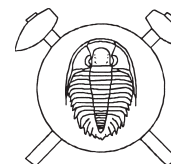


# Interpretation of bidimensional fluid inclusion microthermometric data in terms of pressure and compositional variations in gold-bearing fluids: an example from the Libčice and Kasejovice deposits, Czech Republic



**Interpretace dvourozměrných mikrotermometrických měření  
fluidních inkluzí vzhledem k variacím ve složení a tlaku zlatonosných fluid:  
příklady z ložisek Libčice a Kasejovice, Česká republika**

(10 figs)

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Systematic mapping of selected fluid inclusion microthermometric characteristics is combined with standard microscopy and various cathodoluminescence techniques to provide detailed information on the evolution of pressure, temperature and compositional variations in hydrothermal fluids. The advantage of such a complex approach is demonstrated on samples from Variscan mesothermal gold deposits of Libčice and Kasejovice in Central Bohemia.

Primary fluid inclusions from remnants of original quartz grains were studied at the Libčice deposit. They display systematic zoning of CO<sub>2</sub>-melting and homogenization temperatures [Tm-CO<sub>2</sub>: -57.5 to -65.0 °C and Th-CO<sub>2</sub>: +24 to -21 °C (always to liquid)], and little variation in the other parameters [salinity: 1–5 wt. % NaCl eq., total homogenization: +340 to +370 °C (to liquid, or critical), degree of fill: ~0.5]. These variations reflect an increase in the amount of CH<sub>4</sub> in the gaseous phase of fluid inclusions from 1 to 50 mol. % from the cores towards the rims of quartz grains. In addition, variations in fluid density (0.70–0.88 g/cm<sup>3</sup>) were observed.

The data are discussed in terms of P-T-X variations: the difference in fluid pressure between the grain core and grain rim during quartz gangue precipitation is estimated to equal nearly 2000 bars. The gradual evolution of CH<sub>4</sub>/CO<sub>2</sub> ratio is interpreted as being due to mixing between initial CO<sub>2</sub>-rich fluids of deep provenance with local CH<sub>4</sub>-enriched fluids. The former were probably produced by large-scale regional devolatilization, while the latter are a result of local “in situ” devolatilization of organic carbon-rich Lečice Member black shales in a narrow contact-metamorphic zone of the CBPC.

An example of a trail of secondary aqueous fluid inclusions from the Kasejovice deposit exhibits systematic variations in the total homogenization temperatures (+180 to +130 °C, to liquid). These are interpreted as pressure and temperature variations during sealing of microfractures.

## Introduction

Fluid inclusions represent a useful tool for genetic studies of various geological objects. They allow estimation of the fluid temperature, pressure and composition on the basis of microthermometric studies. The method has been described in detail in numerous papers (e.g., Roedder 1984, Shepherd et al. 1985, De Vivo and Frezzotti, eds. 1995).

Interpretation of microthermometric data, however, may not be simple in some cases. The difficulties may result largely from: 1) our ability to properly distinguish individual inclusion populations, 2) natural variations in P-T-X conditions of hydrothermal systems, and 3) secondary (i.e., post-entrapment) processes (like leakage, diffusion, phase precipitation) that can modify fluid properties.

Microthermometric data are usually collected more or less randomly using the most suitable inclusions found in the studied sample. Systematic measuring of fluid inclusions, with respect to their two-dimensional (2D) distribution on a sample/grain scale is, however, rarely carried out. The main aim of this paper is therefore to demonstrate the advantage of this approach in the interpretation of complex natural assemblages of fluid inclusions. Two examples are given from the Libčice and Kasejovice gold districts in central Bohemia.

## Brief summary of geology and mineralogy of studied localities

### Libčice deposit

The Libčice deposit (Fig. 1, historical gold production < 0.2 t) and two other small districts (Borotice and Nový Knín) in its proximity are located only about 10 km away from the well-known large-tonnage Mokrsko deposit (e.g., Morávek et al. 1989, Morávek ed. 1995, ~100 t of gold reserves). The geology of the deposit was studied by Malachov (1953) and Havlíček (1959). Its petrology and mineralogy were recently summarized by Šrein et al. (1995).

The deposit is situated in Neoproterozoic intermediate to acid volcanic rocks of the Kozí Hory Belt, in a narrow contact-metamorphic aureole of the Variscan Central Bohemian Plutonic Complex (CBPC). The volcanic rocks are overlain by silicified Neoproterozoic black shales (Lečice Member) formed in euxinic conditions during a long period of basin starvation (Suchý 1992). They are rich in organic carbon (kerogen; up to 1.5 wt. % of C<sub>org</sub>) and pyrite (up to 2 wt. % S). The Neoproterozoic volcanic rocks with ore-bearing structures are underlain by peripheral biotite granite (CBPC) at depths of 300–500 m under the surface. In some places in the mine, the peripheral granite cuts and the associated aplite dykes crosscut

the gold-bearing structures (quartz veins). In addition, the thermal effect of Variscan intrusives also caused recrystallization of the original vein quartz, and transformation of the original carbonate gangue to rare calc-silicate (skarnoid) assemblage.

The Libčice deposit thus represents unique evidence for intimate relationships between the Variscan gold-bearing processes and the Variscan late magmatic activity. With respect to other geological aspects, it is unique in its having the form of a single quartz vein system and in the abundance of pyrrhotite (hexagonal) and its predominance over other sulphides (arsenopyrite, loellingite, pyrite).

The ore structure – “main quartz vein” – is 400 m long along the strike and only 0.2 to 0.4 m thick (on an average). It is spatially associated with an E-W striking sub-vertical dyke of lamprophyre (of unknown but pre-granite age). Gold is present in two generations (> 950/1000, 900–850/1000) and accompanied by accessory Bi-Te-S minerals (Šrein et al. 1995, Litochleb and Šrein 1994).

#### Kasejovice district

The Kasejovice ore district (Fig. 1, e.g., Koutek 1944, Váňa et al. 1988) is formed mostly by high-grade Moldanubian migmatites. Mineralization is represented by gold-bearing quartz veins with a minor presence of wolframite, molybdenite, arsenopyrite, pyrite and other min-

erals (Litochleb 1984, Litochleb and Mrázek 1984 and references therein). The studied sample was obtained from the dumps of the abandoned Jakub Mine. Fluid inclusions, stable isotopes and quartz textures (SEM-CL cathodoluminescence) were studied by Zachariáš and Pudilová (2002). The formation of gold bearing quartz veins is related to complex intrusive – metamorphic – hydrothermal event(s) occurring along the northwestern contact of the CBPC. In contrast to the Libčice deposit, the quartz veins at Kasejovice show no signs of thermal recrystallization. A wide variety of Pb-Sb-S minerals (younger than gold) can be related with fluids that now occur in numerous aqueous fluid inclusion trails (healed microcracks with secondary fluid inclusions). These were formed during a period of regional uplift (at  $P < 90$  MPa).

#### Methods

Samples for microthermometric study were selected on the basis of preliminary microscopic and microthermometric studies. The fluid inclusion wafers as well as individual chips of broken wafers were documented by the Olympus CZ-2000 digital camera. These photos were used for construction of inclusion distribution maps on a sample/grain scale. Data isolines were calculated and drawn by Surfer® software.

Microthermometry was carried out using a Linkam THMSG 600 heating-freezing stage mounted on an Olympus BX-50 microscope with 20x and 50x ULWD lenses. The stage was calibrated monthly using synthetic and natural standards at  $-56.6$  °C ( $\text{CO}_2$ ),  $0$  °C ( $\text{H}_2\text{O}$ ),  $+31$  °C ( $\text{CO}_2$ ),  $+307$  °C ( $\text{NaNO}_3$ ) and  $+398$  °C ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), but the  $\text{CO}_2$ -melting ( $-56.6$  °C) and homogenization ( $+31$  °C) temperatures were checked daily during measurements. The temperatures of the measured phase transitions include: first melting temperature ( $T_{\text{fm}}$ ), ice-melting temperature of the last ice crystal ( $T_{\text{m-ice}}$ ), melting temperature of the solid  $\text{CO}_2$  ( $T_{\text{m-CO}_2}$ ),  $\text{CO}_2$ -clathrate dissociation ( $T_{\text{m-cla}}$ ),  $\text{CO}_2$ -homogenization temperature ( $T_{\text{h-CO}_2}$ ), total homogenization temperature ( $T_{\text{h-tot}}$ ) and temperature of decrepitation ( $T_{\text{dec}}$ ). Homogenization occurred mostly to the liquid (L) and rarely to the vapour (V) or the critical (C) state. Salinities were calculated as wt. % equiv. NaCl using the equations of Bodnar (1993; for aqueous fluids) and Diamond (1992; for aqueous-carbonic fluids). The data of Thiery et al. (1994) were used for estimation of the composition and molar volume of the gaseous phase of  $\text{CO}_2$ -bearing inclusions. The isochores were calculated using the equations of Zheng and Frantz (1987) or Bakker (1999), for the  $\text{H}_2\text{O}$ -salt and for the  $\text{H}_2\text{O}$ - $\text{CO}_2$ - $\text{CH}_4$ -NaCl systems, respectively. The bulk fluid composition was calculated using BULK v. 01/02 (Bakker 2001) program, the partial pressures and fugacity coefficients of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  were calculated using Loner 8 program (Bakker 1999).

Quartz textures were studied by the cathodoluminescence method (SEM-CL) in the laboratory of the Slovak Geological Survey, Bratislava (operating conditions: 20–

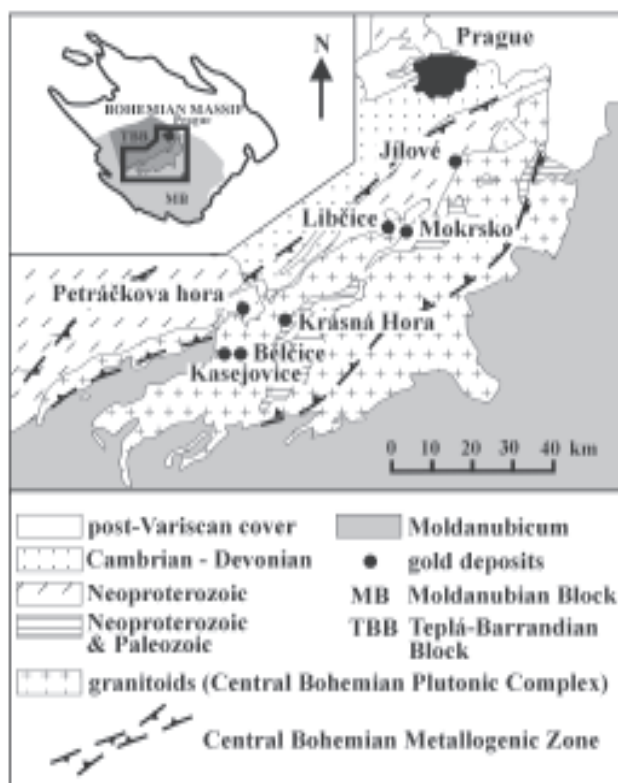


Fig. 1 Distribution of gold deposits within the Central Bohemian Metallogenic Zone. The small insert shows the position of the map area in the Bohemian Massif.

25 kV, 50–100 nA). In order to prevent partial or total decrepitation of fluid inclusions during CL studies (due to a local overheating of a sample surface), wafer chips were studied after fluid inclusion microthermometry and/or an additional polished thin section was prepared from the sample block after the original wafer preparation.

## Results

### Libčice deposit: quartz textures

The quartz of the main vein from the Libčice deposit displays variable degrees of recrystallization: 1) complete recrystallization manifested by saccharoidal texture, regular triple junctions and the absence of any remnants of the original grains (up to ~50 m from the granite contact); 2) partial recrystallization – the grains of the original quartz are more or less randomly preserved and surrounded by newly formed recrystallization-related grains. The disintegration of the original quartz is mediated by the mechanism of grain boundary migration and implies the significant presence of a fluid phase. The grains of the original quartz can be recognized also by their larger size, by more irregular shape (not always) and by dark appearance due to the presence of large quantities of fluid inclusions (Fig. 2a). In contrast to the original grains, fluid inclusions are scarce or absent in the recrystallized quartz. Interfaces of many recrystallized quartz grains also host frequent fluid inclusions, but these usually are not suitable for microthermometry because of their poor transparency. Surprisingly, almost no difference exists in luminescence (studied by SEM-CL) between the original and recrystallized quartz grains. This implies similar trace-element chemistry and similar crystal defects in both types of quartz.

### Libčice deposit: fluid inclusions

Only primary or primary-looking fluid inclusions are discussed in this chapter. They are aqueous-carbonic ( $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{NaCl}-\text{CaCl}_2$ ), mostly two-phase liquid-rich (L+V), rarely three-phase liquid-rich (L, L- $\text{CO}_2$ , V- $\text{CO}_2$ ) or one-phase vapour (V) at room temperature. They vary in size from 10 to 25  $\mu\text{m}$ , their shape is mostly regular and rounded (Fig. 2b). The degree of fill [Fv; expressed as  $L/(L+V)$  ratio] is scattered around a value of 0.5 in the original quartz grains (Fig. 3a,b) but is more variable in the recrystallized quartz ( $Fv = 0-0.95$ ; Fig. 3c). The Fv value was estimated either visually (Fig. 3a and 3c), or calculated using an ellipsoid 3D volume model (Fig. 3b), based on the long and short inclusion axis and on the bubble diameter measurements. The comparison between the visually estimated and calculated Fv values is relatively good (Fig. 3a vs. Fig. 3b); however, the latter is more variable. To simplify the interpretation and calculation of fluid properties, an average Fv value of 0.48 only was used throughout all the calculations in this paper related to original quartz grains.

The homogenization of  $\text{CO}_2$  (Th- $\text{CO}_2$ ) occurred mostly to a liquid from  $-22$  to  $+23$  °C (Fig. 4a). The melting temperatures of  $\text{CO}_2$  (Tm- $\text{CO}_2$ ) vary significantly (from  $-57.5$  to  $-65.0$  °C) in both the original and the recrystallized quartz grains and correlate well with Th- $\text{CO}_2$  (Fig. 4b). This correlation was interpreted in terms of a binary  $\text{CO}_2-\text{CH}_4$  system as an admixture of 1.5 to 52 mol. % of  $\text{CH}_4$  in gaseous phase of fluid inclusions (for Tm- $\text{CO}_2 < -65$  °C, significant admixture of  $\text{N}_2$  can be excluded on the basis of the data of Thiery 1994). In addition to the Tm- $\text{CO}_2$  vs. Th- $\text{CO}_2$  correlation, systematic zoning of Th- $\text{CO}_2$  (Fig. 5) and consequently also of Tm- $\text{CO}_2$  was observed in grains of the original quartz. The Th- $\text{CO}_2$  was always

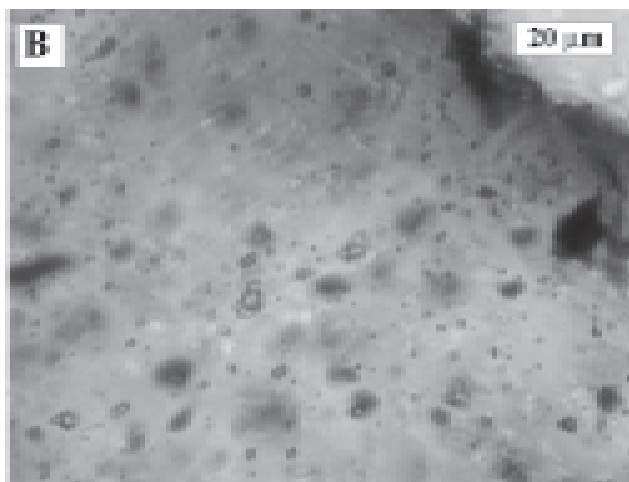
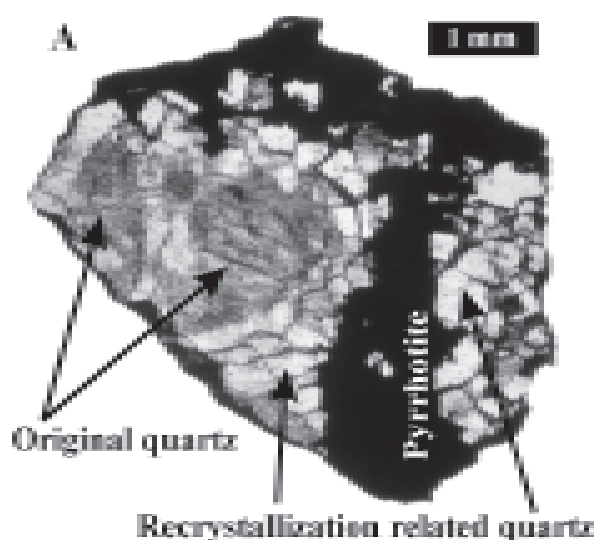


Fig. 2 A – Partially recrystallized quartz gangue from the Libčice deposit. The large dark grains represent remnants of original pre-metamorphic hydrothermal quartz. Sample thickness is 0.25 mm, photo in transmitted light. B – Example of fluid inclusions from the original quartz grain, Libčice deposit, transmitted light.

highest in the cores of the studied grains, but gradually decreased towards the rim (Fig. 5) – usually down to  $-5^{\circ}\text{C}$ , but locally values as low as  $-22^{\circ}\text{C}$  were recorded.

The salinity of the aqueous phase is estimated at 1.5 to 5 wt. % NaCl eq. (a value of 3 wt. % NaCl was used

throughout all calculations presented here). The temperatures of the first melting ( $T_{\text{fm}}$ :  $-49$  to  $-37^{\circ}\text{C}$ ) indicate the presence of  $\text{CaCl}_2$  and  $\text{MgCl}_2$ . The presence of limited amounts of  $\text{FeCl}_2$  and/or  $\text{NaCl}$  cannot be, however, excluded.

The total homogenization temperatures are clustered between  $345$ – $355^{\circ}\text{C}$  (to C),  $360$ – $370^{\circ}\text{C}$  (to V) for sample Li 11 and around  $300 \pm 10^{\circ}\text{C}$  (to L and V; sample Li 7). The inclusions with  $T_{\text{tot}} > 340^{\circ}\text{C}$  frequently decrepitated before inclusion homogenization.

#### Kasejovice deposit: fluid inclusions

A fluid inclusion trail of a suitable subhorizontal orientation (with respect to the sample wafer) was studied. The inclusions are aqueous-only, two-phase liquid-rich with a constant degree of fill ( $F_v = 0.90$ ). A systematic zoning of  $T_{\text{tot}}$  (to L) data was observed (Fig. 6) on a microscopic scale. The higher  $T_{\text{tot}}$  values are confined to the trail core, while towards the microcrack termination the temperatures become lower. In contrast to  $T_{\text{tot}}$ , no significant differences in salinities ( $\sim 7$  wt. % eq. NaCl) and in  $T_{\text{fm}}$  ( $-49^{\circ}\text{C}$ ) were observed between individual “ $T_{\text{tot}}$ ” zones.

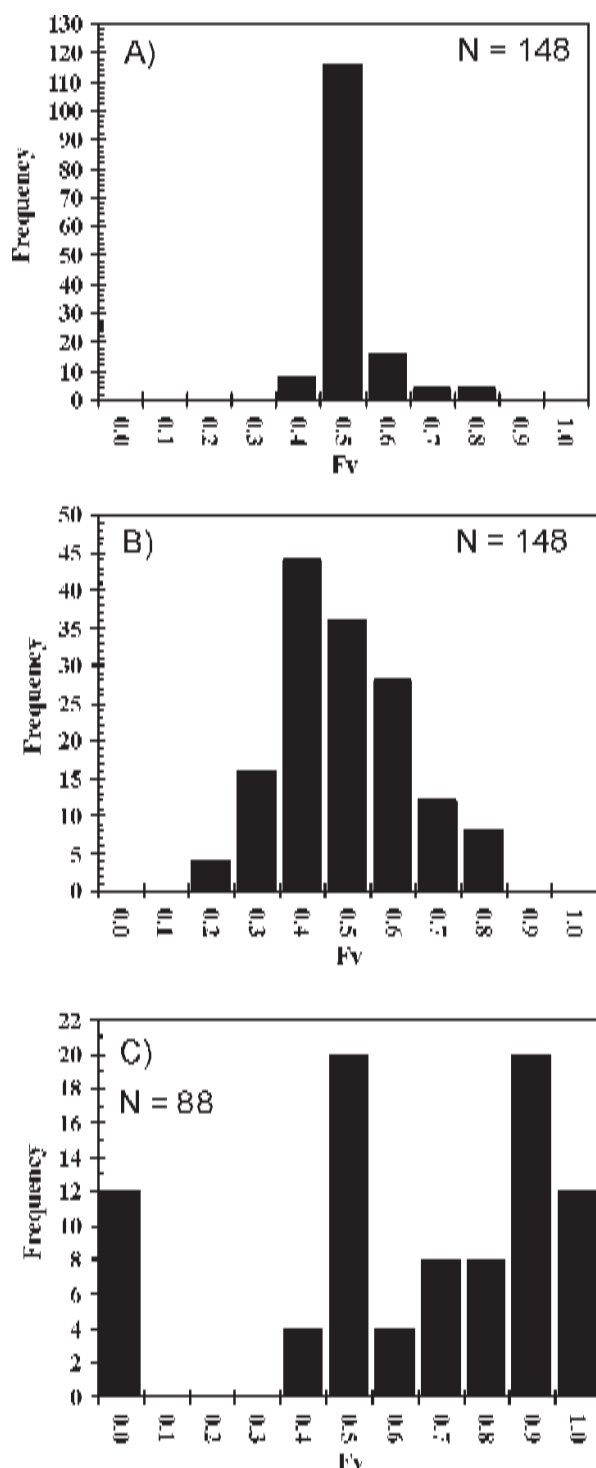


Fig. 3 Liběč deposit: histograms of the degree of fill ( $F_v$ ) in primary  $\text{H}_2\text{O}-\text{CO}_2 \pm \text{CH}_4$  inclusions from original (A–B) and recrystallized quartz /C/. The  $F_v$  was either estimated visually (A, C), or calculated using an ellipsoid model (see text, B).

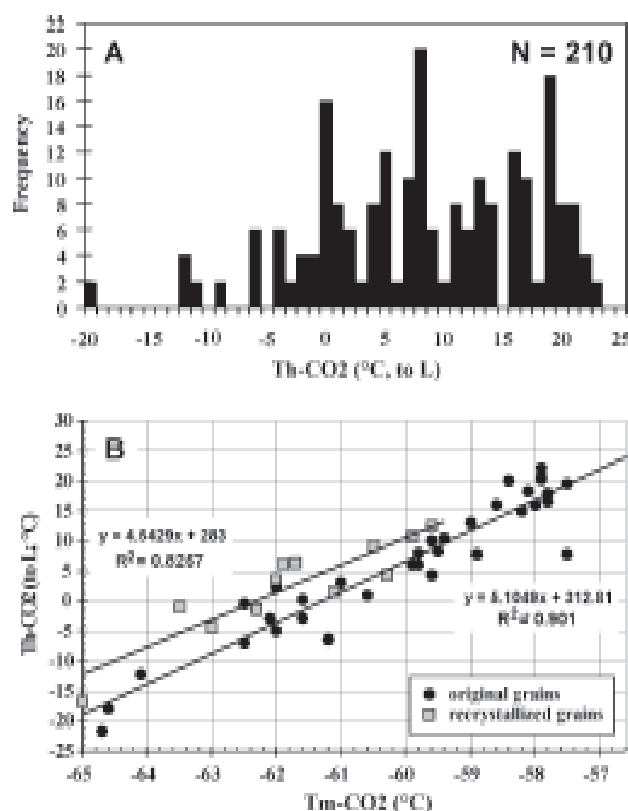


Fig. 4 Liběč deposit: A –  $\text{CO}_2$ -homogenization temperature (always to liquid) histogram – data for primary inclusions in both original and recrystallized quartz. B –  $\text{CO}_2$ -melting ( $T_{\text{m-CO}_2}$ ) vs.  $\text{CO}_2$ -homogenization ( $T_{\text{h-CO}_2}$ ) relationship of primary inclusions in original and recrystallized quartz separately.

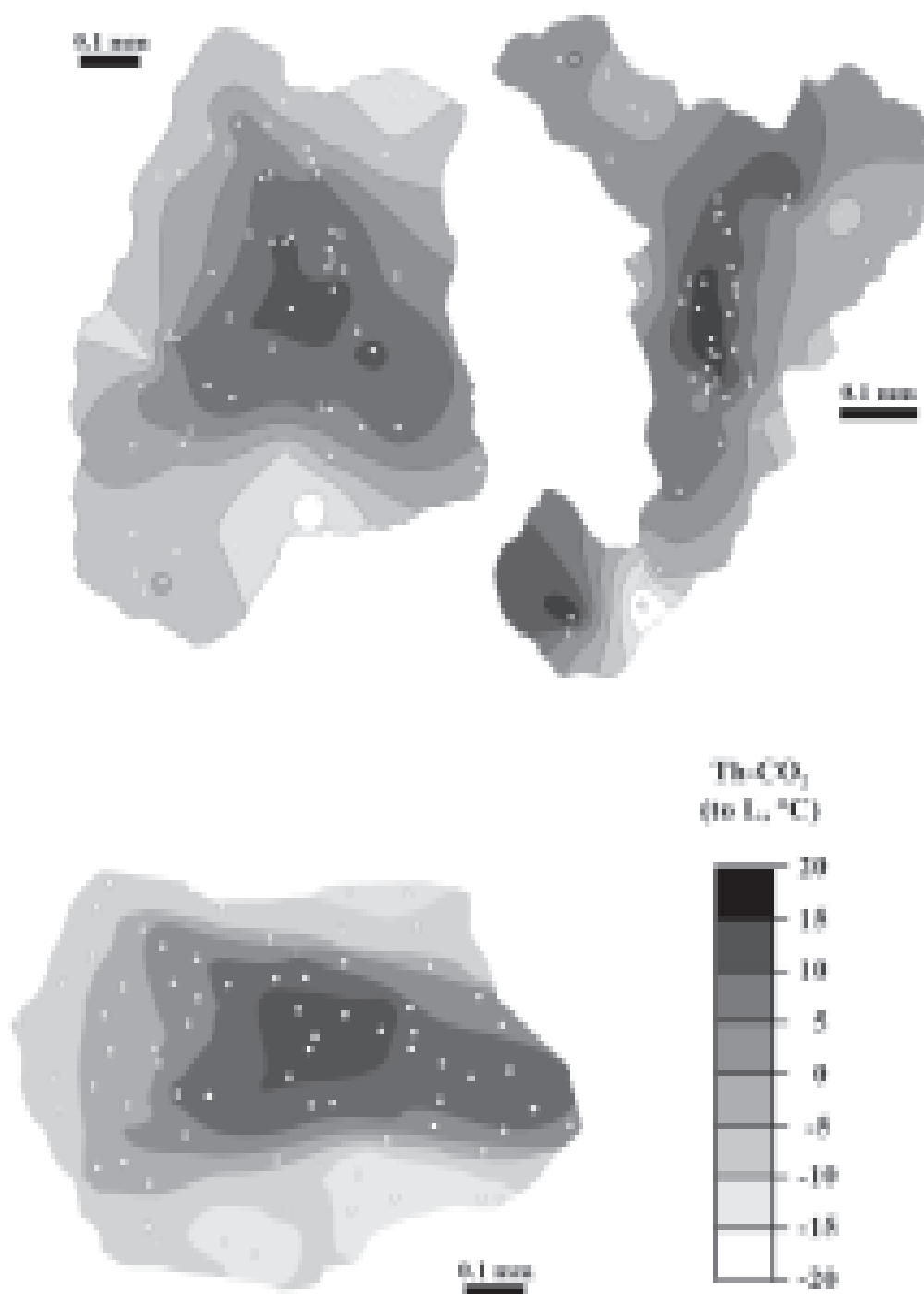


Fig. 5 Maps of iso-Th-CO<sub>2</sub> contours for several studied grains from the Libčice quartz gangue. The open dots represent individual studied inclusions. The Th-CO<sub>2</sub> systematically decreases from the core to the rim in all these grains.

## Discussion

Libčice deposit: genetic aspects of Th-CO<sub>2</sub> – Tm-CO<sub>2</sub> zoning

In order to generalize the following discussion, the maps of Th-CO<sub>2</sub> contour lines (Fig. 5) were transformed into a spherical grain model and the measured data is discussed

with respect to the relative grain ratio (i.e., 0–100 % of core – rim distance; Fig. 8a–g). The variations in Th-CO<sub>2</sub>/Tm-CO<sub>2</sub> observed in the grains of the original quartz reflect the variations in the fluid density and in the CO<sub>2</sub>/CH<sub>4</sub> ratio. These two effects will be discussed separately.

*The fluid density variations* may result from: 1) variable P-T trapping conditions; or 2) post-entrapment changes (re-equilibration). When an isothermal model

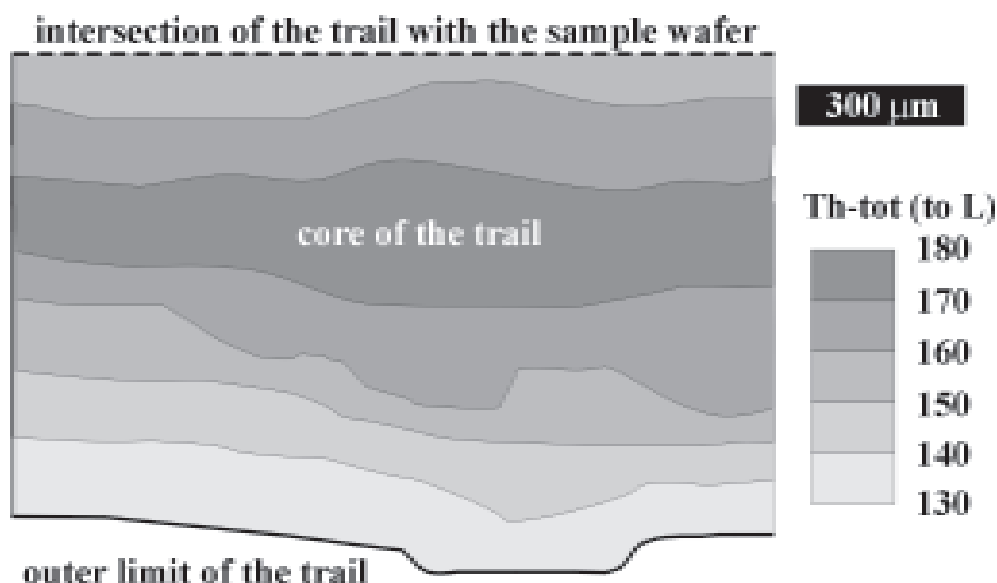


Fig. 6 Zoning of Th-tot data in a trail of secondary inclusions from the Kasejovice quartz gangue.

suggesting negligible temperature variations during original quartz precipitation on a grain scale is employed to explain the fluid density variation, then the grain cores must have been formed at significantly lower pressures (e.g.  $\sim 80$  MPa at  $350^\circ\text{C}$ ) than the middle and peripheral zones (250–290 MPa at  $350^\circ\text{C}$ ) of the studied grains (Figs 7 and 8d). The final pressure difference ( $\sim 200$  MPa) is independent of the temperature used for calculation. A pressure increase accompanying the sealing of the vein structure, as the mineral precipitation proceeds, is a widely accepted phenomenon (e.g., Sibson 1990) and corre-

sponds to a gradual change from the hydrostatic to the lithostatic pressure. However, such large differences were rarely reported. A pressure decrease of about 50 MPa in the outermost zone of some grains (Fig. 8d) contradicts the simple one-stage sealing model. This can be explained either by a decrease in the fluid pressure at the beginning of a new crack-forming/propagation stage or, when leaving the isothermal model, by a temperature increase associated with the incipient thermal-induced recrystallization. An increase of about  $+50$  to  $+60^\circ\text{C}$  would set the fluid pressure to higher values (approx. 300 MPa), thus

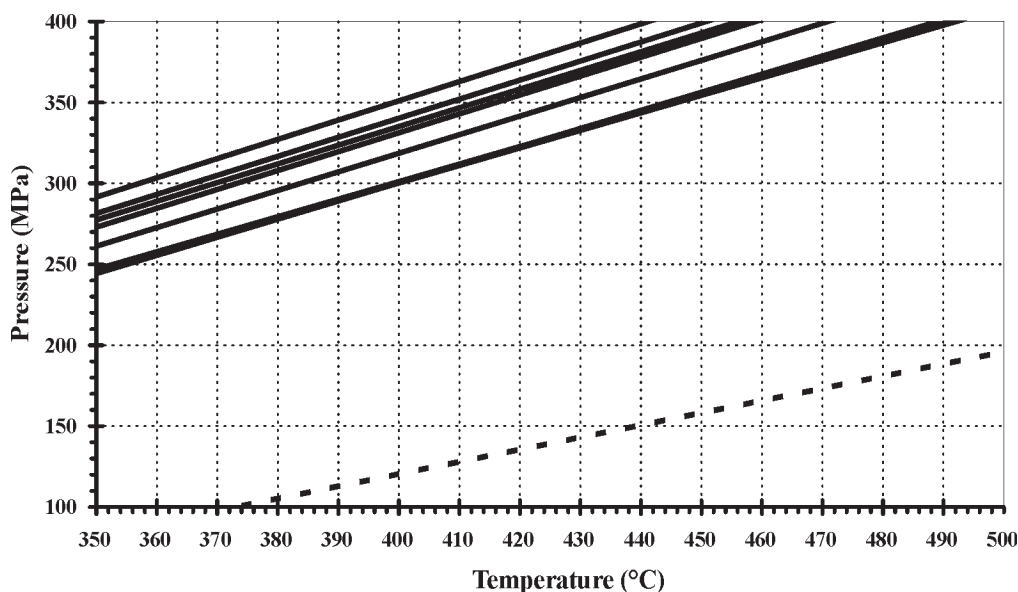


Fig. 7 Libčice deposit: isochores estimated for fluid inclusions from the original quartz grains. The dashed isochore corresponds to fluid inclusions with partial homogenization (Th- $\text{CO}_2$ ) at  $+23^\circ\text{C}$  to liquid, the solid isochores to that with Th- $\text{CO}_2 < 20^\circ\text{C}$  (calculated for 18, 12.5, 7, 2,  $-4$ ,  $-8.5$ ,  $-14$ ,  $-22^\circ\text{C}$ ).



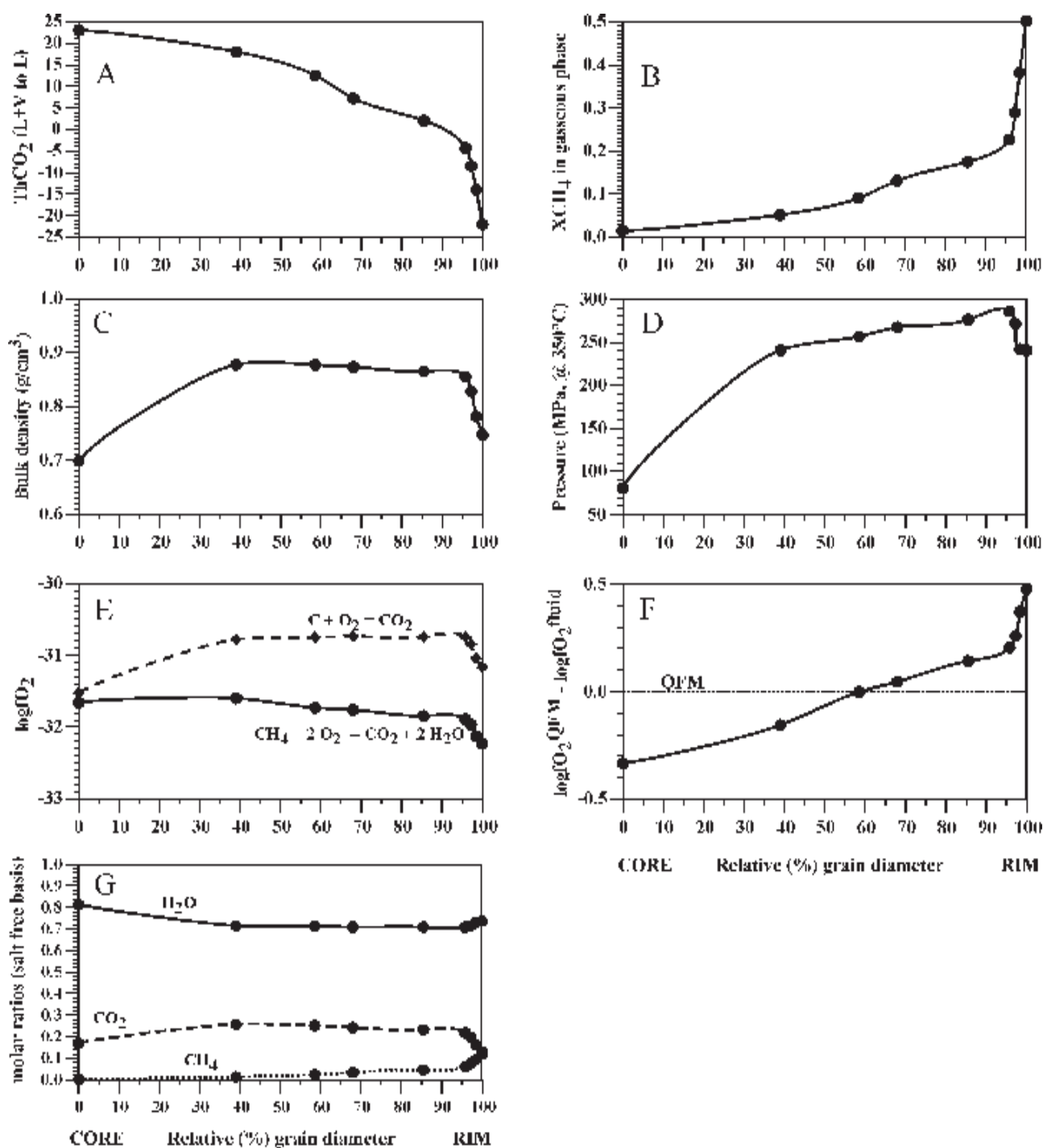


Fig. 8 Various interpretations, based on the isothermal model (see text), of the observed Th-CO<sub>2</sub> vs. Tm-CO<sub>2</sub> zoning in a partially recrystallized quartz gangue from the Liběc deposit shown with respect to relative grain diameter: A – the generalized Th-CO<sub>2</sub> zoning; B – the estimated molar ratio of CH<sub>4</sub> in gaseous phase; C – bulk fluid density; D – corresponding fluid pressure calculated at 350 °C; E – corresponding oxygen fugacity ( $f_{O_2}^{fluid}$ ) calculated for 350 °C and isochoric conditions; F – the same oxygen fugacity as above (based on  $CH_4 + 2O_2 = CO_2 + 2H_2O$  reaction), but expressed as a difference (in log<sub>10</sub> units) with respect to the QFM buffer ( $f_{O_2}^{QFM}$ ) at 350 °C; G – the estimated molar ratios of H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> in fluid inclusions.

eliminating the “pressure drop” of the isothermal model. Unfortunately, neither the standard microscopic methods or SEM-CL studies were able to unambiguously demonstrate the character (i.e., original vs. recrystallization-related quartz) of the outermost zones of the original quartz with  $Th-CO_2 < -10$  °C. On the other hand, the discontin-

uous character of these zones and their spatial association with areas of assumed future grain disintegration support their association with solid-state recrystallization processes.

The compositional variations in the C–O–H–(N–S) system have been extensively modelled theoretically and

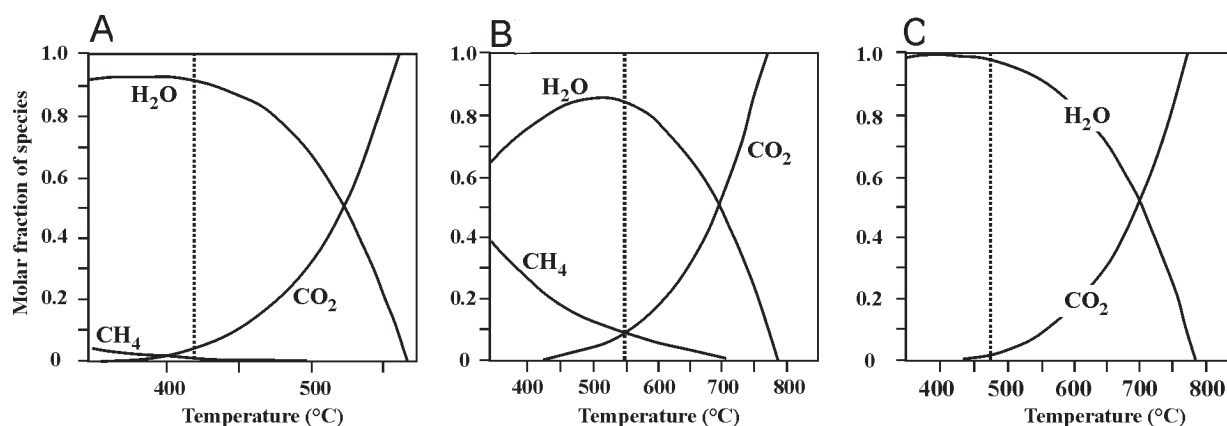


Fig. 9 The molar  $\text{CO}_2$ - $\text{CH}_4$ - $\text{H}_2\text{O}$  proportions of fluids in equilibrium with graphite (carbon) as a function of temperature, oxygen fugacity ( $f_{\text{O}_2}^{\text{fluid}}$ ) and carbon activity ( $a_c$ ). The pressure is constant (3 kbar). The dotted line corresponds to molar ratios of species that were found in the studied fluid inclusions. Variables: A –  $f_{\text{O}_2}^{\text{fluid}} = f_{\text{O}_2}^{\text{QFM}}$ ,  $a_c = 1$ ; B –  $f_{\text{O}_2}^{\text{fluid}} = f_{\text{O}_2}^{\text{QFM}-1}$ ,  $a_c = 1$ ; C –  $f_{\text{O}_2}^{\text{fluid}} = f_{\text{O}_2}^{\text{QFM}}$ ,  $a_c = 0.1$ . Modified after Huzienga (2001).

experimentally over the past 30 years (see Huizenga 2001 and references therein). They may result from: 1) P-T- $f_{\text{O}_2}$  changes/evolution in the fluid source reservoir; 2) modification of the original fluid during its migration; 3) post-entrapment changes in the fluid composition in fluid inclusions.

In the subsequent discussion related to fluid inclusions in the original quartz grains, the term early fluid is employed for fluid trapped in inclusions from grain cores, the term mid-stage fluid is used for that in middle grain zones, and late fluid refers to fluid inclusions in the narrow rim zone.

On the basis of the  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  molar ratios in the studied fluid inclusions and using the minimum trapping temperature of 350 °C, the oxygen fugacity was calculated (Fig. 8e–f) from the fugacity coefficients and equilibrium constant of  $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$  reaction (Ohmoto and Kerrick 1977). This reaction describes equilibrium between  $\text{CH}_4$  and  $\text{CO}_2$  in aqueous-carbonic fluid

and is independent on the mode of  $\text{CO}_2/\text{CH}_4$  formation. The results suggest a gradual decrease in  $f_{\text{O}_2}$  during growth of original quartz grains that is accompanied by a sudden drop in  $f_{\text{O}_2}$  during the final stages of grains growth. The oxygen fugacity calculated for  $\text{C} + \text{O}_2 = \text{CO}_2$  equilibrium (Ohmoto and Kerrick 1977) yielded similar results only for the core of the grain, but it is of about 1 log unit higher for the rest of the grain (Fig. 8e). Therefore we may suggest that the early fluids were in equilibrium with graphite, while the mid-stage and late-fluids not.

Assuming no significant leakage of  $\text{H}_2\text{O}$  (supported by relatively constant  $X_{\text{H}_2\text{O}}$ , Fig. 8g), the mutual proportions of  $X_{\text{H}_2\text{O}} - X_{\text{CH}_4}$  mostly reflect the T –  $f_{\text{O}_2}$  variations and/or changes in the carbon activity ( $a_c$ ). For example: at  $a_c = 1$  and  $P = 300$  MPa, the respective proportions for early fluids could be produced by thermal devolatilization of graphite-bearing rocks at ~420 °C and  $f_{\text{O}_2}$  conditions of the QFM buffer (Fig. 9a). The proportions for mid-stage

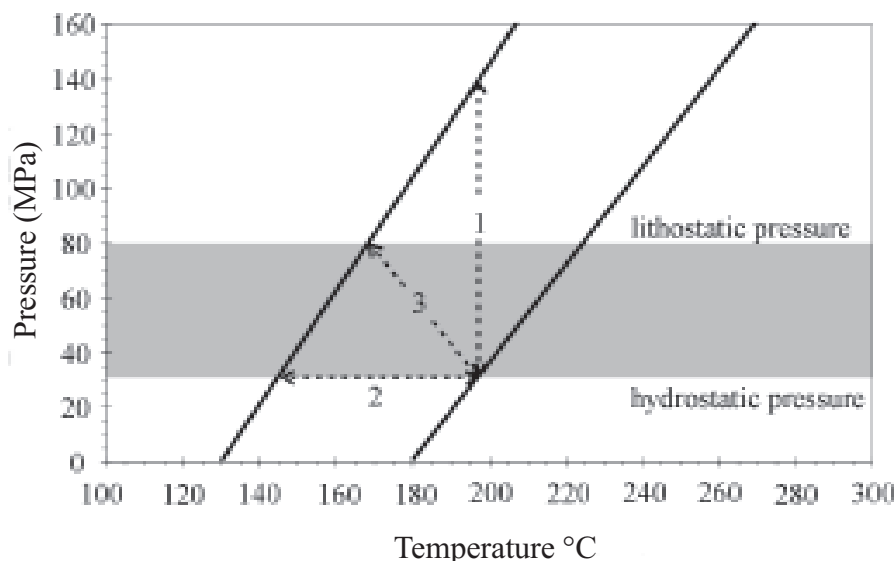


Fig. 10 Possible P-T variations in the measured microcrack from the Kasejovice deposit. Dashed lines indicate three alternative interpretations: (1) isothermal trapping, (2) isobaric trapping and cooling and (3) cooling accompanied by a change from hydrostatic to lithostatic conditions (see the text for details). The thick lines represent isochors for fluid inclusions from the core (Th-tot: 180 °C) and rim (Th-tot: 130 °C) of the secondary fluid inclusion trail.



or late fluids are compatible only with higher temperatures (~450 to ~550 °C respectively) and lower  $f_{O_2}$  ( $f_{O_2}^{fluid} = f_{O_2}^{OFM-1}$  to  $f_{O_2}^{OFM-2}$ ) conditions (Fig. 9b). Another alternative, however, is the formation of early fluids under carbon-undersaturated conditions ( $a_c \approx 0.1$  to  $0.2$ ; Fig. 8c) and formation of mid- and late-fluids under carbon-saturated conditions ( $a_c \approx 1$ ).

Both explanations are possible with respect to the given geological situation and include the local formation of the  $CH_4$ -rich fluid phase by thermal devolatilization of carbon-rich shales of the Lečice Member. In contrast to this, the  $CO_2$ -rich early fluids were probably of much deeper origin than the mid-stage to late fluids and resulted probably from large-scale crustal greenschist-facies devolatilization (undersaturated with respect to carbon).

Pressure and temperature variations in a healed microcrack – an example from the Kasejovice deposit

To explain Th-tot zoning within the healed microcrack, pressure or/and temperature variations simultaneous with the sealing mechanism must be considered. The difference between maximum and minimum Th-tot temperatures in the healed microcrack is 40–50 °C. Three alternatives are possible: (1) Assuming negligible temperature variations in the fluid during the sealing of the fracture, a pressure gradient of about 110 MPa can be calculated (Fig. 10, line 1) for fluid inclusions from the core and rim of the trail. However, this gradient is two times larger than a normal difference between lithostatic and hydrostatic pressures for a depth of 3 km and therefore, this alternative is not realistic. (2) If no pressure fluctuation occurred during trapping of the studied fluid inclusions, the differences in the measured Th-tot would indicate rapid cooling of the fluid when entered the fracture (Fig. 10, line 2). This case represents the maximum cooling gradient. (3) When both temperature and pressure were variable, than a cooling of about 25 °C must have occurred, between the time when the fluid was trapped in the core and in the peripheral zones of the fissure. This alternative represents minimum cooling gradient for maximum pressure variation (hydrostatic to lithostatic). Possible P-T variations within the microcrack are thus delimited by alternatives 2 and 3. The indicated P-T variations derived for the microcracks correlate well with a model of incursion of hotter hydrothermal fluids into an uplifted and relatively cooled crustal block (Zachariáš – Pudilová, 2002).

## Conclusions

Quartz gangue from the Libčice deposit was recrystallized due to the contact-metamorphic effect of intrusions of the CBPC. In some samples, however, remnants of the original quartz have been preserved. They contain, in contrast to the newly formed recrystallized quartz, large quantities of primary  $H_2O-CO_2-CH_4-NaCl-CaCl_2$  fluid inclusions. These inclusions display systematic zoning of

Th- $CO_2$  data: the highest values in the grain cores and a gradual decrease towards the rim. In addition to this, a positive correlation was observed between Tm- $CO_2$  and Th- $CO_2$ . All these data indicate a gradual increase in the  $CH_4$  content in the gaseous phase of fluid inclusions from ~1 to ~50 mol. %, accompanied by variations in bulk fluid density. The difference in fluid pressure between the grain core and rim during the original quartz gangue precipitation is estimated at 200 MPa. The gradual evolution of the  $CH_4/CO_2$  ratio is interpreted as a result of mixing between the initial  $CO_2$ -rich fluids of deep provenance with local  $CH_4$ -enriched fluid. The former were probably produced by large-scale regional devolatilization, while the latter was produced by local *in situ* devolatilization of organic carbon-rich Lečice Member black shales in a narrow contact-metamorphic zone of the CBPC. The Kasejovice deposit provides another example of pressure-fluctuations related 2D zoning of microthermometric data.

The two above-mentioned examples demonstrate the advantage of combined cathodoluminescence and microthermometric studies and of systematic collecting of fluid inclusion data on a two-dimensional scale.

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### Interpretace dvourozměrných mikrotermometrických měření fluidních inkluzí vzhledem k variacím ve složení a tlaku zlatonosných fluid: příklady z ložisek Libčice a Kasejovice, Česká republika.

Systematické měření mikrotermometrických parametrů fluidních inkluzí ve vybrané ploše výbrusu bylo kombinováno se standardním mikroskopickým pozorováním a studiem textur žiloviny v katodové luminescenci (SEM-CL). Na dvou příkladech křemenné zlatonosné žiloviny z ložisek Libčice a Kasejovice je demonstrována užitečnost takového komplexního přístupu pro interpretaci změn ve složení, tlaku a teplotě fluid během mineralizačního procesu.

Na ložisku Libčice je křemenná žilovina do různé míry postižena termální rekrystalizací. Primární fluidní inkluze H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>-NaCl typu v relikttech původního (předrekrystalizačního) křemene vykazují výraznou zonálnost mikrotermometrických charakteristik plynné fáze (Tm-CO<sub>2</sub>: –57.5 až –65.0 °C a Th-CO<sub>2</sub>: +24 až –21 °C /na kapalinu/) ve směru od středu k okrajům křemenných zrn. Tomuto trendu odpovídá postupný nárůst podílu CH<sub>4</sub> v plynné fázi inkluzí z 1 mol. % ve středu zrn až na 50 mol. % při okrajích zrn. Analogické variace v celkové hustotě fluidní fáze (0.70 – 0.88 g/cm<sup>3</sup>) indikují výrazný vzestup tlaku fluid během krystalizace křemene (až o 200 MPa). Změny v poměru CH<sub>4</sub>/CO<sub>2</sub> ve fluidní fázi jsou pravděpodobně důsledkem míšení hlubinných CO<sub>2</sub>-bohatých fluid regionálního původu s lokálními CH<sub>4</sub>-bohatými fluidy vzniklými termální devolatilizací organickým uhlíkem bohatých lečických vrstev v kontaktní aureole středočeského plutonu.

Druhý příklad, z ložiska Kasejovice, popisuje variace teplot homogenizací (+180 to +130 °C, na kapalinu) sekundárních H<sub>2</sub>O-NaCl inkluzí a možné interpretace oscilací tlaku fluid během utěšňování mikrotrhlin v křemenné žilovině.