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Massive formation of lawsonite in subducted sediments from the Schistes Lustrés (W. Alps): implications for mass transfer and decarbonation in cold subduction zones

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ABSTRACT

This study investigates the reactions allowing crystallization of large amounts of lawsonite ($CaAl_2Si_2O_7(OH)_2 \cdot [H_2O]$) found in calcschists metamorphosed in a subduction zone setting. Previous studies of lawsonite-forming reactions in metasediments have highlighted its importance for the large-scale budget of CO_2, as the calcium required to form lawsonite is thought to originate from decarbonation reactions. Yet, thermodynamic modelling as well as isotopic measurements have indicated that 80 to 90% of the carbon is retained in sediments, and there is no evidence of major decarbonation in the field. As lawsonite contains abundant H_2O and has a large stability field, understanding its crystallization is also important to assess fluid migration and mass transfer in a critical part of the subduction system where slow earthquakes are nucleating (such as LFEs or ETS).

The upper units of the blueschist facies metasediments of the Schistes Lustrés complex (Western Alps), buried to depths of ~ 30-40 km, have been selected as an ideal case study as they host up to 40 vol.% of lawsonite. Lawsonite is found crystallized over several generations, in veins, in reactions fronts as well as in the rock matrix. Three types of lawsonite were identified. The most abundant type of lawsonite is associated with quartz and ankerite. This mineral assemblage formed from phyllosilicates and calcite in a continuous reaction: chlorite + calcite + kaolinite = lawsonite + ankerite + quartz + H_2O. According to thermodynamic modelling, this reaction is restricted to a narrow pressure-temperature domain and initiates around 180°C and 0.4 GPa. Lawsonite is also observed and predicted to grow from Fe-Mg-carpholite at higher metamorphic conditions. None of these reactions allow efficient net export of carbon, as one carbonate replaces another, and most observations are consistent with closed-system behaviour at outcrop-scale, in agreement with geochemical studies. At sample-scale and below, crystallization of lawsonite is linked to homogenization of carbonate and pelitic domains in geologically fast reactions. Dissolution of calcite produces reactive fluids prone to react with pelitic domains and crystallize lawsonite and another carbonate. Although metamorphic veins are ubiquitous to the upper units of the Schistes Lustrés Complex, most of them result from local reactions and do no indicate large-scale mass transfer.

Keywords: lawsonite, metasediments, fluid/mass transfer, decarbonation, Schistes Lustrés, seismogenic depths

1. INTRODUCTION

Sediments buried in subduction zones contain large amounts of volatiles (up to ~7 wt.% H_2O and 30 vol.% carbonates according to Plank and Langmuir, 1998; Rea and Ruff, 1996; Clift, 2017). Understanding their behaviour is key to assess the fate of carbon and fluids in subduction settings (Gorman et al., 2006; Bebout, 2007; Cook-Collars et al., 2014; Kelemen and Manning, 2015; Dragovic et al., 2018; Plank and Manning, 2019). Metamorphosed sediments also play an important role along the subduction interface (Agard et al., 2018; Raimbourg et al., 2018): production and expulsion of metasediment-derived fluids is proposed to control the periodicity of slow earthquakes at the base of the seismogenic zone (and more specifically around depths of 35 km) through changes in permeability and dissolution-precipitation creep (Fig. 1a; Rogers and Dragert, 2003; Audet et al., 2009; Osei Tutu et al., 2018; Behr and Becker, 2018). The associated element mobility, metasomatism and changes in rheology must be extensive, for example Audet and Bürgmann (2014) suggest km-scale transfer of silica from metasediments to the overriding plate based on high compressional- to shear-wave velocity ratios (Vp/Vs). The interplay between deformation, mineral reactions and

rheology along and above the plate interface, however, remains largely unknown (Breeding and Ague, 2002; Saffer and Tobin, 2011; Bebout and Penniston-Dorland, 2016).

One target outcropping unit to study this interplay is the Schistes Lustrés complex of the Western/Central Alps and Corsica (Figs. 1b-d), an accretionary prism including several units and subunits preserving seafloor material, i.e. calcschists, metapelites and remnants of crustal material (e.g., Tricart and Lemoine, 1986). Metamorphism of the Schistes Lustrés originates from subduction during closure of the Liguro-Piemontese ocean (see e.g., Lagabrielle and Lemoine, 1997). The selected area belongs to the uppermost units of the Schistes Lustrés complex, which experienced blueschist-facies metamorphism with peak conditions between 1.2 GPa – 300°C and 1.9 GPa – 450°C (yellow dots; Fig. 1d). Mass transfer via metamorphic fluids appears extensive, as shown by the presence of ubiquitous veins bearing high-pressure minerals (Goffé and Chopin, 1986; Agard et al., 2001b, 2009; Bousquet et al., 2002, Plunder et al., 2012; Vitale Brovarone et al., 2014).

A notable feature of the upper unit of the Schistes Lustrés complex is the high abundance of lawsonite ($CaAl_2Si_2O_7(OH)_2 \cdot [H_2O]$), commonly greater than 20 vol.% and frequently associated with quartz (Caron, 1974; Sicard-Lochon, 1987; Agard et al., 2000). With 12 wt.% H_2O, lawsonite is a major carrier of H_2O. Lawsonite is stable up to ultra-high pressures, implying it may release water at depths greater than 200 km in cold subduction zones (Schmidt and Poli, 1998, 1994; van Keken et al., 2011; Faccenda, 2014). Lawsonite allows for many cation exchanges, especially in its large Ca site prone to
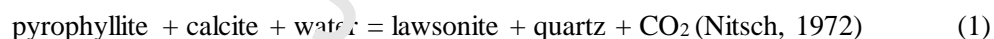
strain (Martin et al., 2011; Vitale Brovarone and Beyssac, 2014; Dubacq and Plunder, 2018). It is

thought to play a key role in trace element cycling into the deep Earth (Schmidt and Poli, 1998, 1994;

Zack and John, 2007; Tsujimori and Ernst, 2014; Fornash et al., 2019).

Yet the formation of lawsonite remains poorly understood and models are fraught with contradictions

(see Clarke et al., 2006). Explaining large modal amounts of lawsonite in metasediments is

problematic due to the low amounts of Ca initially present in pelitic rocks. Decarbonation and

metasomatism are necessarily invoked processes, with a huge impact on modelling the mobility of

carbon in its deep cycle (Kerrick and Connolly, 2001; Gorman et al., 2006; Kelemen and Manning,

2015; Stewart and Ague, 2018). Local accumulations of lawsonite in hybrid metasediments from

Corsica ('lawsonitites'; >75 vol.%) have been interpreted as the result of large-scale metasomatism

through serpentinite-derived metasomatic fluids, with and without decarbonation (Vitale-Brovarone et

al., 2014, Piccoli et al., 2016; respectively).

In contrast to Corsican lawsonitites, the lack of significant isotopic shift in volatiles (C, O, H) from the

Schistes Lustrés suggests limited external fluid infiltration, except possibly along tectonic contacts

(Henry et al., 1996; Cook-Kollars et al., 2014; Collins et al., 2015; Jaeckel et al., 2018; Epstein et al.

2019). Fluid-mobile elements (e.g., H, N, B, Li, Ba, K, Rb, Cs) overall show little evolution along

comparable rocks in the Cottian Alps (Busigny et al., 2003; Bebout et al., 2013; Barnes et al., 2019).

Most fluids percolating through these rocks appear internally-derived and/or derived from similar

lithologies, in support of closed-system behaviour at the meter scale and possibly up to 100 meter-

scale, at least for components other than H_2O. This is in stark opposition to large-scale element

mobility and extensive metasomatism.

Given the volumetric extent of the Schistes Lustrés metasediments, understanding the formation of

lawsonite in terms of reactions, decarbonation, loss or gain of water and silica is crucial to quantifying

the element budget along and across the plate interface. The lawsonite forming reaction is not readily

accessible since lawsonite rarely hosts silicate mineral inclusions and is generally poorly preserved in

exhumed rocks. Lawsonite is commonly pseudomorphed and replaced by a variety of minerals,

including phyllosilicates (mostly chlorite and white mica) and epidote, during burial (as in Syros and

Turkey: Hamelin et al., 2018; Fornash et al., 2019) and exhumation (e.g., in the Cottian Alps: Sicard-

Lochon, 1987; Plunder et al., 2012). Reactions suggested so far for lawsonite crystallization in

metasediments include:

pyrophyllite + calcite + water = lawsonite + quartz + CO_2 (Nitsch, 1972)   (1)

$$Al_2Si_4O_{10}(OH)_2 + CaCO_3 + H_2O = CaAl_2Si_2O_7(OH)_2 \bullet [H_2O] + 2\ SiO_2 + CO_2$$

kaolinite + aragonite = lawsonite + CO_2 (Cook-Kollars et al., 2014)   (2)

$$Al_2Si_2O_5(OH)_4 + CaCO_3 = CaAl_2Si_2O_7(OH)_2 \bullet [H_2O] + CO_2$$

Both reactions involve decarbonation and production of CO_2, since Ca is mobilized from calcium carbonate. Lawsonite, however, was shown experimentally to be unstable in CO_2-rich fluids (reaction 1 being valid for $XCO_2<0.05$; Nitsch, 1972). Based on thermodynamic modelling of reaction (2), Cook-Kollars et al. (2014) suggested that only moderate amounts (10-20 vol.%) of lawsonite could be produced given the bulk composition of the Schistes Lustrés and that the Schistes Lustrés retained 80 to 90% of their initial C content. Yet larger amounts of lawsonite pseudomorphs are found in most of these rocks (Caron, 1974; Sicard-Lochon, 1987), and whether lawsonite formation requires addition of H_2O to the sediments or not is unknown. Based on field, mineralogical and micro-structural observations together with geochemical analysis, the present contribution documents lawsonite concentrations along a representative transect of the uppermost units of the Schistes Lustrés. This study aims at explaining how such concentrations have been reached. Mineral reactions forming lawsonite and the scales of associated fluid/mass transfer are critically discussed to shed light on the involvement of large-scale transfer, silica deposition, and decarbonation.

2. GEOLOGICAL SETTING

2.1 The Schistes Lustrés paleo-accretionary complex in the Alpine orogenic belt

The Schistes Lustrés complex belongs to the internal domain of the Alpine orogenic wedge (Figs. 1b,c, inset; for more details on the overall Alpine structure, see: Coward and Dietrich, 1989;

Lagabrielle and Lemoine, 1997; Rosenbaum and Lister, 2005; Handy et al., 2010). The Western Alps

formed as a result of east-dipping, slow and cold subduction (~8°C/km at a maximum 2 cm/year;

Agard et al., 2001a; Le Pichon et al., 1988; Lapen et al., 2003) of the Valais and Liguro-Piemontese

slow-spreading oceans (Lagabrielle and Cannat, 1990). Oceanic subduction lasted from c. 100 to 40

Ma and was followed by continental subduction and collision of the European plate with Apulia.

The Schistes Lustrés complex is mostly made of metasediments of seafloor origin showing

alternations of thinly bedded carbonate-rich and pelitic layers. It also contains slivers and blocks of

various scales, more abundant in the lower units, of mafic and ultramafic bodies from the Liguro-

Piemontese ocean (Fig. 1b; Lagabrielle and Polino, 1985; Lagabrielle et al., 2015). The Schistes

Lustrés sediments were deposited from the Upper Jurassic (~150 Ma, De Wever and Caby, 1981) to

the Late Cretaceous (~70-65 Ma, Lemoine et al., 1986) and formed a 100-400 m thick sediment pile

(De Wever and Caby, 1981). During subduction and exhumation, metasediments were intensely

folded, leading to an important thickening of the initial sediment pile (Agard et al., 2002).

Approximately 30 to 50% of the total sedimentary cover was eventually exhumed, much more than its

oceanic basement (<5 %; Agard et al., 2009). Based on lithological differences in the Schistes Lustrés

complex, three to four main units have been distinguished (Lagabrielle, 1990; Deville et al., 1992;

Fudral, 1996; Agard et al., 2001a; Tricart and Schwartz, 2006; Lagabrielle et al., 2015). Plunder et al.

(2012) showed that the upper, median and lower units experienced increasing metamorphic conditions.

Thermobarometric estimates show an eastward increase from the upper (1.2 GPa – 300°C west of

Fraiteve) to the lower units (2.1 GPa – 500°C) as shown in figure 1d (Agard et al., 2001a; Beyssac et

al., 2002; Plunder et al., 2012).

2.2 Tectono-metamorphic evolution along the Cottian Alps transect

The Schistes Lustrés complex recorded several deformation stages which are well constrained in terms

of age and pressure-temperature (P-T) conditions (Agard et al., 2001a, 2002; Tricart and Schwartz,

2006). This study focusses on the upper unit of the Schistes Lustrés (LPU) along a ~15 km SW-NE

traverse between Mt. Fraiteve and Colle delle Finestre, in the French-Italian Cottian Alps (Figs. 1b, c;

Caron, 1974; Polino et al., 1984). Four deformation stages are recognized in the LPU (Agard et al.,

2002). The first episode D1 is linked to peak or near-peak burial, as indicated by the crystallization of

Fe-Mg-carpholite and lawsonite, and is thought to correspond to recumbent folding and thin-skinned

stacking of several slices under blueschist facies conditions at ~60-50 Ma. Associated tectonic patterns

are largely erased. A second fabric D2 is dated between 51 and 45 Ma and corresponds to early stages

of exhumation under blueschist facies conditions (~1.2 GPa – 350°C in the area of Monte Triplex). It

is marked by dominant top-to-the east shear senses. A third stage D3, characterized by top-to-the west

ductile to brittle deformation in greenschist facies conditions (~0.7 GPa – 300°C), occurred between

38 and 35 Ma. The final stage D4 (and D5 identified in places) corresponds to brittle deformation

marked by local extension, probably c. 28-20 Ma (Tricart and Schwartz, 2006).

3. FIELD CHARACTERIZATION AND SAMPLING

Lithologies and mineral abundances were investigated along the 15-km traverse through the LPU unit

(Fig.1b). While detailed observations and sampling were carried out along the whole section, this

study documents in greater details the ~200 m long Mt. Triplex locality (Figs. 2, 3; metamorphic pick

conditions of 1.6GPa – 350°C, Fig. 1d).

3.1 Lithologies and distribution of hydrous metamorphic minerals

Figure 2 presents the five types of lithologies distinguished between carbonate-rich and pelite-rich

layers in the LPU unit. Amounts of lawsonite and Fe-Mg carpholite vary systematically between rock

types, although lithologies appear rather similar at first examination. The pelitic endmember (lithology

1) is composed of dark, organic-rich and phyllosilicate-rich material where carbonate layers are absent

or not visible at the cm scale (Figs. 2a, b). By contrast, the carbonate endmember (lithology 5; Fig. 2a)

consists of metric (1-5 m.) carbonate horizons, often with subordinate horizons containing

phyllosilicates (<5 vol.%; Fig. 2b). Lithologies 2, 3 and 4 (hereafter referred to as calcschists) are

composed of a mixture of pelitic layers and carbonate beds in various proportions (Figs. 2a, b).

Lithology 2 contains thinly bedded, typically cm-scale carbonate layers in a shaly matrix (pelite to

carbonate volume ratio ~3:1). Lithology 3 shows regularly alternating pelitic and carbonate horizons with roughly equivalent thicknesses (commonly 5-10 cm, and up to ~20 cm). Lithology 4 is characterized by more compact calcschists in which phyllosilicate-rich layers do not exceed cm-scale (pelite to carbonate ratio ~1:3).

The metasediments contain significant amounts of hydrous minerals typical of blueschist facies metamorphism such as lawsonite and Fe-Mg-carpholite, or preserve evidence of their former presence. Fe-Mg-carpholite is much more sensitive to retrogression and alteration than lawsonite. Fe-Mg-carpholite is readily replaced by chlorite and white mica during exhumation and frequently only preserved as micrometric needles in quartz (Chopin and Goffé, 1986; Agard et al., 2001b). Lawsonite is commonly pseudomorphed, allowing for minimum estimates of its former abundance. Figure 2b displays modal amounts of lawsonite determined in the field. Lawsonite is present in all lithologies but mostly found in calcschists among which it is heterogeneously distributed: it makes up to 40 vol.% of rock type 3 (e.g., at Mt. Triplex and Genevris). Fe-Mg-carpholite is mainly observed in lithology 1, although it may have occurred in other lithologies prior to retrogression. In general, these two minerals are not observed coexisting in hand specimen or thin-section. Along the transect between Mt. Fraiteve and the Assietta pass (Figs. 1b-c, 2c), most rock types correspond to lithologies 2, 3 and 4 (calcschists). Some locations present much more pelitic material classified as lithology 1 (Mt. Fraiteve and Assietta pass). The carbonate-rich endmember of our classification (lithology 5) is only sparsely

encountered; these rocks are found in greater proportions in (and are typical of) the median unit of the

Schistes Lustrés further east.

3.2 Outcrop-scale observations in Triplex

Detailed petrological observations and sampling were performed along the 200 m long, relatively

continuous and homogeneous exposures of Mt. Triplex (along the dirt road and immediately to the

west, Fig. 3). Sampling sites are shown on figure 3a. Observations and representative sampling were

carried out with particular attention to ensure consistent scale transfer from the hm-scale (Figs. 3a, b)

to the cm-scale (Figs. 3c-f, 4, 5, 6). Outcropping rocks are essentially made of lithology 2. They are

pervasively deformed by hundred meter-long shear bands, with cm-scale penetrative shear structures

(C/S or C' bands, vein rotations) consistent with top-to the east deformation attributed to D2. These are

interpreted as marking the onset of exhumation (Agard et al., 2001a). The main schistosity visible on

figure 3 is a composite D1 D2 structural pattern. The D2 shear bands are cross-cut by later, ductile to

brittle and mostly west-vergent planes, corresponding to the D3 deformation stage (Fig. 3d), which are

locally east-vergent when reworking earlier D2 structures. Late, *en échelon* calcite ± quartz ± chlorite

veins are associated with this D3 stage. Metasediments are highly deformed and show many m- to cm-

scale folds of the schistose matrix, along with multiple vein generations. The carbonate layers (~30

vol.%) are heterogeneously distributed across the outcrop. Ankerite-rich reddish haloes are commonly

observed between carbonate and pelitic horizons (Figs. 4a, b, d). Lawsonite is present in the schistose

host-rock (Figs. 3e, 4) and in quartz ± ankerite veins (Fig. 3f). Lawsonite is by far the predominant

metamorphic hydrous phase (rare Fe-Mg-carpholite pseudomorphs are found in some layers), locally

up to 45 vol.% of the host rock.

4. LAWSONITE TYPES

At macroscopic scale, three types of lawsonite have been characterized based on their texture,

association with other minerals, and presence in the schistose matrix or high-pressure veins (Figs. 3e,

f, 5). For simplicity, these different types are termed LwsA, LwsB and LwsC. The lettering does not

imply cross-cutting relationship or relative chronology as these remain unclear, as detailed below.

4.1 Calcschist lawsonite (LwsA in lithologies 2 and 3)

LwsA, by far the most common type of lawsonite in this area, is mostly found in pelitic calcschists

interlayered with carbonate-rich horizons (Figs. 3e, 4a) and makes up to 30% of lithology 2 and 40%

of lithology 3. In addition to lawsonite, the pelite-rich layers are commonly composed of quartz (20 to

30%), calcite (0 to 30%), ankerite (< 20%), phengite (< 20%), chlorite (< 10%) and organic matter

found as inclusions (Figs. 4e, f, g). LwsA forms millimetric to centimetric black prisms (Figs. 4c-g),

generally well-preserved, texturally associated with quartz and oxidized reddish ankerite (Fig. 4d).

Ankerite is found in carbonate layers and all across the pelitic layers. Ankerite is particularly

concentrated at the edge of folded carbonate-rich layers where it forms diffuse, centimetre-thick

domains along lithological contacts (Figs. 4a, b). Well-defined horizons of ankerite are less frequent

(Fig. 4d). The association of LwsA and ankerite is maximum at the interface between carbonate and

pelitic layers, and decreases towards pelitic domains and towards thick carbonate horizons. The

textural relationships between LwsA and ankerite are best preserved in thin carbonate layers (Fig. 4d).

Figures 4e-f-g show fractured, organic-matter-rich, dark lawsonite crystals overgrown with pale

newly-formed lawsonite, indicating incremental growth. When pseudomorphed, LwsA is replaced by

a mixture of chlorite, phengite and calcite, as described in previous studies (Sicard Lochon, 1987;

Vitale-Brovarone et al., 2014).

4.2 Lawsonite-bearing veins (LwsB and LwsC)

The second type of lawsonite (LwsB) is observed in pluri-centimetric to metric quartz veins following

the main schistosity (Fig. 5a). LwsB forms elongated, cream-coloured crystals with long axis parallel

to vein selvages and aligned with quartz fibres (Figs. 5a-c). Crystal size reaches 20 cm long in places.

LwsB shows incremental growth and also crystallized in pressure shadows around boudinaged quartz

veins (Figs. 5c-e). Lawsonite and quartz often evidence ductile deformation in LwsB-bearing veins

(Fig. 5d), advocating for syn-deformation incremental growth and mode II vein opening. LwsB is

generally only associated with quartz, but ankerite crystals have been observed in places, in particular

in the vicinity of pelitic horizons (Fig. 5e). The third type of lawsonite (LwsC) is observed in

millimetric to centimetric tensile veins (Fig. 5f, g) cutting across the host rock. They show the same

cream-coloured, elongated fibres as LwsB-bearing veins but are systematically associated with ankerite and quartz. The LwsC-bearing veins are particularly abundant in calcschists hosting LwsA and mostly located around fold hinges (in extrado domains) and near larger LwsB-bearing quartz veins. LwsC-ankerite-quartz fibres are perpendicular to the vein walls and these veins are dominated by mode I opening (Figs. 5f, g). Sometimes, these veins cross-cut LwsB-bearing veins and apparently opened in a single stage, possibly indicating shorter-lived tensile events than for LwsB formation. Early veins transposed along the schistosity have been identified in places as former, strongly deformed LwsC-bearing veins, suggesting that only the latest generation of LwsC-bearing veins is observed. Local accumulations of LwsB- and LwsC-bearing veins are found in m-scale domains scattered around Mt. Triplex, in lithologies where LwsA is also abundant (Figs. 3d, f).

5. PETROGRAPHY AND MINERALOGY

5.1 Textural relationships

In the calcschists, LwsA forms euhedral rhombi to oval crystals (Figs. 6a, d, e). Inclusions of organic matter, responsible for the black colour of hand specimens, are concentrated in LwsA cores (Figs. 4e-g, 6d). These inclusions form trails related to deformation accompanying burial and may record early episodes like D1 (Caron, 1974). Inclusion trails are found in adjacent crystals of lawsonite and ankerite (Fig. 6a). As for outcrop-scale observations, systematic relationships are found between

lawsonite, ankerite and quartz. These three minerals are commonly found in apparent textural equilibrium (Fig. 6) and included in one another: figure 6f shows LwsA and quartz included in rhombic ankerite crystals, and figure 6c shows ankerite and quartz included in lawsonite (see also Sup. mat.1, 3). The calcite - chlorite assemblage cross-cuts domains with lawsonite, ankerite and quartz. In carbonate-rich layers, the habitus of LwsA is different from that in the adjacent pelite-rich schist (Figs. 6b, c). Crystals are much smaller, better preserved and do not contain organic matter inclusions. Lawsonite crystals in veins never contain organic matter inclusions. Fine-scale alternations of LwsC, quartz and ankerite are observed along small veins, highlighting their close association and co-crystallization. Lawsonite is only partially preserved in LwsC veins (LwsB is better preserved in veins). Crystals of LwsC are fractured, replaced and pseudomorphed by a fine mixture of chlorite, phengite and calcite along cracks.

The amounts of ankerite and lawsonite were estimated for LwsA, LwsB and LwsC-bearing thin sections from optical microscopy images (Fig. 7). LwsA-bearing rocks show Lws/Ank ratios varying around 1.5. Vein samples with LwsB and LwsC show more scattered ratios, between 1 and 3 for LwsB and 0 and 1 for LwsC. Since LwsC are much more overprinted by phengite and chlorite than LwsA, the LwsC/Ank ratios were corrected using pseudomorphs (see Sup. mat. 2). The corrected LwsC/Ank estimates plot around 1.5, as for LwsA/Ank. Large variations in LwsB/Ank ratios reflect the largely varying amounts of ankerite (Figs. 7, 5a, e). Most phyllosilicates appear linked to peak or retrograde

metamorphism. Phengite appears in the main foliation as well as cross-cutting it. Chlorite is found in

lawsonite pseudomorphs together with phengite and calcite, a typical lawsonite retrogression reaction

in the SL (Sicard-Lochon, 1987). Chlorite is also found as retrogression product between lawsonite

and ankerite.

5.2 Rock and mineral composition

Whole-rock major element chemistry was performed with an Agilent 5100 ICP-OES at the ALIPP6

analytical facility (Sorbonne Université, Paris) after acid attack of finely-ground samples. A HF-HNO$_3$

mixture was used for dissolution of samples in closed tubes over 24 hours, and boric acid added

immediately after opening to prevent loss of silicium. Dilution and measurement followed shortly

(within 24 hours). Analytical uncertainties are estimated to be better than 5% of the measured value.

Loss on ignition was obtained by mass loss after heating approximately 4 grams of samples at 110°C

for one night for adsorbed water and at 1000°C for three hours for remaining volatiles. Mineral

analysis was carried out at the CAMPARIS facility (Sorbonne Université, Paris) with a CAMECA

SX-FIVE electron microprobe and the data reducing method of Pouchou and Pichoir (1991).

Analytical conditions were 15 kV-10 nA in WDS mode, for analysis of major elements. Conditions

were changed to 25 kV and 100 nA when measuring Sr and Ti, which are in low concentrations. Fe$_2$O$_3$

(Fe), MnTiO$_3$ (Mn, Ti), diopside (Mg, Si), Cr$_2$O$_3$ (Cr), orthoclase (Al, K), anorthite (Ca) and albite

(Na) were used as standards for elements in parentheses. Representative analyses are provided in Table 1 for lawsonite. All Fe is assumed to be in divalent state and is expressed as FeO.

Figure 8a shows the composition of ankerite, chlorite and white mica. Variations in minor to trace element concentrations of lawsonite are shown in figures 8b, c, d. Figure 9 shows selected chemical maps for major and minor to trace elements. Ankerite shows a composition close to the ideal $Ca_1Fe_{0.5}Mg_{0.5}(CO_3)_2$ with very constant Fe/Mg ratio around 1 (Fig. 8a; Table 1). In places, Mn zoning is observed (Fig. 9d), with rims enriched in Mn. White mica are of muscovite and phengite type (Fig. 8a), a solid solution between muscovite and celadonite with minor (~10%) pyrophyllite content. Crystals with the highest celadonite content probably preserve the high pressure equilibrium stage (Agard et al., 2001b). Chlorite is fairly homogeneous and compares well with previous data, plotting in a restricted composition interval of Figure 8a at low sudoite content. The Mg/Fe ratio of chlorite is similarly homogeneous. Together with textural evidence, this points to chlorite being mostly retrograde (Fig. 9a). Lawsonite is close to its ideal composition, and no difference in major elements was found between the various lawsonite types and samples. Variations in trace amounts of Ti and Sr were detected (Figs. 8b, c, d, 9b, c; Table 1). Optically-zoned LwsA appears also zoned in Ti and shows higher Ti content in the core, linked to hour-glass zoning (Figs. 8b, 9b; see Sup. mat. 3). Crystals of LwsA also show enrichment in Sr at their rims, while LwsA cores are Sr-poor (Figs. 8b, 9b, c). Similarly, LwsC crystals are either slightly enriched in Ti or in Sr (Fig. 8d). Only LwsB can

reach higher Sr contents and contain both Sr and Ti (Fig. 8c).The close association of lawsonite,

ankerite and quartz is readily apparent from chemical mapping (Fig. 9a).

6. DISCUSSION

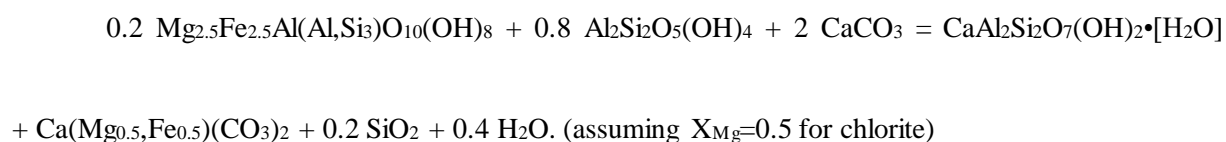### 6.1 Co-crystallization of lawsonite and ankerite

Co-crystallization of lawsonite, quartz and ankerite is supported by their close association, both as

intricate, parallel fibres seeded in vein walls (LwsC; Figs. 5f, g) and in the host-rock (LwsA-rich

domains, Figs. 4, 6). The abundance of lawsonite in calcschists (lithologies 2 and 3) with mixed

carbonate-rich and pelite-rich layers is consistent with the fact that the latter contain most of the

cations needed for lawsonite crystallization, i.e. Al, Si, H. Calcium, however, is not present in

sufficient amounts in pelite-rich layers to explain the formation of up to 30-40 vol% of lawsonite. This

requires adding massive amounts of Ca to pelitic domains via either (i) infiltration of external Ca-rich

fluids, (ii) local decarbonation and/or (iii) reaction between carbonate and pelitic layers.

The first hypothesis is not supported by isotope data on C-O-H which should be concomitantly altered

(Henry et al., 1996; Cook-Kollars et al., 2014). Field and petrographic evidences do not support

significant decarbonation: there is crystallization of ankerite and overall no major dissolution of

carbonate. The third hypothesis is favoured: replacement of primary calcite from the carbonate-rich

lithologies by ankerite allows substituting half of the initial Ca amount with Fe and Mg, with zero net

export of carbon. The net reaction releases sufficient Ca to form lawsonite in the more pelitic layers

from mixed lithologies. An indication on the spatial range of element transfer is provided by the very

low content of lawsonite in pelitic lithologies with no carbonate horizon within a few meters (almost

zero in lithology 1).

Element transfer through dissolution-precipitation reactions explains the systematic association of

lawsonite with ankerite at all scales (e.g., Figs. 4a-d, 5f, g, 6b-f) and the presence of ankerite haloes

between pelitic and carbonate horizons (Figs. 4a, b). Based on (i) observations from this study and

former descriptions (Caron, 1974; Sicard-Lochon, 1986; Caron et al., 1987), in particular that reactants

may have been somewhat similar to minerals overgrowing lawsonite and ankerite on exhumation (i.e.,

chlorite, calcite Fig. 9a), and (ii) the large amounts of hydrous aluminosilicates present in common

sediments (Planck and Langmuir, 1998), lawsonite and ankerite are expected to form at the expense of

chlorite, calcite and kaolinite, themselves formed at the expense of former detrital and early diagenetic

phases. The observed overall 1.5 volume ratio of lawsonite to ankerite (controlled by LwsA-bearing

rocks) corresponds to a 1:1 Lws/Ank molar ratio. This points to a reaction such as:

chlorite + kaolinite + aragonite = lawsonite + ankerite + quartz + water (3)

$0.2\ Mg_{2.5}Fe_{2.5}Al(Al,Si_3)O_{10}(OH)_8 + 0.8\ Al_2Si_2O_5(OH)_4 + 2\ CaCO_3 = CaAl_2Si_2O_7(OH)_2 \bullet [H_2O]$

$+ Ca(Mg_{0.5},Fe_{0.5})(CO_3)_2 + 0.2\ SiO_2 + 0.4\ H_2O.$ (assuming $X_{Mg}=0.5$ for chlorite)

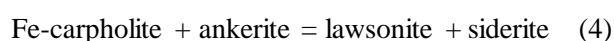## 6.2 Thermodynamic modelling of formation of the lawsonite-ankerite assemblage

In order to locate reaction (3) in P-T space, a first pseudosection was computed using a bulk

composition corresponding to the stoichiometry of reaction (3) assuming excess water in the

CaFMASHC system (Fig. 10a). Computations were made using Perple_X version 6.8.4 with the

updated database of Holland and Powell (1998) and corresponding solution models (for chloritoid,

dolomite, Fe-Mg-carpholite, phengite) except for chlorite (after Holland et al., 1998). As shown on

figure 10a, during burial along a 8°C/km metamorphic gradient, the lawsonite-forming reaction starts

at 170°C and 0.44 GPa (i.e., ~15 km depth) and is completed across a restricted P-T range ending at

190°C (Fig. 10b). This reaction forms ~60 vol.% of lawsonite. In this case all lawsonite crystals would

be formed during a continuous reaction occurring over a short period of time (a minimum of ~250 000

years at a convergence rate of 2 cm y^{-1}).

In order to quantify the extent to which lawsonite and ankerite may co-crystallize from the interaction

between carbonate and pelitic-rich layers, the mineralogical evolution of the calcschists has been

modelled in the KCaFMASHC system using the same thermodynamic set up and water saturated

conditions. Two pseudosections were built using compositions representative of typical pelitic and

carbonate-rich domains (i.e., on either side of the lithological boundary shown in figure 4a). Sample

SL16-11c, a type 3 calcschist from Mt. Triplex, was separated in pelitic (R11SCH) and carbonate-rich

(R11CARB) domains. For these two bulk rock compositions, CO_2 and H_2O are declared as

components. CO_2 content is inferred from the CaO content, assuming that carbonates host all the CO_2 of the rock. H_2O content is fixed at 8 wt.% in R11SCH and 5.2 wt.% for R11CARB. These values ensure water saturation across the whole P-T domain, yet represent the minimum H_2O content to reach water saturation at low P and T conditions. They are fixed to allow chlorite and kaolinite to form at P-T ≤ 0.2 GPa – 150°C while minimizing the amount of stilbite which take over for greater H_2O contents (see Sup. mat. 4). The amount of stilbite in itself does not affect the stability field of lawsonite but the presence of excessive stilbite (hosting Ca instead of calcite) would imply an additional lawsonite-forming reaction with addition of CO_2, which was deemed unlikely. It is also noted that H_2O and CO_2 are immiscible at these conditions (so that presence of CO_2 will not modify water activity, equal to 1 here) and that the mixing model of Holland and Powell (2003) does not reproduce this accurately (see Dubacq et al., 2013). The water content does not affect significantly phase relations at higher grade. It is stressed that the lingering presence of detrital minerals, unobserved in the present rocks but likely dominant in the lowest-grade parts of the pseudosections, will have a greater impact on the reactions experienced by the rocks than details of the modelling before appearance of lawsonite.
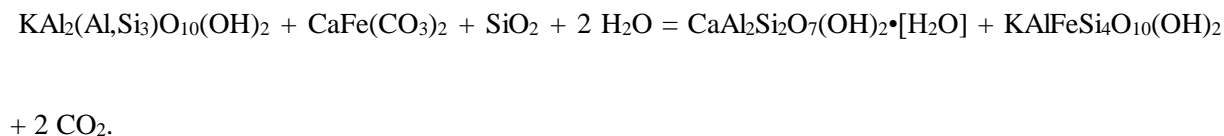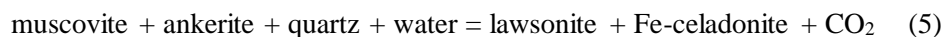
Pseudosections predict up to 34 vol.% of lawsonite for the pelitic domains and 23 vol.% for carbonate-rich domains at peak burial conditions (1.6 GPa and 350°C; Figs. 10c, d). Calculated Lws/Ank volume ratios are close to 1.5 in both cases but this ratio increases slightly close to peak conditions for the pelitic domain. Most of the lawsonite forms through reaction (3) with ankerite and quartz at the

expense of chlorite, kaolinite and calcite, which releases water. This mechanism predominates in carbonate-rich domains. In pelitic domains, lawsonite formation continues during breakdown of kaolinite and chlorite, which is expected to form Fe-Mg-carpholite above 210°C. Above 330°C, a continuous reaction forms lawsonite and siderite from Fe-Mg-carpholite (which provides Al and Si) and ankerite (which becomes the source of Ca after exhaustion of calcite, Figs. 10c, e). The corresponding reaction, written for end-members in the CaFASHC system for simplification, is:
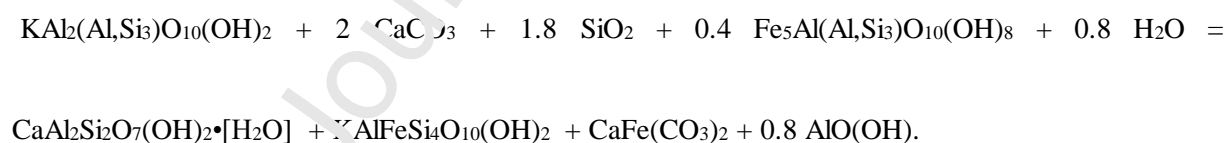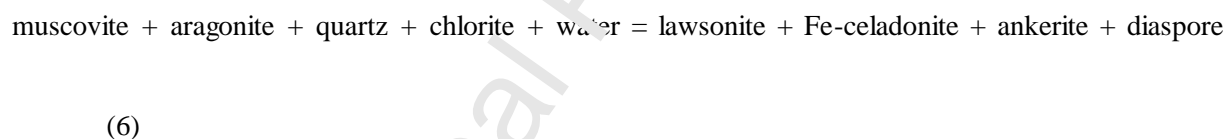
Fe-carpholite + ankerite = lawsonite + siderite   (4)

$FeAl_2Si_2O_6(OH)_4 + CaFe(CO_3)_2 = CaAl_2Si_2O_7(OH)_2 \bullet [H_2O] + Fe_2(CO_3)_2$

Note that in reaction (4), Fe-Mg-carpholite is then consumed: in addition to being much more sensitive to retrogression and alteration than lawsonite, this may explain why both minerals are very rarely found in equilibrium (Plunder et al., 2013). Further quartz production accompanies to the disappearance of kaolinite above 310 °C (Fig. 10e).

The Tschermak exchange in micas ($2\,Al^{3+} = (Mg^{2+}, Fe^{2+}) + Si^{4+}$), which releases Al and consumes Mg, Fe and Si at constant amount of mica, could also contribute to lawsonite formation, as proposed by Cook-Kollars et al. (2014). In pelite-rich domains, the reaction, balanced here for phengite end-members in the KCaFASHC system, would produce CO_2 and consume H_2O, as suggested by Cook-Kollars et al. (2014):

muscovite + ankerite + quartz + water = lawsonite + Fe-celadonite + CO_2 (5)

$KAl_2(Al,Si_3)O_{10}(OH)_2 + CaFe(CO_3)_2 + SiO_2 + 2\ H_2O = CaAl_2Si_2O_7(OH)_2 \cdot [H_2O] + KAlFeSi_4O_{10}(OH)_2 + 2\ CO_2$.

However, such reaction is not supported in our modelling, as shown by the parallel modal evolution of lawsonite, ankerite and quartz until 330°C (Fig. 10e). In carbonate domains, the continuous reaction producing small amount of lawsonite and ankerite above 180°C consumes quartz as well as chlorite and aragonite (as in reaction (3)). Considering that Al is provided by the Tschermak exchange in micas, the reaction would consume H_2O but not release CO_2:

muscovite + aragonite + quartz + chlorite + water = lawsonite + Fe-celadonite + ankerite + diaspore

(6)

$KAl_2(Al,Si_3)O_{10}(OH)_2 + 2\ CaCO_3 + 1.8\ SiO_2 + 0.4\ Fe_5Al(Al,Si_3)O_{10}(OH)_8 + 0.8\ H_2O = CaAl_2Si_2O_7(OH)_2 \cdot [H_2O] + KAlFeSi_4O_{10}(OH)_2 + CaFe(CO_3)_2 + 0.8\ AlO(OH)$.

Presence of white mica is common in lawsonite-bearing rocks, both as high-pressure phengitic mica and as retrogression products (see Sicard-Lochon, 1986; Agard et al., 2002; Hamelin et al., 2018 among others). However it is noteworthy that the Tschermak exchange is limited here, even in the high-pressure phengites (Fig. 8a), showing that reactions (5) and (6) are subordinate to reactions (3) and (4).

6.3. How progressive is lawsonite crystallization?

The large amounts of lawsonite observed in the Triplex area and lawsonite-ankerite relative proportions point to reaction (3) being prominent. Reaction (3) would account for the formation of most of the massive amounts of lawsonite in the Schistes Lustrés, especially LwsA. The relatively small P-T domain over which reaction (3) takes place suggests one large pulse of crystallization. Overstepping may increase this character by delaying nucleation of lawsonite and favouring faster growth due to a large distance to equilibrium. However this reaction is a medium to high-entropy reaction producing free fluid: $\Delta S^0_r \approx$ -2.3 J/K or -2.5 J/K per mole of oxygen for Mg and for Fe end-members, respectively. This entropy production is ~5 times larger than the andalusite-sillimanite reaction (using the database of Holland and Powell, 2011). Reaction (3) is therefore unlikely to be largely overstepped (see Pattison et al., 2011). The carpholite-consuming reaction (4) appears more sensitive to overstepping ($\Delta S^0 \approx$ .5 J/ /K per mole of oxygen; no fluid production) but continuous lawsonite growth may have benefited from the presence of lawsonite crystals nucleated during reaction (3). In addition, deformation during early stages of burial will increase chances of lawsonite crystallization.

Rapid growth of lawsonite is supported by hourglass Ti zoning in LwsA cores (Figs. 4e-g, Sup. mat. 3). Preferential incorporation of Ti on some crystal faces has been related to out-of-equilibrium Ti incorporation (Dowty, 1976) and compares to sector zoning implying fast growth for lawsonite (Ueno,

1999; Vitale-Brovarone et al., 2014). Rapid growth is also supported by the thin, cm-scale reaction fronts (Fig. 4d) showing high reactivity of the fluid (large Damköhler number, the ratio of reaction rate to element advection rate in fluids; see Skelton et al., 1997; Wigley et al., 2013). In this view the production of lawsonite appears transport-limited.

Therefore the restricted P-T window (hence time) over which lawsonite crystallized is likely underestimated by equilibrium modelling and reaction (3) may be more progressive. First, rock compositions considered in the modelling may represent already evolved or mixed lithologies rather than the exact initial protoliths. Instead, calcium may not be readily available in pelite-rich domains, depending on the distance to carbonate layers (i.e., carbonate/pelitic layers alternation), thus transport mechanisms may significantly delay lawsonite crystallization. Around 200°C, cation diffusivity is sluggish yet at least five orders of magnitude faster in free fluid than grain boundary diffusion (e.g., Carlson, 2010; Verlaguet et al., 2016). Therefore the presence of free fluids in otherwise isolated carbonate domains will be key to initiating reactions. Lawsonite-bearing veins also attest the presence of a free fluid phase. It is noteworthy that dehydration of smectite and replacement by illite, precursor to phengitic mica, provides water in pelitic domains over this temperature range (Vidal and Dubacq, 2009).

This points in turn to additional lawsonite-forming reactions not considered in the modelling. Detrital phases such as feldspar and clay minerals are expected at conditions below appearance of lawsonite.

Their breakdown to mineral assemblages including lawsonite will be progressive. In particular in pelitic domains, the smectite - illite - phengitic mica transition may contribute as a source of Fe and Mg to form ankerite and lawsonite from calcite, as in reaction (3), enlarging the P-T field of lawsonite crystallization. This is estimated as subordinate to reaction (3) because chlorite typically contains 10 to 25 times more Fe and Mg than illitic clays equilibrated around 200°C (Dubacq et al., 2010, their figure 2).

In summary, an array of evidence points to fast initial growth of lawsonite at moderate pressure, at least for most of LwsA (cores), which makes up a large volumetric proportion of lawsonite. More progressive events of crystallization and growth of lawsonite along the prograde path are attested and tentatively set in the frame of deformation events below.

6.4 Different lawsonite types and veins: nature and timing of crystallization

- LwsA: The large amounts of LwsA in pelitic layers (Fig. 3) are consistent with relatively rapid lawsonite growth, possibly as early in the burial history as around 0.4 GPa (Fig. 10). LwsA crystals also evidence incremental growth during deformation as shown by the trails of organic matter preserved in their cores and rotation of the cores with respect to the inclusion-free crystals (Figs. 4e-g, 6d; see also Caron, 1974). This event is possibly associated with D1 deformation phase (Agard et al., 2002). Deformation analysis is unfortunately complicated by the succession of deformation stages and

strain localization in the rheologically weak pelitic layers (Agard et al., 2002). Rapid and incremental

growth could result from response to rearrangement of porosity, fluid pressure fluctuations and/or

seismic cycles (Fagereng et al., 2011; Viete et al., 2018; Ganzhorn et al., 2019).

- LwsC: Small (<5 cm) tensile veins hosting LwsC are best preserved around D2 folds (Figs. 11a, 3d,

5f-g). These veins contain all products of reaction (3), i.e. lawsonite-ankerite-quartz, in proportions

similar to those modelled in pseudosections and with textures evidencing co-crystallization before

transposition into the S2 schistosity (Figs. 5, 11c, d). The mineralogical homogeneity of LwsC veins is

interpreted as reflecting growth during progressive deformation, along the prograde path and from

reaction (3), in deformation-controlled sites. These tensile veins evidence mode I opening and point to

short-lived events, possibly repeated over time (through a delayed reaction (3)? Figs. 11d, 12a). Such

fibrous veins are commonly interpreted as the result of mineral growth in volumetrically limited fluid-

filled dilating space (Bons, 2000; Oliver and Bons, 2001; Verlaguet et al., 2011; Fisher and Brantley,

2014). The constant width of fibres across the vein indicates that crystals grew at the same rate,

independent on the mineral or nuclei orientation, suggesting that their growth was limited by the vein

opening rate. The earliest LwsC veins have probably been largely transposed into the schistosity.

- LwsB: Veins hosting LwsB generally lack ankerite or only in subordinate and variable amounts. The

fact that LwsB veins do not show products of reaction (3) (unlike LwsC veins), suggests that LwsB-

bearing veins formed either during replacement of ankerite and carpholite (e.g., through reaction (4),

>330°C on figures 10c, 12a) and/or by pressure solution of lawsonite, in the presence of either local or

external fluids. The latter is supported by the growth of some LwsB in pressure shadows around

former quartz vein boudins. These veins are by far larger and longer (>5-10 cm) than LwsC veins.

They evidence boudinage stretching and internal rotation (Fig. 5a) indicative of formation throughout

progressive deformation.

As a final note, the initial boundaries between the carbonate and pelitic layers are attenuated through

deformation and migration of reaction fronts (Fig. 11b). This contributes to the progressive chemical

mixing of the subducted sediment at the local scale, enhancing the stability of carbonates.

6.5. Implications for mass transfer and the carbon budget in subduction zone

The major lawsonite-in reaction reported here (reaction (3)) for the first time allows explaining the

high lawsonite content observed in the calcschists. Importantly, the mineralogical and petrological

evolution indicates that no significant decarbonation took place during lawsonite formation in the

Schistes Lustrés calcschists up to 1.6 GPa (maximum pressure in Triplex area). Calcite dissolution led

instead to local co-crystallization of lawsonite and ankerite during relatively fast reactions. In the

debate on how much carbon is recycled to subarc depths or even beyond into the deep mantle (i.e.,

significant: Gorman et al., 2008; Cook-Kollars et al., 2014; Epstein et al., 2019; minor: Kelemen and

Manning, 2015), the results of this study show that there is no major decarbonation of slab sediments

at least to depths of ~40km.

Further, in our samples, early-crystallized lawsonite stored much organic matter as inclusions, leading

to minimum C export from the rock, at least until 35-40 km depth (Fig. 12). Assemblages bearing

LwsA and LwsC imply that C remained within centimetres of its dissolution site, consistent with the

isotopic signatures of C, O and H (Henry et al., 1996; Cook-Kollars et al., 2014; Collins et al., 2015;

Jaeckel et al., 2018). There is also no evidence of carbonation by external C-enriched fluid as reported

in ultramafic horizons in Alpine Corsica (Piccoli et al., 2016).

Intense veining together with the high abundance of water-rich minerals are direct witnesses of high

fluid activity in the Schistes Lustrés. Internally-derived fluids contribute to pervasive, cm-scale

element transfer between pelite and carbonate-rich domains (Figs. 4a,b), attenuating lithological

contrasts (Figs. 11b, c) and restricting the scale of carbon mobility (black and blue boxes on figure

12b). Excess fluids may nevertheless be expelled into larger-scale vein networks (i.e., LwsB-bearing

veins; blue arrows on figure 12b), possibly contributing to migration of fluids, silica and volatiles

beyond the cm-m-scale.

Large-scale silica production at seismogenic depths was hypothesized to account for high Vp/Vs ratios

(Figs. 11d, 12; Audet and Bürgmann, 2014). Lawsonite-quartz-bearing veins and reaction (3) do show

mobilization and production of quartz. However, observations of the bulk mineralogy and

thermodynamic modelling imply small amounts of quartz produced, as silica is consumed in other reactions such as the Tschermak exchange of phengitic micas. There is also no field evidence for massive addition of silica via quartz veins, and none was detected by whole-rock chemistry (Henry et al., 1996). We conclude that large-scale silica migration is not likely in paleo-subduction complexes hosting Tethyan-type metasediments such as the Schistes Lustrés.

7. CONCLUSIONS

This study shows that the mineralogical evolution and voluminous formation of lawsonite during prograde metamorphism of the Schistes Lustrés complex indicate element redistribution mediated by fluids from low-grade metamorphic conditions (180°C, 0.4 GPa) to seismogenic depths (Fig. 12b). Lawsonite mostly grows in stoichiometric proportions with ankerite and quartz from calcite and phyllosilicates. Stabilization of a carbonate phase during lawsonite formation precludes any significant decarbonation of the calcschists. While large amounts of fluids are involved, these results are consistent with the Schistes Lustrés complex behaving mostly as a closed system at the m-scale, in agreement with previous studies. Generalized mobilization of elements and dissolution/crystallization of water-rich phases set up rapid reactions leaving a wealth of small reaction fronts and veins consistent with local redistribution. In this view most of the lawsonite crystallized in a relatively short period of time from a continuous reaction in a narrow P-T field. One type of lawsonite-bearing vein

(LwsB) is consistent with progressive and incremental crystallization, and potentially larger transport distances, but is found in lesser amounts.

Declaration of interests

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

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FIGURES CAPTIONS

Figure 1: Geological setting

A) Schematic representation of the Schistes Lustrés paleoaccretionnary prism in the Alpine subduction

zone (modified after Audet and Bürgmann, 2014). The three main units of the Schistes Lustrés are

represented in yellow (upper unit, LPU), orange (median unit, LPM) and red (lower unit, LPL).

Liberation of fluids at the base of the seismogenic portion is conceptually represented by blue arrows.

Potential swarms of slow seismic events and/or Episodic Tremors and Slip (ETS) events are

represented by white stars. B) Simplified geological map of the Cottian Alps (modified after Beyssac

et al., 2002) illustrating the extent of the three Schistes Lustrés units and the sampling areas (stars)

located along the Stradda del Assietta transect. The top-left inset shows the extent of the Schistes

Lustrés units in the western Alps and locate the Cottian Alps. GP: Grand Paradis; FH: Flysch à

Helmintoïdes; SL: Schistes Lustrés; DM: Dora Maira; PF: Pennine Front; ECM: external crystalline

massifs; ICM: internal crystalline massifs. C) Schematic cross-section of the studied transect and

eastward-increasing gradient of peak metamorphic conditions (modified after Agard et al., 2001a). D)

Compilation of thermobarometric estimates of several Alpine units (CH: Chenaillet ophiolite, Mevel

and Kienast., 1980; BR: Briançonnais, Goffe., 1984; 1 to 5: Schistes Lustrés units, Agard et al., 2001a;

MV: Mont Viso, Locatelli et al., 2018 and DM: Dora Maira, Chopin et al., 1991). Sample locations are

reported on the geological map B) and on the cross-section (C).

Figure 2: Distribution of metasediments in the upper unit of the Schistes Lustrés complex

A) Field photographs of the rock types (carbonate content increases from types 1 to 5). B) Average

lawsonite content in each rock type. Calcschists (types 2 to 4) are the lithologies where lawsonite is

clearly predominant. Mg-Fe-carpholite is found in lithology 1 only. Associated schematic logs

illustrate the proportions of metasediment types. C) Rock types distribution along the path between

Fraiteve and the Assietta pass (along the path of Fig. 1b), presented on a simplified cross-section (topography not to scale). Colours as on A) and B). Calcschists are dominant overall and lawsonite is found all across the section apart from the vicinity of Testa dell'Assietta where it is in minor proportions.

Figure 3: Structural framework and field observations on Monte Triplex

A) Schematic representation of the Monte Triplex area (red dot on Fig. 2c). Sample locations are shown with circles. The main structural features corresponding to exhumation phases D2 and D3 (see text) are underlined. B) Photography of a Monte Triplex outcrop where the east-vergent D2 ductile phase and west-vergent D3 brittle phase are best shown. C) Photography of a typical outcrop observed in lithology 3 (calcschists) and corresponding interpretation (D). Structural features are shown for D2 (light black lines) and D3 (large grey lines). Carbonate-rich layers are represented in light brown and lawsonite-bearing veins are represented in cream colour. E) Typical alternations of folded pelite-rich and carbonate-rich layers (lithology 3). Lawsonite (Lws) is ubiquitous in pelitic layers. The black-lined shape represents the location of the hand specimen presented on figure 4. F) Lawsonite-bearing vein where host-rock inclusions of both carbonate-rich and pelite-rich layers are embedded in quartz-rich veins (lithology 2).

Figure 4: Lawsonite in calcschists: LwsA (lithology type 3)

A) Photography of a Monte Triplex sample (lithologies 2, 3, with fine alternations of carbonate-rich and pelite-rich layers) shown on figure 3e. Contacts between layers are magnified on C and D. LwsA crystals appear very dark due to inclusions of organic matter, easily confounded with the similarly black schistose matrix. Ankerite (Ank) is mostly found in the pelitic layers and at the lithological interfaces with the carbonate-rich layers. B) Interpretation of the same sample where LwsA crystals are represented as black prisms and ankerite in dark brown, highlighting the close association between the two minerals at the interface between pelitic and carbonate-rich layers. C) LwsA crystals in a pelitic layer with diffuse ankerite, contrasting with D) where ankerite forms well-defined horizons near lithological interface. E), F) and G) thin section micrographs showing examples of large LwsA black prisms (up to 5 mm in this sample) associated with quartz and ankerite in pelitic layers. Hourglass zonations are highlighted by colour variations and by inclusion trails of organic matter. Pale, inclusion-free lawsonite overgrows zoned, boudinaged and fractured lawsonite cores, sometimes leading to amalgamation of crystals. Qz: quartz; OM: organic matter.

Figure 5: Lawsonite in metamorphic veins: LwsB and LwsC

A) Quartz-lawsonite-bearing vein showing ductile deformation in the pelitic schists. Quartz is associated with elongated cream-coloured LwsB crystals parallel to vein walls. B and C) Close-up views illustrating the association of LwsB and quartz. D) Inclusions of pelite-rich host-rock containing

LwsA and ankerite inside a LwsB-bearing vein. E) Small LwsB vein associated to ankerite and quartz.

F) and G) Tensile LwsC-bearing veins (mode I opening) opened at the hinge of quartz-bearing vein

with ductile deformation in pelite (F) and in hinge of a LwsB vein (G). LwsC fibers are associated

with elongated crystals of ankerite and quartz, all growing perpendicularly to the vein walls. Ank:

ankerite; Qz: quartz.

Figure 6: Textural observations of the LwsA-ankerite-quartz assemblage

A) Thin-section scan of sample SL17-15A (polarized light) showing a lithological interface in rock

type 3. Large zoned, deformed LwsA crystals with inclusion trails of organic matter are found in the

pelitic domains together with quartz (Qz) and ankerite (Ank). Quartz veins, mainly found within

pelitic domains, occasionally cross-cut carbonate domains as shown here. B) Close-up view in the

carbonate-rich layer showing fine crystals of LwsA with quartz, ankerite, calcite and minor

phyllosilicates. C) SEM back-scattered electron image of the carbonate layer focussing on lawsonite

and ankerite included in a quartz-rich domain. D) Close-up view of the pelite-rich domain on image A

(optical microscope in cross-polarised light) showing inclusion-free LwsA overgrowing organic-

matter rich LwsA cores, co-crystallizing with large ankerite crystals and quartz. Phengite is present as

a peak and retrograde phase. E) Lawsonite included in ankerite in the pelite-rich domain (optical

microscope in cross-polarised light). F) SEM back-scattered electron image of inclusions of LwsA and

quartz in a larger ankerite crystal, highlighting co-crystallization of the three minerals.

Figure 7: Volumetric ratio of lawsonite and ankerite in LwsA, LwsB and LwsC-bearing samples.

For LwsC veins, the ratios estimated including pseudomorphs (stars) are significantly higher than without pseudomorphs and are those considered, as LwsC crystals are highly retrogressed compared to LwsA and LwsB.

Figure 8: Mineral composition.

A) Composition of carbonates (ankerite Ank and calcite Calc), chlorite and phengite obtained from electron microprobe. The data of Plunder et al. (2012, from samples equilibrated over a larger range of peak conditions) are shown for comparison with grey symbols for phyllosilicates. B), C) and D) show the Sr and Ti content of LwsA, LwsB and LwsC, expressed in atom per formula unit from electron microprobe measurements. Uncertainties are about 10% of the measured value for each point.

Figure 9: Element maps for lawsonite-ankerite-quartz assemblages.

A) back-scattered electron image of a typical texture from carbonate-rich layers containing lawsonite (LwsA, Fig. 6b). Ca, Al and Fe maps obtained from electron microprobe illustrate the mineral associations. Calcite (Calc), paragonite (Pg) and chlorite (Chl) are seen on the edges of LwsA and ankerite (Ank), and post-date their crystallization. Both ankerite and calcite crystals are observed in inclusions within LwsA. B) back-scattered electron image and Sr and Ti maps obtained from SEM WDS in a LwsA crystal in a pelite-rich layer. The core of the crystal is Ti-rich, Sr enrichment is

observed on parts of the rim. C) back-scattered electron image and Sr and Ti maps obtained from SEM

WDS, in a fragmented LwsA crystal preserved in a retrogressive calcite matrix. LwsA shows sector

zoning with Ti-rich domains globally found in crystal cores and Sr-rich rims. D) back-scattered

electron image and Mn map obtained from SEM WDS, in a LwsA-ankerite assemblage with iron

oxides appearing as bright phases on the back-scattered electron image. The Mn map shows Mn-

enriched domains in the ankerite-rich part of the sample, reflecting several stages of ankerite growth.

Figure 10: Thermodynamic modelling of reactions and phase equilibria

A) Pseudosection calculated in the CaFMASHC system with stoichiometric composition fixed by

reaction (3) (see text). Peak conditions for each unit of the Schistes Lustrés complex are shown in

circles. The appearance of lawsonite is shown with a bold blue line. A geothermal gradient of 8°C/km

is used for the burial history, along which mineral mode evolutions is indicated in B). Along this

gradient, reaction (3) occurs in the 170-190°C range. The volumetric fraction occupied by kaolinite

and chlorite is replaced by lawsonite, and that of calcite by ankerite. C) and D) show pseudosections

calculated for pelite-rich and carbonate-rich domains, respectively in the CaKFMASHC system. The

composition of the system is shown on top of each pseudosection. Compositions are representative of

each side of the lithological interface on figure 4a. Lawsonite iso-volume are represented by coloured

lines and amounts are specified in dark blue. E) and F) show the evolution of mineral modes along a

geothermal gradient of 8°C/km. Successive reactions producing lawsonite are detailed in the text. The

appearance/disappearance of major phases is outlined with grey bars. Temperature scales are similar to those of pseudosections above. Water is in excess in each pseudosection.

Phase equilibria are indicated in each field, numbers in small fields indicate:

A) (1) Chl, Kln, Cc; (2) Chl, Lws, Ank, Kln, Stlb, Arag, H_2O; (3) Chl, Lws, Ank, Kln, Qz, Cc, H_2O; (4) Chl, Kln, Ctd, Qz, Cc, H_2O; (5) Ctd, Car, Qz, Cc, H_2O; (6) Chl, Ctd, Ma, Qz, Ank, H_2O; (7) Chl, Ma, Ank, Qz, H_2O; (8) Chl, An, Qz, Cc, CO_2, H_2O; (9) Chl, An, Ank, Qz, CO_2, H_2O; (10) Ank, An, Qz, H_2O; (11) Chl, Ank, Ma, Zo, Qz, H_2O; (12) Ank, Ma, Zo, Qz, H_2O.

C) (1) Chl, Kln, Cc, Phg, Ank, Qz, Stlp; (2) Chl, Ank, Kln, Phg, Cc, Qz; (3) Chl, Lws, Ank, Kln, Qz, Arag, Phg, Stlb; (4) Phg, Ank, Lws, Kln, Qz, Arag, Stlp, Mstl; (5) Phg, Ank, Lws, Kln, Qz, Stlb, Stlp, Mstl; (6) Phg, Ank, Chl, Lws, Kln, Qz, Cc, H_2O; (7) Phg, Car, Ank, Lws, Kln, Qz, Stlp, H_2O; (8) Phg, Ank, Chl, Kln, Qz, Cc, H_2O; (9) Phg, Ctd, Ank, Chl, Kln, Qz, Cc, H_2O; (10) Phg, Ctd, Car, Ank, Kln, Qz, Cc, H_2O; (11) Phg, Ctd, Ank, Car, Prl, Qz, Cc, H_2O; (12) Phg, Chl, Ank, Ma, Wrk, Qz, H_2O; (13) Phg, Ctd, Ank, Chl, Ma, Qz, Cc, H_2O; (14) Phg, Ctd, Car, Ank, Lws, Ma, Qz, H_2O; (15) Phg, Ctd, Car, Ank, Lws, Prl, Qz, H_2O.

D) (1) Phg, Ank, Chl, Kln, Qz, Stlb, Cc; (2) Phg, Ank, Chl, Lws, Kln, Qz, Arag, Stlp; (3) Phg, Ank, Chl, Lws, Kln, Qz, Cc, H_2O; (4) Phg, Ctd, Ank, Chl, Kln, Qz, Cc, H_2O; (5) Phg, Ank, Chl, Qz, Wrk,

Cc, H_2O; **(6)** Phg, Ctd, Ank, Chl, Prl, Qz, Cc, H_2O; **(7)** Phg, Ank, Chl, Zo, Ma, Qz, Cc, H_2O; **(8)** Phg, Ank, Chl, Zo, Qz, Cc, H_2O; **(9)** Phg, Ank, Lws, Qz, Arag, Act, Stlp, Mstl.

(Ank = ankerite; Act = actinote; Arag = aragonite; Car = carpholite; Cc = calcite; Chl = chlorite; Ctd = chloritoid; Kln = kaolinite; Lws = lawsonite; Ma = margarite; Mstl = Magnesio-stilpnomelane,; Phg = Phengite; Qz = quartz; Stlb = Stilbite; Stlp = stilpnomelane; Wrk = wairakite ; Zo = zoisite)

Figure 11: Petrological evolution scenario at outcrop and hand specimen scale.

A) Progressive reaction and lithological mixing along continuous ductile deformation (D2 tectonic event, see text in section 2.2) in the calcschists. B) Shows close-up views of mineralogy at stages t_0 and t_1, illustrating the main reaction consuming phyllosilicates and producing lawsonite, ankerite, quartz and water (reaction (3)) in the pelitic and carbonate domains and at their interface. C) Outcrop-scale spatial and textural relations between lawsonite types, with close-up views on veins in D). Mineral symbols are common to all subfigures. Water transfer (blue arrows) hypothesizes formation of LwsB from fluid pathways (not necessarily of external origin). LwsC are drawn in tensile veins opening at the hinge of folds and are thought to be derived from fluids with a local origin.

Figure 12: Implications of the petrological scenario at subduction-zone scale.

A) Summary of the inferred metamorphic evolution of the upper unit of the Schistes Lustrés complex. LwsA crystallizes rapidly compared to the complex vein system formed progressively over most of the prograde history in the stability field of lawsonite. The small sketches and the text on the right sum up the main information regarding lawsonite formation at three different step time reported on the P-T grid. B) Schematic model of the varying properties, in particular water retention versus production of the Schistes Lustrés units at seismogenic depths. Hypothetical fluid pathways are likely found in calcschists, which produce the most water (reaction (3)). Insert on the top right as been modified after Audet and Bürgmann, 2009 and locate the studied area at depth (LFSEs = Low-frequency earthquakes).

TABLE CAPTION

Table1: Representative analysis of each type of lawsonite encountered in the studied samples.

SUPPLEMENTARY MATERIALS CAPTIONS

Sup. mat. 1: Back-scattered electron image of ankerite (Ank) included in LwsA and closely associated with quartz (Qz) in a pelite-rich domain. Pg: paragonite.

Sup. mat. 2: The top image shows a compositional map of Ca obtained from SEM on a thin section (sample SL17-08D3), used to estimate the Lws/Ank ratio presented in figure 7. LwsA is represented in dark blue, ankerite in light blue and calcite in red. The two photographs below (optical microscopy)

illustrate the typical textures of lawsonite-bearing veins (LwsB and LwsC). Depending on the retrogression state, Lws/Ank might have been estimated on Lawsonite ghosts (pseudomorphs, LwsC*) as shown for the LwsC bearing vein.

Sup. mat. 3: Optical microscopy (cross-polarized light) image centered on a LwsA crystal with ankerite (Ank) inclusions in a pelite-rich layer. The two chemical maps below illustrate hourglass zonation of Ti and Sr in this lawsonite crystal. Cc: calcite; Phg: phengite; Qz: quartz..

Sup. mat. 4: Supplementary pseudosection calculated for pelite-rich composition (R11SCH, see Fig.10c) in the CaKFMASHC system. The composition of the system is shown on top of the grid. The water content has been fixed to 15wt.% to verify the saturated water state in pseudosection shown in figure 10c. The associated mineral modes are drawn below. The main lawsonite-ankerite forming reaction still occurs at 170-180°C, although the reaction is complicated by the contribution of stilbite breakdown. The mineral mode evolution remains unchanged, as well as carpholite-in and out reactions. The appearance of major phases is outlined with grey bars. All symbols and abbreviations are similar to those in figure 10.

Highlights

- Voluminous lawsonite stable in calcschists at the base of the seismogenic zone
- Co-crystallization of lawsonite and ankerite witnesses carbon retention
- Sequential crystallization of hydrous phases constrains fluid budget and migration
- Vein-forming reactions consistent with closed-system behaviour

Figure 1

Figure 2

a — Samples SL-16 (red), Samples SL-17 (green), Slope instability, Track, 200m

b — W, E, (D₃), (D₂), (D₂), (D₃), 10 m, Triplex Zoom

c — W, E, SL17-14, SL17-02, SL17-01, SL16-15B, SL17-15A, SL16-11E, SL16-11C, 1 m

d — W, E, (D₃), (D₂), (D₂), (D₃), (D₂), (D₃), Lawsonite-bearing vein, Carbonate-rich layer

e — Lithology 3, SL17-06, Fig. 4a, ~ 15 cm

f — SL17-08A, Lws-bearing vein, Lithology 2, ~ 10 cm
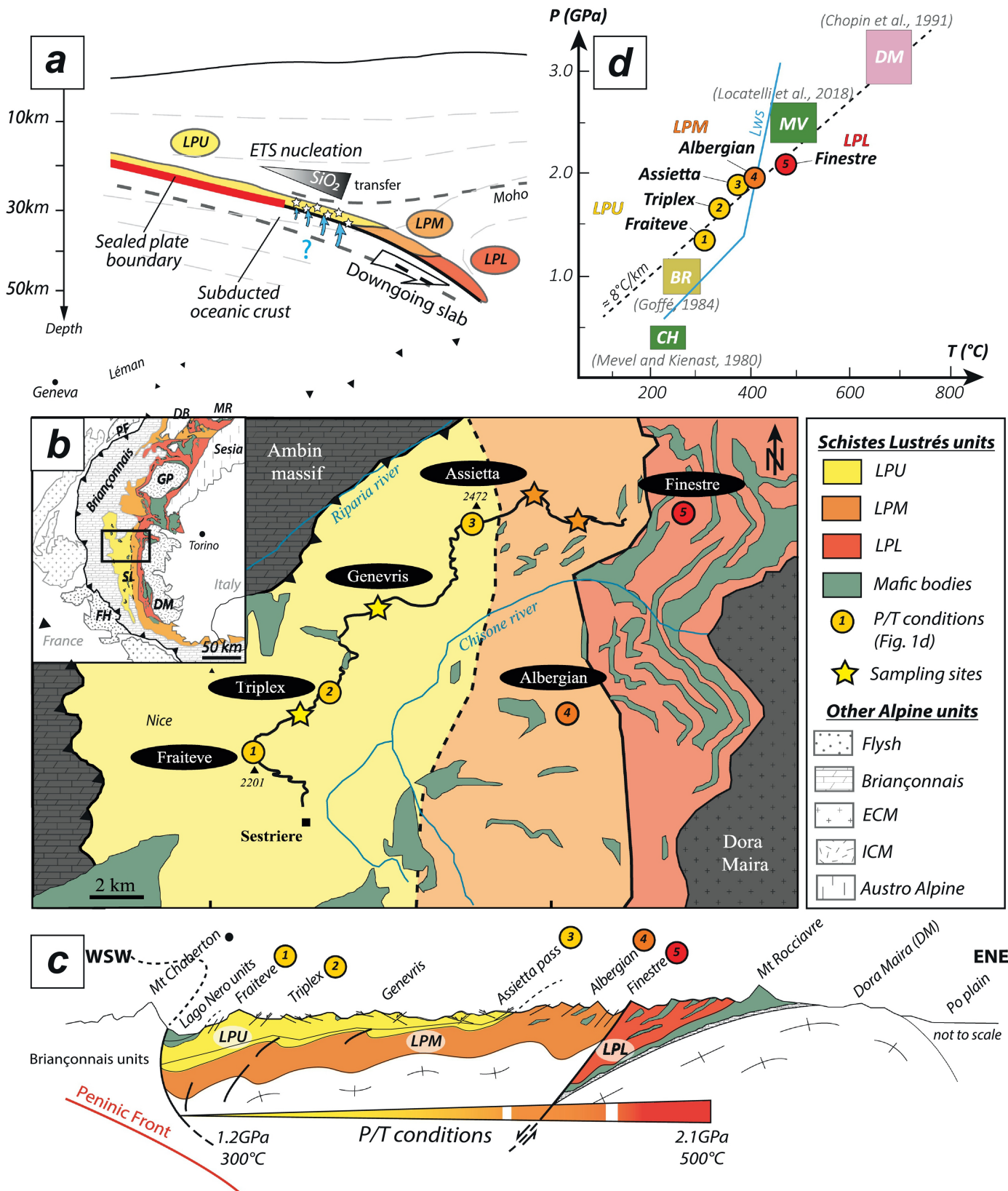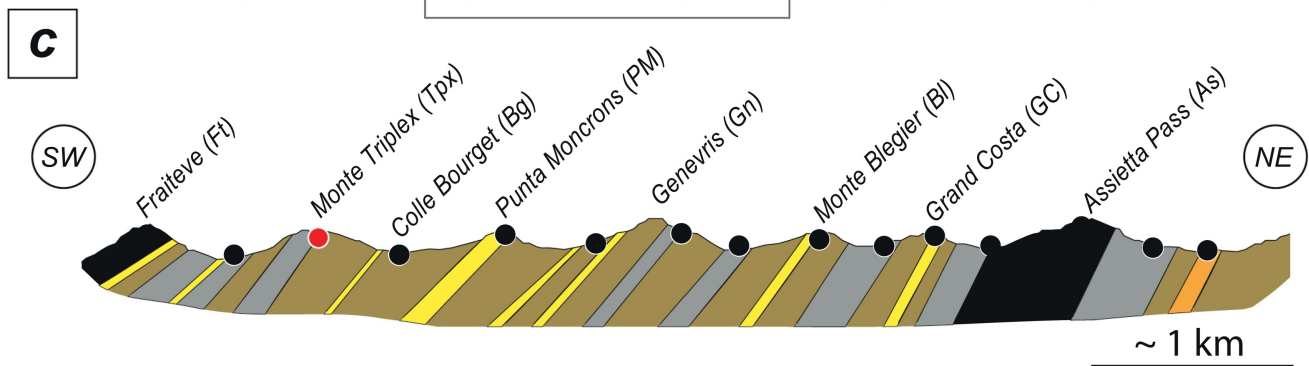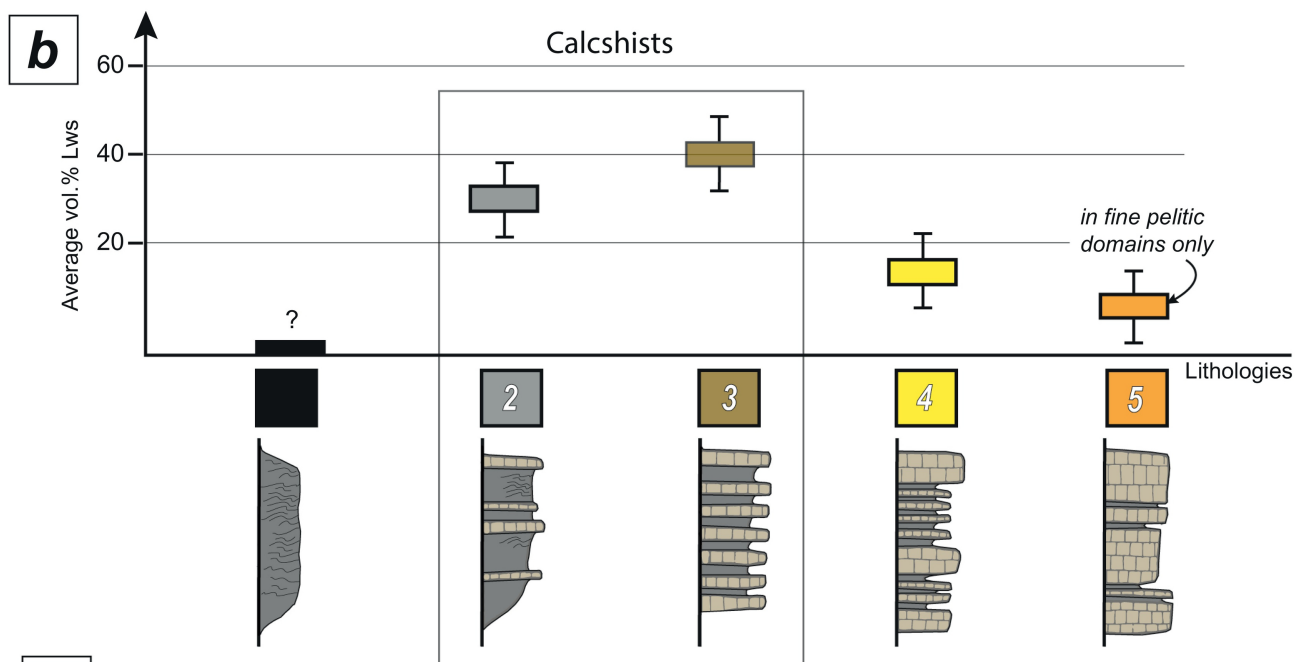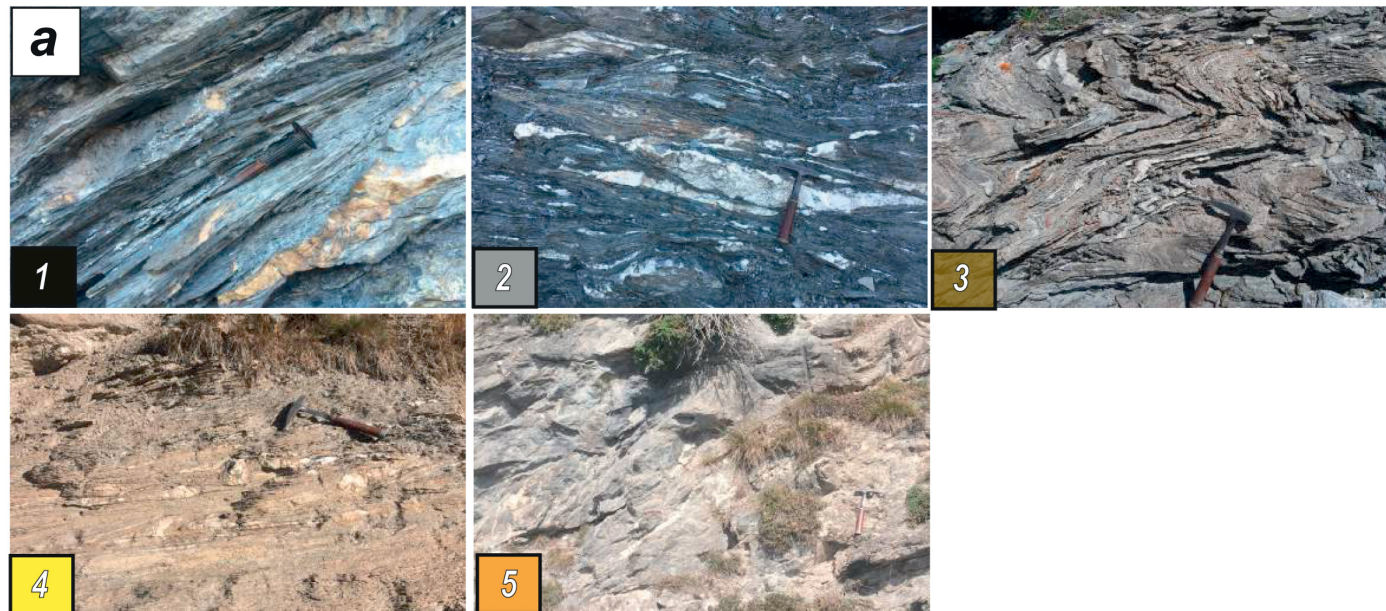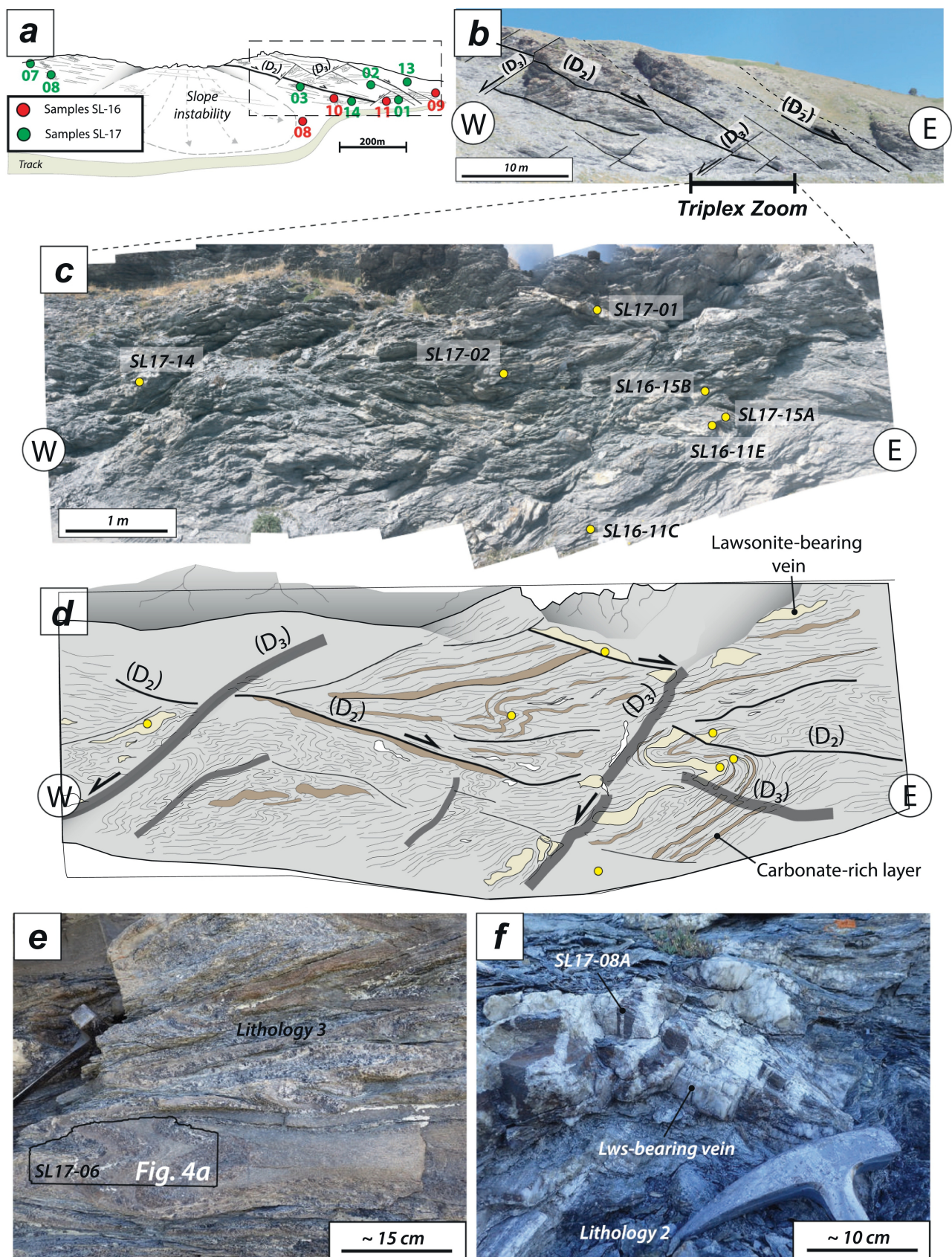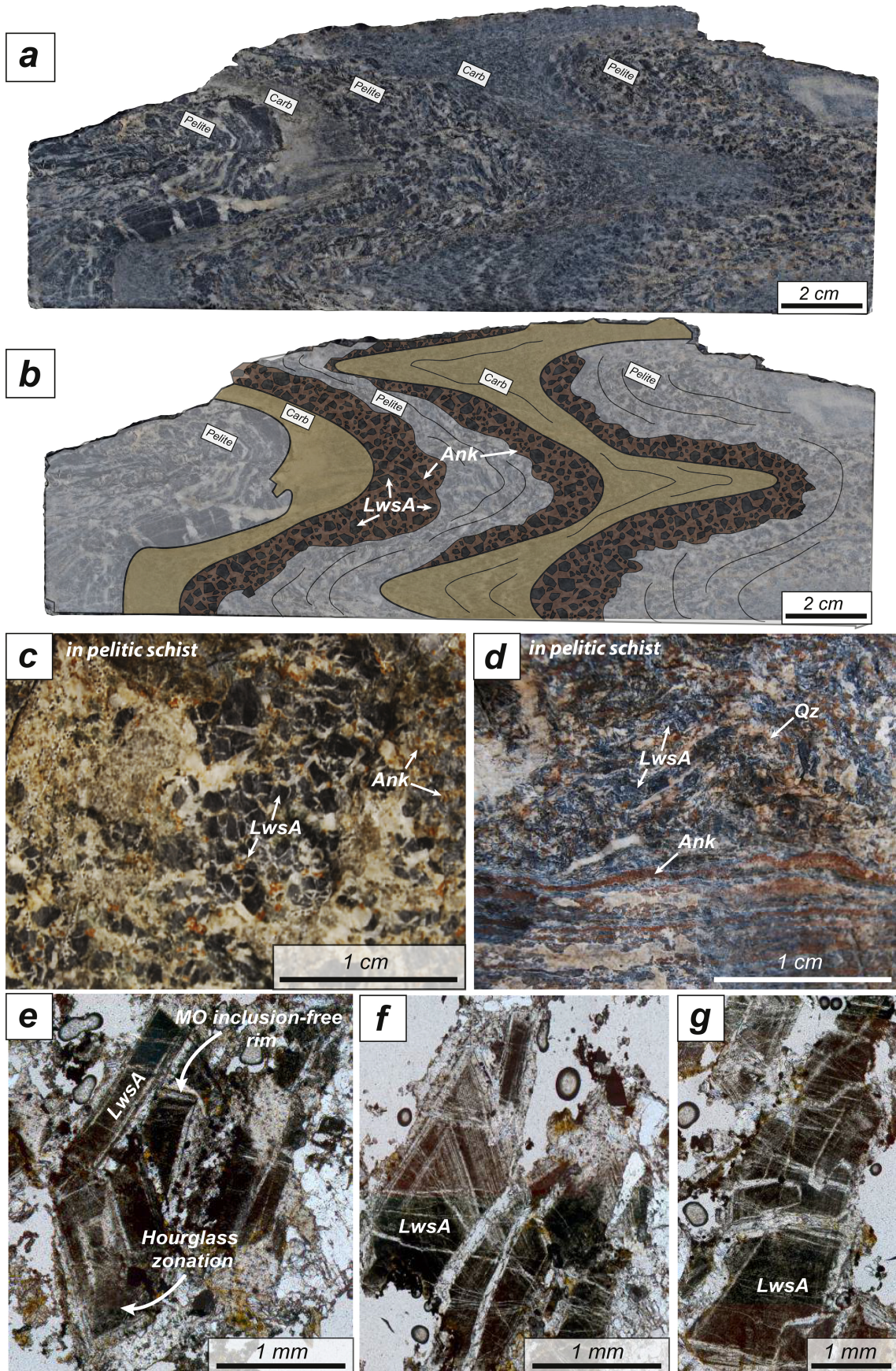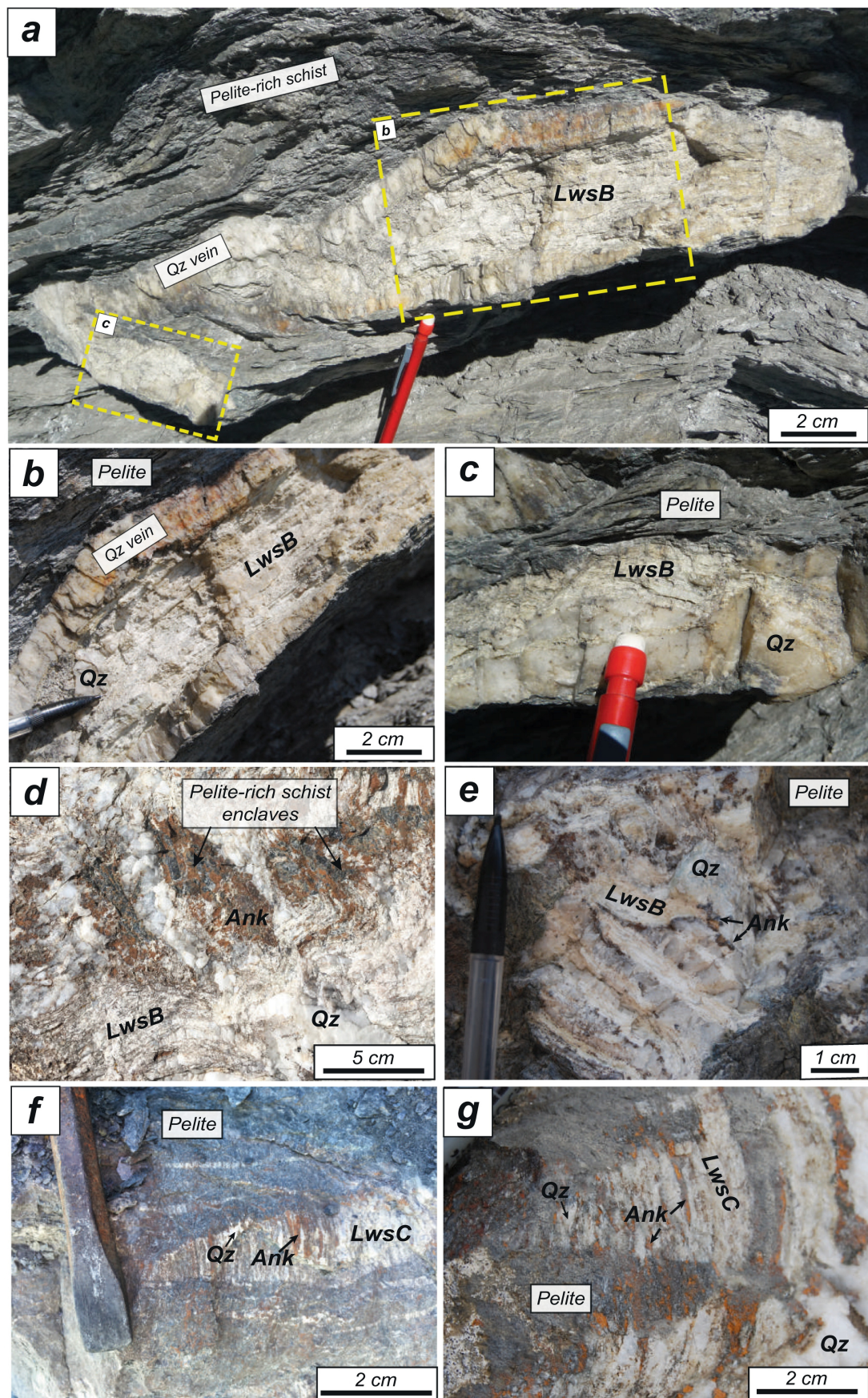
Figure 3

Figure 4

Figure 5
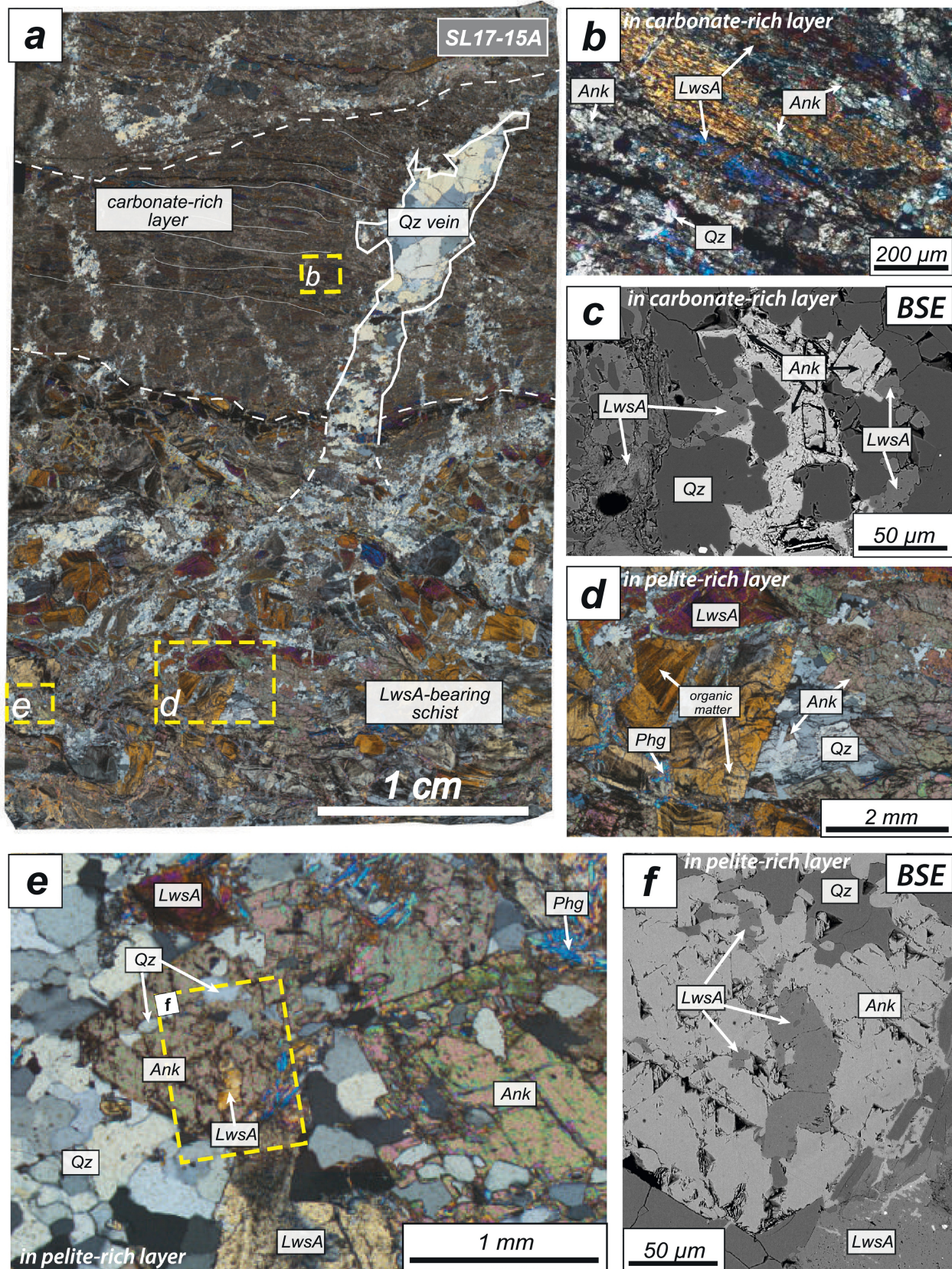
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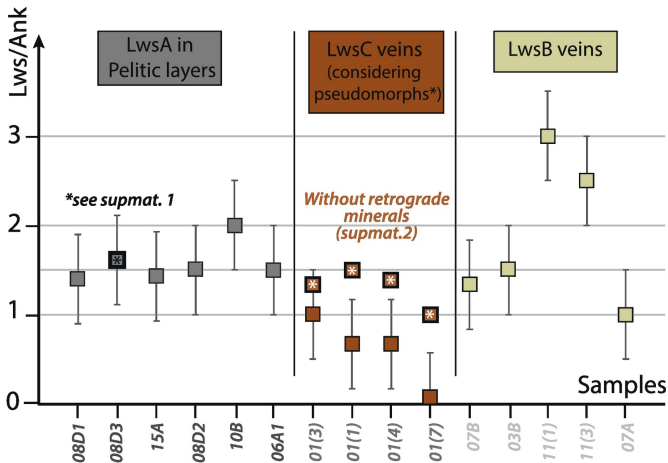
Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12