Deformation-enhanced fluid and mass transfer along Western and Central Alps paleo-subduction interfaces: Significance for carbon cycling models

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ABSTRACT

The interplay between fluid mobility and deformation along subduction zone interfaces, and its influence on subduction C flux and other chemical cycling, can be evaluated through study of exposed paleo-subduction suites. Along traverses of three interface exposures in the Western Alps (Switzerland and Italy), lowering of carbonate δ¹⁸O values toward the fault surfaces is consistent with infiltration by H₂O-rich fluid with δ¹⁸O of +8.5 to +10.5‰ calculated using temperatures of 400–460 °C from Raman spectroscopy of carbonaceous matter. The lowering of δ¹⁸O occurs in rocks showing pervasive mylonitization and flattening parallel to the paleo-interface, and containing abundant deformed carbonate ± quartz veins, consistent with the enhancement of fluid infiltration by this deformation. These δ¹⁸O values could reflect mixtures of far-traveled fluids emanating from metabasaltic, meta-ultramafic, and metasedimentary sources at greater depths in the subducting slab (perhaps including hydrated mantle) and/or along the interface.

Thermal gradients in the uppermost parts of subducting sections and interfaces (particularly at depths of >80 km) could result in flow paths that are initially up-T, thus conceivably promoting carbonate dissolution. This flow would presumably be followed by flow down-T and down-P, and thus down the solubility gradient for calcite in H₂O (potentially precipitating carbonate), as the fluids then move toward the surface along the interface. At all three of the Western Alps localities, the carbonate (and quartz) precipitated in veins could reflect focusing of fluid flow along these zones of enhanced deformation. These observations, and other recently published accounts of carbonation in ultramafic rocks from similar structural settings, indicate precipitation and storage of carbonate in forearcs of a magnitude potentially important for whole-margin C cycling.

1. INTRODUCTION

Subduction zones are major pathways for the cycling of materials between near-surface and deep-Earth reservoirs, influencing the long-term chemical/isotopic evolution of the atmosphere, lithosphere, and deeper mantle, and known to be extremely important avenues for flux influencing whole-Earth C cycling (Berner et al., 1983; Bebout, 1995; Marty and Tolstikhin, 1998; Berner, 1999; Bebout, 2007). Better understanding of the natural C cycle can inform assessments of the role humans have played in altering this cycling. Knowledge of the balance between C subduction inputs into trenches and outputs into the atmosphere via arc volcanism, and the roles that metamorphism plays in this balance, is key to quantifying fluxes of subducting CO₂ into the atmosphere, influencing atmospheric C and N levels and thus global mean surface temperatures (see Bebout, 1995; Kerrick and Connolly, 2001; Hilton et al., 2002; Jarrard, 2003; Sadofsky and Bebout, 2003; Gorman et al., 2006; Bebout, 2007, 2014; Ague and Nolcoscu, 2014; Cook-Kollars et al., 2014; Kelemen and Manning, 2015; Collins et al., 2015; Scambelluri et al., 2016; Clift, 2017; Aiuppa et al., 2017).

Current estimates of the fraction of initially subducted C contributed to arc magmas and retained to depths beyond subarc regions are based upon studies of volcanic gas C emissions (CO₂) in comparison with estimated subduction zone C inputs (Varekamp et al., 1992; Sano and Williams, 1996; Marty and Tolstikhin, 1998; Hilton et al., 2002; Bebout, 2007, 2014; Dasgupta and Hirschmann, 2010). Large uncertainties exist in the global-basis estimates of volcanic arc return efficiency (i.e., balancing of subduction inputs and outputs), as these estimates are confounded by uncertainties in not only volcanic outputs but also a wide array of other factors influencing the C concentrations of rocks entering trenches and physical factors affecting their delivery to beneath arcs (16%–80% estimated by Collins et al., 2015; discussions by Jarrard, 2003; Clift, 2017). High- and ultrahigh-Rocks representing ancient subduction would seem to provide a means of directly assessing the fates of subducting C both in oxidized form (as carbonate) and as variably metamorphosed organic matter (reduced C). However, these metamorphic suites are typically fragmentary records of the processes at depth and, in the worst case, their presence at the surface reflects their metamorphism and exhumation in margins that do not match our view of the “normal” modern (or ancient) subduction zone. The results of processes likely to affect deep C subduction (e.g., decarbonation, carbonate dissolution, redox reactions) can certainly be observed in some of these rocks, but it has been difficult to extend information gained through study of these processes in exhumed suites to quantitative consideration of C cycling on a global basis or at individual subduction margins. Despite this
complexity, such rocks can serve as “analogos” of rocks metamorphosing in modern subduction margins that, when studied in the context of experimental and theoretical knowledge of C mobility, can yield great insight regarding the role of forearc metamorphic processes on whole-Earth C cycling.

Recently, work on decarbonation history in Western Alps high-P and ultra-high-P metamorphic suites by Cook-Kollars et al. (2014) and Collins et al. (2015) demonstrated impressive retention of C in carbonate to depths of up to 90 km in metasedimentary, metabasaltic, and meta-ultramafic rocks located away from major shear zones and having relatively few through-going veins. These authors suggested that the large degree of retention of carbonate in these rocks reflects their having behaved largely as closed systems without significant infiltration by H$_2$O-rich fluids that would drive more extensive decarbonation. This scenario of relatively closed-system behavior, and limited decarbonation, contrasts dramatically with models invoked by Gorman et al. (2006) involving massive infiltration of the upper-slab section by fluids from underlying dehydrating ultramafic rocks, resulting in extensive decarbonation and CO$_2$ flux easily balancing arc outputs.

Collins et al. (2015; see their table 3) argued that, over the 80–120 km depth range (range of slab-surface depths beneath arcs), even closed-system decarbonation alone (i.e., involving no infiltration of the rocks by H$_2$O-rich fluid) could potentially release CO$_2$ in quantities sufficient to match with arc volcanic output. This depth interval corresponds roughly to where subducting slabs are heated by exposure to the convecting asthenosphere in the mantle wedge (see the models of Syracuse et al., 2010; van Keken et al., 2011). Release of CO$_2$ from subducting rocks in forearcs, before they reach 80 km depths, would decrease what is available for addition to arcs, and what can be subducted to greater depths in the mantle (Kerrick and Connolly, 2001; Gorman et al., 2006; Ague and Nicolescu, 2014; Cook-Kollars et al., 2014; Collins et al., 2015). Cook-Kollars et al. (2014) and Collins et al. (2015) suggested some moderate loss (perhaps <20%) of C as CO$_2$ during forearc prograde metamorphism of the Western Alps suites. This would imply that >80% of the initially subducted C is available for addition to magmatic arcs, storage in other reservoirs in the overlying mantle wedge and crust, or transport into deeper parts of the mantle (see Collins et al., 2015; Kelemen and Manning, 2015).

Carbonate dissolution could also result in significant C release beneath arcs and possibly also in forearcs (Ague and Nicolescu, 2014; Kelemen and Manning, 2015). However, like decarbonation, this dissolution seemingly requires infiltration of the rocks by externally generated fluids, perhaps H$_2$O-rich, capable of dissolving the carbonate (see the discussion by Collins et al., 2015). It is possible that both decarbonation and carbonate dissolution can be enhanced in zones of increased permeability such as shear zones (e.g., mélangé zones) and highly fractured rock volumes in which H$_2$O-rich fluid can more readily infiltrate C-bearing rocks (Hacker, 2008; Ague and Nicolescu, 2014; Cook-Kollars et al., 2014; Collins et al., 2015). Therefore, a logical extension of the recent field-based studies in the Western Alps (and elsewhere) is an examination of the extent of fluid infiltration and related C mobilization involving similar rock types (e.g., calcshist of the Schistes Lustrés; metabasaltic and meta-ultramafic rocks) in and adjacent to major shear zones representing ancient subduction interfaces, or at the least analogs of such settings. In this study, calcshist (and other rocks) in the lower-plates of three Western Alps exposures of ancient subduction interfaces previously studied by Bachmann et al. (2009) and Angiboust et al. (2014a, 2015) were examined for evidence of deformation-enhanced fluid infiltration and related decarbonation and/or carbonate dissolution. This work merged field and petrographic observations with analyses of the C and O isotope compositions of carbonate in the calcshist and in veins and other metasomatic features therein.

## 2. GEOLOGIC SETTING

The European Alps record the closure of the Alpine Tethyan oceanic basin and the subsequent collision between the Adriatic and western Eurasian plates. This orogenic belt consists of slices of sediments and continental crust off-scraped from both the Adriatic and European margins, as well as Jurassic oceanic crust (Fig. 1; Rubatto et al., 2011). The Central Alps are dominantly made up of upper plate exposures whereas the Western Alps mostly expose lower plate rocks (Coward and Dietrich, 1989; Handy et al., 2010). In addition, metamorphosed ophiolite complexes were under-thrusted, accreted fragments of the European continental margin, including the Tsaté Ophiolite complex (Fig. 1C; Coward and Dietrich, 1989). This study considered calcshist from Central and Western Alps suites that experienced this orogenic event.

The calcshists considered in this study are Schistes Lustrés–type oceanic sediments deposited in the Alpine Tethyan realm during the Jurassic and Cretaceous (Dal Piaz, 1974; Deville et al., 1992; Trümpy, 2003). The exceptional preservation of prograde to peak mineral assemblages makes the Schistes Lustrés in the Central and Western Alps an excellent location for field investigations related to subduction (Agard et al., 2001). These units experienced subduction-zone metamorphic conditions ranging from sub-greenschist-facies (~300 °C and ~0.5 GPa) to lawsonite blueschist and lawsonite eclogite-facies conditions (up to ~500–550 °C and ~2.3 GPa; Bucher et al., 2005, Angiboust et al., 2009; Plunder et al., 2012). Carbonate-bearing rocks are abundant in the Schistes Lustrés along the basal Austroalpine thrust in the Central Alps (studied by Bachmann et al., 2009; also see Ring et al., 1988, 1990), and at exposures along the Dent Blanche Thrust (DBT), notably near Ollomont and Breuil-Cervinia, Italy (the former investigated by Angiboust et al., 2014a). These include not only metamorphosed oceanic sediments (calcshists), but also opal-carbonate and carbonated metabasalts (Ring et al., 1988, 1990; Deville et al., 1992; Miller et al., 2001; Trümpy, 2003; Garofalo, 2012). Carbonate in veins in the calcshists is generally approximately in C and O isotopic equilibrium with carbonate and silicate phases in the hosts, but its isotopic composition hints at some equilibration with externally derived fluids (Henry et al., 1996; Cartwright and Buick, 2000; Miller et al., 2001; Cook-Kollars et al., 2014; Piccoli et al., 2016).

At the Central Alps St. Moritz locality (Fig. 1A), the contact between the Austroalpine domain (upper plate) and Penninic domain (lower plate) is a basal
thrust interpreted to represent a paleo-subduction interface (Bachmann et al., 2009; Fig. 2A). The Austroalpine domain preserves the westernmost exposure of upper plate nappes and the Penninic domain consists of metamorphosed Alpine Tethys oceanic sediments (Ring et al., 1988, 1990; Bachmann et al., 2009). The Austroalpine domain is composed of a stack of continent-derived slivers, possibly corresponding to former extensional allochthons, individualized during the thinning of the Adriatic margin (e.g., Mohn et al., 2012). These slivers have been accreted in the depth range 10–40 km against the Adriatic buttress during alpine late Cretaceous convergence leading to the nappe-stack presently exposed in the Western and Central Alps (e.g., Platt, 1986; Polino et al., 1990). Remnants of Mesozoic pre-alpine deformation, occasionally visible in the field (e.g., Froitzheim and Manatschal, 1996), have been in many locations pervasively overprinted during the alpine accretionary stage (e.g., Thöni, 1988; Bachmann et al., 2009; Angiboust et al., 2014a). The three local-
ities selected for our study appear to show less of this overprinting and are better-suited for study of the pre-Alpine, subduction-related underplating (see Bachmann et al., 2009; Negro et al., 2013; Angiboust et al., 2014a, 2015). The Penninic domain is Cenozoic in age and preserves a block-in-matrix fabric of intensely deformed oceanic and continental material believed to have developed in the deep parts of an accretionary wedge. This was then subducted to depths of 20–30 km (corresponding to pressures of 0.5–0.8 GPa) and reached peak temperatures of ~300–400 °C (Figs. 1A, 2A; Ring et al., 1988, 1990, Bachmann et al., 2009). Pseudotachylites from the upper plate found in the Engadine window region, along the hanging wall of the main Austroalpine thrust have been interpreted to reflect unstable slip at ~200–300 °C (Bachmann et al., 2009).

Farther west, the DBT preserves a paleo-subduction interface between the Arolla gneiss (upper plate) and the Tsaté Ophiolite Complex (lower plate; Figs. 1A, 1B). Two sites along this interface were chosen for this study (Ollomont and Breuil-Cervinia exposures; locations on the map in Fig. 1A; sketches of these exposures in Figs. 2B, 2C). The Arolla gneiss consists of crystalline basement rocks from the Adriatic Plate studied by Roda and Zucali (2008) and Angiboust et al. (2014a, 2015). Metasedimentary rocks make up the top of the Tsaté Ophiolite Complex and are in direct contact with the DBT (Marthaler and Stampfli, 1989). These rocks were subducted to depths of 30–40 km (corresponding to pressures of 1.0–1.2 GPa) and experienced peak \( T \) of 360–490 °C (Negro et al., 2013; Angiboust et al., 2014a).
3. STABLE ISOTOPE ANALYTICAL METHODS

Samples of carbonate for C and O isotope analyses were obtained largely by microdrilling of veins and host-rocks (using a 2 mm drill bit). Carbonate phases (e.g., calcite and dolomite) were first identified petrographically and using a Phenom XL scanning electron microscope (SEM) with energy-dispersive x-ray spectroscopy (EDS) capability at Lehigh University. The microdrilled powders were reacted with 2 ml of 100% phosphoric acid at 72 °C for a minimum of three hours (see the more detailed description of this method by Collins et al., 2015). The resulting CO₂ gas was measured for C and O isotope compositions using a Gas Bench II with a CombiPAL autosampler interfaced with a Finnigan MAT 252 gas-source isotope ratio mass spectrometer at Lehigh University. Routine analyses of a house standard (HAUS) and international standards (e.g., NBS-19) allowed monitoring and correction of the data, resulting in uncertainties in both δ¹³C and δ¹⁸O of ~0.2‰ (expressed as one standard deviation; 1σ).

A small set of samples collected prior to the primary field season in 2016 was analyzed for C and O isotope compositions following the procedure developed by McCrea (1950) involving off-line extraction (at 25 °C) and cryogenic purification of the gases and analyses by dual-inlet methods also using the Finnigan MAT 252 mass spectrometer at Lehigh University. These methods result in somewhat higher precision, relative to the carrier-gas methods, with uncertainties (1σ) of ~0.15‰ for both δ¹³C and δ¹⁸O. For both the dual-inlet and the carrier-gas results, δ¹³C and δ¹⁸O values are reported in standard delta notation relative to VPDB (Vienna PeeDee belemnite) and VSMOW (Vienna standard mean ocean water), respectively.

4. FIELD OBSERVATIONS

Fieldwork, including sampling, in this study was largely focused in the lower plate exposures mostly consisting of calcschist, with lesser amounts of metamafic and meta-ultramafic rocks. Field relations in the Arolla gneiss at the Dent Blanche localities, and in the hanging-wall at the St. Moritz locality, are described by Angiboust et al. (2014a, 2015) and Bachmann et al. (2009), respectively.

4.1. St. Moritz Locality

Calcschist at the St. Moritz locality, and at the two Dent Blanche localities (described later), exhibits a dominant single foliation parallel to the shear zone that marks the paleo-subduction interface, the basal Austroalpine thrust (Figs. 3A, 3B). This mylonitic foliation overprints any earlier-formed foliations such as those observed in the Schistes Lustrés away from these zones of deformation (Agard et al., 2001; Cook-Kollars et al., 2014). Veining tends to increase in abundance nearer to the interface contacts. Centimeter-thick lens-shaped veins are composed of quartz and fine-grained calcite and are oriented parallel to the basal thrust (Fig. 3A). In many cases, quartz appears to have precipitated first, followed by deformation and precipitation of calcite (Fig. 3A). Strain shadow features, where present, are composed of calcite that precipitated around quartz hosts. Also observed at this locality are 5–10 m blocks of limestone up to a few meters in length and containing calcite veins—calcschist wraps around these blocks and blocks of metamafic rocks. Pseudotachylites were observed in upper plate exposures, as well as in mafic rocks, but not in metasedimentary rocks in the lower plate (see Koch and Masch, 1992; Bachmann et al., 2009).

4.2. Dent Blanche Thrust System Localities

4.2.1. Ollomont Locality

Calcschist at the Ollomont locality exhibits a strong foliation parallel to the DBT, overprinting any earlier-formed foliations and folding in the Schistes Lustrés. These rocks exhibit a block-in-matrix fabric like that described for some localities along the base of the Austroalpine nappe in the Central Alps (see Bachmann et al., 2009). The mylonitic foliation in the calcschist at the Ollomont locality wraps around metamafic and meta-ultramafic blocks. Field-work was undertaken in more accessible parts of the mixing zone and in the calcschist (metasedimentary rocks) beneath the thrust. More detailed field observations concerning the Arolla gneiss and its geological evolution are provided by Diehl et al. (1952), Roda and Zucali (2008), Angiboust et al. (2014a), Manzotti et al. (2017), and Kirst (2017). Kinematic indicators exposed on each side of the DBT exhibit top-to-NW sense of shear frequently reworked by exhumation-related back-shearing associated with top-to-SE tectonic transport (Ring, 1996; Angiboust et al., 2014a; Kirst, 2017).

Large numbers of extensively deformed, transposed veins containing calcite, and occasionally dolomite (the latter in opicarbonate), are more common nearer to the sheared interface (Fig. 3D). Carbonate also occurs as more disseminated grains within cm-scale layers between disparate rock types such as calcschist and talc-schist (Fig. 3C). This form of carbonate precipitation is observed only within ~400 m of the DBT. Where carbonate occurs in deformed veins, quartz is the only other mineral present (Fig. 3D). Veins that are composed solely of carbonate are relatively rare and occur only in metamafic rocks adjacent to the shear zone. In addition to carbonate veining, cm-scale domains (lensoidal in two dimensions) containing talc, pyrite, and actinolite were observed at Ollomont, but only in rocks within ~400 m of the shear zone.

Large variation in deformation features, veining, and rock-type was observed near the shear interface at the Ollomont locality, on the scale of meters. At distances ≥400 m from the DBT, the finite deformation recorded in calcschists becomes less penetrative than in the rocks nearer to the shear zone. Also at greater distance from the shear zone, veins are smaller and far less abundant, and they tend to be monomineralic, containing only quartz or calcite.
Figure 3. Field photographs taken at the three localities, with chisel, coin, sunglasses, or hammer for scale. St. Moritz locality: (A) Photograph of the locality for sample DB16-5 showing a boudinaged quartz-calcite vein in calc schist. This vein is composed almost entirely of calcite, unlike most of the others observed. (B) Photograph of locality for sample DB16-2A of calcite with a high deformed vein. Ollo mon Dent Blanche Thrust (DBT) locality: (C) Photograph of the locality for sample DB16-42 of calcite precipitation within calc schist. (D) Photograph of the locality for samples DB16-36A and DB16-36B of boudinaged quartz-calcite vein, within calc schist, with calcite appearing only on the outer rim of the vein. Breuil-Cervinia DBT locality: (E) Photograph of the locality for samples DB16-63B and DB16-63C of metamafic lens with dispersed carbonate throughout at hand-sample scale. (F) Photograph of the locality for samples DB16-8A and DB16-65 showing contact between calc schist and metamafic lens (white dashed line). (G) Photograph of the locality for sample DB16-5 showing quartz-calcite veins in calc schist. Calcite is fine-grained and deformed. (H) Photograph of the locality for samples DB16-8A and DB16-65 showing quartz-calcite veins with blocky calcite crystals in calc schist.
4.2.2. Breuil-Cervinia Locality

As at the other two localities, the calcschist at the Breuil-Cervinia locality exhibits a strong mylonitic foliation parallel to the DBT (Figs. 3E–3H). This dominant foliation overprints any earlier-formed foliations and folding that formed in the Schistes Lustrés away from major shear zones (see Cook-Kollars et al., 2014).

Variably deformed (transposed) veins at Breuil-Cervinia are more common near the sheared interface (Figs. 3G, 3H), and the overall volume of carbonate-rich veining at this locality is larger than that observed at the St. Moritz and Ollomont localities. In deformed carbonate-bearing veins, quartz is typically the only other mineral present (Figs. 3G, 3H), and veins composed solely of carbonate are relatively uncommon. Some individual veins contain at least two phases of carbonate precipitation, commonly one fine-grained and one more coarse-grained (e.g., Fig. 3H). Scattered minor occurrences of talc, pyrite, and actinolite also were observed at the Breuil-Cervinia locality, largely in lensoidal domains. As at the two other localities, the Breuil-Cervinia traverse contains 1–150-m-thick metamafic lenses strongly foliated and incorporated into the dominant foliation orientation (see Figs. 2C, 3F) and exhibit both prograde topto-NW and kinematically reversed shear sense indicators (e.g., Ring, 1995).

5. PETROGRAPHIC OBSERVATIONS AND RSCM ON CARBONACEOUS MATTER IN THE CALCSCHISTS

This section contains petrographic observations made for samples from the three interface exposures, demonstrating the mineralogy and textures with photomicrographs of representative mineral assemblages and deformation-related features (see Supplemental Item 1). EDS/SEM analyses demonstrated that calcite is the only carbonate phase present in the metasedimentary samples, with dolomite occurring only in veins and matrices of metamafic and meta-ultramafic lenses (e.g., Fig. 3C).

In order to characterize the maximum temperature reached by the calcschist sliver in the St. Moritz transect, we used the RSCM (Raman spectroscopy on carbonaceous material) thermometer based on gradual transformation of organic matter in graphite developed by Beyssac et al. (2002). This method, little-affected by retrogression, yields results with a relative accuracy of ±15 °C (also see Beyssac et al., 2004). These analyses were performed at the Ecole Normale Supérieure in Paris. Fifteen spectra were acquired for one St. Moritz sample within-sample heterogeneity. The average temperature obtained for this sample is 430 ± 19 °C (indicated on Fig. 2A). Similar methods applied to calcschists at Breuil-Cervinia yielded temperatures of ~460 °C (Angiboust and Agard, 2010; Negro et al., 2013) and, for the Ollomont locality, temperatures of ~400 °C (Angiboust et al., 2014a; indicated on Figs. 2B, 2C). Since the P-T trajectories in Western Alps ophiolitic metasomades are characterized by cooling during exhumation or at most isothermal decompression (e.g., Agard et al., 2001; Bousquet et al., 2008; Gabalda et al., 2009; Plunder et al., 2012; Fig. 2D), we posit that the obtained temperatures here are representative of the near-burial metamorphic conditions. Note that since exhumation-related kinematic reworking reused the structures formed during burial, it is difficult in some localities to discard the possibility that some foliations were not affected by exhumation.

5.1. Saint Moritz Locality

Supplemental Item 1 (footnote 1) and Figures 4A and 4B contain petrographic observations for calcschist, veins, and metamafic rocks collected at the St. Moritz locality. Meta-ultramafic blocks collected from the St. Moritz locality are composed primarily of talc and serpentine and contain some dolomite veins. Limestone blocks collected at this locality are fine-grained and composed entirely of calcite. As at the other localities, calcschist at the St. Moritz locality largely contains varying modal proportions of calcite, quartz, and white mica. Quartz and calcite show a moderate shape-preferred fabric defining the foliation along with white mica, talc, and serpentine (Fig. 4B). Sample DB16-15 (see the photomicrograph in Fig. 4A), was collected ~120 m from the basal thrust, and DB16-14 (see Fig. 4B) was collected ~40 m from the thrust. Samples such as DB16-14 near the contact show a stronger foliation and are more fine-grained than those slightly farther (~300 m) from the interface (e.g., DB16-15). Also, more extensive grain size reduction was observed in sheared quartz veins near the basal thrust. Quartz collected farther away from the contact, for example, in samples DB16-15 (~110 m) and DB16-4B (~210 m), does not exhibit grain size reduction but does show non-planar grain boundaries indicative of minor late-stage grain boundary migration possibly during exhumation. Crenulation cleavage is present in phyllosilicate-rich samples farther from the basal thrust. Calcite twinning and bent twins are present in all samples, regardless of proximity to the basal thrust; however, twins are more deformed nearer to the shear zone contact (see Figs. 4A, 4B). Calcium-rich silicates that could reflect carbonation reactions include titanite, clinozoisite, and amphibole, each present in some samples but in minor abundances [see Supplemental Item 1 (footnote 1)]. Titanite is present as subhedral to euhedral crystals within foliated white mica and commonly associated with intergrowths of ilmenite and rutile.

5.2. Dent Blanche Thrust Localities

5.2.1. Ollomont Locality

Supplemental Item 1 (footnote 1) and Figures 4C and 4D present petrographic observations for calcschist, veins, and metamafic rocks collected at the Ollomont locality along the DBTS. The carbonate phase in rocks at this locality is predominantly calcite; however, dolomite occurs in some opificarbonates near the interface contact. As at the St. Moritz locality, calcschists largely consist of varying modal proportions of calcite, quartz, and white mica.
Titanite, clinozoisite, and amphibole, all Ca-silicates, are abundant (up to 50 modal percent, but generally <10 modal percent) in some samples from the Ollomont locality (Supplemental Item 1). Titanite is often euhedral to subhedral and, as at the St. Moritz locality, commonly associated with ilmenite-rutile aggregates.

At thin section scale, lower-plate rocks near the shear zone show greater evidence of deformation, as exhibited by flattened minerals (parallel to the DBT), in addition to a more diverse suite of minerals (e.g., containing some calc-silicate phases; see Supplemental Item 1 [footnote 1]), relative to rocks far from the paleo-subduction interface (Figs. 4C, 4D). Quartz and calcite show weak orientations defining a pervasively developed foliation in rocks up to 1 km from the interface contact. Crenulation cleavage defined by phyllosilicates is observed in samples far from the DBT. Phengite crystals are not zoned and exhibit a very narrow Si content range of 3.20–3.28 p.f.u. (Angiboust et al.,
2014a). It is unsure whether white mica crystals forming the main foliation in Ollomont calcschists grew during peak burial conditions (and were not affected by retrogression) or if they have been completely re-equilibrated during exhumation-related re-equilibration. Mineralized fractures at the mm to cm scale are more voluminous and widespread at the Ollomont and Breuil-Cervinia localities than at the St. Moritz locality. Quartz in the groundmass exhibits sub-grain development, dynamic recrystallization, as well as static recrystallization independent of proximity to the shear zone (see Fig. 4D). Plagioclase feldspar porphyroblasts often appear brittlely deformed, however, where plagioclase feldspar occurs sparingly in veins, it is euhedral and undeformed.

5.2. Breuil-Cervinia Locality

Supplemental Item 1 (footnote 1) and Figures 4E and 4F contain petrographic observations for calcschist, metamafic rocks, and veins collected at the Breuil-Cervinia locality. As at the St. Moritz and Ollomont localities, the calcschist at Breuil-Cervinia is largely composed of varying proportions of calcite, quartz, and white mica. Quartz and calcite show weak preferred orientations that, along with occurrences of mica, define a continuous foliation even in rocks up to 1 km from the interface contact (Fig. 4E). Unlike at the Ollomont locality, rocks more than ~500 m away from the interface still contain quartz and calcite veins, and the veins are in general larger than those observed at the St. Moritz and Ollomont localities. Quartz in the groundmass exhibits sub-grain development, dynamic recrystallization, as well as static recrystallization when in sheared quartz close to the shear zone (see Fig. 4F). Plagioclase feldspar porphyroblasts appear brittlely deformed; however, when plagioclase is present within veins, it appears euhedral. Plagioclase was observed in only a few samples. Titanite is present as subhedral to euhedral wedge-shaped crystals within foliated white mica and chlorite. As in rocks from the other localities, aggregates of ilmenite and rutile are commonly associated with titanite and opaque ilmenite grains are surrounded by anhedral, amber rutile. (See Angiboust and Harlov [2017] for a discussion of similar textures in the adjacent Arolla gneiss.)

6. CARBON AND OXYGEN ISOTOPE COMPOSITIONS

6.1. Saint Moritz Locality

Calcite $\delta^{18}O$ values for carbonate-bearing host-rocks and veins at the St. Moritz locality range from $+12.0$ to $+22.5\%$ (see Figs. 5A, 5C). Multiple microdrilled powders from individual calcschist samples do not show significant variation in calcite $\delta^{18}O$ at the cm scale (Supplemental Item 7 [footnote 1]; data are also in Supplemental Item 2). For individual samples, $\delta^{18}O$ values of veins and adjacent calcite are quite similar, but with the $\delta^{18}O$ values of veins occasionally more positive than those for calcite in the surrounding calcites. However, for one sample, a carbonate vein is $+5\%$ more positive in $\delta^{18}O$ than calcite in the calcite (Fig. 5A). For a limestone block collected at St. Moritz, $\delta^{18}O$ values are lower along the margins of the block ($+14.2$ and $+14.4\%$) than at the center of the block ($+21.7\%$). Small (cm scale) veins cross-cutting the block have $\delta^{18}O$ ranging from $+20.7$ to $+22.6\%$, similar to the values for the center of the block (see the data for samples DB16-7B1, DB16-7B2, DB16-7C, DB16-DV1, and DB16-DV2 in Supplemental Item 2). In general, calcite $\delta^{18}O$ in the calcschists decreases toward the contact along the basal thrust (Fig. 5A).

Carbonate $\delta^{13}C$ shows a range of $-2.9$ to $+3.2\%$ ($\sigma = -0.2\%$). Nearly all of these values fall within the range expected for Tethyan marine carbonate ($-1.5$ to $+2.0\%$, with values as high as $+4\%$ in the Aptian; Figs. 5B, 5C; cf. Menegatti et al., 1998; Deville et al., 1992). Microdrilled regions in individual samples show little variation in carbonate $\delta^{13}C$ at the cm scale (Supplemental Item 7 [footnote 1]). The $\delta^{13}C$ values of veins and adjacent calcschist do not differ significantly from each other, with the largest variation being $+0.6\%$ (Figs. 5B, 5C).

6.2. Breuil-Cervinia Locality

6.2.1. Ollomont Locality

For this locality, carbonate $\delta^{18}O$ ranges from $+11.6$ to $+22.0\%$ ($\sigma = -0.2\%$), with multiple microdrilled samples in individual samples showing little variation (Supplemental Item 7 [footnote 1]). The $\delta^{18}O$ values of veins and host calcschist do not differ significantly, with the largest variation being $+0.5\%$ in sample DB16-48 (see Fig. 6A). $\delta^{18}O$ values in veins are similar to slightly higher than values for adjacent calcschist. $\delta^{18}O$ values in general show decrease toward the DBT contact. Some values do not fall along this trend of decrease but are still lower than the range of values for Schistes Lustres away from such structures ($+18$ to $+22\%$; blue-shaded region; from Cook-Kollars et al., 2014). The reduction in $\delta^{18}O$ begins $600–800$ m from the DBT (Fig. 6A).

Carbon isotope compositions ($\delta^{13}C$) of carbonate range from $–3.8$ to $0\%$ and most of the data, with only a few outliers, fall within the range expected for Tethyan marine carbonate ($–1.5$ to $+2.0\%$; Figs. 6B, 6C; cf. Menegatti et al., 1998; Deville et al., 1992). Analyses of microdrilled samples across individual rock stubs demonstrate little variation in carbonate $\delta^{13}C$ from the mm to cm scale (Supplemental Item 7 [footnote 1]). The $\delta^{13}C$ values of veins and adjacent calcschist do not vary significantly, with the largest difference being $+0.5\%$ in a vein with one of the more positive $\delta^{13}C$ values (Figs. 6B, 6C).

6.2.2. Breuil-Cervinia Locality

Oxygen isotope compositions ($\delta^{18}O$) of carbonate from this locality range from $+13$ to $+21.5\%$ (see Figs. 7A, 7C), with multiple microdrilled samples from single rock stubs showing little variation (Supplemental Item 7 [footnote 1]).
Figure 5. Oxygen and C isotope compositions of carbonate from the St. Moritz locality in the Central Alps. Data are ordered by distance from paleo-subduction interface (as in Figs. 6 and 7). (A) $\delta^{18}$O of carbonate in samples versus distance from the plate interface contact. (B) $\delta^{13}$C of carbonate in samples versus distance from the plate interface contact. (C) $\delta^{13}$C versus $\delta^{18}$O of carbonate. Blue circles—calcschist. Brown squares—carbonate in veins. Lines with double arrows represent the range of $\delta^{18}$O for Schistes Lustrés documented by Cook-Kollars et al. (2014) and Epstein et al. (2018). In general, veins are quite similar in isotopic composition to their host rocks (also see Supplemental Materials [text footnote 1]). VPDB—Vienna Peedee belemnite; VSMOW—Vienna standard mean ocean water.
Figure 6. Oxygen and C stable isotope compositions of carbonate from the Ollomont locality in the Western Alps. Data are ordered by distance from paleo-subduction interface (as in Figs. 5 and 7). (A) δ¹⁸O of carbonate in samples versus distance from the plate interface contact. (B) δ¹³C of carbonate in samples versus distance from the plate interface contact. (C) δ¹³C versus δ¹⁸O of carbonate. Blue circles—calcischist. Brown squares—carbonate in veins. The lines with double arrows represent the range of δ¹⁸O for Schistes Lustrés documented by Cook-Kollars et al. (2014) and Epstein et al. (2018). In general, veins are quite similar in isotopic composition to their host rocks (also see Supplemental Materials [text footnote 1]). VPDB—Vienna PeeDee belemnite; VSMOW—Vienna standard mean ocean water.
Figure 7. Oxygen and C isotope compositions of carbonate from the Breuil-Cervinia locality in the Western Alps. Data are ordered by distance from paleo-subduction interface (as in Figs. 5 and 6). (A) $\delta^{18}O$ of carbonate in samples versus distance from the plate interface contact. (B) $\delta^{13}C$ of carbonate in samples versus distance from plate interface contact. (C) $\delta^{13}C$ versus $\delta^{18}O$ of carbonate. Blue circles—calcite. Brown squares—carbonate in veins. Lines with double arrows represent the range of $\delta^{18}O$ for Schistes Lustrés documented by Cook-Kollars et al. (2014) and Epstein et al. (2018). In general, veins are quite similar in isotopic composition to their host rocks (also see Supplemental Materials [text footnote 1]). VPDB—Vienna Peedee belemnite; VSMOW—Vienna standard mean ocean water.
Where analyzed, the δ18O values of veins and adjacent calcschist do not differ significantly, with the largest difference being +2‰ in one sample (see Fig. 7A) and vein samples having δ18O higher than that of adjacent calcschist. δ18O values in general show decrease toward the DBT and, although there is some scatter, nearly all values still fall well below the δ18O range established for the Schistes Lustrés distal from these interface structures (+18 to +22‰; from Cook-Kollars et al., 2014; blue-shaded region in Fig. 7A). The reduction of δ18O values begins ~600 m from the DBT (Fig. 7A).

Carbon isotope compositions (δ13C) of carbonate at this locality range from ~5.4 to 0.4‰ and all but four of these values are within the range expected for Tethyan marine carbonate (~1.5 to +2.0‰; see Figs. 7B, 7C; cf. Menegatti et al., 1998; Deville et al., 1992). Microdrilled traverses across individual samples show little variation in carbonate δ13C (Supplemental Item 7 [footnote 1]) and δ13C values of veins and adjacent calcschist hosts do not differ significantly, with the largest variation being 0.5‰ (Fig. 7B). Where there are differences, the veins have δ13C values higher than those of the adjacent calcschist.

### 7. DEFORMATION-ENHANCED FLUID INFILTRATION

#### 7.1. Field and Petrographic Evidence of Fluid Infiltration during Deformation

There are two dominant types of veins observed in Schistes Lustrés metasedimentary rocks (see Agard et al., 2000). The first, developed during prograde to peak conditions, are flattened parallel to the main foliation or, in some cases, strongly folded. The second type of vein is less deformed and contains plagioclase feldspar and chlorite. This vein type cross-cuts the foliation and is in some cases slightly folded in retrogressive deformation networks (Agard et al., 2000).

The abundant carbonate-rich prograde to peak veining networks at each of these interface localities reflect transient development of fracture-related permeability and related fluid mobility prior to or during the evolution of the thrust system. In each case, this veining increases in abundance toward the interface and, along the DBT, is variably overprinted by the development of a pervasive mylonitic fabric. The veins show an array of deformation features and evidence of transposition and multiple phases of mineral precipitation. Mineral precipitation occurs within strain shadows or extensional fractures developed by the deformation of earlier-formed vein material (see Figs. 3, 4).

The observed high abundance of prograde to peak veining networks near the faults at the St. Moritz and DBT localities, and the lack of veining more distal to the faults, potentially demonstrate that regions of more intensive shear accommodated larger influxes of fluid, in part as related to the evolution of fracture-related permeability. As further evidence of hydrous conditions, at the Ollomont locality, phengite rich mylonitized gabbro pods are found in the serpentinite-bearing mixing zone as evidence of hybridization and pervasive fluid flux along the DBT (Angiboust et al., 2014a). This macroscopic evidence, in addition to the isotopic results, indicates extensive fluid-rock interaction along the DBT.

Deformation is enhanced along these shear interfaces, relative to more distal rocks, as evidenced by more pronounced crystal plastic deformation of calcschists observed in thin section, bent calcite twins, grain size reduction and subgrains within quartz, and crack-seal veins (Figs. 3, 4). This work complements previous studies in observing two main deformation mechanisms in the Schistes Lustrés metasedimentary rocks; dislocation creep and dissolution precipitation creep (Agard et al., 2001; see also Stöckhert et al., 1999). These two mechanisms may have worked coevaly or may instead reflect differing stages of a slow-creep process.

#### 7.2. Stable Isotope Evidence for Fluid Infiltration

Oxygen and C isotope compositions of carbonate minerals can elucidate metasomatic processes in subduction zones and provide information regarding C mobility in metamorphic fluids (Bebout and Barton, 1989; Cartwright and Barnicoat, 1999; Wang and Rumble, 1999; Ague and Nicolaselu, 2014; Galvez et al., 2013; Cook-Kollars et al., 2014; Collins et al., 2015; Piccoli et al., 2016). The more scattered δ18O values at St. Moritz and Breuil-Cervinia (Figs. 5A and 7A), relative to Ollomont (Fig. 6A), may be due to heterogeneity in permeability within the calcschist adjacent to the shear zone, leading to differing degrees of access to the rocks by infiltrating fluids. Fracture networks of varying densities could also have contributed to the scatter observed in δ18O values at the St. Moritz and Breuil-Cervinia localities. Fractures are transient conduits for fluid flow and there is positive feedback between fluid infiltration and fracture development, with increase in pore fluid pressure leading to further fracture formation (Sibson, 1996). Regions of deformation (such as semi-brittle shear zones with high vein densities) would thus experience larger degrees of infiltration and related possible shift in the δ18O of vein host-rocks.

The δ18O and δ13C values of carbonate in the calcschists and carbonate-bearing metapelites at these traverses, and veins therein, are conceivably explained by some combination of the following factors: (1) retention of protolith δ18O and δ13C during both prograde and any retrograde metamorphism (Wang and Rumble, 1999); (2) carbonate-silicate isotopic exchange (Cook-Kollars et al., 2014); (3) decarbonation reactions (discussion by Cook-Kollars et al., 2014; Collins et al., 2015); or (4) interaction with an O-rich, C-poor fluid (e.g., H2O-rich).

Clearly, these rocks, even far from the shear zones, have not preserved protolith marine carbonate δ18O values (scenario 1 above). Calcschists (Schistes Lustrés) in Alpine Corsica (Cartwright and Buick, 2000; Miller et al., 2001), Western Alps (Cartwright and Barnicoat, 1999; Cook-Kollars et al., 2014), and Cyclades (Ague and Nicolaselu, 2014) show ranges of δ18O (~2 to +2‰) and δ18O (+18 to +22‰), arguing for regional-scale lowering of δ18O from likely protolith values of +28 to +30‰ (see the discussion by Cook-Kollars et al., 2014). Along the interfaces investigated in this study, δ13C overlaps with the range for marine
carbonate protoliths (−1.5 to +1‰); however, the $\delta^{18}$O values display additional shift from the regionally developed range of +18 to +22‰, to values as low as +12‰ (see Figs. 5A, 6A, 7A; regionally developed range shaded blue).

Partial or complete carbonate-silicate O isotope exchange (scenario 2) could also explain some of the lowering of carbonate $\delta^{18}$O (with almost no change in $\delta^{13}$C; see the discussion by Cook-Kollars et al., 2014; Collins et al., 2015; cf. Henry et al., 1996). However, such exchange would not necessarily produce the gradients in $\delta^{18}$O observed at the three traverses. Isotopic exchange by diffusion between two solid phases at the $P$-$T$ conditions, discussed earlier, would be very slow and restricted to grain margins (Piccoli et al., 2016). Interface-coupled dissolution precipitation could also allow for fast isotopic exchange; however, the $\delta^{18}$O values of carbonate after such equilibration should be correlated with silicate content (Wang and Rumble, 1999; Putnis and John, 2010; Cook-Kollars et al., 2014). Comparing Supplemental Items 1 and 2, no apparent correlation exists between the $\delta^{18}$O of carbonate and the silicate content in the rock. Such exchange, facilitated by fluid mobility within the Schistes Lustrés, can explain shifts in the carbonate $\delta^{18}$O from values of marine carbonate (+28 to +30‰) to the values of +18 to +22‰ (see figure 12 in Cook-Kollars et al., 2014; cf. Henry et al., 1996). However, another mechanism is required to explain the further reductions in $\delta^{18}$O, along the interfaces, to values as low as +12‰.

Concerning scenario 3, the calcschists can be compared with carbonates elsewhere known to have experienced decarbonation reactions. For example, carbonates in skarns formed by closed-system decarbonation typically show decrease in $\delta^{13}$C with only very small decreases in $\delta^{18}$O (see the discussion by Cook-Kollars et al., 2014). Also for the rocks studied here, decarbonation in a closed system would produce a reduction of $\delta^{13}$C with little change in $\delta^{18}$O (see the discussion by Collins et al., 2015). Fluid-rock interactions in an open system can cause significant decrease in both $\delta^{18}$O and $\delta^{13}$C in cases where infiltration by externally derived O-rich fluids (e.g., H$_2$O-rich fluids) drives decarbonation reactions (see Collins et al., 2015, and the decarbonation trend in $\delta^{18}$O and $\delta^{13}$C in Fig. 5C). Figures 5, 6, and 7 demonstrate trends of decreasing $\delta^{18}$O toward the interfaces with little or no change in $\delta^{13}$C, with only a small number of samples having $\delta^{13}$C falling outside the range for marine carbonate protoliths (Figs. 5B, 6B, 7B). The O and C isotope compositions across the three traverses show little evidence of decarbonation, consistent with the general lack of Ca-silicate mineral phases that would be produced by such reactions (see Supplemental Item 1 [footnote 1]). Considerable reduction in the carbonate $\delta^{13}$C of some calcschist exposed in the Cottian Alps was attributed to C isotope exchange of the carbonate with co-existing reduced/organic C (see Cook-Kollars et al., 2014). However, those shifts occurred at grades higher than those represented at our traverses and in metapelitic rocks with high ratios of reduced/organic C to carbonate C.

Infiltration by H$_2$O-rich fluids from another source, either at greater depth in the subducting slab or at greater depth along the slab interface (scenario 4), is the most likely explanation for the isotope compositions reported in this study (Figs. 5–7). The fluid, as discussed above, was localized along paleo-subduction interfaces and must have had $\delta^{18}$O of +8.5 to +10.5‰ to lower the carbonate to its present values from the regionally developed values of +18 to +22‰, documented by Cook-Kollars et al. (2014; for temperature of ~450 °C and using calcite-H$_2$O fractionation factors of Zheng, 1999). The increased abundance of calcite-quartz veins along the paleo-subduction interfaces preserved at St. Moritz and DBT localities, relative to rocks farther from these structures, also is consistent with greater fluid infiltration in these zones. It is worth noting here that another possible scenario would involve infiltration by an O-rich fluid also containing considerable C but with $\delta^{13}$C of the fluid already equilibrated with similar rocks, at similar temperatures, and thus incapable of producing a C isotope shift in calcshist it infiltrates.

### 7.3. Source(s) of Fluids

Devolatilizing rocks at greater depths in the slab section (mafic and ultramafic rocks) and along the interface (sedimentary, mafic, ultramafic rocks, and hybrid mixtures thereof) are obvious candidates as sources for the fluids mobilized along these sheared fault surfaces (see van der Straaten et al., 2012; Angiboust et al., 2014b, 2017; Cannaò et al., 2015). Within metasedimentary rocks in shallow parts of the subduction channel, a combination of porosity collapse and the illite-smectite breakdown were the major fluid-producing processes (see Saffer and Tobin, 2011). However, at greater depths, fluid production would dominantly involve devolatilization reactions at higher temperatures (and pressures) and involve breakdown of hydrous phases such as chlorite, serpentine, and phengite (Schmidt and Poli, 1998; Angiboust and Agard, 2010). Previous work in the Western Alps has established that up to ~20% of the H$_2$O from high-pressure and ultrahigh-pressure metapelitic rocks was lost during subduction to depths of 80–90 km, along a $P$-$T$ gradient of ~7–8 °C/km (Busigny et al., 2003; Bebout, 2014). Similarly, Collins et al. (2015) demonstrated that metabasaltic rocks and opal-carbonate can retain large fractions of their initially subducted H$_2$O, at the greater depths largely in phengite, to depths of 80–90 km (see the calculations of Angiboust and Agard, 2010, indicating somewhat greater loss). Considered in the context of more recent thermal models of subduction margins (e.g., Syracuse et al., 2010; van Keken et al., 2011), thermodynamic calculations by Kerrick and Connolly (2001), Cook-Kollars et al. (2014), and by Collins et al. (2015) suggests that a large fraction of the initially subducted H$_2$O can be released from metasedimentary, metamafic, and metabasaltic rocks subducted to depths beneath and beyond arc volcanoes. Particularly significant loss of H$_2$O (and other volatiles; e.g., CO$_2$) likely occurs over the general depth interval of 80–120 km where subducting slab sections have been heated by juxtaposition with convecting mantle wedge (see Collins et al., 2015). The combination of deeply subducted sediment and mafic rock could release significant amounts of H$_2$O-rich fluid (deeper than 80 km) into the subduction interface that could travel up-dip along more permeable pathways (Zack and John, 2007; Angiboust et al., 2014b; Fig. 8).

As discussed in previous sections, $\delta^{18}$O values from the St. Moritz, Ollo-mont, and Breuil-Cervinia localities have been shifted from the values of +18 to +22‰ observed regionally for Schistes Lustrés (see Cook-Kollars et al., 2014) to values of +12 to +13‰. Using fractionation factors from Zheng (1999) for equili-

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temperatures of 500–600 °C would have had δ18O values of some of the calcschists along traverses. The similarity in the δ18O of metasedimentary and other rocks along the main thrust suggest long-range circulation of exotic H2O-rich fluids originating from deeper sources (possibly mantle). Along the plate interface, high pore fluid pressures prevail, maintained at high levels by the relatively low permeability of the subduction hanging wall. Transient slip instabilities (such as slow slip events) may enable periodic flushing of the system through vein systems and grain boundaries.

with the general statement that large-scale fluid circulation was limited during exhumation in the deep Alpine orogen (Philippot and Scambelluri, 1995), confirms the utility of these traverses (which seem largely insensitive to exhumation-related, fluid-deficient conditions) to decipher prograde processes.

The O isotope gradient preserved in the limestone block sampled at the St. Moritz locality demonstrates the isotopic effect of fluid-rock interaction in the actively deforming calc schist adjacent to the interface thrust. The δ18O values in the core of this block fall in the range of values for the Schistes Lustrés on a regional scale (mostly in the range of +18 to +22‰) documented by Cook-Kollars et al. (2014), and believed to reflect fluid-mediated O isotope exchange among carbonate- and silicate-rich rock types mostly within the Schistes Lustrés (cf. Henry et al., 1996). The shift from these values to values near +14‰ reflects exchange at the margins of this block with the more far-traveled H2O-rich fluids with δ18O values near +11‰ that pervasively lowered the calcschist δ18O near these thrust faults and were perhaps in part generated at depth in the mafic and ultramafic parts of the downgoing slab (see the discussion of fluid sources in Angiboust et al., 2017; Fig. 9A).

8. POSSIBLE GLIMPSES OF FLUID PROCESSES INVOKED IN STUDIES OF MODERN FOREARC SEISMICITY

Exposures of paleo-subduction interfaces can yield insight regarding deformation style at depths at which interface earthquakes are generated and the roles of fluids and fluid-rock interactions in generating such events (see Bach-
mann et al., 2008; Konrad-Schmolke et al., 2011; Angiboust et al., 2015). High pore fluid pressure is a critical characteristic often used to explain anomalous weakness of major fault systems in comparison to the surrounding crust (Shelly et al., 2006; Tobin and Saffer, 2009; Gomberg, 2010; Peng and Gomberg, 2010). Increased pore fluid pressure reduces effective stress along faults, lowers fault strength, leads to hydraulic fracturing and reduces friction at the plate or fault boundary (Moore, 1989; Sibson, 1992; Wada et al., 2008). Elevation of fluid pressure can lead to slow-slip phenomena in areas of extreme overpressuring (Peacock and Wang, 1999; Kodaira et al., 2004; Ito et al., 2007; Audet et al., 2009; Tobin and Saffer, 2009; Peng and Gomberg, 2010). The P-T conditions associated with slow slip–phenomena typically range from 350 °C to 600 °C and 0.8 to 1.4 GPa (~20–40 km depth; Peacock and Wang, 1999; Shelly et al., 2006; Ito et al., 2007; Peng and Gomberg, 2010), overlapping the ranges of conditions during the deformation along the St. Moritz and DBT paleo-interfaces. Angiboust et al. (2014a) suggested that the formation of hydrous minerals, such as serpentine and talc, at the Ollomont and Breuil-Cervinia localities resulted from fluid infiltration from the dehydrating downgoing slab or hydrated ultramafic rocks at greater depths along the interface (for the latter scenario, see Cannão et al., 2015). The formation of these mineral phases and fluids along the interface, infiltrating at or near lithostatic pressure, is believed to promote slow-slip behavior and to control the down-dip limit of large thrust earthquakes in many subduction zones (Peacock and Hyndman, 1999; Peacock, 2001; Hacker et al., 2003; Peng and Gomberg, 2010; also see Wada et al., 2008).

The field, petrographic, and geochemical observations made in this study are certainly consistent with what is invoked for these depths along the interface and leading to the generation of earthquakes of various types (see the discussion by Angiboust et al., 2015). At these three localities, rocks nearer the interfaces experienced strong mylonitic deformation, consistent with the temperatures inferred from the RSCM (400–460 °C). The veining record reflects periodic overpressuring leading to hydrofracturing, followed by precipitation of calcite and quartz then strong deformation of these veins. This fracturing, over a range of scales (perhaps grain-scale to meters), facilitated enhanced infiltration of the rocks experiencing the greater degrees of deformation nearer the faults. The fluids that equilibrated with calcite in the host-rocks and veins ranged in δ18O, likely as related to their varying sources and degrees of prior interaction with similar calcshist lithologies. Thus, the lowest calcite δ18O values at each locality probably are the closest representation of the δ18O of the fluids initially entering the Schistes Lustrés section above the subducting oceanic slab (see Fig. 8). This fluid traversing of the large section of calcshists apparently was channelized along larger-scale structures, rather than being pervasive (see the blue dashed arrows in Fig. 8), resulting in the preservation of higher δ18O near +20‰ except along fluid pathways.

Figure 9. Simplified sketch of an ocean-continent subduction zone and P-T diagram illustrating relevant carbonate solubility relationships. (A) Simplified sketch localizing the main characteristic features controlling subduction zone deformation patterns, including the high Vp/Vs region (indicating high pore fluid pressures), the serpentined mantle wedge, and the transition zone (episodic tremors, ETS, and slow slip events, SSE) at the junction between the seismogenic zone and the deeper stable slab region, where plastic deformation dominates. The blue arrows represent the main fluid transfer directions and the black rectangle localizes the study area in the Western Alps (modified after Angiboust et al., 2015). Bs—lower bound of the blueschist-facies field. (B) Isobars of CaCO3 solubility as a function of T indicated by the labeled black-curved lines, modified after Kellemen and Manning (2015). Dashed lines—base of subducting oceanic crust; solid lines—top of subducting volcanics and sediments; green—Kermadec; blue and red—Aleutians; orange—southern Chile. The solid gray curve indicates the stability limit of serpentine. The orange field indicates the P-T conditions above the fluid-saturated solidus for metabasalt and metasediment. The black arrow indicates an approximate P-T path for fluids moving toward the surface along subduction interfaces such as those represented in the Western Alps and described in this study. The slope of this path on this diagram reflects the ~8 °C/km P-T gradient inferred for the Western Alps Schistes Lustrés/Cignana suite (see Agard et al., 2001; Bebout et al., 2013; Cook-Kollars et al., 2014).
9. CARBON MOBILITY IN FOREARC SLAB/SEDIMENT SECTIONS

The Western Alps subduction pathway had an estimated P-T gradient of ~7–8 °C/km (Agard et al., 2001; Busigny et al., 2003; Bebout, 2014). Fluid P-T flow paths traveling along the subduction channel interface would be like those estimated for the upper plate of southern Chile (Fig. 9B; path from van Keken et al., 2011). Fluids traveling along this projected pathway can be H2O-rich and able to in general dissolve carbonate at higher P-T conditions but precipitate carbonate at lower P-T conditions (Kelemen and Manning, 2015). Kelemen and Manning (2015) suggest that the possibility that only a very small fraction of initially subducted C is contributed to the mantle beyond subarc depths, due to large amounts of carbonate dissolution related to fluid infiltration. However, work by Cook-Kollars et al. (2014) and Collins et al. (2015) found limited evidence for large-scale C loss (at the lower end of the range discussed by Kelemen and Manning, 2015), and a general lack of interaction with H2O-rich fluids with isotopic signatures reflecting generation at greater depths in the subducting plate. It can be inferred that most of the C in carbonate can be retained to 80–90 km if it is far removed from regions of enhanced deformation and fluid infiltration, such as the shear zones described in this paper. As observed in this study, even when carbonate-bearing rocks are near regions of enhanced deformation and fluid infiltration, the carbonate can largely be retained in the rock.

Work by Piccoli et al. (2016) showed that rock carbonation can occur at high-P conditions along subduction interfaces by either vein-injection or chemical replacement mechanisms (also see Scambelluri et al., 2016). This implies that carbonic fluids produced by decarbonation reactions and carbonate dissolution may not be directly transferred to the mantle wedge, but could interact with slab and mantle-forming rocks. Carbonate dissolution and decarbonation reactions possibly occurred at some great depth to release carbonate into an up-dip-traveling fluid. The regions of enhanced fluid mobility in shear zones along subduction interfaces allow for a relatively permeable pathway for a C-bearing fluid to travel through. Precipitation of carbonate will likely occur along these pathways as P-T conditions decrease (Fig. 9B). The fluids in the Central and Western Alps were most likely mobilized along major fluid pathways such as the basal thrust preserved at the St. Moritz locality and the DBT preserved at Ollomont and Breuil-Cervinia, perhaps with some small fraction of this fluid entering the hanging-wall (e.g., Angiboust et al., 2015).

Future work at these subduction interface exposures could be directed at attempting to quantify C release through the examination of whole-rock compositional changes (see Bebout and Barton, 2002; Anastasio et al., 2004). In such an investigation, passive concentration could almost completely occur by dissolution of calcite. In this case, it would closely resemble the sedimentological mixing of calcite-rich and calcite-poor rocks throughout the Schistes Lustrés unit. However, it is possible that infiltration by H2O-rich fluids, resulting in calcite dissolution, could also have disrupted other element ratios, in addition to shifting the 87Sr/86Sr values.

Evidence exists for dissolution and decarbonation in some high-P-ultra-high-P suites and for precipitation and carbonation in others (Piccoli et al., 2016; Scambelluri et al., 2016). Recently published carbonate solubilities (Caciagli and Manning, 2003; Kelemen and Manning, 2015) indicate that flow of H2O-rich fluid upward along such interfaces (see the purple arrow in Fig. 9B) should result in the carbonate precipitation, not dissolution, and the large amount of carbonate precipitated in veins along the two paleo-subduction interfaces could reflect fluids moving along similar P-T trajectories. Thermal gradients in the uppermost part of the subducting section and interface (particularly at depths of >80 km) could result in flow paths that are initially up-T, thus conceivably promoting carbonate dissolution. This fluid would presumably then flow down-T and down-P up-dip along the interface and thus down the solubility gradient for calcite in H2O (see Fig. 9B), thus promoting the precipitation of carbonate. Similarly, for quartz, upward flow along such P-T trajectories would in general be expected to lead to precipitation (see the quartz solubility data of Manning, 1994; also see Bebout, 2012), explaining the apparent co-precipitation of quartz and calcite to produce the wide range of vein textures illustrated in Figure 3.

9.1. Implications for Carbon Cycling Models

Arc volcanism, along with magmatism at oceanic spreading ridges, is known to play a key role in the global C cycle (Berner et al., 1983; Alt and Teagle, 1999; Kelemen and Manning, 2015; Bebout and Penniston-Dorland, 2016; Piccoli et al., 2016). Understanding the subduction-zone metamorphic contribution to the subduction-zone C cycle is crucial for quantifying the amount of C being released into the atmosphere and that being contributed to arcs and the deeper mantle. Temporal changes in subduction inputs and outputs could be strongly correlated, particularly as related to change in convergence rates (and thermal structure of individual margins) and sediment input (Edmond and Huh, 2003; recent discussion by Kelemen and Manning, 2015). However, at any individual margin, the efficiency of return of subducted C to the mantle wedge and other reservoirs could be influenced by the degree to which C is mobilized along zones of particularly high flux of metamorphic fluid. The development of these fluid channel-ways presumably relates to the thickness and lithology of the sediment section (and its rheology) and the potentially evolving permeability of any mixing zones developed at the interface (see Bebout and Penniston-Dorland, 2016; Ague, 2007).

It will be difficult to quantify the impact that C mobilization in fluids transported into and along subduction interfaces has for the total C cycling budgets of individual subduction margins or the global budget. Subduction-related metamorphic suites are fragmentary samples of interface environments with varying degrees of exhumation-related metamorphic and structural overprinting. Thus, a study of this type should be regarded as an analog study of such processes, pointing to key factors that could partly govern the efficiencies of removal and transport of C bound in subducting sediments, rock types represented in paleo-slabs, and any mixing zones developed at or near the subduction interface.
10. CONCLUSIONS

- Regions of deformation enhance fluid mobility along paleo-subduction interfaces, as indicated by the large shifts in δ18O near the thrust surfaces at the St. Moritz, Ollomont, and Breuil-Cervinia exposures. These shifts cannot be explained by a closed-system model and, combined with the C isotope compositions, seemingly require infiltration by C-poor fluids (likely H2O-rich) with relatively low δ18O (+8.5 to +10.5‰, taking into account published fractionation factors and estimated temperatures of 400–460 °C for the three localities). Enhanced fluid infiltration leads to a greater potential for open-system mass transfer and, accordingly, the calcshists and other rocks nearer these faults show greater evidence for metasomatism (e.g., more extensive veining) than rocks observed farther from the faults.
- Based on known solubility relations of calcite at appropriate P-T conditions, recently summarized by Kelemen and Manning (2015; Fig. 9B), it appears that fluids moving upward along these thrust surfaces would have precipitated calcite or aragonite rather than dissolving it. The abundant calcite-quartz veins at the St. Moritz, Ollomont, and Breuil-Cervinia localities seemingly reflect this precipitation. The hanging-walls at these interfaces contain varying amounts of carbonate-rich veining, showing varying textures relative to host-rocks, and further work should more thoroughly investigate evidence for fluid infiltration in the upper-plate gneisses (see Fig. 2).
- Evidence for carbonate dissolution, and other evidence for local-scale redistribution of carbonate, does exist in the form of pressure solution features (e.g., cleavage formation; strain shadows around porphyroblasts and concentrations of calcite in fold hinges; see Stöckhert et al., 1999; Ague and Nicolaescu, 2014). However, as demonstrated by Scambelluri et al. (2016) and Piccoli et al. (2016), interaction of C-bearing fluids with disparate rock types can lead to carbonate dissolution and nearby carbonate precipitation. A large amount of C can in this way be retained along the interface, having only been redistributed within the subduction zone, and perhaps not transferred into and stored in other reservoirs (Scambelluri et al., 2016; Piccoli et al., 2016).
- Future work could test for whole-rock compositional change possibly associated with volume strain, specifically, as related to possible removal of calcite by dissolution during infiltration by fluids (and related passive concentration of elements less mobile in H2O-rich fluids; e.g., Cr, Ti, Al; see Bebout and Barton, 2002, and the similar approach taken by Anastasio et al., 2004). Such work will be complicated by the likelihood that a calcshist leached of all carbonate, with little or other metasomatic alteration, could resemble a metapelite formed from a protolith containing no carbonate.
- Because of the fragmentary nature of high-P and ultrahigh-P metamorphic suites representing paleo-interface environments, and the varying degrees of exhumation-related metamorphic and structural overprinting, a study of this type should be regarded as an analog study of such processes pointing to key factors that could partly govern the efficiencies of removal and transport of C bound at depth in forearc regions. Exposures such as these can yield insight regarding deformation style at depths along interfaces at which earthquakes are generated, including the roles of fluids and fluid-rock interactions in generating such events.

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