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Antimony in quartz as a vector to mineralization: A statistical approach from five Variscan Sb occurrences (France).

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Abstract

Using in-situ LA-ICP-MS, the trace elements compositions of hydrothermal quartz from five Sb mineralized Variscan districts, from different parts of France, were compared. Each of these districts is characterized by the presence of stibnite, with quartz being an ubiquitous gangue mineral. The resulting dataset was processed using a set of multivariate statistical analyses (*i.e.* principal component analysis, hierarchical cluster analysis, and permutational multivariate analysis of variance). This approach highlights differences in ore-forming processes (e.g., fluid chemistry), recorded in the trace-elements pattern of the gangue minerals. Using this methodology, we could distinguish different mineralizing events with intricate paragenesis, such as those in the Sioule nappe, which appear to have recorded two different events of Sb precipitation. Results indicate that Sb incorporation in quartz is weakly correlated to other trace elements, but that its contents increase sharply in quartz from stibnite-bearing veins. In this case, Sb shows values >10 ppm and up to 200 ppm, considerably higher than the values measured in quartz unrelated to Sb mineralization (mainly ≤ 1 ppm). Intermediate Sb contents in quartz would point to the potential for a fluid to precipitate Sb ore. It is concluded that incorporation of Sb in quartz can be confidentially correlated to its content in the mineralizing fluid. Based on our data from five Sb districts of the French Variscan belt, supported by published Sb trace-elements data in quartz from a number of other Sb deposits worldwide, this study highlights the strong potential of the Sb content in quartz as a proxy for tracing Sb mineralization.

Keywords

LA-ICP-MS; Trace-elements signature; Quartz; Antimony; Mineralization; Footprint.

1. Introduction

During the last couple of decades, many studies have undertaken to determine the concentration of trace elements in quartz in order to better constrain magmatic and/or hydrothermal processes (Monnier et al., 2018 and references therein, Müller et al., 2018; Wertich et al., 2018; Breiter et al., 2019; Hong et al., 2019; Peterková and Dolejš, 2019; Wang et al., 2019; Feng et al., 2020; Fu et al., 2020; Li et al., 2020; Sun et al., 2020; Yan et al., 2020). In most cases, quartz trace-elements chemistry has been mainly used for geothermometery (e.g., Wark and Watson, 2006; Grujic et al., 2020; Jollands et al., 2020) and as an expression of magmatic fractionation or fluid evolution (e.g., Müller et al., 2005; Rusk et al., 2008; Breiter and Müller, 2009; Breiter et al., 2017; Garate-Olave et al., 2017; Monnier et al., 2018). Monnier et al. (2018) have shown clear evidence for precipitation of quartz with a unique chemical signature when coming from a single mineralizing fluid. Based on this principle, these authors distinguish several overprinting hydrothermal alteration events within the same mineralized district. Their study also emphasizes that quartz trace-elements chemistry can represent the signature of a specific type of mineralization, making for a powerful proxy for prospecting. Recent studies confirm that the concentration of a number of elements in quartz correlates with their abundance in the source, fluid or magma, and therefore that quartz analyses may provide a direct marker of mineralization. This was proposed for Li in igneous quartz (Beurlen et al., 2011; Garate-Olave et al., 2017; Monnier et al., 2018; Maneta and Baker, 2019), although Li-rich quartz in Li-poor intrusives and vice versa has been observed on a few occasions, weakening this argument (Breiter et al., 2014). Good correlations were also found for Rb in igneous quartz (Monnier et al., 2018), as well as for Sb in hydrothermal quartz, the latter seeming to be the most promising (Rusk et al., 2011; Monnier et al., 2018; Pacák et al., 2019). To confirm or discredit this trend, we chose to investigate the potential of Sb in quartz as a tracer for Sb mineralization, given that this metal is considered, after the REE, as the critical commodity with the highest risk of supply by the European Union Commission (2017).

For this study, we have selected five Sb mineralized districts located in the French remnants of the Variscan belt (Bournac, La Lucette, Le Semnon, Pouzol-Servant, Nades; Fig. 1). Some of them are well known, while others have not been the subject of modern scientific studies, yet. Two of these poorly constrained districts, Nades and Pouzol-Servant, are located within the same tectonic unit, the Sioule Nappe (northern part of the French Massif Central), only ca. 3 km apart. They are thus ideal candidate to evaluate the potential of quartz trace-elements signature in complex polyphased systems that are otherwise in the same geological environment. Moreover, the Sioule nappe is known to contain a large variety of mineralized quartz veins (Sb, Cu, W, Li, Sn, Nb-Ta), some of which have already been the subject of trace-elements studies in quartz (Monnier et al., 2018), thus allowing a comparison with systems mineralized to different degrees, or being all together barren. A model linking the greisenification of the nearby Beauvoir rare-metal granite, the formation of proximal veins (W, Sn) around it and of the more distal Sb mineralization was proposed to explain the genesis of the Nades district (Monnier et al., 2018; Monnier et al., 2020). This gave us the opportunity to compare quartz analyses from this district with the chemistry of quartz from the neighbouring Pouzol-Servant veins to evaluate whether or not the latter system was related to the same greisen hydrothermal event.

In order to properly treat the large dataset at our disposal, we made use of a statistical approach implementing three complementary multivariate analytical tools. These are hierarchical cluster and principal component analysis, plus permutational multivariate analysis of variance (HCA, PCA, PERMANOVA). HCA and PCA are statistical tools that are being used increasingly commonly in the geochemical literature (cf., Lin et al., 2014 and Codeço et al., 2020). Although the PERMANOVA test is used regularly in other branches of Sciences, such as biology, to the best of our knowledge, this tool

(Anderson, 2001) was only employed for the first time in geochemistry in the recent study of Monnier et al. (2018). The final purpose of this exercise is to understand whether or not the chemical signature of different quartz generations is an efficient means for distinguishing the five districts considered, and whether it may represent an efficient marker to fingerprint Sb mineralizations.

2. Geological Settings

2.1. Bournac district

Bournac is an epithermal deposit located in the North-East of the Montagne Noire, a metamorphic core complex which exposed gneissic and migmatitic Variscan basement during orogenic collapse at ca. 290 Ma (Rey et al. 2011; Roger et al. 2015; Whitney et al. 2015; Trap et al. 2017). Mineralization occurs as large veins (80 cm thick) oriented N 20° E, hosted within the Brusque nappe at the level of an anticline composed of Lower Cambrian rock (various metasediments and rhyolite-trachyte). These formations are intersected by the Faoulat granite, which form a network of interconnected dykes to the south of the mineralized zone, emplaced about 290 Ma (dating by the Rb-Sr method on total rock; Hamet, 1975). Mineral assemblages related to contact metamorphism of the granite indicate a setting pressure of less than 1 kbar, consistent with a pressure of about 0.5 kb estimated from fluid inclusions (Munoz and Shepherd, 1987). The ore paragenesis consists of a succession of crystallization stages, accompanied by quartz and/or ankerite (for more details, see Munoz and Moëlo, 1982; and Munoz and Shepherd, 1987). The first and second stages comprise As-Fe and Zn-Cu massive suphides (e.g., arsenopyrite, pyrite, sphalerite, chalcopyrite) formed above 300 °C (homogenization temperature of fluid inclusions from 300 to 350 °C). The third stage consists of Pb-Sb ore (galena and antimony sulfosalts) and occurred at approximately 250°C, while Sb ore (stibnite plus quartz) makes up the fourth, and last, stage and was recorded by fluid inclusions displaying homogenization temperatures around 200°C.

2.2. La Lucette district

At La Lucette, Sb mineralization is hosted in the Laval basin, located along the North Armorican shear zone, a structure that delimits the Northern from the Central Armorican Domain. During the Variscan orogeny, this area underwent low-grade regional metamorphism and moderate deformation marked by north-verging open folds (Brun et al., 2001; Gumiaux et al., 2004). Mineralized quartz and carbonate veins of significant width (up to several meters) are hosted by sandstone and pelites, within an anticline oriented N 120° E. The metal stock is estimated at 42 kt antimony and 8.4 t gold (Chauris and Marcoux, 1994). The vein mineralogy was studied by Pochon (2017), who describes a first barren episode, consisting mostly of massive quartz, followed by an As-Zn-Au stage accompanied by minor Sb-sulphosalts, and a last Fe-Pb-Cu-Au stage. Important precipitation of stibnite took place during this last stage. Each of these four episodes was accompanied by quartz precipitation, trapping fluid inclusions which record temperature decrease of the mineralizing fluid would have recorded wide-range temperature of 300 ± 80 °C (microthermometric data on fluid inclusions, Pochon, 2017). In the Armorican Massif, an important Sb-Au mineralization event seems to be spatially correlated with mafic rocks around 360 Ma (Pochon et al., 2016a, 2016b, 2019), nevertheless, the emplacement age of the La Lucette deposit remains unclear and could be late Variscan (Chauris and Marcoux, 1994).

2.3. Le Semnon district

The Le Semnon deposit is located in the central part of Variscan Armorican massif. Here, the central armorican domain consists of Late Neoproterozoic to Late Paleozoic sedimentary rocks metamorphosed to low grade facies moderately deformed. Main structures consist of upright folds with sub-vertical axial planes and E–W sub-horizontal axes, produced by a N120-125-striking dextral wrenching of the CAD (Gapais and Le Corre, 1980; Gumiaux et al., 2004). Gloaguen et al. (2016) estimated the stock at ca. 45 kt of antimony and 3.3 t of gold. The Sb-Au mineralization consists of a network of irregular quartz-carbonate veins, up to 80 cm thick, crosscutting the contact between the dolerite dyke and Lower Ordovician slates. The mineralization would be genetically related to the emplacement of these mafic dykes, which are dated at ca. 360 Ma (U-Pb on apatite; Pochon and al., 2016b, 2018). A first pervasive alteration of the wall rock, induced by orthomagmatic fluids from the dolerites, led to the crystallization of early minerals enriched in Sb such as rutile (ca. 100 ppm). A second As-Fe stage (with minor Au-Sb) occurred during the initiation of fracturing, happening at approximately 360 °C (As-geothermometer in arsenopyrite). The last Sb-Au episode occurred during a crack-sealing process with a fluid temperature around 250 to 300 °C (microthermometric data on fluid inclusions, Pochon et al., 2018). All of these episodes took place at shallow depth, probably less than 2 km. For more details about petrographic and genetic considerations about the Le Semnon deposit, see Pochon et al. (2018).

2.4. Districts from the Sioule nappe: Pouzol-Servant and Nades

To date, there are few data about Sb mineralizations from Pouzol-Servant and Nades. Monnier et al. (2018) describe the petrography of the Sb-bearing veins at Nades and provides trace-elements chemistry of quartz from one sample. The most detailed study about the Nades and the Pouzol-Servant deposits focusses on the structural features (Aubert and Contamine, 1958). The district of Nades contains several veins, (up to meter in size), made up mostly of quartz, stibnite, and lesser arsenopyrite and pyrite. This district is located a few kilometers east of the Sillon Houiller, in the southern zone of an antiform centered on the granitic complex of Colettes/Beauvoir (Fig. 2). The formation of proximal veins and of the Nades veins in the mica schists led to intense alteration of the vein selvages, which consists mostly of muscovitisation (greisen facies). Peak of metamorphism of the host unit has been dated at approximately 360 Ma (Do Couto et al., 2016). Located about 500 m south of Nades, the granite of Pouzol-Servant intruded the host metasediments at 330 ± 9 Ma (Rb-Sr method on whole rock; Pin 1991). On the western edge, its contact with the schist is underlined by a fault, while to the North, laccolitic contacts with the schist can be observed (Aubert and Contamine, 1958). These authors describe several Sb occurrences in the Pouzol-Servant granite, consisting of quartz and stibnite veins with no other metals. The two main veins are those of Cros and Capitraux; the former, referred to as the Fontabourgnon vein in the study by Aubert and Contamine (1958), was prospected at the beginning of the twentieth century and has a maximum thickness of 0.7 m with stibnite modal composition of the order of 10 to 20 %. No information is available on the Capitraux vein. Aubert and Contamine (1958) propose a common hydrothermal event explaining both Sb mineralizations in Pouzol-Servant and Nades districts. Recently, Monnier et al. (2020) described the main petrographic features and provided fluid inclusion data for these two districts. Minimal temperatures for Sb mineralization were estimated at ca. 175 °C and 215 °C for Pouzol-Servant and Nades district, respectively.

3. Petrography

The following chapters contain brief description of the main Sb mineralizing episodes for the five districts. These generally occur during the last hydrothermal stage and consist mostly of quartz and stibnite deposition. For more comprehensive information of each deposit, the reader is invited to consult the studies cited in the geological setting section above.

3.1. Bournac district

Although mineralized quartz veins in the Bournac district contain a wide variety of sulfide and sulfosalt, stibnite occurs in substantial larger proportion. This sulfide precipitated as (i) massive clusters of up to several mm in thickness around quartz crystals (Fig. 3-A), (ii) within fractures in quartz, in sealed fracture plains in the continuity of secondary fluid inclusion trails (Fig. 3-B), (iii) acicular grains within quartz crystals, orthogonal to the quartz facets, underlining their simultaneous growths (Fig. 3-C). Quartz is mostly euhedral, crystals measuring up to 1 mm in width. It commonly contains a large number of inclusions consisting of a majority of secondary fluid inclusions and stibnite acicular crystals (occurrence iii, above). Only quartz rimmed by substantial thickness of massive stibnite (Fig. 3-A) display large patches without inclusions, probably due to the protective role of the stibnite envelop during late fluid circulation.

3.2. La Lucette district

At La Lucette, quartz in veins forms euhedral crystals of millimeter size. Stibnite forms massive interconnected grains around the quartz. An important number of secondary inclusions (fluids and acicular stibnite) can be found in quartz crystals although they are preferentially located in the rims. Primary fluid inclusions (organized hexagonally and parallel to the quartz facets, indicating trapping during crystal growth) were also observed, and these are not accompanied by acicular stibnite (Fig. 3-D,E,F).

3.3. Le Semnon district

In this district, Sb-bearing extensional veins formed after an episode of pervasive alteration at selvages of dolerite dikes (Pochon et al., 2018). The extensional veins occur as lens shapes of mainly a few cm in size, which opened and filled during cyclic fracturing of the host rock. Quartz seals most parts of the veins, though locally calcite and ankerite also occur. The last mineralizing episode is marked by a crack-and-seal texture of quartz, growing perpendicular to the elongation of the lenses (Fig. 3-G,H,I). Locally, this quartz displays rather unique elongation along the c axis, with a very high length to width ratio (more than 10:1). Stibnite occurs as in primary inclusion in quartz, or as acicular grain at the edges of elongated quartz crystals. It can also be found in the metasomatized host rock, albeit in smaller amounts (Fig. 3-G,H,I).

3.4. Pouzol-Servant district

The veins at Pouzol-Servant, Cros and Capitraux, are similar in texture. They are composed of "star" quartz aggregates of ca. one millimeter in diameter which seem to have grown radially (Fig. 3-J,K) around a iron oxide nucleus, of few microns in size. In the periphery of these star quartz crystals, rare acicular stibnite crystals may grow included in the quartz (Fig. 3 L). However, most of the mineralization occurs outside the star quartz (Fig. 3-J,K). Beside quartz and stibnite crystals, porosity can be significant or even predominant in the total volume of the vein in the case of Capitraux veins, in the form of large vacuoles around the star quartz network. Late clay commonly fills these vacuoles.

3.5. Nades district

Veins in the Sioule metasediments of the Nades district can contain stibnite with or without quartz. Tiny stibnite-only veinlets intersect the shale foliation (Fig. 3-M), as do mm- to cm-sized quartz-stibnite veinlets (Fig. 3-N). Stibnite can also occur within flakes of newly formed muscovite, next to these veinlet (Fig. 3-N). Both veinlet types form a dense interconnected network that intersects the foliation in the mica schist. In the quartz-stibnite veinlets, stibnite mostly envelops euhedral to subhedral quartz grains, or fills fractures in quartz (Fig. 3-N), much as the stibnite found in Bournac quartz. Locally, small stibnite crystals are found included in the border of quartz crystals, forming a cloudy area in the crystal (Fig. 3-O), indicating synchronous growth of these two minerals. Few euhedral pyrite crystals also occur in the veinlets and in the schist, texturally predating quartz and stibnite crystallization.

Based on the petrographic evidences detailed above, relationships between stibnite and quartz common to the five districts are as follows: stibnite precipitated towards the end of quartz crystallization and mostly after it at Nades, Pouzol-Servant, and in the La Lucette district. With regards to the Bournac district, stibnite crystallizes mainly contemporaneously to and, to a lesser extent, after quartz crystallization. Lastly, stibnite precipitation in the Le Semnon district mainly took place before and during quartz crystallization.

4. Materials and methods

4.1. Sampling strategy and preparation

Samples from the Le Semnon were collected in the mine's adit (-17 m level) and correspond to samples that were studied by Pochon et al. (2018). Collection samples from Bournac are part of a batch collected for the studies of Munoz and Moëlo (1982) and Munoz and Shepherd (1987). Finally, quartz veins from Nades and Pouzol-Servant districts were sampled on outcrop during the autumn 2016 and 2017, respectively (Monnier et al., 2018; Monnier et al., 2020). Samples from La Lucette, which were taken from different parts on the main mineralized vein, come from the rock collection of the French Geological Survey (BRGM). For each district, several samples were collected from different veins or veinlets, excepted for La Lucette where only the main vein was sampled. All samples were sliced and selected areas prepared into polished thick sections (approximately 200 µm thick). In addition to the above localities, we also used trace-elements data from quartz collected from the Sb-poor Suchot, Mazet and Colettes kaolin quarry vein sets, in order to provide a comparison with similar quartz veins that do not contain Sb mineralization. These veins have been characterized in detail in previous studies (cf. Monnier et al., 2018).

4.2. LA-ICP-MS analyses protocol

LA-ICP-MS analyses were performed using a UV laser-ablation microsampler CETAC® Excite (193 nm) coupled to a ThermoScientific® X serie II quadrupole plasma mass spectrometer, at the BRGM facility in Orleans (France). The laser is equipped with a HelEx® 2 volume ablation chamber. It was used with frequency of 8 Hz, fluency of 7 $J.cm^{-2}$, and an ablation spot diameter of 85 µm. Acquisitions run 40 s (320 pulse), separated, before and after, by 20 s of background recording. The Glitter® software was used to quantify absolute values, using external standard NIST SRM 612 (concentration from Pearce et al., 1997) for calibration. Si was used as internal standard with a value fixed at 99 % of SiO_2 in quartz for all analyses. More details can be found in Monnier et al. (2018), as the analytical protocol was exactly the same. A total of 8 elements (Li, B, Na, Al, Ti, Ge, As, Sb) were measured in quartz from the districts of Bournac, Nades, the La Lucette and the Le Semnon. To these elements, in order to compare our data with other quartz veins of the Sioule nappe studied by Monnier et al. (2018), we added Be, Rb and Sr for the district of Pouzol-Servant, as these elements were also measured in that study. Detection limits (d.l.) are given in Table 1 for each element. Acquisition error are inferior to 10 %, for concentrations at least 1 order of magnitude superior to d.l. Sulfur was monitored (but not calculated) to verify for the presence of micro inclusions of stibnite that may not have been detected during microscopic observation. Although quartz from the Nades district had already been analyzed by Monnier et al. (2018), we perform new analyses from different veins in order to obtain As concentrations, and to obviate to the limited number of analyses (i.e., 7) obtained in the older work. This also allowed comparing the data obtained during the two analytical sessions (cf., Supplementary Materials 1). The two datasets show very good reproducibility; however, we observed a moderate tough significant drop in Sb and Na values in the new analyses. Such slight differences may be attributed to limited chemical variation between different veins, which is commonly observed in multiple expressions of a single hydrothermal episode, as pointed out in Monnier et al., (2018).

4.3. Multivariate analyses protocol

To investigate the trace-elements signature of quartz from each district we used a set of multivariate statistical analyses, namely, principal component analyses (PCA), hierarchical cluster Analyses (HCA), and permutational multivariate analysis of variance (PERMANOVA). Distance measures for HCA and PERMANOVA were calculated using the Bray Curtis similarity index (Bray and Curtis, 1957), which well describes the statistical characteristics (e.g., presence/absence, broad variations) of trace-elements variables (Monnier et al., 2018). All multivariate analyses were performed with the software Past 3.17 (Hammer et al., 2001).

PCA allows reduction of the dimensionality of the variable space by reporting it with a series of new orthogonal (uncorrelated) variables, called principal components, which capture most of the total variability. Results correspond to a number of components according the total variation of the initial data. The principal components represent a large proportion of the total information and, consequently, the last components have a negligible significance. In other terms, PCA reduces the dimensionality, i.e. the number of variables, of a multivariate data to few principal components; that is, newly-calculated variables that can be visualized graphically, with maximal preserved information. In this study, PCA highlights whether the incorporation of one element in quartz is constrained by the presence of any other given element; it also characterizes the main chemical correlations that typify each district. In this way, in order not to give too much weight to the correlations between elements marked in the most represented groups (districts with the highest population analyses), we operate simple random sampling without replacement for 17 analyses in each group (17 corresponds to the number of analyses in the smallest district, i.e., Nades) using the Mersenne Twister algorithm (Matsumoto and Nishimura, 1998). To ensure the representativeness of the data with "only" 17 analyses per group, we repeated the protocol three times, to provide comparable results. This ensued in three PCAs, constructed with 17 (random sample analyses) x 5 (districts) total measures. These three PCAs are strongly similar; consequently, we decide to only depict the first multivariate analyses in the main body of the manuscript while PCA # 2 and PCA # 3 can be found in Supplementary Materials 2.

HCA builds the hierarchy from each individual chemical analysis by merging clusters as a function of distance measures among data. Any given district where quartz was sampled will not constrain the cluster building (all analyses were equally compared). Common HCA representation is done using dendrograms. Linkage criteria are defined by the unweighted pair group average (UPGMA) algorithm. Clusters are joined based on the average distance between all members in the two groups (Sokal and Michener 1958). Stated differently, the more a cluster emerges at low dissimilarity, the more chemical analyses grouped in this cluster are similar. We used HCA to determine whether the several districts display homogeneous and specific signatures, and to test similarities between genetically unconstrained sample groups.

PERMANOVA quantifies the dissimilarity between any two objects (district, vein, etc.) included in the test, considering all trace-elements analyses of the two groups, using an F-ratio constructed by an inter-point geometric approach (scalar correlations based on the distance measure); the lower the F-value, the more the hypothesis of no statistical difference between groups is true (Anderson, 2001). Significance of the variables was tested by 9999 permutation. In other words, PERMANOVA permits to underline the more similar groups among all. In our case, PERMANOVA was performed to test the resemblances between the districts and veins in the Sioule nappe in order to highlight potential genetic links.

5. Results

The eight chemical elements (Li, B, Na, Al, Ti, Ge, As, Sb) measured in all samples were clearly detected (i.e., well above the detection limit, d.l.) for the majority of the districts studied. The additional elements (Be, Rb and Sr) quantified in samples from Pouzol-Servant also resulted largely above d.l. (Table 1). For each district, a specific signature could be delineated, based on correlations among element pairs (Fig. 4). In the following section, we describe the characteristics of each district as revealed by common descriptive statistics and multivariate statistical analyses. Quartz trace-elements data are available in Supplementary Materials 3.

5.1. Descriptive statistics

Quartz from Bournac is the most enriched in Ti and As (median values are 14.1 ppm and 19.3 ppm, respectively) and, compared to other districts, has intermediate Li, B, Na, Al values (respective median values: 295, 14.1, 31 and 3497 ppm; cf. Table 1). Germanium is relatively low whereas Sb is present in higher concentrations than in other districts (2.6 ppm and 86.5 ppm, respectively). Quartz from Bournac has the lowest Ge:Ti ratio of all districts (0.18 on average) (Fig. 4). Quartz from Nades displays intermediate contents for all elements (with median values of 206, 18.1, 65, 2342, 6.6 and 49.4 ppm, respectively), except for Ge which is relatively high (median value of 65 ppm). As it can be visualized in Figure 4, the La Lucette quartz displays low concentration in Na (with a maximum value of 95 ppm) and in B (maximum value of 5.5 ppm). The contents of Li, Al and Ti are intermediate, (median of 116 ppm, 2598 ppm and 6 ppm respectively) with high variability compared to other districts. In the Li vs Al plot (Fig. 4), the La Lucette data stands out from the general correlation displayed by the other districts, with a higher concentration of Al. Concentrations of As and Ge are relatively high (7.7 and 6.1 ppm in median concentrations) and Sb contents are the highest of all districts (median value of 97 ppm). Quartz from the Pouzol-Servant district exhibits high concentrations of trace-elements, with the highest values being for Li, B, Na, Al and Ge (respective median value of 370, 51, 205, 4153, 8.7 ppm), low and unvarying Sb contents (median value of 14 ppm) and intermediate Ti contents (median equals to 4.8 ppm). The concentrations of Be, Rb and Sr are very high (median value of 1.9, 3.3 and 11.3 ppm, respectively) and correspond roughly to the highest concentrations measured for all types of quartz monitored in the Sioule nappe (Monnier et al., 2018). Quartz originating from the Le Semnon deposit contains the lowest amounts of trace-elements (Li, B, Na, Al, Ti, Ge), with the exception of As and Sb, which occur at intermediate concentrations (respective median value of 0.7 and 29 ppm).

Although Sb may vary among districts by about an order of magnitude (e.g., median values of the La Lucette and Pouzol-Servant districts), its concentration remains high for all districts (Fig. 5). For the Le Semnon and Pouzol-Servant district, more than 75% of the analyses show Sb levels above 10 ppm. For Nades, Sb concentrations are always above 10 ppm, and 8 out of 17 analyses are greater than 50 ppm. globally, the highest Sb concentration is recorded in quartz from the Bournac (23 of the 24 analyses are superior to 50 ppm) and the La Lucette districts (75% of the analyses are superior to 75 ppm). Such a high Sb content in quartz has only been rarely reported in the literature, and when so, it is related to Sb mineralization (Rusk et al. 2011; Pacák et al., 2019; Feng et al., 2020; Fu et al., 2020; Li et al., 2020).

5.2. Multivariate analyses

Hierarchical cluster analysis allowed confirmation of homogeneous and specific quartz trace-elements signature for each district (Fig. 6). Overall HCA results for the entire dataset are remarkable, in that they allow a very clear distinction of each district from the others, with the exception of the Nades and La Lucette, which are only poorly distinguished from one another. The first group emerging entirely from the rest of the analyses is the Le Semnon district, probably because of its very low contents of Li, B, Na, Al and Ge. However, a small number of analyses (which represent extreme values in relation to the distribution of elements in the group) are scattered throughout the rest of the HCA. The second cluster which emerges to the rest of the data consists of quartz from Pouzol-Servant district, probably because of its enrichment in most trace elements. A third cluster emerges clearly and corresponds to the Bournac district which is characterized by high concentration of As, Ti and Sb. The rest of the HCA is less straightforward, including the few artefacts of the Le Semnon, and the districts of the La Lucette and Nades. The latter two groups share many similar elemental concentrations, including Na, Al, Ge and Ti, which can explain their ambiguous and similar position in HCA. Nevertheless, the amounts of B and As easily distinguish these two district (Fig. 4).

Principal component analyses were performed to highlight the principal correlations between the different elements and, at a second time, characterize the role of each district on these correlations (Fig. 7). Component 1 of PCA, corresponding to the horizontal axis, represents 45 % of the entire data and reveals that Al, Li, B, Na and Ge show good correlation while As, Sb and Ti have independent behavior. Using component 2, which represents, in addition to component 1, 75 % of the total analyses, we can distinguish two groups of elements already correlated by the first component: Al and

Li on one hand and Ge, Na and B on the other. Consequently, these two groups display strong correlations for three-quarters of the analyses. As, Sb and Ti are almost exclusively projected onto component-2's axis, meaning that their correlation is effective for ca. 30 % of the data and displays an independent behavior in regard to elements projected mostly in component 1 (i.e. Al, Li, Ge, B and Na). If we use the third component, less representative but not negligible (14 % of the total data), the couple As-Ti shows a negative correlation with Sb, becoming negatively correlated. To resume, Sb variation is independent of most of the elements for 45 % of the data, positively correlated to As and Ti for 30 % of them, while it is negatively correlated to the same couple of elements (As and Ti) for 14 % of the analyses. Consequently, we can conclude that the behavior of Sb in quartz is mainly independent of the presence of other elements.

Regarding the position of the five Sb districts in the PCA diagrams, we can observe that the Pouzol-Servant district is characterized mostly by B, Na, Ge, Al and Li. The Bournac district is constrained by the behaviors of Sb, As and Ti. The intermediate content of most of the elements in the Nades quartz puts this group close to the center of the diagram. Finally, the projection of the La Lucette and Le Semnon districts on opposite sides of Al, Li, B and Na likely results from their low content of these elements and their differences in Sb contents, leading to different vertical positions of these two groups in the diagram.

To resume, for most analyses, some trace elements show strong positive correlations, such as Al with Li, Na with B and Ge, and, to a lesser extent, As with Ti. Others vary mostly independently, as Sb, while no element shows a clearly negative correlation to another. This last result can be explained by the fact that trace-element incorporation in quartz is a global process, i.e., the more a quartz crystal incorporates a given element, the higher its capacity to incorporate others elements (Monnier et al., 2018). Once this parameter is met, the nature of the fluid chemistry also comes into play, particularly in controlling the relative proportions of the different elements incorporated.

6. Discussion

6.1. Deciphering polyphase Sb events, the case of the Sioule Nappe

We have seen above how the five districts studied display different quartz trace-element signatures, including the two neighbour districts in the Sioule Nappe, Pouzol-Servant and Nades. Monnier et al. (2018, 2019, 2020) have shown that greisen alteration of the Beauvoir granite developed a regional-scale fluid circulation that gave rise to distal mineralizations, among which is the Nades district. A particular aspect of the latter is that it was the only site showing Sb mineralization, although quartz from all manifestation of the greisen event(s) at Beauvoir showed Sb enrichment in their trace-elements signatures. In the vicinity of the Nades district, occur the Sb-rich veins of Pouzol-Servant, emplaced within the homonymous granite. A question that needs answering at this stage, is whether the latter system is related, or not, to the Beauvoir greisen episode responsible for mineralization at Nades. The statistical data presented above indicate that each of the Sb mineralized sites in the five districts has a specific signature, suggesting that Pouzol-Servant and Nades, and by extrapolation the greisen system, also have distinct origins. This is consistent with the petrographic observations and fluid inclusion data presented in Monnier et al. (2020) showing clear differences in textures (euhedral to subhedral quartz for the Nades veins vs an uncommonly abundant star quartz filling at Pouzol-Servant) and fluid inclusion homogenization temperatures between the two sites (ca. 170 °C and 210 °C for the median Th of the quartz of the Pouzol-Servant and Nades veins, respectively). To verify this hypothesis, we performed new multivariate analyses (HCA and PERMANOVA) using an enlarged signature for quartz from Pouzol-Servant, by adding analyses of Be, Rb and Sr. This allows a direct comparison with the quartz chemistry obtained from the proximal vein system at Beauvoir, and from the distal Nades veins (data from Nades, including Be, Rb and Sr, are from Monnier et al., 2018). The results of HCA analysis show only a weak similarity between the Pouzol-Servant group and the veins from the proximal systems and Nades (Fig. 8). The PERMANOVA analysis also points to the same conclusion (Fig. 9), with the quartz from Pouzol-Servant district showing significant higher F-values when compared to those of Nades and proximal veins. On the contrary, the quartz of the Nades veins and the group of the three proximal veins (Mazet, Colettes kaolin quarry and Suchot veins) show moderate F-values between each of these groups, suggesting a common origin. In summary, it appears clear that two distinct hydrothermal events occurred in the Sioule Nappe, both at the origin of a distinct stibnite mineralization episode. This observation suggests a local fertility for occurrences of Sb mineralization.

6.2. Sb in quartz as vector to mineralization

As already revealed by chemical mapping at the crystal scale (Rusk et al., 2011), PCA shows that there are almost no correlations between Sb and other elements (Fig. 6). This means that Sb incorporation in quartz is mainly controlled by the content of Sb in the mineralizing fluid, and not by the possible presence of other elements, which is crucial for its use as a potential proxy for Sb deposits. Moreover, the different timing of quartz crystallization in the five Sb districts (mainly pre-, syn- or post-dating stibnite crystallization) did not constrain the incorporation of Sb in quartz in trace amounts, suggesting that the competition with stibnite does not represent an inhibiting factor. Considering the high content of Sb (>10 ppm) in quartz from our five Sb districts and the low Sb concentration (not detected or ≤ 1ppm) reported in the literature for hydrothermal or magmatic quartz unrelated to Sb mineralization (Götze et al., 2004; Rusk et al., 2011; Audétat, 2013; Muller et al., 2018; Monnier et al., 2018; Peterková and Dolejš, 2019; Hong et al., 2019; Pacák et al., 2019; Li et al., 2020), it can be inferred that the presence of Sb in hydrothermal quartz is an excellent tracer of Sb mineralization. Moreover, our results agree with preliminary data from Rusk et al. (2011) which show high Sb contents in quartz from epithermal deposits in Comstock (Nevada) and Creede (Colorado), both mineralized in Sb (miargyrite and tetrahedrite for Comstock; Hudson, 2003; and tetrahedrite for Creede; Plumlee and Whitehouse-Veaux, 1994). In addition, Rusk et al. (2011) show that quartz from hydrothermal deposits of other metals (i.e., Carlin, MVT and porphyry deposits, all of which do not show Sb mineralization) contain very little Sb. A recent study of several Au (-Sb) mineralizations in the Bohemian massif came to the same conclusion, i.e., quartz with high trace contents of Sb was only found in Sb-mineralized veins (Pacák et al., 2019). In China, several recent studies have analyzed trace-element in quartz in a number of Sb districts. Quartz from the giant Woxi and Xikuangshan Sb deposits exhibits extraordinary Sb contents, always superior to 10 ppm and commonly higher than

1000 ppm (Fu et al., 2020). Also, the different quartz generations in the Gutaishan Au (Sb) deposit have median Sb concentrations ranging from ca. 10 to 70 ppm (Feng et al., 2020). Finally, in the Youjiang metallogenic province in China, which hosts both Sb and Au deposits, Sb was only detected in quartz from the Sb deposits (Li et al., 2020).

If we use the results from our study, we can define a quartz chemistry that could be considered a potential vector to Sb mineralization. Different generations of quartz from the fluid that led to stibnite mineralization in the Nades district (greisen quartz, proximal veins) have a similar signature marked by unusually high Sb contents (mainly > 1 ppm and < to 10 ppm), even if these quartz are not directly associated to Sb mineralization. In comparison, quartz completely disconnected from Sb mineralizing fluids mostly exhibits less than 1 ppm Sb. Conversely, quartz directly associated to Sb mineralization has Sb content commonly greater than 10 ppm. Therefore, we can conclude that quartz crystallizing from a Sb-enriched fluid can record this pre-enrichment, even if no Sb-bearing minerals occurs in the immediate proximity of this quartz (Fig. 10). This observation can be critical to target potential mineralization along the circulation pathway of a cooling Sb-bearing fluid.

To get an idea of the effectiveness of the protocol for Sb prospecting, at the rate of ca. five LA-ICP-MS analyses per vein tested, the Sb mineralization potential can be apprehended by monitoring 10 to 50 quartz veins per day, and much more in case of automatized LA-ICP-MS. This protocol can be used in strategical zone, such as potential epithermal or orogenic quartz veins, with bad outcrop conditions or poorly constrained samples from drill core. Even if preliminary observations may not be conclusive as to the presence of Sb mineralization, reproducible concentrations of more than 10 ppm Sb in quartz are likely to signify that a vein network has very elevated potential for Sb mineralization in the immediate proximity. Much in the same way as LA-ICP-MS analyses of pyrite and arsenopyrite can help targeting potential Au deposit (e.g., Morey et al., 2008; Cook et al., 2013; Velasquez et al., 2014; Traore et al., 2016; Gourcerol et al., 2018, 2020; Zhang et al., 2020), our approach may help tracking Sb mineralization and improve prospecting during mineral exploration.

7. Conclusion

The results of a study on five Sb mineralized occurrences from five districts in the Variscan belt in France, indicate that the trace-elements composition of vein quartz has an excellent potential as a proxy for Sb mineralization. Concentrations of Sb in quartz predominantly superior to 10 ppm indicate occurrence of Sb mineralization within the considered vein or in close proximity. Intermediate concentrations (between ca. 1 and 10 ppm) would indicate that the magmatic or hydrothermal system is pre-enriched in Sb and could lead to the formation of possible associated mineralization. Concentrations mainly inferior to ca. 1 ppm indicate that quartz is not associated with Sb mineralized systems. It is also possible to differentiate quartz from different mineralization event, and therefore coming from different fluids, using their chemicals signature. The latter may turn useful to distinguish different mineralizing episodes in a same locality. Thus, we have seen that the veins of Pouzol-Servant and Nades, which are located at proximity in the same tectonic nappe, originated from two distinct mineralizing fluids. With regards to the fluid source, new perspectives appear concerning the Sb metallogenic paradigm: in the case of the Echassières district, we highlight the genetical link between greisen alteration, formation of peripheral veins rich in W, Sn, Nb-Ta, and, further away, Sb occurrences. This trace-element signature, specific to each hydrothermal event, can also be used in the identification of the origin of mineralization. Finally, the trace chemistry of quartz could denote the specific signature of many deposits, thereby allowing tracing the original source of an ore sample of controversial origin, provided it contained a few small quartz crystals.

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Captions

Figure 1: A sketch map of France locating the Sb districts in Variscan terranes (in gray) that were the object of this study. AM: Armorican Massif; FCM: French Central Massif. The color code assigned to each district (stars) will be the same in all subsequent Figures.

Figure 2: Geological map of the central part of the Sioule nappe, locating the mineralized occurrences discussed in this study. The rare-metal bearing Beauvoir granite is also shown. Stars locate sampled outcrops. Veins mineralized in Sb: a = Nades; b = Les Cros; c = Capitraux. Proximal veins (Monnier et al., 2018) with no Sb mineralization: d = Suchot; e = Mazet; f = Colettes kaolin quarry.

Figure 3: Photographs and Photomicrographs illustrating textural relationships between stibnite and quartz in: the Bournac district (A to C), the La Lucette district (D to F), the Le Semnon district (G to H), Pouzol-Servant district (J to L) and Nades district (M to O). All photomicrographs are in plane polarized light and were taken from thick section, except for image N, taken from thin section. Photographs J and L show hand samples in the field, while image K is a high-resolution scan of a thick section. A: Euhedral to subhedral inclusion-free quartz surrounded by massive stibnite. B: An altered quartz grain containing abundant stibnite crystals and fluid inclusions, trapped along plane of micro-fracturing. C: Euhedral quartz containing acicular stibnite crystals mostly oriented orthogonally to the quartz faces. Contrarily to the case in B, this texture indicate that stibnite and quartz precipitated at the same time. D; E; F: euhedral quartz with stibnite filling the interstices. In several crystals, the outer rims of quartz are free of fluid inclusions, indicating that those present in the cores are primary or pseudo-secondary. In the upper left corner of image D, a laser ablation hole is visible, where quartz was analyzed. G; H; E: quartz veinlets hosted by metasomatized schist. Stibnite mineralization occurs mainly within the veinlet as inclusions in quartz, plus, in lesser quantity, in the altered schist. J, K: hand sample of the Cros vein, where quartz exhibits a radial texture, detailed in K. Stibnite is

interstitial to the quartz aggregates. L: Close-up view of clusters of acicular stibnite crystals included in a quartz crystal (Capitraux vein). M: A small sample of Sioule schist containing a stibnite veinlet at Nades. N: A quartz veinlet hosted in secondary-muscovite rich schist. Stibnite occurs mostly in the quartz veins, but also in fractures affecting both schist and veinlet. O: Quartz crystal showing a cluster of stibnite inclusions. The quartz crystal is surrounded by massive stibnite and hydrothermal muscovite.

Figure 4: Binary diagrams depicting quartz trace-elements data for each of the five districts.

Figure 5: Box plot diagrams illustrating variations in Sb content for quartz from the five districts. Colored circles represent outliers that plot outside the upper and lower inner fence limits delimited by the whiskers, calculated as 1.5 times the box height from the box.

Figure 6: Hierarchical cluster analysis (HCA) dendrogram illustrating the similarities between each analysis for the entire dataset. For more visibility, the analyses are colored according to their district of origin. Elements included in the HCA are Li, B, Na, Al, Ti, Ge, As, Sb.

Figure 7: A diagram depicting the results of principal component analysis (PCA) of trace-elements data from quartz from the five districts. The three principal components are shown. The envelop for each district is contoured in the corresponding color (cf. Fig 1). Each district is represented by same number of analyses, i.e. 17 (for more details see the Multivariate Protocol section). Elements included in the PCA are Li, B, Na, Al, Ti, Ge, As, Sb.

Figure 8: HCA dendrogram comparing the trace-elements data for quartz from the proximal veins and from the Nades veins, taken from Monnier et al. (2018), with the analyses from the Pouzol-Servant district performed in this study. Elements included in the HCA are Li, Be, B, Na, Al, Ti, Ge, Rb, Sr, Sb.

Figure 9: F-value statistics of a permutational analysis of variance (PERMANOVA) concerning the two Sb districts of the Sioule Nappe and the three proximal vein sets at Mazet, Colettes quarry and Suchot. Larger F-values invalidate the hypothesis of no difference between two datasets. F-value = 0

indicate two data set strictly equals. F-values between 0 and 1 are generally interpreted as no statistical evidence of difference between the two data set analyzed. Elements included in the PERMANOVA are Li, Be, B, Na, Al, Ti, Ge, Rb, Sr, Sb. In this Figure, the color code is only an indication to help reading the values.

Figure 10: Boxplot diagram illustrating the concentration of Sb in quartz as a function of their genetic link to Sb mineralization. Data include all quartz from the five Sb districts (in violet; this study) plus hydrothermal quartz in stibnite-free veins from the Sioule nappe (in orange; data from Monnier et al., 2018). The latter are divided into two groups: to the left, hydrothermal quartz completely unrelated to Sb mineralization, originating from orthomagmatic fluids (i.e., the La Bosse stockwork), alkali alteration (granite apex veins), and supergene alteration (late quartz), while, to the right, quartz from the Beauvoir greisen, i.e., a fluid that transported Sb but did not produce Sb mineralization in the proximity of the Beauvoir granite (pervasive and greisen vein quartz in the granite, and quartz from the proximal veins). More distally, the greisen fluid led to the formation of the Nades veins. (Names in brackets refer to the terminology in Monnier et al., 2018).

Author contributions:

Conceptualization, L.M. and A. P.; methodology, L.M., A.P., J.M. and P.L.; validation, S.S., J.M., D.B., and L.B.; formal analysis, P.L. and L.M.; investigation, L.M.; writing—original draft preparation, L.M. and S.S.; writing—review and editing, A.P. and D.B.; visualization, L.M.; supervision, J.M., D.B., L.B. and S.S.; project administration, J.M., D.B., L.B. and S.S.; funding acquisition, J.M. and L.B.

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Table 1: Descriptive statistics of quartz trace-elements concentrations from the different Sb districts (n.a.: not analyzed; d.l.: detection limit).

		The Lucette n = 93			The Semnon n = 46			Bournac n = 24			Nades n = 17			Pouzol-Servant n = 51		
ppm	d.l.	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.
Li	0.5	31	116	244	3	8	192	166	295	368	87	206	325	248	370	453
Be	0.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.37	1.9	2.93
B	0.5	1.1	3.6	5.5	0.7	1.2	4	9.6	14.1	22.1	10.6	18.1	25.2	31.9	51.0	61
Na	5	5	13	95	5	5	45	6	31	215	5	65	163	19	205	518
Al	10	1029	2598	4427	63	192	5797	2102	3497	416[illegible]	956	2342	3829	3251	4453	5096
Ti	1	2.3	6.0	9.6	1.4	3.3	10.9	7.7	14.1	24.5	4.5	6.6	13.2	3.5	4.8	6.7
Ge	0.5	4.3	7.7	15.1	1.5	2.2	11.8	1.4	[illegible].6	8.6	4.9	8	16.4	5.3	8.7	11.4
As	0.1	0.9	6.1	20.4	0.5	0.7	1.3	3.[illegible]	19.3	38.1	0.1	0.3	0.4	0.1	0.1	0.4
Rb	0.01	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.1	3.3	5.7
Sr	0.01	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.6	11.3	23.1
Sb	0.01	23.2	96.0	304.1	1.4	29.2	291.1	34.7	86.5	123.9	13.9	49.4	102.5	8	14.1	272.9

Highlights

- Sb contents in quartz higher than 10 ppm record deposition of Sb ore.
- Sb concentrations from 1 to 10 ppm reflect potential for Sb mineralization.
- Quartz signature is a useful tool to untangle polyphase mineralizations.