INTRODUCTION

Quartz veins of variable sizes are common features in orogenic settings and their study may shed light on the evolution of orogens (Bons et al., 2012; Sharp et al., 2005, among others). In the Eastern Pyrenees, a number of quartz veins are present that vary from kilometric to metric lengths and decametric to centimetric widths, respectively (Ayora and Casas, 1983; Fonseca et al., 2015). These veins are mostly hosted in Variscan and pre-Variscan rocks, but on the southeastern slope of the chain (Roc de Frausa massif), quartz bodies that crosscut Mesozoic sedimentary rocks have also been recognised.
West of the Roc de Frausa massif, on the southern slope of the Canigó massif, several quartz veins crop out in the Upper Ordovician and underlying Cambrian-Ordovician successions. Casas et al. (2019) and Puddu et al. (2019), based on the veins arrangement and distribution, suggested an Upper Ordovician fluid circulation event, which was genetically linked to the Middle-Upper Ordovician “Sardic” geodynamics. Specifically, Santanach (1972a) described the Upper Ordovician Unconformity in this area for the first time in the Pyrenees, now widely recognised and used for Palaeozoic stratigraphic correlations in southwestern Europe. However, the origin and significance of this so-called Sardic Unconformity are still subject to open debate (Álvaro et al., 2018). As this area has registered complex evolution from Ordovician to Miocene times, more criteria are necessary to establish the age of the veins.

In this paper we deal with the structure, distribution and textural characteristics of quartz veins and their hosting rocks in La Molina area (Canigó massif), together with phyllosilicate chemistry and fluid inclusion microthermometry. The obtained data allow us to discuss: 1) the thermal balance between fluids and host rocks, and 2) the emplacement of quartz veins within the framework of the structural evolution of the pre-Variscan rocks of the Eastern Pyrenees. Moreover, differences in chlorite composition related to vein-generation and vein-location call into question the validity of the applied geothermometers for some of the analysed chlorites.

GEOLOGICAL SETTING

The Pyrenees is an Alpine fold-and-thrust belt formed from the Late Cretaceous to Miocene by the collision between the Iberian and Eurasian plates (Muñoz, 1992a). In the central area of the orogen, cortical-scale Alpine antiformal stacking (Muñoz, 1992a) produced the exhumation of a pre-Variscan metasedimentary succession, Late Neoproterozoic to Carboniferous in age. Pre-Variscan rocks are affected by Sardic (Ordovician), Variscan, and Alpine deformational events and record Cadomian, Ordovician, and Carboniferous magmatic activity together with Variscan regional metamorphism (Casas, 2010; Guittard, 1970; Muñoz, 1992a; Navidad et al., 2018; Padel et al., 2018a; Pereira et al., 2014; Santanach, 1972b; Zwart, 1979).

In La Molina area (southern slope of the Canigó massif; Fig. 1), the Upper Ordovician (Sardic) Unconformity (Santanach, 1972a) splits the pre-Silurian sequence into underlying Cambrian-Ordovician and overlying Upper Ordovician successions, giving rise to a ~20m.y. gap (Margalef et al., 2016) (Fig. 2). The Cambro-Ordovician succession is represented by the uppermost part of the Jujols Schists Series (Cavet, 1957), now referred to as the Sèrdinya Formation (Padel et al., 2018b) within the Jujols Group (Laumonier, 1988). It consists of a rhythmic alternation of sandstone and shale layers of millimetric to centimetric thickness. Late Cambrian (Furongian) to Early Ordovician (Tremadocian) acritarch-based age was established by Casas and Palacios (2012) in its uppermost

FIGURE 1. Geological sketch of the pre-Variscan rocks in the Pyrenees showing the location of the study area.
part, whilst a maximum depositional age of ca. 475Ma (Floian) was proposed by Margalef et al. (2016) on the basis of the youngest detrital zircon population.

The overlying Upper Ordovician succession (Cavet, 1957; Hartevelt, 1970) forms a broad fining-upward siliciclastic package with some limestone key levels, displaying significant (100–1,000m) thickness variations. This succession was originally defined by Hartevelt (1970), who described five formations. These are, from base to top, the Rabassa Conglomerate, Cava, Estana, Ansobell, and Bar Quartzite formations. In the study area only the Rabassa Conglomerate and Cava formations crop out.

The Rabassa Conglomerate Fm. is made up of red-purple matrix-supported unfossiliferous polymictic conglomerates composed of surrounding slate and quartzite heterometric (2–20cm) clasts and its age has been established as Sandbian-Early Katian (former Caradoc) by Hartevelt (1970). In the study area, the Rabassa conglomerates form discontinuous lenses up to 60m thick. These massive-to-channelised sets are interpreted as alluvial-to-fluvial deposits (Hartevelt, 1970). The overlying Cava Fm. is 100–800m thick and covers either the Serdinya or the Rabassa Conglomerate formations. It is made up of feldspathic conglomerates and sandstones in the lower part, showing a characteristic green-purple colour, grading upward into

FIGURE 2. A) Detailed geological map of the study area. Location shown in Figure 1. B) Stratigraphic log of Cambrian–Ordovician and Upper Ordovician successions. C) Geological cross-section through the study area.
variegated shales and fine-grained sandstones, with strongly burrowed quartzites in the uppermost part (Belaustegui et al., 2016). On the basis of abundant brachiopods, bryozoans and echinoderms concentrated in fine-grained sandstones of the middle part of the formation, Gil-Peña et al. (2004) attributed a Katian (former Late Caradoc to Early Asgil) age to this formation.

The Cambrian-Ordovician succession is affected by a pre-Variscan (Middle Ordovician?) deformation (Casas, 2010; Casas et al., 2012; Santanach, 1972a) that gave rise to the formation of the Sardic Unconformity. This unconformity has also been recognised in other Pyrenean massifs (i.e., Lys-Caillouas area, Den Brok, 1989; Kriegsman et al., 1989; Garona Dome, García-Sansegundo and Alonso, 1989; García-Sansegundo et al., 2004 or the La Cerdanya area, Casas and Fernández, 2007; Puddu et al., 2019). The existence of this intra-Ordovician unconformity was first established in other NW Gondwana domains such as in Sardinia (Teichmuller, 1931), where it separates the Cambrian–Ordovician from the Upper Ordovician successions (Pillola et al., 2008), although its origin and meaning are still under debate (i.e., Cocco and Funedda, 2019; Pasci et al., 2008). As a result, the large-scale geodynamic processes that led to its formation have been subject to several interpretations (see a review in Álvaro et al., 2018). Moreover, the pre-Sardic deformation, the Sardic Unconformity and the lowermost part of the post-Sardic succession are cut and offset by several Late Ordovician NNE-SSW-trending synsedimentary extensional faults, which caused variations in the thickness (from a few metres up to 100m) of the lower part of the Upper Ordovician succession (Casas, 2010; Puddu et al., 2019).

A penetrative cleavage parallel to the axial plane of folds is recognisable in both the pre- and post-Sardic successions. Classically, a Variscan age has been attributed to this folding episode (Casas, 2010; Casas et al., 2012; Santanach, 1972b), although the absence of post-Variscan deposits in the study area renders this attribution speculative. This cleavage can be correlated with the pervasive cleavage linked to the east-west trending folds that is the main deformation mesostructure in the Pallaresa, Rabassa, and Orri domes and in the Tor-Casamanya and Llavorsí synclines (Clariana and García-Sansegundo, 2009; Margalef and Casas, 2016; Poblet, 1991; Speksnijder, 1986).

During Alpine deformation the pre- and post-Sardic successions were part of the Rialp-Canigó unit, which is the lowermost Alpine unit including pre-Variscan basement rocks in the Pyrenees (Muñoz, 1992a). This author distinguished three main Alpine thrust sheets, from bottom to top: the Rialp-(Canigó), Orri-(Cadí) and Pedraforca-(Nogueres), which form an antiformal stack with their basal thrusts north-dipping on the northern side of the chain, subhorizontal in the central part, and south-dipping at the southern contact with the Mesozoic-Cenozoic cover. Transverse (N–S-trending) southward displacement related to these Alpine thrust sheets is about 150–160km (Muñoz, 1992a), so the original Palaeozoic basin should be located northward from present-day arrangement, being double the width of what is preserved today. The Rialp-(Canigó) unit is the one originally located further south. Moreover, the Alpine deformation gave rise to important horizontal axes rotation, up to 110°, related to thrust sheet emplacement and antiformal stack development (Muñoz, 1992a). In contrast, Alpine metamorphism is absent and Alpine internal deformation has not been described in the post-Variscan rocks. As a result, the original characteristics of the pre-Variscan rocks may be confidently reconstructed in the Pyrenees, although their original position must have been located further north. Finally, the La Cerdanya Neogene normal fault separates the study area (in the footwall) from the rest of the Cambrian–Ordovician and Upper Ordovician outcrops located further north (in the hanging wall) (Fig. 1).

In the Eastern Pyrenees, besides a number of metric veins spread throughout the Palaeozoic basement, discontinuous kilometric veins with metric to hectometric width massive aligned milky quartz bodies are also known. These larger veins cut metasedimentary sequences, orthogneiss and granitoids, and are crosscut by other very fine-grained quartz micro-veins, some with a few phyllosilicates and calcite. Host rock fragments in the veins are common near their boundary. Examples of these veins, from west to east, are the WNW–ESE Esquedres de Rojà vein in the Canigó massif (Ayora and Casas, 1983), the W–E to NW–SE quartz veins of Roc de Frausa massif (Lieja, 1988), and the NW–SE Roses-Palau sections in the Cap de Creus massif (Fonseca et al., 2015).

In the study area, quartz veins with centimetric thickness and metric lengths crop out. Recently, their possible relationship with the Sardic events has been suggested by Casas et al. (2019) and Puddu et al. (2019), pointing out that the quartz veins encased in the uppermost part of the Jujols Group are subparallel to the trace of the extensional faults, and that they might have served as source of quartz clasts that form the Rabassa Conglomerate Fm. However, the petrography, structure, distribution, and formation conditions of these veins have not yet been described.

**METHODS**

The geological map and cross-section from La Molina area were generated using 3D-software MOVE® from the collected field data. The data corresponding to bedding, mean cleavage, bedding/cleavage intersection
lineation, fold axes, joint sets, normal faults, and two generations of quartz veins, have been plotted in equal-area lower-hemisphere stereographic projections to carry out a classic structural analysis. Spatial distribution throughout the study area of quartz veins was obtained from quantifying the number of each vein family (>0.5 cm thick) in visible outcropping square metre outcrops in the area. Altogether, 299 evenly-distributed outcrops were plotted using a Geographical Information System (GIS) and interpolated using the natural neighbour method. To interpolate a value, this algorithm finds the closest subset of input data to a query point, applying weights to the data based on proportionate areas (Sibson, 1981).

The petrographic study of 27 thin sections from samples of Cambrian–Ordovician and Upper Ordovician rocks and quartz veins was carried out with special emphasis on the texture, microstructure, and vein-rock relationship. Muscovites and chlorites were analysed in a JEOL JXA-8230 Electron Probe Microanalyzer (EPMA) at Centres Científics i Tecnològics of the Universitat de Barcelona (CCITUB). The EPMA was operated using an excitation potential of 20kV and a beam diameter of 1 μm. Peak counting times for each analysed element was 10s with the exception of Na, where 20s was used. Back measurements were made at 50% peak counting time on each side of the analysed peaks. Three semi-empirical geothermometers (Bourdelle et al., 2013; Inoue et al., 2018; Lanari et al., 2014) were used via the spreadsheet from Verdecchia et al. (2019) to estimate vein formation temperatures. Calculations were applied to analysed chlorites without smectite or vermiculite interstratified layers (Na+Ca+K<0.1 atoms per formula unit, a.p.f.u.) and octahedral sites below 5.95a.p.f.u., according to Bourdelle and Cathalineau (2015) and Vidal et al. (2016) under the premise that analyses with very low amounts of octahedral vacancies produce erratic temperature estimations.

Fluid inclusion petrography and microthermometric measurements were performed on 250 μm thick double-polished sections from two quartz vein generations. Data was obtained on a Linkam THMSG 600 heating-freezing stage at the Department de Mineralogia, Petrologia i Geologia Aplicada of the Universitat de Barcelona. The stage was calibrated with fluid inclusions of pure CO₂ and distilled water. The measurement precision was ±0.1°C below 0°C and ±2°C for the homogenisation temperatures. The FLUIDS package from Baker (2003) was used to obtain the trapped-fluid properties. Salinity of fluid inclusions, reported in equivalent mass % NaCl, was calculated using Bodnar’s (1993) equation in BULK software. The corresponding isochore was calculated from the obtained density and molar volume through the state equations of Bodnar and Vityk (1994) and Knight and Bodnar (1989) in ISOC software.

FIGURE 3. Equal-area lower hemisphere stereoplots of bedding (S₀), cleavage (S₂) and intersection lineation (L₀–2), A, C, E) from the Cambrian–Ordovician and B, D, F) Upper Ordovician successions. G) Late Ordovician normal faults and joints. n indicates the number of measurements.
STRUCTURE

A detailed geological map of La Molina area (1:5,000 scale) and a stratigraphic log of the Cambrian–Ordovician and Upper Ordovician successions are shown in Figure 2A, B. The study area is in the WNW–ESE trending vertical-to-subvertical southern flank of the Canigó antiform, truncated in the south by the Alpine Ribes-Campproden thrust (Muñoz, 1992b) that separates the Canigó antiform from a southwards located synform where Silurian, Devonian, and pre-Variscan Carboniferous successions crop out extensively (Figs. 1; 2C).

The most visible mesostructures of the Cambrian–Ordovician and Upper Ordovician rocks are the bedding surfaces ($S_0$), which exhibit different attitude in each succession. In the Cambrian–Ordovician succession, $S_0$ values display a marked dispersion with dips ranging from sub-vertical to sub-horizontal (Fig. 3A). In contrast, the Upper Ordovician $S_0$ bedding surfaces are southwards dipping and exhibit a more regular NW–SE trend (Fig. 3B).

A rough slaty cleavage ($S_1$) is only observed at microscopic scale in the Cambrian–Ordovician rocks. Other deformational mesostructures or folds associated with this cleavage have not been identified.

A roughly NNE-dipping $S_2$ crenulation cleavage parallel to $D_2$ folds axial planes and affecting both Cambrian–Ordovician and Upper Ordovician rocks is the most pervasive deformation structure recognised at micro and meso scales (Fig. 3C, D). As with the $S_2$ cleavage, $D_2$ fold axial surfaces display a moderate-to-subvertical dip (45°–90°) towards the NW (15/320°) (Fig. 3A). In contrast, the Upper Ordovician $S_0$ bedding surfaces are southwards dipping and exhibit a more regular NW–SE trend (Fig. 3B).

PETROGRAPHY

Cambrian–Ordovician shales (Fig. 5A-C) and Upper Ordovician conglomerates and feldspathic sandstones
Cambrian–Ordovician shales, in areas with high amounts of quartz veins, show micrometric to millimetric width bedding surfaces defined by compositionally different bands (Fig. 5A, B). The thinnest bands (60μm–0.5mm) are rich (>90%) in phyllosilicates with chlorite and muscovite (<20μm) and poor (<10%) in quartz, representing a Localised Volume Reduction (LVR) interpreted as bedding-parallel compaction bands (e.g. Aydin et al., 2006; Fossen et al., 2007) (Fig. 5B). Otherwise, the thickest bands (0.5–1.75mm) are mostly formed by quartz (>95%) (Fig. 5A). In both cases quartz grains show a granoblastic texture with intracrystalline deformation and sutured boundaries, indicating recrystallisation processes. Eventually, the rough S1 is transposed by the S2 main cleavage (Fig. 5C). S2 is anastomosed, well-developed, and defined by the preferred orientation of phyllosilicates in the thinnest bands, surrounding in some cases larger euhedral-to-subhedral chlorite crystals (<100μm) (Fig. 5C).

Upper Ordovician Rabassa conglomerates are constituted by rounded to sub-rounded shale, quartzite and monomineralic quartz clasts supported in a quartz (90%) + phyllosilicates (5%) ± opaque minerals (5%) matrix (Fig. 5D). Matrix quartz grains (40–100μm) show a granoblastic texture with sutured boundaries. Shale clasts, 1–4mm in size, are interpreted as Serdinya Fm. sourced. Quartzite clasts (0.01–2cm) are eventually elongated without any preferential orientation and include chlorite-bearing stylolites. Monomineralic polycrystalline quartz clasts (0.3–3mm) are elongated in a preferential orientation and show characteristic textural and microstructural relationships with quartz veins (see below this section). S0 is represented by the alignment of opaque matrix minerals, eventually deformed by open folds with axial surfaces parallel to S2. The preferential orientation of matrix phyllosilicates and the elongation direction of monomineralic quartz define the S2 surfaces that are the only visible surfaces in the matrix since they surround all the clasts (Fig. 5D).
FIGURE 5. Microphotographs of Cambrian–Ordovician and Upper Ordovician rocks: A) V1 vein hosted in the Serdinya Formation with in-vein stripes related to the host rock phyllosilicate compaction bands (Cross-polarised light, XPL); B) interpretation of (A) (see text for further explanation); C) euhedral chlorite (Chl) crystals growing coevally with S2, the latter transposing the S1 cleavage (Plane-polarised light, PPL); D) S2 cleavage surrounding monomineralic quartz and quartzite clasts; Rabassa Conglomerate Formation (PPL); E) grain-size variations (S0) and their relationship with S2 cleavage; Cava Formation (PPL); F) sutured boundaries (blue arrows) from a V2 blocky vein; Cava Formation (XPL); G) complex relationships between monomineralic quartz clast from the Rabassa Conglomerate Formation and a transgranular V1 vein in PPL; and H) XPL (see text for further explanation). Orange arrows indicate Fe-oxide locations. Red arrows indicate the silica dissolution and diffusion pathways. Double red arrows indicate the maximum silica diffusion into the vein. Abbreviations: Py= pyrite; Chl= chlorite.
The Cava Fm. conglomerates are composed of clasts of the same type and origin as those described for the Rabassa Conglomerate Fm. clasts are homometric (generally 1–2mm) and are supported in a quartzo-feldspathic matrix that also includes tourmaline, zircon, and apatite crystals (10–30μm). S1 is well-defined by matrix grain-size variations (from 10–60μm to 0.25–0.5mm; Fig. 5E) and by opaque mineral alignment, whereas S2 is depicted by the preferential orientation of phyllosilicates, monomineralic polycrystalline quartz and shale clasts. Some chlorite grains (0.02–0.25mm in size) unrelated to matrix grain-size variations (Fig. 5E) appear growing coevally to S2. They contain layers showing optical characteristics of biotite, which are also compatible with stilpnomelane and with small-scale interleaving of chlorite with other phyllosilicates (Franceschelli et al., 1986; Mellini et al., 1991).

Host-rocks described above and veins (see below this section) have up to 20% of Fe oxides, which permeate S1 and S2 cleavages, stylolites, clast boundaries, and quartz vein walls (Fig. 5A, C–H). V1 walls are apparently more permeated by Fe oxides than V2 walls. Euhedral to subhedral pyrite crystals (30μm–0.8mm) unlinked to grain-size variations depict quartz and chlorite pressure fringes (Fig. 5A, B) and are also present in both Rabassa Conglomerate and Cava formations.

For the petrographic characterisation, 1–2cm thick veins from both (V1 and V2) generations hosted in Cambrian–Ordovician and Upper Ordovician successions were selected in order to identify possible differences between them. The texture of both V1 and V2 quartz veins varies from blocky to elongated-blocky without any preferential direction. Blocky veins (Fig. 5F) are generally narrow (0.2–4mm), containing homometric grains (50μm–0.3mm) with sutured edges. Elongated blocky veins (Fig. 5A, B) are wider (1–15mm) and quartz crystals have a length/width ratio on the order of 10. The crystals’ long axes are aligned perpendicularly to the vein walls, having a large quantity of smaller crystals on the vein-margins and a reduced quantity of larger crystals towards the veins centres. A concave-convex curvature along the long axis of crystals in V1 veins eventually develops (Fig. 5A, B), indicating syntaxial growth morphology (Bons, 2000; Durney and Ramsay, 1973; Ramsay, 1980).

Properties of vein-filling quartz crystals from Cambrian–Ordovician-hosted V1 veins are variable. This is because quartz-rich and phyllosilicate-rich bands from the Sardinya Fm. match with quantity and grain-size variations inside the veins (Fig. 5A); phyllosilicate-rich compaction bands result in stripes within the veins having larger crystals, whilst quartz-rich bands result in stripes with a higher quantity of smaller crystals. This microstructural variation inside veins has not been recognised in the Upper Ordovician-hosted V1 veins, probably due to the lack of phyllosilicate compaction bands in this succession. Furthermore, complex relationships between V1 veins and monomineralic quartz clasts from the Rabassa Conglomerate Fm. have been identified (Fig. 5G, H). Limits between both show a “net” surface in plane-polarised light (PPL) defined by Fe oxides (Fig. 5G). Otherwise, in cross-polarised light (XPL), the elongation of vein crystals shows different properties when the vein crosses the matrix components or the monomineralic quartz clasts. As the vein crosses a quartz clast, the crystals exhibit elongation parallel to the vein wall, becoming perpendicular to it at the end of the clast when the vein becomes matrix-shrouded again (Fig. 5H).

PHYLLOSILICATES CHEMISTRY AND CHLORITE GEOTHERMOMETRY

Phyllosilicates, white mica and chlorite, from host rocks and veins (Fig. 6) have been chemically characterised by electron microprobe (see Appendix, Tables II, III for compositions and calculated structural formulae of the 14O basis, with the total Fe expressed as FeO). White micas (Fig. 6A, B) are present in host rocks, with no textural differences among Cambrian–Ordovician and Upper Ordovician successions. They occur as tabular or flaky-shaped crystals <20μm in size and are aligned parallel to S2 planes, or more often as white mica-chlorite stacks (intergrowth packets) (1–8μm) (Fig. 6B). Nevertheless, Cambrian–Ordovician white micas (Equation 1) show significantly higher amounts of K, Fe2+, Mg a.p.f.u. and lower Al[VII] a.p.f.u. than the Upper Ordovician succession (Equation 2).

\[ K^+_{0,79±0,04} Al^{III}_{1,70±0,09} Fe^{II}_{2,23±0,08} Mg^{II}_{0,16±0,05} [Al^{IV}_{0,88±0,07} Si^{IV}_{3,16±0,07} O_{10}[OH]_2 \]

\[ K^+_{0,72±0,04} Al^{III}_{1,89±0,04} Fe^{II}_{0,14±0,05} Mg^{II}_{0,05±0,00} [Al^{IV}_{0,84±0,01} Si^{IV}_{3,16±0,01} O_{10}[OH]_2 \]

Chlorites are present in host rocks (Fig. 6A, B, C) in the walls of V1 veins (Fig. 6D, E) and in the centre and walls of V2 veins (Fig. 6F, G, H). All chlorites are classified as rigidopilites according to Hey (1954) chamosites according to the Association Internationale pour l’Étude des Argiles (AIPEA) nomenclature (Fig. 7A). The chlorites that are hosted either in pre- or post-Sardic rocks occur as euhedral to subhedral greenish-brownish crystals, 50–150μm in size and eventually replaced along cleavage planes by iron-oxides (Fig. 6A, B). In some cases, flaky-shaped chlorites occur associated with stylolites in monomineralic polycrystalline quartz clasts of the Rabassa conglomerates (Fig. 6C). Pre-Sardic-hosted chlorites have higher Mg a.p.f.u. and lower Fe2+ a.p.f.u. (Equation 3, n=29) compared with those hosted in post-Sardic rocks (Equation 4, n=5). Altogether they show a
FIGURE 6. Plane-polarised light microphotographs (A, C, E, G) and back-scattered electron images (B, D, F, H) of the analysed phyllosilicates: A) chlorite (Chl) growing coevally with S2 cleavage; Cava Formation; B) chlorite and white mica (Wmca) interstratification; Serdinya Formation; C) chlorite-bearing stylolite in a monomineralic quartz (Qtz) clast; Rabassa Conglomerate Formation; D) chlorite in a Upper Ordovician-hosted V2 vein margin; E) chlorite in a Upper Ordovician-hosted V1 vein margin; F) chlorite in a Cambrian–Ordovician-hosted V2 vein margin; G) and H) chlorite in a Upper Ordovician-hosted V2 vein centre.
positive correlation in an FeT/Mg vs. FeT diagram (Fig. 7B), and a negative correlation in an Al(VI) vs. FeT diagram (Fig. 7C).

\[ (3) \quad (\text{Mg}^{2+}_{1.30 \pm 0.06 \text{ Fe}^{2+}_{3.99 \pm 0.11} \text{ Al}^{3+}_{1.53 \pm 0.05} \text{ Si}^{4+}_{2.88 \pm 0.03} \text{ O}_{10}) (\text{OH})_8 \]

\[ (4) \quad (\text{Mg}^{2+}_{1.22 \pm 0.04 \text{ Fe}^{2+}_{3.17 \pm 0.03} \text{ Al}^{3+}_{1.51 \pm 0.03} \text{ Si}^{4+}_{2.60 \pm 0.02} \text{ O}_{10}) (\text{OH})_8 \]

Chlorites located in V1 and V2 veins walls (Fig. 6D, E, F) occur as isolated euhedral crystals (100–200μm) or more often as aggregates (0.1–0.4mm) of vermicular or chrysanthemum-shaped crystals (20–60μm) (Fig. 6D, E, F). Otherwise, chlorite in V2 veins centre (Fig. 6G, H) only occur as aggregates (0.2–2mm) of crystals (40–150μm). Chlorite in V1 walls (Equation 5, n=7) have the highest amounts of Si and Mg a.p.f.u. and the lowest amount of FeT a.p.f.u. Chlorites in V2 walls (Equation 6, n=6) are compositionally between the chlorites in the V1 wall and in the V2 centre (Equation 7, n=43), the latter having the highest Fe a.p.f.u. and the lowest Si and Mg.

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**FIGURE 7.** A) Si vs. FeT/FeT+Mg (after Hey, 1954), B) FeT/Mg vs. FeT, and C) Al(VI) vs. FeT diagrams of analysed chlorites. Note the two sub-parallel trends for vein- and rock-hosted chlorites in (B) and (C). D) Formation temperatures obtained from the three applied geothermometers for the V2 veins (wall and centre) and host rocks; for each dataset, coloured boxes are the standard deviations (first and third quartiles), while horizontal lines are the median, black points are the mean value and whiskers are the maximum and minimum values (95% interval). E, F) T variations depending on the assumed Fe3+/Fe2+ content for the Lanari et al. (2014) (Chl1) and Inoue et al. (2009) geothermometers, respectively; shaded areas indicate the confidence interval between the V2 wall and V2 centre formation temperatures considering the typical errors (± 30°C) of the methods.
A p.f.u. Altogether, vein-hosted chlorites display a positive correlation in FeT/Mg vs. FeT diagrams (Fig. 7B) and a negative correlation in AlIV vs. FeT diagrams (Fig. 7C). Correlation lines have a similar slope for the vein-hosted and host-rock chlorites, although lines do not overlap due to the aforementioned compositional differences (Fig. 7B, C). Furthermore, if the chlorite location (V2 wall vs. V2 centre) and vein-generation (V1 wall vs. V2 wall) are considered, three compositional groups in FeT, Mg and AlIV a.p.f.u. diagrams are deciphered.

$$\begin{align*}
(5) & \quad (Mg^{2+}_{2.12\pm0.05} \text{ Fe}^{2+}_{2.78\pm0.04} \text{ Al}^{3+}_{1.73\pm0.04} \quad 0.29\pm0.02) \quad [(\text{Si}^{4+}_{2.74\pm0.02} \text{ Al}^{3+}_{1.26\pm0.02})_1 \text{ O}_{10}]_{} \text{(OH)}_6^{} \\
(6) & \quad (Mg^{2+}_{2.07\pm0.02} \text{ Fe}^{2+}_{3.05\pm0.06} \text{ Al}^{3+}_{1.65\pm0.04} \quad 0.22\pm0.04) \quad [(\text{Si}^{4+}_{2.66\pm0.03} \text{ Al}^{3+}_{1.34\pm0.03})_1 \text{ O}_{10}]_{} \text{(OH)}_6^{} \\
(7) & \quad (Mg^{2+}_{1.90\pm0.05} \text{ Fe}^{2+}_{3.32\pm0.08} \text{ Al}^{3+}_{1.56\pm0.01} \quad 0.11\pm0.02) \quad [(\text{Si}^{4+}_{2.61\pm0.02} \text{ Al}^{3+}_{1.39\pm0.02})_1 \text{ O}_{10}]_{} \text{(OH)}_6^{}
\end{align*}$$

Semi-empirical geothermometers (Bourdelle et al., 2013; Inoue et al., 2018; Lanari et al., 2014) were applied to rock- and vein-hosted chlorites. In the analyses, Fe total is expressed as FeO, and Fe₂O₃ content is unknown. For the application of these geothermometers, the lack of XFe³⁺ should be <3, vacancies (Al (VI)-Al (IV)-Na-K/2) >0.05 a.p.f.u. (Lanari et al. 2014 (Chl2)) geothermometer, the Si a.p.f.u. to rock- and vein-hosted chlorites. In the analyses, Fe total is expressed as FeO, and Fe₂O₃ content is unknown. For the application of these geothermometers, the lack of XFe³⁺ should be <3, vacancies (Al (VI)-Al (IV)-Na-K/2) >0.05 a.p.f.u. and an estimated pressure value (0.5 kbar for V1 and 2 kbar for V2 and host rock chlorites) is necessary; for the Inoue et al. (2018) geothermometer, vacancies (6-(Fe²⁺+Mg+X³⁺)) should be <1 a.p.f.u. and NaO+K₂O+CaO<0.5 a.p.f.u.).

All chlorites used here as geothermometers are in agreement with the aforementioned premises. From the analyses plotted in Figure 7A, B, C, only those with the sum of octahedral sites below 0.95 a.p.f.u. were used for the temperature estimations, so the analyses with low amounts (<0.05) of octahedral vacancies have been discarded. Rock and V2 centre hosted chlorites show the maximum temperatures, being slightly higher those obtained from Cava Fm.-hosted ones (Fig. 7D; Table 1). Significantly different formation temperatures from vein-hosted chlorites were obtained for the three geothermometers, depending on the location and vein-generation (Fig. 7D; Table 1). According to all geothermometers applied, temperature increasing towards the vein centre is perceived from the V2 centre and V2 wall comparison, whilst significantly lower temperatures were obtained for the V1 wall (Fig. 7D; Table 1). As only wall-hosted chlorites have been identified in the V1 veins, it cannot be determined whether or not this difference in chlorite formation temperature dependent on vein location occurs for both vein types. Here, only the temperatures obtained from the V2 centre and rock hosted chlorites have been considered representative of the formation conditions during V2 fluid circulation. Temperatures obtained from the V1 and V2 margins and their validity will be discussed below.

**FLUID INCLUSION MICRO-ThERMOMETRY**

Quartz from both vein generations shows numerous micron-sized fluid inclusions. Only a few bigger (3–8μm), liquid rich two-phase inclusions were measured (n=184). Most inclusions are rounded to sub-rounded in shape and aligned obliquely to the main direction of the veins.

Fluid inclusions to the from V1 veins show homogenisation temperatures (Th) between 165 and 204°C (n=50) with a mean value of 176±8°C. Given the paucity of data, the standard deviation is large and no distribution patterns are perceived (Fig. 8A); this is probably due to non-isochoric behaviour. No salinity data were obtained due small inclusion size.

Fluid inclusions from V2 veins show a Th between 164 and 211°C (n=154), with most values ranging between 176 and 191°C. Altogether define a right-skewed normal distribution with a mean value of 184±7°C (Fig. 8A). Measured eutectic temperature (Te) for the two biggest inclusions (~12μm) with a Th of 179 and 186°C indicates that the system corresponds to NaCl-H₂O. The last phase inclusions are rounded to sub-rounded in shape and aligned obliquely to the main direction of the veins.

Measured eutectic temperature (Te) for the two biggest inclusions (~12μm) with a Th of 179 and 186°C indicates that the system corresponds to NaCl-H₂O. The last phase inclusions are rounded to sub-rounded in shape and aligned obliquely to the main direction of the veins. Formation temperature from chlorites hosted in Cambrian–Ordovician and Upper Ordovician rocks (n=20) and in V2 vein centres (n=43) were used together to obtain the pressure conditions through their correlation with the isochore (Appendix, Table III; Fig. 8B). Temperatures of 338±27°C, 369±23°C and 318±12°C obtained from Bourdelle et al. (2013), Lanari et al. (2014) (Chl2) and Inoue et al. (2018) geothermometers correspond to pressure values of 2.78±0.5 kbar, 3.34±0.4 kbar.
and 2.42±0.2kbar, respectively (Fig. 8B). The utility of chlorite formation temperatures obtained from V1 and V2 vein walls (Fig. 7D) will be discussed below.

**DISCUSSION**

**Thermal balance between fluids and host rock**

The obtained chlorite formation temperature for the centre of V2 veins and for the host rock, both for the Serdinya and the Cava fms., is ca. 318±12°C according to the Inoue et al. (2018) geothermometer (Figs. 7D; 8B; Table 1). Bourdelle et al. (2013) and Lanari et al. (2014) (Chl2) geothermometers gave similar mean values but with higher standard deviations (Figs. 7D; 8B; Table 1). This result is in accordance with veins formed under low fluid/rock ratios and therefore, with expected thermal equilibrium between circulating fluids and rocks (Sharp et al., 2005 and references therein). However, these three geothermometers point to different and clearly lower temperature for chlorites in V1 veins, 210±7°C according to the Inoue et al. (2018) geothermometer.

| Chlorite location In-vein location (n) Geothermometer Mean value (°C) Minimum (°C) (95% interval) Maximum (°C) (95% interval) |
|---|---|---|---|---|
| Serdinya Fm. (Cambrian-Ordovician) - (n=17) | Bourdelle et al. (2013) | 349±34 | 299 | 408 |
| | Lanari et al. (2014) | 380±32 | 319 | 431 |
| | Inoue et al. (2018) | 320±13 | 297 | 339 |
| Cava Fm. (Upper Ordovician) - (n=3) | Bourdelle et al. (2013) | 372±24 | 345 | 389 |
| | Lanari et al. (2014) | 407±17 | 396 | 426 |
| | Inoue et al. (2018) | 327±9 | 316 | 333 |
| V1 Wall (n=7) | Bourdelle et al. (2013) | 193±6 | 182 | 200 |
| | Lanari et al. (2014) | 214±13 | 195 | 231 |
| | Inoue et al. (2018) | 210±7 | 197 | 218 |
| V2 Wall (n=6) | Bourdelle et al. (2013) | 250±32 | 232 | 297 |
| | Lanari et al. (2014) | 273±11 | 269 | 279 |
| | Inoue et al. (2018) | 257±22 | 251 | 274 |
| Centre (n=43) | Bourdelle et al. (2013) | 331±21 | 303 | 361 |
| | Lanari et al. (2014) | 362±14 | 336 | 387 |
| | Inoue et al. (2018) | 317±12 | 300 | 335 |

**FIGURE 8.** A) Histogram of the homogenization temperatures (Th) obtained from V1 and V2 fluid inclusions. B) P-T formation conditions of V2 veins obtained from the correlation between the isochore and the V2 centre and host rock formation temperatures.
Thus, specific Fe$^{3+}$ content of the chlorites of this study (2019), they are based on a restricted number of analyses. Verdeccia (2014) (Chl2) and Inoue estimate the Fe$^{3+}$/Fe$^{2+}$ via thermodynamic modelling, according to their balance between the hosting rocks and the circulating fluids, show evidence of low fluid/rock ratios and hence, thermal the giant quartz veins formed at up to 400°C in the Alps fluid inclusions of the V2 wall and centre (Fig. 8A). Even the giant quartz veins formed at up to 400°C in the Alps show evidence of low fluid/rock ratios and hence, thermal balance between the hosting rocks and the circulating fluids, according to their δ$^{18}$O (Sharp et al., 2005 and references therein).

To invoke a high fluid/rock ratio seems unlikely for this context since: i) similar chlorite formation temperatures were found in the host rock and the V2 centre (Fig. 7D; Table 1) and ii) no Th differences were found between fluid inclusions of the V2 wall and centre (Fig. 8A). Even the giant quartz veins formed at up to 400°C in the Alps the differences with the real content of Fe$^{3+}$ in chlorites implicitly assumed by the geothermometer has a significant effect on the temperature obtained, as it modifies the number of vacancies through the formula calculation; this number of vacancies is key to the temperature determination as it determines the di-trioctahedral substitution.

The difference in Fe$^{3+}$ quantity between the V2 wall-hosted chlorites and those in the host rocks and V2 centre could have resulted in apparent differences to their formation temperature. To check the possible effect of differences of Fe$^{3+}$/total Fe ratios, we applied the geothermometers that allow consideration of this ratio, Lanari et al. (2014) (Chl1) and Inoue et al. (2009), for a suitable range of values (Vidal et al., 2016). Figures 7E and F, which display the effect of the Fe$^{3+}$/total Fe ratio on the calculated temperatures, show, for both geothermometers, the same temperature among the V2 wall-hosted chlorites and those in the host-rocks and V2 centre when different values for the Fe$^{3+}$/total Fe ratio are considered. The real value of this parameter is unknown, the temperature of the chlorites may be the same, being the different results a consequence of the Fe$^{3+}$ value assumption, similar to that of the population of samples used for the calibration of each semi-empirical geothermometer. The coinciding field is around 350°C for the Lanari et al. (2014) (Chl1) geothermometer (Fig. 7E) and 300°C for the Inoue et al. (2009) geothermometer (Fig. 7F). This match interval is not far from the values for the Chl2 and Cathalineau, 2015). The Lanari et al. (2014) (Chl2) and Inoue et al. (2018) geothermometers estimate the Fe$^{3+}$/Fe$^{2+}$ via thermodynamic modelling (Verdeccia et al., 2019), but according to Mascii et al. (2019), they are based on a restricted number of analyses. Thus, specific Fe$^{3+}$ content of the chlorites of this study could be more or less out, or in the boundaries, of the application limits of the above mentioned semi-empirical thermometers, which would depend on the collection of the analyses used for their original calibration.

There are chlorite substitutions that involve the incorporation of Fe$^{3+}$ in both tetrahedral (Munoz et al., 2013) and/or octahedral (Trincal and Lanari, 2016; Vidal et al., 2006) positions. According to Masci et al. (2019), the assumed Fe$^{3+}$ increase goes together with an increment in octahedral vacancies. This is a mathematical effect of the normalisation criterion for the calculation of the chlorite formula, which is based on the number of oxygens, or equally the balance of charge. The more Fe$^{3+}$ that is assumed, the lower is the necessary total number of cations needed to balance the 28 negative charges of the chlorite formula. A coupled substitution of three divalent cations by two Fe$^{3+}$-cations, which is a kind of di-trioctahedral substitution ($\delta^{14}$O = 3(Mg, Fe$^{3+}$)) has been proposed (Masci et al., 2019; Trincal and Lanari, 2016). Nevertheless, in the absence of external data on the real Fe$^{3+}$ content, the extent of this substitution unfortunately remains masked by the mathematical relationship mentioned above. To conclude, the differences with the real content of Fe$^{3+}$ in chlorites implicitly assumed by the geothermometer has a significant effect on the temperature obtained, as it modifies the number of vacancies through the formula calculation; this number of vacancies is key to the temperature determination as it determines the di-trioctahedral substitution.
formation in this work is the one obtained from the vein centre, which matches the temperature of host rock chlorite (Fig. 8B; Table 1), pointing to low fluid/rock ratios.

Fluid circulation under low fluid/rock ratios implies static regimes with locally derived fluids (Yardley, 1975), fluid/rock interactions constrained by host rock properties (among them mineralogy, grain size or banding) and their deformational histories (e.g. Sharp et al., 2005; Van Noten and Sintubin, 2010). Quartz dissolution is favoured by pressure variations (e.g. Sharp et al., 2005), grain-grain contacts, high dislocation densities and small grain size (Yardley, 1975). Specifically, pressure solution in quartz-quartz interfaces produces less dissolution than in quartz-mica ones (Renard et al., 1997; Wangen and Munoz, 2004). Considering that the boundaries of the pre-Sardic phyllosilicic compaction banding (LVR) have many quartz-mica interfaces, they might have acted as the main local source of silica (Fig. 5A, B). Upper Ordovician rocks do not show LVR, although some (~5%) mica-quartz interfaces are present in the matrix (Fig. 5D, E).

According to Nakamura and Watson (2001), dissolved silica can diffuse into fractures over meters at a rate as high as 0.1–1 m/year. In the pre-Sardic-hosted V1 veins, diffusion heterogeneities are gathered by matching in-vein stripes with the phyllosilicate compaction bands in the adjacent host rock (Fig. 5A, B). The size and number of quartz crystals within the stripes correlate with the bands in the host rock (Fig. 5A, B). As quartz-mica boundaries support a thicker layer of water than the quartz-quartz ones (Niemeijer and Spires, 2002; Rendard et al., 1997), the diffusion pathways are enhanced by the numerous compaction band boundaries (Fig. 5B). Conversely, inner zones of the phyllosilicate compaction bands probably acted as transmissivity barriers due to the impermeability gain corresponding to increasing phyllosilicate content (Parry et al., 2004). These low-permeability zones prevented silica diffusion into the veins, resulting in inner-vein stripes with minimum nucleation and therefore larger crystals (Fig. 5A, B). In contrast, no evidence of these features was found in veins hosted in the Upper Ordovician rocks.

Quartz vein emplacement and the structure of the pre-Variscan rocks

We differentiated two quartz vein generations (V1 and V2) based on differences in their orientation (Figs. 3A, 4), distribution (Fig. 4), and relationship with the deformational structures (Figs. 4, 5A, B, E, F). Variations in chlorite chemistry (Fig. 7A, B, C) and their corresponding calculated temperatures (Fig. 7D; Table 1) also support this differentiation.

Concerning their age, V1 veins are affected by centimetric scale D2 folds and crosscut by the S2 cleavage, so pre-D2 emplacement may have occurred. Moreover, their occurrence around the Upper Ordovician Unconformity and the Upper Ordovician synsedimentary extensional faults suggest an emplacement that was linked to the sedimentation of the lowermost part of Upper Ordovician succession and to the Late Ordovician faulting episode (Fig. 4). Thus, we can interpret a relationship between the formation of V1 veins and the Sardic events, supporting the interpretations from Casas et al. (2019) and Puddu et al. (2019).

Besides the V1 veins, other deformational structures, previous to D2 and only affecting the Cambrian–Ordovician succession, have been identified in the study area: S1 rough slaty cleavage (Fig. 5C) and pre-D2 folds (Fig. 2). Hartevelt (1970), Bons (1988) and Poblet (1991) also recognised a fabric prior to the development of the main phase cleavage in Central Pyrenees and in the Orri dome, but they concluded that this parallel bedding fabric is the result of sedimentation and compaction processes. Clariana and Garcia-Sansegundo (2009) and Garcia-Sansegundo et al. (2011) also described a S1 cleavage only recognisable in the Cambrian–Ordovician succession and not related to fold development in the Central Pyrenees (Garona and Pallaresa domes). These authors suggest that S1 could be related to a pre-Late Ordovician deformation event. In La Molina area, S1 cleavage has been only identified at a microscopic scale and no relationship with folding structure was observed. Thus, S1 development cannot be unequivocally related to a Middle Ordovician (?) pre-D2 fold system. Alternatively, it could represent a Variscan poorly-developed cleavage near its upper front at shallow metamorphic levels, whereas it is well developed at deeper structural levels where it constitutes the main Variscan deformational mesostructure (Ayora and Casas, 1986; Carreras and Capellà, 1994; Santanach, 1972b). In the La Cerdanya area Puddu et al. (2019) described NE–SW oriented decametric to hectometric folds that were not related to cleavage formation or metamorphism, only affecting the pre-Sardic sequence. The similarities with the pre-D2 folds described in the La Molina area suggest that both fold systems may share a common origin. Finally, the distribution of V1 veins and their relationship with D2 mesostructures point to a pre-Variscan (Sardic-linked) age for this vein type (Fig. 4A).

Veins of V2 are parallel to the S2 cleavage, either where S0 and S1 are perpendicular or oblique, near or far from the D2 fold hinge, respectively (Fig. 4). This points to a post-D2 emplacement for V2 veins. Therefore, V2 veins could be Variscan (after D2 deformation) or Alpine in age.

Classically, a Variscan age has been attributed to the deformation responsible for the main cleavage in the pre-Alpine basement rocks of the Pyrenees (see a review in
Carreras and Capellà, 1994). In the equivalent rocks of the Serdinyà Fm. of the Orri dome, Bons (1998) obtained palaeotemperatures between 250°C and 350°C on the basis of illite crystallinity data, which, for a geothermal gradient of 30°C/km-1 would imply maximum pressures on the order of 2–3kbar. In the same area, Cochelin et al. (2018) obtained similar temperatures, ca. 350°C by using Raman spectrometry analysis of carbonaceous material on muscovite-chlorite bearing metasediments. Cochelin et al. (2018) related these temperatures to Variscan metamorphism developed subsequent to the initiation of regional-scale folding and drawing flat isotherms with an estimated palaeothermal gradient of 45°C/km-1. According to this gradient, a depth of about 7.8km for the cleavage development during Variscan times in the Orri dome can be estimated. Temperatures from Bons (1998) and Cochelin et al. (2018) are similar to those obtained in the study area for V2 veins and host rocks (Fig. 7D; Table 1). However, in the La Molina area this estimated depth is unrealistic unless several repetitions of the overlying Upper Ordovician, Silurian, Devonian and pre-Variscan Carboniferous (ca. 1.000m in thickness, Domingo et al., 1988; Martín-Closas et al., 2018) together with syn-orogenic Carboniferous successions (up to 1.000m in thickness, Sánz-López, 2019) occur. In addition, preserved Variscan structure of the Tossa d’Alp massif, close to la Molina, indicates that the thrust system affecting the post-Silurian rocks only produces a structural relief of ca. 2.000m (Domingo et al., 1988).

Alternatively, an Alpine age can be considered for the V2 veins. On the northern slope of the Canigó massif (Conflent area), Kister et al. (2003) obtained formation conditions of 309–405°C and 2.5–3.5kbar from a set of centimetric-width quartz veins, applying purely empirical chlorite geothermometry and fluid inclusion microthermometry. According to them, these veins are parallel-to or related with fractures, fault sets, or shear zones and are aged as late-Variscan or Alpine. Applying the semi-empirical geothermometers of Bourdelle et al. (2013), Lanari et al. (2014) and Inoue et al. (2018) to their analyses, we have obtained temperature values of 308±54°C, 343±51°C and 308±25°C, respectively, very similar to those from the La Molina V2 veins. In the Gavarnie thrust area, Henderson and McCaig (1996) studied Alpine quartz veins by estimating P-T conditions of 5kbar and 330°C for the Pic Long and La Glère shear zones, and also applying empirical chlorite thermometry and fluid inclusion microthermometry. Semi-empirical thermometry could not be applied to their chlorite analyses since the sum of octahedral sites is >5.95a.p.f.u. Nevertheless, the empirical formation temperatures of these Alpine veins are also similar to those obtained for the La Molina V2 ones with modern geothermometry.

In the Central Pyrenees, Lacroix et al. (2011, 2012) obtained palaeotemperatures of 208 and 240°C and pressures of 570 and 650bars, during the emplacement and fault reactivation of the Monte Perdido thrust sheet in the late Eocene-early Oligocene, respectively. These authors used fluid inclusions, oxygen isotopic fractionation, and chlorite thermometry data. Izquierdo-Lavall et al. (2013) obtained palaeotemperatures up to ca. 215°C based on vitrinite reflectance for the lowermost part of the Palaeogene succession in the Jaca basin. Combining this data with fluid inclusions they obtained a pressure of 800–1,200bars, estimating a burial depth of ca. 6km. Lacroix et al. (2011, 2012) and Izquierdo-Lavall et al. (2013) get the same geothermal gradient of 34°C/km-1 but differently to what is proposed in this work, they assumed hydrostatic pressures. In the La Molina area, higher chlorite formation temperatures give higher pressures, and assuming a lithostatic pressure this gave a calculated burial depth of ca. 9km and a geothermal gradient of 34°C/km-1. From regional stratigraphic data, Carrillo et al. (2014) estimated a thickness of ca. 5.6km for the Eocene sequence in the south eastern Pyrenees. In La Molina area, thicknesses of ca. 500m for the Late Cretaceous-Palaeogene succession and ca. 2,000m for the post-Upper Ordoviciansuccessions should be added. As a result, a burial depth of ca. 8.1km is achieved for Cambrian–Ordovician rocks in Eocene times based on stratigraphic criteria. This depth is comparable to that proposed in the Orri dome, but fitted in Variscan time by Cochelin et al. (2018) and close to that estimated for the La Molina area considering the Inoue et al. (2018) geothermometer.

CONCLUSIONS AND FINAL REMARKS

On the southern slope of the Canigó massif (La Molina area), we have differentiated two sets of decimetric–metric quartz veins (V1 and V2) based on differences in orientation, distribution and relationship with deformational structures. We posit that the generation of V1 veins is related to a Late Ordovician fracture episode, linked to the Middle–Late Ordovician Sardinic events. We deduce that V2 veins were formed in a low fluid/rock ratio regime because analysis of in-vein and host rock chloritites yield the same formation temperatures. For the V2 veins, the combination of chlorite chemistry and fluid inclusion data provides a temperature of ca. 318±12°C and a pressure of 2.4±0.2kbar, with an estimated geothermal gradient of 34°C/km-1, which indicate a burial depth of ca. 9km. After a comparison of these conditions with the ones in other areas of the Central and Eastern Pyrenees and based on stratigraphical criteria, we propose an Alpine age for the V2 veins.

Several questions are raised from these results. For instance, how representative are these data in the broader context of the Central and Eastern Pyrenees, and/or, what is the relationship between these metric veins and the
larger ones spread throughout the pre-Alpine basement of the Eastern Pyrenees (A yora and Casas, 1983; A yora et al., 1984)? Giant veins are classically considered to be the expression of large quantities of circulating fluids that precipitate in regional-scaled brittle-ductile structures, under 200–300°C and 2–3kbar (Bons, 2001; Lemarchand et al., 2012). However, could these large quartz veins have formed at low fluid/rock ratios as has been suggested in the Alps (Sharp et al., 2005)? In the Eastern Pyrenees, although giant veins are mostly hosted by Variscan and pre-Variscan rocks, large fault-related quartz bodies also crosscut Mesozoic sedimentary rocks in some places (Fonseca et al., 2015; L isa, 1988), being therefore Alpine in age.

Veins formed under low fluid/rock ratios are a palaeorecord of the P-T conditions within the enclosing rocks. Fluid inclusions, as a geobarometer through an independent geothermometer, as applied in this work, constitute an effective tool to establish the fluid/rock ratio; however, chlorite geothermometry requires caution. The formation conditions together with a well-known structural and thermal framework can help to establish the age of these large structures, whilst an accurate petrographic and geochemical characterisation can provide information on their formation constraints and mechanisms.

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### APPENDIX I

#### TABLE I. Spatial distribution throughout the study area of V1 and V2 (>0.5cm thick) quartz veins outcropping per m²

| POINT ID | X (UTM) | Y (UTM) | Z (masl) | N_{V1} / 1000 m² | N_{V2} / 1000 m² | N_{V1} + N_{V2} |
|----------|---------|---------|----------|------------------|------------------|-----------------|
| 1        | 414237.86 | 4688362.41 | 1452.2 | 2 | 9 | 11 |
| 2        | 414193.36 | 4688374.91 | 1434.5 | 3 | 8 | 11 |
| 3        | 414222.73 | 4688376.47 | 1445.3 | 2 | 6 | 8 |
| 4        | 414211.05 | 4688354.60 | 1433.5 | 1 | 7 | 8 |
| 5        | 414244.11 | 4688347.06 | 1455.3 | 4 | 6 | 10 |
| 6        | 414265.45 | 4688404.54 | 1479.9 | 4 | 6 | 10 |
| 7        | 414288.10 | 4688402.76 | 1466.1 | 3 | 5 | 8 |
| 8        | 414283.15 | 4688380.37 | 1465.9 | 3 | 6 | 9 |
| 9        | 414311.53 | 4688399.11 | 1475.1 | 3 | 4 | 7 |
| 10       | 414321.94 | 4688418.90 | 1474.9 | 1 | 7 | 8 |
| 11       | 414307.62 | 4688440.50 | 1467.2 | 3 | 3 | 6 |
| 12       | 414082.73 | 4688321.03 | 1432.1 | 0 | 9 | 9 |
| 13       | 414082.99 | 4688304.89 | 1432.0 | 0 | 5 | 10 |
| 14       | 414070.24 | 4688354.60 | 1441.7 | 3 | 3 | 6 |
| 15       | 414242.32 | 4688363.35 | 1453.8 | 4 | 5 | 9 |
| 16       | 414280.22 | 4688424.75 | 1495.7 | 2 | 8 | 10 |
| 17       | 414283.26 | 4688428.28 | 1495.9 | 1 | 5 | 6 |
| 18       | 414431.94 | 4688525.39 | 1454.9 | 1 | 4 | 5 |
| 19       | 414427.92 | 4688442.48 | 1489.6 | 2 | 5 | 7 |
| 20       | 414426.11 | 4688435.83 | 1491.4 | 2 | 3 | 5 |
| 21       | 414431.47 | 4688436.85 | 1491.8 | 1 | 2 | 3 |
| 22       | 414433.17 | 4688440.55 | 1490.4 | 5 | 4 | 9 |
| 23       | 414448.83 | 4688444.90 | 1492.2 | 5 | 5 | 10 |
| 24       | 414449.65 | 4688444.11 | 1492.6 | 5 | 3 | 8 |
| 25       | 414442.99 | 4688437.07 | 1492.8 | 4 | 5 | 9 |
| 26       | 414447.28 | 4688450.62 | 1488.4 | 6 | 6 | 12 |
| 27       | 414459.33 | 4688454.74 | 1488.7 | 2 | 4 | 6 |
| 28       | 414751.46 | 4688347.51 | 1459.5 | 1 | 7 | 8 |
| 29       | 417600.09 | 4688340.46 | 1458.1 | 5 | 5 | 10 |
| 30       | 41761.52 | 4688335.51 | 1453.9 | 0 | 3 | 3 |
| 31       | 41765.55 | 4688329.07 | 1458.9 | 6 | 6 | 12 |
| 32       | 41785.32 | 4688343.54 | 1470.0 | 0 | 5 | 5 |
| 33       | 41790.06 | 4688310.12 | 1460.9 | 1 | 3 | 4 |
| 34       | 41802.25 | 4688312.67 | 1461.5 | 0 | 6 | 6 |
| 35       | 41784.60 | 4688339.67 | 1458.0 | 1 | 7 | 8 |
| 36       | 41669.25 | 4688389.88 | 1498.9 | 1 | 7 | 8 |
| 37       | 41644.14 | 4688390.60 | 1499.3 | 3 | 5 | 8 |
| 38       | 41604.31 | 4688409.79 | 1465.0 | 4 | 4 | 8 |
| 39       | 41608.74 | 4688409.86 | 1464.5 | 1 | 6 | 7 |
| 40       | 41592.84 | 4688428.07 | 1468.9 | 0 | 4 | 4 |
| 41       | 41591.18 | 4688442.41 | 1467.1 | 1 | 4 | 5 |
| 42       | 41595.66 | 4688486.97 | 1471.0 | 0 | 6 | 6 |
| 43       | 41564.19 | 4688472.83 | 1417.1 | 1 | 5 | 6 |
| 44       | 41534.20 | 4688480.89 | 1478.5 | 2 | 4 | 6 |
| 45       | 41449.65 | 4688502.73 | 1467.2 | 2 | 5 | 7 |
| 46       | 41448.88 | 4688499.69 | 1468.9 | 2 | 1 | 3 |
| 47       | 41473.52 | 4688367.51 | 1440.0 | 2 | 1 | 3 |
| 48       | 41452.50 | 4688319.91 | 1430.0 | 7 | 3 | 10 |
| POINT ID | X (UTM) | Y (UTM) | Z (masl) | NV1 (>0.5cm) / m² | NV2 (>0.5cm) / m² | NV1 + NV2 |
|----------|---------|---------|----------|-------------------|-------------------|-----------|
| 99       | 414498,67 | 4688499,70 | 1422,3 | 4                  | 4                 | 8         |
| 100      | 414213,66 | 4688469,55 | 1430,4 | 3                  | 3                 | 6         |
| 101      | 414226,18 | 4688464,49 | 1435,2 | 1                  | 2                 | 3         |
| 102      | 414178,30 | 4688492,28 | 1420,5 | 4                  | 5                 | 9         |
| 103      | 414175,58 | 4688496,47 | 1420,0 | 3                  | 6                 | 9         |
| 104      | 414181,96 | 4688462,81 | 1422,0 | 5                  | 7                 | 12        |
| 105      | 414186,17 | 4688464,44 | 1430,0 | 4                  | 7                 | 11        |
| 106      | 414166,94 | 4688481,36 | 1420,0 | 2                  | 6                 | 8         |
| 107      | 414166,47 | 4688501,21 | 1420,9 | 0                  | 4                 | 4         |
| 108      | 414158,41 | 4688520,96 | 1420,2 | 1                  | 4                 | 5         |
| 109      | 414162,01 | 4688531,47 | 1421,0 | 2                  | 6                 | 8         |
| 110      | 414169,97 | 4688527,91 | 1422,0 | 1                  | 7                 | 8         |
| 111      | 414179,90 | 4688530,07 | 1422,9 | 3                  | 5                 | 8         |
| 112      | 414177,30 | 4688517,41 | 1420,0 | 4                  | 7                 | 11        |
| 113      | 414150,29 | 4688557,70 | 1420,0 | 1                  | 1                 | 2         |
| 114      | 414156,77 | 4688542,92 | 1420,0 | 1                  | 4                 | 5         |
| 115      | 414167,11 | 4688541,00 | 1422,0 | 5                  | 6                 | 11        |
| 116      | 414158,24 | 4688550,35 | 1420,0 | 1                  | 4                 | 5         |
| 117      | 414157,51 | 4688562,63 | 1420,0 | 2                  | 5                 | 7         |
| 118      | 414145,80 | 4688557,30 | 1420,0 | 1                  | 4                 | 5         |
| 119      | 414170,35 | 4688566,13 | 1424,5 | 1                  | 7                 | 8         |
| 120      | 414178,45 | 4688567,02 | 1426,6 | 0                  | 5                 | 5         |
| 121      | 414189,65 | 4688566,34 | 1429,0 | 1                  | 3                 | 4         |
| 122      | 414186,58 | 4688567,32 | 1428,0 | 4                  | 3                 | 7         |
| 123      | 414199,76 | 4688567,81 | 1431,0 | 1                  | 5                 | 6         |
| 124      | 414204,84 | 4688571,53 | 1431,5 | 4                  | 5                 | 9         |
| 125      | 414217,88 | 4688571,50 | 1430,0 | 1                  | 4                 | 5         |
| 126      | 414232,74 | 4688574,47 | 1430,4 | 0                  | 3                 | 3         |
| 127      | 414251,14 | 4688564,44 | 1430,0 | 1                  | 7                 | 8         |
| 128      | 414295,28 | 4688563,59 | 1432,0 | 1                  | 4                 | 5         |
| 129      | 414414,82 | 4688557,78 | 1440,2 | 2                  | 6                 | 8         |
| 130      | 414390,40 | 4688532,75 | 1440,0 | 0                  | 5                 | 5         |
| 131      | 414400,78 | 4688518,60 | 1455,6 | 1                  | 9                 | 10        |
| 132      | 414275,75 | 4688317,44 | 1460,6 | 6                  | 4                 | 10        |
| 133      | 414302,56 | 4688312,65 | 1463,7 | 4                  | 3                 | 7         |
| 134      | 414312,99 | 4688329,31 | 1470,4 | 8                  | 6                 | 14        |
| 135      | 414359,98 | 4688318,31 | 1473,7 | 7                  | 5                 | 12        |
| 136      | 414367,04 | 4688302,52 | 1477,0 | 8                  | 5                 | 13        |
| 137      | 414448,33 | 4688269,72 | 1506,7 | 8                  | 4                 | 12        |
| 138      | 414470,31 | 4688256,79 | 1510,8 | 7                  | 4                 | 11        |
| 139      | 414493,60 | 4688265,56 | 1509,3 | 5                  | 2                 | 7         |
| 140      | 414416,00 | 4688336,24 | 1492,6 | 3                  | 1                 | 4         |
| 141      | 414471,89 | 4688339,93 | 1506,0 | 2                  | 4                 | 6         |
| 142      | 414555,50 | 4688332,54 | 1529,3 | 1                  | 6                 | 7         |
| 143      | 414605,85 | 4688319,61 | 1530,1 | 1                  | 4                 | 5         |
| 144      | 414743,97 | 4688227,68 | 1477,7 | 4                  | 3                 | 7         |
| 145      | 414751,82 | 4688182,88 | 1488,6 | 1                  | 5                 | 6         |
| 146      | 414479,65 | 4688155,16 | 1500,3 | 2                  | 4                 | 6         |
| 147      | 414743,04 | 4688132,99 | 1512,4 | 5                  | 3                 | 8         |
| 148      | 414674,68 | 4688151,00 | 1522,7 | 7                  | 6                 | 13        |
TABLE I. Continued.

| POINT ID | X (UTM) | Y (UTM) | Z (m asl) | N_{V1-2cm}<0.5/m² | N_{V1-2cm}<0.5/m² | NV1 + NV2 |
|----------|---------|---------|-----------|-------------------|-------------------|----------|
| 199      | 414106.30 | 4688191.28 | 1435.0    | 8                 | 2                 | 10       |
| 200      | 414096.70 | 4688207.84 | 1435.0    | 8                 | 4                 | 12       |
| 201      | 414097.69 | 4688220.42 | 1434.2    | 8                 | 3                 | 11       |
| 202      | 414085.77 | 4688231.34 | 1434.9    | 3                 | 3                 | 6        |
| 203      | 414093.05 | 4688241.94 | 1434.0    | 6                 | 4                 | 10       |
| 204      | 414087.43 | 4688278.68 | 1434.3    | 7                 | 5                 | 12       |
| 205      | 414084.78 | 4688295.57 | 1434.2    | 2                 | 7                 | 9        |
| 206      | 414081.47 | 4688311.79 | 1432.5    | 2                 | 8                 | 10       |
| 207      | 414080.14 | 4688327.68 | 1433.0    | 7                 | 6                 | 13       |
| 208      | 414069.88 | 4688352.84 | 1441.2    | 2                 | 4                 | 6        |
| 209      | 414051.67 | 4688240.61 | 1446.4    | 3                 | 3                 | 6        |
| 210      | 414041.74 | 4688194.92 | 1454.8    | 4                 | 5                 | 9        |
| 211      | 413941.76 | 4688531.62 | 1480.7    | 0                 | 1                 | 1        |
| 212      | 413954.67 | 4688490.90 | 1474.8    | 1                 | 3                 | 4        |
| 213      | 413960.30 | 4688386.61 | 1495.6    | 1                 | 4                 | 5        |
| 214      | 414002.34 | 4688300.87 | 1488.3    | 3                 | 5                 | 8        |
| 215      | 413956.99 | 4688331.99 | 1494.1    | 1                 | 7                 | 8        |
| 216      | 413936.46 | 4688289.94 | 1470.6    | 3                 | 8                 | 11       |
| 217      | 413885.15 | 4688246.57 | 1493.9    | 0                 | 6                 | 6        |
| 218      | 414157.71 | 4687754.55 | 1490.8    | 1                 | 5                 | 6        |
| 219      | 414163.99 | 4687712.19 | 1509.5    | 1                 | 3                 | 4        |
| 220      | 414128.95 | 4687675.59 | 1515.0    | 1                 | 2                 | 3        |
| 221      | 414146.73 | 4687608.65 | 1534.5    | 0                 | 5                 | 5        |
| 222      | 414182.29 | 4687622.25 | 1534.0    | 1                 | 4                 | 5        |
| 223      | 414271.32 | 4687638.98 | 1564.4    | 2                 | 7                 | 9        |
| 224      | 414320.06 | 4687397.20 | 1479.4    | 3                 | 8                 | 11       |
| 225      | 414341.55 | 468440.28 | 1476.5    | 1                 | 4                 | 5        |
| 226      | 414502.07 | 468486.66 | 1459.4    | 3                 | 3                 | 6        |
| 227      | 414221.50 | 4685518.27 | 1425.0    | 3                 | 6                 | 9        |
| 228      | 414543.31 | 468498.99 | 1469.4    | 0                 | 8                 | 8        |
| 229      | 414672.83 | 468497.01 | 1452.1    | 0                 | 5                 | 5        |
| 230      | 415755.88 | 468507.14 | 1452.0    | 3                 | 4                 | 7        |
| 231      | 412842.52 | 468664.85 | 1437.9    | 2                 | 5                 | 7        |
| 232      | 412929.89 | 468338.34 | 1469.7    | 4                 | 5                 | 9        |
| 233      | 41240.28  | 468399.62 | 1450.5    | 6                 | 6                 | 12       |
| 234      | 412203.45 | 468425.33 | 1433.5    | 0                 | 7                 | 7        |
| 235      | 412609.94 | 468298.29 | 1452.8    | 7                 | 8                 | 15       |
| 236      | 41301.83  | 468286.42 | 1465.4    | 8                 | 5                 | 13       |
| 237      | 412571.41 | 468119.60 | 1485.7    | 0                 | 3                 | 3        |
| 238      | 412421.66 | 468203.08 | 1455.5    | 1                 | 6                 | 7        |
| 239      | 412535.39 | 468602.71 | 1511.7    | 2                 | 4                 | 6        |
| 240      | 41221.93  | 468731.19 | 1510.7    | 1                 | 3                 | 4        |
| 241      | 41107.22  | 468165.86 | 1436.0    | 6                 | 6                 | 12       |
| 242      | 414887.11 | 468208.44 | 1435.0    | 5                 | 5                 | 10       |
| 243      | 414070.01 | 468262.24 | 1438.8    | 6                 | 3                 | 9        |
| 244      | 414328.45 | 468446.46 | 1491.9    | 6                 | 5                 | 11       |
| 245      | 414021.20 | 468045.15 | 1456.6    | 1                 | 4                 | 5        |
| 246      | 413937.53 | 468717.87 | 1460.6    | 3                 | 3                 | 6        |
| 247      | 413989.82 | 468796.07 | 1448.9    | 5                 | 3                 | 8        |
| 248      | 413941.17 | 468784.67 | 1469.0    | 7                 | 4                 | 11       |
**TABLE II.** Chemical composition and structural formulae (11O basis) of white micas located at hostrocks. Total Fe as FeO.

| Hostrock          | Serdinya Fm. | Serdinya Fm. | Serdinya Fm. | Serdinya Fm. | Serdinya Fm. | Serdinya Fm. | Mean     | Standard deviation | Cava Fm. | Cava Fm. | Cava Fm. | Mean     | Standard deviation |
|-------------------|--------------|--------------|--------------|--------------|--------------|--------------|----------|-------------------|-----------|-----------|-----------|----------|-------------------|
| **Chemical composition (Wt%)** |              |              |              |              |              |              |          |                   |           |           |           |          |                   |
| SiO₂   | 46.62        | 45.03        | 45.04        | 44.87        | 44.34        | 41.61        | 44.92    | 1.72              | 46.75     | 44.72     | 44.65     | 45.37    | 1.19               |
| TiO₂     | 0.40         | 0.65         | 1.06         | 0.28         | 1.57         | 0.06         | 0.39     | 0.52              | 0.03      | 0.05      | 0.03      | 0.04     | 0.02               |
| Al₂O₃    | 30.06        | 30.54        | 31.01        | 33.13        | 29.30        | 34.46        | 31.40    | 1.80              | 34.48     | 32.40     | 32.46     | 33.11    | 1.18               |
| FeO      | 2.84         | 2.98         | 3.28         | 4.09         | 5.65         | 3.32         | 3.98     | 1.23              | 1.56      | 2.92      | 2.85      | 2.44     | 0.77               |
| MnO      | 0.01         | 0.00         | 0.02         | 0.01         | 0.05         | 0.01         | 0.02     | 0.02              | 0.01      | 0.00      | 0.01      | 0.01     | 0.01               |
| MgO      | 1.32         | 1.80         | 1.86         | 1.44         | 1.49         | 0.63         | 1.55     | 1.51              | 0.51      | 0.45      | 0.41      | 0.46     | 0.05               |
| CoO      | 0.03         | 0.03         | 0.02         | 0.03         | 0.04         | 0.06         | 0.03     | 0.01              | 0.02      | 0.04      | 0.08      | 0.05     | 0.03               |
| Na₂O     | 0.24         | 0.21         | 0.19         | 1.42         | 0.25         | 1.02         | 0.64     | 0.57              | 0.32      | 0.52      | 0.43      | 0.43     | 0.10               |
| K₂O      | 9.82         | 10.38        | 10.27        | 7.19         | 9.32         | 7.67         | 7.31     | 8.88              | 8.43      | 8.52      | 7.49      | 8.15     | 0.57               |
| **Total** | 91.83        | 91.63        | 92.76        | 92.46        | 92.27        | 94.03        | 88.68    | 91.95             | 92.12     | 89.63     | 88.41     | 90.08    | 1.89               |

| Structural formulae (11O basis) | T site (apfu) | O Site (apfu) |
|--------------------------------|---------------|---------------|
| Si                              | 2.32          | 2.31          |
| Al IV                          | 0.77          | 0.85          |
| Total T site                   | 4.00          | 4.00          |
| Al VI                          | 1.69          | 1.67          |
| Ti                             | 0.02          | 0.03          |
| Fe²⁺                           | 0.16          | 0.17          |
| Mn                             | 0.00          | 0.00          |
| Mg                             | 0.19          | 0.19          |
| Ca                             | 0.00          | 0.00          |
| Na                             | 0.30          | 0.30          |
| K                              | 0.87          | 0.93          |
| Total O site                   | 2.97          | 3.03          |
| Total Cations                  | 6.97          | 7.03          |
| OH⁻                            | 2.00          | 2.00          |
| Wt% H₂O calculated             | 4.32          | 4.28          |
| **Total Wt% (plus H₂O)**       | 96.16         | 95.91         | 97.09        | 96.83        | 96.53        | 98.51        | 92.82    | 96.26    | 95.54        | 93.88    | 92.64          | 94.35    | 1.99    |
**TABLE III.** Chemical composition (14O basis) and geothermometry from chlorites located in the center and walls of V2 veins, in the walls of V1 veins and in the hostrocks. Total Fe as FeO.

| Vein generation | Chlorite location | Chemical composition (Wt%) | Structural formulae (14O basis) | Geothermometry |
|-----------------|-------------------|---------------------------|-------------------------------|-----------------|
| V1              | V1                | V1                        | V1                            | V1              |
| V2              | V2                | V2                        | V2                            | V2              |
| Wall            | Wall              | Wall                      | Wall                          | Wall            |
| Wall            | Wall              | Wall                      | Wall                          | Wall            |
| Mean            | Mean              | Mean                      | Mean                          | Mean            |
| Standard deviation | Standard deviation | Standard deviation | Standard deviation | Standard deviation |

**Chemical composition (Wt%)**

| SiO$_2$ | 24.77 | 24.73 | 25.27 | 24.79 | 24.99 | 25.16 | 25.27 | 25.03 |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|
| TiO$_2$ | 0.05  | 0.02  | 0.01  | 0.03  | 0.00  | 0.05  | 0.01  | 0.02  |
| Al$_2$O$_3$ | 30.75 | 30.63 | 30.38 | 29.76 | 30.44 | 30.14 | 30.36 | 30.35 |
| FeO     | 0.12  | 0.16  | 0.14  | 0.13  | 0.14  | 0.18  | 0.14  | 0.14  |
| MnO     | 7.24  | 7.55  | 7.56  | 7.68  | 7.02  | 7.13  | 7.86  | 7.38  |
| MgO     | 0.07  | 0.06  | 0.05  | 0.12  | 0.08  | 0.06  | 0.05  | 0.07  |
| Na$_2$O | 0.13  | 0.02  | 0.18  | 0.06  | 0.28  | 0.06  | 0.22  | 0.14  |
| K$_2$O  | 0.22  | 0.26  | 0.12  | 0.15  | 0.21  | 0.22  | 0.21  | 0.22  |
| Total   | 86.23 | 85.80 | 87.56 | 85.04 | 86.94 | 86.47 | 87.85 | 86.56 |

**Applicable? (Inoue et al., 2018)**

| Y | Y | Y | Y | Y | Y | Y | Y |

**Applicable? (Lanari et al., 2014)**

| Y | Y | Y | Y | Y | Y | Y | Y |

**Applicable? (Bourdelle et al., 2012)**

| Y | Y | Y | Y | Y | Y | Y | Y |

**Approximated pressure**

| 0.50 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 | 0.90 |

**Total Fe as FeO.**

**SEMI-EMPIRICAL THERMOMETRY**

| Inoue et al. (2008, 2019) | 219 | 0.27 | 0.28 | 0.29 | 0.27 | 0.31 | 0.31 | 0.28 |
|---------------------------|-----|------|------|------|------|------|------|------|
| Lanari et al. (2014)     | 220 | 0.19 | 0.20 | 0.20 | 0.21 | 0.21 | 0.24 | 0.19 |
| Bourdelle et al. (2013)  | 201 | 0.22 | 0.23 | 0.24 | 0.22 | 0.25 | 0.26 | 0.22 |
### TABLE III.
Continued

| Vein generation | Chlорite location | V2 Centre | V2 Centre | V2 Centre | V2 Centre | V2 Centre | V2 Centre | V2 Centre | V2 Centre | V2 Centre | V2 Centre |
|-----------------|-------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Chemical composition (Wt%) |                  |           |           |           |           |           |           |           |           |           |           |
| SiO₂            | 23.41             | 22.68     | 23.10     | 22.53     | 22.84     | 23.17     | 23.19     | 23.29     | 23.20     | 23.29     | 23.01     | 23.72     | 22.58     | 22.17     |
| TiO₂            | 0.01              | 0.02      | 0.00      | 0.06      | 0.01      | 0.04      | 0.03      | 0.00      | 0.04      | 0.04      | 0.01      | 0.01      | 0.01      | 0.01      |
| Al₂O₃           | 22.43             | 22.91     | 23.18     | 23.28     | 22.29     | 21.88     | 21.92     | 21.25     | 21.29     | 21.99     | 21.74     | 21.77     | 21.39     | 21.19     |
| FeO             | 34.95             | 34.81     | 34.59     | 34.99     | 35.25     | 36.01     | 36.09     | 34.97     | 35.57     | 36.03     | 35.26     | 36.24     | 32.30     | 33.22     |
| MnO             | 0.06              | 0.02      | 0.06      | 0.11      | 0.14      | 0.05      | 0.06      | 0.07      | 0.07      | 0.06      | 0.07      | 0.07      | 0.07      | 0.06      |
| MgO             | 6.56              | 5.83      | 6.12      | 5.84      | 5.87      | 6.22      | 5.69      | 5.87      | 5.62      | 5.93      | 6.08      | 5.78      | 6.33      | 5.89      |
| CaO             | 0.09              | 0.03      | 0.08      | 0.02      | 0.03      | 0.03      | 0.03      | 0.05      | 0.05      | 0.02      | 0.05      | 0.09      | 0.04      | 0.04      |
| Na₂O            | 0.00              | 0.04      | 0.05      | 0.00      | 0.02      | 0.04      | 0.03      | 0.18      | 0.13      | 0.03      | 0.04      | 0.04      | 0.20      | 0.03      |
| K₂O             | 0.05              | 0.02      | 0.02      | 0.01      | 0.01      | 0.02      | 0.01      | 0.16      | 0.02      | 0.02      | 0.05      | 0.08      | 0.02      | 0.04      |
| Total           | 87.57             | 86.36     | 87.20     | 86.75     | 86.49     | 87.84     | 87.13     | 87.51     | 87.90     | 87.42     | 86.30     | 87.74     | 83.03     | 82.64     |

Applicable? (Inoue et al., 2018) | Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y

Applicable? (Lanari et al., 2014) | Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y

Applicable? (Bourdelle et al., 2012) | Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y Y

Approximated pressure (14 O basis)

| Structural formulae (14 O basis) | T site (apfu) | O Site (apfu) | Total O site | Total Cations | OHc | Wt% H₂O calculated | Total Wt% (plus H₂O) |
|---------------------------------|--------------|---------------|--------------|---------------|-----|-------------------|---------------------|
| Si                             | 2.61         | 1.44          | 4.00         | 4.00          | 8.00| 10.77             | 98.33               |
| Al²⁺                           | 1.39         | 1.42          | 2.81         | 2.82          | 5.63| 8.72              | 97.04               |
| Fe³⁺                           | 3.26         | 3.23          | 6.50         | 6.55          | 12.96| 19.67             | 98.49               |
| Mn                             | 0.01         | 0.01          | 0.02         | 0.02          | 0.04| 0.06              | 98.74               |
| Mg                             | 1.09         | 0.98          | 1.97         | 1.97          | 3.94| 5.91              | 98.36               |
| Ca                             | 0.01         | 0.01          | 0.02         | 0.02          | 0.04| 0.04              | 98.74               |
| K                              | 0.00         | 0.00          | 0.01         | 0.01          | 0.02| 0.02              | 98.74               |
| Vacancies                      | 0.00         | 0.00          | 0.01         | 0.01          | 0.02| 0.02              | 98.74               |
| SEMI-EMPIRICAL THERMOMETRY     | Inoue et al. (2018) | 0.10 | 0.11 | 0.13 | 0.09 | 0.10 | 0.15 | 0.12 | 0.09 | 0.09 | 0.11 | 0.16 | 0.11 |
|                               | Lanari et al. (2014) | 0.08 | 0.09 | 0.10 | 0.08 | 0.08 | 0.07 | 0.08 | 0.07 | 0.07 | 0.08 | 0.08 | 0.09 |
|                               | Bourdelle et al. (2013) | 0.08 | 0.09 | 0.10 | 0.08 | 0.08 | 0.07 | 0.08 | 0.07 | 0.08 | 0.07 | 0.09 | 0.11 |

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Geological evolution of the Eastern Pyrenees from quartz veins geothermometry
**TABLE III. Continued**

| Vein generation | Chlorite location | Chemical composition (Wt%) | Si | AlVI | Total T site | O Site | Total O site | Total Cations | Wt% H2O calculated | Total Wt% (plus H2O) | Vacancies |
|-----------------|-------------------|---------------------------|----|------|-------------|--------|-------------|---------------|-------------------|---------------------|-----------|
| V2              | Centre            | V2 Centre                 | 0.03 | 2.59 | 2.39 | 2.60 | 2.59 | 2.58 | 2.57 | 2.61 | 2.60 | 2.62 | 2.64 | 2.60 |
|                 | V2                | V2 Centre                 | 0.03 | 1.41 | 1.41 | 1.40 | 1.41 | 1.42 | 1.43 | 1.39 | 1.40 | 1.38 | 1.36 | 1.40 |
| V2              | Centre            | Total T site              | 0.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |
| V2              | Centre            | O Site                   | 0.04 | 1.58 | 1.61 | 1.59 | 1.57 | 1.60 | 1.59 | 1.62 | 1.58 | 1.59 | 1.58 | 1.55 | 1.56 |
|                 | V2                | AlVI                     | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|                 | V2                | Fe2+                     | 0.06 | 1.32 | 3.11 | 3.27 | 3.30 | 3.20 | 3.25 | 3.25 | 3.28 | 3.24 | 3.26 | 3.25 | 3.29 |
| V2              | Centre            | Mn                        | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
|                 | V2                | Mg                        | 0.02 | 1.06 | 0.96 | 1.02 | 1.03 | 1.09 | 1.03 | 1.02 | 1.03 | 1.02 | 1.05 | 1.02 | 1.06 |
| V2              | Centre            | Ca                        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|                 | V2                | Na                        | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| V2              | Centre            | K                         | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|                 | V2                | Total Cations             | 0.02 | 5.92 | 5.91 | 5.91 | 5.82 | 5.92 | 5.92 | 5.91 | 5.91 | 5.92 | 5.91 | 5.92 | 5.92 |
|                 | V2                | Wt% H2O calculated        | 0.11 | 10.35 | 10.83 | 10.70 | 10.63 | 10.53 | 10.68 | 10.91 | 10.73 | 10.80 | 10.78 | 10.77 | 10.75 |
| V2              | Centre            | Total Wt% (plus H2O)      | 0.87 | 96.36 | 99.11 | 97.71 | 97.25 | 95.95 | 98.46 | 98.60 | 98.06 | 98.50 | 98.43 | 98.24 | 98.34 |

**Semi-empirical Thermometry**

- Inoue et al. (2018)
- Lanari et al. (2014)
- Bourdelle et al. (2013)
| Vein generation | Chlorite location | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 | V2 |
|----------------|-------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
|                |                   | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre | Centre |
| Chemical composition (Wt%)
| SiO2     | 22.89 | 22.94 | 23.16 | 22.98 | 23.18 | 23.35 | 23.04 | 22.91 | 22.95 | 22.85 | 22.95 | 23.22 | 23.04 | 23.16 | 22.89 | 22.85 | 23.49 |
| TiO2     | 0.02  | 0.00  | 0.00  | 0.00  | 0.00  | 0.02  | 0.05  | 0.00  | 0.01  | 0.01  | 0.00  | 0.04  | 0.06  | 0.01  | 0.02  | 0.00  | 0.00  | 0.00  |
| Al2O3    | 21.47 | 21.72 | 21.89 | 21.87 | 21.97 | 22.19 | 22.26 | 21.03 | 21.90 | 21.45 | 22.11 | 21.78 | 22.31 | 21.97 | 22.06 | 22.02 |
| FeO      | 33.39 | 33.65 | 36.35 | 35.91 | 36.21 | 35.92 | 36.10 | 35.66 | 35.44 | 35.60 | 35.92 | 36.15 | 35.38 | 36.85 | 35.21 | 34.65 | 36.05 |
| MnO      | 0.07  | 0.04  | 0.10  | 0.09  | 0.07  | 0.07  | 0.01  | 0.02  | 0.07  | 0.08  | 0.08  | 0.09  | 0.06  | 0.09  | 0.07  | 0.04  | 0.09  |
| MgO      | 5.86  | 5.95  | 5.23  | 5.67  | 5.72  | 5.86  | 5.69  | 5.60  | 5.71  | 5.54  | 5.48  | 5.65  | 6.03  | 5.58  | 5.46  | 5.65  | 5.93  |
| CaO      | 0.10  | 0.11  | 0.02  | 0.04  | 0.02  | 0.02  | 0.03  | 0.01  | 0.06  | 0.02  | 0.01  | 0.04  | 0.03  | 0.11  | 0.02  | 0.11  | 0.02  |
| Na2O     | 0.13  | 0.11  | 0.04  | 0.05  | 0.02  | 0.02  | 0.03  | 0.01  | 0.07  | 0.04  | 0.01  | 0.03  | 0.02  | 0.13  | 0.11  | 0.14  | 0.11  |
| Total    | 84.30 | 84.65 | 86.78 | 86.64 | 87.12 | 87.32 | 87.16 | 86.62 | 85.28 | 85.13 | 85.97 | 87.30 | 86.46 | 88.25 | 85.92 | 85.60 | 87.70 |

Table III. Continued

| Applicable? (Bourdelle et al., 2018) | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
|--------------------------------------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Applicable? (Lanari et al., 2014)    | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |
| Applicable? (Bourdelle et al., 2012) | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y | Y |

Approximatal pressure
3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00 3.00

Structural formulae (14 O basis)

| T site (qfu) |
|-------------|
| Si          | 2.65 |
| Al          | 1.35 |
| Total T site | 4.00 |
| O Site (qfu) |
| Al          | 1.58 |
| Ti          | 0.00 |
| Fe2+        | 3.24 |
| Mg          | 0.00 |
| Ca          | 1.01 |
| Na          | 0.04 |
| K           | 0.02 |
| Total O site | 5.91 |
| OHc         | 3.00 |
| Total Cations | 9.91 |
| WH2O (calculated) | 10.28 |
| Total WH2O+H2O | 10.46 |

Vacancies

| 6x[Fe2+Mg2+Al3+] (Bourdelle et al., 2009, 2018) | 0.17 |
| 3x[Al3+-Na]+(K)+2+Na+ (Lanari et al., 2014) | 0.09 |
| 3x[Al3+-Na]+ (Bourdelle et al., 2013) | 0.12 |

Semi-empirical thermometry

| Inoue et al. (2018) | 282 |
| Lanari et al. (2014) | 344 |
| Bourdelle et al. (2013) | 278 |
| Vein generation | Mean | Standard deviation | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) |
|----------------|------|--------------------|-------------------------|-------------------------|-------------------------|
| Chemical composition (Wt%) | | | | | |
| SiO₂ | 23,11 | 0,33 | 23,38 | 23,61 | 22,74 |
| TiO₂ | 0,01 | 0,02 | 0,00 | 0,02 | 0,03 |
| Al₂O₃ | 22,18 | 0,58 | 22,57 | 22,77 | 22,28 |
| FeO | 35,20 | 0,93 | 32,05 | 33,48 | 33,57 |
| MgO | 0,08 | 0,03 | 0,17 | 0,14 | 0,19 |
| CaO | 5,93 | 0,30 | 8,20 | 7,57 | 7,57 |
| Na₂O | 0,04 | 0,06 | 0,06 | 0,17 | 0,08 |
| K₂O | 0,04 | 0,04 | 0,06 | 0,17 | 0,08 |
| Total | 86,66 | 1,29 | 86,49 | 87,77 | 86,55 |
| Applicable? (Inoue et al., 2018) | Y | Y | N |
| Applicable? (Lanari et al., 2014) | Y | Y | N |
| Applicable? (Bourdelle et al., 2012) | Y | Y | N |
| Approximated pressure | - | - | - |
| Structural formulae (14 O basis) | | | | | |
| T site (apfu) | | | | | |
| Si | 2,61 | 0,02 | 2,60 | 2,60 | 2,56 |
| Al³⁺ | 1,39 | 0,02 | 1,40 | 1,40 | 1,44 |
| Total T site | 4,00 | 0,00 | 4,00 | 4,00 | 4,00 |
| O Site (apfu) | | | | | |
| Al¹¹⁺ | 1,56 | 0,03 | 1,56 | 1,56 | 1,51 |
| Ti | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| Fe²⁺ | 3,33 | 0,08 | 2,98 | 3,09 | 3,16 |
| Mn | 0,01 | 0,00 | 0,02 | 0,01 | 0,02 |
| Mg | 1,00 | 0,05 | 1,36 | 1,24 | 1,27 |
| Ca | 0,01 | 0,00 | 0,01 | 0,00 | 0,00 |
| Na | 0,01 | 0,01 | 0,00 | 0,00 | 0,01 |
| K | 0,01 | 0,01 | 0,01 | 0,00 | 0,01 |
| Total O site | 5,92 | 0,01 | 5,93 | 5,93 | 5,98 |
| Total Cations | 9,92 | 0,01 | 9,93 | 9,93 | 9,98 |
| OHc | 8,00 | 0,00 | 8,00 | 8,00 | 8,00 |
| Wt% H₂O calculated | 10,62 | 0,15 | 10,79 | 10,88 | 10,67 |
| Total Wt% (plus H₂O) | 97,27 | 1,44 | 97,28 | 98,65 | 97,22 |
| Vacancies | | | | | |
| 6-(Fe²⁺ Fe³⁺ Mg) Al³⁺ (Inoue et al., 2009, 2018) | 0,11 | 0,02 | 0,10 | 0,11 | 0,07 |
| (Al³⁺ Al⁵⁺ - Na-K)² (Lanari et al., 2014) | 0,08 | 0,01 | 0,07 | 0,07 | 0,02 |
| (Al³⁺ Al⁵⁺)² (Bourdelle et al., 2013) | 0,09 | 0,01 | 0,08 | 0,08 | 0,03 |
| SEMI-EMPIRICAL THERMOMETRY | | | | | |
| Inoue et al. (2018) | 317 | 12 | 323 | 319 | NOT APPLICABLE |
| Lanari et al. (2014) | 362 | 14 | 373 | 382 | NOT APPLICABLE |
| Bourdelle et al. (2013) | 331 | 21 | 349 | 342 | NOT APPLICABLE |
Vein generation

| Chlorite location | - | - | - | - |
|-------------------|---|---|---|---|
| Hostrock (Serdinya Fm.) | 23.94 | 23.46 | 23.94 | 23.46 |
| Hostrock (Serdinya Fm.) | 0.03 | 0.00 | 0.06 | 0.04 |
| Hostrock (Serdinya Fm.) | 22.76 | 23.18 | 22.52 | 22.35 |
| Hostrock (Serdinya Fm.) | 32.71 | 32.44 | 31.90 | 34.25 |
| Hostrock (Serdinya Fm.) | 0.19 | 0.19 | 0.17 | 0.17 |
| Hostrock (Serdinya Fm.) | 8.22 | 7.85 | 8.47 | 7.05 |
| Hostrock (Serdinya Fm.) | 0.01 | 0.03 | 0.00 | 0.02 |
| Hostrock (Serdinya Fm.) | 0.03 | 0.00 | 0.01 | 0.02 |
| Hostrock (Serdinya Fm.) | 0.02 | 0.02 | 0.03 | 0.17 |
| Hostrock (Serdinya Fm.) | 86.90 | 87.17 | 86.50 | 86.73 |

Chemical composition (Wt%)

| Hostrock (Serdinya Fm.) | 22.94 | 23.46 | 23.34 | 22.66 |
| Hostrock (Serdinya Fm.) | 0.03 | 0.00 | 0.06 | 0.04 |
| Hostrock (Serdinya Fm.) | 22.76 | 23.18 | 22.52 | 22.35 |
| Hostrock (Serdinya Fm.) | 32.71 | 32.44 | 31.90 | 34.25 |
| Hostrock (Serdinya Fm.) | 0.19 | 0.19 | 0.17 | 0.17 |
| Hostrock (Serdinya Fm.) | 8.22 | 7.85 | 8.47 | 7.05 |
| Hostrock (Serdinya Fm.) | 0.01 | 0.03 | 0.00 | 0.02 |
| Hostrock (Serdinya Fm.) | 0.03 | 0.00 | 0.01 | 0.02 |
| Hostrock (Serdinya Fm.) | 0.02 | 0.02 | 0.03 | 0.17 |
| Hostrock (Serdinya Fm.) | 86.90 | 87.17 | 86.50 | 86.73 |

Applicable? (Inoue et al., 2018)

| Hostrock (Serdinya Fm.) | N | Y | Y | N |
| Hostrock (Serdinya Fm.) | N | Y | Y | N |
| Hostrock (Serdinya Fm.) | N | Y | Y | N |

Approximated pressure

| - | - | - | - |

Structural formulae (14 O basis)

| T site (apfu) | 2.55 | 2.59 | 2.59 | 2.55 |
| AlIV | 1.45 | 1.41 | 1.41 | 1.45 |
| Total T site | 4.00 | 4.00 | 4.00 | 4.00 |
| O Site (apfu) | 1.53 | 1.60 | 1.54 | 1.52 |
| Ti | 0.00 | 0.00 | 0.01 | 0.00 |
| Fe²⁺ | 0.02 | 0.02 | 0.02 | 0.02 |
| Mg | 0.13 | 1.29 | 1.40 | 1.18 |
| Ca | 0.00 | 0.00 | 0.00 | 0.00 |
| Na | 0.01 | 0.00 | 0.00 | 0.00 |
| K | 0.00 | 0.00 | 0.00 | 0.03 |
| Total O site | 5.96 | 5.91 | 5.93 | 5.98 |
| Total Cations | 9.96 | 9.91 | 9.93 | 9.98 |
| OH⁻ | 8.00 | 8.00 | 8.00 | 8.00 |
| Wt% H₂O calculated | 10.79 | 10.87 | 10.80 | 10.65 |
| Total Wt% (plus H₂O) | 97.69 | 98.04 | 97.30 | 97.39 |
| Vacancies | 6-(Fe²⁺ Fe³⁺ Mg A)⁻ (Inoue et al., 2009, 2018) | 0.07 | 0.12 | 0.10 | 0.07 |
| (Al³⁺ Al⁶⁺ Na-K)² (Lanari et al., 2014) | 0.04 | 0.09 | 0.07 | 0.07 |
| (Al³⁺ Al⁶⁺)² (Bourdelle et al., 2013) | 0.04 | 0.09 | 0.07 | 0.03 |

SEMI-EMPIRICAL THERMOMETRY

| - | NOT APPLICABLE | 318 | 329 | NOT APPLICABLE |
| Lanari et al. (2014) | NOT APPLICABLE | 344 | 383 | NOT APPLICABLE |
| Bourdelle et al. (2013) | NOT APPLICABLE | 324 | 379 | NOT APPLICABLE |
### Table III. Continued

| Vene generation | Chlorite location | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) |
|-----------------|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Chemical composition (Wt%) | | | | | | | |
| SiO₂ | 22.94 | 23.54 | 22.67 | 22.20 | 23.46 | 23.80 |
| TiO₂ | 0.04 | 0.04 | 0.07 | 0.05 | 0.00 | 0.05 |
| Al₂O₃ | 23.06 | 23.17 | 22.19 | 21.76 | 22.98 | 23.11 |
| FeO | 33.12 | 31.84 | 34.37 | 32.86 | 32.78 | 31.67 |
| MgO | 7.61 | 8.08 | 7.67 | 7.65 | 7.76 | 8.61 |
| CaO | 0.01 | 0.04 | 0.01 | 0.04 | 0.01 | 0.02 |
| Na₂O | 0.02 | 0.02 | 0.05 | 0.06 | 0.02 | 0.02 |
| K₂O | 0.03 | 0.11 | 0.04 | 0.28 | 0.16 | 0.04 |
| Total | 87.90 | 86.93 | 87.24 | 85.04 | 87.35 | 87.59 |

### Applicable? (Inoue et al., 2018)

| | Y | Y | N | N | Y | N |
| | | | | | | |

### Applicable? (Lanari et al., 2014)

| | Y | Y | N | N | Y | N |
| | | | | | | |

### Applicable? (Bourdelle et al., 2013)

| | Y | Y | N | N | Y | N |
| | | | | | | |

### Approximated pressure

| | | | | | | |
| | | | | | | |

### Structural formulae (14 O basis)

#### T site (apfu)

| | Si | 2.55 | 2.60 | 2.54 | 2.54 | 2.59 | 2.60 |
| | Al³⁺ | 1.45 | 1.40 | 1.46 | 1.46 | 1.51 | 1.40 |
| | Total T site | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |

#### O site (apfu)

| | Al³⁺ | 1.57 | 1.61 | 1.46 | 1.48 | 1.58 | 1.58 |
| | Ti | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| | Fe²⁺ | 3.08 | 2.94 | 3.22 | 3.15 | 3.03 | 2.89 |
| | Mn | 0.02 | 0.01 | 0.02 | 0.01 | 0.02 | 0.02 |
| | Mg | 1.26 | 1.32 | 1.28 | 1.31 | 1.28 | 1.40 |
| | Ca | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Na | 0.00 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 |
| | K | 0.00 | 0.02 | 0.01 | 0.04 | 0.02 | 0.01 |
| | Total O site | 5.94 | 5.93 | 6.00 | 6.01 | 5.93 | 5.93 |
| | Total Cations | 9.94 | 9.91 | 10.00 | 10.01 | 9.93 | 9.91 |
| | OH⁻ | 8.00 | 8.00 | 8.00 | 8.00 | 8.00 | 8.00 |
| | Wt% H₂O calculated | 10.79 | 10.87 | 10.72 | 10.47 | 10.86 | 10.98 |
| | Total Wt% (plus H₂O) | 97.79 | 97.81 | 97.96 | 95.51 | 98.22 | 98.57 |

### Vacancies

| 6(Fe²⁺,Fe³⁺,Mg²⁺) (Inoue et al., 2009, 2018) | 0.09 | 0.14 | 0.04 | 0.07 | 0.12 | 0.13 |
| (Al³⁺,Al³⁺-Na-K)² (Lanari et al., 2014) | 0.06 | 0.09 | 0.00 | -0.01 | 0.07 | 0.09 |
| (Al³⁺,Al³⁺)² (Bourdelle et al., 2013) | 0.06 | 0.10 | 0.00 | 0.01 | 0.08 | 0.09 |

### SEMI-EMPIRICAL THERMOMETRY

| Inoue et al. (2018) | 338 | 306 | NOT APPLICABLE | NOT APPLICABLE | 318 | NOT APPLICABLE |
| Lanari et al. (2014) | 424 | 343 | NOT APPLICABLE | NOT APPLICABLE | 386 | NOT APPLICABLE |
| Bourdelle et al. (2013) | 408 | 310 | NOT APPLICABLE | NOT APPLICABLE | 338 | NOT APPLICABLE |
### TABLE II. Continued

| Vein generation | Chalcopyrite location | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) |
|-----------------|----------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Chemical composition (Wt%) | | | | | |
| SiO₂ | 23.51 | 22.55 | 22.92 | 22.42 |
| TiO₂ | 0.00 | 0.04 | 0.04 | 0.08 |
| Al₂O₃ | 23.15 | 22.66 | 21.95 | 22.38 |
| FeO | 32.65 | 33.24 | 34.16 | 34.63 |
| MnO | 0.25 | 0.23 | 0.16 | 0.18 |
| MgO | 8.52 | 7.90 | 7.85 | 7.57 |
| CaO | 0.01 | 0.01 | 0.01 | 0.01 |
| Na₂O | 0.00 | 0.00 | 0.08 | 0.05 |
| K₂O | 0.02 | 0.14 | 0.04 | 0.06 |
| Total | 88.10 | 86.76 | 87.21 | 87.38 |

**Applicable? (Inoue et al., 2018)**

| | N | N | N | N |

**Applicable? (Lanari et al., 2014)**

| | N | N | N | N |

**Applicable? (Bourdelle et al., 2012)**

| | N | N | N | N |

### Approximated pressure

| Structural formulae (14 O basis) | T site (apfu) | O site (apfu) | Total Cations | OHc |
|---------------------------------|--------------|---------------|---------------|-----|
| Si | 2.57 | 1.55 | 1.43 | 1.48 | 1.44 | 1.49 |
| Al⁺³ | 1.43 | 1.48 | 1.44 | 1.49 |
| Total T site | 4.00 | 4.00 | 4.00 | 4.00 |
| Al⁺³ | 1.55 | 1.51 | 1.45 | 1.46 |
| Ti | 0.00 | 0.00 | 0.00 | 0.01 |
| Fe²⁺ | 2.98 | 3.31 | 3.19 | 3.24 |
| Mn | 0.02 | 0.02 | 0.02 | 0.02 |
| Mg | 1.39 | 1.32 | 1.31 | 1.26 |
| Ca | 0.00 | 0.00 | 0.00 | 0.00 |
| Na | 0.00 | 0.00 | 0.02 | 0.01 |
| K | 0.00 | 0.02 | 0.01 | 0.01 |
| Total O site | 5.95 | 5.99 | 6.00 | 6.02 |

**Vacancies**

- 6-(Fe²⁺Mg)⁺³ (Inoue et al., 2009, 2018)
- (Al⁺³-AI⁺³-Na-K)/2 (Lanari & others, 2014)
- (Al⁺³-AI⁺³)/2 (Bourdelle et al., 2013)

**SEMI-EMPirical THERMOMETRY**

| | Inoue et al. (2018) | Lanari et al. (2014) | Bourdelle et al. (2013) |
|----------------------|----------------------|----------------------|------------------------|
| NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
| NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
| NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
| NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
### TABLE III. Continued

| Vein generation | Chlorine location | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) |
|----------------|-------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Chemical composition (Wt%) | | | | | |
| SiO₂ | 23.43 | 23.08 | 23.97 | 23.07 |
| TiO₂ | 0.03 | 0.00 | 0.00 | 0.00 |
| Al₂O₃ | 22.80 | 22.15 | 22.47 | 22.42 |
| FeO | 32.81 | 32.69 | 32.14 | 31.79 |
| MnO | 0.20 | 0.16 | 0.24 | 0.20 |
| MgO | 7.87 | 7.32 | 8.51 | 8.52 |
| CaO | 0.01 | 0.08 | 0.02 | 0.02 |
| Na₂O | 0.08 | 0.07 | 0.04 | 0.03 |
| K₂O | 0.02 | 0.10 | 0.00 | 0.01 |
| Total | 87.25 | 85.85 | 87.39 | 87.06 |

Applicable? (Inoue et al., 2018)  
Applicable? (Lanari et al., 2014)  
Applicable? (Bourdelle et al., 2012)

Approximated pressure

| Structural formulae (14 O basis) |
|---------------------------------|
| T site (apfu) | | | | |
| Si | 2.59 | 2.00 | 2.63 | 2.54 |
| Al³⁺ | 1.41 | 1.40 | 1.37 | 1.46 |
| Total T site | 4.00 | 4.00 | 4.00 | 4.00 |
| O Site (apfu) | | | | |
| Al³⁺ | 1.56 | 1.57 | 1.54 | 1.58 |
| Ti | 0.00 | 0.00 | 0.00 | 0.00 |
| Fe²⁺ | 3.03 | 3.08 | 2.95 | 2.93 |
| Mn | 0.02 | 0.02 | 0.02 | 0.02 |
| Mg | 1.30 | 1.23 | 1.39 | 1.40 |
| Ca | 0.00 | 0.00 | 0.00 | 0.00 |
| Na | 0.00 | 0.00 | 0.00 | 0.00 |
| K | 0.00 | 0.00 | 0.00 | 0.00 |
| Total O site | 5.93 | 5.93 | 5.92 | 5.94 |
| Total Cations | 9.93 | 9.93 | 9.92 | 9.94 |
| OH⁻ | 8.00 | 8.00 | 8.00 | 8.00 |
| Wt% H₂O calculated | 10.85 | 10.65 | 10.32 | 10.88 |
| Total Wt% (plus H₂O) | 98.10 | 96.50 | 98.32 | 97.95 |

Vacancies

| Vacancies | | | |
| 6-(Fe²⁺Fe³⁺Mg) A³⁺ | (Inoue et al., 2009, 2018) | 0.11 | 0.12 | 0.12 | 0.09 |
| (Al³⁺,Fe³⁺,Na,K)2 | (Lanari et al., 2014) | 0.07 | 0.07 | 0.08 | 0.07 |
| (Al³⁺,Fe³⁺)2 | (Bourdelle et al., 2013) | 0.07 | 0.08 | 0.09 | 0.06 |

### SEMI-EMPIRICAL THERMOMETRY

| | Inoue et al. (2018) | 322 | 314 | 312 | 339 |
| | Lanari et al. (2014) | 390 | 390 | 345 | 431 |
| | Bourdelle et al. (2013) | 328 | 337 | 325 | 395 |
### Table III. Continued

| Vein generation | Chlorite location | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) |
|-----------------|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| **Chemical composition (Wt%)** |                   |                         |                         |                         |                         |                         |                         |
| SiO₂            | 23.11             | 23.19                   | 22.82                   | 22.73                   | 23.53                   | 23.12                   |
| TiO₂            | 0.01              | 0.00                    | 0.00                    | 0.01                    | 0.00                    | 0.00                    |
| Al₂O₃           | 22.76             | 23.79                   | 21.35                   | 20.93                   | 21.87                   | 22.25                   |
| FeO             | 31.86             | 32.13                   | 34.24                   | 33.67                   | 34.44                   | 34.05                   |
| MnO             | 0.15              | 0.22                    | 0.15                    | 0.11                    | 0.22                    | 0.16                    |
| MgO             | 8.47              | 8.33                    | 7.64                    | 7.33                    | 7.82                    | 7.72                    |
| CaO             | 0.04              | 0.00                    | 0.02                    | 0.04                    | 0.01                    | 0.01                    |
| Na₂O            | 0.01              | 0.02                    | 0.00                    | 0.01                    | 0.01                    | 0.00                    |
| K₂O             | 0.01              | 0.02                    | 0.00                    | 0.01                    | 0.01                    | 0.00                    |
| Total           | 86.42             | 87.68                   | 85.05                   | 87.91                   | 87.37                   |                         |

| **Applicable?** (Inoue et al., 2018) | Y | Y | N | N | N | N |
|--------------------------------------|---|---|---|---|---|---|
| **Applicable?** (Lanari et al., 2014) | Y | Y | N | N | N | N |
| **Applicable?** (Bourdelle et al., 2012) | Y | Y | N | N | N | N |

| **Approximated pressure** |       |       |       |       |       |       |
|---------------------------|-------|-------|-------|-------|-------|-------|
| **Structural formulae (140 basis)** |       |       |       |       |       |       |
| Total T site              |       |       |       |       |       |       |
| Si                         | 2.57  | 2.54  | 2.59  | 2.61  | 2.61  | 2.57  |
| AlIV                       | 1.43  | 1.46  | 1.41  | 1.39  | 1.39  | 1.43  |
| Total T site               | 4.00  | 4.00  | 4.00  | 4.00  | 4.00  | 4.00  |
| **O Site (apfu)**          |       |       |       |       |       |       |
| AlIV                      | 1.55  | 1.65  | 1.44  | 1.44  | 1.46  | 1.49  |
| Ti                         | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Fe²⁺                       | 2.96  | 2.94  | 3.24  | 3.23  | 3.19  | 3.17  |
| Mn                         | 0.01  | 0.02  | 0.01  | 0.01  | 0.02  | 0.02  |
| Mg                         | 1.40  | 1.36  | 1.29  | 1.29  | 1.29  | 1.28  |
| Ca                         | 0.00  | 0.00  | 0.00  | 0.01  | 0.00  | 0.00  |
| Na                         | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| K                          | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Total O site               | 5.94  | 5.93  | 5.99  | 5.98  | 5.97  | 5.97  |
| Total Cations             | 9.94  | 9.93  | 9.99  | 9.98  | 9.97  | 9.97  |
| OH⁺                       | 8.00  | 8.00  | 8.00  | 8.00  | 8.00  | 8.00  |
| Wt% H₂O calculated        | 10.79 | 10.96 | 10.58 | 10.45 | 10.83 | 10.77 |
| Total Wt% (plus H₂O)       | 97.21 | 98.64 | 96.81 | 95.50 | 98.74 | 98.15 |

| **Vacancies** |       |       |       |       |       |       |
|---------------|-------|-------|-------|-------|-------|-------|
| 6(Fe²⁺Fe³⁺Mg³⁺A⁺) | 0.08  | 0.03  | 0.04  | 0.06  | 0.06  | 0.06  |
| (Al³⁺Al²⁺NaK)/2 | 0.06  | 0.07  | 0.01  | 0.02  | 0.03  | 0.03  |
| (Al³⁺Al²⁺)/2     | 0.06  | 0.07  | 0.01  | 0.02  | 0.03  | 0.03  |

| **SEMI-EMPIRICAL THERMOMETRY** |       |       |       |       |       |       |
|-------------------------------|-------|-------|-------|-------|-------|-------|
| Inoue et al. (2018)            | 339   | 336   | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
| Lanari et al. (2014)           | 416   | 402   | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
| Bourdelle et al. (2013)        | 402   | 381   | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
### Table III. Continued

| Vein generation | Chlorite location | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) |
|-----------------|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Chemical composition (Wt%) | | | | | | | |
| SiO₂ | 23.12 | 23.14 | 23.45 | 22.53 | 22.71 | 23.13 |
| TiO₂ | 0.00 | 0.03 | 0.06 | 0.00 | 0.00 | 0.06 |
| Al₂O₃ | 22.25 | 23.08 | 22.75 | 21.37 | 21.84 | 21.94 |
| Fe₂O₃ | 34.05 | 32.00 | 33.07 | 33.85 | 33.57 | 33.79 |
| MnO | 0.16 | 0.15 | 0.18 | 0.16 | 0.14 | 0.13 |
| MgO | 7.72 | 7.73 | 7.32 | 7.50 | 7.36 | 7.23 |
| CaO | 0.01 | 0.05 | 0.03 | 0.03 | 0.06 | 0.08 |
| Na₂O | 0.06 | 0.15 | 0.32 | 0.02 | 0.03 | 0.08 |
| Total | 87.37 | 86.33 | 87.24 | 85.46 | 85.75 | 86.54 |

| Applicable? (Inoue et al., 2018) | N | Y | Y | N | N | N |
|----------------------------------|---|---|---|---|---|---|
| Applicable? (Lanari et al., 2014) | N | Y | Y | N | N | N |
| Applicable? (Bourdelle et al., 2012) | N | Y | Y | N | N | N |

| Approximated pressure | | | | | | |

| Structural formulae (14 O basis) | T site (apfu) | | | | | |
|----------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Si | 2.57 | 2.58 | 2.60 | 2.57 | 2.58 | 2.60 |
| Al IV | 1.43 | 1.42 | 1.40 | 1.43 | 1.42 | 1.40 |
| Total T site | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |

| O Site (apfu) | | | | | | |
|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Al III | 1.49 | 1.61 | 1.57 | 1.45 | 1.50 | 1.51 |
| Ti | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Fe²⁺ | 3.17 | 2.98 | 3.07 | 3.24 | 3.19 | 3.18 |
| Mn | 0.02 | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 |
| Mg | 1.28 | 1.28 | 1.21 | 1.28 | 1.25 | 1.21 |
| Ca | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 | 0.01 |
| Na | 0.00 | 0.02 | 0.05 | 0.00 | 0.00 | 0.00 |
| K | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.02 |
| Total O site | 5.97 | 5.92 | 5.94 | 5.99 | 5.97 | 5.96 |
| Total Cations | 9.97 | 9.92 | 9.94 | 9.99 | 9.97 | 9.96 |
| OH⁻ | 8.00 | 8.00 | 8.00 | 8.00 | 8.00 | 8.06 |
| Wt% H₂O calculated | 10.77 | 10.77 | 10.81 | 10.50 | 10.56 | 10.67 |
| WE % (plus H₂O) | 98.15 | 97.10 | 98.05 | 95.96 | 96.31 | 97.21 |
| Vacancies | 6-(Fe²⁺Fe³⁺Mg⁺⁺⁺) | 0.06 | 0.13 | 0.15 | 0.07 | 0.10 |
| (Al³⁺Al⁶⁺Na⁺K⁺)² | 0.03 | 0.08 | 0.06 | 0.01 | 0.03 | 0.04 |
| (Al³⁺Al³⁺)² | 0.03 | 0.09 | 0.09 | 0.01 | 0.04 | 0.05 |

| SEMI-EMPIRICAL THERMOMETRY | | | | | | |
|-----------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Inoue et al. (2018) | NOT APPLICABLE | 314 | 303 | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
| Lanari et al. (2014) | NOT APPLICABLE | 368 | 412 | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
| Bourdelle et al. (2013) | NOT APPLICABLE | 329 | 330 | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
### Vein generation

| Chemical composition (Wt%) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) | Hostrock (Serdinya Fm.) |
|---------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| SiO₂                      | 23.04                   | 24.10                   | 23.95                   | 23.12                   | 22.92                   | 23.29                   |
| TiO₂                      | 0.07                    | 0.02                    | 0.03                    | 0.00                    | 0.02                    | 0.02                    |
| Al₂O₃                     | 22.94                   | 21.85                   | 22.98                   | 23.15                   | 22.36                   | 22.64                   |
| Fe₂O₃                     | 32.88                   | 33.94                   | 31.46                   | 33.25                   | 34.73                   | 34.23                   |
| MnO                       | 0.21                    | 0.16                    | 0.28                    | 0.22                    | 0.19                    | 0.16                    |
| MgO                       | 8.03                    | 7.26                    | 8.77                    | 8.20                    | 7.70                    | 7.83                    |
| CaO                       | 0.03                    | 0.08                    | 0.04                    | 0.01                    | 0.01                    | 0.00                    |
| Na₂O                      | 0.02                    | 0.02                    | 0.01                    | 0.00                    | 0.01                    | 0.00                    |
| K₂O                       | 0.05                    | 0.07                    | 0.09                    | 0.02                    | 0.02                    | 0.03                    |
| Total                     | 87.26                   | 87.50                   | 87.60                   | 87.97                   | 87.97                   | 88.20                   |

### Applicable?

- Inoue et al., 2018
  - N
  - Y
  - Y
  - N
  - N

- Lanari et al., 2014
  - N
  - Y
  - Y
  - N
  - N

- Bourdelle et al., 2012
  - N
  - Y
  - Y
  - N
  - N

### Approximated pressure

#### Structural formulae (14 O basis)

| T site (apfu) | Total T site | O Site (apfu) | Total O site | Total Cations | OH⁻ | Wt% H₂O calculated | Total Wt% (plus H₂O) |
|---------------|--------------|---------------|--------------|---------------|-----|--------------------|----------------------|
| Si            | 2.55         | Al³⁺         | 1.45         | 4.00          | 8.00| 10.83              | 98.10                |
| Al³⁺         | 1.45         | Mg            | 1.33         | 4.00          | 8.00| 10.82              | 98.33                |
| Fe²⁺         | 3.04         | Ca            | 0.00         | 4.00          | 8.00| 10.99              | 98.60                |
| Mn            | 0.02         | Na            | 0.00         | 4.00          | 8.00| 10.99              | 98.60                |
| Mg            | 1.33         | K             | 0.01         | 4.00          | 8.00| 10.99              | 98.60                |
| Ca            | 0.00         | Total Cations | 9.95         | 8.00          | 8.00| 8.00               | 98.08                |
| Na            | 0.00         | OH⁻           | 8.00         | 8.00          | 8.00| 8.00               | 98.08                |
| K             | 0.01         | Wt% H₂O calculated | 10.83        | 10.82         | 10.99| 10.80              | 98.88                |
| Total Wt% (plus H₂O) | 98.10      |               |              |               |     |                    | 99.08                |

### Vacancies

- 6(Fe²⁺Fe³⁺Mg⁺⁺⁺) (Inoue et al., 2009, 2018)
  - 0.09
  - 0.13

- (Al³⁺Al³⁺Na⁺K⁺)/2 (Lanari et al., 2014)
  - 0.05
  - 0.09

- (Al³⁺Al³⁺)/2 (Bourdelle et al., 2013)
  - 0.05
  - 0.10

### SEMI-EMPIRICAL THERMOMETRY

| Inoue et al. (2008) | NOT APPLICABLE | 297 | 306 | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
|--------------------|----------------|-----|-----|----------------|----------------|----------------|
| Lanari et al. (2014)| NOT APPLICABLE | 319 | 346 | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
| Bourdelle et al. (2013)| NOT APPLICABLE | 299 | 321 | NOT APPLICABLE | NOT APPLICABLE | NOT APPLICABLE |
| Vein generation | Chemical composition (Wt%) | Mean | Standard deviation | Hostrock (Cava Fm.) | Hostrock (Cava Fm.) | Hostrock (Cava Fm.) | Hostrock (Cava Fm.) | Hostrock (Cava Fm.) | Hostrock (Cava Fm.) |
|-----------------|---------------------------|------|--------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
|                 | SiO₂                      | 23.15| 0.44               | 23.40               | 23.41               | 23.03               | 23.71               | 23.53               |                     |
|                 | TiO₂                      | 0.02 | 0.02               | 0.02                | 0.08                | 0.00                | 0.00                | 0.01                |                     |
|                 | Al₂O₃                     | 22.51| 0.61               | 22.08               | 22.01               | 22.06               | 22.12               | 23.04               |                     |
|                 | FeO                       | 33.34| 0.95               | 33.96               | 33.80               | 34.53               | 33.96               | 34.77               |                     |
|                 | MnO                       | 0.18 | 0.04               | 0.16                | 0.14                | 0.11                | 0.13                | 0.16                |                     |
|                 | MgO                       | 7.86 | 0.41               | 7.40                | 7.72                | 7.56                | 7.38                | 7.19                |                     |
|                 | CaO                       | 0.03 | 0.02               | 0.03                | 0.03                | 0.02                | 0.06                | 0.01                |                     |
|                 | Na₂O                      | 0.03 | 0.01               | 0.05                | 0.04                | 0.01                | 0.11                | 0.03                |                     |
|                 | K₂O                       | 0.07 | 0.01               | 0.05                | 0.04                | 0.01                | 0.11                | 0.03                |                     |
|                 | Total                     | 86.98| 0.79               | 87.30               | 87.28               | 87.26               | 87.53               | 88.80               |                     |

**Approximated pressure**

| Structural formulae (14 O basis) | T site (apfu) | O Site (apfu) | Total O site | Total Cations | OHc | Wt% H₂O calculated | Total Wt% (plus H₂O) | Vacancies |
|---------------------------------|--------------|---------------|--------------|---------------|-----|--------------------|----------------------|-----------|
|                                 |              |               |              |               |     |                    |                      |           |
|                                 |              |               |              |               |     |                    |                      |           |

**Semi-empirical thermometry**

|                                                     | Inoue et al. (2018) | Lanari et al. (2014) | Bourdeille et al. (2013) |
|-----------------------------------------------------|---------------------|----------------------|--------------------------|
| Mean Standard deviation                             | 0.08 0.03           | 0.05 0.01            | 0.02 0.01                |
|                                                     | NOT APPLICABLE      | NOT APPLICABLE       | NOT APPLICABLE           |
|                                                     | 320 313             | 380 400              | 349 383                  |
|                                                     | 0.04 0.01           | 0.02 0.00            | 0.06 0.02                |
|                                                     | 316 333             | 396 426              | 345 389                  |
### Chemical composition (Wt%)

| Chemical  | Mean | Standard deviation |
|-----------|------|--------------------|
| SiO₂      | 23.42| 0.25               |
| TiO₂      | 0.02 | 0.03               |
| Al₂O₃     | 22.26| 0.44               |
| FeO       | 34.20| 0.42               |
| MgO       | 0.14 | 0.02               |
| CaO       | 7.45 | 0.20               |
| Na₂O      | 0.03 | 0.02               |
| K₂O       | 0.04 | 0.04               |
| Total     | 87.61| 0.68               |

### Applicable?

- Applicable? (Inoue et al., 2018)
- Applicable? (Lanari et al., 2014)
- Applicable? (Bourdelle et al., 2012)

### Approximated pressure

#### Structural formulae (14 O basis)

| T site | apfu | Mean | Standard deviation |
|--------|------|------|--------------------|
| Si     | 2.60 | 0.02 |
| AlIV   | 1.40 | 0.02 |
| Total T site | 4.00 | 0.00 |

| O Site | apfu | Mean | Standard deviation |
|--------|------|------|--------------------|
| AlVI   | 1.51 | 0.03 |
| Ti     | 0.00 | 0.00 |
| Fe²⁺   | 3.17 | 0.03 |
| Mn     | 0.01 | 0.00 |
| Mg     | 1.23 | 0.04 |
| Ca     | 0.00 | 0.00 |
| Na     | 0.01 | 0.00 |
| K      | 0.01 | 0.01 |
| Total O site | 5.95 | 0.02 |

#### Total Cations

| Total Wt% (plus H₂O) | Mean | Standard deviation |
|----------------------|------|--------------------|
| 98.42                | 0.77 |

### Vacancies

- 6-(Fe²⁺Fe³⁺Mg)/2 (Inoue et al., 2009, 2018) | 0.08 | 0.02 |
- (Al¹³-Al¹⁰-Na-K)/2 (Lanari et al., 2014) | 0.05 | 0.02 |
- (Al¹³-Al¹⁰)/2 (Bourdelle et al., 2013) | 0.05 | 0.02 |

### SEMI-EMPIRICAL THERMOMETRY

| Geo thermometer | Mean | Standard deviation |
|-----------------|------|--------------------|
| Inoue et al. (2018) | 327  | 9                  |
| Lanari et al. (2014) | 407  | 17                 |
| Bourdelle et al. (2013) | 372  | 24                 |

### SUMMARY (Fig. 8B)

| V₂ FORMATION TEMPERATURE (V₂ CENTRE + HOSTROCK) | Geo thermometer | Mean | Standard deviation |
|--------------------------------------------------|-----------------|------|--------------------|
| Inoue et al. (2018) | 318  | 12 |
| Lanari et al. (2014) | 369  | 23 |
| Bourdelle et al. (2013) | 338  | 27 |