Mineralogy and Petrology

Oxygen and nitrogen isotopes as tracers of fluid activities in serpentinites and metasediments during subduction

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Summary

N and O isotope systematics of a suite of high-pressure (HP) and ultrahigh-pressure (UHP) metasediments of the Schistes Lustrés nappe and metaperidotites of the Erro Tobbio Massif from the Alpine-Appennine system are compared with their un-metamorphosed or hydrothermally-altered equivalent from the same localities and from the South West Indian Ridge (SWIR). The HP and UHP rocks studied represent a sequence of pelagic sediments and altered ultramafic rocks subducted to different depths of down to 90 km along a cold geothermal gradient ($8\,°C/km$). Unmetamorphosed and HP metasediments show the same range in $\delta^{15}N$ values irrespective of their metamorphic grade and bulk nitrogen concentrations. Together with several other geochemical features (K, Rb and Cs contents, δD), this indicates that $\delta^{15}N$ values were unaffected by metamorphism and N was not released during subduction. N isotope analysis of serpentinites coupled with $\delta^{18}O$ systematics suggests the involvement of a mafic (crustal) component during partial deserpentinization of the subducted oceanic mantle at the depth locus of island arc magmatism. This does not imply large-scale fluxes as the metagabbros are spatially associated with the analyzed serpentinites. It rather indicates preservation of presubduction chemical and isotopic heterogeneities on a local scale as documented for the metasediments.

Introduction

Fluids released during subduction of oceanic lithosphere recycle crustal components into the overlying mantle wedge and are ultimately involved in the production of arc magmas. They transfer a characteristic geochemical signature to arc volcanism that can be used to trace mass transfer through subduction processes. Most studies have concentrated on identifying the source of volatile elements in subducting slabs and evaluating the efficiency of volatile recycling in subduction through the use of isotope and gas chemistry of island arc magmas (*Fischer* et al., 2002; *Zimmer* et al., 2004). Data on stable N and C isotopes suggest that most of the carbon is transferred to the mantle (*Shaw* et al., 2003; *Synder* et al., 2001), whereas N is largely returned back to the surface via volcanic degassing (*Fischer* et al., 2002). Another way to document more directly the source and behavior of volatiles in subduction zones is to study oceanic material that has been subducted to different depths. Metasediments and serpentinites are the two main carriers of volatiles at convergent margins. Although the understanding of high-pressures phase relations in pelitic systems and hydrous ultramafites has considerably been improved (*Poli* and *Schmidt*, 2002; *Pawley* and *Holloway*, 1993; *Ulmer* and *Trommsdorff*, 1999; *Hermann* and *Green*, 2001), knowledge about their volatile and mobile element fingerprints (e.g. B, Li, Cl, N) at high and ultrahigh pressures is still incomplete. An inventory of such tracers is available for mafic rocks and metasediments subducted along warm geothermal gradients (*Moran* et al., 1992; *Bebout* and *Fogel*, 1992; *Mingram* and *Braüer*, 2001). Recently, *Busigny* et al. (2003a) showed that the contents of fluid-mobile elements such as N, K, Rb and Cs of metasediments subducted in a cold slab environment remain unaffected by devolatilization and that N is effectively transported down to at least 100 km depths. This is in agreement with experimental data on calcareous metapelites (*Domanik* and *Holloway*, 2000) showing that phengite, the main carrier of N, is stable up to 9 GPa for a geothermal gradient of about 8 °C/km. The interpretation that nitrogen can be deeply recycled to the mantle is also supported by the occurrence of high concentrations of nitrogen (up to 11,000 ppm) in UHP metamorphic diamonds ($P>4$ GPa; *Cartigny* et al., 2001), which contrasts with the interpretation that N can be efficiently recycled in arc lavas associated with hot slab environment (*Fisher* et al., 2002).

Many studies have highlighted the central role of serpentinites as sources of volatiles in subduction zones (*Scambelluri* and *Philippot*, 2001; *Scambelluri* et al., 2004; *Sharp* and *Barnes*, 2004; *Straub* and *Layne*, 2003), yet to date no study has identified serpentinites as a source of N in the genesis of island arc magmas. In the present paper, we investigate the nitrogen contents and N isotope composition of a suite of ultramafic rocks from the Alpine Erro Tobbio complex, which has experienced oceanic hydrothermal alteration and subduction zone metamorphism up to ultra-high pressure conditions (2.5 GPa and 650 °C; *Busigny*, 2004). In order to provide a reference frame to the results obtained on these metamorphic rocks, serpentinites from the South West Indian Ridge were also analyzed. The results are compared with previous oxygen isotope systematics on the same set of samples (*Früh-Green* et al., 2001) and with N isotope systematics on associated mafic rocks and metasediments from the Schistes Lustrés nappe (*Busigny* et al., 2003a). The

data presented represent the first inventory of N behavior in a typical oceanic lithosphere subducted along a 'cold' geothermal gradient ($8\,°C/km$), representative of most current subduction zones.

Samples and analytical technique

The volatile and mobile elements in the oceanic mantle and in metasediments were analyzed in sample suites from the Alpine-Apennine system. The Alpine-Apennine 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 (*Philippot* and *Selverstone*, 1991; *Philippot*, 1993; *Barnicoat* and *Cartwright*, 1995; *Scambelluri* et al., 1997; *Früh-Green* et al., 2001; *Scambelluri* and *Philippot*, 2001). The selected ultramafic rocks record key evolutionary stages of (1) hydration of the oceanic mantle, (2) fluid release during partial dehydration of serpentine (olivine-in reaction) and formation of high-pressure metamorphic veins. Detailed sample descriptions and the relevant bibliographic information are reported in *Scambelluri* et al. (2004) and in *Busigny* (2004) and are only summarized below.

Ultramafics

The sample set selected is from the Erro Tobbio Complex of the Ligurian Alps. The rocks studied show a variety of equilibration stages from shallow alteration in an oceanic environment up to eclogite facies conditions (*Scambelluri* et al., 1995). The early stage of serpentinization occurred at $T < 300\,°C$ and $P < 0.25\,GPa$, as indicated by stable chrysotile. High pressure antigorite serpentinites formed at increasing $P–T$ conditions up to $2.5\,GPa$ and $650\,°C$, which was contemporaneous with eclogitization of associated mafic rocks (*Messiga* et al., 1995). The antigorite serpentinites display 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 ± antigorite; *Scambelluri* et al., 1997). To study the N content and stable isotope systematics during oceanic serpentinization and HP metamorphism and veining, the analytical work was performed on a cross section including low-strain peridotites displaying variable oceanic serpentinization and high-pressure serpentinite mylonites and veins. Samples analyzed here are from the study of *Scambelluri* et al. (2001; their figure 1). These comprise three low strain serpentinized peridotites (ETF1, ETF2, ETF3) and three HP mylonitic serpentinites (ETF4, ETF6, ETF7). One HP vein (ET0903-V) composed of olivine, Ti-clinohumite and antigorite and its host rock (ET0903-WR) serpentinite have been also analyzed (*Busigny*, 2004). In addition, three oceanic serpentinites from the South West Indian Ridge (SWIR) have been analyzed to provide an independent estimate of the N budget in a present day environment. These are DR23-2-1, DR23-2-8 and DR23-3-5 (see *Decitre* et al., 2002 for a detailed petrological and major and trace element analysis). All samples are undeformed spinel lherzolite showing different

degrees of serpentinization (from 67 to 82%) and preserving relics of mantle olivine, orthopyroxyne, clinopyroxene and spinel.

(Meta)sediments

The pelitic rocks sampled include unmetamorphosed oceanic sediments from the Apennines and their high and ultrahigh pressure counterparts of the western Alps. 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 P–T conditions along a cold subduction path. The sediments from the Lavagna Unit consist of unmetamorphosed mid 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 P–T 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). P–T estimates include: Lago Nero ($T = 300\,°C$ and $P \leq 0.8$ GPa; *Martin* and *Polino*, 1984), 2) Fraiteve ($T = 350\,°C$ and $P \leq 1.5$ GPa; *Agard* et al., 2001), Colle di Assietta ($T = 400\,°C$ and $P \leq 1.8$ GPa), Colle delle Finestre ($T = 450\,°C$ and $P < 2.0$ GPa) and Lago di Cignana ($T = 650\,°C$ and $P \leq 3.0$ GPa; *Reinecke*, 1991).

Analytical techniques

The nitrogen contents and the stable nitrogen isotope compositions were measured using the sealed tube combustion technique coupled with static mass spectrometry (*Boyd* et al., 1994; *Ader* et al., 2006; *Busigny* et al., 2005). In a companion paper, it was shown that this technique provides accurate and reproducible results for analyses of rock samples with N contents as low as 2 ppm (*Busigny* et al., 2005). The whole-rock samples were ground to thin powders and homogenized. Nitrogen was extracted from sample powders during a combustion step in quartz tubes sealed under vacuum. Nitrogen was purified and separated from other volatiles (mainly H_2O) using CaO, Cu and CuO. The sealed tubes were loaded into a vacuum line and opened with a tube cracker. Nitrogen was purified and quantified as dinitrogen N_2 by capacitance manometry with a precision better than 8% (2σ). The amount of extracted N ranged between 30 and 300 nmol in sedimentary rocks and between 4 and 17 nmol in the ultramafics. The gas was then analyzed for its nitrogen isotope composition using a triple-collector static mass spectrometer. Variations in the nitrogen isotope composition of the samples are expressed in the usual δ notation (in ‰): $\delta^{15}N_{sample} = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard} - 1] \times 1000$, where the standard is atmospheric N_2. Possible carbon monoxide and atmospheric contamination was monitored in the mass spectrometer using $m/z = 12$, 30 and 40 (Ar). The accuracy of $\delta^{15}N$ values was estimated at ± 0.5‰ (2σ) from the reproducibility of international standards (IAEA-N1 and -N2). The nitrogen blank

amount was 0.65 ± 0.30 nmol N, with a mean $\delta^{15}N$ at -3.7 ± 2.7‰ (2σ; for details see *Busigny* et al., 2005).

In order to test any potential effect of the serpentinization process on the N behavior, it is important to compare N content and isotopic composition to a sepentinization index like water content. While water contents of SWIR ultramafic rocks have been determined previously (*Decitre*, 2000), those of Erro-Tobbio rocks have been measured in the present study. Sample powders ($\sim$30 mg) were loaded in quartz tubes connected to a vacuum line. The powders were degassed during $\sim$12 hr at 150 °C under vacuum. Water was extracted from OH-bearing minerals by fusion of the sample at 1200 °C. Potential traces of hydrogen, as H_2, were oxidized to water with CuO heating at 450 °C. Water was purified from other gases (mainly CO_2 and N_2) on a variable-temperature trap at -145 °C and then converted to H_2 passing through hot uranium (800 °C; *Bigeleisen* et al., 1952). The hydrogen was quantified manometrically using a Toepler pump and the water content was calculated assuming all the hydrogen was initially present as water in the rock. The analytical error for water content is estimated to be better than 0.1% (2σ).

Nitrogen content and isotope composition in the serpentinized oceanic mantle

Bulk rock nitrogen analyses of SWIR and Erro Tobbio ultramafic rocks are given in Tables 1 and 2. Each sample has been analyzed at least twice in order to check analytical reproducibility. SWIR samples show nitrogen contents between 2.0 and 2.9 ppm and $\delta^{15}N$ between $+6.3$ and $+7.5$‰. The nitrogen content of Erro Tobbio serpentinized peridotites ranges between 3.9 and 5.9 ppm, which is slightly higher than the nitrogen content of HP mylonitic serpentinites (1.4–2.8 ppm). With the exception of the HP vein ($\delta^{15}N = 3.7$‰), all Erro Tobbio samples show $\delta^{15}N$ values between $+8.9$ and $+15$‰.

Figure 1 shows that no correlation seems to exist between nitrogen content and $\delta^{15}N$ of all analyzed Erro Tobbio and SWIR samples. Water contents of the ana-

Table 1. *Results of N and H_2O analyses for serpentinized peridotites from South West Indian Ridge (SWIR)*

Sample	Weight (mg)	N (nmol)	N (ppm)	$\delta^{15}N$ (‰)	H_2O (wt%)
DR23-2-1	30.27	8	3.0	$6.2^{+0.6}_{-0.8}$	
	50.43	11	2.8	$6.4^{+0.7}_{-0.7}$	
			2.9	*6.3*	*12.9**
DR23-2-8	49.28	10	2.8	$7.5^{+0.7}_{-0.7}$	
	40.35	9	3.0	$7.4^{+0.8}_{-0.7}$	
			2.9	*7.5*	*13.7**
DR23-3-5	50.57	8	2.0	$6.9^{+0.8}_{-0.8}$	
	35.19	6	2.0	$6.8^{+0.9}_{-1.0}$	
			2.0	*6.9*	*9.6**

Weight corresponds to sample weight used for N isotope analysis. N (nmol) represents the amount of N detected by manometry, and N (ppm) and $\delta^{15}N$ the N content and isotopic composition of samples after blank correction
* Water content from *Decitre* (2000)

Table 2. *Results of N and H_2O analyses for Erro Tobbio metaperidotites*

Sample	Weight (mg)	N (nmol)	N (ppm)	$\delta^{15}N$ (‰)	H_2O (wt%)
Low-strain serpentinite peridotites					
ETF1	34.36	15	5.9	$8.5^{+0.7}_{-0.6}$	
	28.08	12	5.7	n.d.	
	30.32	13	5.7	$9.2^{+0.6}_{-0.7}$	
	39.14	17	5.8	$9.1^{+0.6}_{-0.6}$	
			5.8	*8.9*	*8.42*
ETF2	27.48	9	4.1	$15.1^{+0.7}_{-0.8}$	
	29.57	9	3.8	$15.0^{+0.7}_{-0.8}$	
			4.0	*15.0*	*9.30*
ETF3	36.26	11	4.2	$11.1^{+0.7}_{-0.7}$	
	28.50	9	3.9	$10.9^{+0.7}_{-0.8}$	
	29.09	8	3.7	$10.9^{+0.8}_{-0.8}$	
			3.9	*11.0*	*9.22*
HP mylonitic serpentinites					
ETF4	31.79	6	2.6	$11.3^{+0.8}_{-0.9}$	
	25.63	5	2.5	$11.5^{+1.0}_{-1.0}$	
	25.22	5	2.6	$11.1^{+0.9}_{-1.0}$	
			2.6	*11.3*	*10.23*
ETF6	32.09	7	2.8	$10.6^{+0.8}_{-0.8}$	
	27.42	6	2.8	$10.5^{+0.9}_{-0.9}$	
			2.8	*10.6*	*10.73*
ETF7	27.86	5	2.1	$9.2^{+1.1}_{-1.1}$	
	35.44	5	1.9	$10.3^{+0.9}_{-1.0}$	
	42.03	6	1.9	$8.9^{+0.8}_{-0.9}$	
	28.95	5	2.1	$9.3^{+1.0}_{-1.1}$	
			2.0	*9.5*	*10.63*
ET0903WR	42.55	5	1.3	$8.8^{+1.0}_{-1.0}$	
	33.57	4	1.4	$9.0^{+1.1}_{-1.2}$	
			1.4	*8.9*	*10.92*
HP vein					
ET0903 V	37.36	14	5.1	$3.5^{+0.6}_{-0.7}$	
	35.44	15	5.4	$3.9^{+0.9}_{-1.0}$	
			5.3	*3.7*	*4.79*

Weight corresponds to sample weight used for N isotope analysis. N (nmol) represents the amount of N detected by manometry, and N (ppm) and $\delta^{15}N$ the N content and isotopic composition of samples after blank correction

lyzed SWIR samples were estimated between 9.6 and 13.7 wt%. Figure 2 shows that the SWIR samples display highly variable water content at relatively constant N concentration, indicating that N is unaffected by the degree of serpentinization. Erro Tobbio serpentinized peridotites and HP mylonitic serpentinites show a remarkable negative linear correlation characterized by decreasing nitrogen contents
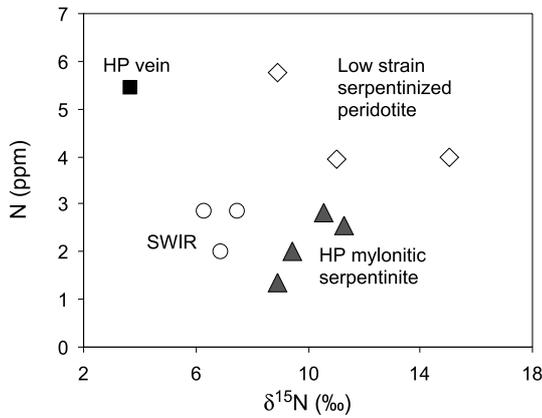
Fig. 1. Whole rock $\delta^{15}N$ values versus N content for the Erro Tobbio serpentinized metaperidotites and HP vein and mylonitic serpentinites, and the South West Indian Ridge (SWIR) serpentinized peridotites
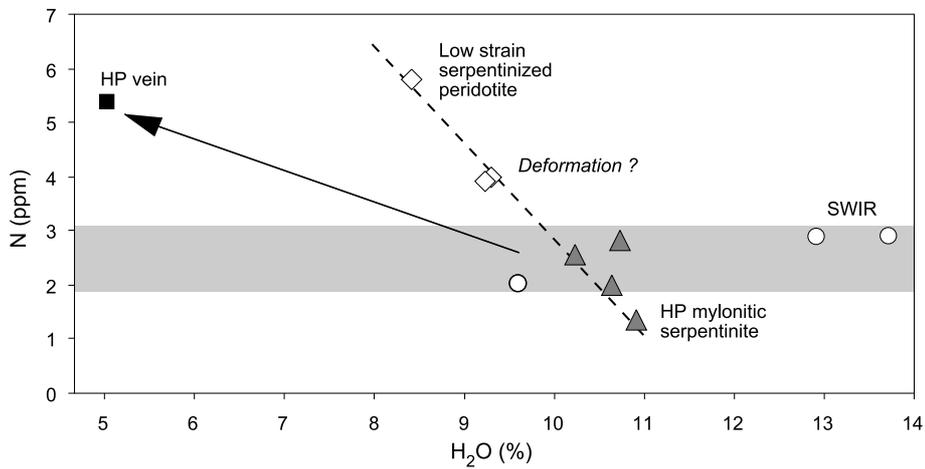

Fig. 2. Whole rock N versus H_2O content for the Erro Tobbio serpentinized metaperidotites and HP vein and mylonitic serpentinites, and the South West Indian Ridge (SWIR) serpentinized peridotites. Shaded area underlines the range of N content of SWIR samples (see text)
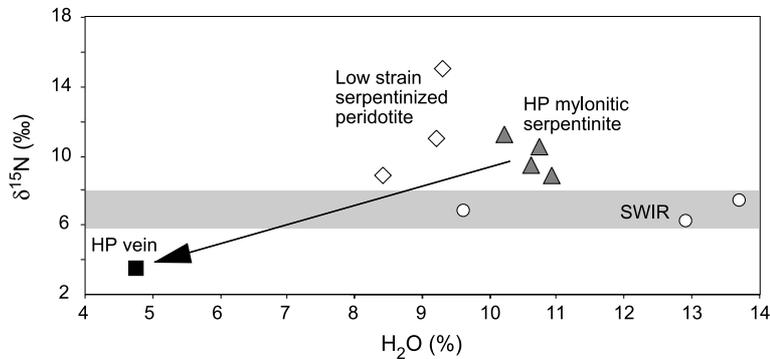

Fig. 3. Whole rock $\delta^{15}N$ values versus H_2O content for the Erro Tobbio serpentinized metaperidotites and HP vein and mylonitic serpentinites, and the South West Indian Ridge (SWIR) serpentinized peridotites. Shaded area underlines the range of N content of SWIR samples (see text)
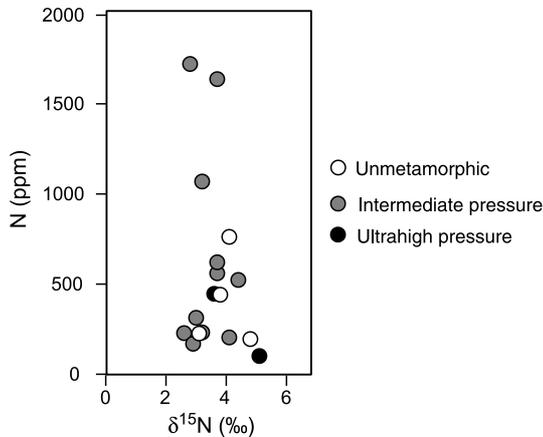
Fig. 4. Whole rock $\delta^{15}N$ values versus N content for the HP and UHP metasediments from the Schistes Lustrés nappe and their unmetamorphosed equivalent from the Appennine (data from *Busigny* et al., 2003a)

at increasing H_2O concentrations. The nitrogen content of the HP vein is about 5 times higher (5.3 ppm) than in the host mylonite (1.4 ppm) with a markedly lower H_2O content (from 11 to about 5 wt% H_2O). $\delta^{15}N$ values of Erro Tobbio and SWIR samples show no correlation with the H_2O contents (Fig. 3). The HP vein is significantly depleted in ^{15}N compared with its HP host rock.

Nitrogen composition of subducted sediments

Figure 4 shows the bulk nitrogen contents versus $\delta^{15}N$ values of the unmetamorphic and HP metasediments from the Lavagna and Schistes Lustrés nappes (data from *Busigny* et al., 2003a). In these rocks, nitrogen occurs mainly as ammonium (NH_4^+) and is substituted for potassium in K-bearing minerals Analysis of individual phengite using FTIR spectrosocopy showed that ammonium is mainly in phengite and that its concentration is homogeneous on a sample scale but varies significantly between samples. Whole rock nitrogen contents vary over a range from about 100 to 1700 ppm (*Busigny* et al., 2003b). This large variation recorded between samples is sedimentary in origin and reflects the proportion of K-bearing minerals in the protolith. Whole-rock $\delta^{15}N$ values range between +2.6 and +4.8‰. As shown in Fig. 4, the different rock types show the same range in $\delta^{15}N$ values irrespective of their metamorphic grade and bulk nitrogen concentrations. Together with other geochemical evidence, such as the constant ratios of K, Rb, Cs and δD (*Busigny* et al., 2003a), these data indicate that $\delta^{15}N$ values were unaffected by metamorphism and nitrogen was not released during subduction down to 90 km depth.

Discussion and conclusions

Figures 2 and 3 show that SWIR serpentinized peridotites display a slight increase in bulk nitrogen concentrations and relatively constant $\delta^{15}N$ values despite a large variability in water content. Considering that the increase in nitrogen content in the most hydrated samples is real, this suggests that the nitrogen budget could be controlled by the serpentinization process. In contrast, the Erro Tobbio serpentinized peridotites and HP mylonitic serpentinites display a marked negative linear correlation between nitrogen and water contents at similar $\delta^{15}N$ values. Dehydra-

tion processes attending subduction are unlikely to explain this correlation as the HP mylonites show a significant enrichment in water compared to the low strain peridotites. We rather favor the idea that nitrogen loss from low strain serpentinized peridotites to HP mylonitic serpentinites can be due to deformation. Recognition that the HP vein contains the same nitrogen amount as the low-strain peridotite suggests that the nitrogen loss associated with mylonitization of the low-strain serpentinized peridotites into the HP mylonites could be balanced by trapping of nitrogen in the HP veins. Alternatively, *Früh-Green* et al. (2001) suggested that two fluid sources could be involved in the hydration processes of the Erro Tobbio peridotites. A typical oceanic fluid origin attending mid-oceanic ridge hydrothermal circulation and a dehydration/compaction-derived fluid released in the sedimentary accretionary wedge and driving secondary serpentinization in the forearc region. In this model, the first fluid source would be responsible for the increase of the nitrogen content of the serpentinites with the degree of hydration of the samples (SWIR samples). The origin and location of nitrogen in the serpentinites is unknown. It may be hypothesized that nitrogen resides in sealed voids and cracks produced during serpentinization as it has been proposed for NaCl derived from seawater (*Sharp* and *Barnes*, 2004). The second fluid source originating in the accretionary wedge would have introduced metamorphic water into the deforming low-strain peridotite, which is now being further serpentinized. This fluid would be poor in nitrogen to the degree it is not derived from dehydrating metasedimentary phengite, which is the main nitrogen carrier (see below). By partly percolating the pre-existing hydrothermally-derived serpentinite, part of the N would be progressively leached out of the deforming HP mylonites and expelled into the local HP veins.

Constraints on the potential role of externally-derived fluid sources during Erro Tobbio dewatering processes attending vein formation can be obtained by using isotope systematics and trace element characteristics of Erro Tobbio rocks and surrounding mafic and metasedimentary protoliths. In order to evaluate the possible source of nitrogen involved in vein formation during HP metamorphism, the isotopic composition of the studied SWIR and Erro Tobbio serpentinites are plotted together with that of metasedimentary rocks (*Busigny* et al., 2003a) and ophiolitic
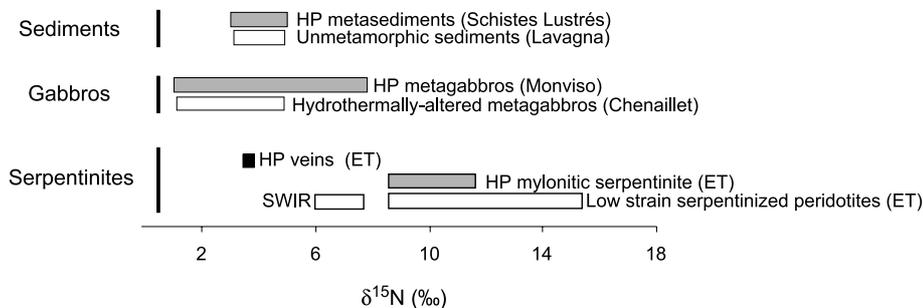

Fig. 5. Whole rock $\delta^{15}N$ values of the Erro Tobbio metaperidotites, HP vein and mylonitic serpentinite, South West Indian Ridge (SWIR) serpentinized peridotites, Monviso UHP metagabbros and their hydrothermally-altered equivalents from Chenaillet, and HP to UHP metasediments from the Schistes Lustrés nappe and their unmetamorphosed equivalent from the Appennine
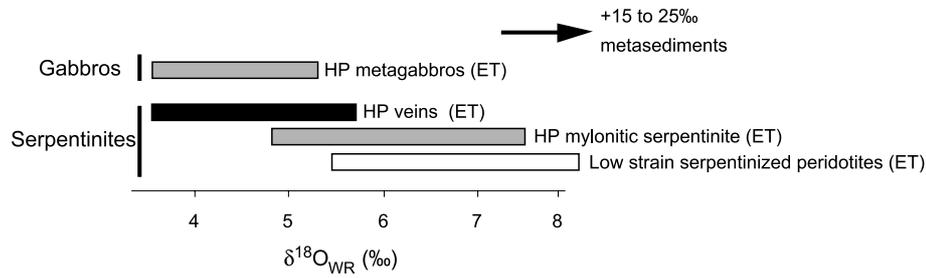
Fig. 6. Whole rock $\delta^{18}O$ values of the Erro Tobbio metaperidotites, HP vein and mylonitic serpentinite and surrounding HP metagabbros (data from *Früh-Green* et al., 2001)

metagabbros (*Busigny* 2004; unpublished data) from the same Schistes Lustrés nappe. Figure 5 shows that a fluid-derived contamination arising from either meta-sediments or metagabbros could account for the observed $\delta^{15}N$ value of the HP vein. Figure 6 plots the oxygen isotope composition of the Erro Tobbio oceanic serpentinites, HP serpentines and veins together with associated eclogitic metagab-bros of *Früh-Green* et al. (2001) as well as the range of $\delta^{18}O$ values of Alpine metasedimentary rocks of *Henry* et al. (1996). The range of $\delta^{18}O$ of the HP ser-pentinite veins is similar to that of surrounding metagabbros but very different from the HP metasediments by more than 10–20‰. In contrast to nitrogen, which is a trace element, hence sensitive to fluid processes, oxygen is a major supporting element of silicate minerals. Modifying the $\delta^{18}O$ signature of a rock would require much greater quantities of exchanging material. Yet, if a fluid phase derived from the sediments was percolating the ultramafic/gabbroic sequence, one would expect to see an effect on the stable isotope composition of the HP serpen-tinite vein. Considering that the sediments $\delta^{18}O$ values range between 15 and 20‰, and that the host serpentinite $\delta^{18}O$ values range between 5 and 8‰, a fluid of sedimentary origin controlling HP serpentinite vein formation should produce a higher ^{18}O imprint than the surrounding HP mylonites. The HP vein shows a sig-nificantly lower $\delta^{18}O$ value than its host mylonitic serpentinite, which is at odd with a sedimentary fluid component involved in its formation. The fact that the HP veins show the same range of $\delta^{18}O$ values as the surrounding metagabbros suggests a local buffering by the metagabbros. Further supports for a local origin of the fluids arises from the large range of $\delta^{18}O$ of the serpentinite veins, hence large heterogeneity of the veins, which is best accounted for by a relatively small-scale of isotopic equilibration. Involvement of a gabbroic component in the formation of the HP veins is also supported, although not demonstrated, by the trace element composition of the veins. As shown in Fig. 7, the normalized trace element pattern of the Erro Tobbio HP veins display a positive Ti anomaly which is not present in the host HP serpentinites (*Scambelluri* et al., 2001). This is best explained by the involvement of surrounding Fe-Ti metagabbros (*Scambelluri* et al., 1995) rather than a metasedimentary source. We conclude that the HP vein is probably not representative of the fluids released during mylonitization. In our view, the most likely explanation is that deformation is the key parameter to account for the negative correlation between water and nitrogen contents found in Fig. 2. Increas-ing water content may have enhanced deformation, which in turn may have favored
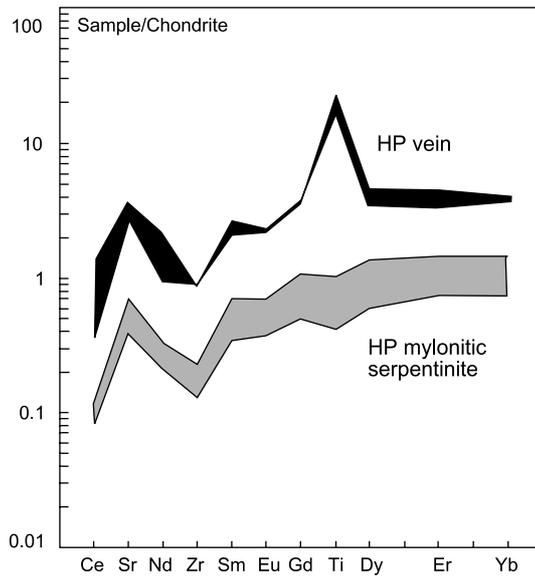
Fig. 7. Extended trace element pattern of Erro Tobbio HP vein and mylonitic serpentinite (data from *Scambelluri* et al., 2001)

nitrogen released from the rock "porosity" or mineral structure depending on where nitrogen is localized in serpentinites. This model relies heavily on the assumption that available data on present-day altered peridotites from the SWIR could be extended to Alpine samples. Additional studies are required to test this hypothesis.

The Erro Tobbio ultramafics studied here and associated metasediments from the Schistes Lustrés nappe investigated by *Busigny* et al. (2003a) can be considered as representative of processes active down to the depth locus of island arc magmatism (i.e. 90–100 km depth) in most modern subduction zones. Our nitrogen isotope analyses of serpentinites coupled with $\delta^{18}O$ systematics suggest involvement of a mafic (crustal) component during partial deserpentinization of the subducted oceanic mantle at the depth locus of island arc magmatism. This does not necessarily imply large scale fluid fluxes as the metagabbros are spatially associated with the analyzed serpentinites. In contrast we rather infer preservation of presubduction chemical and isotopic heterogeneities on a local scale as documented in Alpine metasediments (*Busigny* et al., 2003a) and in mafic protoliths (e.g., *Philippot*, 1993; *Barnicoat* and *Cartwright*, 1995; *Scambelluri* and *Philippot*, 2001). The HP vein contains metamorphic olivine that formed at the expense of antigorite at a minimum pressure of about 2.5 GPa. This indicates that nitrogen could be recycled continuously into newly formed HP minerals during subduction to great depth, hence supporting the notion that nitrogen stored in ultramafic rocks could be subducted far deeper than the depth locus of island arc magmatism.

The role of serpentinites in recycling nitrogen and other volatiles in subduction zones remains largely unknown due to large uncertainties in estimating the degree of serpentinization of the oceanic lithosphere (*Mével*, 2003). In fast spreading ridges, most evidence suggests that the crust is layered and consists of extrusive basalts, a dike complex and a massive gabbro layer overlying mantle peridotites, with little evidence of serpentinized peridotites. In contrast, *Cannat* et al. (1995) suggested that exposure of serpentinites could represent 20% of the seafloor, that is

about 5–15% in volume of the crust for low spreading rates. In modern environments, considering the vast extension of fast spreading ridges compared to slow and ultraslow spreading ridges suggests that the degree of serpentinization should not exceed a few % of the lithosphere (*Mével*, pers. comm.). Estimated fluxes of basalts and gabbros are of the order of 2.0×10^{16} and 4.0×10^{16} g/yr, respectively (*Peacock*, 1990). Considering that serpentinized peridotites represent 5% at most of the oceanic lithosphere leads to a flux of serpentinites of about 3.0×10^{15} g/yr. Considering a mean nitrogen concentration of 3.2 ppm for serpentinites results in nitrogen flux estimates of about 9×10^9 g/yr. This value is 2 orders of magnitude lower than the sedimentary nitrogen flux (7.2×10^{11} g/yr, *Busigny* et al., 2003a), thus suggesting that the contribution of serpentinized peridotites to the nitrogen budget is minor compared to that of sediments and mafic rocks. Clearly, additional constraints on the degree of serpentinization of the oceanic lithosphere are needed to test this hypothesis.

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References

Ader M, Cartigny P, Boudou JP, Oh JH, Petit E, Javoy M (2006) Nitrogen isotopic evolution of carbonaceous matter during metamorphism: methodology and preliminary results. Chem Geol (in press)

Agard P, Jolivet L, Goffé B (2001) Tectonometamorphic evolution of the Schistes Lustrés complex: implications for the exhumation of HP and UHP rocks in the western Alps. Bull Soc Geol Fr 5: 617–636

Barnicoat AC, Cartwright I (1995) Focused fluid flow during subduction: oxygen isotope data from high-pressure ophiolites of the western Alps. Earth Planet Sci Lett 132: 53–61

Bebout GE, Fogel M (1992) Nitrogen-isotope compositions of metasedimentary rocks in the Catalina Schist, California: implications for metamorphic devolatilization history. Geochim Cosmochim Acta 56: 2839–2849

Bigeleisen J, Perlman ML, Prosser HC (1952) Conversion of hydrogenic materials to hydrogen for isotopic analysis. Anal Chem 24: 1356–1357

Boyd SR, Rejou-Michel A, Javoy M (1994) Noncryogenic purification of nanomole quantities of nitrogen gas for isotopic analysis. Anal Chem 66: 1396–1402

Busigny V (2004) Comportement géochimique de l'azote dans les zones de subduction. PhD Thesis, Université Denis Diderot, 301 pp

Busigny V, Cartigny P, Philippot P, Ader M, Javoy M (2003a) Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the schistes Lustrés nappe (western Alps, Europe). Earth Planet Sci Lett 215: 27–42

Busigny V, Cartigny P, Philippot P, Javoy M (2003b) Ammonium quantification in muscovite by infrared spectroscopy. Chem Geol 198: 21–31

Busigny V, Ader M, Cartigny P (2005) Quantification and isotopic analysis of nitrogen in rocks at the ppm level using sealed-tube combustion technique: a prelude to the study of altered oceanic crust. Chem Geol 223: 249–258

Cannat M, Mével C, Maïa M, Deplus C, Gente P, Agrinier P, Belarouchi A, Dubuisson G, Humler E, Reynolds JR (1995) Thin crust, ultramafic exposure and rugged faulting patterns at the Mid-Atlantic Ridge (22–24° N). Geology 23: 49–52

Cartigny P, De Corte K, Shatsky VS, Ader M, De Paepe P, Sobole NV, Javoy M (2001) The origin and the formation of metamorphic microdiamonds from the Kokchetav massif, Kazakhstan: a nitrogen and carbon isotopic study. Chem Geol 176: 265–281

Decitre S (2000) Variations de la composition isotopique du lithium dans les péridotites océaniques serpentinisées et dans le manteau: implications pour le cycle du lithium. PhD Thesis, Institut National Polytechique de Lorraine, 250 pp

Decitre S, Deloule E, Reisberg L, James R, Agrinier P, Mèvel C (2002) Behavior of Li and its isotopes during serpentinization of oceanic peridotites. Geochem Geophys Geosystems 3: 1007 (doi: 10.1029/2001GC000178)

Domanik KJ, Holloway JR (2000) Experimental synthesis and phase relations of phengitic muscovite from 6.5 to 11 GPa in a calcareous metapelite from the Dabie Mountains, China. Lithos 52: 51–77

Fischer TP, Hilton DR, Zimmer MM, Shaw AM, Sharp ZD, Walker JA (2002) Subduction and recycling of nitrogen along the Central American margin. Science 297: 154–1157

Früh-Green GL, Scambelluri M, Vallis F (2001) O–H isotope ratios of high-pressure ultramafic rocks: implications for fluid sources and mobility in the subducted hydrous mantle. Contrib Mineral Petrol 141: 145–159

Henry C, Burkhard M, Goffé B (1996) Evolution of synmetamorphic veins and their wall-rocks through a western Alps transect: no evidence for large-scale fluid flow. Stable isotope, major- and trace-element systematics. Chem Geol 127: 81–109

Hermann J, Green DH (2001) Experimental constraints on high pressure melting in subducted crust. Earth Planet Sci Lett 188: 149–168

Martin S, Polino R (1984) Le metaradiolariti a ferro di Cesana (Valle di Susa-Alpi occidentali). Mem Soc Geol It 29: 107–125

Messiga B, Scambelluri M, Piccardo GB (1995) Formation and breakdown of chloritoid-omphacite high-pressure assemblages in mafic systems: evidence from the Erro-Tobbio eclogitic metagabbros (Ligurian Western Alps). Eur J Mineral 7: 1149–1167

Mével C (2003) Serpentinization of abyssal peridotites at mid-ocean ridges. C R Geoscience 335: 825–852

Mingram B, Bräuer K (2001) Ammonium concentration and nitrogen isotope composition in metasedimentary rocks from different tectonometamorphic units of the European Variscan Belt. Geochim Cosmochim Acta 65: 273–287

Moran AE, Sisson VB, Leeman WP (1992) Boron depletion during progressive metamorphism: implications for subduction processes. Earth Planet Sci Lett 111: 331–349

Pawley AR, Holloway JR (1993) Water sources for subduction zone volcanism – new experimental constraints. Science 260: 664–667

Peacock SM (1990) Fluid processes in subduction zones. Science 248: 329–336

Philippot P (1993) Fluid-melt-rock interaction in mafic eclogites and coesite-bearing metasediments: constraints on volatile recycling during subduction. Chem Geol 108: 93–112

Philippot P, Selverstone J (1991) Trace-element rich brines in eclogitic veins; implications for fluid composition and transport during subduction. Contrib Mineral Petrol 106: 417–430

Poli S, Schmidt MW (2002) Petrology of subducted slabs. Ann Rev Earth Planet Sci 30: 207–235

Reinecke T (1991) Very-high pressure metamorphism and uplift of coesite-bearing metasediments from the Zermatt-Saas Zone, western Alps. Eur J Mineral 3: 7–17

Reinhardt M (1991) Vitrinite reflectance, illite crystalinity and tectonics: results from the Northern Apennines (Italy). Org Geochem 17: 175–184

Scambelluri M, Philippot P (2001) Deep fluids in subduction zones. Lithos 55: 213–227

Scambelluri M, Muentener O, Hermann J, Piccardo GB, Trommsdorff V (1995) Subduction of water into the mantle: history of an alpine peridotite. Geology 23: 459–462

Scambelluri M, Piccardo GB, Philippot P, Robbiano A, Negretti L (1997) High salinity fluid inclusions formed from recycled seawater in deeply subducted alpine serpentinite. Earth Planet Sci Lett 148: 485–500

Scambelluri M, Rampone E, Piccardo GB (2001) Fluid and element cycling in subducted serpentinite: a trace element study of the Erro-Tobbio high-pressure ultramafites (western Alps, NW Italy). J Petrol 42: 55–67

Scambelluri M, Müntener O, Ottolini L, Pettke T, Vannucci R (2004) The fate of B, Cl and Li in the subducted oceanic mantle and in the antigorite-breakdown fluids. Earth Planet Sci Lett 222: 217–234

Sharp ZD, Barnes JD (2004) Water soluble chlorides in massive seafloor serpentinites: a source of chloride in subduction zones. Earth Planet Sci Lett 226: 243–254

Shaw AM, Hilton DR, Fischer TP, Walker JA, Alvarado GE (2003) Contrasting He–C relationships in Nicaragua and Costa Rica: insights into C cycling through subduction zones. Earth Planet Sci Lett 214: 499–513

Straub SM, Layne GD (2003) The systematics of chlorine, fluorine, and water in Izu arc front volcanic rocks: implications for volatile recycling in subduction zones. Geochim Cosmochim Acta 67: 4179–4203

Synder G, Poreda R, Hunt A, Fehn U (2001) Regional variations in volatile composition: isotopic evidence for carbonate recycling in the Central American volcanic arc. Geochem Geophy Geosystems 2 (doi: 10.129/2001GC000163)

Ulmer P, Trommsdorff V (1995) Serpentinite stability to mantle depths and subduction-related magmatism. Science 268: 858–861

Zimmer MM, Fischer TP, Hilton DR, Alvarado GE, Sharp ZD, Walker JA (2004) Nitrogen systematics and gas fluxes of subduction zones: insights from Costa Rica arc volatiles. Geochem Geophy Geosystems 5 (doi: 10.1029/2003GC000651)

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