evidence for the close genetic association between magmatism and epithermal oregenesis.

Geology

The Banska Štiavnica ore-forming system and of the same name orefield is located in Central Slovakia, in the central part of the large-scale (> 2000 km^2) Neogene andesitic stratovolcano. Evolution of the stratovolcano progressed beyond the caldera stage. Final uplifting of the central zone, formed a geologically recent and well defined horst. The magmatic rocks of subvolcanic intrusive complex (granodiorite and quartz-diorite porphyries, diorites and granodiorites) belong to calc-alcali series. Ring-shaped extrusive and dykes of rhyolite formation encompassing horst represent a component of the central zone (Konečny et al., 1995).

The Banska Štiavnica stratovolcano, including an extensive subvolcanic intrusive complex, sizeable caldera and remarkable resurgent horst, host many types of ore mineralization: high-sulphidation (related to the subvolcanic diorite intrusion; Šobov), magnetite skarn (at contacts of subvolcanic granodiorite pluton with Mezozoic carbonate rocks; Vihne-Klocoč), porphyry/skarn Cu±Mo,Au (related to granodiorite / quartz-diorite porphyry dyke clusters and stocks around the granodiorite pluton; Zlatno, Šementlov), stockwork/disseminated base-metals ores (in apical part of the granodiorite pluton; Rozalia mine), intrusion related subepithermal (after R. Sillitoe) gold-quartz vein (in andesitic environment just above the granodiorite pluton: Svetozar-Rozalia mine), and low-sulphidation epithermal precious-base metals vein systems (at faults of the resurgent horst; Biber, Špitaler, Terazia, etc.) (Lexa et al., 1999). The epithermal Au-Ag- base metals type mineralization (nearly of 120 ore vein systems) is situated around subvolcanic intrusive complex and is the most abundant and economically most important in this orefield. The Au-Ag-quartz vein mineralization is associated to rhyolite bodies which are formed after granodiorite massif.

Results and discussion

We are studied primary melt-salt-fluid fluid inclusions in magmatic quartz from granodiorite and rhyolite, and primary and secondary fluid inclusions in hydrothermal minerals of the Banska Štiavnica subepithermal and epithermal vein ores.

The primary melt inclusions (<3 to 42 μm) in magmatic quartz from granodiorites are composed of strongly birefringent silicate crystals, an insterstitial liquid phase and a fluid bubble liquid is likely to be a Mg-Na chloride aqueous solution with eutectic temperatures ranging from -38 to -34°C and estimated total salinity of 19.5-8.3 wt. % eq. NaCl. Dissolution of the vapor bubble into liquid occured at 258-302 °C, and silicate crystals commenced melting at ~600°C. Complete homogenization (melting of all dauther crystals) was achieved at 680-850 °C in several small (< 5 μm) inclusions (table 1). Pressure at these temperatures was estimated to be as high as 3.8-2.9 kbar using the method outlined by Naumov (1979). High H_2O abundances were also calculated in the silicate melt (5.8-4.2 wt%) using the technique described by Naumov (1979). The concentration of chlorine in the melt was calculated to be within 0.80-0.24 wt% (based on the assumption that all chlorides occur as NaCl).

A second population of inclusions (5-30 mm in diameter) containing highly mineralised brine (halite crystals, opaque phases, liquid and a vapour bubble), were observed along linear growth zones in magmatic quartz that also hosted silicate-salt melt inclusions. The salt inclusions typically decrepitate during heating, although in some experiments very small inclusions homogenise (i.e. dissolution of halite crystal) at 640-618 ^{0}C, and dissolution of the vapor bubble into liquid occured at 247- 235 °C. These data correspond to a fluid salinity of 80-77 wt.% eq. NaCl, and pressure of 4.0-3.6 kbar. Secondary fluid inclusions in magmatic quartz from granodiorites vary significantly in terms of their appearance, size and phase composition. The most abundant are multi-phase (liquid + vapour + various daughter minerals), three-phase with a halite crystal, and two-phase liquid-rich inclusions. Two-phase vapour-rich inclusions are relatively rare. From microthermometric work the observed and calculated variations in physical and chemical parameters of these fluid inclusions were: temperature 560 до 225 ^{0}C, salinity 68-1.5 wt% eq.NaCl, density 0.85-1.3 g/cm^3 and pressure from 2850 to 108 bar (table 1). These data indicate a progressive decrease in salinity of the fluid along the NaCl saturation line at high temperatures in the time of passage from magmatic to hydrothermal environments. A similar trend in pressure is also observed.

At 370-260 ^{0}C, the salinity and density of the fluid decreased abruptly. Fluid inclusions in minerals (quartz, barite, fluorite and sphalerite) from the epithermal precious-base metals ore veins comprise aqueous two-phase (liquid + vapour) types. These primary inclusions are often very large in size (up to 100-150 mμ) and are aligned along growth zones in crystals. Coexistence of liquid-rich and vapour-rich inclusions in the same growth zone demonstrates that the fluid was heterogeneous at the moment of trapping. The results of microthermometric work (table 1) on more than 2700 individual fluid inclusions in different vein minerals and sphalerite indicate that hydrothermal fluids were low-salinity (12.1-0.2 wt% eq.NaCl), Mg-Na chloride solutions, and that ore deposition occurred between 380-50 ^{0}C and 245 –7 bar (Kovalenker et al., 2002). The physical and chemical conditions of the oreforming process during this stage imply that the metal-bearing fluids were systematically displaced toward lower salinities, temperatures and pressures in comparison to the magmatic hydrothermal stage defined by inclusions in magmatic quartz.

The primary melt inclusions in magmatic quartz from rhyolite homogenise at 810-800 ºC and contain aqueous fluid. The concentration of water in the melt was estimated to be as high as 12.0- 10.5 wt.. %, the water pressure – as 3.1- 2.4 kbar, and the concentration of Cl in the melt - as 0.27- 0.21 wt. % (based on the assumption that all chlorides occur as NaCl).

Microprobe analysis of homogenious melt inclusions show that the concentration of Cl in the melt was high as 0.28-0.26 wt. %, and F – as 0.11- 0.10 wt. %. The composition of the main components is analogous to the bulk composition of rhyolites. Secondary inclusions of postmagmatic fluids in magmatic quartz from rhyolites have a broad range of temperatures (587-233 ºC), pressures (2220- 1190 bar) and salinities (67.7- 1.2 wt.%).

The occurrence of brine inclusions in magmatic rather than hydrothermal quartz, as well as their spatial and temporal association with silicate-salt melt inclusions, suggests that they represent a trapped late magmatic fluid phase. This implies that this phase was possibly transitional between silicate magma and later metal-bearing fluids involved in the formation of epithermal mineralisation. The evolution of these precursor ore-forming fluids is recorded in the secondary hypersaline to saline fluid inclusions in magmatic quartz. Salinity, density, temperature and pressure of this fluid systematically decrease towards the values of primary fluid inclusions in epithermal veins that host economic mineralisation. The abrupt decrease in salinities of these fluids from the NaCl saturation curve values between 260-370 ^{0}C can be interpreted as a result of mixing with meteoric water and subsequent dilution in the top of the cooling pluton or lower levels of the developing epithermal system.

This magmatic to meteoric evolution is also supported by the isotopic composition of water. Results of δD and δ^{18}O study of illite from Banska Štiavnica Au-Ag-base metals ores indicate that isotope composition of the water of oreforming solutions may be estimated at - 78 to – 95 ‰ δD and 3.3 to 4.5 ‰ δ^{18}O. Also was studied isotope composition of oxigen in quartz and barite from epithermal ores (Kovalenker et al., 2002). In accord with P. Kodera et al.(1999), δD and δ^{18}O values of Banska Štiavnica granodiorite primary magmatic waters changed from –55 to -82‰ and from 7.5 to 9.4‰, respectively. The calculated ranges of δ^{18}O oreforming fluids composition in equilibrium with quartz of IV productive stages (-1.0 to 5.1‰) and barite of V productive stages (-3.9 to – 7.6‰) suggest that the late mineralization formed from dominantly δ^{18}O depleted fluids, probably of meteoric origin.

The physico-chemical evolution of the fluid recorded in salt and fluid inclusions provides a sequential record of the development of the magmatic-hydrothermal system from the magmatic environment to the formation of ore-bearing veins in the epithermal environment. Further evidence in support of this magmatic-hydrothermal connection is the temporal association between the Banska Stiavnica hydrothermal system (alteration of country rocks and mineralisation), and the emplacement of the granodiorite pluton. In addition, possible source magmas were enriched in water (3-7 wt%) and chlorine (up to 0.5 wt%) based on data from primary melt and fluid inclusions in plagioclase from biotite-amphibole andesite, and in quartz and sanidine from biotite-sanidine rhyolite that comprise the comagmatic volcanic pile above the intrusive body (Naumov et al., 1996).

In summary, evidence for the proposed magmatic-hydrothermal transition at the Banska Stiavnica epithermal ore deposit includes: 1). The granodiorite magma was enriched in volatile elements, namely H_2O and Cl; 2). Highly concentrated chloride melts or brines were probably formed as a result of exsolution of H_2O-rich fluid during the later stages of silicate magma crystallisation; 3). Postmagmatic fluids trapped as secondary inclusions in magmatic quartz possess a range of salinities from hypersaline magmatic fluid to relatively low-salinity, epithermal near-surface fluid. Other parameters such as fluid pressure and density display similar variations.

Therefore, it is proposed that the granodiorite magma was the source of the epithermal metal-bearing fluids which form both subepithrmal Au-quartz and epithermal Au-Ag- base metal vein ores at Banska Štiavnica. Upon cooling, the magma exsolved hypersaline fluids that were capable of transporting ore-forming components. During cooling, the salinity of these magma derived brines decreased gradually along the NaCl aqueous solution saturation curve, and then decreased abruptly attaining values typical of epithermal ore-fluids . It is envisaged that this abrupt change in fluid saliniity at low temperature (370-260 ^{0}C) and associated decrease in fluid density and pressure resulted from the dilution of the brines via mixing with convecting meteoric waters (low temperature and salinity). It is also very likely that formation of Au-Ag-quartz vein epithermal ores were related to the emplacement of rhyolite intrusions during the final activity stages of the Banska Štiavnica.ore-forming system.

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Table 1. Summary of microthermometric data of melt, salt and fluid inclusions in magmatic and hydrothermal minerals from granodiorite, ryolite and epithermal vein ores at the Banska Štiavnica deposit

Object	**n**	**T, ºC**	**C, wt.% eq. NaCl**	**P, bar**
Magmatic rocks				
Granodiorite (melt)	20	850- 680	19.5- 8.3	3800- 2900
Granodiorite (magmatic fluid)	9	640- 618	79.7- 76.6	3970- 3640
Granodiorite (postmagmatic fluid)	106	560- 225	68.2- 1.4	2850- 110
Rhyolite (melt)	7	810- 800	10.4- 9.2	3100- 2410
Rhyolite (postmagmatic fluid)	105	587- 233	67.7- 1.2	2220- 1190
Epithermal vein systems				
Terezia	998	353-50	12.1- 0.2	100- 15
Biber	842	378- 145	11.6- 0.5	245- 7
Špitaler	355	295- 150	8.9- 1.4	60-20
Rozalia	70	313- 147	8.0- 1.7	10- 5
Svetozar	453	348- 162	6.5- 0.5	156- 60