

Disentangling the compositional variations of lawsonite in blueschist-facies metasediments (Schistes Lustrés, W. Alps)

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5 6	Benjamin Lefeuvre ^{1,2*} , Benoît Dubacq ¹ , Anne Verlaguet ¹ , Clément Herviou ^{1,3,4} , Stephanie Walker ⁵ , Benoît Caron ¹ , Ethan Baxter ⁵ , Philippe Agard ¹
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25 Abstract

Lawsonite is important as a carrier of H_2O in subduction zones and as a petrological tracer. The trace 26 27 element content of lawsonite in mafic rocks has been used as a record of fluid-rock interactions but has 28 received less attention in metamorphosed oceanic sediments. This study documents the major and trace element composition, together with ⁸⁷Sr/⁸⁶Sr isotopic ratios, of the different lawsonite types identified in 29 the upper units of the Schistes Lustrés complex of the Western Alps, a paleo-accretionary prism of the 30 31 Liguro-Piemont slow-spreading ocean subducted up to 40 km. The lawsonite-rich upper units of the 32 Schistes Lustrés complex are principally composed of metamorphosed pelitic sediments and carbonates. 33 Lawsonite content reaches 40 vol.% in the rock matrix and in veins. All lawsonite types originate from 34 prograde metamorphic reactions which occurred up to peak metamorphism. Lawsonite compositions have been measured in-situ with electron microscopy, microprobe and laser-ablation mass 35 spectrometry. Lawsonite separates have been measured for Sr content and ⁸⁷Sr/⁸⁶Sr isotopic ratios using 36 TIMS. Bulk rock compositions have been measured with ICP-OES and ICP-MS. Analysis contamination 37 by minute retrograde white mica inclusions in lawsonite crystals precluded using univalent cations for 38 39 petrological interpretations. For other trace elements, the variability of lawsonite appears extremely 40 high, with crystal compositions varying between samples and between crystals in individual samples. 41 However, clear patterns emerge between lawsonite types, reflecting equilibrium and out-of-equilibrium 42 processes unrelated to pressure-temperature conditions. At crystal scale, textural hourglass zoning 43 predominates in lawsonite from the schist, while growth zoning is found in both schists and veins. The 44 combination of both mechanisms results in spectacular zoning in Ti and in rare earth element contents 45 spanning four orders of magnitude. Over time, the La/Yb ratio decreases strongly (from ~ 100 to ~ 1), as 46 La appears much more sensitive to surface effects leading to textural hourglass zoning. Interface-47 coupled dissolution-precipitation also contributes to decoupling of less mobile elements in the schist. 48 This is best observed for Ti, but rare earth element and chromium contents are affected too. These 49 processes are considered to occur near closed-system conditions. Late lawsonite overgrowths with 50 higher Sr contents are interpreted as reflecting system opening in the veins, yet sometimes observed in 51 the schists. Strontium isotopic ratios measured on separated lawsonite crystals and on bulk rocks also 52 show very large spreads. This indicates that the system did not equilibrate during blueschist-facies metamorphism, due to bulk rock heterogeneities during deposition and limited mineral reactivity at the 53 54 local scale. Strontium isotopic ratios do not correlate with Sr content which rules out limestone 55 devolatilization as the main driver of lawsonite overgrowths. In places, lawsonite is far more radiogenic 56 than the host rocks, indicating either the destabilization of local Rb-rich phases (such as mica, illite and 57 smectite) or the infiltration of externally-derived fluids. The overall compositional evolution of lawsonite 58 records incremental system opening. However, lawsonite offers no evidence of large-scale mass transfer 59 and external fluid influx in the Schistes Lustrés complex, even though the vein network is abundant and extends over time. 60

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65 **INTRODUCTION**

66 Sediments undergoing subduction contain large amounts of H_2O (up to 7 wt. % entering the trench 67 globally, Plank and Langmuir, 1998; Plank, 2014) and release water via metamorphic reactions through 68 burial (e.g., Schmidt and Poli, 1998; Hacker et al., 2003; Van Keken et al., 2011). At depth, fluids play 69 a major role as their migration induces dramatic changes in the mechanical and chemical properties of 70 rocks. The amount of fluids (e.g., H₂O, CO₂) produced can be estimated (e.g., via thermodynamic 71 modeling as by Hacker and Abers, 2004; Baxter and Caddick, 2013; Ague and Nicolescu, 2014; Kleine 72 et al., 2014; Piccoli et al., 2021, among many others), but pathways and scales of fluid migration remain 73 hard to assess, especially in sedimentary lithologies where alternating horizons show hugely variable 74 permeability, and where connection of vein networks may be transient and poorly recorded. Trace 75 elements, fluid inclusions and/or isotopic signatures of minerals growing in subducted rocks, 76 metamorphic veins or shear zones are useful tracers of fluid migration during prograde metamorphism. 77 Lawsonite is of particular interest as it is stable over an extended pressure-temperature range (Schmidt 78 and Poli, 1994), generally growing as prisms, and can be locally abundant. Lawsonite is also intimately 79 linked to both the water and carbon cycles as a it is a major H_2O host (~12 wt. %) and its formation 80 reactions involve devolatilization and dissolution/crystallization of carbonates (Nitsch, 1972; Cook-81 Kollars et al., 2014; Lefeuvre et al., 2020).

82 Lawsonite has been shown to be remarkably stable around its ideal composition (CaAl₂Si₂O₇(OH)₂.H₂O) 83 regardless of pressure-temperature conditions (e.g., Okamoto and Maruyama, 1999), but it can host 84 various trace elements. Lawsonite incorporates Pb, Sr and rare earth elements (REE), especially light 85 rare earths (LREE), preferentially to other minerals in classical assemblages (e.g., reviews in Fornash et 86 al., 2019; Whitney et al., 2020; Kang et al., 2022). Previous studies of the minor and trace element 87 composition of lawsonite in mafic blueschists, eclogites, and metasomatic rocks have shown that 88 variations of lawsonite composition may reflect reactions between trace element-rich minerals and/or 89 changes in fluid compositions, with implications for element cycling in shallow to deep parts of 90 subduction zones (e.g., Tribuzio et al., 1996; Ueno, 1999; Spandler et al., 2003; Tsujimori et al., 2006; 91 Martin et al., 2011, 2014; Vitale Brovarone et al., 2014; Vitale Brovarone and Beyssac, 2014; Fornash 92 et al., 2019; Whitney et al., 2020; Kang et al., 2022).

Studies on metasedimentary lawsonite are scarce (Martin et al., 2014; Whitney et al., 2020), although
lawsonite is abundant in blueschist-facies calcschists such as in the Schistes Lustrés (SL) complex of
the Western Alps, where lawsonite locally represents up to 40 vol.% of the metasediments (Agard et al.,
2001; Lefeuvre et al., 2020; Manzotti et al., 2021). The SL units correspond to fragments of oceanic
lithosphere successively buried along a cold geothermal gradient (~ 8°C/km, Agard et al., 2001; Agard,
2021; Herviou et al., 2022) during Alpine subduction, exhumed sliced from the downgoing plate at

99 various depths. The SL provide a well-exposed example of a deep accretionary complex (Platt, 1986; Marthaler and Stampfli, 1989; Agard et al., 2009; 2018; Agard, 2021). Metasediments are volumetrically 100 101 dominant and crop out continuously over large distances, allowing studies of the production, 102 composition and behavior of fluids in subducted sediments (Agard et al., 2000; Bebout et al., 2013; 103 Herviou et al., 2021). Oxygen and carbon isotopic data in the metasediments suggest that most of the 104 fluid present during subduction was locally-derived (Henry et al., 1996; Bebout et al., 2013; Cook-105 Kollars et al., 2014; Jaeckel et al., 2018; Epstein et al., 2020), consistently with the composition of fluid 106 inclusions in carpholite and lawsonite-bearing veins (Agard et al., 2000; Herviou et al., 2021; see also 107 Raimbourg et al., 2018; Lefeuvre, 2020). Therefore, metasediments of the SL complex mostly behaved 108 as a rock-buffered system, with volumetrically large but transient and restricted fluid migration. External 109 fluid infiltration was limited, but the scales of fluid migration and element mobility remain poorly known. Lawsonite is found in these rocks in pelitic layers and in a network of high-pressure veins, 110 locally with carpholite (Agard et al. 2000, 2001; Vitale Brovarone et al., 2020; Lefeuvre et al., 2020; 111 Herviou et al., 2021, 2023; Manzotti et al., 2021). Lawsonite is thought to grow during prograde 112 metamorphism of the SL units, with veins providing evidence for incremental lawsonite growth during 113 114 crack-seal events (Herviou et al., 2023). Do trace element compositional variations in lawsonite record 115 variations in fluid signature along the prograde path?

In light of the very large variability of minor and trace element composition of lawsonite (Fornash et al., 2019; Whitney et al., 2020; Kang et al., 2022), this study provides a petrological model to refine the crystallization history of lawsonite and to shed light over the scale of element mobility during prograde and peak metamorphism at blueschist-facies conditions. To address these questions, lawsonite crystals from the SL calcschists and high-pressure veins have been analyzed for major and trace elements, coupled to bulk rock analyses and strontium isotopic analyses on bulk samples and on lawsonite separates.

123 GEOLOGICAL SETTING AND PREVIOUS WORK

124 The Schistes Lustrés complex in the Western Alps

The Western Alps result from an east-dipping, slow and cold subduction (~8°C/km at a maximum of 2 cm/year) of the Valais and Liguro-Piemont slow-spreading oceans below Adria/Apulia microcontinents (Le Pichon et al., 1988; Lagabrielle and Cannat, 1990; Agard et al., 2001; Lapen et al., 2003; Schmid et al., 2017). Subduction of these slow-spreading oceanic domains lasted around 60 Myr (Stampfli et al., 1998; Agard, 2021) and was followed by continental subduction and collision (e.g., Mendes et al., 2023).

- 131 Remnants of Liguro-Piemont oceanic lithosphere are now exposed in the internal domain of the Western
- 132 Alps and form a nappe-stack known as the Liguro-Piemont domain or SL complex (Caron, 1974;
- 133 Lagabrielle and Lemoine, 1997; Agard et al., 2001, 2002; Agard, 2021; Herviou et al., 2022) owing to
- their characteristic sedimentary features (Fig. 1a; for more details on the overall Alpine structure, see:
- 135 Coward and Dietrich, 1989; Lagabrielle and Lemoine, 1997; Rosenbaum and Lister, 2005; Handy et al.,
- 136 2010). Former oceanic sediments (marls, shales and limestones, e.g., Lemoine, 2003) correspond to an
- 137 initial ~200-400 meter thick sequence of Upper Jurassic to Upper Cretaceous pelagic and hemipelagic
- seafloor deposits (De Wever and Caby, 1981; Lemoine et al., 1984; Lemoine and Tricart, 1986; Deville,
- 139 1986; Deville et al., 1992; Lemoine, 2003). Minor and variable amounts of mafic and ultramafic rocks
- are also found in the SL complex (e.g., Lagabrielle et al., 2015; Herviou et al., 2022).

141 During subduction, fragments of the Liguro-Piemont oceanic lithosphere were successively scraped off 142 the downgoing plate, stacked at depths and exhumed to form a deep accretionary complex built by progressive underplating (Platt, 1986; Marthaler and Stampfli, 1989; Agard et al., 2009; 2018; Agard, 143 2021; Agard and Handy, 2021; Plunder et al., 2012., Herviou et al., 2022). Several units corresponding 144 145 to independent subduction slices were identified in the SL complex (Lagabrielle, 1987; Fudral, 1996; 146 Tricart and Schwartz, 2006; Lagabrielle et al., 2015). Herviou et al. (2022) reappraised the overall 147 structure of the complex, highlighting a trimodal distribution of units with near-continuous eastward increase in peak burial conditions from the Liguro-Piemont Upper units (LPU; 320-400°C - 1.2-1.9 148 GPa) to the Middle units (LPM; 415-475°C - 1.7-2.2 GPa) and to the Lower units (LPL; 500-580°C -149 150 2.2-2.8 GPa; Fig. 1c; for peak metamorphic conditions through the domain see also Agard et al., 2001; 151 Beyssac et al., 2002; Gabalda et al., 2009; Plunder et al., 2012; Angiboust et al., 2012; Schwartz et al., 152 2013; Locatelli et al., 2018). The LPU and LPM units metamorphosed under blueschist-facies conditions are dominated by sediments (> 90 %), whereas the LPL units metamorphosed at eclogite-facies 153 154 conditions are richer in mafic-ultramafic rocks (> 40 %; Herviou et al., 2022).

155 Lawsonite-bearing calcschists on the Cottian Alps transect

This contribution focuses on lawsonite-bearing calcschists from the LPU unit of the Cottian 156 Alps (Lago Nero slice; Polino et al., 2002; Herviou et al., 2022) and more specifically on the Strada 157 dell'Assietta transect (Caron, 1974; Lefeuvre et al., 2020; Fig. 1b) between Fraiteve and the Assietta 158 159 pass, along a ~15 km SW-NE traverse in the French-Italian Cottian Alps (Fig. 1b, c; Caron, 1974; Polino, 160 1984). Metasediments recorded four deformation stages described by Agard et al. (2001; 2002) and 161 Ghignone et al. (2020). Kilometer-scale folding associated with thin-skinned stacking during blueschist-162 facies peak burial (D1) is dated at 62-55 Ma. These early fabrics have been largely erased by a D2 event (51-45 Ma) with top-to-the-east shear deformation patterns associated with early exhumation under 163 164 blueschist-facies, and by subsequent west-vergent shear zones (D3) associated with greenschist facies 165 conditions (38-35 Ma; Agard et al., 2002). Late normal faults characterize the final ductile-brittle tran-166 sition during late exhumation. The metasediments along the transect are composed of alternations of 167 carbonates and pelitic horizons (Fig. 1d, e), which are of varying thickness and proportions, ranging 168 from pelites (described as type 1 calcschists by Lefeuvre et al., 2020, Fig. 1d, e) to thick carbonate beds 169 almost lacking pelitic horizons (type 5 in Lefeuvre et al., 2020, Fig. 1d, e).

170 Lawsonite is the dominant hydrous phase stable at peak conditions in LPU metasediments, but 171 its distribution is very heterogeneous. Lawsonite growth has been described as 'massive' by Lefeuvre 172 et al. (2020) because it amounts to about half the volume of large outcrops in the LPU units in type 3 173 calcschists, but it is restricted to fine carbonate-metapelite mixtures (also ubiquitous in type 3 174 calcschists) that allow reaction between Ca, Al, Si and H₂O. Four textural occurrences of lawsonite were identified by Lefeuvre et al. (2020) and were labelled from A to D (LwsA, LwsB, LwsC, LwsD) without 175 implying chronological order. In thin pelitic horizons, lawsonite occurs as millimetric black prisms 176 177 coined LwsA, by far the most abundant lawsonite type. Cream-colored lawsonite fibers labelled LwsB 178 are found in decimeter to meter-long quartz-rich veins elongated parallel to vein walls and recording incremental crack-seal growth (Fig. 2f; Herviou et al., 2023). LwsC-bearing centimetric tensile veins 179 180 contain cream-colored lawsonite fibers in textural equilibrium with ankerite and quartz, all growing 181 perpendicular to vein walls. LwsA in the schist is interpreted as the product of the prograde reaction 182 chlorite + aragonite + kaolinite = lawsonite + ankerite + quartz + H_2O , beginning at conditions possibly 183 as low as 0.4 GPa/180 °C (Lefeuvre et al., 2020). Lawsonite veins likely formed all along the prograde 184 path, in response to pressure-solution processes. While LwsC veins likely opened as single stage, short-185 lived tensile events, LwsB incremental crack-seal fibers may have recorded longer-lived events along 186 the prograde path (Lefeuvre et al., 2020; Herviou et al., 2023). LwsD is restricted in pelitic layers and 187 occurs as white rosette-like prisms in the schist (Fig. 2g). Table 1 presents the mineralogy, rock and 188 lawsonite types for all samples.

189 LAWSONITE OCCURRENCE, TEXTURE AND ASSOCIATED MINERALOGY

This study focuses on three representative lawsonite-bearing outcrops along the Strada dell'Assietta transect (Fig. 1): Desertes, Triplex and Assietta. The Fraiteve location also offers an interesting outcrop of the least metamorphosed rocks of the series. At the 200m long Mt. Triplex outcrop, lawsonite is particularly abundant in both schist and veins (Fig. 2). These type 2 (and type 3 to a lesser extent) calcschists are made of pelitic and carbonate-rich layers alternating every few centimeters, highly folded and affected by D2-related penetrative shear bands. D2 shear structures are cross-cut by later west-vergent D3 shear bands (Fig. 2a, b).

197 LwsA crystallized in the thin pelitic layers as millimetric to centimetric black prisms enriched198 in organic matter (OM). LwsA is systematically associated reddish oxidized ankerite found at the

interface between pelitic and carbonate-rich beds (Figs. 2b, c, 3a). Samples Tpx-A1, Tpx-A2 and Tpx-199 200 A3 (Table 1) contain large amounts of centimetric LwsA crystals reaching 40 vol. % of the whole rock (Fig. 3a, b), and are hereafter referred to as 'host calcschists' (Figs. 2c, 3). LwsA in pelite-rich layers is 201 202 closely associated with ankerite and quartz (Fig. 3c, d, e, f). Fine mixtures of phengite, chlorite and 203 calcite are surrounding LwsA crystals and interpreted as the retrograde assemblage of lawsonite 204 destabilization (Fig. 3c, e; Sicard-Lochon and Potdevin, 1986). Accessory minerals are scarce in the 205 host calcschists; tiny rutile needles were identified in lawsonite, and apatite occurs in one sample (Fig. 206 3f; Tpx-A2). Optical microscopy reveals complex growth patterns for LwsA. Differences in interference 207 colors under crossed polars clearly indicates the presence of hourglass zoning (Fig. 3b, e). In some LwsA 208 crystals, organic matter (OM) inclusions help to illuminate the zoning and identify the hourglass shapes 209 (Fig. 3b). Such chemical zoning has been previously described in metasedimentary lawsonite (Vitale 210 Brovarone et al., 2014; Fornash et al., 2019; Whitney et al., 2020). LwsA cores include OM in trails 211 aligned along crystal faces (Fig. 3c, d), folded and rotated compared to the surrounding schistosity, or 212 highlighting hourglass zoning (Fig. 3c, e). These OM-rich cores are generally rimmed by OM-free lawsonite (Fig. 3b, c, e), suggesting a series of discrete growth events of LwsA (see Rice and Mitchell, 213 214 1991 for details about textural zoning and carbon-rich inclusion bands).

Rare white crystals of prismatic lawsonite, without preferential orientation, are observed in pelitic layers in the vicinity of LwsB-bearing veins. These have been classified as a fourth lawsonite type: LwsD. LwsD is present in sample Tpx-D1 (Fig. 2e, g) collected 1 meter away from LwsB-bearing Tpx-B1, and in Ft-D1 collected in Fraiteve. As with LwsA, LwsD crystals are locally associated with ankerite and quartz (Fig. 2g), and partially retrogressed by phengite, chlorite and calcite. LwsD contains little OM inclusions compared to LwsA.

221 Veins are abundant, especially at Mt. Triplex where they have been estimated to make up to 222 30 % of the outcrops (Herviou et al., 2023). LwsB-bearing veins are decimeter to meter-long, parallel 223 to the main D1/D2 schistosity, ductility deformed (Fig. 2b, f). LwsB-bearing veins collected at Triplex 224 and at Desertes (Table 1, Tpx-B1, Tpx-B2, Ds-B2, Ds-B3) are composed of quartz and fibers of cream-225 colored LwsB often fractured and systematically elongated parallel to vein walls (Fig. 4a-c), 226 highlighting their formation by dilatational shearing (Herviou et al., 2023). Ankerite crystals were found 227 at the selvages of some veins but are rarely observed in association with LwsB (Fig. 4a). LwsB crystals 228 do not contain OM but are often pseudomorphed into a mixture of phengite and chlorite (Fig. 4b, c).

LwsC-bearing veins are millimetric to centimetric tensile veins crosscutting the schistosity. These veins occur in the vicinity of fold hinges, close to LwsB-bearing veins, and are only found where LwsA is widespread in the schist. LwsC fibers are associated with ankerite and quartz, all growing perpendicularly to the vein selvages (Fig. 4d-f). LwsC-bearing veins are easily missed as they are small, scarce, largely sheared and poorly preserved. In most veins, LwsC fibers are pseudomorphed into phengite, chlorite and calcite (Fig. 4f). The freshest LwsC veins, selected for the geochemical study, were found in the vicinity of the 'multiquartz aggregates' described below. Herviou et al. (2023) have shown that the emplacement of the lawsonite vein (LwsB and LwsC) network is continuous and incremental, interpreted as the fossil record of slow slip events. The relative chronology between these events is therefore complicated to establish as the formation of these veins can be related to multiple processes.

240 In places, lawsonite-bearing veins are clustered and intimately folded and sheared with the surrounding schist, resulting in intricate patterns with schistose fragments embedded in high-pressure 241 242 veins with abundant quartz (Figs. 2d, e). These objects, referred to as 'multiquartz aggregates', were 243 sampled both in Triplex (Tpx-AB5 and Tpx-AC4) and Assietta pass (As-AB1 and As-AC2). Lawsonite 244 in these schistose fragments is therefore in direct proximity (< 1 cm) to lawsonite growing in the 245 embedding veins. Lawsonite in schistose fragments (noted LwsA*) forms black prisms including OM 246 trails, similar to those observed elsewhere in the schist, crystallizing with quartz and ankerite (Sup. Mat. 1a-c). Veins contain elongated lawsonite fibers similar to LwsB (labelled LwsB*; Figs. 2e, 5a-d), 247 showing multiple growth steps synchronous with deformation (Figs. 2e, Sup. Mat. 1a, c). LwsB* crystals 248 249 are associated with quartz and are very often pseudomorphosed into phengite and chlorite (Sup. Mat. 250 1c, d). Some multiquartz aggregates display LwsC tensile veins (Figs. 2d, Sup. Mat. 1f), generally at the 251 interface between LwsB*-bearing veins and embedded schistose fragments (Fig. 2e). LwsC fibers are associated with quartz and oxidized ankerite (Sup. Mat. 1g) and are well-preserved compared to LwsC 252 253 in most veins elsewhere and were therefore selected for analysis (Tpx-AC4, As-AC2).

254 ANALYTICAL METHODS

255 Analytical strategy (Table 1)

Major and trace element analysis have been carried out in lawsonite crystals to study whether lawsonite and its zoning patterns record evolving length-scales of element mobility and fluid circulation. Thick sections were made on 20 lawsonite-bearing samples (Table 1) to perform laser ablation ICP-MS and X-ray chemical maps to measure lawsonite trace element content and distribution.

Ten rock samples were selected along the Strada dell'Assietta transect (Fig. 5a) for bulk measurements. Nine of them are calcschists, representative of the types identified by Lefeuvre et al. (2020; Fig. 2a, b). One pelitic (Desertes; type 1) and one carbonate-rich calcschist (Gleise; type 4) were selected to represent end-member lithologies, where lawsonite is not abundant. Most samples (7) were selected in type 2 and type 3 calcschists (Fig. 2a, b) in which lawsonite is widespread (Lefeuvre et al., 2020). In order to identify potential interactions with mafic rocks, one ~10 m long basaltic pillow breccia body embedded in the calcschists was sampled at the Bourget site (Bg-mafic; 20 m away from theBourget calcschist sample) and analyzed.

Strontium isotopic ratios were measured on mineral separates and selected bulk samples because Sr is commonly enriched in both carbonates and lawsonite (Enami, 1999; Martin et al., 2014; Hara et al., 2019; Whitney et al., 2020) and rather mobile in aqueous fluids, therefore useful to study fluid-rock interactions (see Hara et al., 2018).

272 Bulk-rock geochemistry (Table 2)

273 Samples were finely crushed ($< 2\mu m$) in an agate mortar. Sample powders were weighed and heated for 1h at 1100°C to ensure destruction of OM. Powders were dissolved at 80°C in closed beakers 274 275 with HNO₃ and HF overnight. For analysis of major elements, B(OH)₃ was introduced quickly after 276 opening the beakers to avoid loss of silica. Further dilution was carried out with 2% HNO3 before 277 analysis. Major and trace element compositions were analyzed at ALIPP6 (ISTeP, Sorbonne Université, 278 Paris) using an ICP-OES spectrometer (Agilent 5100 HVDV) for major elements and an ICP-MS/MS 279 (Agilent 8800) for trace elements. Calibration was made using a set of international and in-house 280 standards (RGM-1, BIR-1, AGV-2, LIP, M77-2, GSN, COS, BHVO-2). To characterize the major 281 element budget of these rocks, 10 oxides were measured (SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, 282 Na₂O, K₂O and P₂O₅). A total of 37 minor and trace elements were selected for this study (Li, Be, Sc, 283 V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Cs, Ba, Ta, Pb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, 284 Ho, Er, Tm, Yb, Lu, Hf, Th and U).

285 Major element analysis and chemical mapping of lawsonite (Tables 3, 4, 5, 6)

286 Major element analysis of lawsonite crystals has been carried out at CAMPARIS (Sorbonne Université, Paris) with a CAMECA SX-Five electron microprobe and the data reduction method of 287 288 Pouchou and Pichoir (1991). Analytical conditions were 15 kV-10 nA in WDS mode for analysis of 289 major elements. Conditions were changed to 25 kV-100 nA when measuring minor elements (Sr, Ti, 290 and Cr). Fe₂O₃ (Fe), MnTiO₃ (Mn, Ti), diopside (Mg, Si), Cr₂O₃ (Cr), SrSi (Sr), orthoclase (Al, K), 291 anorthite (Ca) and albite (Na) were used as standards for calibration of elements in parentheses. 292 Quantitative mapping was performed using the same analytical conditions in WDS mode. Qualitative 293 element mapping was also carried out with a SUPRA-55VP SEM at ISTeP (Sorbonne Université, Paris) 294 in energy-dispersive spectroscopy (EDS) mode at 15 keV acceleration voltage, 30 nA beam current with a dwell time of 256 µs, analyzing each area up to 10 times for increased signal/noise ratio. 295

296 Trace element analysis of lawsonite (Table 7)

297 Trace element lawsonite concentrations were measured at ALIPP6, using a laser ablation ICP-298 MS/MS (Teledyne Analyte G2 193 nm ArF excimer laser ablation system coupled to an Agilent 8800 299 ICP-MS/MS) on polished thick sections (100 μ m). Lawsonite crystals were ablated for 60 s (frequency 300 of 8 Hz) in a He atmosphere using a 40 μ m beam and a laser fluency of 3.54 J/cm². Background was measured 18 s before and after sampling ablation. Standardization was carried out using BCR2-G 301 international glass standard, and ²⁷Al as internal standard obtained from electron microprobe analyses. 302 303 Instrument drift and accuracy were controlled with repeated analyses of the international standards ATHO-G and BHVO2-G. Every ablation pattern was verified with an in-house spreadsheet to check for 304 305 absence of impurities and/or inclusions during ablation (89 out of 400 analyses were discarded).

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Strontium isotopic ratios (Table 8)

307 Lawsonite strontium isotopic ratios were determined at the Boston College Center for Isotope 308 Geochemistry using an IsotopX Phoenix Thermal Ionization Mass Spectrometer (TIMS). First, lawsonite crystals were separated from the bulk rock after crushing and sieving (see Sup. Mat. 2). 309 310 Mineral fractions between 500µm and 125µm were separated using sodium polytungstate (density of 311 2.9 g.cm⁻³) allowing isolation of the heavy fraction containing lawsonite, ankerite and oxides. Lawsonite 312 grains were separated using magnetic separation, cleaned in ultrasonic baths and handpicked before 313 dissolution for TIMS analysis. Dissolution followed a four-step protocol (Sup. Mat. 2). Lawsonite 314 separates were partially dissolved in 2mL of glacial acetic acid in an ultrasonic bath to remove remaining 315 carbonates. This first step was repeated twice to purify the lawsonite fraction. Samples were 316 subsequently dissolved in HF-HNO₃-HCl. Cleaned lawsonite fractions were attacked with 100 µL of 317 HF together with 2 mL of HNO₃ at 120°C overnight. After 12 hours, the sample was dried down. The 318 same step was repeated with 2 mL of HNO_3 at 120°C. Dissolved samples were prepared for chemistry 319 in 2 mL of HCl at 120°C. Strontium was separated using 100 µL micro-columns and pre-cleaned Sr-320 spec resin. Approximately 100 ng of Sr were loaded onto Re filaments with a TaF activator solution. 321 Samples were analyzed using a multidynamic method, and repeated analysis of Sr standard SRM987 322 during the duration of the project gave 0.710240 ± 0.000010 (n = 5; 2sd), which is within the long-term average of 0.710242 ± 0.000005 (n=114; 2sd). 323

This procedure has been applied to bulk rock samples (without preliminary partial dissolution). In total, 7 bulk rocks and 17 lawsonite separates have been analyzed (8 LwsA, 6 LwsB, 1 LwsC and 2 LwsD samples). These same dissolved lawsonite samples were also aliquoted for ICP-MS analysis to determine the Sr and Rb concentrations and ⁸⁷Rb/⁸⁶Sr ratios reported in Table 8. Uncertainty in ⁸⁷Rb/⁸⁶Sr is 2.8 % RSD based on repeat analysis of standard solutions.

329

330 **RESULTS**

331 Bulk rock geochemistry

332 Bulk rock compositions reflect the petrographic variability of the metasediments along the 333 Strada dell'Assietta transect (Fig. 1d-e; Table 2): compositions evolve gradually in ACF (Al₂O₃-CaO-FeO; Fig. 5a) space between pelitic horizons (Desertes, lithology type 1 in Fig. 1d-e) and carbonate-rich 334 endmembers (Gleise, lithology type 4 in Fig. 1d-e). These rocks exhibit similar FeO contents around 335 336 20 % in ACF except for the mafic sample (Bg-mafic) described below. CaO and Al₂O₃ contents are 337 inversely correlated (Fig. 5b). Pelitic horizons (Desertes; type 1) contain > 25 wt. % of Al₂O₃ and < 10wt. % of CaO, whereas carbonate-rich calcschists (Gleise; type 4) contain up to 58 wt. % of CaO and 338 ~5 wt. % of Al₂O₃. Type 2 calcschists contain between 15 and 25 wt. % of Al₂O₃ and 10-25 wt. % of 339 CaO, whereas more carbonated type 3 calcschists contain 7 to 15 wt. % of Al₂O₃ and 25 to 50 wt. % of 340 CaO. At first order, TiO₂ and Ce are anti-correlated to CaO content (as for Al₂O₃), but Sr is positively 341 correlated to CaO content (Fig. 5b). TiO_2 is a major component of the SL calcschists (ranging between 342 343 0.1 and 1.9 wt. %) and is more concentrated in type 1 pelitic lithologies (> 1 wt. %) than in the more 344 carbonated type 2 (0.5-1 wt. %) and type 3-4 (< 0.5 wt. %) rocks. Most of the calcschists analyzed here 345 contain less than 100 ppm of Sr (types 1, 2) but Sr reaches 180 ppm in carbonate-rich type 4.

The most pelitic type 1 and type 2 calcschists are generally the most concentrated in LREE (Ce > 100 ppm, Fig. 5c) while the lowest concentrations are found in type 4 calcschists (Ce < 25 ppm, Fig. 5c). Chondrite-normalized REE patterns (Fig. 5c) show similarly decreasing trends from LREE to HREE for all calcschists, with La/Yb ratios around 20 and negative Eu anomalies (except for the Bourget sample). These patterns compare well with those of Corsican calcschists metamorphosed around 500-550 °C and ~ 2.3 GPa reported by Piccoli et al. (2016). However, Al₂O₃-rich calcschists from the present study (types 1 to 3) are one order of magnitude richer in REE (Fig. 5c).

Compared to the calcschists described above, the mafic sample from the Bourget locality (Bgmafic: metamorphosed pillow breccia) shows higher contents in FeO (up to 55 % in the ACF, Fig. 5a), MgO (~15 wt. %), Na₂O (~3 wt. %; Table 2), TiO₂ (~2 wt. %; Fig. 5b) and enrichments in V, Cr, Co and Ni (Table 2), elements typically enriched in mafic rocks. Bg-mafic is depleted compared to calcschists in CaO (5 wt. %), HREE, and in most LILE such as Sr (~10 ppm) Rb, Ba, Cs and Pb (Fig. 5c; Table 2).

359 Lawsonite composition

As major elements of the different lawsonite types are very similar (see tables 3, 4, 5, 6), we focused on the trace element contents. In the following, chemical maps (obtained by electron microscopy) are presented next to corresponding extended trace element patterns from LA-ICP-MS spotanalyses for each lawsonite type.

364 Univalent cations and white mica contamination

365 Even though preservation of lawsonite crystals has been a prevalent criterion for selection before laser ablation, and each lawsonite ablation pattern has been carefully inspected to detect contamination 366 367 from inclusions, contamination remains apparent. A strongly positive correlation between K content and 368 Na, Ba, Rb and Cs contents is observed (Sup. Mat. 3). These elements are classically enriched in white mica, in substitution of K. Because lawsonite is generally devoid of K, these specific enrichments are 369 370 attributed to white mica contamination via minute inclusions in lawsonite (see also Whitney et al., 2020). 371 Therefore, interpretation of analytical results does not incorporate Na, K, Ba, Rb and Cs in the following. It is also noteworthy that Li appears to show a positive correlation with K, yet much weaker than for 372 other univalent cations (Sup. Mat. 3). Significant white mica contamination appears limited to these 373 374 elements as no other correlation with K is observed.

375 *Lawsonite composition in host calcschists (LwsA)*

376 Five areas have been analyzed in a pelitic schist (sample Tpx-A1). They contain dark LwsA 377 crystals with hourglass zoning, easily recognized on Ti maps (Fig. 6a, c). Crystals may exhibit both 378 sides of the hourglass (Fig. 6c) or only one (Fig. 6a) due to their orientation. In chemical maps (Fig. 6a, c), hourglass zoning is faintly observed for Ce, with enriched domains similar to Ti (blue spots 30-32 379 380 and 34-35 in C1; spots 13, 14, 16 and 18 in C4) whereas Al is slightly depleted in these domains (C1, 381 Fig. 6a). Ce also shows enrichment in angular sectors in the center of lawsonite crystals, again anti-382 correlated to Al (Fig. 6a) but not linked to specific Ti enrichment (close to spots 37 and 29 in Fig. 6a, 383 close to spot 15 of Fig. 6c).

Ti-rich hourglass domains (blue dots 30-32 and 34-35; Fig. 6a, b) show the highest 384 concentrations in Ti, Zr and Hf and the lowest concentrations in Sr, Y and Mn. REE patterns also show 385 386 large variations, in terms of slope and absolute values, whether located within or without the Ti-enriched 387 domains. Even though barely seen on elemental maps (Fig. 6a, c), core to rim variations appear 388 superimposed to the hourglass domain, in particular in Ti-rich domains (e.g., blue curves 30-32 and 34-389 35 in Fig. 6b, blue and green curves in Fig. 6d): LREE content decreases from core to rim, while HREE values remain almost constant, which tends to flatten the REE pattern slope and generate spoon-shaped 390 391 patterns. Ti also tends to decrease from core to rim in the Ti-rich domain (Fig. 8a). In the crystal core 392 (spot 15 on Fig. 6c), the Ce-enriched Ti-depleted domain shows the highest U, Zr, Y, Hf, REE, Fe, Mn and Cr contents. 393

The LwsA crystal investigated in the third area (Fig. 6e) shows intricate zoning as tentatively 394 395 schematized (Fig. 6f). Overall, Ti and Sr maps (Fig. 6e) show a lawsonite core (spots 1 and 8) rimmed 396 by Ti-enriched lawsonite, itself rimmed by a Ti-poor, Sr-rich lawsonite border (green and blue zones in 397 Fig. 6f, respectively). In the lawsonite core, hourglass zoning is observed with two domains: Ti-enriched 398 (spots 01 and 08) and Sr-enriched (depleted triangle-shaped domain immediately below). Additionally, 399 the Ti-rich domain shows variable Ti content (Fig. 6e, f, g), the lowest contents in Zr, Hf and Ni, and 400 low LREE contents (spots 01 and 08, Fig. 6g). The enclosing lawsonite (spots 2 to 9) is generally Tirich and Sr-poor, with much dispersion and patchy domains. LA-ICP-MS analyses in this zone (spots 401 402 02, 03, 07, 09) show variable LREE contents, but almost similar HREE contents, resulting in flattened 403 and curved patterns like those observed earlier (Fig. 6b, d). The Sr-rich Ti-poor border (spots 10 and 12) 404 rimming LwsA (Fig. 6f) is enriched in Y and HREE, showing spoon-shaped REE patterns (Fig. 6g).

405 *Lawsonite composition in quartz-rich veins (LwsB)*

Cream-colored LwsB crystals have more homogeneous composition than LwsA crystals. None of the investigated LwsB crystals displays hourglass zoning. Other zoning patterns have been identified in LwsB crystals (Fig. 7). The first Ti map (Fig. 7a) features angular Ti-rich domains in crystal cores (LA-ICP-MS spots 38 to 41) surrounded by Ti-depleted rims (spots 42 and 43, Fig. 7a, b). These differences are highlighted in the interpretative sketch and a second map for Ti and Sr (Fig. 7c); it is tempting to interpret these as successive generations of lawsonite. The Ti-poor crystals are enriched in U, Sr, Y and HREE compared to the Ti-rich crystals (Fig. 7b).

413 *Lawsonite composition in multiquartz aggregates (LwsA* & LwsB*)*

Compositions of LwsA* and LwsB* from multiquartz aggregate Tpx-AB5 from Triplex are
provided in Supplementary material 4. LwsB* shows the same features as LwsB with Ti-rich cores (Sup.
Mat. 4a) and Ti-depleted rims corresponding to high Sr contents (Sup. Mat. 4b). The composition and
distribution of the other trace elements (Sup. Mat. 4b) compare also well with LwsB.

In the schistose fragments included in veins, dark LwsA* cores often show pale rims (Sup. Mat.
4d) enriched in Ti and Cr (Sup. Mat. 4c) but not in Ce (spots 2 to 5, Sup. Mat. 4c). LwsA* cores (spots
06 to 09) show heterogeneous and patchy Ti-zoning, they are generally enriched in most LILE (and
HFSE to a lower extent) but depleted in Pb and Sr (Sup. Mat. 4e).

422 Minor and trace elements in lawsonite types along the Strada dell'Assietta transect

In situ lawsonite compositions (Fig. 8, normalized to C1 chondrite, McDonough and Sun, 1995)are provided in Table 7 for each lawsonite type and each locality.

425 Dark LwsA crystals in host calcschist from Triplex area (Tpx-A1, Fig. 8b) display high values 426 for U, Th and REE. Most LILE (K, Cs, Rb, Ba, Pb, Sr) display large variations between samples, sharing 427 high Pb and Sr contents (10 to 100 times chondritic values) but low contents in the other LILE (down 428 to 10^{-3} chondritic values). The dispersion is much lower for Pb and Sr than for other LILE. High field 429 strength elements (HFSE; Zr, Ti, Hf) are also hugely variable: Zr content varies over four orders of 430 magnitude, Hf and Y over three, Ti over two. These lawsonite crystals show peculiar REE patterns, with 431 marked enrichment in LREE content for some, leading to a four order of magnitude dispersion. HREE 432 are also scattered but enriched between 10 and 1000 times the chondritic values. Two signatures appear: 433 LREE-enriched LwsA with a negative slope from LREE to HREE (La/Yb ~ 100), and LwsA with flat 434 to positive REE profiles, with an inflection point around Gd. Metallic elements (Fe, Mn, Cr and Ni) are generally low with considerably smaller dispersion. 435

436 LwsB in isolated quartz-bearing veins from Triplex (Tpx-B1, Fig. 8c; Tpx-B3, Fig. 8d) and Desertes (Ds-B3, Fig. 8a) shows very similar patterns for most elements. LwsB shows less dispersion 437 than LwsA, except for LILE in Tpx-B1 (Fig. 8c) that compare well with those of LwsA (Fig. 8b). U and 438 Th contents are either comparable to those in LwsA (Fig. 8a-d) or lower (between 10- and 200-times 439 440 chondritic values in Tpx-B1). Pb contents are comparable to those of LwsA, and Sr is slightly higher in 441 LwsB (up to 1000 times the chondritic values). For HFSE, Zr and Hf contents are lower than in LwsA (10⁻¹ to 10⁻² chondritic values) while Ti is similar (1-10, Fig. 8c). However, LwsB from Desertes shows 442 higher LILE and HFSE than those from Triplex (Fig. 8a, c, d). REE patterns of LwsB show a slightly 443 444 negative slope from LREE to HREE, as commonly observed in lawsonite (see compilation of Whitney 445 et al., 2020). These patterns are consistent with some of the LwsA patterns in the host calcschist (Fig. 446 8b). A small positive anomaly in Eu is observed in sample Tpx-B1 only (Fig. 8c). Metallic element 447 contents in LwsB from Triplex are comparable to those in LwsA crystals, although Ni is systematically 448 very low (Fig. 8c, d). The Desertes locality shows LwsB with the highest content in metallic elements 449 (Fig. 8a).

LwsD crystals (Tpx-D1, Fig. 8e) show trace element patterns generally like those of LwsA and LwsA*, with somewhat higher Sr and Y values, reaching 2000 times chondritic values. LILE, U, Th and all metallic elements are as high as for LwsA* and LwsC in the multiquartz aggregate Tpx-AC4. Part of LwsD crystals show relatively flat patterns from LREE to MREE and an enrichment of HREE starting from Ho, resulting in La/Yb ~10⁻². These patterns are similar to some of LwsA* and LwsC in multiquartz aggregate Tpx-AC4. (Fig. 8g). The other half of LwsD crystals is comparable with the most REE-enriched LwsA crystals in host calcschist (Fig. 8b, e).

Lawsonite crystals in multiquartz aggregates (LwsA* and LwsB*) in Triplex (Tpx-AB5, Fig.
8f) and Assietta Pass (As-AB1, Fig. 8h) show compositions overall similar to those of LwsA and LwsB,
respectively (Fig. 8b, c). LILE and HFSE contents are generally consistent with similar variability

between lawsonite types (LwsA* are comparable to LwsA and LwsB* to LwsB). Yet LwsA* and LwsC 460 461 from multiquartz aggregate Tpx-AC4 (Fig. 8g) show higher LILE, U, Th and metallic elements (Cr in 462 particular) than LwsA in host calcschist and LwsA* from other samples. REE patterns are more 463 distinctive: LwsA* and LwsC from multiquartz aggregate Tpx-AC4 (Fig. 8g) show pronounced spoon-464 shaped REE patterns similar to some of LwsA in host calcschist, while LwsA* from sample Tpx-AB5 465 (Fig. 8f) displays flat REE patterns around 10 to 100 times chondritic values, with one crystal showing 466 a spoon-shaped REE pattern. Most LwsB* crystals from Triplex and sample As-AB1 from Assietta Pass show REE patterns consistent with those of LwsB (Fig. 8a, b, d, h), i.e. with a slightly negative slope 467 and slightly curved. However, in sample As-AB1 from the Assietta pass, LwsB* growing with ankerite 468 469 (Fig. 8h) shows convex REE patterns (i.e., richer in MREE; Fig. 8h), which is also observed for a few 470 LwsB* crystals from Triplex (Fig. 8f). In the multiquartz aggregate from the Assietta Pass, LwsC crystals show trace element patterns similar to those of neighboring LwsA* (Fig. 8i), with both spoon-471 472 shaped and convex REE patterns.

Overall, two key observations can be made in the context of expected lawsonite composition
from the literature (Martin et al., 2014; Vitale Brovarone et al., 2014; Whitney et al., 2020; Kang et al.,
2022). First, enrichment in some elements (LREE, U, Th, Pb, Sr) stands out, in particular for LwsA,
LwsA* and LwsD crystals. Second, the dispersion of analyses is huge, even within samples.

477 Lawsonite ⁸⁷Sr/⁸⁶Sr ratios

Comparing ⁸⁷Sr/⁸⁶Sr ratios from lawsonite crystals and corresponding whole rocks from each location 478 479 reveals no viable isochron relationships (Fig. 9). To correct the isotopic ratios to the time of blueschist-480 facies metamorphism, the data were corrected by assuming lawsonite growth ages of 60, 50 or 40 Ma 481 (Table 8). At first order, lawsonite separates display different signatures along the transect (Fig. 9a), varying between 0.7113 near the Piemont margin units (westward) and ratios around 0.7140 at the As-482 483 sietta pass (eastward). Near the contact with the Piemont margin units, LwsA at Desertes shows similar 484 ⁸⁷Sr/⁸⁶Sr ratios to LwsB collected on the same outcrop (DS02A). The sample collected at Fraiteve (Ft-D1) containing LwsD shows an 87 Sr/ 86 Sr ratio of 0.712635 (± 0.000013). At Triplex, where the lawsonite 485 content is maximum (see Fig. 1d), all four LwsA samples show similar ⁸⁷Sr/⁸⁶Sr ratios (Table 8) around 486 487 0.7128, very close to the LwsC sample. The LwsB sample collected at Triplex shows higher ⁸⁷Sr/⁸⁶Sr ratios than LwsA and reaches 0.713708 (\pm 0.000015). LwsD contained in sample SL07B shows values 488 489 higher to LwsB and reaches up to 0.714352 (± 0.000008). LwsA at Bourget has higher ⁸⁷Sr/⁸⁶Sr ratio than LwsA in Triplex. At the Assietta pass, LwsA and LwsB show comparable ⁸⁷Sr/⁸⁶Sr ratios around 490 491 0.7140.

492 Overall, ⁸⁷Sr/⁸⁶Sr ratios in lawsonite apparently increase eastward (Fig. 9a), though with
493 significant local variability best demonstrated at Triplex, from 0.7112 at Desertes to .7138 at Assietta.

494 The ⁸⁷Sr/⁸⁶Sr ratios in lawsonite are not correlated with Sr and Rb concentrations (Fig. 9b-c) nor with

495 87 Rb/ 86 Sr ratio. In the bulk rocks, Sr isotopic ratios are inversely correlated to Sr concentration for the

- least radiogenic group, but not for the most radiogenic samples and the entire dataset appears scattered.
- 497 Whole rock and lawsonite values are relatively close to each other at Fraiteve and Triplex (to the west)
- 498 whereas whole rock and lawsonite values are markedly disparate at Bourget and Assietta (to the east).

499 DISCUSSION AND GEOLOGICAL IMPLICATIONS

500 Composition of lawsonite in calcschists

501 Lawsonite is increasingly suggested as a proxy for fluid/rock interactions during subduction through its geochemistry, as reviewed by Whitney et al. (2020) and Kang et al. (2022). However, 502 503 metasedimentary lawsonite is less frequently observed in outcropping rocks and has not been much 504 studied compared to metamafic lawsonite. Comparing the Fe and Al + Cr + Ti contents to the 505 compilation of exhumed lawsonite worldwide (Fig. 10a; Kang et al., 2022) shows that calcschist lawsonite follows a specific trend, different from those identified by Kang et al. (2022). Here, calcschist 506 lawsonite does not contain more than 0.04 Fe a.p.f.u. (regardless of the lawsonite type, Tables 3, 4, 5, 507 508 6) which may be linked to the incorporation of Fe in ankerite co-stable with lawsonite. The Pb and Sr 509 contents have been used by Whitney et al. (2020) to classify lawsonite compositions, where Sr/Pb ratio 510 below 40 are related to metasedimentary lawsonite (in Qz-rich metasediments, Kang et al., 2022); higher 511 Sr/Pb ratios were interpreted as reflecting metamafic lawsonite (characterized by moderate Sr/Pb below 130 and high Sr/Pb for greater values). Most analyses of the Alpine SL lawsonite types fall in the 512 513 moderate metamafic lawsonite field of Whitney et al. (2020; Fig. 10b) inconsistent with the lithology. 514 Abundance of lawsonite in type 2 and type 3 lithologies of the SL is linked to the presence of carbonates 515 involved in lawsonite crystallization. Here lawsonite compositional trends reflect local fluid-rock interactions rather than larger-scale fluid migrations. 516

517 Distribution of trace elements in lawsonite types

Lawsonite easily incorporates trace elements into its structure owing to multiple potential substitutions on Al and Ca sites, the latter being easily deformed and therefore prone to hosting large cations (Ueno et al., 1999; Dubacq and Plunder, 2018). Itoigawaïte has been recognized as the Sr equivalent of lawsonite, where Sr occupies the Ca site (Miyajima et al., 1999), suggesting extensive solid solution between the two.

523 *Hourglass sector zoning*

Hourglass zoning, observed in LwsA only, dramatically affects Ti (Fig. 6a, c, e). Ti-rich 524 525 domains also correspond to high LREE concentrations, as illustrated on Ce maps (Fig. 6a, c), to Zr and 526 Hf enrichment (Figs. 6b, d, 10c) but correspond to Sr depletion (Figs. 6e, 10d). Preferential incorporation 527 of Ti and LREE is commonly observed in metasedimentary lawsonite (Ueno et al., 1999; Martin et al., 528 2011, 2014; Vitale Brovarone et al., 2014), while Ti and Fe hourglass zoning are reported for lawsonite 529 in mafic rocks (Fornash et al., 2019). Hourglass zoning is classically observed in magmatic clinopyroxene and metamorphic staurolite (e.g., Hollister, 1970; Hollister and Gancarz, 1971; Dowty, 530 1976) and appears restricted to specific mineral groups, including tournaline (Van Hinsberg, 2006). 531 532 Hourglass zoning is attributed to differential uptake of elements on crystal faces exposed to fluids (Van 533 Hinsberg, 2006). Dowty (1976) showed that this preferential incorporation is controlled by the crystal 534 structure: some elements show a higher affinity with some crystal faces due to electrostatic interactions, increasing their adsorption rate during growth. Fornash et al. (2019) identified potential correlations 535 536 between the presence of subgrains and the shape of the hourglass zoning, potentially indicating that deformation processes might also play a key role in trace element partitioning while lawsonite 537 crystallizes. Hourglass zoning has therefore been identified as an out-of-equilibrium feature, linked to 538 539 rapid crystallization (Vitale Brovarone et al., 2014). Practically, crystals showing hourglass zoning 540 provide support that equilibrium was not reached, at least for some elements, with the consequence that 541 thermodynamic modeling and/or partition coefficients based on formula unit properties will fail at 542 reproducing the incorporation of these trace elements in lawsonite.

543 *Concentric growth zoning*

544 In Ti-enriched domains, concentrations of Ti and LREE are not constant. LREE are observed to decrease from core to rim, resulting in flattened REE patterns (Fig. 6b, d). Ti also uniformly decreases 545 546 from core to rim (Fig. 6c; patchy domains can be related to interface-coupled dissolution-precipitation, 547 see below). These core-to-rim depletions, also observed in tourmaline by Van Hinsberg et al. (2006), are interpreted as reflecting a reservoir effect consistent with closed-system behavior, as for the classical 548 549 Mn bell-shaped zoning in prograde garnet sometimes referred to as "garnet fractionation" (Tropper and 550 Recheis, 2003; Kohn, 2005; Skora et al., 2006; Dubacq et al., 2019). Here concentric zoning is observed 551 for immobile elements (large trivalent and quadrivalent cations) in lawsonite from pelitic parts, with the 552 lowest permeability, after low-temperature crystallization (180 to 300°C). Assuming at least transient 553 closed-system behavior is therefore reasonable, and backed by previous studies (Henry et al., 1996; 554 Cook-Kollars et al., 2014; Lefeuvre et al., 2020; Herviou et al., 2021). The lack of systematics between 555 cores and rims reflects the transient and local character, with homogenization over small length-scales in isolated parts of the schist. In other words, LwsA preferentially incorporates mobilized Ti and LREE 556 557 to its hourglass domains, but these elements are probably not distributed homogeneously at any given 558 time in the surrounding schist over more than tens of centimeters, linked to the thickness of 559 pelitic/carbonate alternations in the original sediment.

- The combination of hourglass zoning and reservoir effects explains the dramatic variations in
 La/Yb ratios in LwsA crystals (Fig. 10e). Most of the available LREE are incorporated into Ti-enriched
 domains of LwsA while HREE contents remain homogeneous (Fig. 6b, d, g).
- 563 Patchy zoning due to interface-coupled dissolution-precipitation

564 A third feature observed on lawsonite chemical maps in the schistose lithologies (calcschists types 1 to 3 containing LwsA and/or LwsA*) relates to patchy zoning, consisting of enriched or depleted 565 566 domains for some trace elements, and cross-cutting homogeneous or differently zoned domains for other 567 elements. This is best seen on the Ti maps of LwsA* in Sup. Mat. 4c, f, where thin Ti-depleted domains are found together with hair-like Ti-enriched domains with a vague preferred orientation. Patchy Ti 568 569 zoning is also observed for LwsA, either in the hourglass domain (Fig. 6c) or in overgrowths (Fig. 6e, f). Ce and Cr also show patchy or angular zoning in LwsA (Fig. 6a, c) and LwsA* (Sup. Mat. 4c, f). 570 571 This contrast with hourglass zoning and concentric growth zoning in that the domains appear blurry and not linked to crystal axes. The domains cannot be attributed to contamination as depleted and enriched 572 573 domains alternate (Figs. 6a, c, e). Interpretation of these patchy domains involves faster crystal growth 574 than the homogenization rate of Ti (or Cr, Ce) in the fluid feeding the crystal at grain boundaries. This has been recognized as similar to interface-coupled dissolution-precipitation, a mechanism leading to 575 spectacular zoning in many mineral groups (including carbonates, apatite, chloritoid, clinopyroxene and 576 577 garnet) over all metamorphic grades (Martin, 2009; Martin et al. 2011; Ruiz-Agudo et al., 2014; Ague and Axler, 2016; Renard et al., 2019; Figowy et al., 2020). This mechanism is not observed in LwsB 578 579 (grown from fluids in veins), where element mobility is likely much higher than in schistose lithologies 580 and where crystals grew with much more open space, as the veins may represent incrementally opened 581 structures (Lefeuvre et al., 2020; Herviou et al., 2023). Interface-coupled dissolution-precipitation may 582 lead to zoning reflecting the distribution of immobile elements before crystallization of neoblasts, as 583 suggested by Carlson (2002) and Martin (2009). Combined with sensitivity on element mobility, 584 interface-coupled dissolution-precipitation will therefore lead to the decoupling of poorly mobile 585 elements from one another (variably affected) and from more mobile elements (unaffected). Here, this 586 translates as adding noise to correlations with Ti (Fig. 10c, d).

587 Lawsonite overgrowths and system opening

In the schist, LwsA shows overgrowths with distinct chemical fingerprints (Sr-enriched, Tidepleted), as well as LwsB and LwsB* in HP veins and multiquartz aggregates (Figs. 6f, 7a, d, Sup. Mat. 4a). Overgrowths are Ti-depleted (Figs. 6e, 7a, d, Sup. Mat. 4a) but enriched in Sr, Y and HREE (Figs. 6e, g, 7d) whether found in veins or in the schist. LREE contents in lawsonite overgrowths are
variable but do not show clear systematic differences compared to cores (Figs. 6g, 7c, Sup. Mat. 4b).

593 Strontium-rich overgrowths (Fig. 7c) show that Sr is released in the fluid during lawsonite crystallization. Contrary to out-of-equilibrium element incorporation described above for LwsA cores, 594 this likely reflects an increased length-scale for element transfer. Given that Sr is positively correlated 595 596 with CaO in the bulk rocks and more concentrated in type 4 (carbonate-rich) calcschists (Fig. 2b) and considering that carbonates are the primary reservoir of Sr in these rock units, Sr-rich overgrowths may 597 be interpreted as evidence of opening of the system to carbonates via fluids. Quantifying this requires 598 599 modeling the origin and source of Sr in the rocks, for which bulk rock and lawsonite Sr isotopic 600 signatures can yield constraints.

Strontium isotopic ratios for all samples (Fig. 9) are more radiogenic than expected from 601 Cretaceous limestones (in the range 0.7073 – 0.7077; McArthur et al., 2001). The data from Triplex 602 603 perhaps hint at inheritance from a Mesozoic protolith $(139 \pm 65 \text{ Ma}; \text{MSWD}=160; \text{Sup. Mat. 5})$ but this 604 'errorchron' age is far too old for Alpine HP metamorphism and lawsonite growth. Clearly these rocks 605 failed to isotopically re-equilibrate at the local mineral scale during the Alpine metamorphism of these 606 rocks which occurred around 40-60 Ma (e.g., Agard et al., 2002; Ghignone et al., 2021; Herviou and 607 Bonnet, 2023; Gyomlai et al., 2023). Owing to the low temperatures of blueschist-facies metamorphism, this is not surprising. In bulk samples, the high Sr isotopic ratios are thought to reflect incorporation of 608 609 terrestrial-derived sediments. This is motivated by the high Sr isotopic ratios of the ~300 to ~500 Ma 610 crystalline basement from Massif Central, Piemont micro-continent and Adria, being eroded at the time 611 of deposition of the SL: commonly in the range 0.703-0.715, ratios as high as 0.731 are reported (e.g. Talbert and Duthou, 1983; Duthou, 1984; Downes et al., 1990, 1991; von Raumer et al., 1999) and high 612 613 Rb/Sr phases like micas deriving from these rocks could have even higher values. Non-metamorphic 614 Upper Cretaceous sediments of the "nappe des Gets" and Helminthoid flysch, taken as approximate equivalents of the SL before subduction, contain variable and locally high amounts of terrigenous 615 sediments, mostly in the form of clays but including plagioclase feldspar (Caron and Weidmann, 1967; 616 617 Caron, 1972; Caron et al., 1981), a major host of Sr. Rock samples in the least radiogenic group (with 618 ⁸⁷Sr/⁸⁶Sr ratios around 0.709) show decreasing isotopic ratios with Sr and Rb concentrations (Fig. 9b, c) 619 possibly reflecting the rock pelitic/carbonate proportions. However, for the more radiogenic samples 620 and the lawsonite separates, the absence of correlation between Sr content and isotopic ratio (Fig. 9b) is explained by the wide range of ⁸⁷Sr/⁸⁶Sr ratios in the pelitic fraction of the sediments: a unique mixing 621 622 curve is not obtained because of the variability of the pelitic endmember. Incorporation of variable fractions of Hercynian basement-derived, variably radiogenic Sr into the rock and/or the lawsonite 623 624 overgrowths leaves a blurry relationship between content and isotopic signature.

625 This small-scale variability of ⁸⁷Sr/⁸⁶Sr ratios and the lack of data on isotopic signatures for 626 lawsonite cores vs rims precludes defining precisely the source of Sr feeding overgrowths. Therefore, 627 Sr-rich overgrowths are proof of increased Sr mobility and consistent with limited system opening, but 628 do not reflect increasing devolatilization of the limestones.

Evolution of fluid circulation and element mobility length-scale in the Schistes Lustrés metasediments

631 Trace element distribution and zoning patterns in the different lawsonite types give insights into
632 the evolution of element mobility and fluid circulation length-scales in the calcschists during burial (see
633 Fig. 11).

LwsA (and LwsA*) in host calcschists appears first (Fig. 11a-b; Lefeuvre et al., 2020). 634 Hourglass zoning indicates out-of-equilibrium incorporation for some trace elements, including Ti and 635 LREE. Fine zoning in LREE and Ti shows small-scale migration of immobile elements via interface-636 coupled dissolution-precipitation. LREE core-to-rim depletion suggests progressive depletion in the 637 638 surrounding fluid, explaining the high variability of trace element concentrations and the decreasing La/Yb ratios over time, correlating positively with Ti but negatively with Sr (Figs. 6e, f, 7d, 10d). This 639 is consistent with a closed-system behavior and element transfer restricted to µm to mm scale. As LwsA 640 641 starts crystallizing early during burial (predicted crystallization at ~0.4 GPa and 180°C; Lefeuvre et al., 642 2020), element mobility was likely restricted by the small amount of fluid available at grain boundaries and by sluggish diffusivity at such low temperature. The Sr-rich overgrowths in LwsA (Fig. 6e, f) are 643 644 interpreted as recording a slightly more open-system behavior, with length-scales of element mobility 645 reaching tens of centimeters (Fig. 11b). Increasing element mobility is likely due to the on-going 646 dehydration reactions (mostly from the pelitic fraction, Lefeuvre et al., 2020), occurring until peak conditions (Fig. 11c, d). The similar Sr isotopic ratios of LwsA separates and bulk samples from Triplex 647 648 also show evidence of local-scale element redistribution during LwsA crystallization.

649 The significance of the apparent eastward increase of Sr isotopic ratios in LwsA across the 650 Strada dell'Assietta transect (Fig. 9a) remains unclear. However, metamorphic reactions occurring in 651 the pelitic fraction with increasing P-T conditions, including destabilization and dehydration of clay 652 minerals (see Vidal and Dubacq, 2009) and/or increasing dissolution of detrital plagioclase are likely to 653 account for Sr isotopic changes. A denser sampling and further analyses on other phases (calcite and 654 ankerite from the SL; plagioclase and clays from the Pre-Alps Gets unit, a non-metamorphic analog) are required to clarify this, as the evolution of the average Sr isotopic ratio of the detrital sediments during 655 deposition is unknown. The large difference between lawsonite separates and whole rock ⁸⁷Sr/⁸⁶Sr for 656 all locations east of Triplex is also an unresolved first-order problem. There, lawsonite separates are far 657 658 more radiogenic than their host rocks, unlike locations further to the west. It is possible that the lawsonite crystals grew from Rb-rich phases out-of-equilibrium with the rest of the whole rock (e.g., detrital micas
and mica-like clay minerals), inheriting their elevated ⁸⁷Sr/⁸⁶Sr. Alternatively, this could reflect open
system influx of a radiogenic Sr rich fluid that was more significant in the east than in the west.

Although interpretations for LwsC and LwsD cannot be generalized due to a lack of data for these scarce lawsonite types, it is noteworthy that LwsC veins in multiquartz aggregate present mineral assemblages and trace element patterns similar to the neighboring LwsA* in the calcschists (Fig. 8g), and LwsD in the host rocks is very similar to LwsA and LwsA* (Fig. 8b, e, f). Therefore, LwsC and LwsD may have formed from the same local fluid, transferring elements only at the meter scale or smaller, restricted to the meter.

The elemental homogeneity of LwsB and LwsB* cores (Fig. 8a, c, d, f, h) suggests that the vein 668 network collecting internally derived fluids allowed efficient homogenization and element 669 redistribution. As for LwsA, Sr-rich overgrowths (LwsB2, Fig. 7b, c) likely reflect an increasing 670 671 distance of element transfer during LwsB crystallization, in agreement with the incremental growth patterns of LwsB fibers (Lefeuvre et al., 2020). LwsB ⁸⁷Sr/⁸⁶Sr ratios are higher than those of LwsA at 672 673 Triplex but lower at Desertes and similar at Assietta, which is also consistent with opening of the LwsB 674 vein network to surrounding pelitic/carbonate layers with variable Sr isotopic ratios. LwsB and LwsB* 675 show similar trace element patterns all along the Strada dell'Assietta transect, suggesting that similar 676 small-scale processes acted synchronously along the transect, regardless of the varied pressure-677 temperature conditions. However, the heterogeneity of their Sr isotopic signature (Fig. 9) suggests that 678 the scale of fluid homogenization in LwsB vein network did not reach the km-scale but was efficient on 679 the order of hundreds of meters (sub-unit scale; Fig. 11c) in a transiently connected LwsB vein network, 680 continually evolving with ductile deformation.

681 Overall, our results are in line with previous isotopic, trace elements and fluid inclusions studies 682 suggesting a closed-system behavior with a limited scale of fluid circulation inside the SL units during subduction (Henry et al., 1996; Agard et al., 2000; Bebout et al., 2013; Cook-Kollars et al., 2014; Epstein 683 684 et al., 2020; Herviou et al., 2021). This small scale and pervasive fluid circulation is also supported by 685 the distribution of veins across outcrops (Herviou et al., 2023). However, a local and limited influx of 686 fluid containing radiogenic Sr cannot be ruled out at Triplex and locations further east, where lawsonite separates show both the highest and most variable ⁸⁷Sr/⁸⁶Sr ratios, and where multiquartz aggregates are 687 688 numerous.

689 During prograde and peak metamorphism, fluids are internally produced via dehydration 690 reactions in pelitic horizons and react with carbonate layers (see also Herviou et al., 2021) but mobilized 691 elements are rapidly trapped in lawsonite and newly formed carbonates. Growth of LwsA in the schist 692 leads to rapid, effective immobilization of poorly mobile elements like Ti, in addition to consuming water. Crystallization of lawsonite follows a continuum (see Lefeuvre et al., 2020) starting early in the subduction history and lasting until peak metamorphic conditions (Fig. 11d). Along this continuum, opening of the system appears progressive, with increasing fluid-rock interaction scales (from mm-scale to m-scale, Fig. 11a-c.), as shown by i) incremental growth of LwsA, ii) appearance of other lawsonite types in veins, iii) reaction fronts along the carbonate/pelite interfaces, with rock mixing and reaction rates enhanced by deformation (Lefeuvre et al., 2020), and iv) isotopic disequilibrium of Sr between lawsonite veins and the surrounding schist. Despite evidence for increasing fluid circulation and system

opening over time, no evidence for large-scale mass transfer, even close to tectonic contacts, is found.

The limited fluid flux inside the SL units compared to the larger fluid circulation suggested in tectonic
contacts and in lithological boundaries (e.g., Angiboust et al., 2014; Locatelli et al., 2019; Herviou and
Bonnet, 2023) explains the important differences in the geochemical behavior of elements during
crystallization of lawsonite from lawsonitite found in metasomatic aureoles (e.g., Piccoli et al., 2018;
Vitale Brovarone et al., 2020).

706 CONCLUSIONS

707 The upper units of the Schistes Lustrés deep accretionary complex show an intricate record of 708 extensive fluid/rock interactions in sediments metamorphosed at blueschist-facies conditions. In these 709 units, lawsonite is ubiquitous in veins and in the surrounding schists, crystallized from early prograde 710 to peak burial conditions. This study based on major, trace elements and Sr isotopic ratios provides a 711 detailed framework for petrological and geochemical interpretation of the complex geochemical record 712 of lawsonite. White mica contamination has been found to be difficult to avoid and hinders 713 interpretations based on content of univalent cations. For other minor and trace elements, this study 714 shows that several processes affected the composition of lawsonite, decoupling elements from one 715 another, mostly based on their mobility. These processes take place at equilibrium and out-of-716 equilibrium, resulting in zoning, apparently unrelated to the changing pressure-temperature conditions. 717 At crystal scale, two main types of zoning are observed: hourglass zoning in the calcschists and growth zoning both in the schists and in the veins. Hourglass zoning preferentially affects Ti and LREE. 718 Concentric growth zoning is best observed for Ti, REE, Hf and Zr, and likely involves many other 719 720 elements less dramatically. Combination of these mechanisms results in large variability of trace element 721 contents, especially REE that vary over four orders of magnitude. Over time during prograde metamorphism, the La/Yb ratio decreases strongly (from ~100 to ~1) as La appears much more sensitive 722 723 than Yb to crystal surface effects leading to hourglass zoning.

Interface-coupled dissolution-precipitation is a third mechanism decoupling elements in the
calcschists and involving poorly mobile elements. It is again best observed for Ti, but affects REE and
Cr too, resulting in poor correlations between elements.

Lastly, overgrowths, best observed in varying Sr content, show system opening in the veins. 727 728 System opening remains limited in the host calcschists. Sr isotopic ratios that are consistently more 729 radiogenic than the marine carbonate protolith rule out limestone devolatilization as the main driver of 730 fluid flow and source of the Sr. The overall mineral compositional evolution records progressive and 731 incremental system opening, first limited to tens of centimeters, then to the subunit scale, at the order of 732 hundreds of meters at most. Large-scale mass transfer and fluid influx from external sources are not 733 supported even though the vein network extends over time until peak conditions. This vein network 734 appears fed by internal fluids and enhanced by deformation. In the schists, transfer via fluid advection 735 was limited to mobile elements like Sr during the last growth increments. Comparison between the 736 composition of lawsonite in veins and in the schist has been found critical for interpretation of varying 737 fluid composition over space and time.

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1039 Fig. 1
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1288 **Figures captions**

1289 Fig1. Geological settings

1290 (a) Simplified geological map of the Western Alps modified after Herviou et al. (2022). GP: Gran 1291 Paradiso; DB: Dent Blanche; MR: Monte Rosa; DM: Dora Maira. SL units are in yellow for upper units 1292 (LPU), orange for middle units (LPM) and red for lower units (LPL). Raman spectra on carbonaceous 1293 material temperatures of Beyssac et al. (2002) are reported. (b) Close-up of simplified geological map 1294 of the zone of interest. Mafic bodies are shown in green. Bulk rock samples collected along the Strada 1295 dell'Assietta transect are shown as colored circles and diamonds. (c) WSW-ENE simplified cross section 1296 of the SL illustrating the geometry and distribution of the stacked units of the SL. Peak pressure-1297 temperature conditions from west to east are reported according to Agard et al. (2001). (d) Simplified 1298 cross-section of the transect between Fraiteve and the Assietta pass (see Fig. 1). The color code 1299 (schematized in (e)) indicates the rock type, from 1 (pelite) to 5 (carbonate with very few pelite layers). 1300 Samples are located and labeled along the transect (colored circles). (e) Average volumetric content of 1301 lawsonite (regardless of lawsonite type) for each lithology.

1302 Fig2. Several types of lawsonite observed at Triplex

1303 (a) Schematized Triplex outcrop where main deformation structures (D2, D3) are highlighted. Samples 1304 Tpx-A1, Tpx-B1, Tpx-B2 and Tpx-D1 are located with colored dots. (b) Triplex outcrop photograph 1305 overlaid by a sketch of the structural framework with locations of samples Tpx-A2, Tpx-A3, Tpx-B3, 1306 Tpx-AC4 and Tpx-AB5. Carbonate horizons are in light brown and lawsonite-bearing veins in white. 1307 Yellow rectangles locate following subfigures. (c) Field photograph of intensely folded metasediments 1308 composed of centimeter-scale alternations of pelite-rich and carbonate-rich domains (carb). LwsA black 1309 prisms are abundant in pelite-rich layers and associated with ankerite (Ank). Quartz (Qz) and thin calcite 1310 veins are numerous. (d) Centimeter-scale multiquartz aggregate in which all lawsonite types are 1311 observed, schematically interpreted in (e). In these aggregates, clasts of pelitic schists are often embedded in LwsB bearing veins ductilely deformed. (f) Isolated quartz-rich LwsB vein in the SL 1312 1313 metasediments. (g) LwsD in the host calcschist, next to LwsB-bearing veins.

1314 Fig3. Mineralogy of LwsA-bearing host calcschists

(a) Hand specimen of a LwsA-bearing calcschist (Tpx-A1) with LwsA as black prisms, associated with
ankerite and quartz. Note retrograde chlorite (Chl) and phengite (Ph replacing lawsonite. (b), (c)
Photographs of the associated thin section (Tpx-A1) underlining the high abundance of LwsA in the
calcschist. Lawsonite crystal cores contain abundant organic matter (OM) inclusions. (d) Interpretative
sketch of the area in yellow rectangle in (c) highlighting hourglass zonations commonly observed in

1320 LwsA. (e) Close-up view of a hourglass-zoned LwsA associated with quartz and ankerite and partly 1321 retrogressed in phengite. (f) LwsA located in the carbonate horizon of sample Tpx-A2 where ankerite 1322 is predominant and where apatite crystals have been observed, a rare accessory mineral.

1323 Fig4. Mineralogy of LwsB and LwsC-bearing veins

(a) Hand specimen of a LwsB-bearing vein (Ds-B2). LwsB cream-colored crystals is associated with
quartz and grows as fibers elongated parallel to the vein selvages. (b), (c) Photographs of Qz and LwsBbearing vein thin sections (Tpx-B3, Tpx-B1, cross-polarized). These lawsonite crystals never contain
OM inclusions but are often retrogressed into Ph + Chl mixture. (d), (e) LwsC vein in the calcschists,
with ankerite and quartz. (f) Photograph of the sample Tpx-AC4 thin section centered on a LwsCbearing vein. LwsC are often pseudomorphed into a mixture of phengite, chlorite and calcite,
complicating geochemical analysis.

1331 Fig5. Representative geology and whole rock geochemistry

(a) Al_2O_3 , FeO, CaO relative weight fractions in bulk rock samples. Average pelite composition is represented in gray and the GLOSS composition is shown for reference. (b) Major and trace element contents for bulk rocks. From left to right: Al_2O_3 (wt. %), TiO₂ (wt. %), Ce (ppm) and Sr (ppm) contents against the CaO (wt. %) content, the latter reflecting carbonate proportion. (c) REE concentrations of the calcschists, normalized to chondritic values from McDonough and Sun (1995). Alpine Corsican calcschists from Piccoli et al. (2016) are reported for comparison.

1338 Fig6. Incremental growth recorded in host calcschist (Tpx-A1)

1339 (a) Al, Ti and Ce chemical maps (SEM) of a LwsA crystal from Tpx-A1 (map C1). These maps highlight 1340 hourglass zoning. (b) Spider diagram showing element contents normalized to C1 chondrite, for ablation 1341 spots 29 to 38 located on maps from Fig. 7a. (c) Cr, Ti and Ce chemical maps (SEM) of a LwsA crystal 1342 from Tpx-A1 (map C4). Hourglass zoning is best seen on the Ti map. (d) Spider diagrams showing 1343 element contents normalized to C1 chondrite, for ablation spots 13 to 18 located on maps from Fig. 7c. 1344 (e) Ti and Sr chemical maps (EPMA) of a LwsA crystal from Tpx-A1 (map C3). These maps highlight 1345 a complex history of incremental growth interpreted in sketch (f). The crystal core shows hourglass 1346 zoning entrapped in a Ti-rich domain presenting a patchy distribution overgrown by a Sr-rich, Ti-1347 depleted rim. (g) Spider diagram showing element contents normalized to C1 chondrite (ablation spots 01 to 12 located in Fig.7e). 1348

1349 Fig7. Incremental growth recorded in quartz-rich LwsB-bearing vein (Tpx-B1)

- (a) Ti chemical map (SEM) of a LwsB crystal from Tpx-B1 (map C3). This map highlights angular Ti-
- 1351 rich domains in LwsB cores, rimmed by Ti-poor lawsonite, interpreted as incremental growth during
- 1352 the vein formation. Below: interpretative sketch of LwsB incremental growth in the quartz-rich vein.
- 1353 $LwsB_1$ cores are Ti-enriched whereas $LwsB_2$ rims are Ti depleted. (b) Spider diagram with element
- 1354 contents normalized to C1 chondrite (ablation spots 38 to 43 located in Fig.8a). (c) Optical microscopy,
- 1355 Ti and Sr chemical maps (SEM) of a LwsB crystal from Tpx-B1.

1356 Fig8. Trace element patterns of lawsonite

Spider diagrams of 35 elements analyzed by laser-ablation ICP-MS in the lawsonite types encounteredin the field. All 311 spectra are normalized to C1 chondrite from McDonough and Sun (1995) and are

1359 presented by sampling sites and lawsonite types to ease reading. The color code refers to the lawsonite

1360 type even when encountered in the same sample (in multiquartz aggregates: Fig. 10f-i).

1361 Fig9. Strontium isotopic signal of lawsonites

(a) ⁸⁷Sr/⁸⁶Sr ratios in lawsonite separates, plotted against the sample distance to the Piemont margin
units westward. Sampling locations are reported in Fig. 1b. The different types of lawsonite are
highlighted by specific colors (LwsA: red, LwsB: dark blue; LwsC: yellow; LwsD: green). TIMS
⁸⁷Sr/⁸⁶Sr data have been corrected considering an age of crystallization of 50 Ma for lawsonite. Estimated
errors are smaller than point size. All the data and corrections are available in Table 8. (b, c) ⁸⁷Sr/⁸⁶Sr
ratios plotted against Sr (b) and Rb (c) concentrations (ICP-MS).

1368 Fig10. Geochemical correlations

1369 (a) Al + Ti + Cr content (a.p.f.u.) in function of the Fe (a.p.f.u.) content of the Alpine Schistes Lustrés 1370 lawsonites compared to the compilation of worldwide lawsonites collected in different geodynamical 1371 contexts after Kang et al. (2022). The samples are detailed in the legend and color-coded to identify the 1372 different lawsonite types. (b) Sr content (in ppm) plotted against Pb content (in ppm). The three 1373 highlighted domains (gray, light and dark green) are plotted according to Whitney et al. (2020) where 1374 these Pb/Sr ratios have been inferred to discriminate sedimentary lawsonite from mafic rocks lawsonite. 1375 (c) Ti content (in ppm) plotted against Zr content (in ppm). (d) Ti content (in ppm) plotted against Sr 1376 content (in ppm). (e) La/Yb ratio plotted against Sr content (in ppm). (f) Yb content (in ppm) plotted 1377 against Sr content (in ppm).

1378 Fig11. Scenario of fluid circulation and element mobility length-scale

(a) Early crystallization of LwsA in the pelitic schists results from restricted, mm-scale element 1379 migration through locally released fluid. LwsA zoning patterns reveal out-of-equilibrium growth 1380 1381 processes occurring at low temperature (i.e., sluggish diffusivity) in a rather closed system: hourglass 1382 zoning, growth zoning (i.e., reservoir effect) and interface-coupled dissolution-precipitation processes 1383 (i.e., patchy zoning) affecting poorly mobile elements (Ti, LREE, Cr). (b) Along burial, increasing 1384 temperature, deformation and fluid release contribute to progressively increase the scale of fluid-rock 1385 interactions. Sr-rich LwsA overgrowths and local homogeneity of Sr isotopic ratios suggest that fluid 1386 homogenization between pelitic and carbonate-rich layers remained restricted to the dm-scale. LwsC 1387 tension gashes were likely fed by local element transfer. (c) Close to peak burial conditions, the 1388 transiently connected vein network allowed fluid homogenization at the m- to hm-scale (sub-unit scale). 1389 Incremental growth of LwsB veins with Sr-rich rims records the progressive increase of element mobility length-scale. LwsB incremental veins and multiquartz aggregates acted as drains for fluids. 1390 However, the lack of homogeneity of Sr isotopic signature suggests that the SL unit remained a closed-1391 1392 system and did not record massive infiltration of external fluids. (d) Integration of this petrological 1393 scenario at subduction-zone scale. The P-T conditions correspond to the LwsA massive formation (around 0.4 GPa, 180°C; Lefeuvre et al., 2020). At this stage, fluids are locally produced through 1394 metamorphic dehydration reactions and are internally recycled forming large amounts of lawsonite. 1395 1396 Incremental formation of lawsonite veins induces progressive opening of the system, mass transfer likely reaching the hm-scale. Reaching peak burial (1.6 GPa, 350°C; Agard et al., 2001), the SL units were 1397 1398 scrapped off and progressively stacked to the upper plate allowing their later exhumation. This implies 1399 a shift in the mechanical behavior of the sedimentary pile.

1400

1401 **Table captions**

1402 (tables and supplementary materials are available contacting the1403 corresponding author)

1404 Table 1. Sample characterization

Samples investigated here, sorted by locations (Desertes, Fraiteve, Bourget, Triplex, Assietta).
Lawsonite types are provided, together with the mineralogy, performed analyses and GPS coordinates.
LwsA* and LwsB* relate to multiquartz aggregates. Mineral proportions are given with a qualitative
scale ('-': not seen; '+': rarely seen; '++': present in the entire thin section in proportions < 50 %; '+++':
ubiquitous).

1410 Table 2. Bulk rock geochemistry (ICP-OES and ICP-MS)

- 1411 Bulk rock analyses. Major elements are expressed in weight %, trace elements in ppm. Bulk rocks are
- 1412 calcschists, except for sample Bg-Mafic which is a pillow breccia embedded in the Bourget calcschists.

1413 Table 3. Major elements of LwsA from microprobe analysis

- 1414 Weight percentages of investigated oxides for each analysis made on LwsA crystals. TiO₂, SrO and
- 1415 Cr₂O₃ are given with a greater precision because of special analytical conditions for these elements (see
- 1416 methods). B.d.l.: below detection limits. The formula units are calculated on 8 oxygen atoms.

1417 Table 4. Major elements of LwsB from microprobe analysis

- 1418 Weight percentages of investigated oxides for each analysis made on LwsB crystals. TiO₂, SrO and
- 1419 Cr_2O_3 are given with a greater precision because of special analytical conditions for these elements (see
- 1420 methods). B.d.l.: below detection limits. The formula units are calculated on 8 oxygen atoms.

1421 Table 5. Major elements of LwsC from microprobe analysis

Weight percentages of investigated oxides for each analysis made on LwsC crystals. TiO₂, SrO and Cr_2O_3 are given with a greater precision because of special analytical conditions for these elements (see methods). B.d.l.: below detection limits. The formula units are calculated on 8 oxygen atoms.

1425 Table 6. Major elements of LwsD from microprobe analysis

- 1426 Weight percentages of investigated oxides for each analysis made on LwsD crystals. TiO₂, SrO and
- 1427 Cr_2O_3 are given with a greater precision because of special analytical conditions for these elements (see
- 1428 methods). B.d.l.: below detection limits. The formula units are calculated on 8 oxygen atoms.

1429 Table 7. Lawsonite geochemistry (LA-ICP-MS/MS)

1430 Trace element concentrations (in ppm) of different types of lawsonite obtained by laser ablation ICP-1431 MS/MS.

1432 Table 8. Strontium isotopic ratios (TIMS)

- 1433 Strontium isotopic ratios of bulk rocks and lawsonite separates. The Rb and Sr concentrations (in ppm)
- 1434 and ⁸⁷Rb/⁸⁶Sr ratios measured with ICP-MS/MS have been added to the dataset. The ⁸⁷Sr/⁸⁶Sr have been
- 1435 corrected assuming three different crystallization ages for the lawsonite: 40 Ma, 50 Ma and 60 Ma.

1436 Supplementary material captions

1437 Sup. Mat. 1. Mineralogy of LwsA* and LwsB*-bearing samples in multiquartz aggregates

1438 (a) Multiquartz aggregate observed in the Triplex area with coalescent LwsB-bearing veins. Fragments 1439 of the host calcschists are included in the veins, as schematized on (b). (c) Hand specimen of a 1440 multiquartz aggregate (Tpx-AC4) where schistose clasts containing LwsA* are embedded in a LwsB*-1441 bearing quartz-rich vein. LwsB* crystals are sometimes associated with ankerite where located next to 1442 the pelitic fragments. (d) LwsB* crystals thin section illustrating elongation of lawsonite fibers 1443 (polarized light). In this sample (Assietta, As-AB1), LwsB* crystals are essentially associated with 1444 quartz and retrogressed to phengite and chlorite. (e) Photograph of the Tpx-AC4 centered on a calcschist 1445 clast where LwsA* are ubiquitous, presenting the same microstructures as LwsA: association with 1446 ankerite and quartz, inclusions of OM in the cores and OM-free rims. (f) Field photograph of a multiquartz aggregate presenting LwsA* in a host rock fragment and a LwsC-bearing vein. (g) Close-1447 1448 up view of the sharp interface between LwsA* bearing clasts and the LwsC bearing vein (As-AC2). 1449 LwsC crystals grow perpendicularly to the vein selvages (polarized light).

1450 Sup. Mat. 2. Lawsonite separation protocol

Schematized protocol followed in this study to isolate lawsonite crystals from the bulk rocks. Each step
is specified from crushing to the hand picking. SEM imaging was used to ensure purity after heavy
liquids and Frantz magnetic separation.

1454 Sup. Mat. 3. Univalent contamination of lawsonite by white micas

1455 Mica contamination evidenced by positive correlations between K (ppm) and several other elements 1456 (Na, Ba, Rb, Li and Cs). Symbols code for lawsonite types.

1457 Sup. Mat. 4. Distribution of trace elements in multiquartz aggregates (LwsA* & LwsB*)

1458 (a) Ti chemical map (EPMA) of a LwsB* crystal from Tpx-AB5 (zone C1, see location on the thick 1459 section in Sup.Mat. 4). Ti-rich cores rimmed by Ti-poor borders suggest incremental growth during vein 1460 formation. Spots show locations of the laser ablation analyses (Fig.9b). (b) Spider diagram of C1 1461 chondrite-normalized element contents for spots 29 to 35 (localized in (a). (c) Ti, Cr and Ce chemical maps (EPMA) of a LwsA* crystal from Tpx-AB5 (zone C3, see location on the thick section in Sup.Mat. 1462 4). (d) Plane polarized photography of LwsA* highlighting OM-enriched core surrounded by a clear 1463 1464 outer rim. (e) Spider diagram of C1 chondrite-normalized element contents for spots 02 to 09 localized in (c) and (d). (f) Optical microscopy, Ti and Sr maps (SEM) centered on a LwsC-bearing vein and the 1465

- 1466 LwsA*-bearing clast. Note that the OM and the Ti are restricted to the LwsA* crystal, illustrating
- 1467 hourglass zonation.

1468 Sup. Mat. 5. Strontium isotopic "errorchron"

- 1469 ⁸⁷Sr/⁸⁶Sr versus ⁸⁷Rb/⁸⁶Sr for both bulk rocks and lawsonite separates collected at Triplex. The respective
- 1470 errors are reported on the graphic.
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