Fluid inclusion and stable isotope study of the Kasejovice gold district, central Bohemia

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A b s t r a c t. Quartz gangue from the Variscan gold-bearing Kasejovice district (Jakub Mine) of the Moldanubian Drosendorf Unit, Bohemian Massif, was studied by fluid inclusion, stable isotope and SEM-CL techniques. Quartz of the early mineralization stage precipitated from a heterogeneous, unmixed, low-salinity (3.0–1.5 wt% NaCl eq.), H₂O-CO₂ fluid with minor admixture of other gases (CH₄, N₂, H₂S) at 2–1 kbar and 220–300 °C. Oxygen isotope signature of these fluids (δ^{18} O: +8.0 to +6‰ SMOW at 360–300 °C) is ambiguous with respect to the discrimination between deep crustal metamorphic and magmatic fluid sources, but the former one is more likely with respect to CO₂-CH₄-H₂O ratios. The late mineralization stages occurred mostly from aqueous-only fluids under decreasing temperatures (from ~200 to ~100 °C) and pressures (< 0.5 kbar). The observed variety of SEM-CL quartz textures includes oscillatory, growth and sector zoning and deformation related textures.

Key words: gold ores, hydrothermal processes, geochemical controls, fluid inclusions, stable isotopes, oxygen, pressure, temperature, Moldanubicum

Introduction

Gold deposits and occurrences in the intimate vicinity of the Central Bohemian plutonic complex (CBPC) formed during a narrow time interval (350–340 Ma, Zachariáš and Stein 2001), almost identical with that of intrusions of the CBPC (Holub et al. 1997a). They can be generally classified as mesothermal gold mineralizations that are, with respect to descriptive characteristics, more similar to Phanerozoic counterparts (e.g. Nesbitt 1991) than to the Precambrian ones (e.g. Groves and Foster 1991). Recently, the term orogenic-gold (Groves et al. 1998, Goldfarb et al. 2001) has been introduced instead of mesothermal.

The Kasejovice gold-mining district is one of numerous small-sized gold districts/occurrences (Fig. 1) located along the northwestern margin of the Central Bohemian plutonic complex, in the so-called Central Bohemian Metallogenic Zone (CBMZ; e.g. Morávek ed. 1995). Early mineralization stages of gold deposits within the CBMZ are usually characterized by deep crustal, low to moderate salinity, aqueous-carbonic metamorphic fluids, while the late stages by low-salinity, aqueous-only fluids (Zachariáš et al. 1997). In addition to this general pattern, a limited presence of magmatic fluids has been recently described from early stages of the Mokrsko (Boiron et al. 2001) and Petráčkova hora (Zachariáš et al. 2001) deposits.

The Kasejovice district is separated by a narrow, 3–5 km wide and N-S-trending, ore-barren zone from the Bělčice gold district in the east. The two districts are mineralogically quite similar, but differ mostly in the character of the host rock: metamorphic rocks (Kasejovice) vs. granitoids (Bělčice), and in relative abundance of molybdenite and scheelite. In addition, the Kasejovice district is the only gold district (within the CBMZ) with the presence of wolframite. Mining at Kasejovice took place mostly in

the 18th and 19th centuries and at the beginning of the 20th century. Total gold production (14th–20th centuries) is not known but was probably much less than 1 t.

Geology of the Kasejovice district and of the individual ore bodies was studied by Koutek (1946) and Váňa et al. (1980), mineralogy was studied by Hofmann (1906), Hofmann and Slavík (1913), Sobotka (1959, 1960), Litochleb (1984), Litochleb and Mrázek (1984), Litochleb et al. (1990), Litochleb and Šrein (1994) and more recently by Vymazalová (1997). In contrast to the extensive mineralogical studies, no research focused on the character of mineralizing fluids was conducted here. Only the presence of plentiful secondary fluid inclusion planes in quartz gangue was noted by Koutek (1946). The first results of the ongoing study of the Kasejovice district are presented and discussed in this paper.

Geology

The area of the Jakub Mine near Kasejovice (80 km SW of Prague) lies in the easternmost part of the Kasejovice outlier of the Drosendorf Unit of the Moldanubicum (e.g. Vrána et al. 1997, Matte 1991, Matte et al. 1990). It is built by LP-HT biotite-cordierite migmatites (migmatitized gneisses) with rare intercalations of calc-silicate gneisses and scarce intrusions of granite-porphyry and aplite dykes. In the north, east and south, the area under study is bordered by the Blatná granodiorite (dated by Pb-Pb single zircon evaporization at 346 ±10 Ma, Holub et al. 1997a) of the CBPC (Holub et al. 1997b, Janoušek et al. 1995, 2000). Low-grade rocks of the Kasejovice metamorphic islet (Proterozoic) are exposed further in the east.

Molybdenite of the gold-bearing quartz veins of the Bělčice district has been recently dated by Re-Os method at



Fig. 1. Distribution of the most important gold deposits within the Central Bohemian Metallogenic Zone. Small insert shows the position of Fig. 1 in the Bohemian Massif.

 338 ± 2 Ma (Zachariáš and Stein 2001). Molybdenites of other CBMZ gold deposits are slightly older (349–342 Ma, Zachariáš and Stein 2001) than the dated Bělčice sample.

Ore geology and mineralogy

The gold-bearing quartz veins are either hosted by mylonite zones (NE-SW) in the Moldanubian rocks or bound to local faults, subparallel to metamorphic foliation. Principal quartz veins strike NE-SW and dip 40–80° SE. Their along-strike length is 30 to 250 m and down-dip width 50–70 m. They are usually up to 0.5–1 m thick and irregular (lenticular) in shape. Gold grade varies from 2 to 20 g/t, exceptionally reaching 50 g/t. Small quartz veinlets, usually less than 20 mm thick and showing no preferred orientation, have much lower gold content (~ 1 g/t Au).

Litochleb (1984) and Litochleb and Mrázek (1984) distinguished four mineralization stages: *quartz stage* (wolframite ± scheelite, quartz-1, apatite, rutile, tourmaline, arsenopyrite and pyrite-1); *gold-bearing stage* (quartz-2, muscovite, chlorite, pyrite-2, pyrrhotite, chalcopyrite-1, molybdenite, native bismuth, bismuthinite, various Bi-Te-S phases and gold-1); *base metal "polymetallic"* (Sb-bismuthinite, cobellite, Bi-jamesonite, Biberthierite, Bi-andorite, Ag-tetrahedrite, chalcopyrite-2 and gold-2); and *calcite stage* (calcite, dolomite, pyrite-3).

Methods and samples used

The fluid inclusion microthermometry was conducted using Linkam THMSG 600 heating-freezing stage mounted on the Olympus BX-50 microscope with 20× and 50× ULWD objectives. The stage was calibrated using synthetic and natural standards at -56.6 °C (CO₂), 0 °C (H₂O), +31 °C (CO₂), +307 °C (NaNO₃) and +398 °C (K₂Cr₂O₃). Temperatures of measured phase transitions include: first melting temperature (T_{FM}), ice-melting temperature of last ice crystal (Tm-ice), melting temperature of solid CO2 (Tm-CO2), CO2-clathrate dissociation (Tm-cla), CO₂-homogenization temperature (Th-CO₂), total homogenization temperature (Th-tot) and temperature of decrepitation (Tdec). Homogenization occurred either to liquid (to L), or vapour (to V) states, or via critical mode (to C). Salinities were calculated as wt% equiv. NaCl using the equations of Bodnar (1993; for aqueous fluids) and Diamond (1992; for aqueous-carbonic fluids). Data of Thiery et al. (1994) were used to estimate the composition and molar volume of the gaseous phase of CO₂-bearing inclusions. The isochores were calculated using the equations of Zhang and Frantz (1987) or Bakker (1999) for H₂O-salt and H₂O-CO₂-CH₄-NaCl systems respectively.

The oxygen isotope composition of quartz and wolframite samples was determined by standard methods. Oxygen was liberated using bromine pentafluoride (Clayton and Mayeda 1963) at 500 °C at the Faculty of Science, Charles University, Prague. Isotope measurements were done with a Finnigan MAT 251 mass spectrometer in the laboratory of the Czech Geological Survey, Prague (by K. Žák). The total error of isotope measurement and of preparation procedure is not greater than $\pm 0.2\%$. Fluid composition was calculated using the Clayton et al. (1972) quartz-water fractionation equation.

Quartz textures were studied using the cathodoluminescence (SEM-CL) method at the laboratory of Slovak Geological Survey, Bratislava (operating conditions: 20–25 kV, 50–100 nA).

All the studied samples come from abandoned mine dumps of the Jakub Mine, 2 km NW of Kasejovice. Only vein quartz (quartz-1, see above) was studied.

Quartz textures (cathodoluminescence study)

Cathodoluminescence study revealed complex relationships not apparent from classic microscopic study. Small euhedral quartz grains growing directly on the wall-rock are usually sector-zoned (Fig. 2A, B). They are, in some cases, crosscut by narrow deformation zones (Fig. 2C) and overgrown by intimately zoned quartz (Fig. 2D). The volumetrically dominant massive coarse-grained quartz that corresponds to a vein core is usually relatively CL-homogeneous (Fig. 2E), or shows



Fig. 2. SEM-CL images of quartz gangue from the Jakub Mine, Kasejovice: A - quartz crystal with combination of sector and concentric zoning (section perpendicular to c-axis); B - sector-zoned quartz (section subparallel to c-axis); C - zone of younger quartz (arrow) related to a deformation prior to the growth of main quartz masses; D - intrasectorial growth zoning with a slight flexure – deformation (arrow) of growth zones at the boundary of two neighbouring quartz grains; E - CL-homogeneous quartz from the core of the vein. Bright tiny zones correspond to recrystallized quartz associated with the formation of fluid inclusion trails (secondary inclusions); F - mutual crosscutting of two fluid inclusion trails (subvertical trail is younger than the horizontal one).

only weak growth zoning in the youngest parts of quartz grains). In addition to these primary CL-features, zones

of quartz recrystallization related to secondary fluid inclusion trails can be identified (Fig. 2E, F).



Fig. 3. Aqueous-carbonic fluid inclusions: CO₂-melting (Tm-CO₂) vs. CO₂-homogenization (Th-CO₂) relationships of primary and pseudosecondary inclusions.



Fig. 4. Histograms of CO₂-homogenization temperatures for primary and pseudosecondary inclusions.

Fluid inclusion petrography

Two basic types of fluids were identified: aqueous-carbonic and aqueous. The aqueous-carbonic fluid inclusions are usually of primary or pseudosecondary origin, and occur as isolated 3D clusters or as short fluid inclusion secondary as "S" (in general sense), or as "S0 to S7 and S?" (when individual generations are discriminated; S0 being the oldest, S? are of unknown relative age). The S0 inclusions are aqueous-carbonic, the others (S1 to S7 and S?) are aqueous-only.

planes, respectively. They are usually subisometric, 20–5 μ m large and either two-phase (aqueous phase and liquid CO₂), or three-phase (aqueous phase, liquid and vapour CO₂) at room temperature. The degree of fill (F), expressed as CO₂-volume/total inclusion volume is highly variable (~0 to ~1). Secondary (S0, see below) aqueous-carbonic inclusions are very rare.

The aqueous fluid inclusions are of secondary origin only. They form numerous planes, frequently crosscutting one another. Individual inclusions are either two-phase, liquid-rich (2Lr), or one-phase, liquid (1L). The degree of fill (F; liquid volume/total inclusion volume) is relatively constant (0.9-0.95; 2Lr inclusions). In addition to planes with one type of fluid inclusions only (2Lr or 1L), planes with "mixed" (i.e. both 1L and 2Lr together) inclusions are common. The "mixed" fluid inclusion populations maintain constant degree of fill of the 2Lr inclusions. The relative amounts of 1L and 2Lr inclusions are constant for each individual secondary plane, but vary significantly when different planes are compared. Several generations of secondary fluid inclusion planes were distinguished, based on: a) crosscutting relationships; b) variations in relative amounts of 2Lr and 1L inclusions; and c) microthermometric data. In addition to this, the relative timing of some secondary fluid inclusion planes was tested using the SEM-CL.

The primary and pseudosecondary inclusions are further abbreviated as "P" or "PS", the

Microthermometry

The first melting temperatures (T_{FM}) of both primary and secondary inclusions (Table 1) vary significantly: -49 °C (P), -56 to -52 °C (PS, S0, S1, S3), -42 °C (S2c), -39 to -35 °C (S2b, S2d, S4, S5) and ~ -32 °C (S?, S7). With respect to published data (e.g. Borisenko 1977, Crawford 1981), they can be interpreted in terms of dominating salt systems: H₂O-CaCl₂ (P-inclusions); H₂O-NaCl-CaCl₂ (PS, S0, S1, S3); H₂O-NaCl-FeCl₂-(MgCl₂?) (S4, S5) and H₂O-MgCl₂ (S?, S7).

Primary (P) aqueous-carbonic inclusions: Tm-CO₂ varies from -62.0 °C to -56.6 °C. Temperatures lower than -58 °C are scarce (Fig. 3). Th-CO₂ (always to L) is largely scattered (-8.1 to +28.8 °C; mode at 23.0 °C, Fig. 4) and positively correlates with the degree of fill (Fig. 5). Tm-cla (+8.1 to +9.8 °C, mode at +8.7 °C) indicates low salinities from 0.4 to 3.7 wt% eq. NaCl. The final homogenization (Th-tot) is either to vapour state (+350 to +268 °C), or to liquid (+297 to +220 °C) or critical (+297 to +288 °C). Correlation of Tm-CO₂ and Th-CO₂ (Fig. 3) indicates low admixture (from 0 to 4.5 mol%) of CH₄ and/or N₂ in gaseous phase, with the exception of scarce inclusions with $Tm-CO_2 < -60$ °C where 10-20 mol% of CH₄ is present. Raman microanalyses of three P-inclusions indicated the following composition of the gaseous phase: 87.9-94.4 mol% CO2, 1.6-2.0 mol% CH₄, 3.1–9.6 mol% N_2 , 0.5-0.9 mol% H₂S.

Pseudosecondary (PS) aqueous-carbonic inclusions: Tm-CO₂: -56.9 to -56.6 °C; Tm-cla: +8.9 to +9.3 °C; salinity: 1.4 to 2.2 wt% eq. NaCl; Table 1. A summary of microthermometric characteristics of secondary fluid inclusions. The S0 ones are aqueous-carbonic, the S1 trough S7 are aqueous-only.

| Туре | T _{FM} | Tm-ice | wt% NaCl eq. | Th-tot ¹ | Th-tot (mode) | Note: |
|------------|-----------------|--------------|--------------|---------------------|---------------|------------------|
| S0 | -53.0 | | ? | 368-349 (to L) | 350 | *(+8.3 to +12.3) |
| | | | | 360-350 (to V) | | |
| | | | | 350 (to C) | | |
| S1 | -56.0 | -6.5 to -6.1 | 9.9–9.3 | 210-95 | 165 | |
| S2a | ? | -6.2 to -5.7 | 9.5-8.8 | | | |
| S 3 | -56 to -52 | -3.6 to -0.1 | 5.9-0.2 | 174–154 | 169 | |
| S2b | -42 | -0.7 | 1.2 | 149-105 | 127 | *(+8.2 to +8.4) |
| S2c | -38 to -35 | -3.7 to -3.3 | 6.0-5.4 | 158-129 | 155 | |
| S2d | -35.4 | -5.2 to -3.7 | 8.1-6.0 | 122–95 | 115 | |
| S 4 | -39 | -1.6 to -0.2 | 2.7-0.4 | 139-133 | 138 | |
| S5 | -38 | -1.4 to -0.3 | 2.4-0.5 | 138-118 | 126 | |
| S? | -32 | -2.8 to -2.3 | 4.6-3.9 | 187-165 | 172 | |
| S7a | -32 | -1.6 to -1.5 | 2.7-2.6 | 174–165 | 169 | |
| S7b | -32 | -0.8 to -0.7 | 1.4-1.2 | 149-126 | 143 | |

Notes: ¹homogenization to liquid state (if not indicated otherwise), total range; * clathrate-like melting behaviour (an exceptional feature of some inclusions only)



Fig. 5. Relation of partial (Th-CO₂) and total (Th-tot) homogenization temperatures to the bulk ratio of CO₂ and H₂O (i.e. degree of fill, $F = H_2O/(CO_2+H_2O)$). Absence of Th-CO₂ lower than 10 °C for primary fluid inclusions with visible H₂O-phase (F > 0.2) allows to suggest that CO₂-inclusions with Th-CO₂ < 10 °C are not related to fluid unmixing processes indicated by large variations in F for both primary and pseudosec-ondary inclusions. The lowest range (200–240 °C) of Th-tot may be indicative of real trapping temperatures of primary and secondary inclusions.



Fig. 6. Salinity vs. total homogenization temperature diagram of primary (P), pseudosecondary (PS) and secondary (S) inclusions. Primary (square symbols) and pseudosecondary (diamond symbols) inclusions with vapour, liquid and critical total homogenization are shown by open, black-filled and grey-filled symbols, respectively. Individual groups of secondary inclusions with $T_{FM} \sim -32$ °C and -49°C to -56 °C are highlighted by open and filled ellipses, respectively, and by thick lines labelled trend A and trend B, respectively.

Th-CO₂: +11.0 to +28.3 °C (always to L, Fig. 2), Th-tot: +300 to +257 °C (to V), +251 to +215 °C (to L) and +237 °C (to C).

The microthermometric characteristics of secondary inclusions are summarized in Table 1. Individual inclusion populations, represented by data for each individual secondary plane, are relatively homogeneous (Fig. 6).

Oxygen isotopes

Two samples of vein quartz (quartz-1, massive type from vein core) with wolframite were analysed for oxygen isotopes. The measured δ^{18} O (SMOW) compositions of quartz-1 are quite homogeneous (+13.8 and +13.7‰), while that of wolframite slightly varies (+7.6 and +8.0‰). There are three different fractionation factor curves for quartz-wolframite mineral pairs known to date: Landis and Rye (1974), Zheng (1992) and Zhang et al. (1994). Of these only the theoretical equation of Zheng (1992) gives reasonable estimated temperatures for our quartz and wolframite data – 360 ±20 °C. [That of Landis and Rye (1974) is not applicable because of small $\Delta_{qtz-wolf}$ difference of 6‰ only. Experimental equation of Zhang (1994) yielded too high temperature of 500 ±20 °C that is not supported by our fluid inclusion data from cogenetic quartz.]

The estimated fluid composition (δ^{18} O) is +8‰ SMOW at 360 °C. If temperatures obtained from primary fluid inclusion (Th-tot: 350–225 °C) are combined with the quartz-isotope data, then the δ^{18} O composition of corresponding hydrothermal fluid would lie in the interval of +8 to +3‰ SMOW.

Discussion of a hydrothermal model for the Kasejovice district

The precipitation of the quartz gangue (quartz-1) is related to low salinity aqueous-carbonic fluids (P and PS inclusions), oxygen isotopic signatures ($\delta^{18}O_{fluid}$: +8 to

+6‰ SMOW at 360 to 300 °C) of which do not allow distinguishing between deep crustal metamorphic or magmatic fluids. Salinities and homogenization temperatures (Th-tot) of primary (P) inclusions are slightly higher than those of pseudosecondary (PS) ones (Fig. 6). Both P and PS inclusions have highly variable H₂O/CO₂ ratios (Fig. 5) and homogenize both to vapour and liquid states (few inclusions displayed also the critical behaviour). This may be indicative for a trapping from a heterogeneous fluid. Unambiguous interpretation, however, is not possible. If heterogeneous trapping occurred, the lowest Th-tot (250-220 °C) could be interpreted as trapping temperatures; otherwise (i.e. for homogeneous trapping) the trapping temperatures could be 300-350 °C or higher. Temperatures estimated by oxygen isotope thermometry (quartz-wolframite mineral pair) correspond to 360 °C.

In contrast to the primary and pseudosecondary inclusions, the salinities of secondary (S) inclusions vary significantly (Fig. 6). The T_{FM} data indicate unambiguously at least two distinct salt systems (H2O-NaCl-CaCl2 and H₂O-MgCl₂). In addition, the presence of FeCl₂ cannot be excluded. Both salt systems evolve from a higher salinity - higher temperature fluids towards low salinity - lower temperature fluids during the evolution of individual types of secondary fluid inclusions (Fig. 6; trends A and B for H₂O-NaCl-CaCl₂ and H₂O-MgCl₂ fluids, respectively). Such a large decrease in salinity, accompanied by minor changes in Th-tot, can be explained by a mixing with a low-salinity, 120-100 °C hot fluid only. A concomitant decrease in temperature and salinity (trend C, dotted arrows, Fig. 6), indicated by one-phase liquid fluid inclusions, could be induced by rapid fluid cooling due to a large temperature difference between the fluid and the host quartz.

Sector zoning of the oldest quartz grains (within one vein structure) indicates rapid growth and disequilibrium partitioning on crystallographically non-equivalent faces (Reeder 1991, Kerestedjian 1997). Euhedral habitus of such grains testifies for open-space filling. Subsequent sudden increase in the grain-size and general absence of remarkable CL-zoning in such grains testify for a change in kinetics of quartz precipitation and probably also in fluid dynamics during the precipitation of vein core zones.

Isochores for representative fluids trapped in primary and in secondary inclusions are shown in Fig. 7. Conditions of supposed quartz-1 deposition are marked by a shadowed polygon. This region corresponds to trapping of H₂O-rich and CO₂-rich end-members of the unmixed H₂O-CO₂-CH₄-salt fluid. Based on comparison with experimental H₂O-CO₂-NaCl solvus (dashed-dotted lines labelled 5, 10, 30 for fluids containing 5, 10, 30 mol% CO₂ and 2 wt% NaCl; interpolated from data of Bowers and Helgeson 1983) it can be deduced that the CO₂ content in the original homogeneous fluid (i.e. before unmixing) varied approximately between 25 and 7 mol%. The absence of primary inclusions trapped unambiguously from a homogeneous fluid can be explained by extensional



Fig. 7. Fluid inclusion isochores for representative fluid types. Thick double arrowed line represents a hypothetical P-T path of mineralizing stages. The shadowed polygon corresponds to the most probable field of trapping of unmixed aqueous-carbonic fluids representative of the quartz stage, the ellipses correspond to younger mineralization stages (goldbearing ?, base-metal and calcite). The dashed-dotted lines correspond to H₂O-CO₂ solvi for 5, 10 and 30 mol% CO₂ and 2 wt% NaCl (interpolated from the data of Bowers and Helgeson 1983).

character of quartz veins, the formation of which was accompanied by a sudden decrease in fluid pressure and subsequent fluid heterogenization.

In contrast to the quartz stage, exact P-T-X conditions of the gold-bearing stage are difficult to assess. It is clear that the fluid responsible for precipitation of gold must be one (or more) of those trapped in pseudosecondary or secondary inclusions. It should therefore correspond to isochores for either late aqueous-carbonic inclusions (PS or S0) or early secondary aqueous-only ones (S1-S3). The presence of H₂S in the gaseous phase of P inclusions allows to suggest that the Au(HS)⁻² complex can be held responsible for gold transport. The mineralogical variety of gold-bearing and base-metal mineralization stages could be related to the complexity of salt systems of aqueous fluids.

The evolution (P-T path and fluid composition) of the Kasejovice mineralization is generally similar to other Variscan gold deposits in the Central Bohemian Metallogenic Zone (Zachariáš et al. 1997, Morávek et al. 1992, Boiron et al. 2001). In details, however, it differs in slightly lower temperatures of the first (i.e. quartz) mineralization stage and in much larger compositional variety of aqueous fluids during the late hydrothermal stages. The P-T-X fluid evolution of the Kasejovice district is similar also to the characteristics of the general model of European Variscan gold mineralizations (Cathelineau et al. 2000).

Conclusions

The early mineralization stages of the Kasejovice district evolved from a complex H₂O-CO₂-CH₄-N₂-H₂S-CaCl₂-NaCl (XCO₂: 0.25–0.07), low salinity (3.0–1.5 wt% NaCl eq.) fluid. The precipitation of quartz gangue occurred most probably at 2–1 kbar and 220–300 °C from unmixed aqueous-carbonic fluid. The late mineralization stages occurred from aqueous fluids at temperatures from ~200 to ~100 °C and pressures of about < 0.5 kbar. Isotope composition of early fluids (i.e. quartz stage; δ^{18} Of_{fluid}: +8 to +6‰ δ^{18} O SMOW at 360–300 °C) does not allow discriminating between deep-crustal metamorphic and magmatic fluids. With respect to the suggested temperatures of quartz precipitation and fluid composition (i.e. CO₂-CH₄-H₂O ratio), a metamorphic source is, however, more likely.

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