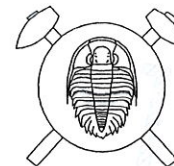


## Formation conditions of calcite veins in the quarry "V Kozle (Hostim I, Alkazar)" in the Bohemian Karst

Podmínky vzniku kalcitových žil v lomu V Kozle (Hostim I., Alkazar) v Českém krasu  
(Czech summary)



(4 text-figs., 1 photo)

VÁCLAV CÍLEK<sup>1</sup> - PETR DOBEŠ<sup>2</sup> - KAREL ŽÁK<sup>2</sup>

<sup>1</sup> *Geologický ústav AVČR, Rozvojová 135, 165 00 Praha 6*

<sup>2</sup> *Český geologický ústav, Klárov 131/3, 118 21 Praha 1*

In the quarry "V Kozle" (also called Hostim I., Alkazar) situated on the left bank of the Berounka river in the central part of the Bohemian Karst, Devonian limestones are crosscut by several steeply dipping calcite veins. The largest vein occurs in the NW section of underground galleries, which were excavated here by the German army in 1944-1945 to construct an underground production plant. Later, in the early sixties, part of the underground workings was used as a repository of low-level radioactive waste.

The steeply dipping calcite vein of NNW-SSE direction (160°) reaches maximal thickness of about 1.9 m and is accompanied by zones of brecciation and locally by dolomitization. A 15-cm calcite scalenohedron from a cavity in the central part of the vein was used for a detailed fluid inclusion and stable isotope study.

Based on the data obtained, formation of the studied vein as a result of karstic processes can be excluded. Fluid inclusion data indicate that the central part of the scalenohedron was formed from fluids with temperature above 100 °C. Based on carbon isotope data, formation of the vein during diagenetic processes and derivation of the vein-forming fluids from the limestone sequence itself can be excluded as well. The vein-forming fluids probably originated in deeper parts of the Barrandian sedimentary basin where clastic rocks and volcanites predominate. This idea is supported by local dolomitization of the brecciated zone. Oxygen isotope data indicate that fluids that formed the main calcite accumulation were either deep circulating meteoric waters or pore-waters from deeper sections of the basin. The youngest calcite in the vein filling was deposited from fluids with temperatures of up to 60 °C and with very low salinities.

### Introduction

The limestone quarry "V Kozle" (also called quarry Hostim I. or Alkazar) is located in the central part of the Bohemian Karst on the left bank of the Berounka river near the mouth of the stream Kačák. A system of underground galleries was excavated here by the German army in 1944-1945 during the construction of an underground production plant. Some parts of the underground galleries were used as a repository of low-level radioactive waste during the early sixties (e.g. Lysenko 1992, see Fig. 1).

Within the galleries and in the quarry itself, Devonian limestones of Prag and Zlíchov stages are cut by several steeply dipping calcite veins. The thickest vein occurs in the NW part of the galleries, about 70 m NE from the repository. Similar, steeply dipping and coarse-crystalline calcite veins are quite common in the Bohemian Karst and can be found within a belt stretching from the Dalejské valley near Prague to the quarry "VČS-Západ" and to Kotýz near Koněprusy. A north-south trending steeply dipping calcite vein with thickness up to 2 m and more than 400 m in length has

been reported recently from the "VČS-Východ" quarry by Bosák (1994). The origin of fluids which formed these veins was studied by Žák et al. (1987). The thick calcite vein outcropping in the galleries of the quarry "V Kozle", representing one of the biggest vein structures of this type in the whole Bohemian Karst, was selected for a detailed fluid inclusion and stable isotope study.

A genetic study of calcite veins at this locality close to the radioactive waste repository is important due to the fact that these veins represent a distinct inhomogeneity in the limestone massif and form zones of increased permeability.

### Vein description

The studied calcite vein (see Fig. 1) is of NNW-SSE strike (160°) and dips almost vertically. The vein development is irregular, lens shaped, with maximum known thickness of 1.9 m. The vein filling is monotonous, represented by coarse-crystalline, often milky calcite with average grain size from 3 to 10 cm. The eastern vein boundary is straight, modified by younger



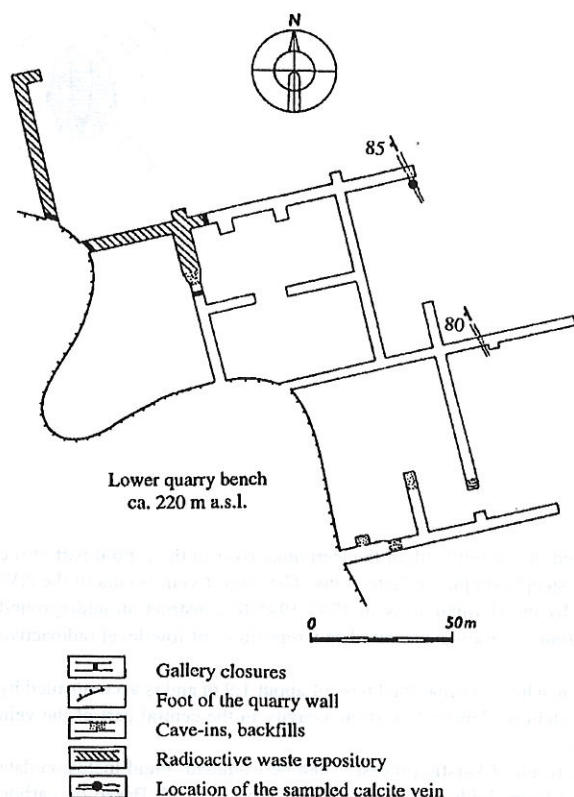


Fig. 1 Location of the studied calcite vein in the underground galleries of the quarry "V Kozle". Map modified after V. Lysenko (1992)

tectonics, while the western vein margin is made of tectonic breccia - blocks and fragments of surrounding limestone cemented by coarse-crystalline calcite. The limestone fragments are up to 30 cm large and locally dolomitized. Similar dolomitization can be observed in the vicinity of calcite veins elsewhere in the quarry.

Within the central zone the vein contains several cavities. The largest cavity is flat, subhorizontal, 30 to 70 cm high with a length of about 2.7 m. Originally, the cavity displayed druses of calcite scalenohedrons of up to 15 cm in size, best developed in the central part of the cavity. One calcite scalenohedron from this cavity was sampled for detailed study (see Photo 1). The samples analyzed thus represent only younger filling stages of the vein. Recently the cavity filling was completely destroyed by collectors.

Calcite scalenohedrons, together with younger generations of calcite crystals covering them, can provide information on the development of fluids which were present during the growth of the crystals inside the cavity.

#### Detailed description of the scalenohedron zoning and calcite types studied

The main scalenohedron with dimensions 50x70x150 mm displays an almost transparent to slightly yellowish core with perfect cleavage. Towards the top and to

the margins of the scalenohedron there is a transition zone of dull yellow up to yellowish-brown color with the same coarse cleavage. The crystal rim proper is cleavable and displays brownish-red tint. The main crystal is covered by younger calcite types: on one side an about 25 mm thick layer of fine-grained calcite material composed of small calcite crystals, only poorly cemented together, on the opposite side there is a cover of 5 to 10 mm large transparent calcite rhombohedrons with slight local signs of younger dissolution. The interrelation of this fine-grained layer and young crystals on the opposite side of the scalenohedron is hard to determine. These younger crystals are partly covered by the fine-grained calcitic mass, but contrary relation can be observed, too. It is possible, that both types of the younger calcite could be more or less contemporaneous, but due to the deposition in a dynamic fluid flow conditions prevailing locally on both scalenohedron sides were different.

Seven carbon and oxygen isotopic analyses of calcite (see Tab. 1 and Photo 1) are presented. Fluid inclusions were studied in the central part of the scalenohedron and in young transparent rhombohedrons (i. e., samples 1 and 7).

#### Methods

Seven chip samples were taken of the calcite scalenohedron and younger calcite types (see Tab. 1 and Photo 1), weighing about 0.5 g each (from samples 1 and 7 suitable cleavage flakes were selected for fluid inclusion study). The samples were homogenized in an agate pan. From the homogenized sample a 10 mg subsample was used for isotope determinations. The  $\text{CO}_2$ -gas for carbon and oxygen isotope determinations was prepared by reaction of calcite with 100 %  $\text{H}_3\text{PO}_4$  at 25 °C under vacuum (after McCrea 1950). Carbon and oxygen isotope determinations were performed on a Finnigan MAT 251 mass spectrometer in the laboratories of the Czech Geological Survey, Prague. Results are expressed in usual  $\delta$  notation relative to international V-PDB standard. The  $\delta^{18}\text{O}$  values related to V-SMOW standard were derived by recalculation.

Fluid inclusions were studied in cleavage flakes using optical microthermometrical methods of homogenization and cryometry on a CHAIXMECA heating and freezing stage, which enables observation of phase changes inside fluid inclusions in the temperature range from -180 °C to +600 °C. The apparatus was calibrated using MERCK chemical standards and the triple points of water and  $\text{CO}_2$ .

#### Carbon and oxygen isotopic compositions of calcite

Results of carbon and oxygen isotope determinations are presented in Table 1 and Fig. 2.



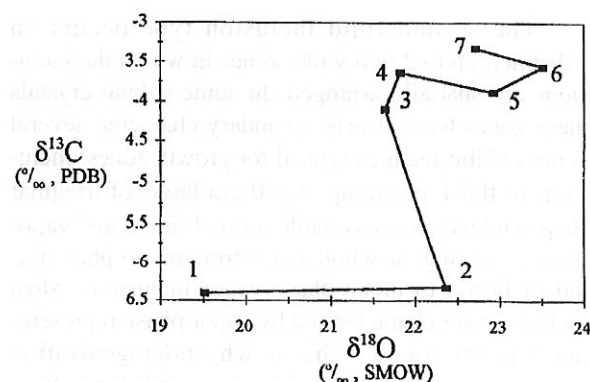


Fig. 2. Carbon and oxygen isotopic composition of calcite in a profile across the studied sample (1 - the oldest, 7 - the youngest; see description in Tab. 1 and sampling points in Photo 1)

### Fluid inclusion study

#### Sample 1 - the central, oldest part of the crystal

Secondary inclusions only were found in this calcite generation, i.e., inclusions which were trapped after the final growth of the mineral during the healing of the cracks by solutions responsible for the growth of more marginal crystal parts or even during younger processes. Fluid inclusions occur either on planes parallel to the cleavage (fluid inclusions of flat, elongated or irregular shape with maximum size of up to 80  $\mu\text{m}$ ) or

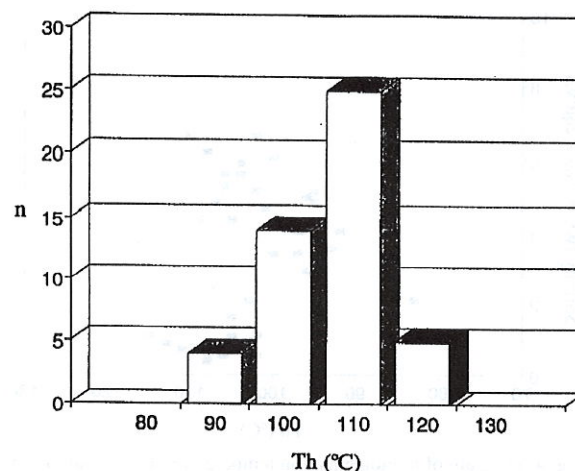


Fig. 3. Homogenization temperatures of fluid inclusions in calcite from the central part of the studied scalenohedron (sample 1 in Tab. 1, Fig. 1 and Photo 1)

on healed fissures (fluid inclusions of oval shape, irregular shape or of a negative crystal shape, size from 5 to 30  $\mu\text{m}$ ).

Fluid inclusions contain aqueous solution with more or less consistent ratio of liquid and vapor phase - vapor bubbles occupy from 5 to 20 vol. % under laboratory temperature. All fluid inclusions homogenized to liquid in a temperature range from 83 to 115  $^{\circ}\text{C}$  (see

Fig. 3). Melting temperature of the last ice crystal ( $T_m$ ) oscillated in the range from -0.2 to -4.9  $^{\circ}\text{C}$ , which corresponds to the salinity of 0.35 to 7.70 wt. % NaCl equiv. (after Bodnar 1993). Inclusions situated in one fluid inclusion trail exhibit similar salinities, while different fluid inclusion trails (zones) differ. Some fluid inclusion trails are characterized by low salinities ranging from 0.35 to 2.0 wt. % NaCl equiv., while other show slightly higher values, from 3.8 to 7.7 wt. % NaCl equiv. On some larger fluid inclusions an eutectic temperature ( $T_e$ ) was measured, according to which the salt system of the solution can be estimated. The  $T_e$  temperatures ranging from -48.0 to -53.6  $^{\circ}\text{C}$  suggest that  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , NaCl and also KCl are likely components of the solution (Borisenko 1977).

#### Sample 7 - younger calcite rhombohedrons

Two types of fluid inclusions were observed. The first type is represented by secondary fluid inclusions on the healed fissures with virtually liquid-only fluid. One fluid inclusion zone only contained two-phase liquid-dominated inclusions with small vapor bubble representing from 5 to 10 vol. %. Inclusions usually have a negative crystal shape with dimensions from 5 to 20  $\mu\text{m}$ . The two-phase inclusions homoge-

Table 1. Carbon and oxygen isotopic composition of calcite

Sample No.	Sample description	$\delta^{13}\text{C}$ (‰ V-PDB)	$\delta^{18}\text{O}$ (‰ V-PDB)	$\delta^{18}\text{O}$ (‰ V-SMOW)
1.	Central part of the main crystal with perfect cleavage, transparent to yellow tint	- 6.40	- 11.01	+ 19.51
2.	Marginal zone of the main crystal with perfect cleavage, yellowish-brown tint	- 6.32	- 8.25	+ 22.36
3.	The main crystal rim, narrow zone of reddish-brown tint	- 4.09	- 8.94	+ 21.64
4.	Growth-layer of fine-grained calcite near the main crystal rim	- 3.63	- 8.77	+ 21.82
5.	Growth-layer of fine-grained calcite in its central part	- 3.88	- 7.70	+ 22.92
6.	Growth-layer of fine-grained calcite, the youngest zone	- 3.55	- 7.13	+ 23.51
7.	Transparent young crystals with perfect cleavage on the opposite side of the main crystal	- 3.32	- 7.91	+ 22.71



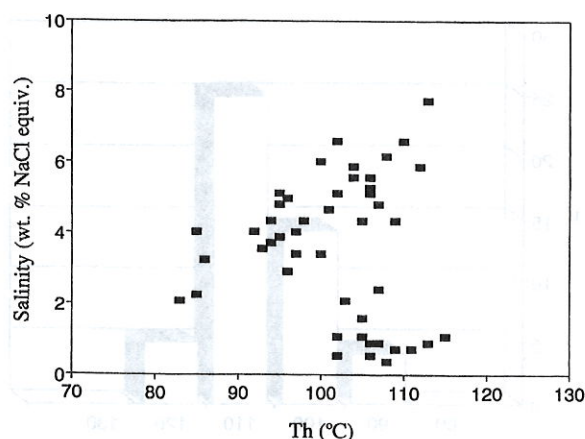


Fig. 4. Diagram of homogenization temperature (Th) vs. salinity of fluid inclusions in calcite from the central part of the studied scalenohedron (sample 1 in Tab. 1, Fig. 1 and Photo 1)



Photo 1. Studied scalenohedron from the calcite vein from the quarry "V Kozle"

Photo N. Hrdličková

nized to liquid in the temperature range from 41 to 58 °C. During the temperature drop after the homogenization the vapor phase was usually not separated again and the inclusions remained mono-phase. Melting of the last ice crystal was observed at temperatures above 0 °C. This phenomenon can be explained by metastable behavior of ice, which is often observed in liquid-only inclusions. Based on these data exact determination of the fluid salinity is impossible, but the presence of a fluid characterized by very low salinity is evident.

The second fluid inclusion type occurs on a distinct, up to 2 mm wide, zones in which the inclusions are spatially arranged. In some calcite crystals these zones have clearly secondary character, several zones exhibit features typical for growth zones. Inclusions of this type are up to 200 µm large, of irregular shape and have very variable ratio of liquid and vapor phase, covering the whole range from mono-phase liquid inclusion to mono-phase vapor inclusions. Most inclusions are characterized by vapor phase representing 5 to 90 vol. %. This is why homogenization temperatures (Th) oscillated in a very wide range from 48 to 172 °C for inclusions with vapor phase of up to 30 vol. %, while inclusions with higher volume of vapor phase either decrepitated before homogenization or did not reach homogenization below 300 °C. Salinity of fluids is very low, up to 1 wt. % NaCl equiv. ( $T_m = 0.0$  to  $-0.2$  °C).

#### Interpretation of fluid inclusion and stable isotope data

The cavity within the vein filling of the calcite vein is substantially older than numerous karst cavities found in this area. At present, the cavity is dry, with no evidence of speleothem formation.

On several localities in the Bohemian Karst large calcite crystal druses covering the walls of paleokarstic cavities can be found. These calcite types probably precipitated in the zones of karstic activity of freatic waters below the erosion base level. For example the walls of the cave "Big Crystalline" 5.5 m in length were fully covered with up to 20 cm large milky calcite crystals (quarry "VČS-Západ", at present mined out, documentation is available in the Czech Speleological Society archives).

The vein structure and the studied calcite crystals from the underground galleries of the quarry "V Kozle" are different. They resemble the so called post-ore calcites from hydrothermal veins of the uranium deposits in the Příbram area.

Based on the geological position and on the carbon isotopic composition of calcite, the formation of the studied vein during early diagenetic processes can be excluded. Diagenetic carbonate types are characterized by  $\delta^{13}C$  values usually very close to those of limestones. For the limestones of Bohemian Karst a range of  $\delta^{13}C$  values from + 1.0 to + 3.5 ‰ was obtained (Žák et al. 1987, Kolářová 1993, J. Hladíková unpublished data), which is quite different from those of the "V Kozle" calcite vein.

Both fluid inclusion and stable isotope data excluded a possibility that the calcite vein was formed as a result of low-temperature karstic processes. Any relationship to karst processes are doubtful due to high homogenization temperatures of fluid inclusions in calcite, which indicate temperatures above 100 °C, and



high salinities of the fluids reaching up to 7.7 wt. % NaCl equiv. Karstic calcite types (speleothems) typically exhibit  $\delta^{13}\text{C}$  values in the range from -6 to -11 ‰. Also the  $\delta^{18}\text{O}$  values of typical speleothems are different from those of the studied calcite. Calcite veins with similar carbon and oxygen isotopic composition and similar strike have been recorded in the Bohemian Karst already in the Koněprusy area by Žák et al. (1987).

Both studied calcite generations contained fluid inclusions of rather low and slightly variable salinity. Secondary fluid inclusions from the central part of the main scalenohedron do not have direct relationship to the crystallization of this crystal zone, but they can be related to the fluids responsible for the formation of more peripheral crystal zones. With respect to constant filling of these inclusions of the central crystal part it seems evident, that they were not trapped during boiling conditions.

The homogenization temperatures ( $T_h$ ) represent minimum formation temperatures. A recalculation of  $T_h$  of fluid inclusions to actual temperatures of trapping requires the knowledge of pressure of trapping. No data on pressures during this mineralization event are known, nevertheless the pressure correction would be probably relatively small (under a hydrostatic pressure regime and depth of 500 m the pressure correction for fluids of this salinity is only of about 10 °C, after Potter 1977).

Fluid inclusions with very variable ratio of vapor and liquid phase found in the calcite rhombohedrons covering the main scalenohedron (sample 7) probably represent a period of coexistence of two separate phases - vapor and liquid - i. e., conditions of a heterogeneous fluid. Under such conditions fluid inclusions trap a mechanical mixture of both phases and the homogenization temperatures do not reflect the trapping temperatures. The calcite of this type covers the main scalenohedron on one side only and probably precipitated under conditions of dynamic fluid flow. The coexistence of a vapor and liquid phase can be a result of separation of dissolved gases from the solution or a result of simple mechanical mixing of two phases during fluid flow under low temperature and pressure.

The group of secondary inclusions with  $T_h$  close to 50 °C found in sample 7 represents probably the youngest generation of fluid inclusions. Trapping temperatures close to measured  $T_h$  can be estimated.

For the estimation of possible origin of the fluids responsible for the formation of the vein, carbon and oxygen isotope compositions of the fluids must be calculated based on the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of calcite and temperature. With respect to the host rock chemistry and the temperatures below 150 °C,  $\text{HCO}_3^-$  was supposed to be the dominant carbon species of the solution. The temperatures of 115 °C for the central part and 50 °C for the peripheral part of the sample were used as the most reliable temperature estimate. The calculated parameters of the solutions are then as follows:

Sample No.	Temperature (°C)	$\delta^{13}\text{C}_{\text{fluid}}$ (‰ V-PDB)	$\delta^{18}\text{O}_{\text{fluid}}$ (‰ V-SMOW)
1.	115	-9.0	+ 3.5
7.	50	-5.8	+ 0.2

This oxygen isotopic composition of the fluids is quite different from those typical for karstic waters or meteoric waters with shallow circulation. Relatively low  $\delta^{13}\text{C}_{\text{fluid}}$  values indicate that the dominant part of carbon was derived from a source outside of the sequence of Paleozoic limestones of the Bohemian Karst. Based on fluid inclusion data, it can be concluded that the fluids could be either deep circulating meteoric waters, which were heated during circulation in clastic rocks of the deeper parts of the sedimentary basin to temperatures above 100 °C and obtained the salt content there, or directly pore waters from these clastic horizons.

In the carbonate rocks of the Paleozoic Prague basin higher temperatures between 100 and 150 °C during late diagenesis, folding and local intensive dolomitization were suggested by Suchý et al. (1992). These dolomitization events connected with intensive fluid migration are widespread in the Prague basin in the basal horizons of the limestone sequences. The find of the calcite vein in the quarry "V Kozle" is another piece of evidence for movement of higher-temperature fluids through the carbonate rocks of this region. At this locality the fluid movement is connected with local dolomitization of the limestone. Similar stable isotope data found previously in similar calcite veins in the Koněprusy area by Žák et al. (1987) indicate that this fluid movement through steep structures of generally N-S direction was more widespread in the area of Bohemian Karst.

Submitted June 2, 1994

## References

- Bodnar, R. J. (1993): Revised equation and table for determining the freezing point depression of  $\text{H}_2\text{O}$ -NaCl solutions. - *Geochim. cosmochim. Acta*, 57, 683-684. Oxford.
- Borisenko, A. S. (1977): Izučeniye solevogo sostava rastvorov gazovožidkych vključenij v mineralach metodom kriometrii. - *Geol. i Geofiz.*, 8, 16-28. Novosibirsk.
- Bosák, P. (1994): Nové geologické struktury ve VČS-Východ. - *Český kras*, 19, 37-39. Beroun.
- Lysenko, V. (1992): Úložiště radioaktivních odpadů v lomu Na Kozle (Hostim I.). - *Český kras*, 17, 33-35. Beroun.
- McCrea, J. M. (1950): On the isotopic chemistry of carbonates and a paleotemperature scale. - *J. Chem. Phys.*, 18, 849-857. London.
- Potter II, R. W. (1977): Pressure corrections for fluid-inclusion homogenization temperatures based on the volumetric properties

of the system  $\text{NaCl-H}_2\text{O}$ . - U. S. Geol. Survey J. Res., 5, 603-607.

Suchý, V. - Dobeš, P. - Horák, J. - Hyršl, J. - Mráz, L. - Rozkošný, I. - Žák, K. (1992): Deep diagenesis of organic matter-rich marine mudrocks: Tentative model for the Lower Paleozoic Barrandian Basin, Czechoslovakia. - *Metallogeny and anoxic*

*ic environments*, Proceedings of the IVth Czech and Slovak Working Group of the IGCP No. 254, 15-16. Guliver, Prague.

Žák, K. - Hladíková, J. - Lysenko, V. - Slačík, J. (1987): Izotopické složení uhlíku a kyslíku jeskynních sintrů, žilných kalcitů a sedimentárních vápenců z Českého krasu. - *Český kras*, 13, 5-28. Beroun.

## Podmínky vzniku kalcitových žil v lomu V Kozle (Hostim I., Alkazár) v Českém krasu

V kalcitovém skalenoedru z mohutné kalcitové žíly o mocnosti až 1,9 m, prorážející masivní devonské vápence Českého krasu v sz. části podzemních chodeb v lomu V Kozle (lom Hostim I., též zvaný Alkazár) byly studovány fluidní inkluze a distribuce stabilních izotopů uhlíku a kyslíku.

Lom se nachází na levém břehu řeky Berounky nad ústím Kačáku. Strmě zapadající kalcitová žíla směru SSZ-JJV je doprovázena zónou drcení a její okolí je místy dolomitizováno. K detailnímu studiu byl zvolen 15 cm velký kalcitový skalenoedr z dutiny v centrální části žíly.

Vznik uvedené kalcitové žíly v souvislosti s nízkoteplotními krasovými procesy lze zcela vyloučit. Ze studia fluidních inkluzí vyplývá, že kalcit v centrální části studovaného skalenoedru vznikl za teplot nad 100 °C. Na základě vypočteného izotopického složení uhlíku a kyslíku zdrojových roztoků lze vyloučit jejich původ v karbonátových horninách samotných. Jak naznačuje i lokální dolomitizace okoložilných drcených pásem, roztoky (buď hluboko cirkulující meteorické vody nebo pórové vody ze sedimentární pánve) pocházely z hlubších částí pánve, z podložních souvrství nekarbonátových hornin. Nejmladší kalcit v žilné výplni vznikl nejspíše z roztoků s velmi nízkou salinitou a teplotou do 60 °C.