Regional low-temperature fluid flow indicated by quartz mineralization in Silesicum, NE Bohemian massif

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Abstract: The crystalline rocks of the Silesicum unit of the Bohemian Massif host two principal types of hydrothermal quartz veins. Veins associated with granitoids are primarily quartz with wollastonite and epidote and accompanied by hydrothermal alteration of host rocks whereas others are of the more complex “Alpine-type”. L+V+S (liquid + vapour + solid phase) fluid inclusions within quartz crystals contain muscovite and ±calcite (±haematite) as solid phases and homogenisation temperatures are between 124 and 176°C. Trapped fluids are uniformly of the H2O–NaCl–CaCl2–MgCl2±KCl system with a salinity between 9.1 and 26.8 mass % (NaCl+CaCl2). The variable Na/Ca ratios result from different intensity of fluid-rock reactions. The ubiquitous muscovite is a product of fluid-rock interactions. Oxygen isotope evidence indicates that the fluids were a mixture of meteoric and marine waters in deep regional-scale convection systems. The studied type of fluids represents a post-Variscan hydrothermal system and shows the extent of migration pathways in the upper crust on the north-eastern edge of the Bohemian Massif.

Keywords: Bohemian Massif, Silesicum, regional fluid flow, hydrothermal alteration, quartz veins, fluid inclusions, muscovite.

Introduction

Quartz crystals including a pure variety, occur in the Silesicum, in the Jegłowka area of Poland and in the Žulová area of the Czech Republic with a relationship to the Žulová granite (Figs. 1, 2) and are different from the typical metamorphic “Alpine-type veins” as described by Parker (1923). These widespread later veins, related to Variscan metamorphic events, occur within fissures in amphibolites and are closely connected to epimetamorphic conditions of the Silesicum unit (Kruňa 1973; Sládek 1973; Jedlička 1995; Gadas 2002).

The nature and genesis of the hydrothermal fluids and the conditions of quartz crystallization in the different geological settings within the area have not been published yet. Slobodník et al. (2010a) suggested three genetic models for quartz mineralizations in Silesicum, namely: a) pegmatite-related of Variscan age; b) metamorphic hydrothermal including Alpine-type veins of Variscan age; c) late- and post-Variscan hydrothermal.

Previous studies of the fluids have been focused on quartz and quartz veins related to Variscan pegmatite bodies genetically linked to the Strzegom-Sobótka, Karkonosze, Szczylnia and Žulová granite plutons in Lower Silesia, SW Poland (Kozłowski 1986, 2002; Kozłowski & Metz 2003; Kozłowski & Marcinowska 2007; Slobodník et al. 2010b). They concluded that different types of fluids trapped as fluid inclusions (FIs) in quartz crystals represent distinct stages of fluid flows.

Variscan quartz veins designated as “Alpine-type fissure veins” occurring within amphibolite bodies of the Silesicum area show a complex mineral assemblage with a genetic link to metamorphic fluids (e.g., Sládek 1973; Staněk 1997; Novotný & Zimák 2003). Investigations of FIs within quartz crystals revealed that the fluids were dominantly low salinity aqueous solutions, with variable amounts of CO2, generated by low-grade metamorphism (Slobodník et al. 2010a; Kontár 2011).

The results of fluid inclusion studies from late and post-Variscan quartz veins from the Silesicum area and the Žulová Pluton (Fig. 2) are discussed in Slobodník et al. (2010a). The mineralogical composition of late quartz veins, principally within granites, is rather simple and kaolinite, chlorite and epidote also occur in addition to the predominant quartz (Novotný 1997). A different range of homogenization temperatures of FIs, the chemical composition of the aqueous fluids and their salinity are also known (Novotný & Dobeš 1999). However, a number of fundamental questions on the overall genetic context remain unanswered.

A variety of quartz crystals at the Jegłowka site were studied by Karwowski & Kołowski (1975) who reported the presence of aqueous chloride solutions in FIs. They mentioned three-phase fluid inclusions which contained aggregates of kaolinite–smectite (identified on the basis of infrared absorption spectrum, Wiewióra 1973) as trapped solid phases. However, their study does not address genetic aspects of the fluids. Sachanbinski et al. (2008) focused only on tiny solid phases (anatase, kaolinite, chlorite, Fe-oxy-hydroxides, pyrite and haematite) in quartz crystals from the Jegłowka area using Raman spectroscopy.

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The above studies do not consider the age relationships of the veins. The broad range of temperature and salinity of the enclosed fluids, however, suggest that the late- and post-Variscan fluid systems are more complex than previously thought.

The quartz veins that occur in the magmatic and metamorphic rocks of the Silesicum (Fig. 2) show a simple mineral assemblage associated with kaolinization (Kužvart 1965; Kruťa 1973; Karwowski & Kozłowski 1975) with the implication that their origin is different from that commonly reported for the veins of the Silesicum area which are considered to be pegmatite or Alpine-type veins.

The current categorization of the veins needs to be extended and this paper presents evidence for the nature of the parent fluids of the late/post Variscan quartz veins, which host well-formed clear quartz crystals, in the Strzelin Massif and Žulová Pluton area and the physico-chemical conditions during their formation with the aim to provide a refined definition for the late stage veins.
Regional geological setting

The investigated sites are in the northern part of the Silesicum, Moravo–Silesian region. The north-eastern Bohemian Massif (Fig. 1) is a structurally complex of pre-Carboniferous metamorphosed volcano-sedimentary succession with igneous bodies. These rocks are the most north-easterly exposed part of the Variscan crystalline basement in the Bohemian Massif surrounded by Mesozoic and Cenozoic sedimentary sequences. The Variscan basement comprises a nappe pile of a detached Bruno-Vistulian fragment of basement overridden from the west by the Central Sudetic Orlica–Śnieżnik Dome and the Staré Město Belt (Fig. 2). Further to the East, the Velké Vrboň and Keprník nappes rest on parautochthonous gneisses of the Desná unit (Schulmann & Gayer 2000) and are covered by the Devonian volcano-sedimentary Vrboň Group (Fig. 2). Towards the east, they adjoin the thrusted and folded Lower Carboniferous fill of the Moravo–Silesian flysch basin. The compressional regime of the European Variscides persisted until the Carboniferous – a time period dominated by intense granitic plutonism coupled with unroofing of metamorphic complexes and simultaneous inversion of foreland basins (Tait et al. 2000).

The main Variscan tectonic phases are associated with the collision of the Central Sudetic orogenic wedge with the Bruno-Vistulian terrane, which commenced during the earliest Carboniferous and lasted until Late Carboniferous times (Schulmann & Gayer 2000). During these times, tectonic activity in other parts of the area was dominated by strike-slip movements along major faults and shear zones, localized gravitational collapse, and intense granitic plutonism. Dextral strike-slip displacements dated at 340 Ma occurred along the WNW–ESE trending fault zones (Aleksandrowski et al. 1997; Mattern 2001). Contemporaneous sinistral displacements occurred along the NNE–SSW striking Niemcza Shear Zone (Mazur & Puziewicz 1995). Variscan tectonics in total resulted in a complex network of large faults, shear zones and thrusts (N–S, NW–SE, WNW–ESE, NE–SW). Granitic plutonism climaxed at 310–300 Ma, resulting in the emplacement of several large plutons, such as those of Krkonoše far to the WNW, Strzegom–Sobótka, Zlota Stok, Strzelin and Žulová (Fig. 2).

The Jegłowa area is composed of metamorphic rocks which form the central and eastern parts of the Strzelin Massif (Oberc-Dziedzic et al. 2005). This metamorphic complex was intruded by granitoids between 350 and 330 Ma (Oberc-Dziedzic et al. 1996). The Strzelin Massif consists of a core unit, an inner envelope of older schists, and an outer envelope of younger schists, the latter referred to as the Jegłowa Beds (Oberc-Dziedzic et al. 2005). The outer envelope (Jegłowa Beds) consists of metaquartzites, quartz–sericite schists and metaconglomerates deposited during early- to mid-Devonian times (Patočka & Szczepański 1997). Bederke (1931) and Obrec (1966) compared these rocks to the fossiliferous Lower Devonian metaquartzites of the East Sudetes (Vrboň Group).

Metamorphites of Paleozoic and Proterozoic ages in the envelope of Žulová Pluton include various types of gneiss,
migmatite and, as minor occurrences, marble, mica schist and metaquartzite. This geologically coherent region is divided by the Sudetic Boundary Fault (Fig. 1, 2) into two morphologically contrasting domains, namely the low-mountainous ridge to the SW and the penepanned lowland to the NE. The fault is a Late Variscan fracture zone rejuvenated during the latest Cretaceous–Paleocene uplift of the Bohemian Massif and again during its Neogene reactivation (Badura et al. 2003).

Towards the north, the East Sudetic nappe pile (Variscan basement) is covered by Cenozoic sediments. Crystalline rocks emerge at the surface mostly within the Strzelin Massif. The final stage of sedimentation is represented by Quaternary glacial sands, gravels and loess.

**Strzelin Massif and Žulová Pluton**

The Variscan post-orogenic granitoid intrusions in the Strzelin Massif and the Žulová Pluton are the principal geological features of the study area. The Žulová pluton was intruded along the Sudetic Boundary Fault into the Lower Paleozoic rocks of the Silesicum crystalline unit (Figs. 1, 2).

Igneous rocks of the Strzelin Massif comprise granodiorites, quartz diorites, tonalites, biotite- and two-mica granites as isolated bodies, mostly stocks and flat-lying dykes up to tens of metres thick (Oberc-Dziedzic et al. 1996). Whole-rock geochemical data indicate metaluminous, calc–alkaline features for the constituent tonalite, quartz diorite and biotite granite. These rocks are described as HCa (low K–high Ca) calc–alkaline granitoids by Oberc-Dziedzic (1998) following the classification of Barbarin (1990).

The biotite granite and the two-mica granite have been dated at 347±12 Ma and 330±6 Ma, respectively (Rb–Sr whole-rock data, Oberc-Dziedzic et al. 1996). The other Rb–Sr age values obtained for the tonalite, range from 293.8±0.3 Ma to 296.7±0.7 Ma (Mazur et al. 2007). Equally young Pb-evaporation zircon age values of 291±5.5 Ma and 301±7 Ma are reported by Turniak et al. (2006) for the tonalite, quartz diorite and biotite granite. K–Ar cooling age values for the granitoids, range from 278 to 288 Ma (Depciuch & Lis 1972), are in general agreement with Ar–Ar results obtained on a molecular sieve (5 Å) and subsequently expanded into the inlet of a Finnigan MAT 253 isotope ratio mass spectrometer. Oxygen isotope ratios were expressed in per mil (‰) relative to V-SMOW standard by use of the standard δ-notation. Replicate oxygen isotope analyses of the NBS-28 quartz standard (n=4) had an average precision of ±0.1 ‰. The accuracy of the obtained δ18O values was better than 0.2 ‰ compared to the accepted value of 9.64 ‰ for the NBS-28 standard. To calculate the isotopic equilibrium composition of oxygen in the parent solution, the water–quartz fractionation equation (Zheng 1993) was used.

**Methods and materials studied**

Samples of rocks, crystalline quartz, and pure transparent colourless quartz, were collected at quarries near Jegłowa (JGL), outcrops and pits near Žulová (ZAD) and at Stará Červená Voda (SCV) village (Fig. 2) as the principal sampling areas.

**Fluid inclusions microthermometry**

Thin sections and doubly polished thin sections were prepared for fluid inclusion studies. A Linkam stage THMSG600 mounted on a Nikon Eclipse80i was used for microthermometric measurements. The stage was calibrated by synthetic fluid inclusions. Homogenization temperature (T_h), melting temperature of ice (T_m,ice), melting temperature of hydrohalite (T_m,hh) and eutectic temperature (T_e) were measured. Salinity and the mass fraction of NaCl relative to NaCl+CaCl₂ (Φ) of solutions in aqueous inclusions were calculated according to the method of Steele-MacInnis et al. (2011). FLUIDS 1 programmes (Bakker 2003) were used to calculate isochores.

**Stable isotopes**

Oxygen isotope ratios in quartz were measured at the Institute of Mineralogy and Geochemistry, University of Lausanne, Switzerland. A sample of 0.5–2 mg was loaded onto a small Pt-sample holder and pumped out to a vacuum of about 10⁻⁶ mbar. After prefluorination of the chamber overnight, the samples were heated with a CO₂-laser in pure F₂ atmosphere at a pressure of 50 mbar. Excess F₂ was separated by reaction with KCl at 150 °C. The extracted O₂ was collected on a molecular sieve (5 Å) and subsequently expanded into the inlet of a Finnigan MAT 253 isotope ratio mass spectrometer. Oxygen isotope ratios were expressed in per mil (‰) relative to V-SMOW standard by use of the standard δ-notation. Replicate oxygen isotope analyses of the NBS-28 quartz standard (n=4) had an average precision of ±0.1 ‰. The accuracy of the obtained δ¹⁸O values was better than 0.2 ‰ compared to the accepted value of 9.64 ‰ for the NBS-28 standard. To calculate the isotopic equilibrium composition of oxygen in the parent solution, the water–quartz fractionation equation (Zheng 1993) was used.

**Powder X-ray diffraction (PXRD)**

PXRD was used for the identification of mineral assemblages within the wall-rock along quartz veins and checked by the EDX analysis in thin section. Two representative samples were assembled from the rock material at several locations in the alteration zones along the quartz veins. The samples were pulverised in isopropyl alcohol by use of a McCrone micronizing mill. PXRD analyses were conducted on a Rigaku Smartlab diffractometer, equipped with a copper tube (λ = 0.15418 nm), powered at 40 kV and 30 mA at Bragg–Brentano parafocussing Θ–Θ reflexion geometry; step size – 0.02 °/step, time per step – 0.3 s, angular range 5°–80°/2Θ. The data obtained were processed by the use of a Panalytical High Score 3 plus software and ICSD 2012 database. Quantitative phase analysis was done by the Rietveld method.
Raman spectroscopy

Raman spectra were acquired at laboratories of the Department of Geological Sciences, Masaryk University in Brno and at the laboratory of the Slovak Academy of Sciences in Banská Bystrica equipped with a JY/Horiba LabRam HR Raman system by use of 532 nm (Nd–YAG) and 633 nm (He–Ne) laser excitation, a 100× Olympus BX-41 objective with a 0.25 numerical aperture, a slit of 80 μm and a 1800 grooves/mm grating with a spectral resolution of approximately 1 cm⁻¹. Laser power on the sample of approximately 50 and 10 mW was used (for green and red laser alternatively) and the spectra were collected between 70 and 4000 cm⁻¹ for 40 s with two accumulations per spectrum.

Electron probe microanalysis (EPMA)

The Cameca SX-100 electron microprobe, at the Laboratory of Electron Microscopy and Microanalysis, the joint facility of the Masaryk University and the Czech Geological Survey in Brno was used to determine the composition of wollastonite, epidote and allanite. The wavelength-dispersion mode and the following analytical conditions were applied: acceleration voltage 15 kV, beam diameter 2–5 μm, beam current 10–20 nA and peak and background counting times of 10–30 seconds and 5–15 seconds respectively. The following standards and analytical lines were applied: albite (Na; Kα), gahnite (Al; Kα, Zn; Kα), haematite (Fe; Kα), sanidine (Si; Kα), MgAl₂O₄ (Mg; Kα), titanite (Ca; Kβ), Mn₂SiO₄ (Mn; Kα), TiO₂ (Ti; Kα). The data were reduced by the use of the PAP routine of Pouchou & Pichoir (1985).

Petrography and sample description

Jegłowa (JGL)

At this locality crystals of quartz had formed on the walls of fractures in metaquartzite and metaquartzite schist. The rocks show a white hue as a result of kaolinization (Fig. 3A,B). They display plain parallel or linear structures, the most altered parts of rock being fairly soft with a porous texture, the pores being filled with kaolinite as small nests and pockets. The alignment of microscopic phyllosilicate (kaolinite) flakes does not follow the foliation of the rock suggesting that the kaolinite is a younger filling of pores. Quartz crystals are spatially associated with the kaolinite nests and occur on the inside of pockets and open fractures. White amorphous kaolinite fills tiny nests on uneven rough surfaces of some quartz crystals. Kaolinite and other mineral inclusions inside the crystals such as anatase, chlorite, Fe-oxy-hydroxides, pyrite and haematite have been identified (Sachanbiński et al. 2008). Quartz in drusy cavities shows a prismatic and acicular habit (hexagonal prisms are frequent faces) with positive and negative rhombohedra. Steep rhombohedral faces are rare (Fig. 4A).

Žulová (ZAD)

Quartz veins with massive and drusy structures cut granites and granodiorites (south-east of the Žulová town) of the Žulová Pluton. The host rocks are hydrothermally altered to different intensities showing white colouration along veins. The altered zones are composed of quartz, albite, epidote, white mica (most likely muscovite, illite) and rare gypsum (Table 1). EDX analyses completed the assemblage with sporadic occurrence of titanite, apatite and zircon. The most progressive stages of granite alteration produce totally decayed rocks in which the fragments of quartz veins and crystals float in a clay mass (see text on the Stará Červená Voda site). The same settings were documented in boreholes at the nearby Vidnava kaolin deposit where quartz veins are present in kaolinized granitoids (Milický et al. 1985).

Generally, the direction of the veins is NW–SE, and rarely NNE–SSW, with lens-like sections of up to 5 m thick (Albrechtová et al. 1970). Two principal generations of quartz veins cut through a biotite granite. The older veins are less frequent and are composed of massive quartz with a milky
hue; elongated cavities up to 1 m in length were also observed. The younger veins are accompanied by characteristic alteration of wall-rocks with dominant albite (Figs. 5, 6; Table 1). Thickness of the younger veinlets vary mostly between 1–40 cm and frequent cavities show drusy structures of quartz crystals (rock crystals up to 10 cm in length), which are overlain by a greyish clay. The quartz crystals (Fig. 4B) show prismatic habits with rhombohedral faces. Quartz is the dominant mineral phase of veins and other mineral phases such as rutile, chlorite-clinochlore, Fe-oxyhydroxides and epidote are minor phases, forming tiny mineral inclusions in quartz (Němcová & Němec 1970). Epidote occurs in hydrothermally altered host rocks and in quartz along vein contacts (Fig. 5). Novotný (1997) reported needle-like crystals of epidote as long as 1.5 cm. Tiny grains of epidote (X0–X00 µm) occur along some growth zones of quartz crystals as well. A network of white fibres with a composition close to that of wollastonite (Table 2) can be found at the bottom part of crystals (Fig. 4) in association with very small crystals (up to 20 µm) of fluorite and calcite.

**Table 1**: Representative results of PXRD quantitative analyses (mass %) of hydrothermally affected granite from the Žulová site.

<table>
<thead>
<tr>
<th>Sample/Mineral</th>
<th>ZAD 1</th>
<th>ZAD 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>18.5</td>
<td>20.6</td>
</tr>
<tr>
<td>Albite</td>
<td>61.4</td>
<td>63.9</td>
</tr>
<tr>
<td>Epidote</td>
<td>17.3</td>
<td>13.5</td>
</tr>
<tr>
<td>Mica</td>
<td>2.8</td>
<td>1.7</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.1</td>
</tr>
</tbody>
</table>

**Stará Červená Voda (SCV)**

Quartz veins occur in biotite gneiss, which forms an envelope of granitoids at the eastern part of the Žulová Pluton. Veins show a sharp contact with gneiss wall-rock which underwent intense kaolinitization. Kaolinite shows a light grey hue and fills cavities and fractures in veins. A general strike direction of the veins is NW–SE with steep dips to N and S. The thickness of veins is up to 0.5 m, the quartz showing a slight greyish or milky hue and in cavities it is terminated by pure clear quartz. Cavities are filled with a kaolinite-rich clay containing individual quartz crystals.
well. Principal crystallographic shapes of the quartz crystals are prisms (Fig. 4C) with positive and negative rhombohedral faces, tiny trigonal bipyramid faces and steep rhombohedra as uncommon faces. Individual crystals reach up to 10 cm in length and are commonly doubly terminated.

Rarely, in some crystals, small grains (up to 2–5 mm) of epidote occur along growth zones. Epidote shows sector zoning with the ratio $\text{Fe}^{2+}/(\text{Fe}^{3+}+\text{Al})=0.09–0.19$ (Table 2). Thin to acicular crystals of allanite-Ce (Fig. 7) rarely appear within the youngest growth zones of quartz.

**Fluid inclusion study**

Fluid inclusions (FIs) occur randomly distributed, in clusters, and along growth zones (primary FIs) or rarely they appear to be arranged in short trails (commonly regarded as pseudo-secondary FIs) (Fig. 8A–H). Secondary inclusions (all FI arrangements after Roedder 1984) arranged along planes are rare and too small to investigate. Most fluid inclusions have sizes between 15 and 40 μm, with the biggest inclusion 62 μm. Small inclusions below 5 μm were unable to be measured exactly. Different shapes of FIs could be recognised, regular or rounded (Fig. 8A,C), rather irregular (Fig. 8B,E) or slightly elongated and cylindrical (Fig. 8G) or nearly spherical (Fig. 8D). No differences among samples and studied localities were observed either in shape or in size of FIs and in basic types of inclusions with respect to phase composition. The assemblage of FIs could be divided into two groups:

- 2-phase FIs (Fig. 8A,B), with liquid (L)+vapour (V) and
- 3-phase FIs (Fig. 8C–G), L+V+solid phases (S).

The estimation of the vapour volume fraction (φ or F) in FIs (Bakker & Diamond 2006) is constant and ranges between 0.90 and 0.95. Three categories of trapped solid phases were recognized by optical microscopy:

- colourless solid phases, recognized only at Žulová, occur as individual small grains (Fig. 8F)
- small flakes, fans of flakes or clusters (occur at JGL and SCV). These solids fill inclusion cavities by up to 80–85 % of their volume. They are fairly frequent and occur (microscopically recognised) in 70 % of all inclusions at the two sites (Fig. 8C,D,E).
- very rare small grains (1–2 μm), slightly translucent with a reddish hue (possibly haematite or lepidocrocite – impossible to focus and fix for Raman spectroscopy) have been found in inclusions at Žulová (Fig. 8G).

**Analytical results**

**Raman spectroscopic determinations**

Raman spectroscopy has been applied to all three categories of solids enclosed in FIs and moreover also on vapour phases. White clay matter on the surface of quartz crystals from Jegłowa was subjected to Raman spectroscopy as well.

Colourless grains recognised in FIs at Žulová were identified as calcite (Fig. 8F) since they yielded a distinct Raman spectrum (bands 279, 709, 1083 cm⁻¹) which fits well with the principal bands of calcite: 282, 713, 1089 cm⁻¹ (Fig. 9, spectra 1 and 2).

Raman spectra of flaky phases inside FIs, which have been observed in JGL and SCV samples, could be identified as muscovite (compared with Frezzotti et al. 2012 and RRUFF Raman database). The Raman spectrum involves clear OH-stretching bands at positions 3631, 3627, 3626 cm⁻¹ which fit with OH-group within a broad band of water belonging to the surrounding liquid water present within multiphase inclusions (Fig. 9, spectra 6, 7, 8). Other characteristic bands are at the position of triple-band with values of principal peaks at 699 and 707 cm⁻¹.

Identification of grains with reddish hue failed due to the small size of the grains. On the basis of the hue it is assumed that they are haematite grains.

Small amounts of gas components in the vapour phase in fluid inclusions (undetectable by microthermometry) were found in samples from Jegłowa. Small but distinct Raman bands of $\text{N}_2$ (2330 cm⁻¹) and $\text{CH}_4$ (2919 m⁻¹) were detected indicating small amounts of these gases (Fig. 9, spectrum 6).

White clay matter from kaolinized quartzite in Jegłowa and clays sampled from the surface of quartz crystals, as reference material, were tested by RTG and Raman spectroscopy. Samples yielded typical double-peak values 3618 and 3698 cm⁻¹ of the OH-group (spectrum 4, Fig. 9) that correspond to reference data of kaolinite (3620, 3692 cm⁻¹, Wiewióra et al. 1979).
Homogenization temperatures of all fluid inclusions are between +124 and +176 °C and only a little difference among the median values of $T_h$ of individual localities is obvious (+152 and +155 °C, see Fig. 10; Table 3). The lowest $T_h$ values occurred at the Žulová site and the highest ones at Jegłowa.

The solid phases in FIs neither dissolved nor changed during heating experiments so they all (calcite, muscovite, reddish unidentified grain) represent minerals dispersed in the original hydrothermal solution.

The ranges of eutectic temperatures ($T_e$) are as follows: −59 to −51 °C in JGL, −66 to −46 °C in SCV, −67 to −45 °C in ZAD, with most values around the ranges −51 to −52 and −65 to −67 °C, suggesting the presence of a chloride solutions with Ca$^{2+}$, Na$^+$, and, possibly, K$^+$ and Mg$^{2+}$ cations (Borisenko 1977, 1982; Davis at al. 1990; Spencer et al. 1990). Hence, the chemical type of solution was interpreted as H$_2$O–NaCl–CaCl$_2$±MgCl$_2$±KCl.

Some solid phases that have crystallised during cryothermo-metric runs, helped in specifying the composition and salinity of the aqueous solutions. During reheating of frozen inclusions, after the melting of the first solid ($T_h$), subsequent solids present in the inclusions were either hydrohalite or ice. Overall salinity (CaCl$_2$±NaCl) ranges between 9.1 and 32.3 mass % (Table 3) and no trends between salinity and $T_h$ at any of the investigated sites were noted (Fig. 11).

<table>
<thead>
<tr>
<th>No.</th>
<th>wollastonite</th>
<th>wollastonite</th>
<th>epidote</th>
<th>epidote</th>
<th>allanite–Ce</th>
<th>allanite–Ce</th>
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<tr>
<td>SiO$_2$ wt. %</td>
<td>52.35</td>
<td>51.32</td>
<td>38.39</td>
<td>38.13</td>
<td>36.02</td>
<td>37.81</td>
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</tr>
<tr>
<td>CaO</td>
<td>47.30</td>
<td>48.44</td>
<td>23.36</td>
<td>23.85</td>
<td>13.59</td>
<td>13.66</td>
</tr>
<tr>
<td>MnO</td>
<td>0.38</td>
<td>0.17</td>
<td>0.25</td>
<td>b.d.l.</td>
<td>0.15</td>
<td>b.d.l.</td>
</tr>
<tr>
<td>Total</td>
<td>100.27</td>
<td>100.09</td>
<td>96.49</td>
<td>96.10</td>
<td>97.58</td>
<td>97.45</td>
</tr>
</tbody>
</table>

Microthermometry of FIs

The solid phases in FIs neither dissolved nor changed during heating experiments so they all (calcite, muscovite, reddish unidentified grain) represent minerals dispersed in the original hydrothermal solution.

The ranges of eutectic temperatures ($T_e$) are as follows: −59 to −51 °C in JGL, −66 to −46 °C in SCV, −67 to −45 °C in ZAD, with most values around the ranges −51 to −52 and −65 to −67 °C, suggesting the presence of a chloride solutions with Ca$^{2+}$, Na$^+$, and, possibly, K$^+$ and Mg$^{2+}$ cations (Borisenko 1977, 1982; Davis at al. 1990; Spencer et al. 1990). Hence, the chemical type of solution was interpreted as H$_2$O–NaCl–CaCl$_2$±MgCl$_2$±KCl.

Some solid phases that have crystallised during cryothermo-metric runs, helped in specifying the composition and salinity of the aqueous solutions. During reheating of frozen inclusions, after the melting of the first solid ($T_h$), subsequent solids present in the inclusions were either hydrohalite or ice. Overall salinity (CaCl$_2$±NaCl) ranges between 9.1 and 32.3 mass % (Table 3) and no trends between salinity and $T_h$ at any of the investigated sites were noted (Fig. 11).
Fig. 8. Different types of fluid inclusions in quartz from the studied areas. **A** — regular, nearly negative crystal shape of a two-phase FI (L — liquid, V — vapour), JGL; **B** — irregular shape of a two-phase FI, JGL; **C** — three-phase FI (S — solid) with a fan of flakes (muscovite), JGL; **D** — solid-dominated three-phase FI (muscovite), JGL; **E** — three-phase FI with a crystal-shaped solid (muscovite), JGL; **F** — three-phase FI with a grain of calcite, ZAD; **G** — three-phase FI with a small grain of reddish hue (haematite?), ZAD; **H** — the most characteristic distribution of FIs (of L + V ± S phase composition) in clear quartz, vapour bubbles inside the inclusions are clearly recognizable, ZAD.
Measurements of $T_{\text{mhh}}$ and $T_{\text{mice}}$ (Table 3, Fig. 12) demonstrate a large compositional variability in the Na/Ca ratio and salinity in samples from the Žulová area where the highest and lowest Na/Ca ratios and salinities of fluids were determined. The Na/Ca ratios and total salinities are negatively correlated (Fig. 12, Table 3). The values of Na/Ca ratio are lower at JGL indicating a slightly higher concentration of Ca$^{+2}$ ions compared to that at SCV.

The measurements of $T_{\text{mhh}}$ within the youngest growth zone of quartz crystals at the SCV site are about −26 °C suggesting higher concentrations of Ca$^{+2}$ ions in younger fluids, while, in core zones of crystals, temperatures about −22 °C are more common.

Oxygen isotope data

The investigated quartz yielded values of δ$^{18}$O between +8.4 and +12.9 ‰ V-SMOW (Table 4). The lowest values occur in samples from veins in weakly altered granitoids at the ZAD site and the highest positive values produced quartz crystals from totally altered gneisses as country rocks at the SCV site.

Discussion

Pressure and temperature conditions

The results obtained show that all studied fluid inclusions can be considered as primary (even in seemingly short trails) because there are no systematic deviations within microthermometric parameters. The consistent values of $T_h$, salinity and chemical composition of the fluids indicate a uniform fluid system. These circumstances allow data interpretation from all sites and all veins together. The concept of fluid trapping conditions could be performed using marginal isochores (Fig. 13) which were calculated with application of minimal and maximal $T_h$ and salinity parameters. Because the fluid state is not favourable for determining the fluid trapping temperature using the pressure correction calculation, published pressure conditions proposed for the Jeglowa site were
used (50–60 MPa, Karwowski & Kozlowski 1975, based on the difference in the homogenization and decrepitation temperatures of fluid inclusions). These pressure conditions define fluid trapping and quartz crystallization temperatures in the range of 155–210 °C. The delimited $p$–$T$ area also lies at the intersection with the thermal gradient of 30 °C/km for hydrostatic pressure conditions (Fig. 13). These conditions, which are close to the current thermal gradient (Hurtig & Čermák 1992), can be considered as reasonable values for the post-Variscan regime corresponding to the depth of formation of the studied mineralization of approx. ≤5 km. The other indicated gradients represent higher thermal or pressure conditions, which are close to higher $p$–$T$ conditions common to the orogen (e.g., Schneider et al. 2014).

The nature of fluids and their origin

Determined eutectic temperatures (between −67 and −45 °C), correspond to metastable (lower range) and stable eutectic temperatures (upper range) for the Na–Ca–Cl system with possible admixture of other cations, such as K$^+$, Mg$^{2+}$ (Borisenko 1977, 1982; Davis et al. 1990; Spencer et al. 1990). Fluids of that composition and with high salinity are largely discussed in terms of the basement and basinal brines (Yardley & Bodnar 2014 and references therein; Walter et al. 2016). Two models of the basement brines are proposed. One is based on enrichment of low-salinity fluids by solutes during water-rock interaction (e.g., Fritz & Frape 1982; Markl & Bucher 1998; Stober & Bucher 2004). The alternative model proposes that the high salinity can be inferred from external sources, such as evaporites in the sedimentary cover (e.g., Bottomley et al. 1994; Gleeson & Yardley 2002; Bejaoui et al. 2014 and references therein), generally derived from sea water (e.g., Behr et al. 1993; Emmermann & Lauterjung 1997). However, mass-balance calculations indicate that fluid-rocks reactions alone cannot explain the high salinity of basement brines and an external source of salinity is expected (Savoye et al. 1998). Such external source can be low-temperature formation (basinal) brines (e.g., Freeman 2007) which generally show the same chemical composition as that discussed for the fluids in this study (e.g., Houston et al. 2011).

High salinity fluids, with Ca–Na–Cl composition, may have a magmatic origin, but they are of higher temperatures (Yardley & Bodnar 2014; Harlaux et al. 2017) and hence it is unlikely that the studied solutions would be of magmatic origin.

![Fig. 12. Diagram with isotherms for the system H$_2$O–NaCl–CaCl$_2$ (Janatieva 1946; Vanko et al. 1988; Oakes et al. 1990; Williams-Jones & Samson 1990) with fluid data from investigated quartz showing the extent of NaCl/CaCl$_2$ ratios for all three studied sites. Some data are used from Peša (2008).](image)

![Table 3: Ranges of microthermometric data and fluid characteristics of the studied localities in Silesicum.](table)

<table>
<thead>
<tr>
<th>Locality</th>
<th>(N)</th>
<th>$T^\dagger$</th>
<th>$T_e$</th>
<th>$T_{hh}$</th>
<th>$T_{ice}$</th>
<th>Salinity</th>
<th>$\Phi$ (NaCl/NaCl+CaCl$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jegłowa – JGL</td>
<td>52</td>
<td>132/176</td>
<td>−59/−51</td>
<td>−26.5/−8.0</td>
<td>−30.5/−24.0</td>
<td>25.1/26.8</td>
<td>0.30/0.70</td>
</tr>
<tr>
<td>Žulová – ZAD</td>
<td>81</td>
<td>124/174</td>
<td>−67/−45</td>
<td>−27.0/−5.8</td>
<td>−38.5/−5.6</td>
<td>9.1/32.3</td>
<td>0.16/0.95</td>
</tr>
<tr>
<td>Stará Červená Voda – SCV</td>
<td>49</td>
<td>134/169</td>
<td>−66/−46</td>
<td>−27.0/−12.8</td>
<td>−23.9/−9.5</td>
<td>13.5/25.6</td>
<td>0.44/0.90</td>
</tr>
</tbody>
</table>

Fig. 11. Microthermometric data from FIs in quartz from studied sites and the extent of salinity and $T_e$ from some other localities in the region where Ca–Na–Cl fluids occur: A — Cracow ore district (dolomite, calcite, Heijlen et al. 2003); B — Zálesí uranium deposit (quartz, calcite, Dolníček et al. 2009); C — Horní Město ore district (quartz, calcite, Fojt et al. 2007); D — Vernířovice (secondary FIs in Variscan quartz, Kontár 2011).
The source of studied fluids will have been a rather low temperature one. Brines of marine origin documented according to their I–Br–Cl systematics (Carpenter 1978) are reported from many European platforms (see overview in Schmidt Mumm & Wolfram 2004; Muczez et al. 2005). These brines are parental solutions of the Kupferschiefer mineralization (Muczez et al. 2005; Brown 2009), the post-Variscan polymetallic mineralization in the Moravo–Silesian Paleozoic region (Slobodník et al. 1999; Kučera et al. 2010), the Cracow Ore District (e.g., Heijlen et al. 2003) with Pb–Zn deposits dated at 135 Ma by the Rb–Sr method, and also of the uranium ore district, revealed a mixture of meteoric water with evaporated seawater (Heijlen et al. 2003; Dolníček et al. 2009). The authors discussed the origin of these fluids based on both oxygen isotopic composition (δ¹⁸O ≤ 0‰) and I–Br–Cl systematics. Thus the sea brines and meteoric water could be common fluid components within the post-Variscan mineralization in this region.

**Geological context of the quartz mineralization**

The occurrence of low-temperature saline fluids was found not only in primary inclusions of investigated quartz crystals but also in secondary inclusions in Variscan Alpine-type quartz veins in the Silesicum (Kontár 2011). Furthermore, the same type of saline fluids was also found in fluid inclusions in quartz of the post-Variscan mineralization stage at the strataform polymetallic deposit Horní Město (Fojt et al. 2007).

In view of the low temperature conditions of saline fluids of a consistent composition, supported by the oxygen isotopic composition of the fluids and their distribution in the wider region, the metamorphic or magmatic origin for the fluids can be rejected.

### Table 4: Isotopic composition of quartz and of aqueous fluid in isotopic equilibrium with quartz

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ¹⁸O (‰ V-SMOW) quartz</th>
<th>Range of T (°C)</th>
<th>δ¹⁸O (‰ V-SMOW) fluids</th>
</tr>
</thead>
<tbody>
<tr>
<td>JGL 1</td>
<td>+11.8</td>
<td>+155/+210</td>
<td>−3.3/+0.7</td>
</tr>
<tr>
<td>JGL 3 (apex of crystal)</td>
<td>+11.4</td>
<td>+155/+210</td>
<td>−3.7/+0.3</td>
</tr>
<tr>
<td>ZAD 1</td>
<td>+10.1</td>
<td>+155/+210</td>
<td>−4.9/+0.9</td>
</tr>
<tr>
<td>ZAD 2</td>
<td>+8.4</td>
<td>+155/+210</td>
<td>−6.6/−2.7</td>
</tr>
<tr>
<td>SCV 2 (apex of crystal)</td>
<td>+12.9</td>
<td>+155/+210</td>
<td>−2.2/+1.8</td>
</tr>
</tbody>
</table>

The released ions have influenced the chemical nature of fluids in fluids corresponds to the geochemical type of pluton wall-rocks (low K–high Ca discussed here, Řober-Dziedzic 1998).

The observed occurrence of wollastonite in quartz also fits well into the chemical environment of the studied low temperature hydrothermal process although the formation of wollastonite is generally associated with contact metamorphism and higher temperatures. However, the formation of wollastonite, as a product of the interaction of rocks with low-temperature fluids, was also found at several other places in the world (Kristmannsdóttir 1981; Ronoh 2015; Camprubí et al. 2019).

Gaseous fluid components are common, in particular, for metamorphic fluids in the deep crust (Yardley & Bodnar 2014). The detected gaseous components in the studied samples are present only in a very small amounts (undetectable by microtermometry). Therefore, their occurrence in brines can be interpreted rather as a product of maturation of organic matter as discussed by Essarraj et al. (2016) and Warren (2016).

The δ¹⁸O values of aqueous fluid in equilibrium with quartz (−6.6 and +1.8 ‰, see Table 4) are close to that of seawater with the addition of meteoric water. The obtained values differ from the isotopic values of Variscan fluids in the Silesicum, which show positive values above +1.9 ‰ (Slobodník et al. 2010a) and between +6 and +10 ‰ δ¹⁸O (Fojt et al. 2007). Generally, positive values are characteristic of magmatic or metamorphic waters (e.g., Taylor 1974; Giggenbach 1992; Hoefs 2015). On the other hand, there is an overlap of our data with the values of post-Variscan fluids parental to the regionally widespread mineralization throughout the Moravo–Silesian Paleozoic rocks, showing a range of δ¹⁸O between −0.9 and +3.0 ‰, suggesting the presence of seawater in the fluids (Kučera et al. 2010). Moreover, a detailed examination of fluids, at the nearby deposits at Zálesí and at the Cracow ore district, revealed a mixture of meteoric water with evaporated seawater (Heijlen et al. 2003; Dolníček et al. 2009).

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The authors discussed the origin of these fluids based on both oxygen isotopic composition (δ¹⁸O ≤ 0‰) and I–Br–Cl systematics. Thus the sea brines and meteoric water could be common fluid components within the post-Variscan mineralization in this region.
Consistent genetic features of fluids and the geological setting of investigated quartz mineralization within a regional scale indicate a connection with large-scale migration of fluids. The conditions for such migration was provided by the geological structure of the region.

The region shows a complex geological structure disrupted by a dense network of long-active faults (Aleksandrowski et al. 1997; Mazur et al. 2006; Zuchiewicz et al. 2007) resulting in seismicity (Štěpančíková et al. 2008; Havíř 2018) providing a suitable environment for an enhanced expulsion and migration of fluids. The nearby crystalline basement with Mesozoic and Cenozoic sedimentary cover sequences is indicative of a stable platform (e.g., McCann ed. 2008). This is supported by the paleogeographic models of the north-eastern part of the Bohemian Massif where extensive seas between the Vindelic Ridge, as the Bohemian Massif and the Fennosarmatian Land, existed during the Triassic and Jurassic periods. Later, this area became a part of the Cretaceous ocean, together with the West Carpathian foredeeps which were widespread to the North and East of the post-Variscan continent for tens of millions years during the Tertiary (Ziegler 1988, 1992).

These conditions could provide migration pathways for basinal fluid infiltration from the overlying sediments into the crystalline basement, a process which has been thoroughly discussed elsewhere (e.g., Gleeson et al. 2003; Warren 2016).

The spatial association of quartz mineralization with the occurrence of kaolinite and its relation to regional faults with NW–SE orientation is significant (Kužvart 1965; Krufa 1973; Milický et al. 1985; Fig. 2). Such a setting for kaolinite, with respect to the complex tectonic structure of the region, gives an impression of a genetic link between kaolinite and the hydrothermal activity associated with quartz mineralization (c.f. Boulvais et al. 2000). However, hydrothermal alteration of rocks can also prepare pathways, producing secondary permeability (Bongiolo et al. 2007; Frolova et al. 2014) for subsequent penetration of waters which decompose aluminosilicates in rocks (e.g., muscovite into kaolinite – Hemley & Jones 1964; Sheppard 1977; Boulvais et al. 2000; Dekov et al. 2008).

On the other hand, direct hydrothermal formation of kaolinite is not a rarity and it is documented in several regions in Europe and elsewhere (Merceron et al. 1992; Yuan et al. 2014). However, a detailed isotopic study is necessary to do to decide whether kaolinite is hydrothermal or formed during weathering.

**Conclusion**

The studied quartz mineralization in Silesicum and the genetically associated type of fluids have a regional distribution throughout the whole northeast part of the Bohemian Massif. The $P–T$ properties and fluid composition of the quartz mineralization and its oxygen isotopic signatures are consistent with the nature and migration of post-Variscan lower temperature fluids in the wider area of the north-eastern part of the Bohemian Massif. The findings discussed here indicate that the investigated fluid activity could be related to some post-Variscan platform stages or to the regime and development of the adjacent domain of the Western Carpathian system.

Hydrothermal fluids were most likely generated as transformed marine brines mixed with meteoric waters. The tectonic structure of the wider region of the north-eastern part of the Bohemian Massif indicates the likelihood that the long-active fault network provided deep-seated pathways for fluid migration. The studied mineral association of quartz veins and crystals with other minor minerals as well as those enclosed in inclusions and linked with rock alteration corresponds to the interaction of brines with rocks of granitic composition.

An interesting phenomenon of the vein quartz mineralization is the concomitant co-occurrence of kaolinite. The geological context indicates a possible link with the hydrothermal process, but without an isotopic study, the origin of kaolinite remains unresolved.

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**References**


Boderke E. 1931: Die moldanubische Überschiebung im Sudetenvorlande. Zentralblatt für Mineralogie, Geologie und Paläontologie Abt. B. 349–408.
Bongiolo E.M., Bongiolo D.E., Sardini P.M.A.S., Siitari-Kauppi E., González-Partida E., Richard A., Boiron M-Ch., Brown A.C. 2009: A process-based approach to estimating the copper...
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