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# Serpentinization as a Tape Recorder of (Dis)Continuous Mantle Exhumation along the Alpine Tethys Ocean-Continent-Transition

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Serpentinization has been widely documented and investigated at mid-ocean ridges (MOR) and subduction zones. In contrast, at magma-poor rifted margins serpentinization has received much less attention, despite its importance in controlling rheology and mass fluxes during breakup and establishing of a steady-state MOR. In this study, we present new petrological and geochemical data on subcontinental exhumed serpentinized peridotites from the spectacularly exposed Platta, Tasna and Totalp nappes in the Eastern Central Alps in SE Switzerland, belonging to the Alpine Tethys Ocean Continent Transition (OCT). The results testify of a complex history of fluid-rock interactions recorded by several serpentinization events starting with lizardite mesh and bastite textures (S1), subsequently followed by a succession of serpentine-filling veins with distinct textures and serpentine polysomes that include spherical polyhedral serpentine (S2); chrysotile ± polygonal ± lizardite banded veins (S3); lamellar antigorite veins and patches (S4) and chrysotile crack-seal (S5). The serpentinization sequence differs at proximal (i.e. continentwards) and distal (i.e. oceanwards) domains of the OCT. At proximal domains of the OCT (Upper Platta, Tasna) serpentinites record the complete serpentinization sequence (S1 to S5), whereas at distal domains (Lower Platta) serpentinization is restricted to pseudomorphic mesh and bastite (S1) and chrysotile crack-seal (S5). We attribute this discrepancy to contrasted mechanisms of mantle exhumation along the OCT. While at proximal domains mantle is unroofed along continuous and single large offset detachment faults allowing for the formation of all serpentine generations, mantle exhumation at distal domains is a more discontinuous process, controlled by sequential out-of-sequence detachment and flip-flop faults preventing the full development of all serpentine generations. In this frame, the nature and order of formation of the serpentine polysomes are directly controlled by the conditions of serpentinization (i.e. temperature, mantle composition and fluid/rock ratio). We propose that this new conceptual model can be extrapolated to serpentinization at slow to ultra-slow MORs, where close similarities in the serpentinization sequences have been recently reported.

Key words: serpentinization; magma-poor rifted margin; mantle exhumation; serpentine geochemistry; fluid-rock interaction

#### INTRODUCTION

At slow and ultra-slow spreading ridges (<40 mm $\bullet$ yr<sup>-1</sup>), mantle peridotites are either exhumed at the seafloor along large offset normal faults, also referred to as detachment faults (Karson & Rona, 1990; Cannat, 1993; Cann et al., 1997; Lavier et al., 1999; Smith et al., 2006), or flip-flop faults (Sauter et al., 2013). Mantle exhumation at MORs is closely linked to hydrothermal activity that significantly modifies the mineralogy of mantle peridotites, turning them into serpentinites (e.g. Bonatti, 1968; Aumento & Loubat, 1971; Früh-Green et al., 1990, 1996; Paulick et al., 2006; Bach et al., 2004, 2006; Schwarzenbach et al., 2016, 2021). The serpentinization process stores about 13 wt % H<sub>2</sub>O, leading to a strong volume expansion (up to ~40%, O'Hanley, 1992; Klein & Roux, 2020), and a density drop from 3.3 to 2.6  $gecm^{-3}$ . Serpentinization also results in strain localization along faults and the subsequent rapid exhumation from depths of 3 to 4 km to the seafloor (Raleigh & Paterson, 1965; Christensen, 1972, 2004; Reinen et al., 1994; Escartin et al., 1997, 2001; Morrow et al., 2000).

While serpentinization and mantle-fluid interactions at Mid-Ocean Ridges (MORs) were largely documented over the past two decades, at magma-poor Ocean-Continent Transitions (OCT) these processes remain less well understood, despite the ubiquity of serpentinites at these settings. The presence of serpentinites at OCTs was first proposed from the Apennines (Boccaletti *et al.*, 1971) before it has been proofed along the Iberia margin (ODP Leg 103, Boillot *et al.*, 1980, 1989). Since then, more and more occurrences have been reported and described from present-day OCTs (Agrinier *et al.*, 1996; Albers *et al.*, 2021; Beslier *et al.*, 2004; Bonatti, 1976; Hopkinson *et al.*, 2004; Kodolányi *et al.*, 2012; Nicholls *et al.*, 1981) as well as from fossil examples (Lagabrielle & Bodinier, 2008; Manatschal & Müntener, 2009; Picazo *et al.*, 2013). At present, it is assumed that ~50% of the world rifted margins are formed by serpentinized exhumed mantle (Minshull, 2009).

Similar to MOR settings, serpentinization plays also at OCTs a key-role during mantle exhumation (e.g. Whitmarsh *et al.*, 2001; Gillard *et al.*, 2019). However, the nature of the mantle strongly differs between the two settings: while lherzolites are common in OCTs, harzburgites are dominant in MORs. How far the more fertile, pyroxene-rich composition of the mantle at OCTs controls the serpentization pathways and the nature of secondary mineral phases is yet little understood and will be discussed in this paper. Previous studies have demonstrated that temperature of serpentinization also differs between OCTs and MORs. At slow spreading centers, seawater-mantle interaction takes place in the range of 200°C to 400°C (e.g. Früh-Green et al., 2004; Barnes et al., 2009; Vesin et al., 2024), while serpentinization at OCT is assumed to occur at T < 250°C (Agrinier et al., 1996; Schwarzenbach et al., 2013, 2016; Vesin et al., 2023). This discrepancy is mainly attributed to the presence of punctual gabbroic intrusions in the mantle section at slow spreading centers that significantly increase the local geothermal gradient that can range between 45 and 150°C•km<sup>-1</sup> (Bach et al., 2011; Cannat et al., 2019). At OCTs, the volume of intrusive magma increases oceanward, suggesting that the thermal gradient increases in the same direction reaching at its oceanward termination similar conditions like those at ultraslow MORs (Cannat et al., 2009, 2019). The extent of serpentinization is likely controlled by access of seawater at depth, which is influenced by the presence or absence of magma. Low temperature of serpentinization was estimated from samples from the Iberia Abyssal Plain OCT (60-190°C, e.g. Agrinier et al., 1996; Vesin et al., 2023) and the Newfoundland OCT (100-130°C, Vesin et al., 2023). Higher temperatures of serpentinization were primary reported at the MAR (>350°, e.g. Agrinier & Cannat, 1997), but recent in-situ oxygen data in MOR serpentinites indicate lower temperatures (~290 and 115°C; Vesin et al., 2024). These new temperatures only partly cover the range of those expected at OCTs. As the mantle composition, geothermal gradients and depths of fluid penetration differ between OCTs and MORs, these two systems may record distinct histories of fluid-rock interaction, mass fluxes and deformation. However, to date, only very few studies looking more systematically at serpentinization reactions and sequences exist at OCTs.

The large variety of serpentine textures reported for MOR settings has been interpreted in terms of variation in the conditions and mechanisms of serpentinization, including temperature, fluid/rock ratio, fluid chemistry and/or tectonic unroofing (e.g. Dilek et al., 1997; Andréani et al., 2007; Rouméjon et al., 2015, 2019). To date, detailed investigations of serpentine textures at magmapoor OCTs remain scarce and mostly incomplete, mainly due to the limited accessibility of the exhumed mantle in presentday OCTs and the complexity of restoring remnants of fossil OCTs emplaced in collisional orogens back to their pre-orogenic position (Albers et al., 2021; Tichadou et al., 2021).

In this study we investigate serpentinized peridotites from the Jurassic OCT of the Alpine Tethys realm now exposed in the southeastern Swiss Alps. We discuss the serpentine textures in terms of fluid/rock ratio, fluid chemical composition, mass fluxes and temperature conditions, and integrate the importance of tectonic modes during the exhumation of subcontinental mantle at the seafloor. We propose a conceptual model to explain serpentinization sequences at OCTs and discuss how our results can reconcile observations made at MORs.

#### **GEOLOGICAL SETTING**

Remnants of the Jurassic OCT of the Alpine Tethys are exposed as so called ophiolitic nappes in the Central Alps in southeastern Switzerland (Fig. 1A and C; Manatschal & Nievergelt, 1997; Müntener *et al.*, 2004, 2010). They represent remnants of the Adriatic-European conjugate margins (Fig. 1B; Florineth & Froitzheim, 1994; Manatschal, 2004). In our study, we focus on three sites, the Platta and Totalp nappes, both deriving from the SE OCT of the Adriatic margin, and the Tasna nappe, which derives from the conjugate European margin (Manatschal & Müntener, 2009; Fig. 1).

#### The Platta nappe

The Platta nappe belongs to the lower Austro-Alpine and South Pennine nappe stack that was emplaced during Late Cretaceous along top to the NW thrust faults (Fig. 1C). The Platta nappe is subdivided into two units separated by a main reactivated pre-Alpine shear zone (Fig. 1D; Epin et al., 2019). The Upper Platta Unit, in the hanging wall, was originally located in a more proximal position in the OCT (Fig. 1D). This unit consists of mantle rocks (the Upper Serpentinite Unit; Fig. 2A) derived from the inherited subcontinental Adriatic mantle (i.e. Schaltegger et al., 2002; Müntener et al., 2004, 2010; Picazo et al., 2016; Epin et al., 2019). The Lower Platta Unit, in the footwall of the main shear zone, was originally located in a more distal position (Fig. 1D). This unit consists of a large mantle domain (i.e. the Lower Serpentinite Unit, Fig. 2A) locally intruded by gabbros dated at  $161 \pm 1$  Ma (Schaltegger et al., 2002) and covered by lavas of late Middle to early Late Jurassic age (165 to ~155 Ma; Desmurs et al., 2001; Amann et al., 2020). Contrarily to peridotites from the Upper Platta Unit that are almost free from any syn-exhumation melt imprint and equilibrated at ~920°C, peridotites from the Lower Platta Unit have been largely percolated by MORB-type melts during final rifting and breakup, leading to a significantly higher equilibrium temperature of  $1100 \pm 50^{\circ}$ C (Müntener *et al.*, 2010). Slivers of continental origin also occur in the Platta nappe and have been interpreted as extensional allochthons (Froitzheim & Manatschal, 1996). Mantle rocks in the Platta nappe display ophicalcites at their contact with mafic rocks and deep-water sediments (Fig. 2C; Dietrich, 1970, Coltat et al., 2021), and were weakly affected by Alpine metamorphism (lower greenschist facies, <350°C; Trommsdorff & BW, 1974, Frey & Ferreiro Mählmann, 1999, Coltat et al., 2021). However, an increase in Alpine metamorphism from north to south is documented by the transition from lizardite-chrysotile to antigorite. In the northern Platta nappe, temperatures were assumed to remain below 150°C, whereas in the Malenco nappe, south of the Engadine line, temperatures reached up to 400°C (Fig. 1C; Dietrich, 1969; Trommsdorff & Evans, 1977; Trommsdorff, 1983; Burkhard & O'Neil, 1988; Vils et al., 2011).

#### The Totalp nappe

The Totalp nappe is located to the north of the Platta nappe (Fig. 1B). It belongs to the Late Cretaceous Upper Austro-Alpine and South Pennine nappe stack that was thrust northward over the Middle and Lower Pennine units during the late Eocene, (Froitzheim & Manatschal, 1996; Fig. 1C). The slightly more complex polyphase Alpine tectonic overprint makes that its position in the former OCT is less well defined than that of the Platta nappe. However, there is consensus in admitting that the Totalp nappe is derived from the SE OCT of the Alpine Tethys (Weissert & Bernoulli, 1985). The Totalp nappe consists of serpentinized spinel lherzolites, locally containing pyroxenites and ophicalcites, resulting from the carbonation of serpentine under static conditions at the seafloor. The ophicalcites preserve depositional contacts with Upper Jurassic to Lower Cretaceous pelagic sediments (Fig. 3; Picazo et al., 2013). Magmatic rocks are very rare and mainly consist of flaser gabbros and dolerite dykes (Peters & Mathews, 1963). The Alpine metamorphic overprint is below prehnite pumpellyite facies at around 250°C (Peters, 1965). Serpentinized mantle is often crosscut by calcite veins, and similarly to the Platta nappe, relics of the pre-Alpine contacts between exhumed mantle rocks, ophicalcites and deep-water sediments are locally





**Fig. 1.** (A) Present-day location of ophiolitic units of the Central–Western Alps and Apennines (modified after Manatschal & Müntener, 2009). (B) Schematic reconstruction of the Piemonte–Ligurian oceanic basin at Late Jurassic time, with the location of the major ophiolitic sequences (modified after Manatschal & Müntener, 2009). (C) Simplified geological map of the Pennine and Austro-Alpine nappes showing sample locations (modified after Froitzheim *et al.*, 1994). D) Distribution of subcontinental and infiltrated mantle domains along the ocean-continent-transition of the Alpine Tethys (modified after Müntener & Piccardo, 2004). CH, Chenaillet; PL, Platta; TA,: Tasna; TO, Totalp.

well-preserved (Bernoulli & Weissert, 1985; Weissert & Bernoulli, 1985; Picazo *et al.*, 2013). Results from  ${}^{40}$ Ar/ ${}^{39}$ Ar dating on phlogopite from pyroxenites gave a cooling temperature  $\leq$  300°C and exhumation age of 160±8 Ma (Peters & Stettler, 1987a, 1987b).

#### The Tasna nappe

The Tasna nappe was derived from the European OCT (Fig. 1B; Florineth & Froitzheim, 1994; Manatschal et al., 2006; Ribes et al.,

2020). It belongs to the Tertiary Alpine nappe stack made of Austro-Alpine and Pennine units (Fig. 1C) emplaced during the Eocene to Oligocene (Ribes *et al.*, 2020). As for the Platta and Total nappes, the Tasna nappe exposes primary contacts between exhumed and serpentinized mantle rocks and sediments (Fig. 3). The Alpine metamorphism did not exceed 350°C (greenschist facies; Florineth & Froitzheim, 1994; Bousquet *et al.*, 2008). The Tasna nappe is made of a wedge of continental crust separated



**Fig. 2.** (A) Geological map of the Platta nappe with sample locations (modified after Schaltegger *et al.*, 2002). (B) Photograph of the Falotta area, and (C) interpretative drawing of the Falotta area showing the various lithologies and their respective structural relations (the basalts overlie the lower Platta Unit made of serpentinized mantle separated by a rift-related detachment surface.

from the underlying mantle by a detachment fault, referred to as the Lower Tasna Detachment (LTD; Froitzheim & Rubatto, 1998, Fig. 4C).a The Upper Tasna Detachment (UTD) is the topbasement fault responsible for the exhumation of the crust and mantle rocks at the seafloor (Froitzheim & Rubatto, 1998, Manatschal et al., 2004, 2006). It is overlain by the undeformed postrift sediments (Fig. 4C) interpreted as Upper Jurassic (Ribes *et al.*, 2020). Mantle rocks consist of highly serpentinized spinel lherzolites with abundant spinel websterite layers and preserving a high temperature foliation marked by spinel grains (Manatschal *et al.*, 2006). The <sup>40</sup>Ar/<sup>39</sup>Ar dating of phlogopite provides an age of 170.5 ± 0.4 Ma (Manatschal *et al.*, 2006), similar to that obtained for mantle exhumation at Totalp (160 ± 8 Ma; Peters & Stettler, 1987a). The clinopyroxene compositions and the calculated equilibrium temperatures of mantle peridotites from Tasna are similar to those from the Upper Platta unit and Totalp, demonstrating that all of these ultramafic units belonged to the same, inherited mantle domain (Manatschal *et al.*, 2006; Picazo *et al.*, 2016).

#### MATERIALS AND METHODS Sampling and analytical strategies

A total of 40 moderately to completely serpentinized peridotites have been sampled (Table 1). The sampling was done with the aim of characterizing fluid–rock interactions at the two opposed positions along the OCT of the former Alpine Tethys, i.e. at the proximal domain (continentwards, Upper Platta, Tasna and Totalp) and



Fig. 3. (A) Geological map of the Totalp area with sample locations (modified after Picazo *et al.*, 2013). (B) South–north oriented cross-section across the Totalp area showing Alpine thrusts and folds. (C) Photograph of massive serpentinite outcrop. D) Photograph of the serpentinite wall near Weissfluhjoch (samples Tot 19–01,02).

the distal domain (oceanwards, Lower Platta; Fig. 1D). A comprehensive set of petrographical and geochemical analyzes was performed on each sample, including: i) petrographic observations in thin sections; ii) X-ray diffraction, to identify minerals and their respective proportions in serpentinites; iii) bulk-rock major and trace element analyses. Among the samples, 18 were selected for: i) Raman spectroscopy to identify serpentine polysomes, and ii) in situ major and trace element analyses to constrain fluid–rock interactions during mantle exhumation.

#### X-ray diffraction

XRD analyses were performed on sample powders using a Bruker D8 advance Eco diffractometer at the Institut Terre et Environnement de Strasbourg (ITES, University of Strasbourg). A large Xray beam was emitted by a copper source with a 40-kV accelerating voltage and a 25-mA current. Intensities were recorded at 0.014° 20 step intervals from 3 to 80° 20, with a dwell time of 0.8 s. Size of the divergence slit was 0.4°. Table 1 provides the quantitative mineralogical compositions determined by Rietveld refinement using Profex-BGMN software (Doebelin & Kleeberg, 2015),



**Fig. 4.** (A) Simplified geological map of the western Engadine window in SE Switzerland and Austria and location of the Tasna nappe (modified after Trümpy & Dössegger, 1972; Florineth & Froitzheim, 1994; Manatschal *et al.*, 2006). (B) Panoramic view of the Tasna Ocean–Continent Zone. (C) Geological interpretation of the Tasna area showing the serpentinized mantle that is separated from the continental crust (in the SSW) and post-rift sediments (in the NNE) by rift-related detachment faults. The base of the mantle is an Alpine thrust fault (modified from Florineth & Froitzheim, 1994; Manatschal *et al.*, 2006).

as well as the list of the reference structures used for refinement. The diffraction patterns, Rietveld refinements and the references of mineral structures used for the refinements are given in supplementary materials.

#### Raman spectroscopy

Raman spectra were acquired on 30  $\mu$ m thick polished thin sections, using a HORIBA LabRAM ARAMIS spectrometer at the Laboratoire des sciences de l'ingénieur, de l'informatique et de l'imagerie (ICube, University of Strasbourg). A 100× objective (Olympus) and a 632-nm (Ar+) laser at 9 mW were used, resulting in a laser spot size of ~1  $\mu$ m. All analyses were performed

using integration times of 15 or 30 s to optimize the signal/noise ratio. Raman spectra were recorded in two wavelength intervals: 100–1120 cm<sup>-1</sup> for structural bonding characterization and 3500–3750 cm<sup>-1</sup> for the characterization of hydroxyl bonds. The serpentine polysomes were identified by comparison with reference spectra taken from the literature, in particular on the stretching range of the OH groups (e.g. Auzende *et al.*, 2004; Groppo *et al.*, 2006; Tarling *et al.*, 2018; Compagnoni *et al.*, 2021).

#### Bulk-rock chemistry

The major element concentrations were measured on pressed pellets of calcined powder (i.e. after loss on ignition) using a micro-

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	Fal 18-02b	Massive + veins	46°32′51.17″N	9°40'9.42''E	97.8	1.8	<1	
	Fal 18-03*	Massive	46°32′51.08"N	9°40'10.14"E	9.66	<1	<1	
	Fal 18-04	Vein	46°32′51.12″N	9°40′9.94″E	6.99	·	ı	
	Fal 18-05	Vein	46°32′51.13″N	9°40′9.92″E	2.99.7	<1		
	Fal 18-06*	Massive	46°32′51.25″N	9°40′10.02″E	95.0	J	<1	
	Fal 18-07	Massive	46°32′51.25″N	9°40′10.02″E	81.0	1.3		
	Fal 18-08	Massive + veins	46° 32′ 56.63" N	9°40′7.09″E	97.0	2.3		
	Fal 18-09	Massive	46°32′56.63″N	9°40′7.09″E	8.66	<1		
	Fal 18-10	Massive + veins	46°32′56.63″N	9°40′7.09″E	98.9	1.1		
Lower Platta	Fal 18-11*	Massive	46°32′44.74"N	9°39'38.65″E	99.3	<1		
	Fal 18-12	Massive	46°32′43.75″N	9°39'33.72″E	85.7	<1	1.6	8.1
	Fal 18-13*	Massive	46° 32′ 42.24" N	9°39′34.87″E	99.5	~1	<7	
	Fal 18-14	Massive	46°32′29.95″N	9°39′40.02″E	9.99	<1	ı	
	Mar 18-01*	Massive + veins	46° 30′ 19. 19"N	9°37′41.28″E	98.8	1.2	<1	,
Totalp	Tot 19-01	Massive	46°49′56.97″ N	9°48′ 18.71″ E	58.9	-	ı	·
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	Tot 19-03a*	Massive + veins	46°50′18.49″ N	9°48′ 13.85″ E	92.0	~1	ı	
	Tot 19-03b	Vein	46°50′ 18.55″ N	9°48′ 13.94″ E	9.99	·	ı	
	Tot 19-04*	Massive + veins	46°50′18.40″ N	9°48′ 14.23″ E	96.7	0.38		
	Tot 19-05	Massive	46°50′18.40″ N	9°48′ 14.23″ E	90.8	<1	ı	
	Tot 19-07*	Massive	46°50′19.58″ N	9°48′ 16.68″ E				
	Tot 19-09*	Massive	46°54′56.61″ N	9°51′27.98″ E	97.1	~1	ı	
	Tot 19-10a	Foliated	46°50′23.31″ N	9°48′ 24.48″ E	95.9	<1	ı	
	Tot 19-10b*	Massive	46°50′24.37″ N	9°48′ 26.62″ E	98.7	~~~	^1	,
Tasna	Tas 19-01	Massive	46°50′17.28″ N	10°15′37.79″E	94.0	1.3	<1	
	Tas 19-02*	Foliated	46°49′24.33″ N	10°15′6.11″E	98.7	<1	<1	
	Tas 19-03*	Massive	46°49′35.23″ N	10°15′4.26″E	96.3	$^{<1}$	<1	·
	Tas 19-04*	Massive + veins	46°49′35.08″ N	10°15′4.12″ E	94.1	~1	<1	
	Tas 19-06a	Vein	46°49′34.70″ N	10°15′4.69″ E	99.9	ı	ı	
	Tas 19-06b	Massive + veins	46°49′34.70″N	10°15′4.69′′E	98.2	~1	<1	
	Tas 19-07	Vein	46°49′34.73″ N	10°15′5.02″ E	99.9	ı	ı	
	Tas 19-08*	Massive + veins	46°49′34.59″ N	10°15′4.74″E	99.4	$^{<1}$	<1	·
	Tas 19-09	Vein	46°49′34.38″ N	10°15′4.30″E	9.99	,	,	
	Tas 19-10*	Massive + viens	46°49′27.28″ N	10°16′9.17″E	98.5	<1		
	Tas 19-11	Vein	46°49′54.23″N	10°14′56.57″E	97.9	<1	·	
	Tas 19-12	Massive	46°49′54.06″ N	10°14′56.78″E	98.7	~1	^1	
	Tas 19-13	Massive	46°50′ 0.71″ N	10°15′9.73″E	2.66	<1		
	Tas 19-14	Massive	46°50′1.07′′ N	10°15′9.70″E	90.1	<1	<1	
	Tas 19-15	Massive	46°50′ 1.07″ N	10°15′9.70″E	99.5	<1	ı	ı

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X-ray fluorescence ( $\mu$ -XRF) Bruker M4 Tornado at ITES. For each sample, 10 measurements were performed at random location on each pellet to ensure the reproducibility at the pellet surface. A collimated Rh source operating at 700  $\mu$ A with an accelerating voltage of 50 kV was used, resulting in a 1-mm spot-size in diameter at the sample surface. Two energy-dispersive silicon drift detectors of 125 eV resolution, and with an active area of 60 mm<sup>2</sup> each were used to measure fluorescence spectra (300 s counting time per spectrum). Measurements were performed in a vacuum chamber at 2 mbar to minimize air absorption and ensure the best signal/noise ratio.

The bulk-rock trace element concentrations were determined at ITES using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Thermo Scientific X series II instrument and ICAP RQ Thermo Scientific instrument. The analytical procedure was adapted from the method of Chauvel *et al.* (2011): about 100 mg of rock powder was precisely weighed and dissolved in Savillex beakers in a HF-HNO<sub>3</sub>-HClO<sub>4</sub> (5:1:1) mixture, during a minimum of 7 days at 140°C on a hot plate. The solution was then evaporated, and the residue was taken in a 3:1 3 M HCl–H<sub>3</sub>BO<sub>3</sub> mixture for 12 hours in a hot plate at 90°C to avoid any fluoride precipitation. This mixture was then evaporated and further dissolved in concentrated HNO<sub>3</sub>. After another evaporation, the residue was finally diluted in 40 ml of 7 M HNO<sub>3</sub>.

Analyzes performed on international standard are consistent with preferred reference values from GeoREM for UB-N serpentinite (Govindaraju, 1982). Differences between reference values from the literature and our analyses of UB-N are  $\pm 1.1\%$  for all other major oxides except for Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> which are present in very low concentrations. For most trace element concentration, the deviation from the reference value of UB-N is in average  $\pm 5\%$  (see Supplementary Table S3).

#### Mineral chemistry

The major element concentrations were measured on 30  $\mu$ mthick polished sections using a  $\mu$ -XRF Bruker M4 Tornado at ITES. Measurements were performed using a Rh anode operating at 400  $\mu$ A with an accelerating voltage of 50 kV. Polycapillary lenses were used to focus the X-ray beam down to 20  $\mu$ m fullwidth-at-half-maximum at the sample surface. The counting time per point was set to 180 s.  $\mu$ -XRF spectra were calibrated after repeated analyses of Smithsonian National Museum of Natural History mineral standards (Jarosewich *et al.*, 1980) of diopside (NMNH 117733) and San Carlos olivine (NMNH 111312–44), and some in-house mineral standards of clinochlore, chrysotile and antigorite. Total Fe content was calculated on a divalent basis, as FeO<sub>tot</sub>.

The structural formulae for lizardite, chrysotile, polygonal and polyhedral serpentines was calculated on the basis of 7 oxygens. Antigorite has a distinct formula  $Mg_{3m-3}Si_{2m}O_{5m}(OH)_{4m-6}$  that slightly differs from the idealized serpentine formula  $(Mg_3SiO_5(OH)_4)$ , where m is the number of tetrahedra along an entire wavelength of the crystalline structure. Here, the structural formula of antigorite was calculated based on m = 17 (Mellini et al., 1987). The Fe<sup>2+</sup> and Fe<sup>3+</sup> contents of serpentine mineral were estimated following the approach of Ulrich et al. (2020) based on the initial study of Beard & Frost (2017). The calculations assume a full dioctahedral substitution, i.e. ferric iron is accommodated in the serpentine by substitution for divalent cation plus the addition of a vacancy in the octahedral sheet.

Serpentine trace element compositions were acquired on 30  $\mu m$  polished thin sections by laser ablation inductively

coupled plasma mass spectrometry (LA-ICP-MS) at Géosciences Montpellier (University of Montpellier, AETE regional facility of the OSU OREME). The instrument includes a pulsed 193 nm ArF excimer laser (Compex 102 instrument from LambdaPhysik) coupled to a ThermoScientific Element XR mass spectrometer. Laser ablation was performed with an energy density of 12 J/cm<sup>2</sup> at a frequency of 6 Hz. Few laser pulses with a spot size of 130  $\mu$ m were applied before each ablation to clean up the sample surface. Then each acquisition was performed with a total of 240 pulses with a spot size of 110  $\mu$ m, sufficient to obtain a long and stable signal for integration. The ablated material was transported using a constant He flow of 1 l/min and mixed with Ar flow of 0.6 l/min in a cyclone coaxial mixer before entering the ICP torch and being ionized. The ions are then sampled, accelerated and focused before being separated and analyzed in the mass spectrometer.  $^{29}$ Si content known from prior  $\mu$ -XRF analyses were used as internal standard and concentrations were calibrated against the NIST 612 rhyolitic glass using reference values from Pearce et al., 1997. In order to evaluate the precision of the measurements the reference basalt glass BIR-1G was analyzed repeatedly each 5 samples to (the complete dataset, including standard reference values, is available in supplementary materials). Data reduction was operated with Matlab-based SILLS program (Guillong et al., 2008), following the standard methods of Pettke et al. (2012). Detection limits were between 1 ppb and <0.3 ppm for most trace elements.

# RESULTS

#### Petrographic description

All samples analyzed in this study derived from the proximal domain (Tasna, Totalp and Upper Platta) are spinel-lherzolites, while those from the distal domain (Lower Platta) are dominantly plagioclase-bearing lherzolites. Macroscopically, all samples are extensively serpentinized (Fig. 5). This is confirmed by microscopic observations (Fig. 6) and Rietveld refinements made on X-Ray diffraction patterns (Table 1), showing that most of the samples contain ~96% (n = 40) serpentine. Rare exceptions were found at Tasna and mostly Totalp, where relics of primary clinopyroxene and more occasionally olivine are preserved.

The serpentinites from the Lower and Upper Platta nappe are typically of a dark green color (Massive serpentinite; Fig. 5A). Serpentinites from the Lower Platta, display rare imprint of several serpentine veins. Some serpentinites contain clasts of massive dark serpentinite that are locally embedded in a fibrous and light-green colored serpentine matrix (Fig. 5B). For the Upper Platta (proximal domain) serpentinites are occasionally crosscut by centimeter-thick light green serpentine veins (Fig. 5A), and most samples are characterized by several generations of serpentine veins (Fig. 5C). At Tasna (Fig. 5D, E) and Totalp (Fig. 5F), massive serpentinites are locally surrounded by a late foliated serpentinite, characterized by a light blueish color and a fibrous aspect. At Totalp, some relics of primary minerals are present, like olivine in the center of mesh texture (Fig. 5G) or clinopyroxene in massive dark serpentinite (Fig. 5H). It should be noted that some samples contain minute amounts of calcite (<1%, Table 1) when picked up in the vicinity of ophicalcites (e.g. Picazo et al., 2013).

Based on microscopic observations and Raman spectra made on thin sections, we firstly described the textures and determined the polysomes of serpentine. Secondly, we attributed the succession of serpentine to a sequential evolution regarding the position along the OCT, i.e. proximal and distal domains.



Fig. 5. Representative photographs of the diversity of textures in serpentinites sampled in the three distinct sites (Platta, Totalp, Tasna). (A) Massive dark green serpentinite crosscut by a fibrous serpentine vein of pale green color (Fal 18-02, Upper Platta unit). (B) Clasts of massive dark serpentinite embedded in a serpentine matrix of a fibrous texture (Fal 18-12, Lower Platta Unit). (C) Green serpentinite crosscut by several generations of thick dark and thin green pale serpentine veins (Fal 18-08, Upper Platta unit). (D) Massive dark green serpentinite (Tas 19-03) surrounded by a foliated pale green fibrous serpentinite (Tas 19-04, Tasna Unit). (E) Massive green serpentinite from Totalp (Tot 19–01). (F) Blueish serpentine fibers (Tot 19-04). (G) Massive green serpentinite sample crosscut by thick dark serpentine veins forming a mesh texture (Tot 19-05, Totalp Unit). (H) Pyroxene relics in a massive dark green serpentinite (Tot 19-09).

#### Serpentine mesh and bastite textures S1

Serpentine mesh and bastite textures constitute the bulk and first generation of serpentinization in most samples from all domains. They correspond to the pseudomorphic replacement of olivine and pyroxenes by serpentine mesh (Fig. 6 A, B) and bastite textures (Fig. 6 C, D). Some relics of primary minerals, especially clinopyroxene and to a lesser extent olivine, can be

occasionally preserved in samples from Totalp (Fig. 6B, E). In these samples, olivine is preserved within the mesh network and hydration of clinopyroxene has progressed with the development of serpentine veins along cleavages. Orthopyroxene relicts are scarcely observed in our samples, at the opposite of spinel grains which are preserved even in the most serpentinized samples and only show minor evidence of hydrothermal alteration with the



**Fig. 6.** Photomicrographs of serpentinite thin sections showing the diversity of serpentine textures and their respective Raman spectra. P, point where the Raman spectra was done. All photos were taken under plane-polarized light (PPL; A, C) or cross-polarized light (XPL; B, D to H). (A–B) First generation of serpentine (S1) made of lizardite, forming a typical mesh texture replacing olivine grains, or (C) Bastite texture replacing primary pyroxene associated with magnetite grains. (D) Bastite under XPL, cut by serpentine veins. (E) Second generation of serpentine formed of polyhedral serpentine (S2) in clinopyroxene cleavage. (F) Focus on S2 serpentine vein in clinopyroxene cleavage showing the close association of this serpentine polysome and the formation of andradite grains. (G) Third generation of serpentine (S3) with a typical banded vein texture made of polygonal serpentine crosscutting the bastite and mesh textures (S1). (H) Polyhedral serpentine (S2) and andradite at rims of bastite (S1), cut by a banded vein (S3).

local formation of chlorite aureoles. The dominant serpentine polysome is lizardite, as shown by the typical OH stretching bands at 3685 cm<sup>-1</sup> and 3707 cm<sup>-1</sup> on Raman spectra (Fig. 6). In all these samples, magnetite is ubiquitous, with amounts between 0.38 and 5% (Table 1). Magnetite mainly occurs as small grains (<5  $\mu$ m) disseminated along the mesh rims, and also

observed in cleavages and surrounding the bastite grains (Figs. 5 and 6C).

#### Serpentine veins

The background mesh and bastite textures (S1, lizardite type) are usually crosscut by at least one generation of serpentine veins in



**Fig. 7.** (A) Microphotography under plane polarized light (PPL) and cross polarized light (XPL) of a serpentinite sample from the lower Platta unit (Fal 18–06) showing the primary mesh texture (S1) crosscut by successive generations of serpentine veins. (B) Focus on the primary serpentine mesh (S1) and associated magnetite grains crosscut by a thick fracture opened in pull-apart mode and filled by antigorite (S4) with a typical lamellar texture. (C–D) Focus of (A) showing the chronology of formation of serpentine polysomes between lizardite mesh (S1), lamellar antigorite vein (S4), chrysotile crack-seal (S5) and late calcite veins.

the distal domain, and usually several generations of serpentine veins in the proximal domain. We have identified four main generations of serpentine veins representing a serpentinization sequence.

Spherical serpentine (S2): The second generation of serpentine, here referred to as 'spherical serpentine S2', was occasionally observed in partially serpentinized samples from Totalp and Tasna and barely in fully serpentinized samples from Upper Platta. It forms a typical spherical texture that is characterized in microscopic view in crossed-polarized light by an extinction cross in the polarization directions (Fig. 6 E, F, H). Such typical spherical texture and the Raman signature (Fig. 6) are robust features in favor of a polyhedral serpentine. This serpentine polysome occurs in a few of our samples, mainly in clinopyroxene cleavages (Fig. 6E, F) and occasionally as veins crosscutting the previous serpentine mesh and bastite S1 (Fig. 6H). The occurrence



**Fig. 8.** Representative microphotographs and schematical representations of the five different types of serpentines described in this study.

of small and radite grains ( $\sim$ 10  $\mu$ m diameter) is closely associated to polyhedral serpentine veins, almost exclusively at the vicinity of clinopyroxenes (Fig. 6F, H).

Banded veins (S3): The third generation of serpentine (S3, Fig. 6G), is usually observed in serpentinites from proximal domains and very sparsely and rarely in serpentinites from the distal part (Lower Platta). It consists of veins ranging from tens of  $\mu$ m- to cm-thick. The centimetric veins are observable at the macroscopic scale and are characterized by a fibrous green texture (e.g. Fig. 5A). These veins are made of finely spaced bands

of low birefringence that alternate between white and black colors under the cross-polarized light (Fig. 6G, H). All bands are parallel to each other and mimic the irregular shape of the vein margins, preserving the initial geometry of the fracture. The Raman spectra shows that serpentine polysomes filling these banded veins are diverse. Although recent studies have shown that the distinction between lizardite and polygonal serpentine is not obvious using Raman spectroscopy (Tarling *et al.*, 2018; Compagnoni *et al.*, 2021). Based on the Raman spectra, most of the banded veins exhibiting the typical OH stretching bands at 3685 cm<sup>-1</sup> and 3707 cm<sup>-1</sup> are filled by lizardite. Other spectra showing two peaks at 3692 cm<sup>-1</sup> and 3700 cm<sup>-1</sup> (Fig. 6) rather correspond to polygonal serpentine, whereas only rare occurrences of chrysotile were observed (main peaks at 3689 cm<sup>-1</sup> and 3699 cm<sup>-1</sup>).

Lamellar veins (S4): The fourth generation of serpentine (S4) is exclusively observed at Tasna and Upper Platta (proximal domains). Only one has been observed in a sample from Lower Platta (distal domain) and none from Totalp (proximal domain). It consists of disoriented serpentine lamellae with a first order grey to pale yellow birefringence under the cross-polarized light. It occurs mostly as veins crosscutting the pseudomorphic mesh and bastite and serpentine veins, which are highlighted by magnetite grains at the serpentine vein rims (Fig. 7). Lamellar veins are typically between 50- and 150-µm-thick, but they can also form large patches interconnected by veins of the same textures (Fig. 7). Lamellar veins appear to spread within the mesh textures, resulting in blurred rims (Fig. 7D). The Raman spectral signature indicates that these lamellar veins are made of a mixture of antigorite and chrysotile, with peaks at 3670 cm<sup>-1,</sup> 3690 cm<sup>-1</sup>and 3700 cm<sup>-1</sup> (Fig. 7). Occasionally, some of these veins and patches display an additional peak at 3685 cm<sup>-1</sup>, which likely indicates the local presence of small lizardite grains. Some carbonates, identified as calcite, are occasionally observed inside some of these lamellar veins (Fig. 7C).

Fibrous veins (S5): The last generation of serpentine (S5) is systematically observed in samples from Lower Platta and regularly observed in the other units. It forms crack-seal structures characterized by lens-shape extending along several mmlong and tens of  $\mu$ m width (Fig. 7 D). This serpentine polysome displays a typical fibrous aspect. The fibers are preferentially oriented perpendicular to the vein edge and are characterized by a high birefringence under cross-polarized light. The characteristic shoulder at 3690 cm<sup>-1</sup> preceding a peak at 3701 cm<sup>-1</sup> matches the Raman spectral signature of chrysotile in high wavelength domain (Fig. 7D).

To sum up, the different serpentine textures and polysomes described in this section are presented as an evolutionary sequence, comprised of five stages of serpentinization (Fig. 8).

#### Bulk-rock geochemistry

Most samples show typical concentrations of SiO<sub>2</sub> and MgO for serpentinites (41.33 wt % and 38.96 wt % in average, respectively; Fig. 9). They cover a wide range of concentrations in CaO (0.04– 4.1 wt %) and Al<sub>2</sub>O<sub>3</sub> (0.21–7.73 wt %). The presence of clinopyroxene and/or plagioclase in the samples can explain the high CaO measured in bulk, while higher Al<sub>2</sub>O<sub>3</sub> content attests of the presence of spinel or plagioclase. Fig. 10 presents the MgO/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratios of serpentinites from Totalp, Tasna, Upper and Lower Platta (Jagoutz *et al.*, 1979; Hart & Zindler, 1986). The serpentinized peridotites plot along the terrestrial mantle array. Most samples display fertile compositions (Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> > 0.05) while only few samples derive from a refractory protolith. Mg# is around 0.94 for most serpentinites (Fig. 10), close to the Mg#



**Fig. 9.** Binary diagrams of bulk-rock compositions of serpentinites (recalculated in anhydrous basis) from Upper and Lower Platta, Tasna and Totalp showing MgO versus (A) SiO<sub>2</sub>, (B) Fe<sub>2</sub>O<sub>3</sub>, (C) CaO and (D) Al<sub>2</sub>O<sub>3</sub>. Our data are compared to serpentinized peridotites from Platta and Malenco (Müntener et al., 2010), the Iberia Margin (Kodolányi et al., 2012; Albers et al., 2021), Newfoundland, Mid Atlantic Ridge (MAR) and Hess Deep (Kodolányi et al., 2012). South West Indian Ridge (SWIR; Rouméjon et al., 2015). DMM: Depleted MORB Mantle Salters & Stracke (2004).

values of initial peridotites (Müntener et al., 2010). Ni and Cr concentrations are mainly in the range 1500 to 2500  $\mu$ g/g and 2000 to 3500  $\mu$ g/g, respectively (Fig. 11). Interestingly, samples with abundant veining are characterized by high Mg# (up to 0.96, corresponding to samples with low FeO<sub>tot</sub>, <5 wt %; Figs. 8 and 10) and very low Cr and Ni concentrations (<500  $\mu$ g/g Table 2; Fig. 11).

from the overall trends by highly depleted HREE concentrations (HREE<sub>N</sub>  $\sim 0.1-1$  C1-Chondrite; Fig. 12) and positive Eu anomalies (Eu/Eu<sup>\*</sup> = 1.41 in average, n = 40). Spider diagrams show enrichment in fluid mobile elements (FME), as highlighted by positive anomalies in Cs, B and Li. Locally, a slight enrichment in U is observed (up to 10 times PM in Tasna serpentinites), Pb and Sr (0.1-1 time PM in Upper and Lower Platta and Tasna serpentinites).

Bulk-rock serpentinites normalized to Chondrite-C1 display homogeneous patterns, characterized by flat Heavy to Middle rare earth elements (REE) with relatively fertile compositions with HREE<sub>N</sub> > 2 and depletion in Light (L)REE ((La/Sm)<sub>N</sub> = 0.80, in average n = 40; Fig. 12). Some samples from Tasna and Platta differ

#### Serpentine geochemistry Major elements

In average, serpentine mesh contains 40.91 wt% SiO\_ (Si=1.91 apfu), 1.40 wt% Al\_2O\_3 (Al=0.08 apfu), 38.87 wt% MgO (Mg=2.74

Upper Platta	ple Fal 18-02a Fal 18-02b	2 40.18 36.13 0.098 0.096	<b>0</b> 3 1.903 2.453	<b>0</b> <sub>3</sub> 3.498 10.421	0 0.065 0.123	00.55 55.00 0.065 0.031	1000 Pd  Pd	0 0.242 0.084	<b>D</b> <sub>2</sub> 0.013 0.482	0.021 0.285	14.74 13.34	1 100.4 98.5 • 0.953 0.857		e (ppm) 8.200 11.90	15.11 40.42	9.177 48.73	33.40 3170 541 541	47.40 116.0	147.0 2050	166.5 2242	0.860 9.920 1130 4350	b.d.l b.d.l	0.090 0.170	0.700 2.400	1.710 2.910	1.200 0.855	0.260 0.320	0.140 0.140	0.100 0.150	0.150 0.410	0.037 0.078	0.080 0.239	0.018 0.045 0.065 0.253	0.032 0.104	0.020 0.050	0.044 0.166 0.014 0.031	0.060 0.223	0.019 0.054	0.048 0.165 0.012 0.026	0.053 0.180	0.013 0.030	0.173 0.210 0.041 0.039	0.081 0.176	
	Fal 18-03	38.52 0.133	2.261	8.316	0.173	30.80 0 106	0.100 h d l	0.108	0.421	0.259	13.75	100.9 0.888		21.80	98.49	45.59	2480 b d 1	99.10	1810	2036	39.20	8.000	0.390	6.100 1.690	3.000	0.519	0.240	0.130	0.120	0.960	0.070	0.258	0.052	0.142	0.110	0.220	0.313	0.069	0.209	0.224	0.035	0.181 0.029	0.260	0.150
	Fal 18-04	41.13	1.328	3.092	0.079	C0.75	тор.о Р д 1	0.116	0.018	0.035	15.02	100.5 0.958		5.700	26.74	7.881	12.20	29.00	316.0	272.7 5 660	26 50	b.d.1	0.175	0.900	6.270	0.096	0.020	0.050	0.037	0.268 1 E 00	0.050	0.110	0.015	0.025	0.016	0.037	0.053	0.013	0.041	0.044	0.008	2.320 0.038	0.835	
	Fal 18-05	38.82 0.077	2.079	10.602	0.176	54.89 0 107	hdl	0.078	0.488	0.270	13.20	100.9 0.854		3.000	25.98	61.11	364.0 노卢 1	33.20	347.0	2192	1.160 23 40	b.d.1	0.090	0.500	2.280	0.372	0.140	0.140	0.060	0.020	0.041	0.126	0.026 0.164	0.084	0.030	0.162 0.033	0.250	0.059	0.180	0.178	0.026	0.143	2.460	
J	Fal 18-06	39.71 0.008	0.209	7.372	0.121	01.00	L h d	0.489	0.327	0.262	13.80	100.3 0.901		7.200	82.74	0.997	2440 b.d.1	95,10	1850	2062 5 200	07 40	2.100	0.450	4.100	0.730	0.269	0.240	0.180	0.080	1.250	0.070	0.198	0.032	0.045	0.070	0.044	0.041	0.006	0.017 hdl	0.021	l.b.d	0.049	0.290	
4	Fal 18-07	39.85 0.254	3.439	8.594	0.115	25.15 2.15	0.006	000.0	0.364	0.221	10.51	100.1 0.873	0	10.40	113.8	75.22	2170 b d l	82.10	1370	1736	16.5U	b.d.l	0.960	13.400 3.060	5.970	0.304	0.160	0.230	b.d.l	1.740 2 260	0.179	0.661	0.125 0.793	0.313	0.140	0.4/8 0.084	0.608	0.131	0.388	0.389	0.057	0.273	0.299	1 000
	Fal 18-08	38.15 0.040	1.662	9.262	0.102	58.1/ 0.004	-00-0 1 h d 1	0.056	0.379	0.255	12.84	100.9 0.880		4.600	56.45	23.27	2440 노卢 1	94.80	1650	2004	10.80 46 50	p.d.l	0.120	1.600 0.627	1.130	0.156	0.180	0.060	l.b.d.l	0.080	0.056	0.122	0.015	0.029	0.020	0.058 0.013	0.113	0.026	0.091	0.112	0.017	0.058	0.065	
	Fal 18-09	39.21 0.066	3.332	6.916	0.121	50.05 0.021	170.0	0.205	0.454	0.294	13.06	100.5 0.905		7.300	66.79	99.26	2750 b.d.l	117.0	1940	2307	16.8U 38.10	17.000	0.550	3.500	0.760	0.145	0.070	0.100	0.220	0.640	0.009	0.037	0.007	0.051	0.030	0.120 0.027	0.220	0.051	0.166 0.026	0.194	0.031	0.063	1.020	
	Fal 18-10	38.09	1.411	8.407	0.126	38.2U 0.012	7700 1 P q	0.170	0.521	0.303	13.58	100.9 0.890		2.400	73.04	21.42	3020 b 4 1	98.40	1840	2379	12.70 52.10	p.d.l	0.070	1.400 0.487	0.840	0.085	0.160	0.050	0.080	0.030	0.036	0.071	0.012	0.020	0.020	0.042 0.014	0.078	0.023	0.071	0.093	0.017	0.175	0.987	
Lower Platts	Fal 18-11	39.91 0.022	0.317	7.372	0.100	38.8U	100.0	0.163	0.426	0.000	12.74	99.9 0.904	•	15.40	54.42	1.087	3070 5 4 1	105.0	2030	2362	50.10 50.10	b.d.l	0.120	1.500 0.292	0.610	0.130	0.080	0.100	0.110	0.250	0.079	0.167	0.024	0.040	0.030	0.060	0.058	0.011	0.030 h d l	0.031	b.d.l	0.132 0.029	0.169	0000
5	Fal 18-12	35.50 0.174	3.289	8.793	0.126	30.19 7 464	-04.7	0.041	0.408	0.222	13.84	100.0 0.860		10.40	42.42	73.41	2270 b.d.1	163.0	1540	1742	7.830 40 40	38.000	0.580	13.500 2 200	2.860	0.132	b.d.l	0.110	0.100	1.050	0.247	0.581	0.086 0.486	0.198	0.090	0.312	0.431	0.096	0.287 0.043	0.302	0.048	0.202	0.483	
	Fal 18-13	39.06 0.059	3.003	9.964	0.170	55.82 0.210	017-0	0.455	0.437	0.275	13.20	100.7 0.858		10.60	152.4	105.5	2760 b.d.1	104.0	1910	2164	14.30 59 90	b.d.l	1.240	5.000 1.350	0.800	0.033	b.d.1	0.110	0.070	2.970 1.970	0.009	0.013	b.d.1 0.042	0.051	0.060	0.126	0.238	0.057	0.181	0.212	0.031	0.116	0.177	010.0
	Fal 18-14	38.84 0.066	2.160	8.777	0.120	5/.U8 0.030	l þ d	0.241	0.419	0.272	12.84	100.8 0.883		11.30	50.76	52.86	2320 b_d_1	101.0	1780	2141	18.80 51 70	10.00	0.440	2.000	0.510	0.026	b.d.l	0:030	0.070	0.580	l.b.d	0.011	1.b.d 0.055	0.059	0.040	0.136	0.244	0.054	0.174 0.026	0.191	0.029	0.085	0.168	0100
	Mar 18-01	38.20 0.018	0.884	9.824	0.154	50.99 0000	0.000 h d l	0.033	0.291	0.247	13.84	100.5 0.870		2.800	46.75	6.68	1840 노卢 1	91.90	1780	1940 12.20	104.0 104.0	2.000	0.590	4.400 0.336	0.370	0.109	b.d.l	0.420	0.100	0.520	0.228	0.409	0.044	0.036	0.100	0.043 0.008	0.051	600.0	0.030 h.d.l	0.047	0.007	0.053	0.424	0800

9.00         1.00         1.00         1.00         1.00         1.00         1.01 <th< th=""><th>Totalp Tot Tot Tot Tot</th></th<>	Totalp Tot Tot Tot Tot
8.2         1.1         1.1         2.2 <th>101 101 101 101 101 101 101 101 101 101</th>	101 101 101 101 101 101 101 101 101 101
75         1.4         21.0         2.0.0	38.66 38.20 38.41 38.00 38.65 38.13 38.90 38.36 37.20 0.153 0.190 0.087 0.007 0.171 0.186 0.203 0.176 0.164
1         1	3.090 3.810 2.366 5.771 2.803 2.988 3.093 2.805 2.919 8.069 7.834 8.440 6.003 8.385 8.460 9.455 8.580 8.619
10         11         2.79         3.49         9.49         1.40         1.41         0.4	0.127 0.123 0.130 0.075 0.122 0.120 0.132 0.111 0.137 ( 0.000 0.000 0.070 0.075 0.120 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.1         1         1.4.1	3.317 5.993 1.895 0.024 2.885 3.067 2.788 1.154 3.169 0.
Mit         Mit <th>b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.</th>	b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.
37.1         ui         0.000         0.0	0.023 0.000 0.143 0.000 0.072 0.033 0.141 0.102 0.028 0. 0.441 0.468 0.429 0.013 0.398 0.354 0.452 0.375 0.413 0
35         nd         127         130         110	0.219 0.173 0.256 0.019 0.240 0.219 0.243 0.222 0.213 0
000         111         955         1000         1000         2000         111         2300         200	12:04 10:87 12:17 13:24 11:92 12:66 11:82 12:74 13:08
46         413         100         1300         740         850         520         550 <th>100.1 100.1 99.7 100.5 100.1 100.1 100.0 100.0 100.0 0.882 0.881 0.882 0.917 0.880 0.877 0.861 0.880 0.876 (</th>	100.1 100.1 99.7 100.5 100.1 100.1 100.0 100.0 100.0 0.882 0.881 0.882 0.917 0.880 0.877 0.861 0.880 0.876 (
4.66         4.30         5.30         5.40         1.30         3.90 <th< td=""><th></th></th<>	
N. 7         Systery         X-14	4.500 3.800 2.800 2.400 0.900 5.100 10.80 10.40 24.70 2 <sup>-</sup>
57.0         57.0 <th< td=""><th>6.5.10 5.950 n.d n.d n.d 13.31 106./3 68.55 48.40 4 55.22 78.94 72.08 3.381 62.28 62.89 70.06 63.29 57.55 5</th></th<>	6.5.10 5.950 n.d n.d n.d 13.31 106./3 68.55 48.40 4 55.22 78.94 72.08 3.381 62.28 62.89 70.06 63.29 57.55 5
220         86.0         88.10         17.10         85.40         81.10         45.00         80	2630 2790 1290 29.00 2610 2300 2420 2230 2300 1
15.30         15.40 <th< td=""><th>909.0 912.0 629.0 441.0 931.0 887.0 873.0 833.0 962.0 8</th></th<>	909.0 912.0 629.0 441.0 931.0 887.0 873.0 833.0 962.0 8
30         110         1200         12	96.70 88.60 56.30 14.20 105.00 98.50 94.90 106.0 93.00 94 4650 4470 040.0 4000 4000 4700 4770 4000 4660 47
11         11         290         2660         118         2170         2350         5500         550 </td <th>1650 1470 942.0 120.0 1940 1700 1773 1880 1660 17 1717 1358 1538 145.9 1887 1724 1912 1742 1675 16</th>	1650 1470 942.0 120.0 1940 1700 1773 1880 1660 17 1717 1358 1538 145.9 1887 1724 1912 1742 1675 16
(1)         (1) <th>36.10 25.90 2.140 10.50 30.80 27.30 25.80 25.70 15.80 25</th>	36.10 25.90 2.140 10.50 30.80 27.30 25.80 25.70 15.80 25
add         badd	59.20 51.00 16.90 28.50 54.60 47.90 51.20 50.50 51.50 40
350         18.30         26.41         17.0         17.30         17	D.d.I. D.d.I. D.d.I. D.d.I. D.d.I. D.d.I. D.d.I. D.d.I. D.d.I. D 0.131 0.021 0.012 0.040 0.049 0.188 0.750 0.557 0.104 0.
228         17.10         15.90         0.258         0.238         0.238         1.230         11.00         11.00         17.00         1	8.940 5.470 1.050 0.360 9.610 12.400 13.900 4.710 3.560 1
7.20         7.20         0.233         0.440         0.230         0.441         0.413         0.411         0.411         0.015         0.411         0.015         0.110         0.015         0.013         0	2.500 3.720 1.460 0.129 2.880 2.800 2.820 2.590 2.510
0.00         0.050         0.050         0.050         0.040         0.280         0.050         0.041         0.025         0.011         0.017         0.002         0.011         0.010         0.010         0.010         0.010         0.010         0.010         0.010         0.010         0.010         0.010         0.010         0.010         0.010         0.011         0.011         0.011         0.011         0.011         0.011         0.011         0.011         0.010         0.010         0.010         0.010         0.010         0.010         0.010         0.010         0.011	2./90
0330         0132         0101         0111         0101         0111         0101         0111         0111         0101         01111         0111         0111 <t< td=""><th>0.040 0.030 0.030 0.030 0.070 0.050 0.080 0.070 0.070</th></t<>	0.040 0.030 0.030 0.030 0.070 0.050 0.080 0.070 0.070
0000         0000 <th< th=""><th>0.003 0.031 b.d.I 0.056 0.013 0.002 0.020 0.018 0.021 0.060 0.130 0.140 0.050 0.140 0.130 0.130 0.160 0.150</th></th<>	0.003 0.031 b.d.I 0.056 0.013 0.002 0.020 0.018 0.021 0.060 0.130 0.140 0.050 0.140 0.130 0.130 0.160 0.150
.042         1060         1340         0.129         0.293         0.247         bdll         0.023         bdll         0.011         0.017         0.005         0.006         0.130         0.566         0.11         0.150         0.143         0.011         0.150         0.143         0.013         0.150         0.130         0.150         0.131         0.150         0.131         0.150         0.131         0.037	b.d.l b.d.l b.d.l b.d.l b.d.l 0.029 0.080
5.20         2.7/10         1.520         0.630         0.130         0.330         2.450         1.940         1.940         5.310         2.500         0.123         0.047         0.026         0.033         0.047         0.026         0.033         0.047         0.026         0.033         0.047         0.026         0.033         0.047         0.026         0.033         0.047         0.026         0.033         0.047         0.026         0.033         0.047         0.026         0.033         0.031         0.026         0.033         0.033         0.033         0.033         0.033         0.033         0.033         0.033         0.033         0.033         0.036         0.031         0.031         0.036         0.031         0.033         0.033         0.033         0.033         0.033         0.033         0.033         0.033         0.035         0.041         0.031 <th< th=""><th>0.013 0.003 b.d.l 0.002 0.028 0.115 0.190 0.176 0.029</th></th<>	0.013 0.003 b.d.l 0.002 0.028 0.115 0.190 0.176 0.029
393         0051         012         0079         0071         0141         0175         0107         0079         0071         0135         0137         0137         0137         0137         0137         0137         0137         0137         0137         0137         0136         0138         0131         0131         0131         0131         0131         0131         0131         0131         0132         0133         0132         0133         0132         0132         0131         0131         0131         0131         0131         0131         0131         0131         0131         0132         0133         0131         0131         0132         0132         0131         0131         0131         0131         0131         0131         0131         0132         01311         0131         0131	0.090
072         0.008         0.017         0.018         0.275         0.013         0.011         0.014         0.016         0.008         0.013           185         0.071         0.134         0.176         0.173         1.060         0.065         0.073         0.012         0.013         0.014         0.013         0.013         0.013         0.013         0.013         0.013         0.013         0.013         0.013         0.013         0.014         0.013         0.014         0.013         0.014         0.013         0.014         0.013         0.014         0.013         0.014         0.013 </th <th>0.189 0.253 0.237 0.174 0.409 1.430 0.440 0.361 0.449</th>	0.189 0.253 0.237 0.174 0.409 1.430 0.440 0.361 0.449
455         0071         0.134         0.164         0.075         0.073         0.025         0.173         1.060         0.065         0.073         0.023         0.0129         0.275         0.1129         0.066         0.087         0.063         0.083         0.094         0.013         0.056         0.073         0.065         0.073         0.065         0.073         0.065         0.073         0.065         0.073         0.065         0.073         0.065         0.073         0.065         0.073         0.065         0.073         0.065         0.074         0.073         0.065         0.074         0.073         0.065         0.074         0.073         0.065         0.074         0.037         0.065         0.074         0.037         0.065         0.074         0.037         0.065         0.074         0.037         0.066         0.035         0.040         0.051         0.031	0.053 0.068 0.054 0.018 0.082 0.192 0.089 0.076 0.086
0.00         0.036         0.036         0.044         0.017         0.036         0.047         0.027         0.037         0.037         0.047	0.380 0.518 0.335 0.077 0.541 0.937 0.571 0.507 0.536 0.185 0.272 0.132 0.019 0.237 0.284 0.245 0.215 0.215
306         0.157         0.163         0.219         0.239         0.332         0.034         0.101         0.019         0.085         0.040         0.152         0.138         0.137         0.138         0.138         0.137         0.138         0.137         0.138         0.137         0.037         0	0.081 0.108 0.120 0.006 0.096 0.107 0.092 0.086 0.119
.055         0.036         0.044         0.048         0.059         0.006         0.018         0.003         0.014         0.043         0.0371         0.347         0.038         0.004         0.033         0.037         0.038         0.037         0.038         0.037         0.033         0.032         0.031         0.021         0.033         0.032         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.032         0.033         0.032         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.031         0.032         0.031         0.031         0.031         0.031         0.031         0.031         0.032         0.031         0.031 <th< td=""><th>0.285 0.413 0.186 0.020 0.348 0.378 0.383 0.336 0.339 (</th></th<>	0.285 0.413 0.186 0.020 0.348 0.378 0.383 0.336 0.339 (
.417         0.283         0.290         0.371         0.434         0.037         0.156         0.023         0.147         0.043         0.228         0.181         0.289         0.197         0.337         0.341         0.535         0.095         0.065         0.065         0.062         0.044         0.068         0.062         0.044         0.068         0.062         0.044         0.068         0.062         0.044         0.068         0.062         0.044         0.068         0.062         0.044         0.068         0.062         0.044         0.068         0.062         0.044         0.068         0.062         0.044         0.062         0.044         0.062         0.044         0.062         0.041         0.022         0.033         0.002         0.033         0.002         0.033         0.002         0.033         0.002         0.033         0.014         0.042         0.033         0.002         0.033         0.002         0.033         0.002         0.033         0.014         0.046         0.022         0.034         0.049         0.022         0.032         0.024         0.040         0.023         0.014         0.025         0.041         0.024         0.032         0.024         0.040	0.061 0.086 0.036 0.003 0.071 0.073 0.071 0.065 0.061
0.001         0.068         0.068         0.068         0.068         0.066         0.064         0.068         0.066         0.044         0.068         0.060         0.044         0.068         0.061         0.044         0.068         0.061         0.044         0.068         0.061         0.044         0.068         0.061         0.044         0.068         0.061         0.044         0.068         0.061         0.110         0.023         0.013         0.0110         0.023         0.013         0.023         0.0110         0.023         0.013         0.023         0.013         0.0110         0.023         0.013         0.023         0.013         0.023         0.013         0.023         0.013         0.023         0.013         0.023         0.013         0.023         0.013         0.023         0.033         0.033         0.023         0.013         0.023         0.024         0.040         0.023         0.033         0.013         0.024         0.041         0.023         0.031         0.013         0.024         0.040         0.024         0.040         0.024         0.040         0.024         0.040         0.024         0.040         0.024         0.040 <th0.024< th="">         0.040         0.024         &lt;</th0.024<>	0.432 0.640 0.261 0.020 0.511 0.510 0.506 0.466 0.442 (
	0.096 0.143 0.056 0.004 0.111 0.109 0.108 0.101 0.094
2.29         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001	0.299 0.451 0.1/1 0.010 0.350 0.343 0.350 0.314 0.302 20043 0.066 0.024 0.001 0.040 0.048 0.050 0.047 0.042
0.44         0.037         0.041         0.041         0.042         0.044	0.043 0.000 0.024 0.001 0.049 0.046 0.030 0.047 0.042 0.305 0.450 0.171 0.012 0.344 0.333 0.350 0.311 0.303
.142       1.340       0.132       0.893       0.073       0.074       0.090       0.680       0.400       0.032       b.dl       b.dl </th <th>0.046 0.067 0.025 0.001 0.049 0.050 0.052 0.048 0.046</th>	0.046 0.067 0.025 0.001 0.049 0.050 0.052 0.048 0.046
.004 0.028 0.003 0.022 b.d.l 0.038 b.d.l b.d.l 0.005 b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l .118 0.207 0.166 0.215 0.237 0.162 0.580 b.d.l 0.530 0.056 0.306 0.041 0.274 0.515 0.413 b.d.l 0.13 .018 0.101 0.025 0.078 0.014 0.104 0.300 0.010 0.010 0.009 0.013 0.009 0.005 0.010 0.012 0.00 .002 0.004 0.008 b.d.l 0.003 0.049 0.053 b.d.l 0.013 0.001 0.032 0.111 0.003 -b.d.l 0.006 0.001 0.05	0.274 0.348 0.169 0.052 0.180 0.211 0.890 0.409 0.350
	0.006 0.005 0.004 b.d.l b.d.l 0.029 0.014 0.003 0.004
.002 0.004 0.008 b.d.l 0.003 0.049 0.053 b.d.l 0.013 0.001 0.032 0.111 0.003 -b.d.l 0.006 0.001 0.02	0.005 0.077 0.048 6.010 0.096 0.050 0.011 0.122 0.296 2067 0.048 0.040 0.036 0.036 0.072 0.020 0.052 0.034
	0.003 0.001 b.d.l 0.007 b.d.l 0.019 0.001 0.002 0.005 0



**Fig. 10.** Bulk rock major element ratios of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (anhydrous) versus MgO/SiO<sub>2</sub> (anhydrous) of serpentinites. The blue line corresponds to the Terrestiral array (Jagoutz *et al.*, 1979; Hart & Zindler, 1986). References are the same as in Fig. 9.



**Fig. 11.** Mg# versus bulk-rock Ni (A) and Cr (B) concentrations (in  $\mu g/g$ ) of serpentinites from Upper and Lower Platta, Tasna and Totalp. References are the same as in Fig. 9.

apfu) and 5.30 wt% FeO<sub>tot</sub> (Fe<sub>tot</sub> = 0.21 apfu), giving a Mg# of  $\sim$ 0.93. Bastite texture slightly differs in composition relative to mesh texture, with less SiO<sub>2</sub> (39.81 wt%; Si = 1.9 apfu), MgO (37.49 wt%; Mg = 2.6 apfu) and  $FeO_{tot}$  (4.74 wt%;  $Fe_{tot} = 0.18 apfu$ ) and more  $Al_2O_3$  (4.12 wt%; Al = 0.23 apfu), because they retain part of Al from primary pyroxene (Table 3). Consequently, serpentine mesh plots close to the Mg-pure lizardite or chrysotile end-members in the Si versus Mg + Fe diagram (Fig. 13A), whereas bastite composition extends along the Tschermak trend (Al replacing an octahedral and tetrahedral cation; Fig. 13A, B). Bastite has Mg# near identical to mesh textures (0.94 in average, Table 3; Fig. 14).

The polyhedral serpentine (S2) is generally characterized by lower FeO<sub>tot</sub> content (4.19 wt%, Fe<sub>tot</sub> ~0.16 apfu) at given SiO<sub>2</sub> and MgO concentrations relative to serpentine mesh (S1; 3A). As a consequence, this second generation of serpentine has higher Mg# values (>0.94 in average; Fig. 14). It is also characterized by relatively high  $Al_2O_3$  concentrations (2.84 wt%, Al = 0.16 apfu) and thus plots between mesh and bastite serpentines along the Tschermak trend (Fig. 13A, B).

The banded serpentine veins (S3) mainly plot within the field defined by serpentine mesh (S1) in the Si versus Mg+Fe diagram (Fig. 13C, Table 3). However, these banded veins can be distinguished by higher Mg# values (>0.95 Table 3, Fig. 14) due to lower Fe<sub>tot</sub> content relative to the two previous generations. More specifically, the banded veins can be subdivided into two groups based on their Mg# and Raman signature (Figs. 14 and 15): the first group made of polygonal serpentine is characterized by Mg# of ~0.95 (Fe<sub>tot</sub> = 0.07–0.28 apfu, Mg = 2.6–2.8 apfu), whereas the second group made of lizardite has Mg# >0.97 (Fe<sub>tot</sub> < 0.10 apfu, Mg = 2.7–2.9 apfu). The banded veins also contain Al apfu higher than the serpentine mesh S1 at a given Si apfu (Al ~0.1 versus ~0.05, respectively at Si ~1.95 apfu). Some veins even extend along the Tschermak trend towards the bastite field (Fig. 13C, D).

The lamellar antigorite veins and patches (S4) display the highest SiO<sub>2</sub> concentrations of all serpentine generations (42.48  $\pm$  1.08 wt%, Si = 1.99 apfu), and Mg + Fe in the range of 9.79–2.93, close to the pure antigorite end-member (Fig. 13C). Interestingly, unlike the gradual increase in Mg# described in previous generations of serpentine from the initial mesh, antigorite veins have lower Mg# (<0.95 in average) due to higher Fe concentrations (FeO<sub>tot</sub> = 4.15 wt% in average, Fe<sub>tot</sub> = 0.16 apfu, Fig. 14). Al<sub>2</sub>O<sub>3</sub> concentrations are low (1.15  $\pm$  1.07 wt %, Al = 0.06 apfu).

The last generation of serpentine veins (crack-seal filled by chrysotile; S5) have Mg+Fe content within the range of previous generations of serpentine veins, with nevertheless slightly higher MgO=39.76±0.97 wt % and lower FeO<sub>tot</sub>= $3.99\pm1.18$  wt % concentrations (Mg=2.79 apfu, Fe<sub>tot</sub>=0.16 apfu, Mg#=0.95; Figs. 13C and 14). They also show very similar SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations to those of the antigorite (SiO<sub>2</sub>= $42.17\pm0.94$  wt %, Si=1.98 apfu; Al<sub>2</sub>O<sub>3</sub>= $0.76\pm0.62$  wt %, Al=0.04 apfu; Fig. 13D).

Interestingly, none of the serpentine composition plots along the brucite trend (Fig. 13). This is consistent with the fact that brucite was never observed in our samples, neither on microscopic observations nor through the different techniques used (i.e. XRD and Raman spectroscopy).

#### Trace elements

The representative trace element concentrations of each serpentine generation are given in Table 4, Figs. 16 and 17. REE and spider diagrams of all samples analyzed in this study are given in supplementary materials. The REE concentrations of serpentine polysomes (Figs. 16 and 17) vary between 0.001 and < 10 times the chondrite C1 and mimic the REE pattern of their respective bulkrocks. They are similar in shape and concentration to exhumed

Unit	Upper Plat	ta				Lower Platts					Totalp				Tasna			
Sample Texture	Fal 18-06 mesh (S1)	Fal 18-02 bastite (S1)	Fal 18-03 banded vein (S3)	Fal 18-06 lamellar vein (S4)	Fal 18-06 fibrous vein (S5)	Mar 18-01 mesh (S1)	Mar 18-01 bastite (S1)	Mar 18-01 banded vein (S3)	Mar 18-01 lamellar vein (S4)	Mar 18-01 fibrous vein (S5)	Tot 19-02 mesh (S1)	Tot 19-02 bastite (S1)	Tot 19-02 spherical vein (S2)	Tot 19-07 banded vein (S3)	Tas 19-02 mesh (S1)	Tas 19-03 bastite (S1)	Tas 19-08 banded vein (S3)	Tas 19-02 lamellar vein (S4)
Type	lizardite	lizardite	polygonal	antigorite	chrysotile	lizardite ol	lizardite	lizardite	antigorite	chrysotile	lizardite ol	lizardite	polyhedral	polygonal	lizardite	lizardite	lizardite	antigorite
minerals	10	xdo				10	xdo				5	cbx			10	cpx		
sio <sub>2</sub>	41.54	39.40	41.24	42.87	41.41	40.52	40.14	42.10	42.26	42.28	40.57	38.67	40.70	42.51	42.05	40.68	42.50	43.29
Tio <sub>2</sub>	0.028	0.088	0.660	0.026	0.020	0.035	0.035	0.035	0.028	0.030	0.027	060.0	0.030	0.040	0.245	0.100	0.040	0.054
Al <sub>2</sub> O <sub>3</sub>	0.265	4.704	2.123	0.233	0.290	1.335	1.180	0.665	0.965	0.880	1.977	5.515	3.530	0.890	0.640	2.790	1.500	0.974
$Fe_2O_3$	5.135	3.907	4.010	4.574	4.600	5.023	4.995	3.055	4.258	3.820	4.900	4.635	2.787	2.530	4.020	4.135	1.570	3.465
MnO	0.125	060.0	0.200	0.206	0.160	0.155	0.135	0.120	0.272	0.180	0.117	0.110	0.093	0.110	0.155	0.105	0.070	0.133
MgO	39.80	38.12	38.39	38.94	41.09	39.59	39.90	41.07	38.93	39.84	39.17	37.52	39.59	40.83	39.42	38.22	40.75	38.38
CaO	0.088	0.175	0.607	0.063	0.180	0.063	0.055	0.065	0.064	0.080	0.147	0.535	0.443	0.210	0.565	0.845	1.190	0.431
K <sub>2</sub> 0	b.d.1	l.b.d	b.d.l	b.d.1	b.d.l	b.d.l	b.d.1	b.d.l	b.d.l	b.d.l	b.d.l	b.d.1	b.d.l	b.d.l	b.d.l	b.d.l	b.d.1	b.d.l
Na <sub>2</sub> 0	b.d.1	l.b.d	b.d.l	b.d.1	b.d.l	b.d.l	b.d.1	b.d.l	b.d.l	b.d.l	b.d.l	b.d.1	b.d.l	b.d.l	l.d.l	b.d.l	b.d.1	b.d.l
$Cr_2O_3$	060.0	0.786	0.143	0.031	0.060	0.483	0.905	0.073	0.049	0.070	0.027	0.210	0.017	0.030	0.070	0.355	0.010	0.051
NiO	0.323	0.058	0.020	0.083	0.050	0.195	0.135	0.025	0.079	0.050	0.427	060.0	b.d.l	b.d.l	0.150	0.060	0.020	0.097
Total	87.39	87.29	87.39	87.02	87.32	87.38	87.47	87.21	86.91	87.22	87.36	87.32	87.19	87.16	87.32	87.27	87.20	86.88
p.f.u	0.0	L			C LC	000	100	10	1	100 7	000 7	000			200	000	000	000
ភា	1.968 2.222	CC8.1	1.94.1	1.9/8	1.953 1.052	1.922	1.90/	1.9/1	1.94/	C86.1	1.922	1.829	1.904	1.984 1.525	1.981	1.92U	1.98U	1.98U
	0.001	0.003	0.024	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.003	0.001	0.001	600.0	0.004	0.001	0.002
AI	0.015	0.261	0.118	0.013	0.016	0.075	0.066	0.037	0.051	0.049	0.110	0.308	0.195	0.049	0.036	0.155	0.058	0.053
Fe <sup>2+</sup>	0.180	0.154	0.105	0.164	0.144	0.189	0.162	0.120	0.174	0.150	0.194	0.184	0.109	0.099	0.110	0.162	0.020	0.116
Fe 3+	0.022	0.000	0.048	0.011	0.014	0.00	0.034	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.044	0.001	0.038	0.015
Mn	0.005	0.004	0.008	0.008	0.007	0.006	0.006	0.005	0.012	0.007	0.005	0.005	0.003	0.005	0.006	0.004	0.003	0.005
Mg	2.811	2.678	2.694	2.679	2.889	2.799	2.826	2.867	2.663	2.789	2.766	2.646	2.762	2.841	2.768	2.689	2.830	2.617
Ca	0.004	0.009	0.031	0.003	600.0	0.003	0.003	0.003	0.002	0.004	0.007	0.027	0.022	0.011	0.029	0.043	0.059	0.021
К			ı								ı			ı				
Na	ı	1	ı	ı	I	ı		1		ı	ı		1	ı	ı	ı		ı
ç	0.003	0.029	0.005	0.001	0.002	0.019	0.034	0.003	0.000	0.003	0.001	0.008	0.001	0.001	0.003	0.014	0.000	0.002
ïZ	0.012	0.002	0.001	0.003	0.002	0.008	0.006	0.001	0.001	0.002	0.016	0.001	0.000	0.000	0.006	0.002	0.001	0.004
Mg#	0.940	0.946	0.963	0.942	0.953	0.937	0.946	0.960	0.939	0.949	0.934	0.935	0.962	0.966	0.962	0.943	0.993	0.958
Fe <sup>3+/Fe</sup> T	0.107	0.000	0.314	0.053	0.053	0.045	0.174	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.286	0.006	0.655	0.117
The struct $m = 17$ in t	ural formuls the antigorit	a for all serf :e general fc	entine mine rmulae Mg	erals and ve 3 m – 3 Si 2	ins have be m0 5 m(OH	en calculate 1) 4 m – 6.	d on the ba	isis of 7 oxy	gens, excep	t for antigo	rite for whi	ch calculati	ons have be	een done on	the basis o	f 6.823 oxy	gen, corresp	onding to

**Table 3**: Representative major element concentrations (in wt %) of serpentine minerals and veins measured by µXRF



Fig. 12. Representative rare earth element (REE) patterns normalized the Chondrite C1 (left) and Primitive Mantle (PM)-normalized extended trace element patterns (right) of bulk-rock serpentinites from Tasna, Totalp and Platta (green: Upper Platta, brown: Lower Platta), in comparison with bulk-rock serpentinites from Iberia (orange field) and Newfoundland (purple field), data from Kodolányi et al., (2012).

mantle peridotites from other places in the Alps (e.g. the Chenaillet unit, Lafay *et al.*, 2017). At sample scale, the REE patterns of the diverse serpentine polysomes are similar in shape: LREE-depleted ((La/Sm)<sub>N</sub> ~ 0.35), with relatively flat middle (MREE) to HREE patterns. Noteworthy a progressive depletion from the first to the last serpentine generation is documented. Two samples from the Lower and Upper Platta units exhibit very different REE concentrations, both forming a U-shaped pattern characterized by enrichment of LREE and HREE over MREE and strong positive Eu anomalies (Eu/Eu\* > 2; Figs. 16 and 17).

At sample scale, the primitive mantle-normalized patterns of serpentine minerals and veins exhibit similar shapes, with a global depletion relative to the PM. As for concentrations in bulkrock, all serpentines are enriched in FME with positive anomalies in Cs, B, As, Sr and Li (concentrations between 0.1 and > 100 times the PM; Figs. 16 and 17). Additionally, a significant enrichment in U relative to Th is observed (U/Th = 14.84 in average; N = 183).

#### DISCUSSION

In this study, we report a sequence of four stages of serpentinization with distinct five serpentine textures and specific chemical compositions (Fig. 8). These stages are likely indicative of a variety of fluid–rock interactions during mantle exhumation along the OCT of the Alpine Tethys. In the following, we first discuss each of the serpentinization stages in terms of local variations of temperature, pressure, fluid/rock ratio and fluid chemistry with the aim to determine the variation of fluid–rock interactions from initial to more advance mantle exhumation, recorded from proximal to distal parts across the OCT (Fig. 19). Finally, we compare serpentinization sequences as documented at OCTs with serpentinization sequences observed at present-day MORs.

#### Serpentinization as a tape recorder of multi-stage mantle exhumation Stage 1: Formation of mesh and bastite textures (serpentine S1)

Pseudomorphic serpentine mesh and bastite textures, here referred to as serpentine S1 (Fig. 8), are not only the oldest, but also the most common textures found in serpentinites from OCTs. Previous studies proposed that serpentinization at magma-poor rifted margins likely begins when the subcontinental lithospheric mantle is still capped by a thin, <6 km thick hyperextended continental crust (Manatschal, 2004; Epin et al., 2019; Hochscheid et al., 2022). Serpentinizing fluids at OCTs are assumed to reach down to ~6 km depth below seafloor through circulation along high-angle normal faults, as indicated by refraction seismic experiments (Boddupalli et al., 2022). At such depth, a combination of anisotropic thermal contraction and tectonic stresses induce micro-fractures into the mantle rocks allowing the channeling of fluids necessary for serpentinization (Rouméjon & Cannat, 2014). These micro-fractures are at the origin of a connected porosity allowing the transport of hydrothermal fluids resulting in a typical mesh texture even at low fluid/rock ratio (<F/R mass

	•				•	•			,								
Unit	Upper Platt	в			Lower Platta					Totalp				Tasna			
Sample	Fal 18-06	Fal 18-06	Fal 18-06	Fal 18-06	Mar 18-01	Mar 18-01	Mar 18-01	Mar 18-01	Mar 18-01	Tot 19-02	Tot 19-02	Tot 19-02	Tot 19-07	Tas 19-02	Tas 19-03	Tas 19-02	Tas 19-08
	ua23	ua15	ua35	ca6	ua39	ua36	ua46	ua50	ca16	vb6	ca_49	ca_50	cb25	ub1	ub21	ub8	cb6
Texture	mesh (S1)	bastite (S1)	lamellar vein (S4)	crack-seal (S5)	mesh (S1)	bastite (S1)	banded vein (S3)	lamellar vein (S4)	crack-seal (S5)	mesh (S1)	relic cpx	spherical vein (S2)	banded vein (S3)	mesh (S1)	bastite (S1)	lamellar vein (S4)	banded vein (S3)
Type	lizardite	lizardite	antigorite	chrysotile	lizardite	lizardite	lizardite	antigorite	chrysotile	lizardite	lizardite	polyhedral	polygonal	lizardite	lizardite	antigorite	lizardite
Primary minerals	ol	xdo		ı	ol	xdo	1			ol	cpx	ı	ı	ol	cpx	ı	
Li	2.852	13.79	11.15	13.71	3.977	2.708	4.957	2.542	12.32	0.213	3.900	2.238	1.656	7.331	26.86	6.134	0.360
В	48.30	36.63	94.50	37.92	43.63	30.92	34.86	37.34	35.25	19.43	15.16	18.49	46.74	25.12	52.70	23.74	15.94
v	5.893	76.84	10.23	4.371	17.20	85.45	17.33	29.26	9.754	6.558	163.7	7.064	7.789	111.9	129.1	18.24	18.28
Ç	136.2	3465	2.115	303.8	553.8	4809	358.4	38.20	253.0	8.755	2853	32.82	78.57	2665	4054	43.96	74.98
ů	111.0	14.58	6.678	43.83	73.56	52.54	9.357	10.96	8.970	162.3	10.79	1.272	2.187	56.96	53.00	35.88	147.6
Ni	2951	1019	210.4	708.5	1977	1053	187.5	223.6	233.2	2987	179.8	16.57	20.37	1663	909.2	1222	2897
Zn	19.17	24.32	19.00	18.16	59.07	65.87	52.24	68.98	38.80	21.99	9.710	7.109	5.471	26.82	34.97	24.24	21.39
As	2.854	0.147	1.326	0.952	1.665	1.057	0.103	0.219	0.195	n.d	0.128	0.130	0.061	0.093	0.063	<0.05	0.040
Rb	0.101	0.178	1.510	0.167	0.748	0.379	0.556	1.352	1.070	0.069	0.026	0.047	0.189	0.508	1.612	1.484	0.010
Sr	1.994	5.386	1.250	3.159	4.103	3.087	2.878	2.053	4.220	1.896	17.43	0.616	4.934	3.291	2.159	1.557	1.264
Y	0.374	2.001	0.136	0.324	0.281	0.176	0.200	0.110	0.338	0.433	12.85	0.142	0.423	1.362	1.281	0.851	0.782
Zr	0.107	3.951	0.066	0.301	0.116	0.086	0.125	0.244	0.106	0.531	10.81	0.258	1.958	0.253	0.770	0.374	0.459
Nb	0.018	0.033	0.010	0.018	0.101	0.094	0.069	0.038	0.061	0.001	0.012	0.004	0.002	0.016	0.010	0.011	0.001
Cs	0.276	0.545	4.999	0.162	0.549	0.329	0.464	1.378	0.725	n.d	0.010	0.013	0.046	1.108	1.401	4.294	0.003
Ba	0.812	3.474	0.589	1.276	1.218	0.863	0.738	0.545	1.151	0.099	0.136	0.091	0.625	0.992	0.364	0.914	0.204
La	0.064	0.057	0.041	0.049	0.299	0.155	0.151	0.071	0.126	0.008	0.108	0.003	0.008	0.031	0.002	0.019	0.001
Ce	0.197	0.252	0.144	0.143	0.397	0.308	0.293	0.153	0.235	0.056	0.774	0.011	0.035	0.078	0.018	0.066	0.007
Pr	0.031	0.040	0.021	0.028	0.039	0.025	0.029	0.015	0.024	0.013	0.212	0.003	0.007	0.012	0.010	0.010	0.004
Nd	0.149	0.233	0.116	0.144	0.136	0.087	0.110	0.045	0.095	0.065	1.605	0.025	0.044	0.097	0.074	0.062	0.054
Sm	0.042	0.115	0.028	0.054	0.029	0.026	0.010	0.011	0.024	0.028	0.865	0.007	0.020	0.049	0.060	0.032	0.041
Eu	0.062	0.054	0.039	0.081	0.088	0.050	0.054	0.033	0.081	0.008	0.346	0.010	0.010	0.020	0.039	0.017	0.014
Gd	0.065	0.226	0.031	0.085	0.032	0.019	0.019	0.00	0.042	0.045	1.393	0.033	0.044	0.111	0.119	0.100	060.0
Тb	0.008	0.049	0.004	0.018	0.004	0.003	0.004	0.002	600.0	0.010	0.302	0.009	0.009	0.031	0.028	0.016	0.016
Dy	0.055	0.354	0.016	0.071	0.034	0.019	0.021	0.018	0.043	0.059	2.158	0.024	0.066	0.232	0.195	0.129	0.107
Но	0.010	0.080	0.004	0.010	0.007	0.005	0.005	0.003	0.010	0.015	0.485	0.005	0.019	0.057	0.048	0.032	0.027
Er	0.029	0.251	0.014	0.034	0.021	0.00	0.013	0.006	0.025	0.045	1.470	0.017	0.049	0.186	0.135	0.104	0.096
Tm	0.003	0.037	0.001	0.007	0.003	0.003	0.003	0.001	0.005	0.009	0.220	0.003	0.008	0.025	0.028	0.018	0.015
ЧЪ	0.022	0.298	0.008	0.032	0.037	0.022	0.018	0.013	0.033	0.062	1.435	0.013	0.071	0.194	0.213	0.103	0.089
Lu	0.004	0.049	0.001	0.011	0.007	0.004	0.004	0.002	0.007	0.012	0.214	0.006	0.012	0.029	0.035	0.020	0.019
Hf	<0.003	0.145	<0.003	0.001	0.005	<0.002	0.003	0.003	0.001	0.023	0.453	0.006	0.057	0.033	0.052	0.033	0.030
Ta	<0.001	0.003	<0.001	0.006	0.002	0.001	0.002	0.002	0.004	<0.0002	0.003	<0.002	0.000	< 0.0010	<0.0006	<0.0008	<0.0002
Pb	0.261	0.019	<0002	0.057	0.520	0.165	0.010	0.011	0.037	0.142	0.064	0.038	0.144	0.071	0.051	0.006	0.033
Th	0.000	0.007	0.000	0.000	0.000	0.001	0.002	0.001	0.001	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000
n	0.001	0.002	<0.001	0.006	0.001	0.000	0.001	0.003	0.000	0.002	0.000	<0.0002	0.001	0.004	0.000	600.0	0.000

Table 4: Representative trace element concentrations (in ppm) of serpentine minerals measured by HR-LA-ICP-MS.



**Fig. 13.** A-C) Plots of Mg + Fe versus Si and B-D) Al versus Si. All cations are given in per formula units and are calculated based on 7 oxygen atoms in the serpentine formula, except for antigorite, which was calculated based on 6.823 oxygens and converted to 7 oxygens for comparison with other serpentine polysomes. Lz/Ctl: pure Mg lizardite/chrysotile endmember. Atg: pure Mg antigorite endmember. Data of Chenaillet serpentinites are from Schwartz et al., (2013) and those of Malenco antigorites are from Liu et al., (2020). Data from Iberia and newfoundland margin are from Vesin et al., (2023).

ratio 1; e.g. Moody, 1976; Wicks & Whittaker, 1977; Rouméjon & Cannat, 2014). This is evidenced by trace element patterns that mimic those of the primary minerals showing lower trace element concentrations (Fig. 16D, H). In addition, compared to mineral precursor serpentine minerals are also enriched in up to several orders of magnitude in FME (Cs, B, Li, ± Rb), evidencing an imprint of oceanic hydration. The FME enrichments in serpentine minerals from the Alpine OCT are similar to those of serpentinites from the Iberia and Newfoundland rifted margins (Kodolányi *et al.*, 2012; Vesin *et al.*, 2023). Experimental studies have shown that the hydrolysis of olivine is optimal at temperature <300°C, whereas orthopyroxene react faster than olivine at greater temperatures (Martin & Fyfe, 1970; Janecky & Seyfried, 1986; Allen & Seyfried Jr., 2003; Bach *et al.*, 2004). In our partially serpentinized samples from Totalp and Tasna, relics of clinopyroxene are preserved in

both units, olivine relics are frequently observed at Totalp while it is rarely preserved in other units (Fig. 6). Similar observations were also reported by Müntener *et al.* (2010) for serpentinized peridotites from Upper and Lower Platta, where some relics of clinopyroxene were observed while olivine is completely serpentinized. In addition, spinel is almost free of chlorite aureoles, indicating low temperatures of serpentinization as the alteration of spinel to chlorite typically occurs at temperature above 400°C. Therefore, based on petrological evidence and the temperatures of serpentinization estimated for Iberia-Newfoundland passive margins and the Mid-Atlantic Ridge (15°20'N Fracture zone and Hess Deep; see Vesin *et al.*, (2024) and references therein), we propose that an uppermost temperature limit of  $\pm$ 300°C can be assumed for this initial stage of serpentinization.



**Fig. 14.** Comparison of Mg# values in the suite of serpentine minerals and veins from this study, independently of their respective locations. The thick bars illustrate the typical variation range of Mg# for each serpentine polysomes.



**Fig. 15.** Fe<sub>tot</sub> versus Mg of serpentine banded veins showing two tendencies depending on the nature of the serpentine polysomes (polygonal serpentine versus lizardite).

#### Stage 2: Serpentine veining (serpentine S2 and S3)

Formation of polyhedral serpentine veins (S2): The first generation of veins coincides with the formation of polyhedral serpentine (S2, Fig. 8) that exhibits a typical spherical texture (Fig. 6). These veins

are mainly located in clinopyroxene relics and bastite cleavages, where a systematic association with andradite grains is reported. The S2 veins mostly occur in partially serpentinized samples, especially at Totalp, while in fully serpentinized samples S2 veins are scarce. The polyhedral serpentine (S2) veins contain significant Al (~0.16 apfu in average; Table 3). Such Al enrichment together with precipitation of andradite are consistent with the alteration of Al-rich mineral phases like clinopyroxene. Spinel and plagioclase are also important Al carriers in peridotites but the textural vicinity of polyhedral serpentine-andradite assemblage with clinopyroxene rather indicates that the latter is the source of Al. In addition, hydrothermal alteration turns spinel into ferritchromite rims and chlorite aureoles, where all Al released from spinel is consumed by the formation of chlorite (e.g. Mellini et al., 2005). Similarly, in plagioclase lherzolite from the Lower Platta unit, Al derived from plagioclase is consumed by the formation of chlorite as evidenced by petrographic observations (e.g. Müntener et al., 2010). Most trace element concentrations are significantly depleted (except for boron) in polyhedral S2 veins showing 1 to 2 orders of magnitude lower concentrations relative to bastite (S1) and primary clinopyroxene precursors (Fig. 16D, H). This suggests a high fluid/rock ratio. Therefore, it is likely that the saturation degree of the serpentinizing fluids forming polyhedral S2 veins is low. Our results agree with Andreani et al. (2008), who proposed that the formation of polyhedral serpentine veins require: (i) an open space, (ii) a temperature <200–300°C, and (iii) Al content >0.1 apfu.

Relatively to bastite (S1), polyhedral serpentine (S2) veins are enriched in Si and Mg and depleted in Ca and Fe (Fig. 13; Table 3). This may be explained by the preferential absorption of Ca and Fe by andradite (Plümper et al., 2014). The absence of magnetite associated to polyhedral serpentine (S2) veins is thus likely a consequence of andradite formation, since andradite consumes the Fe that is released either during pyroxenes serpentinization or after magnetite dissolution. Plümper et al., (2014) assume that andradite forms as a consequence of a Ca-metasomatism process in which the addition of Ca, here likely released after clinopyroxene serpentinization, destabilizes the magnetite. In addition, the oxidation of Fe for incorporation into andradite likely contributes to decrease fO2, as proposed by Beard & Hopkinson (2000) in serpentinites from Hole 1068 (Abyssal Plain). This lowered fO2 likely affects the stability of magnetite, which allow proposing that magnetite dissolution in favor to andradite resulted from both processes. Plümper et al., (2014) also showed that no additional source of Ca is required if the protolith contains between 8 and 12% of clinopyroxene. The subcontinental mantle exposed in the Platta, Tasna and Totalp nappes was originally composed of fertile, i.e. clinopyroxene-rich lherzolites (Müntener et al., 2010). Therefore, it is likely that serpentinization of these spinel or plagioclase lherzolites released enough Ca and Fe to form andradite synchronously with polyhedral serpentine. According to Frost & Beard (2007), the andradite + serpentine assemblage is strongly dependent on silica and calcium activities and on pH rather than temperature. However, these authors claim that a temperature range of 200-230°C is most favorable for the formation of andradite, which becomes the main Ca-bearing phase in serpentinites as long as CO<sub>2</sub> activity remains low, inhibiting the formation of calcite (Beard & Hopkinson, 2000; Kodolányi et al., 2012). This temperature range is consistent with that reported by Plümper et al., (2014), who showed that clinopyroxene can be replaced by an assemblage of serpentine + andradite at temperatures <280°C and low pressure (<0.5 kbar). As mentioned above, andradite is systematically observed at the rims of polyhedral serpentine, the



Fig. 16. Representative rare earth element (REE) patterns normalized to C1-Chondrite (left) and PM-normalized extended trace element patterns (right) of serpentine minerals and veins depending on their localities. Blue field correspond to serpentinites Grade 0 (sub-greenschist facies conditions) from the Chenaillet (data from Lafay *et al.*, 2013).

latter mostly occurring in clinopyroxene and cpx-bastite cleavages (Fig. 6F, G).

Considering that serpentine S1 formed at  $\pm 300^{\circ}$ C and at  $\leq 6$  km depth, serpentine S2 most likely formed shallower and under lower temperature ( $\pm 280^{\circ}$ C, and < 5 km). The presence of andradite closely associated to polyhedral serpentine (S2) is indicative for reducing conditions as iron oxidation prior incorporation into andradite keeps fO<sub>2</sub> of the serpentinizing fluid relatively low and can be accompanied by considerable generation of molecular

hydrogen (Plümper et al., 2014). Even if textural and chemical evidence suggests that polyhedral serpentine (S2) formed under slightly lower temperatures than serpentine S1, serpentine S2 is nevertheless assumed to develop during an early stage of fluid-rock interaction, likely soon after or simultaneously to pseudo-morphic mesh and bastite S1 formation (Fig. 19B – S2).

Formation of banded veins (S3): Banded veins S3 are frequently observed crosscutting the previous serpentine generations (S1 and S2 Fig. 6, Table 1). Similar occurrences of banded veins have



Fig. 17. Rare earth element (REE) patterns normalized to C1-Chondrite (A-C), and extended trace elements patterns normalized to Primitive mantle (B-D) of serpentine minerals and veins of two serpentinite samples for the Lower (Mar 18-01) and the Upper Platta (Fal 18-06) units, showing U-shaped patterns with strong Eu positive anomaly. The compositions of MARK serpentinites (Hole 1268A, Atlantic ridge) and hydrothermal fluids from Rainbow and Logatchev are shown for comparison (Paulick *et al.*, 2006).

been reported in oceanic serpentinites (e.g. Andreani *et al.*, 2004; Andréani *et al.*, 2007; Rouméjon *et al.*, 2015). The nature of the filling serpentine polysomes, however, can evolve from an unstable (proto-serpentine, chrysotile, polygonal) to a more stable serpentine polymorph (lizardite) as suggested by experimental studies of Grauby *et al.* (1998) and Normand *et al.* (2002) and recently strengthened by Raman spectroscopy on naturals samples (Tarling *et al.*, 2021). At sufficient degree of supersaturation (i.e. open system), several metastable phases like chrysotile may crystallize (Normand *et al.*, 2002). However, if the degree of supersaturation of the fluid is not maintained sufficiently high, the transition from a metastable to a more stable form (i.e. chrysotile -> polygonal -> lizardite) can occur spontaneously (Viti & Mellini, 1997; Normand *et al.*, 2002).

In our samples, banded veins (S3) are mostly made of lizardite and polygonal serpentine, whereas chrysotile remains scarce. The banded veins made of polygonal serpentine contains more Fetot and less Mg than banded veins made of lizardite (Fig. 14). Therefore, we attribute this isochemical evolution to the decreasing degree of supersaturation of the solution with respect to serpentine in a response to an increase of fluid/rock ratios, and a longer interaction time with the serpentinizing fluid as proposed by Normand et al. (2002) and Andréani et al. (2007). This is also supported by lower concentrations of most trace elements compared to the primary mesh and bastite S1, accompanied by an increase in FME like B (Fig. 16). According to Andréani et al. (2007), we propose that the formation of these banded veins (S3) begins when the ultramafic rocks are almost fully serpentinized, at shallower depth than the first two serpentine generations (S1 and S2), likely at <3 km depth along a detachment fault (Gillard et al., 2019). At this point, there is not enough results to discriminate if the banded veins attested of crack opening due to: i) an accommodation of volume expansion due to serpentinization, or ii) the

incremental stress release during unroofing of serpentinites (e.g. Ramsay, 1980; O'Hanley, 1992; Andreani *et al.*, 2004).

# Stage 3: Local overpressure and/or SiO<sub>2</sub>-rich fluid circulation – Formation of antigorite (S4)

Antigorite (S4) was identified in some fully serpentinized samples from Upper Platta, Tasna and in one sample from Lower Platta. It mostly occurs as patches, replacing the mesh texture, or as veins opening in all directions (Fig. 7A). Locally, these veins opened in pull-apart mode, showing a close relation with small chrysotile fibers (Fig. 7B). This is highlighted by the Raman spectra signature of antigorite (S4), which is systematically a mixture between serpentine chrysotile and antigorite, with typical peaks at 3670  $\rm cm^{-1},~3690~\rm cm^{-1}$  and 3700  $\rm cm^{-1}$  (Fig. 7). In addition, antigorite (S4) is frequently crosscut by later chrysotile crack-seal (S5) (Fig. 7D). Those antigorite veins may have been initially filled with chrysotile, suggesting the replacement of the latter by the former. Such replacement was also documented in samples from MORs (Hébert et al., 1991; Kodolányi et al., 2012; Klein et al., 2017; Ribeiro Da Costa et al., 2008; Rouméjon et al., 2015, 2019) and the Guatemala forearc (Kodolányi & Pettke, 2011). In Alpine ophiolites, antigorite is mostly considered as a fingerprint of Alpine prograde metamorphism (Dietrich, 1969; Burkhard & O'Neil, 1988; Scambelluri et al., 1995; Früh-Green et al., 2001; Debret et al., 2013; Lafay et al., 2013; Piccardo, 2013; Liu et al., 2020), and was, for long time, considered to be an evidence of HT-HP conditions of formation of serpentine (e.g. Ulmer & Trommsdorff, 1995; Wunder & Schreyer, 1997; Evans, 2004). Thus, high fluid-rock interaction temperatures and an additional heat source linked to melt emplacement (e.g. Beard et al., 2009; Frassi et al., 2022) have been invoked to explain antigorite at spreading ridges. However, neither evidence for the former nor the latter have been found at the Tasna and Upper Platta. At both units, where antigorite is observed, magmatic

additions are extremely rare and are not observed in the vicinity of the sample locations. In contrast, at lower Platta, where numerous gabbroic bodies and mafic dikes intruded the mantle, antigorite is absent, except of one sample. Therefore, the antigorite formation in our samples can hardly be attributed to the heat released by melt intrusions.

Alternatively, antigorite occurrences at Hess Deep (East Pacific Rise; Rouméjon et al., 2019), Atlantis Massif (Mid-Atlantic Ridge, MAR; Rouméjon et al., 2018, 2019), Puerto Rico Trench (Klein et al., 2017) and the Southwest Indian Ridge (SWIR; Rouméjon et al., 2015) were explained by interaction of the predating serpentine with Si-rich hydrothermal fluids derived from the alteration of mafic bodies (dikes and gabbros) or pyroxenes. Linking the antigorite formation to Si-metasomatism of mafic magmatic additions is hardly reconciled with observations and data from Tasna and Upper Platta, since such rocks are not observed in the field. However, peridotites from both Tasna and Upper Platta are pyroxene-rich, and at both sites pyroxenes are largely replaced by serpentine (Fig. 6). Therefore, the silica released after pyroxene alteration may have contributed to the formation of antigorite, which is consistent with the fact that some samples plot below the peridotite melting residue line in Fig. 10. Kodolányi & Pettke (2011) provided a detailed study on the major role played by SiO<sub>2</sub> during the chrysotile to antigorite transition. The authors suggest that if no brucite is produced during antigorite formation, either SiO<sub>2</sub> addition or Mg and Fe removal are needed to balance antigorite growth at the expense of chrysotile. This can explain the absence of brucite in our samples. Another hypothesis is that the chrysotile/lizardite-to-antigorite transition is linked to deformation or fluid infiltration. Ribeiro Da Costa et al., (2008) argued that chrysotile could be replaced by antigorite through a dissolution-recrystallization process favored by intense shearing stress at relatively low temperatures (<300°C). Alternatively, Kodolányi & Pettke (2011) proposed also that the replacement of chrysotile by antigorite occurred by dissolution (and precipitation) at T ~ 300°C due to fluid infiltration (i.e. fluid-assisted chrysotileantigorite transition). The recent discovery of seismic events in the footwall of oceanic core complexes showing compressional focal mechanisms (Parnell-Turner et al., 2017) may reflect a small amount of shortening due to the plate unbending at very shallow levels along an exhumed detachment fault (see also model of Sandiford et al., 2021). Therefore, we can barely exclude that local shortening during unbending of the downward concave detachment resulting in local overpressure did not affect the replacement of lizardite/chrysotile by antigorite, although we agree that this transition is rather promoted by (SiO<sub>2</sub>-rich) fluid circulation.

The transition from oceanic serpentine to antigorite formed in subduction zones is accompanied by a strong mobility of some trace elements, in particular fluid mobile elements (FME) like B, Li, Cs and Sr (e.g. Deschamps et al., 2012; Peters et al., 2017, Pettke & Bretscher, 2022). A loss of such elements was documented in several places in the Alps, such as the Lanzo Massif (Debret et al., 2013) or the Piedmont zone (Chenaillet-Queyras-Montviso; Lafay et al., 2013) of the Western Alps. These elements are transferred to the mantle wedge during the lizardite to antigorite transition. The ophiolitic nappes in Eastern Switzerland and Northern Italy, i.e. Totalp, Platta and Malenco discussed here (Fig. 1C), recorded a prograde and increasing Alpine metamorphism from north to south (Peters & Mathews, 1963; Dietrich, 1969, 1970; Vils et al., 2011). These units remained, however, in the hanging wall of the subduction zone and were not subducted, preserving them from high P-T conditions. This suggests that Alpine serpentinization, if it existed in any of these units, remained rare (Manatschal



**Fig. 18.** (A) Li versus B and (B) Cs versus Sr ( $\mu$ g/g) in the suite of serpentine minerals and veins from this study compared to other serpentinites from the Alps (Malenco Liu *et al.*, (2020), Chenaillet Lafay *et al.*, (2013) and from Iberia margin and Newfoundland margin from (Kodolányi *et al.*, 2012 and Vesin *et al.*, 2023). The two black arrows illustrate the depletion trend of FME during the prograde Alpine metamorphism.

and Müntener, 2006; Picazo et al., 2013). This may explain why antigorite from Upper Platta and Tasna displays no depletion in FME in contrast to the subducted serpentinites, and why it shows concentrations of B, Li, Cs and Sr within the range of earlier serpentines (S1 to S3; Fig. 18). In addition, the shapes of the antigorite spider-diagrams are also comparable to patterns of serpentine mesh within a sample, albeit with an order of magnitude of depletion (Figs. 16 and 17). These results are much in favor of a formation of the antigorite by recrystallization of earlier serpentine generations during mantle exhumation, promoted by SiO<sub>2</sub>-rich fluid circulation, as stated above, rather than a subduction-derived origin. This recrystallization may be accompanied by magnetite dissolution, which could explain why magnetite is so scarce in association with antigorite (Fig. 7A). Based on constant Mg# measured in serpentine mesh and antigorite in abyssal peridotites, Rouméjon *et al.*, (2019) postulated that antigorite does not integrate additional iron, even if magnetite is dissolved with mesh. However, a constant increase in Mg# is observed in our samples from S1 to S3 (Fig. 14), while Mg# decreases in antigorite (S4), suggesting that slight amount of iron may be integrated in antigorite veins and patches during serpentine mesh recrystallization.

#### Stage 4: Stress relaxation—Formation of crack-seal (S5)

Chrysotile crack-seal (S5) are the last generation of serpentine veins and are ubiquitous in our samples. They are also commonly recognized as the latest serpentinization event during mantle exhumation at MORs (e.g. Andréani *et al.*, 2007; Rouméjon *et al.*, 2015, 2018). Evans (2004) proposed that formation of cross-fiber chrysotile (i.e. crack-seal S5) is not really different from slip-fiber chrysotile (i.e. banded veins S3), although the latter is promoted by the presence of fluids rather than shear stress. We propose that the formation of chrysotile crack-seal (S5) occurred mainly at shallower depths than banded veins, but probably in similar levels than antigorite (S4). They are certainly formed as the consequence of late strain release during mantle exhumation at seafloor.

# Serpentine REE compositions: Evidence of fluid-dominated systems

Serpentine REE compositions mostly reflect those of their magmatic mineral precursors (olivine, clinopyroxene and orthopyroxene; see Figs. 16 and 17 and supplementary materials). Regarding the REE compositions of serpentinite whole rocks, they cover the range of peridotite compositions reported by Müntener et al. (2010). The variation of the  $(La/Sm)_N$  ratio from primitive-like to highly depleted signatures is due to variable degrees of partial melting or refertilization by syn-rift melt percolation (case of Lower Platta peridotites). It is a pre-serpentinization feature, consistently with what was documented along the Iberia passive margin (Kodolányi et al., 2012; Vesin et al., 2023). Hence, REE contents of serpentinite samples are inherited from the magmatic processes that affected the subcontinental mantle prior its exhumation at seafloor. Interestingly, two samples from the Lower and the Upper Platta units show particular U-shaped REE patterns with a strong positive Eu anomaly (Fig. 17). Similar patterns were reported in oceanic serpentinites, and two main processes have been proposed in the literature: (i) plagioclase crystallization during melt percolation (i.e. refertilization process; Müntener et al., 2004, 2010; Rampone et al., 1998, 2020); or (ii) large fluid-fluxes during serpentinization (Paulick et al., 2006). Regarding the first assumption, the crystallization of melt-derived plagioclase could be consistent with the formation of LREE-enriched serpentinites in the Lower Platta unit since the latter was largely impregnated by melts during Jurassic rifting (Müntener et al., 2004). However, this explanation cannot account for serpentinites from the Upper Platta, since this unit remained preserved from syn-rift melt percolation (Müntener et al., 2010). Therefore, serpentinization was likely responsible of the U-shape REE pattern which, by comparison, resembles those black smokers (e.g. Rainbow and Logatchev, Fig. 17; Klinkhammer et al., 1994; Douville et al., 2002).

Paulick et al., (2006) proposed that such shapes in serpentines are only possible under very high fluid/rock ratios so that the LREE concentration is entirely controlled by the fluid, erasing the LREE-depleted character of the protolith. At the opposite, HREE are less affected since their concentrations in hydrothermal fluids are negligible relative to the initial peridotite. Accordingly, the U-shape patterns observed in two serpentinites may resulted from intense fluid-rock interactions, similar to some mature hydrothermal systems described along MOR (Paulick *et al.*, 2006). This inference is consistent with the recent discovery of a well-preserved fossil ultramafic-hosted hydrothermal system, namely the Marmorera-Cotschen hydrothermal system in the Lower Platta unit (i.e. distal domain; Coltat *et al.*, 2019, 2021; Hochscheid *et al.*, 2022).

#### **Serpentinization across the OCT** Contrasting serpentinization from proximal to distal domains in the OCT

An important result of this study is that the full sequence of all serpentine generations (S1 to S5) is only observed in the proximal part of the OCT at Upper Platta and Tasna (Fig. 19C). In contrast, at the Lower Platta, which is derived from a more distal part of the OCT, only serpentine (S1) and chrysotile crack-seal (S5) can be observed (Fig. 19C). Interestingly, serpentinites from the Chenaillet unit, which is interpreted to be located more oceanward (distal) than the Lower Platta unit (see Fig. 1D), is dominated by mesh  $\pm$ bastite textures (S1) and devoid of serpentine veins (Lafay et al., 2013; Schwartz et al., 2013). This suggests that intensity of veining in serpentinites decreases oceanwards. Possible controlling factors are: (i) mantle composition, which changes from proximal to distal from spinel to plagioclase lherzolites (Müntener et al., 2004, 2010), and (ii) thermal gradients and presence of magma, which increase from proximal to distal. Both may account for a different rheology of the serpentinized basement and different composition of secondary minerals (e.g. Klein et al., 2013). Likewise, local magmatic intrusions could potentially increase the temperature of serpentinization and change the serpentinization rates (e.g. Rimstidt et al., 2012) and thus the degree of serpentinization at the distal domain. However, there is no difference in mineralogy nor degree of serpentinization between samples from the proximal and distal OCT, allowing us to propose that mantle composition and temperature seem not to be the main factors controlling the presence of serpentine generations. Alternatively, intensity of veining and the occurrence of serpentine generations (S1 to S5) may be linked to the mechanism of mantle exhumation. Indeed, Sauter et al. (2013), Epin & Manatschal (2018); Epin et al. (2019), Reston (2018), and Gillard et al. (2019) showed that mantle exhumation processes differ from proximal to distal domains of the OCT and at MORs. While at proximal OCTs mantle exhumation is mainly controlled by large offset detachment faults, at distal domains fault offsets tend to decrease and a transition to out-of-sequence detachments, and flip-flop faulting is observed. As a consequence, in the proximal domain (e.g. Tasna and Upper Platta) continuous mantle exhumation sequences, favor the development of all serpentine generations S1 to. In contrast, sequential flip-flop faulting or out of sequence detachment faulting at distal domains (i.e. Lower Platta) have the tendency to omit the development of intermediary serpentine generations (S2, S3 S4), allowing solely the development of the initial (S1) and final (S5) serpentine generations (Fig. 19B). It is, therefore, conceivable that the local absence of the intermediate serpentine (S2 to S4) at more distal domains (e.g. Chenaillet; proto-oceanic domain, Fig. 1D) reflects the involvement of flip-flop detachment faults (i.e. flip-flop exhumation mode, Fig. 19A). This is also in line with the studies of Reston & McDermott, (2011), Epin *et al.* (2019), Gillard *et al.* (2019) and Theunissen & Huismans (2022) showing evidence that mantle exhumation processes are undoubtedly more complex and discontinuous at distal parts of OCTs. Our simple model shown in Fig. 19 proposes that occurrence of all serpentine generations S1 to S5 indicates exhumation along one single exhumation fault, while complicated, polyphase flip-flop systems have the tendency to omit intermediate generations (S2 to S4).

Exceptions to this model may exist. At Totalp, that belongs to the proximal OCT, not all serpentine generations are observed. The mantle rocks in this unit are particularly well preserved, displaying serpentinization degrees ~60%. This is expected to occur for peridotites located near a fossil hydration front, in a rock-dominated hydration system. Serpentines consist essentially of lizardite in pseudomorphic mesh and bastite (S1), polyhedral serpentine (S2) inside orthopyroxene cleavages and few banded veins (S3). The low degree of serpentinization may also indicate that only small amounts of fluid penetrated the mantle, which could explain the absence of some serpentine generations (S3 to S5, Fig. 19C). Limited fluid–rock interactions at Totalp are also evidenced by very low FME concentrations (except B, Sb and Li) in bulk rock (Fig. 11).

# Serpentinization at OCT and MOR: Similarities and differences

Mantle exhumation is a common process at slow and ultra-slow spreading centers and at OCTs of magma-poor rifted margins (e.g. Cannat, 1993; Blackman *et al.*, 2002; Cannat *et al.*, 2009; Sauter *et al.*, 2013). Recent studies have proposed that at ultra-slow MOR settings, mantle exhumation involves successive detachment faults (flip-flop model; Sauter *et al.*, 2013 along the SWIR) similarly to distal parts of OCTs (e.g. Iberia-Newfoundland; Reston & McDermott, 2011, Theunissen & Huismans, 2022), Australia-Antarctica (Gillard *et al.*, 2016) and Lower Platta (Epin *et al.*, 2019). In contrast to ultra-slow spreading systems and distal OCTs, at slow spreading MORs and proximal OCTs flip-flop detachment systems have not so far been identified (Cannat *et al.*, 2019; Epin *et al.*, 2019).

Similarities in hydrothermal processes and conditions of serpentinization at slow to ultra-slow MORs and OCT are suggested by the occurrence of similar serpentine polysomes. Studies at 30°N (Atlantis massif; Rouméjon et al., 2018), 23°N (the Kane fracture zone, MARK area Dilek et al., 1997; Andréani et al., 2007), and along the (slow) MAR, at 62–65°E, as well as along the SWIR corresponding to a magma-poor end-member of an ultra-slow MOR (Rouméjon & Cannat, 2014; Rouméjon et al., 2015) show similarities with observations made at serpentinites from the Iberian OCT (Agrinier et al., 1996; Beard & Hopkinson, 2000, Kodolányi et al., 2012; Vesin et al., 2023). All studies revealed that serpentinites recorded multiple serpentinization events, involving a large variety of serpentine veins, textures and polysomes. However, the proportion, morphology and texture of serpentine veins can differ depending on the setting. Along the SWIR 62-65°E and the Atlantis Massif (hole M0076B; Rouméjon et al., 2015, 2018) described very similar serpentine sequences with the same serpentine polysomes to those reported at proximal OCT domains (Upper Platta, Tasna) reported in this study. This supports the idea that the presence or absence of serpentine generations are not controlled by the conditions of serpentinization (temperature and composition of mantle peridotites) but more likely by the mechanisms of mantle exhumation, i.e. exhumation along a single large offset fault vs along flip-flop faults (see model in Fig. 19). This is also supported by observations made along the SWIR, where mantle exhumation occurred during the past 7–10 Myr by flipflop faulting (Sauter et al., 2013). As predicted by our model, only a minor part (~25%) of the analyzed samples are overprinted by several serpentine veins (Rouméjon et al., 2015, 2018) with most of the samples composed only by pseudomorphic mesh and bastite textures (S1). Similar observations were also reported from the Atlantis Massif (Rouméjon et al., 2015, 2018).

#### Polyhedral serpentine: A fingerprint of OCTs?

A substantial difference between OCTs and MORs is the composition of the peridotites undergoing serpentinization. The nature of mantle constituting the OCT typically consists of spinel and plagioclase lherzolites, while at MORs the mantle is mostly harzburgitic (e.g. Andréani et al., 2007; Rouméjon et al., 2018). One notable difference in the serpentine paragenesis between OCT and MOR settings is the occurrence of polyhedral serpentine. In our samples, polyhedral serpentine occurs either in veins crosscutting the mesh texture or in alteration of pyroxenes, while it was not reported in Atlantis massif serpentinites and expected to occur rarely (<15%) in latest serpentine veins at SWIR (Rouméjon et al., 2015, 2018). In serpentinites from MARK, however, serpentine polyhedral is described as the latest generation of veins (Andréani et al., 2007; Andreani et al., 2008). According to Andreani et al. (2008), all Fe in polyhedral serpentine is ferrous, which is in favor of a formation under reducing conditions. This is, therefore, more consistent with a formation at depth rather than close to the seafloor, where oxidizing conditions are more likely. Its close association with andradite, as reported above, is also in favor of reducing conditions (Plümper et al., 2014).

The reason why polyhedral serpentine formed deeper in OCT serpentinites relative to those at MOR is thus unclear. A possible explanation could be the availability of Al that may control the formation of polyhedral serpentine (Andreani et al., 2008). The nature of the protolith may thus play a role in the early crystallization of polyhedral serpentine. The OCT peridotites from the Alps are fertile lherzolites that are up to three to four times more enriched in Al than the harzburgites that outcrop mainly at MAR and SWIR (Fig. 9). In lherzolite, Al is mainly stored in clinopyroxene, spinel and occasionally plagioclase. As in the distal OCT lherzolite was refertilized by melt percolation, forming secondary clinopyroxene-plagioclase assemblage. As stated above (section 5.1.2), we postulate that Al released during spinel and plagioclase alteration is unlikely to contribute to the formation of polyhedral serpentine. Rather, we assume that clinopyroxene contains enough Al to form polyhedral serpentine. This is consistent with the systematic observation of polyhedral at the vicinity of clinopyroxene relicts. Consequently, we assume that OCT lherzolites are more suitable to form polyhedral serpentine and associated andradite at early time of serpentinization relative to MOR harzburgites where Al and Ca are significantly more depleted. The distribution of serpentine generations (S1 to S5) occurring in exhumed mantle rocks depend on the exhumation mode (e.g. long-offset vs flip-flop). The development of polyhedral serpentine in the early stages of serpentinization may be related to the fertility of the protolith.

## CONCLUSION

In this study, we present new petrological and geochemical investigations of 18 serpentinized peridotites out of a set of 40 samples



**Fig. 19.** (A) Simplified cross-section across an ocean continent transition (OCT) highlighting a long detachment fault continentwards (red) and flip-flop faults (blue) oceanwards (Figure modified from Gillard *et al.*, 2016). (B) Conceptual model proposed for the footwall vs. flip-flop mantle exhumation in OCT and the related (C) type sequence of serpentinization: At proximal domains of the OCT, mantle exhumed along a continuous detachment fault, from ±6 km depth up to the seafloor, favors intense fluid–rock interactions and the development of a complete serpentinization sequence. At distal domains of the OCT, the mantle is exhumed discontinuously through asymmetric detachment faults (flip-flop). At this setting, one or more serpentine generations are missing, forming an incomplete serpentinization sequence.

collected in the OCT of the former Alpine Tethys, nowadays exposed in the Central Alps in SE Switzerland. Our results show that serpentinites record complex serpentinization sequences, resulting of successive episodes of fluid–rock interactions related to the progressive mantle exhumation. Four stages of serpentinization are identified giving rise to five serpentine generations with first pseudomorphic serpentine mesh and bastite made of lizardite (S1), which are then crosscut by several serpentine veins with different vein textures and serpentine polysomes (S2 to S5). These include spherical polyhedral serpentine (S2), banded (chrysotile  $\pm$  polygonal  $\pm$  lizardite) serpentine veins (S3), lamellar antigorite veins and patches (S4) and chrysotile crack-seal (S5). A major observation is that while in proximal (i.e. continentwards) parts of the OCT all serpentine sequences were formed (S1 to S5), in distal domains (i.e. oceanwards) of the OCT only the initial and final serpentine generations (S1 and S5) can be found. We explain this observation with a simple model (Fig. 19), suggesting that omission of intermediate serpentinization stages (S2 to S4) is reflecting a change in the mechanisms of mantle exhumation. In this model, a complete serpentinization sequence (S1 to S5) is formed, if the mantle is exhumed continuously along a single large offset detachment fault, as is the case at proximal domains of OCTs or at some oceanic core complexes at slowspreading ridges. At the opposite, an incomplete serpentinization sequence (S1 and S5) is recorded where mantle exhumation process is discontinuous and controlled by either out-of-sequence detachments or flip-flop faults as is the case at distal OCTs or ultra-slow spreading centers. Our model can explain why serpentinization sequences observed at proximal OCTs present close similarities with those observed at large offset faults at slow MORs as well as the similar observations made at distal OCTs and ultra-slow MORs. Our study suggest that formation of serpentine generations is controlled by the mode of exhumation (i.e. continuous vs discontinuous), while the formation of each serpentine generation is controlled by the conditions of serpentinization, (i.e. temperature and pressure, composition of mantle peridotites, fluid rock ratios).

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## SUPPLEMENTARY DATA

Supplementary data are available at Journal of Petrology online.

## DATA AVAILABILITY

The data underlying this article are available in the article and in its online supplementary material.

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