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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 f luid/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; f luid–rock interaction

#### **INTRODUCTION**

<span id="page-1-42"></span><span id="page-1-16"></span><span id="page-1-15"></span>At slow and ultra-slow spreading ridges (*<*40 mm•yr−1), mantle peridotites are either exhumed at the seaf loor along large offset normal faults, also referred to as detachment faults [\(Karson](#page-31-0) [&](#page-31-0) [Rona,](#page-31-0) [1990](#page-31-0); [Cannat,](#page-30-0) [1993](#page-30-0); [Cann](#page-30-1) *[et al.,](#page-30-1)* [1997](#page-30-1); [Lavier](#page-32-0) *[et al.,](#page-32-0)* [1999](#page-32-0); [Smith](#page-34-0) *[et al.,](#page-33-0) 2006*), or flip-flop faults ([Sauter](#page-33-0) *et al., [2013](#page-33-0)*). Mantle exhumation at MORs is closely linked to hydrothermal activity that significantly modifies the mineralogy of mantle peridotites, turning them into serpentinites (e.g. [Bonatti,](#page-30-2) [1968](#page-30-2); [Aumento](#page-29-0) [&](#page-29-0) [Loubat,](#page-29-0) [1971;](#page-29-0) [Früh-Green](#page-31-1) *[et al.,](#page-31-1)* [1990,](#page-31-1) [1996;](#page-31-2) [Paulick](#page-32-1) *[et al.,](#page-32-1)* [2006;](#page-32-1) [Bach](#page-29-1) *[et al.,](#page-29-1)* [2004,](#page-29-1) [2006;](#page-29-2) [Schwarzenbach](#page-34-1) *[et al.,](#page-34-1)* [2016,](#page-34-1) [2021\)](#page-34-2). The serpentinization process stores about 13 wt %  $H_2O$ , leading to a strong volume expansion (up to ∼40%, [O'Hanley,](#page-32-2) [1992;](#page-32-2) [Klein](#page-31-3) [&](#page-31-3) [Roux,](#page-31-3) [2020\)](#page-31-3), and a density drop from 3.3 to 2.6 g•cm−<sup>3</sup> . Serpentinization also results in strain localization along faults and the subsequent rapid exhumation from depths of 3 to 4 km to the seaf loor ([Raleigh](#page-33-1) [&](#page-33-1) [Paterson,](#page-33-1) [1965](#page-33-1); [Christensen,](#page-30-3) [1972,](#page-30-3) [2004;](#page-30-4) [Reinen](#page-33-2) *[et al.](#page-33-2),* [1994](#page-33-2); [Escartin](#page-31-4) *[et al.,](#page-31-4)* [1997,](#page-31-4) [2001](#page-31-5); [Morrow](#page-32-3) *[et al.,](#page-32-3)* [2000\)](#page-32-3).

<span id="page-1-40"></span><span id="page-1-32"></span><span id="page-1-21"></span><span id="page-1-20"></span><span id="page-1-19"></span><span id="page-1-17"></span><span id="page-1-10"></span>While serpentinization and mantle-fluid interactions at Mid-Ocean Ridges (MORs) were largely documented over the past <span id="page-1-29"></span><span id="page-1-25"></span><span id="page-1-13"></span><span id="page-1-12"></span>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](#page-30-5) *[et al.](#page-30-5)*, [1971\)](#page-30-5) before it has been proofed along the Iberia margin (ODP Leg 103, [Boillot](#page-30-6) *[et al.,](#page-30-6)* [1980](#page-30-6), [1989\)](#page-30-7). Since then, more and more occurrences have been reported and described from present-day OCTs ([Agrinier](#page-29-3) *[et al.,](#page-29-3)* [1996](#page-29-3); [Albers](#page-29-4) *[et al.,](#page-29-4)* [2021](#page-29-4); [Beslier](#page-29-5) *[et al.,](#page-29-5)* [2004;](#page-29-5) [Bonatti,](#page-30-8) [1976;](#page-30-8) [Hopkinson](#page-31-6) *[et al.,](#page-31-6)* [2004;](#page-31-6) [Kodolányi](#page-32-4) *[et al.,](#page-32-4)* [2012](#page-32-4); [Nicholls](#page-32-5) *[et al.,](#page-32-5)* [1981\)](#page-32-5) as well as from fossil examples ([Lagabrielle](#page-32-6) [&](#page-32-6) [Bodinier,](#page-32-6) [2008;](#page-32-6) [Manatschal](#page-32-7) [&](#page-32-7) [Müntener,](#page-32-7) [2009;](#page-32-7) [Picazo](#page-33-3) *[et al.,](#page-33-3)* [2013\)](#page-33-3). At present, it is assumed that ∼50% of the world rifted margins are formed by serpentinized exhumed mantle ([Minshull,](#page-32-8) [2009](#page-32-8)).

<span id="page-1-43"></span><span id="page-1-41"></span><span id="page-1-39"></span><span id="page-1-38"></span><span id="page-1-37"></span><span id="page-1-36"></span><span id="page-1-35"></span><span id="page-1-34"></span><span id="page-1-33"></span><span id="page-1-31"></span><span id="page-1-30"></span><span id="page-1-28"></span><span id="page-1-27"></span><span id="page-1-26"></span><span id="page-1-24"></span><span id="page-1-23"></span><span id="page-1-22"></span><span id="page-1-18"></span><span id="page-1-14"></span><span id="page-1-11"></span><span id="page-1-9"></span><span id="page-1-8"></span><span id="page-1-7"></span>Similar to MOR settings, serpentinization plays also at OCTs a key-role during mantle exhumation (e.g. [Whitmarsh](#page-34-3) *[et al.,](#page-34-3)* [2001;](#page-34-3) [Gillard](#page-31-7) *[et al.,](#page-31-7)* [2019](#page-31-7)). 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

<span id="page-2-34"></span><span id="page-2-33"></span><span id="page-2-17"></span><span id="page-2-6"></span><span id="page-2-3"></span>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](#page-31-8) *[et al.,](#page-31-8)* [2004;](#page-31-8) [Barnes](#page-29-6) *[et al.,](#page-29-6)* [2009;](#page-29-6) [Vesin](#page-34-4) *[et al.,](#page-34-4)* [2024](#page-34-4)), while serpentinization at OCT is assumed to occur at T *<* 250◦C ([Agrinier](#page-29-3) *[et al.,](#page-29-3)* [1996](#page-29-3); [Schwarzen](#page-33-4)bach *[et al.,](#page-33-4)* [2013](#page-33-4), [2016](#page-34-1); [Vesin](#page-34-5) *[et al.](#page-34-5),* [2023\)](#page-34-5). 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](#page-29-7) *[et al.,](#page-29-7)* [2011](#page-29-7); [Cannat](#page-30-9) *[et al.,](#page-30-9)* [2019\)](#page-30-9). 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](#page-30-10) *[et al.,](#page-30-10)* [2009,](#page-30-10) [2019](#page-30-9)). 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](#page-29-3) *[et al.,](#page-29-3)* [1996](#page-29-3); [Vesin](#page-34-5) *[et al.,](#page-34-5)* [2023](#page-34-5)) and the Newfoundland OCT (100–130◦C, [Vesin](#page-34-5) *[et al.,](#page-34-5)* [2023](#page-34-5)). Higher temperatures of serpentinization were primary reported at the MAR (*>*350◦, e.g. [Agrinier](#page-29-8) [&](#page-29-8) [Cannat,](#page-29-8) [1997\)](#page-29-8), but recent in-situ oxygen data in MOR serpentinites indicate lower temperatures (∼290 and 115◦C; [Vesin](#page-34-4) *[et al.,](#page-34-4)* [2024\)](#page-34-4). 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.

<span id="page-2-25"></span><span id="page-2-2"></span><span id="page-2-0"></span>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, flu-id/rock ratio, fluid chemistry and/or tectonic unroofing (e.g. [Dilek](#page-30-11) *[et al.,](#page-30-11)* [1997](#page-30-11); [Andréani](#page-29-9) *[et al.,](#page-29-9)* [2007;](#page-29-9) [Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015,](#page-33-5) [2019](#page-33-6)). 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](#page-29-4) *[et al.,](#page-29-4)* [2021](#page-29-4); [Tichadou](#page-34-6) *[et al.,](#page-34-6)* [2021](#page-34-6)).

<span id="page-2-29"></span>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**

<span id="page-2-21"></span><span id="page-2-19"></span><span id="page-2-18"></span><span id="page-2-14"></span>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](#page-3-0); [Manatschal](#page-32-9) [&](#page-32-9) [Nievergelt,](#page-32-9) [1997](#page-32-9); [Mün](#page-32-10)tener *[et al.,](#page-32-10)* [2004](#page-32-10), [2010\)](#page-32-11). They represent remnants of the Adriatic-European conjugate margins ([Fig. 1B;](#page-3-0) [Florineth](#page-31-9) [&](#page-31-9) [Froitzheim,](#page-31-9) [1994](#page-31-9); [Manatschal,](#page-32-12) [2004\)](#page-32-12). 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](#page-32-7) [&](#page-32-7) [Müntener,](#page-32-7) [2009](#page-32-7); [Fig. 1](#page-3-0)).

#### **The Platta nappe**

<span id="page-2-28"></span><span id="page-2-27"></span><span id="page-2-24"></span><span id="page-2-13"></span><span id="page-2-9"></span><span id="page-2-7"></span><span id="page-2-4"></span><span id="page-2-1"></span>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](#page-3-0)). The Platta nappe is subdivided into two units separated by a main reactivated pre-Alpine shear zone ([Fig. 1D;](#page-3-0) [Epin](#page-30-12) *[et al.,](#page-30-12)* [2019](#page-30-12)). The Upper Platta Unit, in the hanging wall, was originally located in a more proximal position in the OCT ([Fig. 1D\)](#page-3-0). This unit consists of mantle rocks (the Upper Serpentinite Unit; [Fig. 2A\)](#page-4-0) derived from the inherited subcontinental Adriatic mantle (i.e. [Schaltegger](#page-33-7) *[et al.,](#page-33-7)* [2002;](#page-33-7) [Mün](#page-32-10)tener *[et al.,](#page-32-10)* [2004,](#page-32-10) [2010](#page-32-11); [Picazo](#page-33-8) *[et al.,](#page-33-8)* [2016](#page-33-8); [Epin](#page-30-12) *[et al.,](#page-30-12)* [2019\)](#page-30-12). The Lower Platta Unit, in the footwall of the main shear zone, was originally located in a more distal position ([Fig. 1D\)](#page-3-0). This unit consists of a large mantle domain (i.e. the Lower Serpentinite Unit, [Fig. 2A](#page-4-0)) locally intruded by gabbros dated at  $161 \pm 1$  Ma [\(Schal](#page-33-7)tegger *[et al.,](#page-33-7)* [2002\)](#page-33-7) and covered by lavas of late Middle to early Late Jurassic age (165 to ∼155 Ma; [Desmurs](#page-30-13) *[et al.,](#page-30-13)* [2001](#page-30-13); [Amann](#page-29-10) *[et al.,](#page-29-10)* [2020\)](#page-29-10). 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 ± 50◦C ([Müntener](#page-32-11) *[et al.,](#page-32-11)* [2010](#page-32-11)). Slivers of continental origin also occur in the Platta nappe and have been interpreted as extensional allochthons ([Froitzheim](#page-31-10) [&](#page-31-10) [Manatschal,](#page-31-10) [1996\)](#page-31-10). Mantle rocks in the Platta nappe display ophicalcites at their contact with mafic rocks and deep-water sediments ([Fig. 2C](#page-4-0); [Dietrich,](#page-30-14) [1970,](#page-30-14) [Coltat](#page-30-15) *[et al.](#page-30-15),* [2021](#page-30-15)), and were weakly affected by Alpine metamorphism (lower greenschist facies, *<*350◦C; [Trommsdorff](#page-34-7) [&](#page-34-7) [BW,](#page-34-7) [1974,](#page-34-7) [Frey](#page-31-11) [&](#page-31-11) [Ferreiro](#page-31-11) [Mählmann,](#page-31-11) [1999](#page-31-11), [Coltat](#page-30-15) *[et al.,](#page-30-15)* [2021](#page-30-15)). 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](#page-3-0); [Dietrich,](#page-30-16) [1969](#page-30-16); [Trommsdorff](#page-34-8) [&](#page-34-8) [Evans,](#page-34-8) [1977](#page-34-8); [Trommsdorff,](#page-34-9) [1983;](#page-34-9) [Burkhard](#page-30-17) [&](#page-30-17) [O'Neil,](#page-30-17) [1988](#page-30-17); [Vils](#page-34-10) *[et al.,](#page-34-10)* [2011\)](#page-34-10).

#### <span id="page-2-35"></span><span id="page-2-32"></span><span id="page-2-31"></span><span id="page-2-30"></span><span id="page-2-26"></span><span id="page-2-16"></span><span id="page-2-15"></span><span id="page-2-12"></span><span id="page-2-11"></span><span id="page-2-10"></span><span id="page-2-8"></span><span id="page-2-5"></span>**The Totalp nappe**

<span id="page-2-36"></span><span id="page-2-23"></span><span id="page-2-22"></span><span id="page-2-20"></span>The Totalp nappe is located to the north of the Platta nappe ([Fig. 1B\)](#page-3-0). 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](#page-31-10) [&](#page-31-10) [Manatschal,](#page-31-10) [1996;](#page-31-10) [Fig. 1C\)](#page-3-0). 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 [\(Weissert](#page-34-11) [&](#page-34-11) [Bernoulli,](#page-34-11) [1985](#page-34-11)). The Totalp nappe consists of serpentinized spinel lherzolites, locally containing pyroxenites and ophicalcites, resulting from the carbonation of serpentine under static conditions at the seafloor. The ophicalcites preserve depositional contacts with Upper Jurassic to Lower Cretaceous pelagic sediments ([Fig. 3;](#page-5-0) [Picazo](#page-33-3) *[et al.,](#page-33-3)* [2013\)](#page-33-3). Magmatic rocks are very rare and mainly consist of flaser gabbros and dolerite dykes [\(Peters](#page-32-13) [&](#page-32-13) [Math](#page-32-13)ews, [1963](#page-32-13)). The Alpine metamorphic overprint is below prehnite pumpellyite facies at around 250◦C [\(Peters,](#page-32-14) [1965\)](#page-32-14). 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





<span id="page-3-0"></span>**Fig. 1.** (A) Present-day location of ophiolitic units of the Central–Western Alps and Apennines (modified after [Manatschal](#page-32-7) [&](#page-32-7) [Müntener,](#page-32-7) [2009](#page-32-7)). (B) Schematic reconstruction of the Piemonte–Ligurian oceanic basin at Late Jurassic time, with the location of the major ophiolitic sequences (modified after [Manatschal](#page-32-7) [&](#page-32-7) [Müntener,](#page-32-7) [2009](#page-32-7)). (C) Simplified geological map of the Pennine and Austro-Alpine nappes showing sample locations (modified after [Froitzheim](#page-31-12) *[et al.,](#page-31-12)* [1994](#page-31-12)). D) Distribution of subcontinental and infiltrated mantle domains along the ocean-continent-transition of the Alpine Tethys (modified after [Müntener](#page-32-15) [&](#page-32-15) [Piccardo,](#page-32-15) [2004\)](#page-32-15). CH, Chenaillet; PL, Platta; TA,: Tasna; TO, Totalp.

<span id="page-3-5"></span><span id="page-3-3"></span><span id="page-3-1"></span>well-preserved [\(Bernoulli](#page-29-11) [&](#page-29-11) [Weissert,](#page-29-11) [1985](#page-29-11); [Weissert](#page-34-11) [&](#page-34-11) [Bernoulli,](#page-34-11) [1985;](#page-34-11) [Picazo](#page-33-3) [et al.,](#page-33-3) [2013\)](#page-33-3). Results from <sup>40</sup>Ar/<sup>39</sup>Ar dating on phlogopite from pyroxenites gave a cooling temperature ≤ 300◦C and exhumation age of 160 ± 8 Ma ([Peters](#page-33-9) [&](#page-33-9) [Stettler,](#page-33-9) [1987a](#page-33-9), [1987b](#page-33-10)).

#### <span id="page-3-6"></span>**The Tasna nappe**

<span id="page-3-4"></span>The Tasna nappe was derived from the European OCT [\(Fig. 1B](#page-3-0); [Florineth](#page-31-9) [&](#page-31-9) [Froitzheim,](#page-31-9) [1994;](#page-31-9) [Manatschal](#page-32-16) *[et al.,](#page-32-16)* [2006;](#page-32-16) [Ribes](#page-33-11) *[et al.](#page-33-11)*, <span id="page-3-8"></span><span id="page-3-7"></span><span id="page-3-2"></span>[2020\)](#page-33-11). It belongs to the Tertiary Alpine nappe stack made of Austro-Alpine and Pennine units ([Fig. 1C](#page-3-0)) emplaced during the Eocene to Oligocene ([Ribes](#page-33-11) *[et al.](#page-33-11)*, [2020](#page-33-11)). As for the Platta and Total nappes, the Tasna nappe exposes primary contacts between exhumed and serpentinized mantle rocks and sediments [\(Fig. 3](#page-5-0)). The Alpine metamorphism did not exceed 350◦C (greenschist facies; [Florineth](#page-31-9) [&](#page-31-9) [Froitzheim,](#page-31-9) [1994;](#page-31-9) [Bousquet](#page-30-18) *[et al.,](#page-30-18)* [2008\)](#page-30-18). The Tasna nappe is made of a wedge of continental crust separated



<span id="page-4-0"></span>**Fig. 2.** (A) Geological map of the Platta nappe with sample locations (modified after [Schaltegger](#page-33-7) *[et al.,](#page-33-7)* [2002\)](#page-33-7). (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](#page-31-13) [&](#page-31-13) [Rubatto,](#page-31-13) [1998](#page-31-13), [Fig. 4C\)](#page-6-0).a The Upper Tasna Detachment (UTD) is the topbasement fault responsible for the exhumation of the crust and mantle rocks at the seafloor [\(Froitzheim](#page-31-13) [&](#page-31-13) [Rubatto,](#page-31-13) [1998,](#page-31-13) Manatschal et al., 2004, 2006). It is overlain by the undeformed postrift sediments ([Fig. 4C](#page-6-0)) interpreted as Upper Jurassic [\(Ribes](#page-33-11) *[et al.](#page-33-11)*, [2020](#page-33-11)). Mantle rocks consist of highly serpentinized spinel lherzolites with abundant spinel websterite layers and preserving a high temperature foliation marked by spinel grains [\(Manatschal](#page-32-16) *[et al.,](#page-32-16)* [2006](#page-32-16)). The 40Ar/39Ar dating of phlogopite provides an age of 170.5 ± 0.4 Ma [\(Manatschal](#page-32-16) *[et al.,](#page-32-16)* [2006](#page-32-16)), similar to that obtained for mantle exhumation at Totalp (160 ± 8 Ma; [Peters](#page-33-9) [&](#page-33-9) [Stettler,](#page-33-9) [1987a\)](#page-33-9).

<span id="page-4-1"></span>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](#page-32-16) *[et al.,](#page-32-16)* [2006;](#page-32-16) [Picazo](#page-33-8) *[et al.,](#page-33-8)* [2016](#page-33-8)).

#### **MATERIALS AND METHODS Sampling and analytical strategies**

A total of 40 moderately to completely serpentinized peridotites have been sampled ([Table 1](#page-7-0)). 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



<span id="page-5-0"></span>**Fig. 3.** (A) Geological map of the Totalp area with sample locations (modified after [Picazo](#page-33-3) *[et al.,](#page-33-3)* [2013](#page-33-3)). (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](#page-3-0)). 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**

<span id="page-5-1"></span>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◦ 2θ step intervals from 3 to 80◦ 2θ, with a dwell time of 0.8 s. Size of the divergence slit was 0.4◦. [Table 1](#page-7-0) provides the quantitative mineralogical compositions determined by Rietveld refinement using Profex-BGMN software ([Doebelin](#page-30-19) [&](#page-30-19) [Kleeberg,](#page-30-19) [2015](#page-30-19)),



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<span id="page-6-0"></span>**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](#page-34-12) [&](#page-34-12) [Dössegger,](#page-34-12) [1972;](#page-34-12) [Florineth](#page-31-9) [&](#page-31-9) [Froitzheim,](#page-31-9) [1994](#page-31-9); [Manatschal](#page-32-16) *[et al.,](#page-32-16)* [2006\)](#page-32-16). (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](#page-31-9) [&](#page-31-9) [Froitzheim,](#page-31-9) [1994;](#page-31-9) [Manatschal](#page-32-16) *[et al.,](#page-32-16)* [2006](#page-32-16)).

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 μm 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 100x objective (Olympus) and a 632-nm (Ar+) laser at 9 mW were used, resulting in a laser spot size of ∼1 μm. 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](#page-29-12) *[et al.,](#page-29-12)* [2004](#page-29-12); [Groppo](#page-31-14) *[et al.,](#page-31-14)* [2006](#page-31-14); [Tarling](#page-34-13) *[et al.,](#page-34-13)* [2018](#page-34-13); [Compagnoni](#page-30-20) *[et al.,](#page-30-20)* [2021\)](#page-30-20).

#### <span id="page-6-4"></span><span id="page-6-3"></span><span id="page-6-2"></span><span id="page-6-1"></span>**Bulk-rock chemistry**

The major element concentrations were measured on pressed pellets of calcined powder (i.e. after loss on ignition) using a micro<span id="page-7-0"></span>**Table 1:** Location and description of the 40 sementinized peridotites and sementinites from the Eastern central Alps analyzed in this study **Table 1:** Location and description of the 40 serpentinized peridotites and serpentinites from the Eastern central Alps analyzed in this study





Mgt, magnetite; Cc, calcite; Chlorite; And, andradite; Tr, tremolite; Ol, olivine; Opx, clinopyroxene; Opx, orthopyroxene; Spl, spinel; b, banded; f, fibrous; g, granular; l, amellar; s, spherical. \*Selected samples for

detailed mineralogical and geochemical investigations.

X-ray f luorescence (μ-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 μA 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 mm2 each were used to measure f luorescence 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.

<span id="page-9-1"></span>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](#page-30-21) *[et al.](#page-30-21)* [\(2011\):](#page-30-21) 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–H3BO3 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 HNO3. After another evaporation, the residue was finally diluted in 40 ml of 7 M HNO3.

<span id="page-9-2"></span>Analyzes performed on international standard are consistent with preferred reference values from GeoREM for UB-N serpentinite ([Govindaraju,](#page-31-15) [1982\)](#page-31-15). 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](https://academic.oup.com/petrology/article-lookup/doi/10.1093/petrology/egae063#supplementary-data)).

#### **Mineral chemistry**

The major element concentrations were measured on 30  $\mu$ mthick polished sections using a μ-XRF Bruker M4 Tornado at ITES. Measurements were performed using a Rh anode operating at 400 μA 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](#page-31-16) *[et al.](#page-31-16),* [1980](#page-31-16)) 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 FeOtot.

<span id="page-9-4"></span>The structural formulae for lizardite, chrysotile, polygonal and polyhedral serpentines was calculated on the basis of 7 oxygens. Antigorite has a distinct formula Mg3*<sup>m</sup>* <sup>−</sup> 3Si2*m*O5*m*(OH)4*<sup>m</sup>* <sup>−</sup> <sup>6</sup> 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 [\(Mellini](#page-32-17) *[et al.,](#page-32-17)* [1987\)](#page-32-17). The Fe<sup>2+</sup> and Fe<sup>3+</sup> contents of serpentine mineral were estimated following the approach of [Ulrich](#page-34-14) *[et al.](#page-34-14)* [\(2020\)](#page-34-14) based on the initial study of [Beard](#page-29-13) [&](#page-29-13) [Frost](#page-29-13) [\(2017\)](#page-29-13). 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.

<span id="page-9-0"></span>Serpentine trace element compositions were acquired on 30 μm 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. <sup>29</sup>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](#page-32-18) *[et al.,](#page-32-18)* [1997.](#page-32-18) 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 [\(Guillong](#page-31-17) *[et al.,](#page-31-17)* [2008\)](#page-31-17), following the standard methods of [Pettke](#page-33-12) *[et al](#page-33-12).* [\(2012\).](#page-33-12) Detection limits were between 1 ppb and *<*0.3 ppm for most trace elements.

#### <span id="page-9-7"></span><span id="page-9-6"></span><span id="page-9-3"></span>**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 [\(Fig. 5\)](#page-10-0). This is confirmed by microscopic observations ([Fig. 6\)](#page-11-0) and Rietveld refinements made on X-Ray diffraction patterns ([Table 1](#page-7-0)), 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](#page-10-0)). 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\)](#page-10-0). For the Upper Platta (proximal domain) serpentinites are occasionally crosscut by centimeter-thick light green serpentine veins ([Fig. 5A](#page-10-0)), and most samples are characterized by several generations of serpentine veins [\(Fig. 5C\)](#page-10-0). At Tasna ([Fig. 5D, E\)](#page-10-0) and Totalp ([Fig. 5F](#page-10-0)), 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\)](#page-10-0) or clinopyroxene in massive dark serpentinite [\(Fig. 5H](#page-10-0)). It should be noted that some samples contain minute amounts of calcite (*<*1%, [Table 1\)](#page-7-0) when picked up in the vicinity of ophicalcites (e.g. [Picazo](#page-33-3) *[et al.,](#page-33-3)* [2013](#page-33-3)).

<span id="page-9-8"></span><span id="page-9-5"></span>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.



<span id="page-10-0"></span>**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 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](#page-11-0) A, B) and bastite textures ([Fig. 6](#page-11-0) 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\)](#page-11-0). 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



<span id="page-11-0"></span>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](#page-11-0)). In all these samples, magnetite is ubiquitous, with amounts between 0.38 and 5% ([Table 1](#page-7-0)). Magnetite mainly occurs as small grains (*<*5 μm) disseminated along the mesh rims, and also

observed in cleavages and surrounding the bastite grains ([Figs. 5](#page-10-0) and [6C\)](#page-11-0).

#### *Serpentine veins*

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



<span id="page-12-0"></span>**Fig. 7.** (A) Microphotography under plane polarized ligth (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 [\(Fig. 6](#page-11-0) E, F, H). Such typical spherical texture and the Raman signature ([Fig. 6\)](#page-11-0) 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\)](#page-11-0) and occasionally as veins crosscutting the previous serpentine mesh and bastite S1 [\(Fig. 6H\)](#page-11-0). The occurrence



<span id="page-13-0"></span>**Fig. 8.** Representative microphotographs and schematical representations of the five different types of serpentines described in this study.

of small andradite grains (∼10 μm diameter) is closely associated to polyhedral serpentine veins, almost exclusively at the vicinity of clinopyroxenes ([Fig. 6F, H\)](#page-11-0).

*Banded veins (S3):* The third generation of serpentine (S3, [Fig. 6G](#page-11-0)), 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 μm- to cm-thick. The centimetric veins are observable at the macroscopic scale and are characterized by a fibrous green texture (e.g. [Fig. 5A\)](#page-10-0). 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](#page-11-0)). 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](#page-34-13) *[et al.,](#page-34-13)* [2018](#page-34-13); [Compagnoni](#page-30-20) *[et al.,](#page-30-20)* [2021](#page-30-20)). 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  $cm^{-1}$ and 3700 cm−<sup>1</sup> [\(Fig. 6\)](#page-11-0) rather correspond to polygonal serpentine, whereas only rare occurrences of chrysotile were observed (main peaks at 3689 cm−<sup>1</sup> and 3699 cm−1).

*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](#page-12-0)). 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](#page-12-0)). Lamellar veins appear to spread within the mesh textures, resulting in blurred rims [\(Fig. 7D](#page-12-0)). The Raman spectral signature indicates that these lamellar veins are made of a mixture of antigorite and chrysotile, with peaks at 3670 cm−1, 3690 cm−1and 3700 cm−<sup>1</sup> [\(Fig. 7\)](#page-12-0). Occasionally, some of these veins and patches display an additional peak at 3685 cm−1, 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](#page-12-0)).

*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](#page-12-0) 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\)](#page-12-0).

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\)](#page-13-0).

#### **Bulk-rock geochemistry**

<span id="page-13-2"></span><span id="page-13-1"></span>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\)](#page-14-0). They cover a wide range of concentrations in CaO (0.04– 4.1 wt %) and  $Al_2O_3$  (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  $Al_2O_3$  content attests of the presence of spinel or plagioclase. [Fig. 10](#page-17-0) 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](#page-31-18) *[et al.,](#page-31-18)* [1979;](#page-31-18) [Hart](#page-31-19) [&](#page-31-19) [Zindler,](#page-31-19) [1986](#page-31-19)). The serpentinized peridotites plot along the terrestrial mantle array. Most samples display fertile compositions  $(Al_2O_3/SiO_2 > 0.05)$ while only few samples derive from a refractory protolith. Mg# is around 0.94 for most serpentinites ([Fig. 10](#page-17-0)), close to the Mg#



<span id="page-14-0"></span>**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 [\(Müntener](#page-32-11) *[et al.,](#page-32-11)* [2010\)](#page-32-11), the Iberia Margin ([Kodolányi](#page-32-4) *[et al.,](#page-32-4)* [2012](#page-32-4); [Albers](#page-29-4) *[et al.,](#page-29-4)* [2021](#page-29-4)), Newfoundland, Mid Atlantic Ridge (MAR) and Hess Deep [\(Kodolányi](#page-32-4) *[et al.,](#page-32-4)* [2012\)](#page-32-4). South West Indian Ridge (SWIR; [Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015\)](#page-33-5). DMM: Depleted MORB Mantle [Salters](#page-33-13) [&](#page-33-13) [Stracke](#page-33-13) [\(2004\).](#page-33-13)

values of initial peridotites [\(Müntener](#page-32-11) *[et al.,](#page-32-11)* [2010](#page-32-11)). Ni and Cr concentrations are mainly in the range 1500 to 2500 μg/g and 2000 to 3500 μg/g, respectively ([Fig. 11\)](#page-17-1). 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](#page-13-0) and [10\)](#page-17-0) and very low Cr and Ni concentrations (*<*500 μg/g [Table 2](#page-15-0); [Fig. 11\)](#page-17-1).

<span id="page-14-1"></span>from the overall trends by highly depleted HREE concentrations (HREEN ∼ 0.1–1 C1-Chondrite; [Fig. 12](#page-19-0)) 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\)](#page-19-0). Some samples from Tasna and Platta differ

#### **Serpentine geochemistry** *Major elements*

In average, serpentine mesh contains 40.91 wt%  $SiO<sub>2</sub>$  (Si = 1.91 apfu), 1.40 wt%  $Al_2O_3$  (Al = 0.08 apfu), 38.87 wt% MgO (Mg = 2.74

<span id="page-15-0"></span>



**Table 2:** Continued



<span id="page-17-0"></span>**Fig. 10.** Bulk rock major element ratios of  $Al_2O_3/SiO_2$  (anhydrous) versus MgO/SiO2 (anhydrous) of serpentinites. The blue line corresponds to the Terrestiral array ([Jagoutz](#page-31-18) *[et al.,](#page-31-18)* [1979;](#page-31-18) [Hart](#page-31-19) [&](#page-31-19) [Zindler,](#page-31-19) [1986](#page-31-19)). References are the same as in [Fig. 9.](#page-14-0)



<span id="page-17-1"></span>**Fig. 11.** Mg# versus bulk-rock Ni (A) and Cr (B) concentrations (in μg/g) of serpentinites from Upper and Lower Platta, Tasna and Totalp. References are the same as in [Fig. 9](#page-14-0).

apfu) and 5.30 wt% FeO<sub>tot</sub> (Fe<sub>tot</sub> = 0.21 apfu), giving a Mg# of ~0.93. Bastite texture slightly differs in composition relative to mesh texture, with less  $SiO_2$  (39.81 wt%;  $Si = 1.9$  apfu), MgO (37.49 wt%;

 $Mg = 2.6$  apfu) and FeO<sub>tot</sub> (4.74 wt%; Fe<sub>tot</sub> = 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\)](#page-18-0). Consequently, serpentine mesh plots close to the Mg-pure lizardite or chrysotile end-members in the Si versus  $Mg + Fe$  diagram [\(Fig. 13A](#page-21-0)), whereas bastite composition extends along the Tschermak trend (Al replacing an octahedral and tetrahedral cation; [Fig. 13A, B\)](#page-21-0). Bastite has Mg# near identical to mesh textures (0.94 in average, [Table 3;](#page-18-0) [Fig. 14](#page-22-0)).

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](#page-22-0)). 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\)](#page-21-0).

The banded serpentine veins (S3) mainly plot within the field defined by serpentine mesh (S1) in the Si versus  $Mg + Fe$  diagram ([Fig. 13C,](#page-21-0) [Table 3\)](#page-18-0). However, these banded veins can be distinguished by higher Mg# values (*>*0.95 [Table 3,](#page-18-0) [Fig. 14](#page-22-0)) 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](#page-22-0) and [15\)](#page-22-1): the first group made of polygonal serpentine is characterized by Mg# of ∼0.95 (Fetot = 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 [\(Fig. 13C, D\)](#page-21-0).

The lamellar antigorite veins and patches (S4) display the highest  $SiO<sub>2</sub>$  concentrations of all serpentine generations  $(42.48 \pm 1.08 \text{ wt\%}, \text{Si} = 1.99 \text{ aptu}), \text{and Mg} + \text{Fe in the range of } 9.79 -$ 2.93, close to the pure antigorite end-member [\(Fig. 13C](#page-21-0)). 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  $(FeO<sub>tot</sub> = 4.15 wt\% in average, Fe<sub>tot</sub> = 0.16 aptu, Fig. 14). Al<sub>2</sub>O<sub>3</sub> con (FeO<sub>tot</sub> = 4.15 wt\% in average, Fe<sub>tot</sub> = 0.16 aptu, Fig. 14). Al<sub>2</sub>O<sub>3</sub> con (FeO<sub>tot</sub> = 4.15 wt\% in average, Fe<sub>tot</sub> = 0.16 aptu, Fig. 14). Al<sub>2</sub>O<sub>3</sub> con$ centrations are low  $(1.15 \pm 1.07 \text{ wt \%}, \text{Al} = 0.06 \text{ apr}$ u).

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 =  $39.76 \pm 0.97$  wt % and lower FeO<sub>tot</sub> =  $3.99 \pm 1.18$  wt % concentrations ( $Mg = 2.79$  apfu,  $Fe<sub>tot</sub> = 0.16$  apfu,  $Mg# = 0.95$ ; [Figs. 13C and](#page-21-0) [14](#page-22-0)). 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  $\pm$  0.94 wt %,  $Si = 1.98$  apfu;  $Al_2O_3 = 0.76 \pm 0.62$  wt %,  $Al = 0.04$  apfu; [Fig. 13D](#page-21-0)).

Interestingly, none of the serpentine composition plots along the brucite trend [\(Fig. 13\)](#page-21-0). 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](#page-20-0), [Figs. 16](#page-23-0) and [17](#page-24-0). REE and spider diagrams of all samples analyzed in this study are given in supplementary materials. The REE concentrations of serpentine polysomes [\(Figs. 16](#page-23-0) and [17](#page-24-0)) 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

<span id="page-18-0"></span>



<span id="page-19-0"></span>**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](#page-32-4) *[et al.](#page-32-4)*, [\(2012\)](#page-32-4).

<span id="page-19-3"></span>mantle peridotites from other places in the Alps (e.g. the Chenaillet unit, [Lafay](#page-32-19) *[et al.,](#page-32-19)* [2017](#page-32-19)). At sample scale, the REE patterns of the diverse serpentine polysomes are similar in shape: LREEdepleted ( $(La/Sm)_{N}$  ~ 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<sup>∗</sup> *>* 2; [Figs. 16](#page-23-0) and [17\)](#page-24-0).

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](#page-23-0) and [17](#page-24-0)). 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 [\(Fig. 8\)](#page-13-0). 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\)](#page-28-0). 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)*

<span id="page-19-4"></span><span id="page-19-2"></span><span id="page-19-1"></span>Pseudomorphic serpentine mesh and bastite textures, here referred to as serpentine S1 [\(Fig. 8](#page-13-0)), are not only the oldest, but also the most common textures found in serpentinites from OCTs. Previous studies proposed that serpentinization at magma-poor rifted margins likely begins when the subcontinental lithospheric mantle is still capped by a thin, *<*6 km thick hyperextended continental crust ([Manatschal,](#page-32-12) [2004;](#page-32-12) [Epin](#page-30-12) *[et al.,](#page-30-12)* [2019;](#page-30-12) [Hochscheid](#page-31-20) [et al.,](#page-31-20) [2022\)](#page-31-20). Serpentinizing fluids at OCTs are assumed to reach down to ∼6 km depth below seaf loor through circulation along high-angle normal faults, as indicated by refraction seismic experiments [\(Boddupalli](#page-30-22) *[et al.,](#page-30-22)* [2022\)](#page-30-22). 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](#page-33-14) [&](#page-33-14) [Cannat,](#page-33-14) [2014\)](#page-33-14). 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 f luid/rock ratio (*<*F/R mass

<span id="page-20-0"></span>



<span id="page-21-0"></span>**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.,  $(2023)$ 

<span id="page-21-4"></span><span id="page-21-3"></span><span id="page-21-2"></span>ratio 1; e.g. Moody, 1976; [Wicks](#page-34-15) [&](#page-34-15) [Whittaker,](#page-34-15) [1977;](#page-34-15) [Rouméjon](#page-33-14) [&](#page-33-14) [Cannat,](#page-33-14) [2014](#page-33-14)). This is evidenced by trace element patterns that mimic those of the primary minerals showing lower trace element concentrations ([Fig. 16D, H\)](#page-23-0). In addition, compared to mineral precursor serpentine minerals are also enriched in up to several orders of magnitude in FME (Cs, B, Li,  $\pm$  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](#page-32-4) *[et al.,](#page-32-4)* [2012;](#page-32-4) [Vesin](#page-34-5) *[et al.,](#page-34-5)* [2023\)](#page-34-5). 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](#page-32-20) [&](#page-32-20) [Fyfe,](#page-32-20) [1970;](#page-32-20) [Janecky](#page-31-21) [&](#page-31-21) [Seyfried,](#page-31-21) [1986](#page-31-21); [Allen](#page-29-14) [&](#page-29-14) [Seyfried](#page-29-14) [Jr.,](#page-29-14) [2003](#page-29-14); [Bach](#page-29-1) *[et al.,](#page-29-1)* [2004](#page-29-1)). In our partially serpentinized samples from Totalp and Tasna, relics of clinopyroxene are preserved in

<span id="page-21-1"></span>both units, olivine relics are frequently observed at Totalp while it is rarely preserved in other units ([Fig. 6\)](#page-11-0). Similar observations were also reported by [Müntener](#page-32-11) *[et al.](#page-32-11)* [\(2010\)](#page-32-11) 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](#page-34-4) *[et al.](#page-34-4)*, [\(2024\)](#page-34-4) and references therein), we propose that an uppermost temperature limit of ±300◦C can be assumed for this initial stage of serpentinization.



<span id="page-22-0"></span>**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.



<span id="page-22-1"></span>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](#page-13-0)) that exhibits a typical spherical texture [\(Fig. 6](#page-11-0)). 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\)](#page-18-0). 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](#page-32-21) *[et al.,](#page-32-21)* [2005\)](#page-32-21). 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](#page-32-11) *[et al.,](#page-32-11)* [2010\)](#page-32-11). 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 [\(Fig. 16D, H\)](#page-23-0). 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](#page-29-15) *[et al.](#page-29-15)* [\(2008\)](#page-29-15), 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.

<span id="page-22-6"></span><span id="page-22-5"></span><span id="page-22-4"></span><span id="page-22-3"></span><span id="page-22-2"></span>Relatively to bastite (S1), polyhedral serpentine (S2) veins are enriched in Si and Mg and depleted in Ca and Fe ([Fig. 13](#page-21-0); [Table 3](#page-18-0)). This may be explained by the preferential absorption of Ca and Fe by andradite [\(Plümper](#page-33-15) *[et al.,](#page-33-15)* [2014](#page-33-15)). 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](#page-33-15) *[et al.](#page-33-15)*, [\(2014\)](#page-33-15) 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 fO<sub>2</sub>, as proposed by [Beard](#page-29-16) [&](#page-29-16) [Hopkinson](#page-29-16) [\(2000\)](#page-29-16) in serpentinites from Hole 1068 (Abyssal Plain). This lowered  $fO<sub>2</sub>$ likely affects the stability of magnetite, which allow proposing that magnetite dissolution in favor to andradite resulted from both processes. [Plümper](#page-33-15) *[et al.](#page-33-15)*, [\(2014\)](#page-33-15) 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](#page-32-11) *[et al.,](#page-32-11)* [2010](#page-32-11)). 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](#page-31-22) [&](#page-31-22) [Beard](#page-31-22) [\(2007\),](#page-31-22) 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℃ 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](#page-29-16) [&](#page-29-16) [Hopkinson,](#page-29-16) [2000](#page-29-16); [Kodolányi](#page-32-4) *[et al.](#page-32-4)*, [2012](#page-32-4)). This temperature range is consistent with that reported by [Plümper](#page-33-15) *[et al.](#page-33-15)*, [\(2014\)](#page-33-15), 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



<span id="page-23-0"></span>**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](#page-32-22) *[et al.,](#page-32-22)* [2013\)](#page-32-22).

<span id="page-23-1"></span>latter mostly occurring in clinopyroxene and cpx-bastite cleavages [\(Fig. 6F, G\)](#page-11-0).

Considering that serpentine S1 formed at ±300◦C and at ≤6 km depth, serpentine S2 most likely formed shallower and under lower temperature (± 280◦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](#page-33-15) *[et al.,](#page-33-15)* [2014\)](#page-33-15). 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 fluidrock interaction, likely soon after or simultaneously to pseudomorphic mesh and bastite S1 formation [\(Fig. 19B](#page-28-0) – S2).

*Formation of banded veins (S3):* Banded veins S3 are frequently observed crosscutting the previous serpentine generations (S1 and S2 [Fig. 6,](#page-11-0) [Table 1](#page-7-0)). Similar occurrences of banded veins have



<span id="page-24-0"></span>**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 f luids from Rainbow and Logatchev are shown for comparison ([Paulick](#page-32-1) *[et al.,](#page-32-1)* [2006](#page-32-1)).

<span id="page-24-12"></span><span id="page-24-7"></span>been reported in oceanic serpentinites (e.g. [Andreani](#page-29-17) *[et al.,](#page-29-17)* [2004](#page-29-17); [Andréani](#page-29-9) *[et al.,](#page-29-9)* [2007](#page-29-9); [Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015\)](#page-33-5). 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](#page-31-23) *[et al](#page-31-23).* [\(1998\)](#page-31-23) and [Normand](#page-32-23) *[et al.](#page-32-23)* [\(2002\)](#page-32-23) and recently strengthened by Raman spectroscopy on naturals samples ([Tar](#page-34-16)ling *[et al.,](#page-34-16)* [2021\)](#page-34-16). At sufficient degree of supersaturation (i.e. open system), several metastable phases like chrysotile may crystallize [\(Normand](#page-32-23) *[et al.,](#page-32-23)* [2002\)](#page-32-23). 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](#page-34-17) [&](#page-34-17) [Mellini,](#page-34-17) [1997;](#page-34-17) [Nor](#page-32-23)mand *[et al.,](#page-32-23)* [2002](#page-32-23)).

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 [\(Fig. 14\)](#page-22-0). 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](#page-32-23) *[et al.](#page-32-23)* [\(2002\)](#page-32-23) and [Andréani](#page-29-9) *[et al.](#page-29-9)* [\(2007\).](#page-29-9) 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 [\(Fig. 16\)](#page-23-0). According to [Andréani](#page-29-9) *[et al.](#page-29-9)* [\(2007\),](#page-29-9) 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 [\(Gillard](#page-31-7) *[et al.,](#page-31-7)* [2019](#page-31-7)). At this point, there is not enough results to discriminate if the banded veins attested of crack opening due to: i) an accommodation of volume expansion due to serpentinization, or ii) the <span id="page-24-1"></span>incremental stress release during unroofing of serpentinites (e.g. [Ramsay,](#page-33-16) [1980](#page-33-16); [O'Hanley,](#page-32-2) [1992;](#page-32-2) [Andreani](#page-29-17) *[et al.,](#page-29-17)* [2004\)](#page-29-17).

#### <span id="page-24-14"></span>*Stage 3: Local overpressure and/or SiO2-rich fluid circulation – Formation of antigorite (S4)*

<span id="page-24-19"></span><span id="page-24-18"></span><span id="page-24-17"></span><span id="page-24-16"></span><span id="page-24-15"></span><span id="page-24-13"></span><span id="page-24-11"></span><span id="page-24-10"></span><span id="page-24-9"></span><span id="page-24-8"></span><span id="page-24-6"></span><span id="page-24-5"></span><span id="page-24-4"></span><span id="page-24-3"></span><span id="page-24-2"></span>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\)](#page-12-0). Locally, these veins opened in pull-apart mode, showing a close relation with small chrysotile fibers [\(Fig. 7B](#page-12-0)). This is highlighted by the Raman spectra signature of antigorite (S4), which is systematically a mixture between serpentine chrysotile and antigorite, with typical peaks at 3670 cm<sup>-1</sup>, 3690 cm<sup>-1</sup> and 3700 cm<sup>-1</sup> ([Fig. 7](#page-12-0)). In addition, antigorite (S4) is frequently crosscut by later chrysotile crack-seal (S5) ([Fig. 7D\)](#page-12-0). 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](#page-31-24) *[et al.](#page-31-24)*, [1991](#page-31-24); [Kodolányi](#page-32-4) *[et al.,](#page-32-4)* [2012](#page-32-4); [Klein](#page-32-24) *[et al.,](#page-32-24)* [2017](#page-32-24); [Ribeiro](#page-33-17) [Da](#page-33-17) [Costa](#page-33-17) *[et al.,](#page-33-17)* [2008;](#page-33-17) [Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015,](#page-33-5) [2019\)](#page-33-6) and the Guatemala forearc ([Kodolányi](#page-32-25) [&](#page-32-25) [Pettke,](#page-32-25) [2011](#page-32-25)). In Alpine ophiolites, antigorite is mostly considered as a fingerprint of Alpine prograde metamorphism ([Dietrich,](#page-30-16) [1969](#page-30-16); [Burkhard](#page-30-17) [&](#page-30-17) [O'Neil,](#page-30-17) [1988;](#page-30-17) [Scam](#page-33-18)belluri *[et al.](#page-33-18)*, [1995;](#page-33-18) [Früh-Green](#page-31-25) *[et al.,](#page-31-25)* [2001](#page-31-25); [Debret](#page-30-23) *[et al.,](#page-30-23)* [2013](#page-30-23); [Lafay](#page-32-22) *[et al.,](#page-32-22)* [2013](#page-32-22); [Piccardo,](#page-33-19) [2013;](#page-33-19) [Liu](#page-32-26) *[et al.,](#page-32-26)* [2020\)](#page-32-26), and was, for long time, considered to be an evidence of HT-HP conditions of formation of serpentine (e.g. [Ulmer](#page-34-18) [&](#page-34-18) [Trommsdorff,](#page-34-18) [1995](#page-34-18); [Wunder](#page-34-19) [&](#page-34-19) [Schreyer,](#page-34-19) [1997;](#page-34-19) [Evans,](#page-31-26) [2004\)](#page-31-26). Thus, high fluid-rock interaction temperatures and an additional heat source linked to melt emplacement (e.g. [Beard](#page-29-18) *[et al.,](#page-29-18)* [2009](#page-29-18); [Frassi](#page-31-27) *[et al.,](#page-31-27)* [2022](#page-31-27)) 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.

<span id="page-25-3"></span>Alternatively, antigorite occurrences at Hess Deep (East Pacific Rise; [Rouméjon](#page-33-6) *[et al.,](#page-33-6)* [2019\)](#page-33-6), Atlantis Massif (Mid-Atlantic Ridge, MAR; [Rouméjon](#page-33-20) *[et al.](#page-33-20),* [2018,](#page-33-20) [2019\)](#page-33-6), Puerto Rico Trench [\(Klein](#page-32-24) *[et al.,](#page-32-24)* [2017](#page-32-24)) and the Southwest Indian Ridge (SWIR; [Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015\)](#page-33-5) 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](#page-11-0)). 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.](#page-17-0) [Kodolányi](#page-32-25) [&](#page-32-25) [Pettke](#page-32-25) [\(2011\)](#page-32-25) 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](#page-33-17) [Da](#page-33-17) [Costa](#page-33-17) [et al.](#page-33-17), [\(2008\)](#page-33-17) 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](#page-32-25) [&](#page-32-25) [Pettke](#page-32-25) [\(2011\)](#page-32-25) proposed also that the replacement of chrysotile by antigorite occurred by dissolution (and precipitation) at T ∼ 300◦C due to f luid infiltration (i.e. f luid-assisted chrysotile– antigorite transition). The recent discovery of seismic events in the footwall of oceanic core complexes showing compressional focal mechanisms ([Parnell-Turner](#page-32-27) *[et al.,](#page-32-27)* [2017\)](#page-32-27) may ref lect a small amount of shortening due to the plate unbending at very shallow levels along an exhumed detachment fault (see also model of [Sandiford](#page-33-21) *[et al.,](#page-33-21)* [2021\)](#page-33-21). 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.

<span id="page-25-4"></span><span id="page-25-1"></span>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](#page-30-24) *[et al.](#page-30-24)*, [2012](#page-30-24); [Peters](#page-33-22) *[et al.](#page-33-22)*, [2017](#page-33-22), [Pettke](#page-33-23) [&](#page-33-23) [Bretscher,](#page-33-23) [2022](#page-33-23)). A loss of such elements was documented in several places in the Alps, such as the Lanzo Massif [\(Debret](#page-30-23) *[et al.,](#page-30-23)* [2013\)](#page-30-23) or the Piedmont zone (Chenaillet–Queyras–Montviso; [Lafay](#page-32-22) *[et al.,](#page-32-22)* [2013](#page-32-22)) 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](#page-3-0)), recorded a prograde and increasing Alpine metamorphism from north to south [\(Peters](#page-32-13) [&](#page-32-13) [Mathews,](#page-32-13) [1963;](#page-32-13) [Dietrich,](#page-30-16) [1969](#page-30-16), [1970;](#page-30-14) [Vils](#page-34-10) *[et al.,](#page-34-10)* [2011\)](#page-34-10). 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



<span id="page-25-2"></span><span id="page-25-0"></span>**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](#page-32-26) *[et al](#page-32-26)*., [\(2020\)](#page-32-26), Chenaillet [Lafay](#page-32-22) *[et al.](#page-32-22)*, [\(2013\)](#page-32-22) and from Iberia margin and Newfoundland margin from ([Kodolányi](#page-32-4) *[et al.](#page-32-4)*, [2012](#page-32-4) and [Vesin](#page-34-5) *[et al.,](#page-34-5)* [2023](#page-34-5)). The two black arrows illustrate the depletion trend of FME during the prograde Alpine metamorphism.

and Müntener, 2006; [Picazo](#page-33-3) *[et al.,](#page-33-3)* [2013](#page-33-3)). 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](#page-25-0)). 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](#page-23-0) and [17](#page-24-0)).

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](#page-12-0)). Based on constant Mg# measured in serpentine mesh and antigorite in abyssal peridotites, [Rouméjon](#page-33-6) *[et al.](#page-33-6)*, [\(2019\)](#page-33-6) 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](#page-22-0)), 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](#page-29-9) *[et al.,](#page-29-9)* [2007;](#page-29-9) [Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015](#page-33-5), [2018](#page-33-20)). [Evans](#page-31-26) [\(2004\)](#page-31-26) 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 f luid-dominated systems**

<span id="page-26-6"></span><span id="page-26-5"></span><span id="page-26-4"></span><span id="page-26-1"></span>Serpentine REE compositions mostly reflect those of their magmatic mineral precursors (olivine, clinopyroxene and orthopyroxene; see [Figs. 16](#page-23-0) and [17](#page-24-0) and supplementary materials). Regarding the REE compositions of serpentinite whole rocks, they cover the range of peridotite compositions reported by [Müntener](#page-32-11) *[et al.](#page-32-11)* [\(2010\)](#page-32-11). The variation of the  $(La/Sm)<sub>N</sub>$  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](#page-32-4) *[et al.](#page-32-4),* [2012;](#page-32-4) [Vesin](#page-34-5) *[et al.](#page-34-5),* [2023](#page-34-5)). Hence, REE contents of serpentinite samples are inherited from the magmatic processes that affected the subcontinental mantle prior its exhumation at seaf loor. Interestingly, two samples from the Lower and the Upper Platta units show particular U-shaped REE patterns with a strong positive Eu anomaly [\(Fig. 17\)](#page-24-0). 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](#page-32-10) *[et al.,](#page-32-10)* [2004](#page-32-10), [2010;](#page-32-11) [Rampone](#page-33-24) *et al.*, [1998](#page-33-24), [2020\)](#page-33-25); or (ii) large fluid-fluxes during serpentinization [\(Paulick](#page-32-1) *[et al.,](#page-32-1)* [2006](#page-32-1)). 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 [\(Müntener](#page-32-10) *[et al.,](#page-32-10)* [2004](#page-32-10)). However, this explanation cannot account for serpentinites from the Upper Platta, since this unit remained preserved from syn-rift melt percolation ([Müntener](#page-32-11) *[et al.](#page-32-11),* [2010\)](#page-32-11). 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;](#page-24-0) [Klinkhammer](#page-32-28) *[et al.,](#page-32-28)* [1994](#page-32-28); [Douville](#page-30-25) *[et al.,](#page-30-25)* [2002\)](#page-30-25).

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](#page-32-1) *[et al.,](#page-32-1)* [2006\)](#page-32-1). 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](#page-30-26) *[et al.,](#page-30-26)* [2019](#page-30-26), [2021](#page-30-15); [Hochscheid](#page-31-20) *[et al.,](#page-31-20)* [2022](#page-31-20)).

#### <span id="page-26-0"></span>**Serpentinization across the OCT** *Contrasting serpentinization from proximal to distal domains in the OCT*

<span id="page-26-9"></span><span id="page-26-8"></span><span id="page-26-7"></span><span id="page-26-3"></span><span id="page-26-2"></span>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\)](#page-28-0). 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\)](#page-28-0). Interestingly, serpentinites from the Chenaillet unit, which is interpreted to be located more oceanward (distal) than the Lower Platta unit (see [Fig. 1D\)](#page-3-0), is dominated by mesh  $\pm$ bastite textures (S1) and devoid of serpentine veins [\(Lafay](#page-32-22) *[et al.,](#page-32-22)* [2013;](#page-32-22) [Schwartz](#page-33-26) *[et al.,](#page-33-26)* [2013](#page-33-26)). 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 [\(Müntener](#page-32-10) *[et al.,](#page-32-10)* [2004,](#page-32-10) [2010\)](#page-32-11), 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](#page-31-28) *[et al.,](#page-31-28)* [2013\)](#page-31-28). Likewise, local magmatic intrusions could potentially increase the temperature of serpentinization and change the serpentinization rates (e.g. [Rimstidt](#page-33-27) *[et al.,](#page-33-27)* [2012\)](#page-33-27) 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](#page-33-0) *[et al.](#page-33-0)* [\(2013\)](#page-33-0), [Epin](#page-30-27) [&](#page-30-27) [Manatschal](#page-30-27) [\(2018\)](#page-30-27); [Epin](#page-30-12) *[et al.](#page-30-12)* [\(2019\),](#page-30-12) [Reston](#page-33-28) [\(2018\),](#page-33-28) and [Gillard](#page-31-7) *[et al.](#page-31-7)* [\(2019\)](#page-31-7) 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 [\(Fig. 19B\)](#page-28-0). 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\)](#page-3-0) reflects the involvement of flip-flop detachment <span id="page-27-3"></span><span id="page-27-2"></span>faults (i.e. f lip-f lop exhumation mode, [Fig. 19A](#page-28-0)). This is also in line with the studies of [Reston](#page-33-29) [&](#page-33-29) [McDermott,](#page-33-29) [\(2011\),](#page-33-29) [Epin](#page-30-12) *[et al.](#page-30-12)* [\(2019\),](#page-30-12) [Gillard](#page-31-7) *[et al.](#page-31-7)* [\(2019\)](#page-31-7) and [Theunissen](#page-34-20) [&](#page-34-20) [Huismans](#page-34-20) [\(2022\)](#page-34-20) showing evidence that mantle exhumation processes are undoubtedly more complex and discontinuous at distal parts of OCTs. Our simple model shown in [Fig. 19](#page-28-0) 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](#page-28-0)). Limited fluid–rock interactions at Totalp are also evidenced by very low FME concentrations (except B, Sb and Li) in bulk rock [\(Fig. 11\)](#page-17-1).

#### *Serpentinization at OCT and MOR: Similarities and differences*

<span id="page-27-0"></span>Mantle exhumation is a common process at slow and ultra-slow spreading centers and at OCTs of magma-poor rifted margins (e.g. [Cannat,](#page-30-0) [1993](#page-30-0); [Blackman](#page-30-28) *[et al.,](#page-30-28)* [2002;](#page-30-28) [Cannat](#page-30-10) *[et al.,](#page-30-10)* [2009](#page-30-10); [Sauter](#page-33-0) *[et al.](#page-33-0),* [2013\)](#page-33-0). Recent studies have proposed that at ultra-slow MOR settings, mantle exhumation involves successive detach-ment faults (flip-flop model; [Sauter](#page-33-0) *et al.*, [2013](#page-33-0) along the SWIR) similarly to distal parts of OCTs (e.g. Iberia-Newfoundland; [Reston](#page-33-29) [&](#page-33-29) [McDermott,](#page-33-29) [2011,](#page-33-29) [Theunissen](#page-34-20) [&](#page-34-20) [Huismans,](#page-34-20) [2022](#page-34-20)), Australia-Antarctica [\(Gillard](#page-31-29) *[et al.,](#page-31-29)* [2016\)](#page-31-29) and Lower Platta [\(Epin](#page-30-12) *[et al.,](#page-30-12)* [2019](#page-30-12)). 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](#page-30-9) *[et al.,](#page-30-9)* [2019](#page-30-9); [Epin](#page-30-12) *[et al.,](#page-30-12)* [2019](#page-30-12)).

<span id="page-27-1"></span>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](#page-33-20) *[et al.](#page-33-20),* [2018\)](#page-33-20), 23◦N (the Kane fracture zone, MARK area [Dilek](#page-30-11) *[et al.,](#page-30-11)* [1997;](#page-30-11) [Andréani](#page-29-9) *[et al.,](#page-29-9)* [2007](#page-29-9)), 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 [\(Rouméjon](#page-33-14) [&](#page-33-14) [Cannat,](#page-33-14) [2014](#page-33-14); [Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015](#page-33-5)) show similarities with observations made at serpentinites from the Iberian OCT ([Agrinier](#page-29-3) *[et al.,](#page-29-3)* [1996](#page-29-3); [Beard](#page-29-16) [&](#page-29-16) [Hopkinson,](#page-29-16) [2000,](#page-29-16) [Kodolányi](#page-32-4) *[et al.,](#page-32-4)* [2012;](#page-32-4) [Vesin](#page-34-5) *[et al.,](#page-34-5)* [2023\)](#page-34-5). 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](#page-33-5) *[et al.,](#page-33-5)* [2015](#page-33-5), [2018](#page-33-20)) 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 mecha-

nisms of mantle exhumation, i.e. exhumation along a single large offset fault vs along flip-flop faults (see model in [Fig. 19](#page-28-0)). This is also supported by observations made along the SWIR, where mantle exhumation occurred during the past 7-10 Myr by flipf lop faulting [\(Sauter](#page-33-0) *[et al.,](#page-33-0)* [2013\)](#page-33-0). As predicted by our model, only a minor part (∼25%) of the analyzed samples are overprinted by several serpentine veins [\(Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015,](#page-33-5) [2018\)](#page-33-20) with most of the samples composed only by pseudomorphic mesh and bastite textures (S1). Similar observations were also reported from the Atlantis Massif [\(Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015](#page-33-5), [2018](#page-33-20)).

#### *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](#page-29-9) *[et al.,](#page-29-9)* [2007;](#page-29-9) [Rouméjon](#page-33-20) *[et al.,](#page-33-20)* [2018\)](#page-33-20). 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 [\(Rouméjon](#page-33-5) *[et al.,](#page-33-5)* [2015,](#page-33-5) [2018](#page-33-20)). In serpentinites from MARK, however, serpentine polyhedral is described as the latest generation of veins ([Andréani](#page-29-9) *[et al.,](#page-29-9)* [2007;](#page-29-9) [Andreani](#page-29-15) *[et al.](#page-29-15),* [2008\)](#page-29-15). According to [Andreani](#page-29-15) *[et al.](#page-29-15)* [\(2008\),](#page-29-15) 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](#page-33-15) *[et al.,](#page-33-15)* [2014](#page-33-15)).

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 [\(Andreani](#page-29-15) *[et al.,](#page-29-15)* [2008\)](#page-29-15). 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](#page-14-0)). 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



<span id="page-28-0"></span>**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](#page-31-29) [et al.,](#page-31-29) [2016](#page-31-29)). (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 seaf loor, favors intense f luid–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 f luid–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](#page-28-0)), 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](https://academic.oup.com/petrology/article-lookup/doi/10.1093/petrology/egae063#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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