

PERIODICO di MINERALOGIA  
established in 1930

An International Journal of  
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,  
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY  
and applied topics on Environment, Archaeometry and Cultural Heritage

## Volatile and mobile element recycling during subduction of the oceanic lithosphere. Insights from metasediments and serpentinites of the Alps

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**ABSTRACT.** — We discuss some aspects of the release of light elements and volatile components during subduction of serpentinite and metasedimentary systems. Enrichment in B, Cl, and Sr during serpentinization of the oceanic mantle is followed by their progressive release in the subduction fluids. Olivine-orthopyroxene rocks formed after significant serpentinite dehydration still contain bulk B, Cl and Li considerably higher than in mantle reservoirs and may introduce light element anomalies into the upper mantle. The high to ultrahigh pressure metasediments underwent little or no devolatilization, nor N release, down to at least 90 km, acting as closed systems to the infiltration of externally derived fluids. They therefore reflux to the mantle appreciable amounts of exogenic N. This behaviour is supported by the oxygen isotope geochemistry of high and ultrahigh pressure rocks, showing closed system behaviour and limited fluid mobility at these depths. Many high pressure rocks thus do not represent the levels of fluid extraction from slabs; we suggest that the antigorite breakdown may represent a dehydration reaction creating a mobile, trace element-enriched, subduction fluid.

metasedimenti. L'arricchimento in B, Cl e Sr durante la serpentinizzazione del mantello oceanico è seguito dal rilascio progressivo di questi elementi nei fluidi di subduzione. Le rocce a olivina e ortopirosseno originate dalla disidratazione delle serpentiniti contengono quantità di B, Cl e Li molto più alte di quelle ospitate dalle rocce di mantello e generano un flusso di elementi leggeri nel mantello terrestre. I metasedimenti di alta e altissima pressione registrano un basso grado di disidratazione e rilascio di N sino ad circa 90 km, introducendo nel mantello quantità significative di N esogenico. Questo comportamento è confermato dagli isotopi O-H delle rocce di facies eclogitica, che si mantengono a sistema chiuso e registrano una bassa mobilità dei fluidi. Di conseguenza, molte rocce di alta pressione non provengono dai livelli delle placche in subduzione da cui vengono estratti i fluidi. Sugeriamo che la destabilizzazione dell'antigorite possa rappresentare un evento di disidratazione che produce un fluido mobile ed arricchito in elementi incompatibili.

**RIASSUNTO.** — Vengono discussi alcuni aspetti del rilascio di elementi leggeri e composti volatili durante la subduzione di serpentiniti e

### INTRODUCTION

Subduction of oceanic lithosphere recycles crustal material into the Earth's mantle: the dehydration fluids released from subducting

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plates are the agents enabling element transfer from down-going slabs to the overlying mantle. Experimental studies of such fluids, joined with the analysis of fluid inclusions in eclogite-facies rocks, show that volatiles and incompatible elements are discharged in the released fluids, likely enhancing hydrous metasomatism in the overlying mantle (Philippot and Selverstone, 1991; Brenan *et al.*, 1995; Ayers *et al.*, 1997; Stalder *et al.*, 1998; Philippot *et al.*, 1998; Scambelluri *et al.*, 1997; Stoeckhert *et al.*, 2001; Svensen *et al.*, 1999; Andersen *et al.*, 1993; Frezzotti *et al.*, 2004). However, the majority of stable isotope studies points to a short-range mobility of these fluids. The O-H isotope signatures of subducted ophiolites and continental crust largely mirror the ones of the pre-subduction protholiths, thus reflecting lack of re-equilibration at high and ultrahigh pressures: this is likely due to low water/rock ratios and to a restricted length-scale of fluid migration (Matthews and Schliestedt, 1984; Nadeau *et al.*, 1993; Barnicoat and Cartwright, 1997; Philippot *et al.*, 1998; Frueh-Green *et al.*, 2001; Yui *et al.*, 1995; Baker *et al.*, 1995).

Recent studies document that eclogites are trace element repositories transferring fluids to 300 Km through the stability of several hydrous minerals (Poli and Schmidt, 1995; 2002). However, the amount of fluids evolved from eclogites is small if compared with serpentinite and meta-sedimentary reservoirs. Although the understanding of high-pressures phase relations in hydrous ultramafites and in pelitic systems has considerably improved (Poli and Schmidt, 2002; Pawley and Holloway, 1993; Ulmer and Trommsdorff, 1999; Hermann and Green, 2001), still incomplete is the knowledge about their volatile and mobile element fingerprints (e.g. B, Li, Cl, N) at high and ultrahigh pressures. An inventory of such tracers is available for mafic rocks and metasediments subducted at  $P < 1.5$  GPa along hot gradients (Moran *et al.*, 1992; Bebout and Fogel, 1992; Bebout *et al.*, 1993; 1999; Domanik *et al.*, 1993), but is still lacking for rocks recording cool

subduction. For this purpose, the Alpine ophiolites are important natural observatories for the progressive subduction of variably altered oceanic lithosphere and can be used as monitors of deep fluid and element loss into the Earth's mantle. This paper aims to review these aspects of deep fluid budgets, particularly the variability of light elements, N and O-H isotopes in the oceanic lithosphere and its sedimentary covers, to discuss the crust-to-mantle element transfer at subduction zones.

#### TRACE ELEMENT VARIABILITY OF BULK-ROCKS, MINERALS AND ASSOCIATED FLUIDS

The volatile and mobile elements in the oceanic mantle and in metasediments were analyzed in sample suites from the Alpine-Apennine system and from the Betic Cordillera. The selected ultramafic rocks record key evolutionary stages of (1) hydration of the oceanic mantle, (2) fluid release at partial dehydration of serpentine (olivine-in reaction) and (3) full antigorite breakdown to olivine and orthopyroxene. The pelitic rocks sampled include unmetamorphosed oceanic sediments from the Apennines and their high and ultrahigh pressure counterparts (schistes lustrés) of the western Alps. Detailed sample descriptions and the relative bibliographic information are reported in Scambelluri *et al.* (2004a) and in Busigny *et al.* (2003a).

#### *Light element variability in the serpentinized oceanic mantle*

The sample set selected encompasses the whole subduction history of the oceanic mantle, from shallow alteration to deep antigorite-breakdown. Samples are from localities (Apennine, Alps and Betic Cordillera) recording one, or several evolutionary stages: despite the different provenance, the selected rocks share the same petrologic roots and exhibit comparable compositional features (Rampone *et al.*, 1996; Hoogerdujin Strating *et al.*, 1993; Scambelluri

*et al.*, 2001a, b; Trommsdorff *et al.*, 1998; Puga *et al.*, 1999).

Serpentinized oceanic mantle peridotites (Northern Apennine and Erro-Tobbio Unit, Ligurian Alps) are the starting materials and the volatile reservoirs for subduction. These rocks were hydrated at  $T < 300$  and  $P < 0.25$  GPa, as indicated by stable chrysotile and prehnite in ultramafic cumulates. High pressure antigorite serpentinites (Erro-Tobbio Unit and Nevado Filabride Units, Betic Cordillera, Spain), and olivine-orthopyroxene-chlorite metamorphic harzburgites (Betic Cordillera) formed at increasing subduction depths, and are associated with eclogites (Messiga *et al.*, 1995; Puga *et al.*, 1999). The antigorite serpentinites display the overgrowth of pre-subduction chrysotile assemblages by eclogite-facies olivine + antigorite + Ti-clinohumite + chlorite + diopside, formed after partial dehydration of the precursor serpentinite (olivine-in reaction). Presence of a fluid phase is documented by olivine-veins (olivine + Ti-clinohumite + chlorite + diopside  $\pm$  antigorite) and by primary saline aqueous inclusion changing from 10 to about 50 wt% NaCl equivalent (Scambelluri *et al.*, 1997; Scambelluri *et al.*, 2001a). Estimated pressures and temperatures are 500-650 °C and 2-2.5 GPa (Scambelluri *et al.*, 1995; Puga *et al.*, 1999). Comparable antigorite serpentinites also occur in the Zermatt Saas ophiolite associated with coesite cherts (Reinecke, 1991), suggesting that they may survive to ultrahigh pressures. Prograde metamorphism beyond the antigorite stability (650-700 °C and 2 GPa) produces rocks such as the Betic metamorphic harzburgites due to reaction antigorite = olivine + orthopyroxene + fluid (Trommsdorff *et al.*, 1998; Puga *et al.*, 1999). These display coarse olivine, orthopyroxene, chlorite (locally Ti-clinohumite), as well as spinifex-like textures indicating growth in the presence of abundant fluid. At this stage ultramafites lose much of the initial water and only chlorite and Ti-clinohumite survive as fluid repositories. Remnants of the antigorite breakdown fluid occur as primary aqueous inclusions with solid daughter phases (olivine,

magnetite-ilmenite, chlorite, apatite) in olivine and orthopyroxene.

The Cl, B, Li contents of minerals formed at increasing pressures and temperatures are listed in Table 1 and in Figure 1: the analyses were performed by means of ion probe (SIMS) and laser ablation ICP-MS (for details see Scambelluri *et al.*, 2004a). Relict mantle olivine has the lowest Cl, B and Li concentrations (Table 1), in the ranges measured in mantle xenoliths (Chaussidon and Libourel, 1993; Seitz and Woodland, 2000). Chlorine and boron rise significantly in the oceanic chrysotile and lizardite, which contain hundreds to thousand ppm Cl (up to 6100 ppm) and B (30 - 200 ppm). In the oceanic serpentines Li (0.02 and 2 ppm) does not rise significantly above the original mantle value, these contents corresponding to the lower range of concentrations measured in oceanic serpentinites (0.1 to 19 ppm; Decitre *et al.*, 2002).

Oceanic serpentinization causes an increase in bulk-rock Sr with increasing hydration, and the positive Sr-H<sub>2</sub>O correlation at the transition from peridotites to strongly serpentinized rocks (Fig. 2A) demonstrates the concomitant increase of these components. The Sr trend of Figure 2A can thus be attributed to secondary enrichment; comparable Sr enrichments were obtained by Menzies *et al.* (1993) after peridotite-seawater experiments at 300 °C and were measured in abyssal serpentinites (Bonatti *et al.*, 1970). This suggests that the Sr and H<sub>2</sub>O increase is related to the oceanic serpentinization: during this event alkalis are also fixed in mixed-layer phyllosilicates (Scambelluri *et al.*, 1997). Serpentinization is thus accompanied by uptake of Sr, Cl, B and alkalis, as the result of exchange with seawater-derived solutions. This enrichment process exerted an important control on the composition of fluids produced subsequently during subduction.

B and Cl progressively decrease from oceanic serpentinites through high-pressure antigorite serpentinites to olivine-orthopyroxene rocks (Fig. 1A, B). Remarkably,

TABLE 1

Rock	Assemblage	Mode	Clppm			Lippm			Bppm		
			Max	Min	Av	Max	Min	Av	Max	Min	Av
Oceanic serpentinite	lizardite, chrysotile	75%	6210	81	967	2.1	0.02	0.5	200	11	59
	chlorite	20			15			4.4			4.8
	other minerals	5									
	bulk-rock				729			1.3			47
High-P serpentinite	antigorite	63%	745	70	276	0.2	0.02	0.1	39	11	22
	olivine	25	120	24	66	3.7	1.5	2.2	36	5.6	17
	diopside	5	422	21	155	9.6	0.6	3.9	26	0.6	11.9
	Ti-clinohumite	7	741	8	323	1.2	6.3	1.9	41	13	27
	Bulk-rock				221			0.9			19.7
Olivine-opx	olivine	52%	18	6.9	11	11.6	4.5	6.7	4.7	22.2	10.8
	orthopyroxene	25			25	0.5	0.4	0.5	3.6	4.7	4.2
	chlorite	16	243	176	204	0.3	0.1	0.2	1.6	4.6	2.7
	Ti-clinohumite	7			8	24.4	11.7	16.7	33.5	27.3	30.8
	Bulk-rock				45			4.9			9.4

the olivine formed at the highest grade of this subduction trend still contains appreciable Cl and B (Table 1). On the other hand, the high-pressure serpentinites broadly share the same Li concentrations as their oceanic protoliths, whereas Li increases significantly in the olivine – orthopyroxene rocks. This feature may suggest an external (crustal) source for Li during the antigorite breakdown event.

First development of metamorphic olivine is accompanied by the release of about 2 wt% water, while the remaining antigorite and chlorite still enable the storage of 10 wt% bulk water (Scambelluri *et al.*, 2001b). The alkalis originally hosted in the oceanic phyllosilicates are absent in the high pressure minerals, B decreases from 46 to about 20 ppm, and Cl decreases markedly, 500 ppm being released in the fluid produced at this stage. Variations in the Cl and water contents of rocks were used to calculate the salinity of the fluid produced at this stage, yielding a 4 to 8 wt% NaCl fluid salinity, which compares with a low salinity 10 wt% NaCl of fluid inclusions in a number of antigorite serpentinites (Scambelluri *et al.*, 2001a). Formation of hypersaline fluids with

up to 50 wt% NaCl likely requires water-consuming reactions and precipitation of hydrous vein-forming minerals during high pressure metamorphism (desiccation), which increase the salt content in the residual fluid phase (Scambelluri *et al.*, 1997). Comparable processes are described for other eclogite-facies terrains (Andersen *et al.*, 1993; Svensen *et al.*, 1999). Scambelluri *et al.* (2001b) showed that the olivine + Ti-clinohumite veins share the same mineralogy and trace element patterns as the host antigorite serpentinites, indicating rock control on the fluid and suggesting lack of externally-derived fluids and components. Appreciable Sr in the veins (Fig. 2B) is compelling evidence for local derivation of the fluid components and for cycling of marine Sr in the high-pressure fluid. These data indicate closed-system behaviour of the analysed serpentinites during eclogitization with internal cycling of oceanic components.

The antigorite breakdown reaction releases 6.5 wt% water, based on the bulk analyses by Scambelluri *et al.* (2001b) and Puga *et al.* (1999). Further loss of 10 ppm B and 176 ppm Cl occurs at this stage, whereas the Li bulk

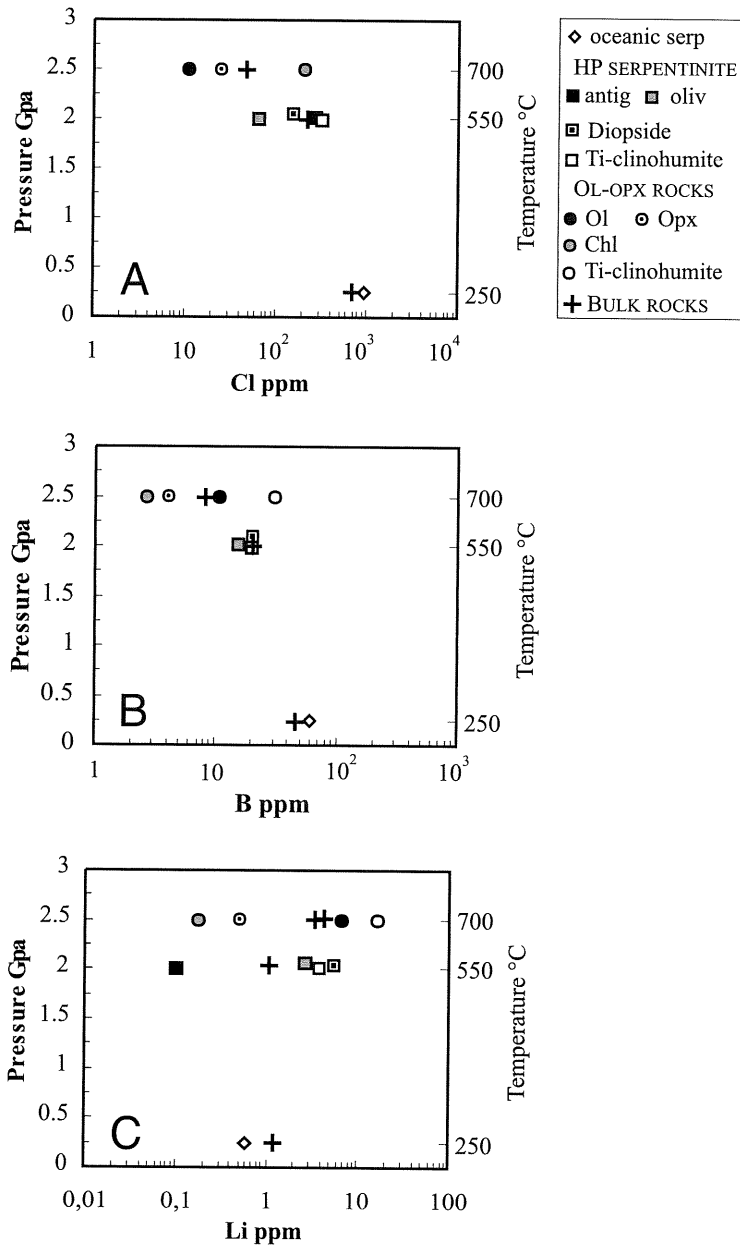


Fig. 1 – Average chlorine (A), boron (B) and lithium (C) variability in minerals and estimated bulk compositions of the selected samples as a function of the metamorphic pressures and temperatures.

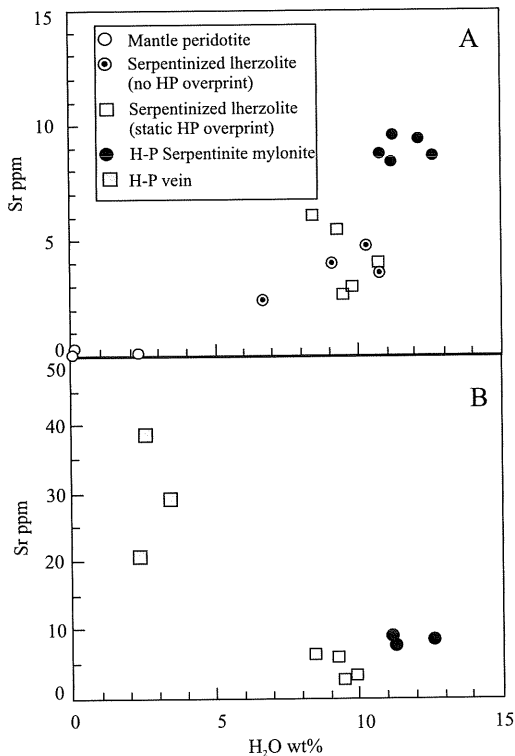


Fig. 2 – Bulk-rock water vs Sr diagrams reporting samples of the Northern Apennine and Erro-Tobbio peridotites showing increasing intensities of serpentinization (A) and high pressure serpentinites with the associated veins (B) (after Scambelluri *et al.*, 2001b).

budget increases up to 5 ppm. This latter feature suggests open system behaviour and influx of externally-derived Li. Based on the above water and Cl loss, the salinity of the antigorite-breakdown fluid was estimated between 0.4 and 2 wt % NaCl<sub>equiv</sub> (Scambelluri *et al.*, 2004a). Comparison with the fluid present in the antigorite serpentinites suggests a decrease in the salinity of the fluids during progressive subduction: ‘differentiation’ in the chlorine content of fluids can thus be expected, with shallower more saline fluids being followed by production of less saline solutions at greater depth.

Despite light element release during antigorite dehydration, appreciable amounts of

such elements are still retained in the metamorphic harzburgites. Figure 1 shows that B and Li entrainment in olivine and Ti-clinohumite enables a bulk rock storage of about 10 ppm B and 5 ppm Li, i.e. concentrations much higher than in normal mantle reservoirs. Olivine and Ti-clinohumite stable beyond the antigorite dehydration will thus re-inject B and Li into the mantle (Weiss, 1997; Ulmer and Trommsdorff, 1999). The altered oceanic mantle thus carries B and Li to the source regions of arc magmas and well beyond these depths, potentially introducing geochemical anomalies in the upper mantle.

#### *Nitrogen and LILE composition of subducted sediments*

The (meta)sediments studied are from the Lavagna Unit in the Internal Liguride zone (northern Apennine) and the schistes lustrés nappe from the Penninic zone (western Alps) (Busigny *et al.*, 2003a). These rocks represent pelagic sediments equilibrated under increasing PT conditions along a cold subduction path. The sediments from Lavagna Unit consist of unmetamorphosed middle Jurassic to late Cretaceous radiolarian chert, Calpionella-limestone and Palombini-shale which experienced diagenesis at  $P < 0.17$  GPa and  $T < 300$  °C (Reinhardt, 1991). Samples contain variable proportions of calcite, clay minerals and quartz. Calc-schists from the Schistes Lustrés nappe consist of quartz, phengite, paragonite and carbonate, subordinate chlorite, rutile and graphite. The rock suite equilibrated at increasing PT conditions as attested by the presence of lawsonite and carpholite (Lago Nero and Fraiteve), chloritoid (Colle di Assietta), garnet (Colle delle Finestre) and coesite (Lago di Cignana). PT estimates include: Lago Nero ( $T = 300$  °C and  $P = 0.8$  GPa; Martin and Polino, 1984), 2) Fraiteve ( $T = 350$  °C and  $P = 1.5$  GPa; Agard *et al.*, 2001), Colle di Assietta ( $T = 400$  °C and  $P = 1.8$  GPa), Colle delle Finestre ( $T = 450$  °C and  $P = 2.0$  GPa) and Lago di Cignana ( $T = 650$  °C and  $P = 3.0$  GPa; Reinecke, 1991). This sample set

provides a direct means for evaluating volatile and incompatible element (N, Cs, Rb) evolution in a cold slab environment.

The bulk ammonium contents vary significantly between samples, from about 100 to 1700 ppm (Figure 3) (Busigny *et al.*, 2003a). Analysis of individual phengite using FTIR spectroscopy (see Busigny *et al.*, 2003 b, for detail of the method) shows that ammonium is mainly preserved in phengite and that its concentration is homogeneous on a sample scale. This suggests that the large variation in ammonium contents recorded between samples is sedimentary in origin.  $\delta^{15}\text{N}$  whole rock values range between 2.6 and 4.8 ‰. As shown in Figure 3, the different rock types show the same range in  $\delta^{15}\text{N}$  values independently of their PT conditions and bulk ammonium

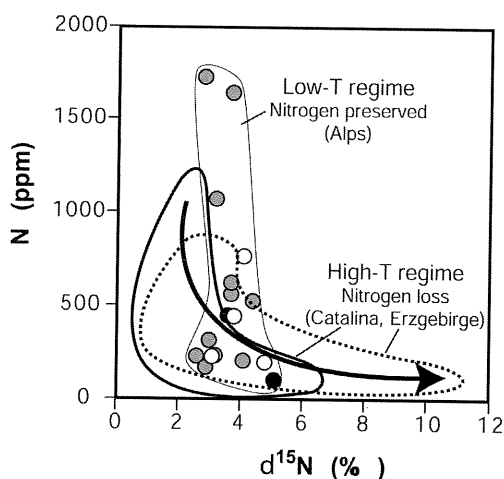


Fig. 3 – Whole-rock N content as a function of  $\delta^{15}\text{N}$  values of HP and UHP metasedimentary rocks from the Alps and their unmetamorphosed equivalent (Busigny *et al.*, 2003), and the Catalina Schists (Bebout and Fogel, 1992) and Erzgebirge Schists (Mingram and Bräuer, 2001). Large arrow indicates the evolution of N concentration and  $\delta^{15}\text{N}$  values of the Catalina and Erzgebirge Schists with increasing metamorphism. Alpine rocks N content and  $\delta^{15}\text{N}$  values are constant independently of the degree of metamorphic equilibration (open circles, unmetamorphosed pelagic sediments from Lavagna Unit; grey dots; HP metamorphic metasediments from Lago Nero, Fraiteve, Colle di Assieta and Colle delle Finestre; black dots, UHP coesite-bearing metasediments from Lago di Cignana).

concentrations. The  $\delta^{15}\text{N}$  values were thus unaffected by metamorphism and N was not released during subduction down to 90 km depth. This is in striking contrast with the results obtained on HP metasediments from the Catalina schists (Bebout and Fogel, 1992) and Erzgebirge schists (Mingram and Bräuer, 2001), showing a major increase in  $\delta^{15}\text{N}$  values and decrease in N concentration with increasing metamorphism. This evolution has been interpreted in terms of large-scale transport of aqueous fluids controlling drastic nitrogen loss with prograde metamorphism. The difference in nitrogen behaviour between the Alpine vs Erzgebirge and Catalina rocks is likely due to difference in thermal regime during subduction. Alpine rocks equilibrated along a cool geothermal gradient (8°C/km) characteristic of «mature» subduction zones whereas the Catalina and Erzgebirge schists were metamorphosed in a relatively «hot» slab environment (15-20 °C/km), characteristic of «immature» subduction zones (Catalina) or the deep roots of continental collision zone (Erzgebirge).

A further illustration of the contrasting volatile behaviour in the Alps relative to the Catalina accretionary wedge is given in Figure 4, which plots bulk Cs/K versus Cs/Rb molar ratios of Catalina Schists metasediments (Bebout *et al.*, 1999) and Alpine and Apennine (meta)sediments (Busigny *et al.*, 2003a). The major Cs loss (shown by the arrow in Figure 4) in the Catalina metasediments was attributed to large-scale devolatilisation and transport attending prograde metamorphism. In contrast, the Alpine (meta)sediments and their unmetamorphosed equivalent show constant Cs/K and Cs/Rb ratios independently of their degree of metamorphic equilibration. This clearly indicates little or no devolatilization of Alpine rocks to at least 90 km depth and a closed-system to external fluid infiltration during HP and UHP metamorphism. Otherwise the fluid-mobile element ratios of HP rocks and their unmetamorphosed equivalents would have been modified. These results indicate that a clear understanding of the geodynamic

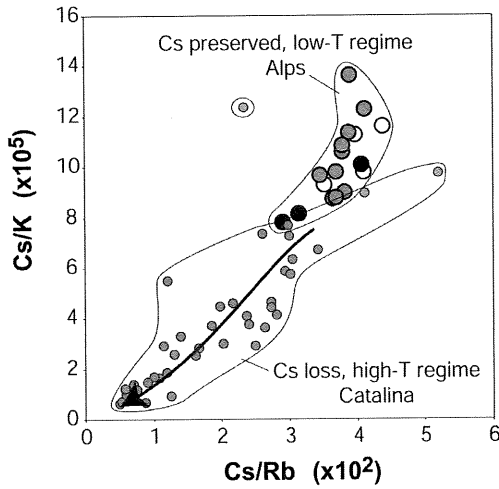


Fig. 4 – Whole-rock Cs/K versus Cs/Rb molar ratios of HP and UHP metasedimentary rocks from the Alps and their unmetamorphosed equivalent (Busigny *et al.*, 2003), and the Catalina Schists (Bebout *et al.*, 1999). Large dashed arrow indicates the evolution of Cs/K and Cs/Rb ratios of the Catalina Schists with increasing metamorphism. Alpine rocks Cs/K and Cs/Rb ratios are constant independently of the degree of metamorphic equilibration (same symbols as in Figure 6).

environment studied is a prerequisite to any extrapolation to a global scale of the geochemical results obtained on a field example.

STABLE ISOTOPE SYSTEMATIC AND THE LENGTH-SCALES OF FLUID MIGRATION

Figure 5 portrays the oxygen isotope compositions of the oceanic serpentinites and of the high-pressure antigorite serpentinites (Erro-Tobbio Unit, data from Früh-Green *et al.*, 2001). The mantle clinopyroxene preserved in the oceanic serpentinites has a large  $\delta^{18}\text{O}$  variability (5 to 7‰) and is both enriched and depleted with respect to reference mantle clinopyroxene (shaded bar in Fig. 5; Chazot *et al.*, 1993). Remarkably, the high pressure diopside of the serpentinites has similar compositions ( $\delta^{18}\text{O}$  from 4.1 to 6.5‰). Oceanic chrysotile and lizardite are in general  $^{18}\text{O}$ -enriched (5.8 to 7.6‰) compared to reference unaltered mantle. As with the clinopyroxenes, the  $\delta^{18}\text{O}$  of high pressure

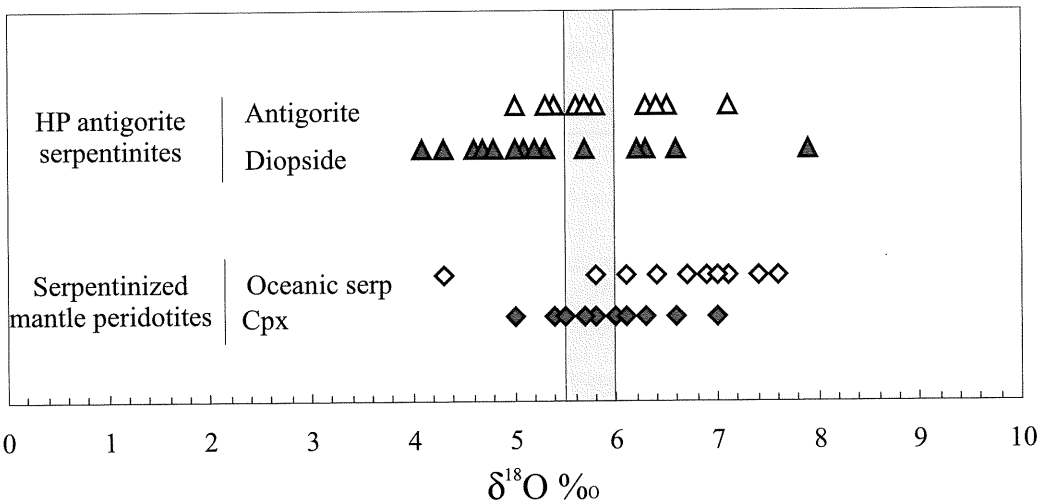


Fig. 5 – Oxygen isotope compositions of serpentines and clinopyroxenes from the Erro-Tobbio (i) serpentinized peridotites (oceanic cpx and serp) and (ii) high pressure serpentinites (data after Früh-Green *et al.*, 2001).



antigorite (5.0 to 7.1‰) largely overlap those of pre-subduction serpentines. The above range of oxygen isotope ratios is comparable to variations measured in serpentinites from modern oceans and from non subducted ophiolites (e.g. Wenner and Taylor 1973; Sakai *et al.* 1990; Lécuyer and Fourcade 1991; Früh-Green *et al.* 1996; Agrinier and Cannat, 1997), which were acquired during both low and high temperature alteration by seawater-derived fluids at varying fluid fluxes. In particular, the depleted  $\delta^{18}\text{O}$  values  $< 5\text{‰}$  of several clinopyroxenes suggest high temperature ( $T > 300^\circ\text{C}$ ) exchange with seawater, whereas the serpentine  $\delta^{18}\text{O}$  compositions  $> 5\text{‰}$  suggest low temperature hydration at crustal levels (Agrinier *et al.* 1997). In general, the  $^{18}\text{O}$  compositions of high pressure minerals largely mirror the ones of precursor pre-eclogitic phases: such a preservation of pre-eclogitic  $\delta^{18}\text{O}$  signatures suggests an absence of large-scale fluid flushing that would have reset precursor isotopic signatures. The stable isotope analysis of the antigorite serpentinites, joined with their trace element imprint, indicate internal recycling of oceanic fluids during high pressure metamorphism.

These results are in agreement with the oxygen isotopic data on mafic rocks (basalts and gabbros) and their eclogitic equivalent, which all argue in favour of a lack of isotopic reset and limited fluid flow during HP to UHP metamorphism (e.g. Matthews and Schliesedt 1984; Nadeau *et al.* 1993; Philippot, 1993; Barnicoat and Cartwright 1997; Philippot *et al.* 1998; Putlitz *et al.* 2000). This was shown by Philippot *et al.* (1998), who compared the oxygen isotope and fluid inclusion data available for non subducted oceanic and ophiolitic mafic rocks with those of their eclogitic counterparts (Fig. 6). Low-temperature alteration of superficial oceanic rocks ultimately results in  $^{18}\text{O}$ -enriched signatures (Gregory and Taylor, 1981), whereas deep oceanic gabbros are  $^{18}\text{O}$  depleted due to high-temperature interactions with salty fluids. The variable  $^{18}\text{O}$  signatures and fluid salinities of eclogites reflect the alteration

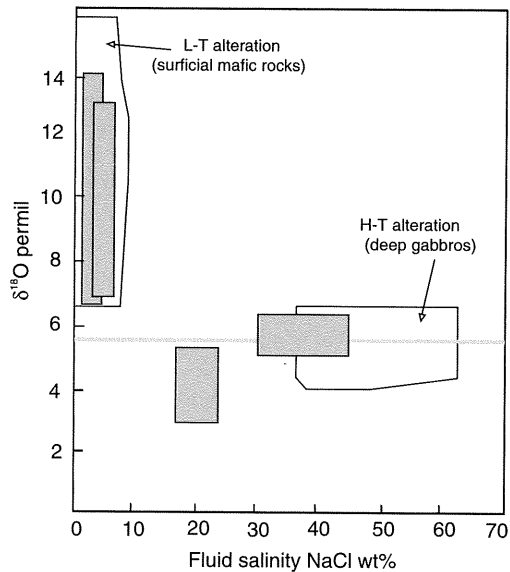


Fig. 6 – Fluid inclusion salinities versus  $\delta^{18}\text{O}_{(\text{whole rock})}$  or  $\delta^{18}\text{O}_{(\text{omphacite})}$  in oceanic rocks (white boxes) (Kane fracture zone, Holes 504B, 735B, Semail and Troodos ophiolites) which underwent high- and low temperature alterations, and in eclogites (grey boxes) (Franciscan Complex, California USA; Sifnos, Greece; Monviso and Rocciavère, Western Alps). Data sources in Philippot *et al.* (1998).

patterns recorded by the un-metamorphosed equivalents. The  $^{18}\text{O}$ -enriched eclogites of Figure 6 derive from superficial crustal materials: same as the superficial oceanic rocks, they still preserve a low-temperature,  $^{18}\text{O}$ -enriched, imprint and contain low-salinity inclusions. In contrast, the  $^{18}\text{O}$ -depleted signatures and high salinity fluid inclusions of the eclogitic metagabbros (Fig. 6) are very similar to those of deep oceanic gabbros. The systematic similarities of Figure 6 imply that subduction did not significantly modify the chlorine and oxygen isotope variability of altered oceanic precursors due to the lack of a significant flux of fluids to reset the initial imprints. These high-pressure rocks thus appear to behave as grossly closed systems that internally cycle their own fluids and elements; this indicates that oceans are the primary

sources of water and chlorine cycled in deep subduction fluids and at other metamorphic settings (Yardley and Graham, 2001).

These features suggest that fluids remain entrapped in the slab (Philippot *et al.*, 1998; Scambelluri and Philippot, 2001). The apparent controversy between the limited fluid flow in such eclogitic rocks and the evidence that fluids move in the overlying mantle wedge can be explained considering that these eclogite-facies rocks do not represent the levels where fluids are extracted from slabs, as considerable fluid retention at these depths ensured by the serpentine stability. Other regions of important fluid loss must be consequently considered, and the antigorite breakdown zone can be one of these regions. Studies on the trace element compositions of fluid inclusions produced at antigorite breakdown document a LILE and light element-enriched signature of this fluid, sharing many features of the geochemical signatures of arc lavas (Scambelluri *et al.*, 2001a; 2004b). Crossing the antigorite breakdown reaction can produce a mobile fluid which may play a role in metasomatism of the sub-arc mantle. The contribution of serpentinite systems to the process of crust to mantle transfer of elements and their role in mantle metasomatism at subduction zones should be therefore considered and re-evaluated in current geochemical models.

#### ACKNOWLEDGMENTS

We acknowledge Bruce Yardley and Maria Luce Frezzotti for their constructive reviews, Daniele Castelli and Bernardo Cesare for their careful editorial handling and for their patience. Funds to M.S. by the Italian MIUR and by the Genoa University.

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