



Reconstruction of Hydrothermal Processes in the Cyprus Type Fe-Cu-Zn Deposits of the Italian Northern Apennines: Results of Combined Fluid Inclusion Microthermometry, SEM-CL Imaging and Trace Element Analyses by LA-ICP-MS

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Abstract: Quartz from the stockwork zone of various Cyprus type volcanogenic massive sulfide deposits (Boccassuolo, Reppia, Campegli, Bargone and Vigonzano) from the unmetamorphosed, Jurassic Northern Apennine ophiolites was studied in order to provide details on the submarine hydrothermal conditions and the characteristics for ore formation. Our detailed SEM-CL investigation of quartz contributed to a robust characterization and interpretation of primary fluid inclusions and microthermometry data. SEM-CL imaging was also useful for reconstructing the consecutive steps of quartz precipitation. The determination of trace element contents according to growth zoning in quartz by LA-ICP-MS constrained the compositional variations of parent fluids during the hydrothermal activity. A continuously cooling fluid regime characterized each studied volcanogenic massive sulfide (VMS) occurrence although the minimum formation temperatures were different (Bargone: 110–270 °C; Boccassuolo: 60–360 °C; Campegli: 110–225 °C; Reppia: 50–205 °C; Vigonzano: 260–330 °C), the range of temperature most probably depends on the original position of sampling in relation to the centers of the hydrothermal systems. Compositional changes are reflected by variations in the methane content (0.13-0.33 mol/kg) and salinity (2.6-9.3 NaCl equiv. wt. %) in the fluid inclusions of quartz and calcite as well as a changeable Al content (11–1526 ppm) in quartz. This study demonstrates that the combined use of SEM-CL imaging and LA-ICP-MS analyses, coupled with fluid inclusion microthermometry, can constrain the different fluid conditions of ore forming and the barren stages of evolving submarine hydrothermal systems.

Keywords: quartz precipitation; VMS stockwork ore; Italian Northern Apennine ophiolites

1. Introduction

Over the past decades, numerous case studies and reviews have been published on modern and ancient submarine hydrothermal systems [1–6]. This has resulted in robust genetic and descriptive models for different types of volcanogenic massive sulfide (VMS) deposits (e.g., Kuroko type, Abitibi type, Cyprus type) [4]. Although many studies have been completed on different VMS systems, a significantly larger number of publications are available for Precambrian deposits and Phanerozoic Kuroko type systems compared with Cyprus type deposits (e.g., [1–11]). This latter type of Cu-bearing VMS deposits are typically hosted in mafic rocks of the upper oceanic crust and are often preserved in ophiolite sequences. Although their economic significance is smaller than the other types of VMS



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deposits, they have historically been major sources of copper for the ancient civilizations in the Mediterranean region. Furthermore, many mineral exploration companies still consider these deposits as attractive targets.

VMS deposits are composed of massive sulfide lenses with zones of stringer sulfides beneath and are formed at or near the seafloor from circulating hydrothermal fluids (e.g., [1–11]). Based on abundant fluid inclusion data gathered from various types of VMS deposits (including microthermometry, stable and noble gas isotope data, e.g., [5,7–9,12,13]), the source of the hydrothermal fluid is understood to be modified seawater. However, there is also some debate regarding the modification of this fluid through fluid-rock interaction in the oceanic crust and/or the admixture of magmatic fluid. Phase separation can also play a role in some systems. However, these complex modification processes as well as the evolution of the hydrothermal fluid are often hard to trace (either due to complex overprinting processes or analytical difficulties) and it may make the interpretation uncertain (e.g., [5,12,13]). This is especially true in the case of Cyprus type deposits where the mode of preservation includes the process of obduction and often orogenic deformation [2,4]. In the present study, we contribute to this topic through the application of a methodology that is seldom used in the field of VMS research.

Textural analyses of minerals by cathodoluminescence, especially quartz, have several fields of applications in the geosciences. It is a powerful tool for understanding complex mineral formation processes (e.g., [14–16]). The use of scanning electron microscopy cathodoluminescence (SEM-CL) to reveal textural properties and growth zoning of quartz is essential to reliably interpret fluid inclusion data (e.g., [17,18]). This is especially true for mineral systems that may have suffered some overprinting processes as it makes the distinction between primary and secondary fluid inclusions more straightforward. In spite of these advantages, SEM-CL supported fluid inclusions studies are almost exclusively limited to Cu-porphyry and epithermal systems (e.g., [19–25]). Notably fewer examples are known from other deposit types (e.g., orogenic gold, Mississippi Valley Type and VMS deposits) (e.g., [26–28]). In addition to the above technique, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is capable of mapping the variation in the trace element content of hydrothermal quartz according to the textural features revealed by SEM-CL (e.g., [27–29]). This analytical technique could also be applied to evaluate changes in fluid composition in an evolving hydrothermal system.

In this study we have targeted the Cyprus type Fe-Cu-Zn deposits of the Northern Apennines, Italy, which occur in an ophiolitic series accumulated in the western limb of the Jurassic Neotethyan Ocean. These deposits have been known since the Bronze Age [30] and detailed mineralogical, petrographic and geochemical studies completed on them since the 1950s [31–37] provide a solid basis for their interpretation as Cyprus type VMS deposits. However, recent studies have mainly addressed the mineral chemical, geochemical and geotectonic aspects of ore deposit formation [33–37] and only a few have focused on the reconstruction of hydrothermal processes by fluid inclusion studies [38]. In addition to this, these locations provide an excellent opportunity to model the fluid evolution of Cyprus type VMS deposits. As metamorphic overprinting is not a characteristic feature of these deposits (orogenic deformation occurred in a cool regime), only the results of oceanic hydrothermal alteration are observable [39].

2. Geological Background

Ophiolite units representing the Piedmont-Ligurian Basin of the Neotethyan Ocean occur in the Western Alps and the Northern Apennines. While the former (west of the Sestri-Voltaggio Line) underwent high pressure low temperature metamorphism, the latter (east from the Sestri-Voltaggio Line) shows only the effects of low pressure and low temperature sea floor alteration without the overprinting of Alpine metamorphism. The non-metamorphosed oceanic crust fragments form the Liguride Nappe (Figure 1). The Ligurian Ophiolites consist of fragments of the lithosphere underlying the Liguria-Piedmont Ocean that was formed by the Jurassic divergence of the European and the

Adriatic plates in the western limb of the Neotethys ocean [40,41]. This ophiolite unit consists of an incomplete ophiolitic sequence in which the sheeted dyke complex and the transition zone are missing [42]. The Ligurian Ophiolites are conventionally divided into Internal and External Ligurides that represent the oceanic crust in two different paleogeographic environments: one in proximity to the rifting zone of an opening ocean (Internal Ligurides) and the other closer to the narrow Adria continental marginal basin (External Ligurides) [41].



Figure 1. Structural sketch map of the External and Internal Ligurides (based on [36]) with locations of the studied Cyprus type volcanogenic massive sulfide (VMS) deposits.

Several Fe-Cu-Zn sulfide deposits are known in the non-metamorphosed ophiolitic units [34,37] (Figure 1). Although copper mining was already ongoing during the Bronze Age in Eastern Liguria [30], systematic exploitation only started during the Industrial Era. Mining between 1850 and 1910 produced more than 1.5 Mt of ore with an average grade of 2%–7% Cu [43]. These occurrences contained more than 65% of the Italian ophiolite-hosted Cu reserves [37]. These deposits consist of stratiform massive sulfide lenses in serpentinite breccia within pillow basalt units or at the top of the volcanic pile. Stockwork-style mineralization occurs separately or under the massive sulfide bodies. The stockwork ore is hosted by serpentinite, gabbro and pillow basalt [31,34,37]. The peculiar situation with several different host rocks is the result of the geodynamic evolution of the Mesozoic Ligurian Ocean [36].

Stockwork mineralization in gabbro is known at Campegli and Bargone (Internal Ligurides) while the Boccassuolo deposit exposes stockwork mineralization in basalt and basalt breccia (External Ligurides). In these deposits, the quartz veins containing the disseminated sulfide phases are commonly between 0.1 to 1 meter wide. The ore deposit at Reppia (Internal Ligurides) contains stratabound and stratiform mineralization in pillow basalt and basalt breccia and stratiform mineralization in serpentinite breccia as well as a related stockwork mineralization in basalt. The stratiform and stratabound sulfide ores show massive textures. Quartz veins, up to several tens of centimeters in thickness containing inclusions of disseminated sulfide minerals, are located in the stockwork zones underlying the massive sulfide lenses. Stockwork mineralization in peridotite is also present at Vigonzano where blocks of serpentinite host the networks of quartz veins up to 1 m thickness

containing disseminated to semi-massive sulfide accumulations (Figure 1) [31,34]. The summary of mineral compositional data based on previous studies is shown in Table 1.

Table 1. Basic geological-mineralogical data of the studied localities (based on [32,37] and observations from this study).

Locality	Setting	Sulfide Assemblage	Gangue Minerals	Accessory Minerals		
Bargone	Stockwork in gabbro	Pyrite, chalcopyrite (sphalerite)	Quartz, prehnite (calcite, chlorite)	Bornite, covellite, Mn minerals		
Boccassuolo	Stockwork in basalt	Pyrite, chalcopyrite, sphalerite	Quartz, calcite, chlorite, epidote, titanite	Galena, rutile, zircon		
Campegli	Stockwork in gabbro	Pyrite, chalcopyrite (sphalerite)	Quartz, chlorite, epidote (pumpellyite)	Monazite, other REE minerals		
Reppia	Stockwork in basalt	Pyrite, chalcopyrite	Quartz	Limonite		
Vigonzano	Stockwork in serpentinite	Pyrite, chalcopyrite, pyrrhotite	Quartz, calcite, chlorite, siderite, epidote, titanite, prehnite	Marcasite, millerite, chromite, magnetite, hematite, zircon, serpentine		

The formation temperature of chlorite from the various stockwork, stratiform and stratabound deposits vary between 50–360 °C [37] pointing to various conditions during the hydrothermal process. These data are in good agreement with the preliminary fluid inclusion data for Boccassuolo (minimum formation temperature of quartz between 70–360 °C [38]).

Previous mineralogical and geochemical studies have recorded the differences among the deposits listed in Table 1. Serpentinite-hosted ores are depleted in Zn and have higher Ni/Co, Mg/Al and Cr/Mn ratios and the composition of the hydrothermal alteration related chlorite is characteristically different. Sulphur isotope data indicate that seawater sulphate is the most important source of S in these deposits [33–37].

3. Materials and Methods

Representative samples (n = 170) of quartz-sulfide veins were collected from the zones of stockwork type mineralization at Boccassuolo, Reppia, Campegli, Bargone and Vigonzano (Figure 1). Based on macroscopic observations, 24 samples were chosen for further analyses reported in this study.

Petrography of the studied samples was carried out with a Zeiss Axioplan microscope at the Department of Mineralogy, Eötvös Loránd University, Budapest, Hungary, on polished slabs and thin sections.

Fluid inclusion petrography was carried out on doubly polished 100–150 μ m thick sections with an Olympus-BH2 type microscope at the Department of Mineralogy, Eötvös Loránd University. Microthermometric measurements were performed by means of a Linkam FT-IR 600 type heating-freezing stage mounted on an Olympus-BX51 type microscope equipped with up to 100× long working distance objectives providing optical magnification up to 1000×. For the calibration of the microthermometric stage, quartz-hosted synthetic CO₂ and H₂O inclusions were used allowing 0.1 °C precision during the freezing runs and 1 °C precision during the homogenization experiments. Salinity calculations were performed based on the final ice melting temperatures using the equation of [44] except in inclusions with a formation of voluminous methane clathrate during the freezing runs. In these latter inclusions, the determination of salinities was based on the Raman spectra of the aqueous phase [45]. In a few cases, the calculation of salinity was not possible due to technical reasons (metastability during freezing, the small size of inclusions or the strong luminescence of calcite).

Raman spectroscopy analyses of fluid inclusions were performed at the Research and Instrument Core Facility, Faculty of Science, Eötvös Loránd University, by using a Horiba Jobin Yvon LabRAM HR 800 edge filter based confocal dispersive Raman spectrometer with 800 mm focal length coupled with an Olympus BXFM type microscope. During the three 20 s measurements, analyses were performed using a frequency-doubled Nd:YAG 532 nm laser, 600 grooves/mm grating, 50 μ m confocal aperture and 50 \times and 100 \times long working distance objectives. The methane content of fluid inclusions was determined using a method based on the spectra of the stretching bands of water and methane in the aqueous phase at temperatures above the homogenization temperature of the fluid inclusion (the peak of dissolved methane appears at around 2912 cm⁻¹) [46]. The high temperature Raman analyses were performed by mounting the Linkam heating-freezing stage on the microscope of the Raman equipment.

For SEM-CL analyses, an Amray 1830I scanning electron microscope was used at the Department of Petrology and Geochemistry, Eötvös Loránd University, equipped with a Gatan MiniCL detector. An accelerating voltage of 10 kV and a beam current of 8 nA were used during the measurements. For these analyses, the same doubly polished thick sections were used in order to gain the most valuable interpretation.

The concentrations of trace elements in quartz were determined by LA-ICP-MS. The analyses were performed using a New Wave UP213 Nd:YAG laser ablation system attached to a Perkin Elmer Elan DRCII type quadrupole ICP-MS at the Geochemical Laboratories of the Mining and Geological Survey of Hungary. These analyses were performed after careful SEM-CL study on doubly polished thick sections. The operating parameters of the ICP-MS were optimized by reference solutions. The ablated aerosol was delivered to the mass spectrometer by He gas mixed with Ar. The laser worked at around $8-10 \text{ J/cm}^2$ (energy density) with a pulse duration of 4 ns at repetition rate of 5 Hz. The spot size was $55 \ \mu m$ fitted to the average width of the growth zones in quartz. Two analytical spots were placed in each analyzed growth zones. The analytes were ²³Na, ²⁷Al, ³¹P, ⁴⁹Ti, ⁵⁷Fe (50 ms dwell time) and ⁷Li, ¹¹B, ²⁹Si, ³⁹K, ⁴⁸Ti, ⁶⁹Ga, ⁷¹Ga, ⁷⁴Ge (20 ms dwell time). NIST 610 reference material was measured as an external standard and Si²⁹ was used as an internal standard. BCR-2G and GSE-1G were analyzed as unknown for checking the quality of analyses. The external standard (NIST 610) and control materials (BCR-2G and GSE-1G) were measured after every 15-23 spots for calibration and checking. The results of QCM (quality control material) for ²³Na, ²⁷Al, ³¹P, ³⁹K, ⁴⁹Ti, ⁵⁷Fe, ⁷¹Ga and ⁷⁴Ge in BCR-2G were 13, 4, 11, 12, 13, 12 and 44%, respectively. In the case of GSE-1G they were 7%, 8%, 18%, 4%, 7%, 10%, 7% and 26%, respectively, and 5% for ⁷Li. The evaluation of data was made by software Sills. Two calculations were made with a spike and without spikes but no characteristic change was observed in the final concentrations.

4. Results

4.1. Petrography of Veins and SEM-CL Properties of Vein Filling Quartz

The veins from Bargone, Boccassuolo, Campegli, Reppia and Vigonzano are mostly composed of quartz, calcite, chlorite, prehnite and pumpellyite as gangue minerals and pyrite, chalcopyrite, sphalerite, pyrrhotite and galena as sulfide minerals.

In all of the studied stockwork zones, the most abundant ore mineral in the veins was pyrite, which occurs as anhedral to euhedral grains in association with other sulfide minerals. Pyrite shows various textural relationships with quartz. It fills up open spaces among euhedral-drusy quartz crystals and also penetrates quartz along fractures. However, quartz also fills up fractures of pyrite and pyrite inclusions in growth zones of quartz also occur. These textures indicated that several generations of quartz and pyrite precipitated during the formation of the veins (Figure 2A,C–F). Pyrrhotite exclusively occurs as inclusions in early pyrite and it appeared that these inclusions were remnants of replacement processes (Figure 2A). This pyrite-pyrrhotite association was the earliest precipitation in the veins. Sphalerite has two varieties. One type of sphalerite shows chalcopyrite disease suggesting interaction with later Cu-bearing fluids [47]. The other type of sphalerite is homogeneous without chalcopyrite disease suggesting that it was precipitated later than the interaction with the Cu-bearing fluids (Figure 2B,C,F). Chalcopyrite is also common as inclusion in late pyrite and also along fractures and boundary surfaces between pyrite crystals where chalcopyrite replaces pyrite (Figure 2A,C,D). Rare galena occurs in the form of anhedral grains precipitated in spaces between other sulfides and is therefore among the latest sulfide phases in the ore mineral assemblage (Figure 3).



Figure 2. Typical petrographic features of the studied VMS stockwork samples. (**A**) Pyrrhotite found as inclusions in pyrite while chalcopyrite formed later grains among pyrite crystals (Vigonzano). (**B**) Chalcopyrite disease in early sphalerite (Bargone). (**C**) Coarse grained pyrite containing chalcopyrite and sphalerite inclusions. Coarse grained quartz precipitated later among pyrite crystals (Campegli). (**D**) Coarse grained pyrite is cut by a younger chalcopyrite veinlet. Opaque minerals are cut by a younger coarse grained quartz (Boccassuolo). (**E**) Early quartz (Qtz 1) is surrounded by younger pyrite and cut by late quartz (Qtz 3) (Vigonzano). (**F**) Sulfide inclusions (sphalerite and pyrite) in growth zones of early quartz (Qtz 1) prove their co-precipitation (Vigonzano). (**G**) Rosetta-like early chlorite in early quartz (Qtz 1) (Vigonzano). (**H**) Early quartz (Qtz 1) showing growth zoning is brecciated by later, fine grained quartz (Qtz 3) (Vigonzano). Abbreviations used: chl: chlorite; cpy: chalcopyrite; po: pyrrhotite; py: pyrite; ser: sericite, sp: sphalerite; Qtz: quartz.



Figure 3. Typical precipitation series of the commonly observed paragenesis at the various study sites.

Three quartz generations were observed at most of the locations apart from Bargone and Boccassuolo. The earliest quartz (Qtz 1) is coarse grained (~0.5–3 mm) and forms euhedral-subhedral transparent-translucent crystals in which growth zones are visible even using a polarizing microscope (Figure 2H). This generation is overgrown by medium grained (~0.3–0.5 mm) subhedral, translucent quartz (Qtz 2) while the latest stage is represented by fine grained (~0.1 mm) anhedral quartz (Qtz 3) (Figure 2H) that may either fill up open spaces between Qtz 1 and Qtz 2 or show brecciation with earlier generations of quartz. At Bargone, only two generations (Qtz 1 and Qtz 3) were observed whereas in a few samples from Boccassuolo a fourth, transparent anhedral quartz generation filling up some 0.1–0.15 mm thick epigenetic veins was also observed.

These textural features suggest that the ore minerals formed mostly before or together with the earliest quartz (Qtz 1) at each location although some overlap with the younger quartz (Qtz 2) did occur (Figure 2A–F). Rosetta-like chlorite formed earlier or together with a euhedral, coarse grained quartz (Qtz 1) (Figure 2G) while anhedral chlorite filled up spaces among Qtz 1 grains and was overgrown by later subhedral quartz (Qtz 2). Sericite was found disseminated in the samples as well as inclusions of Qtz 1 and Qtz 2. Calcite filled the last open spaces together with fine grained quartz (Qtz 3); thus, they can be interpreted as the latest minerals to precipitate (Figure 2H). The typical mineral precipitation series deduced from the petrographical observations is shown in Figure 3.

The following textural features of quartz were identified by SEM-CL according to the classification in [7]: (1) euhedral growth zoning (Figure 4A,C,D), (2) quartz crystals showing homogeneous CL intensity (i.e., CL-bright, CL-dark, CL-grey) (Figure 2F), (3) CL-bright and CL-dark quartz in microfractures of quartz (Figure 4A–D,F) and (4) mottled textures (Figure 4E,F).



Figure 4. Petrographic and SEM-CL characteristics of quartz from the ore deposits studied. (**A**) CL-grey early quartz (Qtz 1) with euhedral growth zones. CL-dark microfractures occurred only in the core of early quartz (Reppia). (**B**) CL-bright early quartz (Qtz 1) was cut by cobweb textured CL-dark microfractures. Late CL-grey, mottled textured quartz (Qtz 3) was microbrecciating; fragments of early quartz (Qtz 1) could be unequivocally identified (Campegli). (**C**) CL-grey, mottled textured early quartz (Qtz 1) with a few euhedral growth zones. CL-dark and younger CL-bright late microfractures crosscut the whole sample (Vigonzano). (**D**) Early quartz (Qtz 1) showing euhedral growth zones. CL-dark microfractures occurred in the core of early quartz. A mosaic of medium (Qtz 2) and fine grained (Qtz 3) quartz with irregular growth zones filled the space among the coarse crystals (Boccassuolo). (**E**) CL-grey early quartz (Qtz 1) with a CL-dark growth zone. Later CL-dark quartz (Qtz 3) was microbrecciating. The breccia may contain fragments of the early quartz (Bargone). (**F**) CL-grey early quartz (Qtz 1) with a CL-dark microfracture. Later CL-dark quartz (Qtz 3) was microbrecciating. The breccia may contain fragments of the early quartz (Bargone).

The early, euhedral quartz (Qtz 1) was most commonly CL-bright or grey. Euhedral growth zones with CL-bright/grey/dark/mottled shades were typical for each location. The thicknesses of the growth zones were between 10 and 150 μ m. Individual crystals contained up to 10 growth zones from the center to the rim. At Reppia, Boccassuolo and Vigonzano, the core of the crystals contained CL-dark microfractures. Homogenous and mottled CL-grey textures as well as splatter and cobweb textures of dark microfractures did overprint the above-mentioned primary features though the former was quite rare (Figure 4A–F).

The medium grained, subhedral quartz (Qtz 2) formed a mosaic of CL-bright, grey and dark colored crystals, filling the space between the early quartz grains at each study site except in Bargone. Irregular growth zones did occur and overprinting by CL-dark and more rarely CL-bright microfractures was common (Figure 4D).

The late, fine grained quartz (Qtz 3) was commonly CL-grey or dark at each study site. Subordinately, a homogeneous or mottled texture was visible in Qtz 3. This quartz generation precipitated during the fracturing and brecciation of earlier quartz stages. However, microfractures also formed before and after the microbrecciation. Based on the different SEM-CL characteristics, fine grained fragments of the earlier quartz generations were also recognizable within this late quartz matrix (Figure 4B,D–F).

The observed textural features supported the following relative timing of the precipitation of quartz varieties (Figure 5):

- 1. The crystallization of CL-bright grey early quartz (Qtz 1) was interrupted by CL-dark quartz microfracturing, now restricted to the core of the crystals;
- 2. The formation of euhedral growth zones still belonging to the early quartz (Qtz 1) generation;
- 3. The precipitation of medium grained Qtz 2;
- 4. The deposition of fine grained interstitial and microbreccia vein filling quartz (Qtz 3);
- 5. CL-dark/bright quartz in microfractures that cross-cut all quartz generations (Qtz 1–3) and crystal boundaries.



Figure 5. Typical SEM-CL texture with the identified steps of the quartz formation process (Boccassuolo). 1. Core of early quartz (Qtz 1) formed at the highest temperature. 2. Quartz growth was interrupted by microfracturing. 3. Early quartz (Qtz 1) precipitation continued with euhedral growth zones. 4. Medium (Qtz 2) to fine grained (Qtz 3) interstitial quartz and calcite precipitated from continuously cooling hydrothermal fluid. 5. Low temperature fine grained quartz (Qtz 3) may cause microbrecciation. 6. A few generations of microfractures are filled with low temperature quartz.

4.2. Trace Element Contents in Quartz

Trace element analyses by LA-ICP-MS were completed on samples representing the oldest and youngest quartz generations (Qtz 1 and 3) from the localities at Boccassuolo and Campegli. The summary of our results is presented in Appendix A Table A1. Among the elements selected for measurements according to the analytical setup (see Materials and Methods section) B, Ga, Ge, Ti and Fe were below the detection limits (detection limits were 10 ppm, 0.3 ppm, 1 ppm, 4 ppm and 16 ppm, respectively). Al was the most common trace element (11–1526 ppm), followed by K (up to 482 ppm), Na (up to 181 ppm), Li (up to 132 ppm) and P (up to 127 ppm). Due to the relatively large sampling volume (the spot size was 55 μ m), the results might be the average of multiple domains with slightly different compositions in finely zoned parts of the crystals (e.g., Figure 4D). Although we aimed to avoid fluid inclusion rich parts of the quartz crystals during analyses, the presence of a few small inclusions could not be excluded. Therefore, we may assume that some Na and K data are affected by contamination of fluid inclusions.

In Boccassuolo we observed some correlation between the SEM-CL color and the Al content although there was some overlap between the data ranges (Figure 6). The highest Al contents were measured in the CL-bright cores and euhedral growth zones. Moderate Al contents characterized the CL-grey and CL-dark euhedral growth zones while the lowest Al concentrations were always occurred in the CL-mottled textured outer growth zones (Figure 6).



Figure 6. Al content of quartz (Qtz 1) with different CL signatures. Some positive correlation is observable (Boccassuolo) (legend: red: max; green: mean; blue: min concentrations; rectangles: standard deviation).

On the contrary, CL-dark early microfractures contained the highest Al values in Campegli followed by the CL-bright crystals and finally the CL-grey late matrix.

A positive correlation was observed between mono and trivalent cation concentrations (Al-monovalent cations $R^2 = 0.65$; Figure 7) in the whole data set. The highest correlation coefficient ($R^2 = 0.58$) occurred between Na and Al while K–Al and Li–Al were weakly correlated ($R^2 = 0.39$ and 0.31, respectively).





4.3. Fluid Inclusion Petrography, Microthermometry and Raman Spectroscopy

Primary fluid inclusions hosted by the different quartz generations as well as late calcite were studied in detail at each location. Commonly, at least 2–3 assemblages of secondary fluid inclusions were also identified. As primary fluid inclusions provide insights into the processes of mineral formation, the present work focused on their study.

Based on our fluid inclusion observations, the sizes of primary fluid inclusions in quartz were from <1 μ m to 10 μ m (most of them were between 2–5 μ m) and occurred along growth zones (Figure 8A,B) or rarely in 3-dimensional cloud structures that did not cross-cut the growth zones in the core of the crystals. Calcite contained fluid inclusions that range from <1 μ m to 20 μ m in size. These were rectangular-shaped (i.e., negative crystal shape) primary fluid inclusions, occurring in 3-dimensional cloud structures far from any secondary fracture hosted inclusion generations and cleavage planes of crystals.



Figure 8. Fluid inclusions in the studied samples. (**A**,**B**) primary, liquid + vapor fluid inclusions in a growth zone of an early quartz grain (Qtz 1). Secondary trails cross-cut the crystal boundaries (Campegli). (**C**) Large liquid + vapor + solid secondary fluid inclusions in an early quartz grain (Qtz 1) (Vigonzano). The solid phase is an accidentally trapped sericite grain (determined by Raman spectroscopic analyses).

The primary liquid + vapor (+ solid) (L+V(+S)) inclusions in quartz showed identical L/V ratios (80–90 area% L and 20–10 area% V), suggesting a homogeneous parent fluid at each study locality. However, an insoluble accidentally trapped solid phase was also present in a few of these inclusions. Based on Raman spectroscopy analyses, this trapped solid phase was sericite. The homogenization temperature of the liquid phase was variable depending on the study site and the quartz generation (see Appendix A Table A2). Trends in homogenization temperatures (T_h (L – V)L) were present among the various quartz generations as well as from the core to the rim of single quartz crystals. In the latter cases, a temperature drop of up to 40 °C was observed. Homogenization temperature values

commonly decreased from early (Qtz 1) through transitional (Qtz 2) to late stage quartz (Qtz 3) (from 360 °C to 50 °C) (Figure 9). The exact ranges of homogenization temperatures for each quartz generation in each study site are listed in Appendix A Table A2. Due to the small size of the studied inclusions, we were only able to determine the final melting temperatures during the freezing runs. Two data ranges were determined: (1) $T_m^{final} -1.7$ to -4.1 °C where ice was the last phase to melt therefore we could calculate the salinity based on the ice melting temperature (T_{m-ice} from -1.7 to -4.1 °C corresponding to 2.9–6.6 NaCl equiv wt% salinity) and (2) $T_m^{final} -0.5$ to -1.5 °C where methane clathrate formation hindered the ice melting phenomenon and this methane clathrate was the last phase to melt at a markedly higher temperature. Thus, in these cases, salinities were from 2.6–9.3 NaCl equiv. wt%.) According to the results of the Raman analyses, the methane content of the homogenized inclusions was also variable between 0.13 and 0.33 mol/kg based on the method of [46]. The calculation of homogenization pressures was performed based on the equation of state for the NaCl-H₂O-CH₄ system in [48]. The calculated values were between 21–59 MPa at each study site.



Figure 9. Homogenization temperature vs. salinity diagram of the fluid inclusions from the various Cyprus type VMS deposits in the Northern Apennines. A decreasing T_h trend was observable among the different quartz generations as well as from the core to the rim of early Qtz 1. Where it was not possible to measure salinity, only the T_h range of those inclusions is shown. Fields of the fluid inclusion homogenization temperature-salinity data for VMS deposits according to [12] are also shown.

At least 2–3 assemblages of secondary fluid inclusions were identified at each locality. These secondary fluid inclusion assemblages contained L+V(\pm S) fluid inclusions of 5–50 µm in size (Figure 8C) and were confined to trails that cross-cut the earlier quartz generations (Qtz 1 and Qtz 2) (Figure 8A). Presumably younger, one-phase (L) secondary fluid inclusions of <1–5 µm in size also occurred in cross-cutting trails. The homogenization

temperatures and salinity values of L + V(+S) inclusions ($T_h(LV - L) = 50-100$ °C and 3.5–7.2 NaCl equiv. wt%) were similar to the ones observed in the primary fluid inclusions of the late Qtz 3 and calcite. The methane content in the gas phase as well as accidentally trapped sericite were also identified by Raman spectroscopy in these inclusions.

The primary liquid + vapor (L + V) inclusions in calcite showed identical L/V ratios (80–90 area % L and 20–10 area % V), suggesting a homogeneous parent fluid at each study locality. The homogenization temperature and salinity values ($T_h(LV - L) = 60-169$ °C and 3.1–6.6 NaCl equiv. wt%) were similar to those observed in the primary fluid inclusions of late Qtz 3.

5. Discussion

5.1. Characteristics of Hydrothermal Processes on the Basis of Fluid Inclusion Data

As the fluid inclusion data from the various study sites showed similarities, we will discuss most of the results collectively. The observed SEM-CL textures of quartz were indicative of dynamically changing hydrothermal systems. The growth zones were related to physicochemical changes during quartz precipitation [27] while microfracturing and microbrecciation were the results of renewed hydrothermal activity [20]. The common occurrence of growth zoning, similar to other VMS quartz case studies [49], proved that recrystallization did not affect quartz in the stockwork zone of the different deposits. This is in agreement with their known geological background; i.e., the host ophiolitic series was non-metamorphosed and only exhibited seafloor hydrothermal alteration [39,42]. Therefore, the microthermometry and Raman spectroscopy data from primary fluid inclusions in quartz reflected the original variability of the parent fluid.

Our petrographic study of primary fluid inclusions hosted by quartz indicated the homogenous state of the parent fluid. Therefore, the homogenization temperatures and pressures could be interpreted as minimum formation conditions. The quite wide range of homogenization temperature values observed at the various locations (Figure 9; Appendix A Table A2) cannot be related to the variable pressure conditions of their entrapments. This is because the isochores of fluid inclusions are so steep that the entrapment of inclusions with low homogenization temperatures could not have happened at the same temperature as the inclusions with a high homogenization temperature. The entrapment pressure for the low temperature inclusions at the temperature of homogenization of the high temperature inclusions is geologically not reasonable (e.g., over 250 MPa in the case of Bargone). The correlations between Th, salinity and methane content data were also not present (see the rather constant salinity values on Figure 9 and also the similar salinity and methane content data despite the changeable temperature values in the various quartz generations in Appendix A Table A2). The correlation of the homogenization temperature data with growth zoning and the relative timing of different quartz generations (Figure 9) were indicative of the variability and cooling of the hydrothermal fluids during the deposition of several superimposing quartz generations.

Beside the minimum formation temperature and pressure variations, changes in the composition of the hydrothermal fluid were also reflected in the variation of methane content (between 0.13 and 0.33 mol/kg) and salinities (between 2.6 and 9.3 NaCl equiv. wt. %). This salinity range is typical of VMS systems [7,12,13]. Salinities slightly higher than sea water salinity can be interpreted most likely as a result of fluid-rock interaction [7,12] while lower values may occur due to the effects of phase separation at depth even if petrographical evidence for this phenomenon is lacking in the studied samples [8,12]. Although methane is not the most common gas phase in the parent fluids of Cyprus type VMS systems, its presence is mentioned in a few deposits (e.g., the Iberian Pyrite Belt [5,6,12]). The presence of methane in the hydrothermal systems of a few Cyprus type VMS deposits is most commonly related to direct magmatic degassing, thermal decomposition of organic material or reduction due to the serpentinization of ultramafic rocks [50].

Methane clathrate melts at significantly higher temperatures than ice [51], which could explain the higher and lower temperature groups that were observed for the final melting

temperatures in inclusions. Variations in pressure, salinity and methane content affect clathrate formation [51]. This observation is also indicative of changing fluid conditions during the growth of quartz.

5.2. Constraints on the Hydrothermal Conditions from Trace Element Fingerprints and CL Behavior of Quartz

Identification of growth zones in quartz by SEM-CL was essential to robustly classify fluid inclusions according to their origin. It provided a basis for the interpretation of the homogenization temperature variation within a single crystal (Figure 10A). The SEM-CL imaging also revealed the presence of microfractures with secondary fluid inclusions in the spongy core of early coarse grained quartz (Qtz 1) and thus provides a likely explanation for the occurrence of two markedly different homogenization temperature ranges within the same growth zone of a single crystal (Figure 10C). In the microbreccias, small pieces of early quartz (Qtz 1) within the late fine grained brecciating quartz (Qtz 3) were also identified. This is important as the former contains fluid inclusions with obviously different characteristics compared to the latter (Figure 4F, Appendix A Table A2).



Figure 10. SEM-CL images of various quartz grains with interpreted fluid inclusion microthermometry data. (**A**) T_h drop from the core to the rim of a single crystal (Qtz 1) contributed to wide T_h ranges. Correlation between Al content and SEM-CL characteristics is also observable (Boccassuolo). (**B**) Methane clathrate was the last phase to melt in the CL-bright core of the quartz grain while ice melting (at a markedly lower temperature) was observed in the CL-dark outer growth zone (Bargone). (**C**) T_h drop from inner to outer growth zones within a Qtz 1 grain was observable. Besides high T_h primary inclusions (found in CL-bright areas), the spongy core contained many CL-dark microfractures with low T_h secondary inclusions (Vigonzano).

A correlation between methane clathrate formation and the SEM-CL characteristics of quartz was observed at the Bargone deposit. The CL-bright core of quartz crystals contained methane clathrate forming primary inclusions ($T_{m-clathrate} = -1.3 \,^{\circ}$ C) while CL-dark outer zones did not show the formation of methane clathrate during the freezing runs and ice was the last phase to melt ($T_{m-ice} = -3.5 \,^{\circ}$ C) (Figure 10B). According to [51], this probably indicates a change in the fluid composition due to a slight change of pressure during the deposition of quartz (higher pressure/salinity/methane content promoted clathrate formation and vice versa).

Based on earlier studies (e.g., [24,25]), either pressure change or compositional variation of the parent fluid may have affected the SEM-CL characteristics of quartz. Our results also support these findings. However, the CL signature of quartz is also dependent on the density of intrinsic (i.e., structural imperfections) and extrinsic defects (i.e., chemical impurities). In hydrothermal quartz, intrinsic defects may include an abundance of fluid inclusions trapped during a specific period of crystal growth and extrinsic defects may be caused by a localized variability in the trace element concentrations. As the intrinsic and extrinsic defects can both affect the SEM-CL characteristics, this had to be evaluated on a case by case basis (e.g., [24,27]).

The results of the LA-ICP-MS study indicated that Al and its charge compensating cations (e.g., Na, K,) affected the SEM-CL properties of quartz (see Figures 6 and 10A) but this correlation was not obvious [24,29]. Al is generally the most abundant trace element in hydrothermal quartz [28]. In agreement with this, the quartz crystals from the VMS deposits of the Northern Apennines contained up to 1526 ppm Al. The observed positive correlation between Al and the monovalent cations indicated their coupled substitution in quartz. The positive correlation between the monovalent cations and Al as well as the low Ti concentrations (in our case, below a detection limit of 4 ppm) are commonly present in low temperature hydrothermal quartz (i.e., below 300–400 °C [23,24]). This is also in good agreement with our fluid inclusion data (see Figure 9 and Appendix A Table A2).

The systematic variation in the trace element content of hydrothermal quartz from various ore deposit types probably also reflects the different formation conditions though these relationships are not well constrained. However, the results of research presented in [23,24,28] suggest that changes in temperature, pressure, pH and fluid composition as well as crystallization rate may have combined effects on the trace element content of hydrothermal quartz. For example, Rusk et al. [22] suggested that fluctuations in Al concentrations reflected the changes in pH of the hydrothermal fluids and the rates of quartz precipitation. Therefore, the compositional differences among the core and euhedral growth zones (especially in case of the outer, CL-mottled zone) of Qtz 1 and the CL-dark microfractures as well as the microbrecciating CL-dark/grey (Qtz 3) quartz may reflect the remarkable formation condition changes especially the significant drop in the minimum temperature of crystallization.

5.3. A Generalized Model for the Submarine Hydrothermal Processes in the VMS Stockwork Deposits of the Northern Apennines

Over the past few decades, detailed genetic and descriptive models of the various types of VMS deposits have been established based on extensive case studies (e.g., [6]). Our knowledge on hydrothermal fluid composition, source and evolution is also extensive (e.g., [5,12]) though several questions remain. One of these questions is how to reliably reconstruct the fluid characteristics and evolution in ancient systems. In the present study, we contribute to this topic using a methodology rarely applied to the field of VMS research.

Although a few slight differences existed among our various study sites, the most important characteristics such as mineral paragenesis, hydrothermal fluid temperature and composition were very similar. Therefore, a generalized model for the evolution of Cyprus type VMS stockwork deposits of the Northern Apennines can be established on the basis of the results of this study.

The deposition of early sulfide minerals as well as the formation of the core of early quartz (Qtz 1) occurred at the highest temperature. The properties of fluid inclusions suggest a homogenous parent fluid. Therefore, the quartz cores formed at a minimum temperature ranging from 170 to 270 °C in Bargone (mean: 207 °C), 250–360 °C in Boccassuolo (mean: 299 °C), 170–205 °C in Campegli (mean: 187 °C), 150–205 °C in Reppia (mean: 158 °C) and 290–330 °C in Vigonzano (mean: 312 °C). The salinity of the methane-bearing hydrothermal fluid was around that of seawater (~3.5%). Syntectonic processes in the ridge setting resulted in the interruption of quartz growth and the formation of microfractures in the crystal cores in Boccassuolo and Reppia. These processes may have affected the composition of the hydrothermal fluid as the fluid-rock interaction could reach new rock masses and gas contents of fluids could have also changed during fracturing. Later, early quartz (Qtz 1) precipitation continued with euhedral growth zones at all localities. Remarkable changes in Al content as well as differences in methane clathrate formation and slight changes in salinity point to possible variations in fluid pressure, pH, fluid composition and temperature. Compared to the early stage of hydrothermal activity, the minimum formation temperature was markedly decreasing during this phase and was commonly between 135–180 °C in Bargone (mean: 155 °C), 125–180 °C in Campegli (mean: 138 °C), 120–160 °C in Reppia (mean: 142 °C), 150–280 °C in Boccassuolo (mean: 215 °C) and 260–310 °C in Vigonzano (mean: 285 °C). Such variation in the temperature of the hydrothermal activity was also commonly observed at other VMS deposits especially in the stockwork zones [5,7,9,12]. These variable conditions and superimposing steps could efficiently promote ore mineral precipitation [52,53] and thus the main ore formation stage was mostly synchronous with early quartz precipitation (Figure 3).

Apart from this, the superimposing hydrothermal pulses were mirrored by the precipitation of the ore minerals as well (Figure 3). The formation of early sphalerite was associated with a pulse of a Cu-rich fluid, resulting in the occurrence of chalcopyrite disease in sphalerite [47] as well as the co-precipitation of chalcopyrite. This was followed by the precipitation of late, chalcopyrite-free sphalerite. A similar temporal evolution has been observed in other (Kuroko type) VMS deposits [11].

These main ore formation stages were followed by the precipitation of scarce pyrite, medium (Qtz 2) to fine grained interstitial quartz (Qtz 3), calcite and sericite from a continuously cooling hydrothermal fluid (Figure 3). The formation of this mineral paragenesis represented the waning stage of the hydrothermal activity [6]. The minimum formation temperature was commonly between 100–140 °C in Bargone, 60–160 °C in Boccassuolo, 110–170 °C in Campegli and 50–170 °C in Reppia. The salinity of the hydrothermal fluid was around that of seawater or slightly higher and the methane content was characteristic just like in the earlier stages. Locally, low temperature fine grained quartz (Qtz 3) caused microbrecciation suggesting multiple hydrothermal events. The low trace element content as well as fluid inclusion and SEM-CL characteristics were similar to the above-mentioned fine grained interstitial quartz (Qtz 3). Therefore, it is possible that this late event was still a part of the submarine hydrothermal activity.

Finally, at least 2–3 generations of quartz filled microfractures formed, which cut across the ore and gangue mineral assemblages at each study site. These microfractures were often hardly distinguishable from the host primary quartz. The secondary fluid inclusions of the primary quartz were related to these microfractures. In Vigonzano, they formed at low minimum temperatures (50–100 °C) and the oldest secondary generation contained a fluid of a similar composition (salinity, methane content, \pm sericite solid phase) to the ones observed in the primary inclusions of the late stage primary quartz (Qtz 3). Therefore, the first generation of these microfractures represented the waning stage of the submarine hydrothermal processes.

In addition to the reconstruction of the hydrothermal process in the Cyprus type VMS stockwork ores of the Northern Apennines, the results of our study also support to understand the original structure of the deposits. The original structure of the VMS stockwork zones is barely traceable due to later tectonic movements (obduction). Therefore, the primary location of the studied deposits within the commonly up to 1 km deep [5] stockwork zone is unknown. Our observations, however, can help in positioning the study sites. Although the most important characteristics were similar, a few features showed differences. While in Vigonzano, quite narrow minimum formation temperatures and salinity ranges were observed; at the other deposits, these values in Qtz 1 and 2 were more variable. This finding can also be explained by the possible different original position within a large scale VMS stockwork system. Proximal zones in relation to the main fluid flow are characterized by a narrow temperature range due to the high water-rock ratio and continuous supply of high temperature fluids while distal zones are characterized by a rapid cooling of the hydrothermal fluid [54]. This interpretation is also supported by the observed ore mineral paragenesis. The suggested more proximal Vigonzano contained more pyrrhotite while the most likely more distal other locations (Boccassuolo, Bargone, Campegli and Reppia) contained more sphalerite and galena (see Table 1) [6].

6. Conclusions

In the present work we applied the combination of fluid inclusion studies with SEM-CL imaging and trace element analyses by LA-ICP-MS in quartz. The aim was to gather texturally well constrained fluid inclusion data about the formation of Cyprus type VMS deposits in the Northern Apennines. While a similar approach has previously been used in other ore deposit types (e.g., Cu-porphyry or epithermal systems), it has been seldom used in Cyprus type Fe-Cu-Zn volcanogenic massive sulfide deposits.

Our detailed SEM-CL study of quartz provided a solid basis to interpret the results of fluid inclusion study while the combination with LA-ICP-MS analyses helped better understand the SEM-CL characteristics. The observed complex SEM-CL textures in quartz can be correlated with variable trace elements, especially Al content, which also reflect changes in the conditions (e.g., drop of a minimum formation temperature and a possible variability of quartz precipitation rate, pH and pressure) of the hydrothermal processes.

Our results support that a dynamically changing hydrothermal system was responsible for the formation of the stockwork zones in the studied VMS deposits. In each pulses of hydrothermal activity, the major trend was the cooling of fluids and this process was combined with variable salinities and methane contents. The hydrothermal conditions were particularly variable in those deposits that probably represent distal positions relative to the main sites of fluid flow. However, a late low temperature phase was identified at each location, which correspond to the waning stages of the hydrothermal activity without ore deposition.

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Appendix A

BOCCASSUOLO																					
ppm	det. lim.	Qtz 1	l: CL-H Ca (n :	Bright I ore = 9)	nner	Qtz 1: CL-Bright Euhedral Growth Zones (n = 7)			Qtz 1: CL-Grey Euhedral Growth Zones (n = 2)			Qtz 1: CL-Dark Euhedral Growth Zones (n = 8)				Qtz 1: CL-Mottled Outer Zone (n = 9)					
⁷ Li	15	79	23	46	120	87	28	50	132	5	1	5	5	37	14	20	61	41	23	24	92
²³ Na	6	67	34	27	105	89	64	10	181	2.	5	1	4	67	50	9	125	19	13	8	48
²⁷ Al	10	834	367	408	1309	767	446	206	1526	38	33	45	50	223	159	49	483	42	29	11	85
³¹ P	17	33	7	21	42	35	14	22	66	3	2	34		35	8	17	42	30	8	21	40
³⁹ K	16	66	32	26	124	151	104	94	360	2	8	b.0	1.l.	65	38	30	138	22	0	22	23
		mean	st.de	v. min	max	mean	st.de	v. min	max	an	1	ar	n 2	mear	ı st.de	v. min	max	mean	st.de	v. min	max
CAMPEGLI																					
ppm	det. lim.	Qtz 1: CL-bright crystals (n = 7) CL-dark mic in Qtz 1				crofrac (n = 2	ctures Qtz 3: CL-grey matrix 2) (n = 5)														
⁷ Li	15	38	17	29	76	32	2	b.c	1.1.	63	20	49	77								
²³ Na	6	72	23	46	110	11	3	13	30	10	2	7	12								
²⁷ Al	10	583	164	416	802	95	0	11	68	22	12	12	43								
^{31}P	17	59	22	43	105	52	7	5	9	71	34	40	127								
³⁹ K	16	112	45	44	162	35	2	48	32	30	5	24	34								
		mean	st.de	v. min	max	an	1	an	12	mean	st.de	v. min	max								

 Table A1. Summary of LA-ICP-MS study results.

st. dev. = standard deviation; det. lim. = detection limit in ppm; b.d.l. = below detection limit; an 1-2 = analysis number (in the case where only two measurements were possible, whole datasets are presented instead of mean, standard deviation, min and max).

			Bargone	Boccassuolo *	Campegli	Reppia	Vigonzano
		min	170		170	150	290
	T_{h} (°C) (core)	max	270		225	205	330
		mean	207		187	158	312
Coarse		min	135		125	120	260
grained	T_{1} (°C) (rim)	max	180		180	160	310
quartz (Otz 1)	- <u>n</u> (C) (IIII)	mean	155		138	142	285
quarte (QLE I)	Salinity	mean	100		100	1 12	200
	(NaCl equiv	rango	26-57		26-17	31_39	7 2_9 3
	(ivaci equiv.	Tunge	2.0 0.7		2.0 4.7	5.1 5.7	7.2 9.0
	Methane						
	content	range	v		0 13_0 22	v	v
	(mol/kg)	Tange	А		0.15-0.22	A	~
	(IIIOI/ Kg)		53		58	70	18
	11		55		50	70	10
		min		250			
	T_h (°C) (core)	max		360			
Coarse and		mean		299			
medium		min		150			
grained	T _h (°C) (rim)	max		280			
quartz (Qtz		mean		215			
1–2)	Salinity						
	(NaCl equiv.	range		3.3-8.3			
	wt%)						
	Methane						
	content	range		0.19-0.26			
	(mol/kg)	-					
	n			98			
		min			110	122	
	T _b (°C)	max			158	171	
Medium		mean			132	146	
grained	Salinity						
quartz (Qtz 2)	(NaCl equiv.	range				3.1-4.7	
	wt%)	runge				0.1 1.7	
	Methane						
	content	range			x	0 22-0 33	
	(mol/kg)	runge			Х	0.22 0.00	
	(mor/ kg)				9	41	
		•	107	00		50	
	\mathbf{T}	min	107	80 1(0		50	
Fine grained	$I_h(C)$	max	118	160		125	
quartz (Qtz 3)		mean	112	102		97	
1	Methane		2			2	
	content		?	Х		?	
	(mol/kg)		2	15		-	
	n		3	15		5	
		min	110	60	132		
	T_h (°C)	max	135	160	169		
Calcito		mean	116	89	147		
Calcite	Salinity						
	(NaCl equiv.	range	3.1-6.6				
	wt%)						
	Methane						
	content		?	х	х		
	(mol/kg)						
	n		13	35	6		

x: methane content proven by Raman spectroscopy but not quantified. ?: methane content was not possible to check due to the small size of inclusions or strong luminescence of calcite. *: data including the previous preliminary results of [38].

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