



Devolatilization history and trace element mobility in deeply subducted sedimentary rocks: Evidence from Western Alps HP/UHP suites



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ABSTRACT

Metapelitic rocks of the Schistes Lustrés in the Cottian Alps, Italy (peak metamorphic conditions of 350–500 °C, 1.2–2.0 GPa) and at the UHP Lago di Cignana locality (Valtournenche, Italy; ~550 °C, 2.5–3.0 GPa) preserve records of prograde devolatilization in their mineral modes and chemistry, contents of volatiles and fluid-mobile elements (elements relatively mobile in aqueous fluids), and B and N isotope compositions. This suite allows study of prograde devolatilization history, across a wide range in metamorphic grade, in metasedimentary rocks that experienced high-P/T prograde paths similar to those experienced in most modern subduction zones.

Across grade, whole-rock samples are in general uniform in their concentrations of relatively fluid-mobile elements N, B, Li, Cs, Ba, and Rb, normalized to the concentrations of the less mobile K₂O and Al₂O₃, showing only hints of loss in several of the highest-grade samples. With increasing grade, ion microprobe analyses of phengites show subtle decrease in B concentration, uniformity in Ba and Cs concentrations, and increase in Li concentrations, the latter likely due to release from chlorite during its breakdown. In one Cignana sample, phengite inclusions in garnets are enriched in B relative to matrix phengite, consistent with either whole-rock B loss after garnet growth or, more likely, closed-system behavior and partitioning of B into paragonite or tourmaline stabilized after garnet growth. In samples with both paragonite and phengite, paragonite shows relative enrichment in B and Sr, and phengite is enriched in Cs, Ba, and presumably also N and Rb (the latter showing strong whole-rock correlations with K₂O).

Whole-rock δ¹⁵N shows a hint of shift to higher values in the highest grade rocks (Cignana) and, accordingly, calculated prograde dehydration histories for appropriate bulk compositions, using the Perple-X database, indicate that significant (~20%) dehydration would for some rocks occur over the temperature interval of 450 to 550 °C, largely related to the breakdown of chlorite (and to a lesser extent carpholite). Small amounts of loss of N into these fluids could have resulted in minor shift in δ¹⁵N, with decrease in whole-rock N concentration masked by heterogeneity inherent with the sedimentary protoliths. Partitioning of Cs and Li (possibly also Rb and Ba) from white micas into H₂O-rich fluids largely produced by chlorite breakdown could similarly have produced the subtle decreases in the concentrations in these elements noted in several high-grade samples. Neoblastic tourmaline in higher-grade rocks likely sequestered some fraction of the B lost from micas, resulting in a lack of obvious whole-rock B loss to accompany the up-grade trend of decreasing B concentrations in phengite. This tourmaline shows core-to-rim decrease in δ¹¹B consistent with growth during small amounts of progressive B loss from phengites.

Taken together, the whole-rock and SIMS data presented here, and the whole-rock dataset of Busigny et al. (2003), demonstrate impressive retention, during prograde forearc devolatilization, of elements thought to be relatively fluid-mobile (particularly H, N, B, Li, Ba, and Cs). Retention of these elements in metasedimentary rocks subducted to depths overlapping those beneath arc volcanic fronts (~90 km estimated for subsolidus, peak Cignana metamorphism) implies their availability for transfer into arc source regions, in aqueous fluids or silicate melts, or into the mantle to depths beyond subarc regions.

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1. Introduction

Models of modern or ancient whole-Earth chemical cycling incorporate assumptions regarding the efficiency with which chemical components of interest are conveyed from shallow reservoirs (oceans, crust)

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into the deep Earth via subduction (Allègre, 1982; Berner et al., 1983; Javoy, 1998; Tolstikhin and Marty, 1998; Hilton et al., 2002; Dasgupta and Hirschmann, 2010; Johnston et al., 2011). Examples of these models include those evaluating the geochemistry of arc lavas, the production of geochemical heterogeneity in the mantle, and long-term change in atmospheric CO₂ concentrations. Geochemical study of subduction-related metamorphic suites, aimed at identifying chemical change during HP/UHP metamorphism, can help reconcile records of subducting lithologies obtained from the study of crust and sediment on the modern seafloor with the geochemistry of lavas produced in modern volcanic arcs (see Bebout, 1995, 2007a, Bebout, 2007b; Li et al., 2007; Marin-Ceron et al., 2010; Mitchell et al., 2010).

Compared with subducting altered oceanic crust (AOC), sediments are subducted in smaller volumes (see Ishikawa and Nakamura, 1994; discussions by Hacker, 2008; van Keken et al., 2011) but tend to be enriched in elements such as the LILE (K, Rb, Cs, Ba), B, Li, and N, all thought to be relatively mobile in hydrous fluids and silicate melts. However, studies of HP and UHP metasedimentary suites aimed at understanding chemical cycling are relatively few (for the Catalina Schist, California: Bebout et al., 1993, 1999, 2007a; for the Sambagawa Belt, Japan: Nakano and Nakamura, 2001; for the Franciscan Complex, California: Sadofsky and

Bebout, 2003; for the Alps in NW Italy, SE France, and Switzerland: Busigny et al., 2003; Garofalo, 2012). As discussed in these previous studies, the assessment of element losses as a function of metamorphic grade requires the availability of suitable protoliths with which more highly metamorphosed units can be compared and metamorphosed equivalents for which exhumation did not result in significant mineralogical and geochemical overprinting of prograde records.

The Western Alps HP and UHP metamorphic suites (Fig. 1) are known to have experienced isothermal to down-temperature exhumation paths affording the survival of prograde records of devolatilization and element mobility (Reinecke, 1991, 1998; Agard et al., 2001a, 2002; Angiboust et al., 2009, 2012) and the Catalina Schist is thought to have experienced rapid cooling during early decompression, in an overall progressively cooling subduction regime (Grove and Bebout, 1995; Grove et al., 2008). By contrast to the Catalina Schist and the Franciscan Complex, the Western Alps provide an opportunity to study devolatilization beyond 30–40 km depths (Agard et al., 2001a,b) to at least 90 km (perhaps > 110 km; Frezzotti et al., 2011) through the study of the Schistes Lustrés exposed in the Cottian Alps (Italy) and the metasedimentary rocks exposed at the UHP Lago di Cignana locality (Valtournenche, Italy; see Fig. 1). For this Schistes Lustrés-Cignana suite, Busigny et al. (2003) analyzed

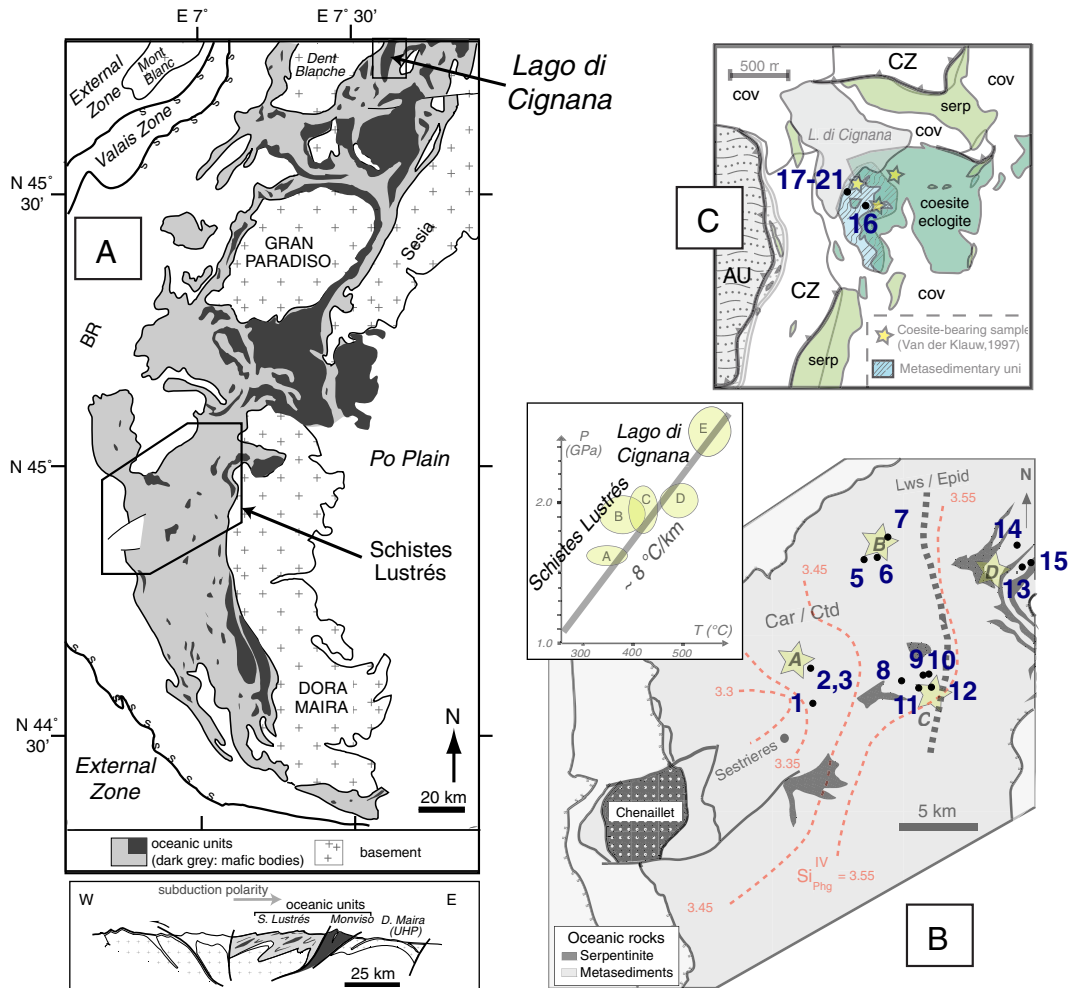


Fig. 1. (A) Geological locality map, showing the locations of the Cottian Alps Schistes Lustrés locality and the UHP Lago di Cignana locality, and (below) schematic cross-section along an east–west traverse at the approximate latitude of “Dora Maira.” Abbreviation: BR (Briançonnais). (B) Enlargement map of the area in the box on the larger geological map (A), showing the traverse of the Schistes Lustrés in the Cottian Alps and sampling localities for this study in blue type (from areas labeled A–D, studied in detail by Agard et al., 2001a,b; 2002) smaller inset P–T diagram shows the estimated peak conditions for each of the units along this traverse). The Chenaillet unit consists of obducted, low-grade ophiolitic rocks. Abbreviated mineral names: Car (carpholite), Ctd (chloritoid), Lws (lawsonite), and Epid (epidote). The location of the village of Sestriere is included for reference. (C) Simplified geological map of the Lago di Cignana locality (sampling area E; map modified after van der Klauw et al., 1997), indicating sampling locations in blue type. Abbreviations: CZ (Combin Zone); AU (Austroalpine undifferentiated; see van der Klauw et al., 1997); serp (serpentinized ultramafic rocks); cov (scree, moraine deposits, and wetland).

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