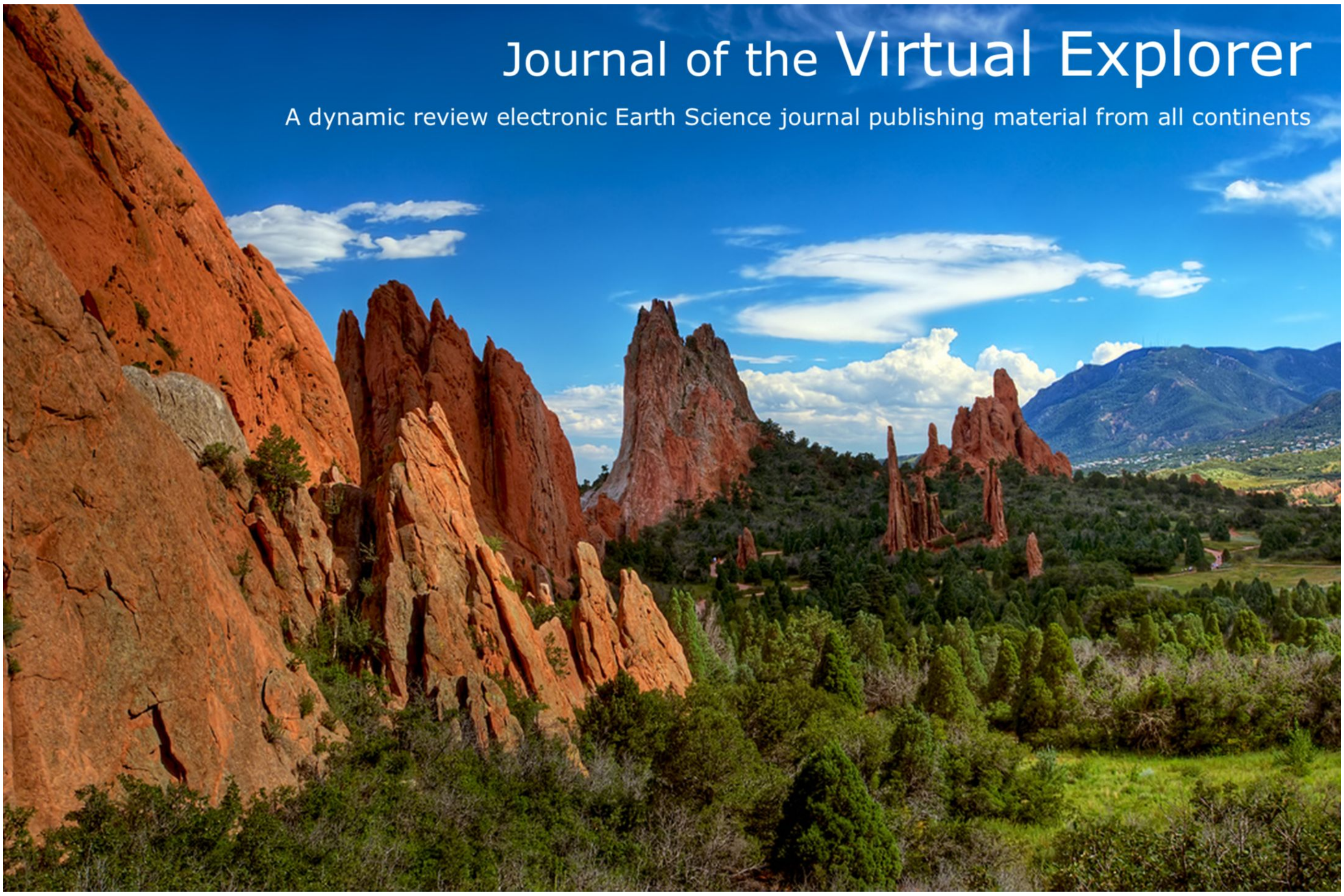

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Abstract: Earth's CO_2 emission in Italy includes both volcanic and non-volcanic degassing, with measured CO_2 fluxes of about 35 - 60 Mt/y. Zones of non-volcanic CO_2 emission include Tuscany, Latium, Campania, the Apennines, Sicily, and Sardinia. Volcanic emissions are particularly abundant at Mt. Etna in Sicily, but also at Vesuvio, Campi Flegrei, Ischia, Vulcano, and Stromboli, in Central-Southern Italy. The anomalous CO_2 emission in Italy is related to the complex geodynamic evolution of this area, in which upper crustal rocks, including carbonate sediments, have been introduced into the upper mantle by Oligocene to present subduction processes. Integrated petrological, geochemical and geophysical data allow us to work out a model for the generation of anomalously high lithospheric CO_2 fluxes. Melting of sediments and/or continental crust of the subducted Adriatic-Ionian (African) lithosphere at pressure greater than 4 GPa (130 km) is proposed to represent an efficient mean for deep carbon cycling into the upper mantle and into the exosphere in the Western Mediterranean area. Melting of carbonated lithologies, induced by the progressive rise of mantle temperatures behind the eastward retreating Adriatic-Ionian subducting plate formed a carbonated partially molten CO_2-rich mantle in the depth range from 130 km to 70 km. Further upwelling of carbonate-rich melts induces massive outgassing of CO_2. Buoyancy forces, probably favored by fluid overpressures, are able to allow migration of CO_2 from the mantle to the surface, through deep lithospheric faults, and its accumulation beneath the Moho, and within the lower crust.

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Introduction

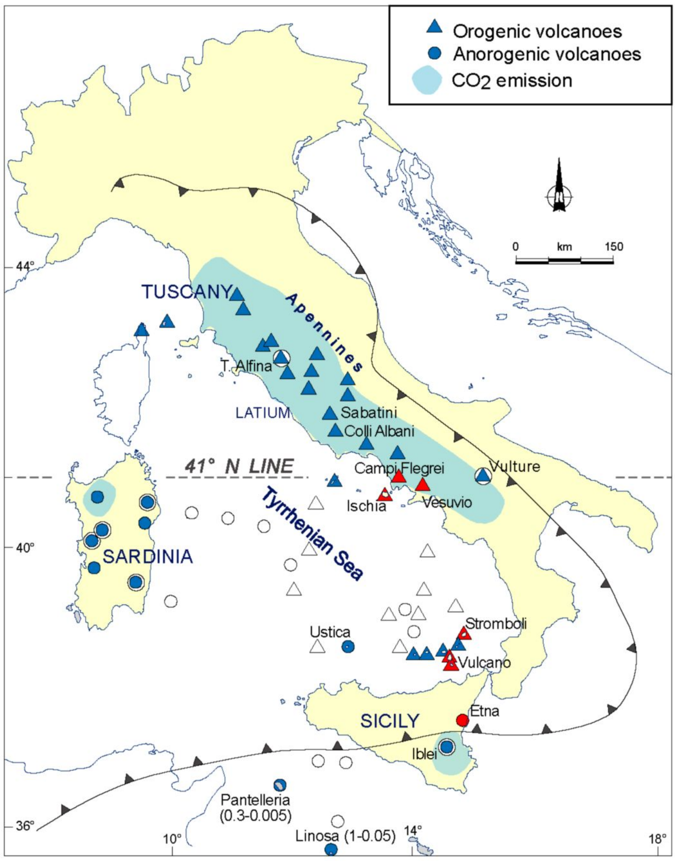
Italy is the site of extensive CO_2 degassing by active volcanoes and by direct soil emission: active Italian volcanoes (e.g., Etna, Vesuvio, Campi Flegrei, Ischia, Vulcano, Stromboli, and Pantelleria) represent a relevant CO_2 source, distributed along Central-Southern peninsular Italy, and in Sicily; in addition, hundreds of zones of CO_2 soil degassing are located in Tuscany, Latium, Campania, the Apennines, Sicily, and Sardinia (Fig. 1; e.g., Allard *et al.*, 1991; Chiodini *et al.*, 1999, 2004; Rogie *et al.*, 2000; Chiodini and Frondini, 2001). Present day Earth's degassing in Italy amounts to 35 - 60 Mt CO_2/year (Mörner and Etiope, 2002, and references therein), about 7 – 12 % of the national anthropogenic CO_2 emissions (457 Mt CO_2/year in 2004; Bassani *et al.*, 2009). Thus, secular variations of Earth's degassing, at the Quaternary scale, may bear influence the present-day atmospheric natural carbon budget.

Cycling of carbon within the solid Earth represents the fundamental basis to understand the long-term (millions to billions of years) global carbon cycle, and influences the solid Earth's CO_2 contribution to the atmosphere. Global estimates of volcanic mantle degassing, based on computations - involving C cycle modeling and the mass flux of volcanic material - indicate 100 -370 Mt CO_2/y (cf., Table 1, and references therein). More difficult appears an evaluation of the non-volcanic CO_2 direct degassing from the lithosphere at the global scale: conservative estimates are in the order of 100 to 600 Mt/y (Table 1; Kerrick *et al.*, 1995; Mörner and Etiope, 2002).

The mantle represents the largest Earth's carbon reservoir (about 80 - 200 x 106 Gt), containing greatly much more carbon than the atmosphere (600 Gt), oceans (39,000 Gt), and other near-surface reservoirs combined (cf., Shcheka *et al.*, 2006, and references therein). Thus, the starting point to understand the deep carbon cycle resides in the theory of plate tectonics: in order to balance the continuous natural CO_2 emission, carbon must be recycled in the mantle (Zhang and Zindler, 1993). Carbon directly deposited on the ocean floor (i.e., pelagic carbonates and organic carbon) and carbonates formed by seawater alteration of basalts may account for an yearly CO_2 flux of about 100 - 150 Mt into the mantle by subduction (Alt and Teagle, 1999; Coltice *et al.*, 2004).

Experimental petrology has demonstrated how melting of subducted lithosphere may extract carbon from the subducting crust, whereas refractory carbonate minerals could allow transport of carbon to the 400 km and 600 km transition zones or to the lower mantle (e.g., Kerrick and Connolly, 2001a and b; Dasgupta *et al.*, 2004; Thomsen and Smith, 2008). When melting occurs, return of subducted carbonated rocks by mobile carbonate melts through the mantle is geologically rapid, less than a few million years (Hammouda and Laporte, 2000). A first quantitative evaluation of deep CO_2 fluxes from the deep upper mantle beneath mid ocean ridges (MOR) has been presented by Dasgupta *et al.* (2006), based on petrological modeling. Estimated mantle CO_2 fluxes are between 120 - 3,400 Mt /y, and although quite variable, are compatible with estimates of MOR-volcanism CO_2 emission (Table 1; Cartigny *et al.*, 2008).

Figure 1. Earth's CO_2 emission in Italy



Earth's CO_2 emission in Italy, as derived from the online catalogue of Italian gas emissions (blue area; http://googas.ov.ingv.it; Chiodini and Valenza, 2007), and from the distribution of the main Plio-Quaternary volcanoes (Peccerillo, 2005). Active volcanoes in red. Open symbols refer to outcrops below the sea level). Volcanic centers marked by white circle bear peridotite xenoliths.

Table 1. Earth's CO_2 degassing

Reference	Volcanic CO_2		Total	Non-Volcanic CO_2
	Sub Aerial	Sub Aqueous		Soil Emission
	Mt/y	Mt/y	Mt/y	Mt/y (km^2)
Global Extrapolations *				
Gerlach, 1991a	80	22-40	102-120	
Allard, 1992	66			
Marty & Le Cloarec, 1992	66-110			
Brantley & Koepenick, 1995	88-132			
Kerrick, 2001	88-110			
Morner & Etiope, 2002			300	>600
Kerrick *et al.*, 1995				44
Global Estimates +				
Williams *et al.*, 1992	64			
Varekamp *et al.*, 1992	145	66-97		
Sano & Williams, 1996	136	44-132		
Marty & Tolstikhin, 1998	242	57-136	367	
Cartigny *et al.*, 2008, Atlantic MOR		101		
* flux measurements and extrapolations to the total number of active volcanoes.				
+ Computations involving C cycle modeling, and the mass flux of volcanic material				

At the regional scale, deep cycling of Earth's carbon - i.e. how decarbonation or melting of carbonate-rich lithologies from a subducted lithosphere may affect the efficiency of carbon release in the lithosphere-asthenosphere system - was recently investigated in the western Mediterranean region by Frezzotti *et al.* (2009), who presented an integrated petrological and geophysical model that explains the present-day CO_2 degassing in Italy. In this paper, we summarize the main data on Earth's CO_2 emission in Italy, and review the mechanical properties of the lithosphere-asthenosphere system along some key sections in the western Mediterranean region to discuss the possible origin of deep CO_2 emission in volcanic and non-volcanic areas, in the light of the main geophysical and geochemical features of the upper mantle in the Italian region.

Earth's CO_2 emissions in Italy

In Italy, the CO_2 degassing from both zones of active volcanism and also from non-volcanic areas, represents an important and widespread phenomenon mainly observed in the central and southern part of the country, where Plio-Quaternary volcanoes are located (Fig. 1; Table 2).

Volcanic CO_2 emissions

Active volcanism represents a fundamental process by which deep CO_2 is released to the atmosphere. Although relevant CO_2 emissions occur during volcanic eruptions, non-eruptive diffuse degassing at the vent or through the flanks of active volcanoes has been recognized as the principal CO_2 release mechanism to the atmosphere (Table 2; and references therein).

Table 2. Selected measurements of volcanic and non-volcanic CO_2 emissions

Locality	**Volcanic CO_2**	**Non-volcanic CO_2**
	Mt/y	Mt/y (km^2)
Italy		
Etna crater 1976-1985 - Allard *et al.*, 1991	25.5	
Etna crater 1993-1997 - Allard, 1998	4-13	
Etna flanks - D'Alessandro *et al.*, 1998	0.6-6	
Stromboli crater - Allard *et al.*, 1994	1-2	
Stromboli flanks - Carapezza & Federico, 2000	0.07-0.09	
Vulcano fumaroles, Italiano *et al.*, 1998	0.13	
Vulcano crater - Baubron *et al.*, 1990	0.06	
Vesuvio - Frondini *et al.*, 2004	0.50	
Ischia diffuse - Pecoraiano *et al.*, 2005	0.47	
Campi Flegrei, Solfatara diffuse, Chiodini *et al.*, 2001	0.55	
Pantelleria diffuse - Favaro *et al.*, 2001	0.39	
Ustica - Etiope *et al.*, 1999		0.26 (9)
Central Appennine - Chiodini *et al.*, 2000		4-13.2 (12,000)
Tuscany and N. Latium - Chiodini *et al.*, 2004		6
Campania - Chiodini *et al.*, 2004		3
Mefite D'ansanto - Rogie *et al.*, 2000		0.3
Larderello and Amiata (Tuscany) - Chiodini *et al.*, 2000		2.2
Mofeta dei Palici, Sicily - De Gregorio *et al.*, 2002		0.1
Siena basin - Etiope, 1996		0.5 (200)
Regional		
Pinatubo 1991 eruption (Philippines) - Gerlach *et al.*, 1996	42	
Popocatepetl crater - Varley & Arminta, 2001	21.9	
Nyiragongo crater (Congo) - Saywer *et al.*, 2008	23	
Masaya Caldera diffuse (Nicaragua) - Perez *et al.*, 2000	10.5	
Kilauea crater (Hawaii) - Gerlach *et al.*, 2002	3.3	
Oldonio Lengai crater (Tanzania) - Koepnick, 1995	2.2 -2.6	
Masaya crater (Nicaragua) - Burton *et al.*, 2000	0.8-1.13	
Rabaul Caldera (Papua N.G.) - Perez *et al.*, 1998	0.88	
Erebus crater (Antarctica) - Wardell & Kyle, 2003	0.7	
Teide flanks (Tenerife, Spain) - Salazar *et al.*, 1997	0.2	
Usu crater (Japan) - Hernandez *et al.*, 2001	0.04-0.12	
Mout Baker crater (Washington, USA) - Mc Gee *et al.*, 2001	0.07	

Locality	Volcanic CO_2	Non-volcanic CO_2
Back arc Pacific Rim - Seward & Kerrick, 1996		44
Nisyros soil (Greece) - Brombach *et al.*, 2001		0.8
St. Andreas fault (California, USA) - Lewicki & Brantley, 2000		0.3 (60)
Mammoth Mount. (California) - Rahn *et al.*, (1996)		0.15 (0.4)
Himalaya Mount. (India) - Becker *et al.*, 2008		39.6

Active volcanoes (Fig. 1) are located in the southern part of continental Italy; (e.g., Vesuvio; Campi Flegrei; Ischia), in Sicily (e.g., Etna) and Sicily channel (e.g., Pantelleria), and in the Southern Tyrrhenian sea (Fig. 1; e.g., Vulcano; Stromboli; Lipari). Based on direct source-point measurements, the overall volcanic CO_2 emission budget is conservatively (lower bound) estimated at about 30 Mt CO_2/y (see references in Table 2). Measured Etna CO_2 fluxes through time vary from 13 to 43.8 Mt/y (average 25 Mt/y; Allard *et al.*, 1991; Gerlach, 1991b). Further CO_2 (about 1-5 Mt/y) emission occurs from the flanks and the summit area of the volcano. Other active volcanoes (i.e., Stromboli, Vesuvio, Campi Flegrei, Ischia, Vulcano, Pantelleria) emit considerably lower - although quite variable - amounts of CO_2 (in the order of 0.2 – 2 Mt/y; Table 2).

Etna represents one of the strongest CO_2-emitting volcanoes at the global scale (Table 2). Gerlach (1991a and b) indicated Etna as a point-source "singularity", contributing alone to about one third of the global CO_2 by subaerial volcanism (cf., Table 1). More recently, the increase of measurements has shown diffuse CO_2 emission from other active volcanoes in the same order of magnitude than Etna, i.e. Nyariagongo, and Popocaptel (Table 2).

The reasons behind extreme CO_2 enrichments in magmas are debated (Gerlach, 1991a and b; Kerrick, 2001). The CO_2 content of degassing magmas reflects mantle source composition, but can be modified by crustal processes during magma rise and rest. In Italy, interaction between magmas and carbonate wall-rocks at crustal levels (i.e., magma chambers) has been proved to contribute substantial CO_2 at Vesuvio and Colli Albani volcanoes, via magma assimilation processes of carbonates. This is testified as by a wealth of petrological and geochemical data, including high oxygen isotopic compositions of igneous rocks and minerals, and by the effects on paths of magma evolution at these centers, which are dominated by clinopyroxene separation induced by heavy carbonate assimilation (e.g., Dallai *et al.*, 2004; Gaeta *et al.*, 2006; Iacono Marziano *et al.*, 2007a and b; Peccerillo *et al.*, 2010).

The relative contributions of these processes and of direct mantle provenance to the overall emission of volcanic CO_2 is highly debated (Iacono Marziano *et al.*, 2007b, 2009; Gaeta *et al.*, 2009). CO_2 degassing at Etna mostly reflects mantle-derived carbon from aa MORB type source enriched by metasomatic fluids, with only subordinate crustal CO_2 contribution (Allard *et al.*, 1997; Nakai *et al.*, 1997). Since Etna alone contributes to more than 90 % of the overall CO_2 emissions from Italian active volcanoes, the bulk of volcanic CO_2 degassing budget in Italy should represent a deep mantle-related process.

Non-volcanic CO_2 emissions

CO_2 degassing occurs in Central and Southern Italy via diffuse soil emission and focused vents, located in wide areas where volcanism is absent or is not anymore active. This is indicated as non-volcanic CO_2 emission, and includes degassing from crustal carbonate rocks, fluxing from the upper mantle, and from geothermal fields (Fig. 1; Table 2; e.g., Chiodini *et al.*, 1998; 1999; 2000; 2004; Etiope, 1999; Italiano *et al.*, 2000; Rogie *et al.*, 2000; Mörner and Etiope, 2002; Gambardella *et al.*, 2004). According to Mörner and Etiope (2002), non-volcanic CO_2 fluxes in Italy are in the same order of magnitude of volcanic degassing (from > 4 to 30 Mt/y). For example, the regional mapping of diffuse CO_2 fluxes from an area of 45,000 km^2 in Central Italy, including Tuscany, Northern Latium geothermal fields, and Central Apennine chain, indicates about 9.7 - 17 Mt CO_2/y (Fig. 1; Gambardella *et al.*, 2004).

A direct association between CO_2 soil emission and location of fault and fractures, often of deep origin, is observed (Table 2): in the axial zones of the Apennines CO_2 emission totals to 4-13 Mt /y (Chiodini *et al.*, 2004 and references therein). In the Mefite of the Ansanto valley (Irpinia; external parts of the southern Apennines), CO_2 fluxes from 0.1 to 0.3 Mt CO_2/y have been measured from gas vents over the hypocenter area of the 1980 earthquake (Italiano *et al.*, 2000; Rogie *et al.*, 2000). In Sardinia, CO_2 degassing occurs in the northern part of the Campidano Graben, (Minissale *et al.*, 1999). In Sicily, high CO_2 fluxes are measured from mofetes distributed along major fault systems that cut the eastern part of the island (De Gregorio *et al.*, 2002).

Non-volcanic CO_2 source might be located in the middle-lower crust, or at greater depth in the mantle, due to decarbonation reactions induced by increasing temperatures, or by active tectonics. Chiodini *et al.* (2000) proposed that about 40 % of the inorganic carbon of non-volcanic CO_2 derives from a source characterized by a δ13C of -3 ‰, compatible with mixed crust + mantle source, or with a mantle metasomatized by crustal fluids. Also 3He/4He ratios measured in CO_2-rich gases in non-volcanic soil emissions indicate an important mantle component (R/Ra up to 4.48; Minissale, 2004), and, interestingly, are close to values measured in lavas of recent and active volcanoes(cf., Martelli *et al.*, 2008, and references therein).

The Italian Mantle

It is generally agreed that the bulk of the CO_2 degassing in Italy should reflect deep mantle processes, with crustal contributions being significant only at a few active or recent volcanoes (Allard *et al.*, 1997; Chiodini *et al.*, 2000; Minissale, 2004; Gaeta *et al.*, 2009; Iacono Marziano *et al.*, 2009). Therefore, the clue to understand present-day massive Earth's CO_2 degassing in Italy ultimately resides in a careful knowledge of mantle processes and of their geodynamics.

The evolution of the Italian region and of the entire Western-Central Mediterranean area has been the effect of the Oligocene to Present convergence between the African and Eurasian plates. This led to the opening of the Ligurian-Provençal, Algerian, and Valencia and Tyrrhenian basins, the formation of the Apennine chain and the emplacement of a wide variety of both orogenic and anorogenic magmas (see Alagna and Peccerillo, this issue; Bianchini *et al.*, this issue; Carminati *et al.* this issue).

Orogenic magmatism started in Provence, Balearic sea and Sardinia (Oligo-Miocene) and migrated eastward in the Tyrrhenian Sea floor, in the Italian peninsula and Aeolian arc (Miocene to present). Compositions are mainly calcalkaline but potassic ultrapotassic rocks dominate in the Italian peninsula (e.g. Francalanci *et al.*, 1993; Peccerillo, 2003; Alagna and Peccerillo, this issue). Eastward migration of orogenic magmatism is related to slab rollback in the same direction (Carminati *et al.*, 1998; Doglioni *et al.*, 1999, and references therein). Anorogenic magmatism around the Tyrrhenian Sea is also variable in composition, from tholeiitic to Na-alkaline, but does not show any apparent regional migration with time, although in single areas (e.g. Sardinia) it follows orogenic activity (Savelli and Gasparotto, 1994; Lustrino *et al.* 2004, 2007a, for a review).

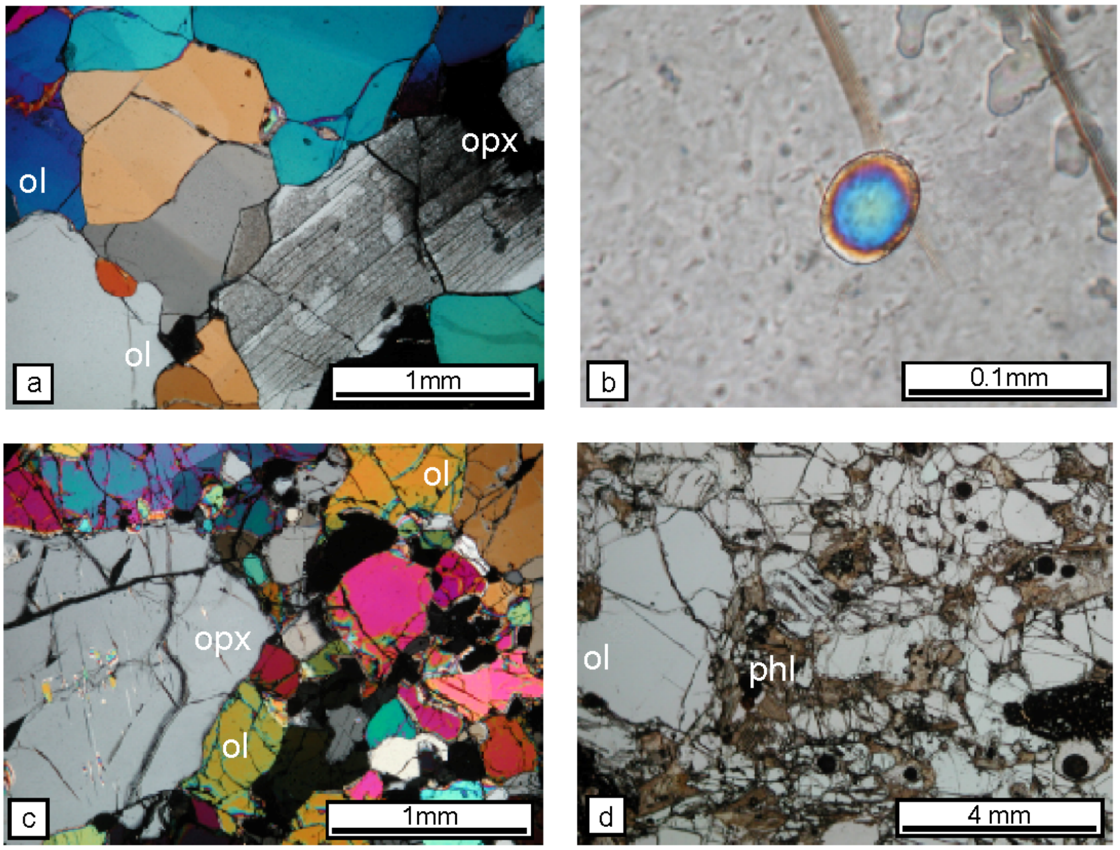
Peridotite xenoliths

Peridotite xenolith suites are present in Pliocene-Quaternary orogenic volcanics in continental Italy at Monte Vulture (0.2 M.y.), and at Torre Alfina (0.9 M.y.), and in the Miocene-Quaternary anorogenic mafic volcanics of Monti Iblei in Sicily, and in Sardinia (Fig. 1; e.g., Conticelli and Peccerillo, 1990; Conticelli, 1998; Jones *et al.*, 2000; Sapienza and Scribano, 2000; Downes, 2001; Beccaluva et la., 2001; Downes *et al.*, 2002, and references therein).

Peridotite suites consist mainly of spinel lherzolites, harzburgites, and dunites, and may contain variable amounts of metasomatic phlogopite and amphibole (Table 3). Overall, geochemical and petrological features of peridotite xenolith suites indicate a depleted mantle lithosphere beneath the Italian region resulting from ancient melting events, variably enriched by subsequent fluxes of metasomatic melts and/or fluids. In orogenic mantle settings, carbonate and hydrous-silicate melts have been proposed as the main mantle metasomatic agents by various authors (Conticelli and Peccerillo, 1990; Conticelli, 1998; Jones *et al.*, 2000; Downes *et al.*, 2002; Rosatelli *et al.*, 2007).

At Monte Vulture volcano, spinel peridotites consist of lherzolites and harzburgites, with subordinate dunites, and wehrlites, and pyroxenites (Fig. 2a), which may contain metasomatic phlogopite, amphibole, and carbonate. Peridotites equilibrated at pressures of 1.8 - 2.2 GPa (about 60-80 km of depth), and temperatures of 990 – 1150°C in the lower part of the spinel stability field (Table 3). Metasomatic enrichment processes in peridotites are testified by presence of mica, carbonates, and silicate glass in melt inclusions and microveins (Fig. 2b), and by LILE and LREE enrichments in clinopyroxene (Downes *et al.*, 2002; Rosatelli *et al.* 2007). According to Downes *et al.* (2002), peridotites show $^{87}Sr/^{86}Sr$ ratios higher than in most of the European continental lithosphere ($^{87}Sr/^{86}Sr$ = 0.7042–0.7058), suggesting that metasomatic melts could have been subduction related.

Figure 2. Photomicrographs of xenolith spinel peridotites from Vulture and Torre Alfina volcanoes.



a) harzburgite from Vulture. Olivine porphyroclasts show undulouse extinction, crossed polars (CP). b) Isolate carbonate inclusion in olivine neoblast from Vulture dunite. Rounded contours of the carbonate inclusion suggest trapping as melt phase, CP. c) Harzburgite from Torre Alfina. Two generations of olivine are recognized: large olivine porphyroclasts surrounded by medium-grained neoblasts, CP. d) Phlogopite from dunite, Torre Alfina. Phlogopite is mainly interstitial, but locally crosses single grains of anhydrous minerals. thick section, plane-polarized light.

In the orogenic lamproitic lavas of Torre Alfina volcano (Tuscany), spinel peridotite suites consist of dunites, harzburgites, and minor spinel lherzolites that may contain metasomatic phlogopite (Fig. 2c and d). Peridotites represent samples of a “hot” lithosphere, close to the asthenosphere-lithosphere boundary: recent geothermobarometric studies indicate equilibrium pressures of about 1.6 GPa, corresponding to a depth of 50 to 60 km, and temperatures of 950 – 1080°C (Table 3; Pera *et al.*, 2003).

In Torre Alfina peridotite xenoliths, metasomatic phlogopite may be present in traces, disseminated through the rock, or may constitute up to 10% of the rock by mode, distributed along short alignments (Fig. 2d). Phlogopite-rich xenoliths have been interpreted as remnants of pervasive metasomatic events in the upper mantle (Conticelli and Peccerillo, 1990). These have Sr-Nd ($^{87}Sr/^{86}Sr$ ~ 0.716 - 0.717; $^{143}Nd/^{144}Nd$ ~ 0.5121) isotopic signatures close to those of the host ultrapotassic rocks and have been suggested to represent the metasomatic veins, whose melting gave ultrapotassic magmas (Conticelli, 1998).

Table 3. Peridotite xenolith suites in Italy

Location	Rock	Ol	Mg#	Opx	Mg#	Cpx	Spinel	Amph	Phlog	Temperature	Pressure	Citation
		vol. %		vol. %		vol. %	vol. %	vol. %	vol. %	C	GPa	
Torre Alfina	Harzburgite Dunite Lherzolite	80-95	0.90-0.92	4-12	0.91-0.93	<1-8	1-2		<1 -10	950-1080	1.6 ± 0.2	Peccerillo & Conticelli 1990; Conticelli 1998; Pera *et al.* 2003
Vulture	Cpx-poor Lherzolite Harzburgite	60-86	0.90-0.91	8-30	0.91-0.93	1-10	1-2	1	<1	992-1150	1.8 ± 0.3	Jones *et al.* 2000; Downes *et al.* 2002; Rosatelli *et al.* 2007
Sardinia	Cpx-poor Lherzolite Harzburgite	60-80	0.89-0.91	10-30	0.90-0.92	4-16	1-3			950-1050	1.4 ± 0.2	Beccaluva *et al.* 2001; unpublished data
Iblei	Harzburgite Lherzolite	60-77	0.90-0.92	10-30	0.87-0.91	3-10	1-4	<1	<1	950-1050	1.1	Sapienza *et al.* 2005; Cristofolini *et al.* 2009

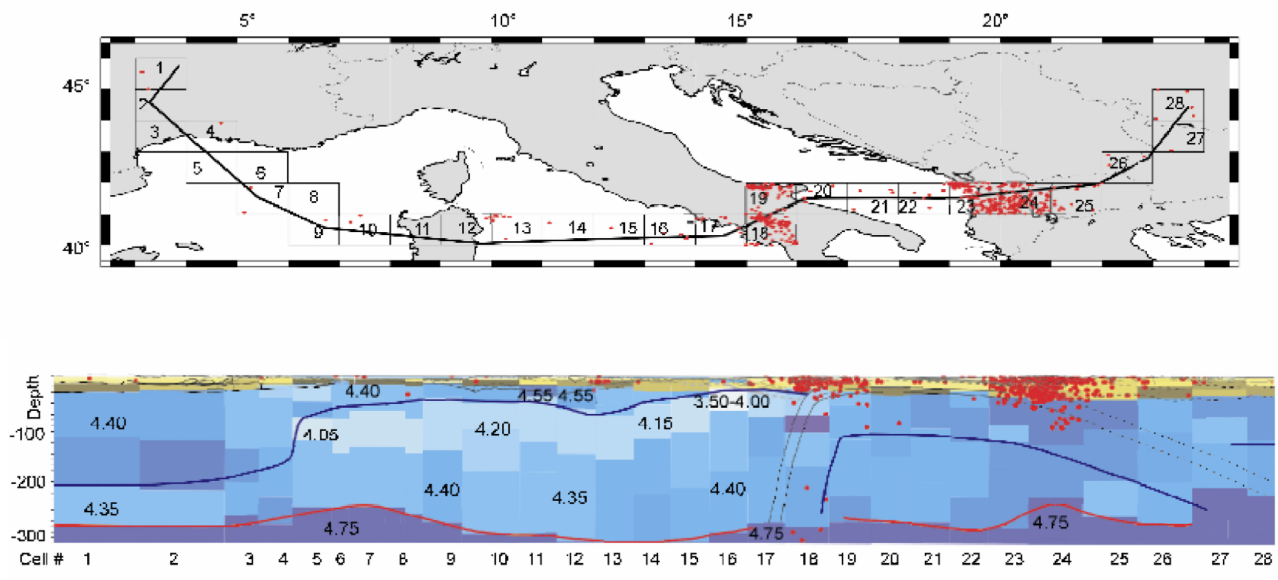
Ol= Olivine; Opx= Orthopyroxene; Cpx= Clinopyroxene; Amph= Amphibole; Phlog= Phlogopite; Mg#= Mg/(Mg/Fe_{tot})

V_S tomography

S-wave velocity tomography in the western Mediterranean and the Thyrrenian sea area is illustrated in Fig. 3. All reported data have been recently published in Panza *et al.* (2007a, and b), Boyadzhiev *et al.* (2008), and Peccerillo *et al.* (2008), where detailed information about the data, path coverage, resolution, etc. can be found. Updated information is given by Brandmayr *et al.*, this issue. Section 1 (Fig. 3a) goes from Provence to Central Sardinia and to the Campanian area, running along the 41° Parallel Line in its central and eastern segments (Panza *et al.*, 2007a). Section 2 (Fig. 3b) runs from offshore southern Sardinia to the Aeolian arc and Calabria following an E-W and then NW-SE direction (Boyadzhiev *et al.*, 2008; Peccerillo *et al.*, 2008). Section 3 (Fig. 3b) is located in the central-northern Tyrrhenian Sea and goes through the Tuscany and Roman magmatic provinces (Panza *et al.*, 2007b).

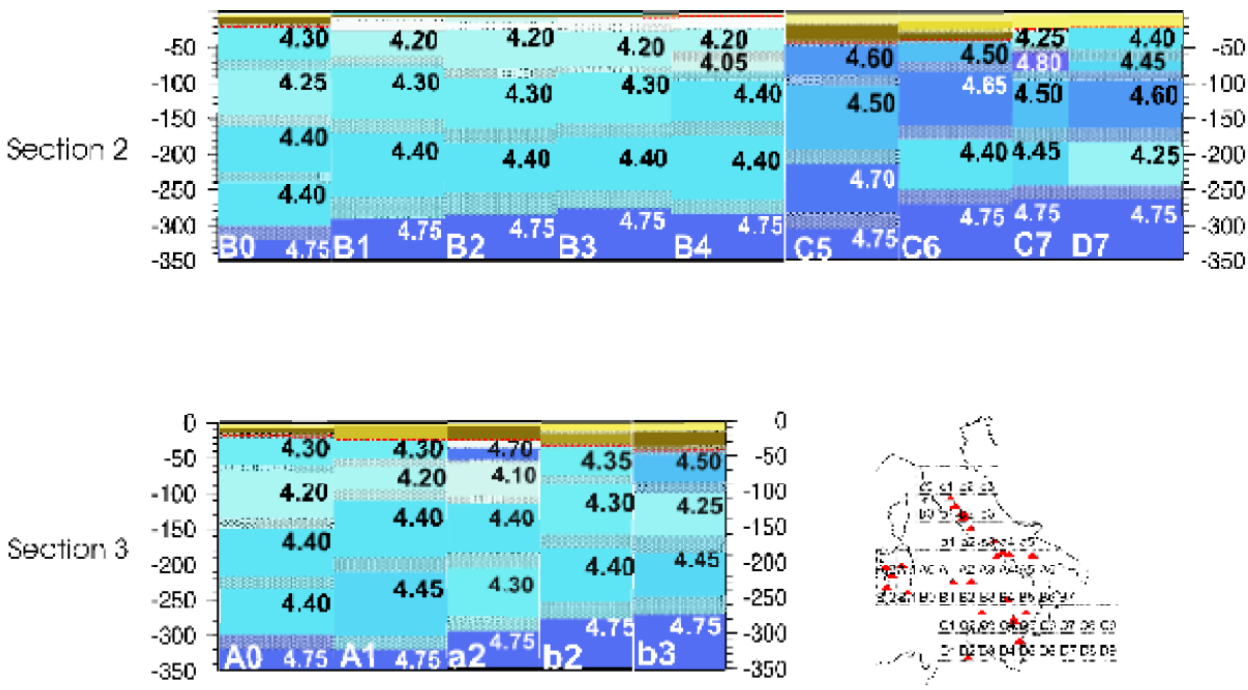
Section 1 running from Provence to Sardinia, central Tyrrhenian Sea, up to the Campanian volcanoes (Vesuvio, Campi Flegrei) (Fig. 3) shows variable features in the lithosphere-asthenosphere system. The upper mantle beneath continental France shows rather constant S-wave velocities (V_S ~ 4.3-4.5 km/s) down to 250 km of depth. Starting from off-coast Provence, the upper mantle structure changes significantly because of the presence of a layer with relatively low S-wave velocities (V_S = 4.0-4.1 km/s) at a depth of about 70-120 km.

Figure 3. V_S models of the lithosphere-asthenosphere system along the TRANSMED III geotraverse



Modified from Panza *et al.* (2007a); the geometry of the base of the lithosphere is indicated by the blue line; the limit between upper and lower asthenosphere is indicated (red line).

Figure 4. Sections 2 and 3, built from the cellular V_S model of the Tyrrhenian Sea and surroundings (Panza, 2007a).



In each labeled cell, the hatched zone stands for the thickness variability, while, to avoid crowding of numbers, only the average shear velocity is reported. The V_S ranges of variability are given in Panza *et al.* (2007a and b). Red triangles indicate recent and active volcanoes.

This low velocity layer is delimited, at the top and at the bottom, by high-velocity material (V_S ~ 4.30-4.55 km/s) and it extends eastward from offshore Provence to the Magnaghi and Vavilov basins, with almost constant thickness. From the Pontine Island to the Campanian area, the low velocity layer raises to a shallower level, with a decrease of V_S that can be as low as about 3.4 km/s. A low velocity layer beneath the Western Mediterranean area was also detected by P-wave tomography (Hoernle *et al.* 1995) and was interpreted as an isolated portion of a large scale mantle up-welling affecting the Western Atlantic and Central-Southern Europe.

In section 2 (Fig. 4), which goes from Sardinia to the southeast, crossing the Aeolian Arc and Calabria, the low velocity layer is much shallower being detected at 30 km to 70 km of depth and rising to 0-30 km beneath the eastern active Aeolian volcanoes. An almost vertical seismically active high-velocity body with V_S from 4.50 to 4.80 km/s likely representing the descending Ionian slab (Panza *et al.*, 2003), interrupts the low velocity layer beneath Calabria.

Finally, section 3 (Fig. 4) goes across the central Tyrrhenian Sea, the Tuscany and Roman magmatic province and the Apennines. In its western segment, it is characterized by a low velocity layer with V_S = 4.1-4.2 km/s at about 60-120 km of depth that becomes shallower in the Roman Province (about 30-50 km).

Carbon-cycling through subduction beneath the Italian region

Mantle structure

Peridotite xenolith suites testify for a depleted mantle lithosphere, refertilized in orogenic regions by conspicuous metasomatic processes induced by hydrous silicate ± carbonate melts of subductive origin. At greater pressures, the most prominent feature evidenced by geophysical data is the occurrence of a low-velocity layer from about 70 to 120 km depth (1.8-4.0 GPa) that extends from the south-eastern Provence to the south-eastern Tyrrhenian Sea areas (Fig. 3). This coincides with the zone of slab migration from Oligocene to present and it is associated with orogenic magmatism of the same age, which migrated east- and southeast-ward as an effect of slab rollback (Panza *et al.*, 2007a). In this view, the low-velocity layer represents a sort of tail of mantle anomalies left behind by the retreating slab. According to Panza *et al.* (2007a), the upraise to shallow depths of this layer beneath the Campanian area is related to the eastward mantle flow above the retreating slab. Peccerillo *et al.* (2008) explain this low-velocity layer as the effect of geochemical anomalies generated by the subducting slab during rollback. An important piece of evidence in support of this possibility is the absence of such a layer in zones which were not affected by recent subduction (i.e., continental France and Spain, and Southern Sicily). In the latter, where the well-known ephemeral volcano of Ferdinandea (Graham) island was formed in 1831, the thin low-velocity layer observed offshore, west and south-west Sicily, likely reveals local zones of melting, possibly due to lithospheric decompression along strike-slip faults.

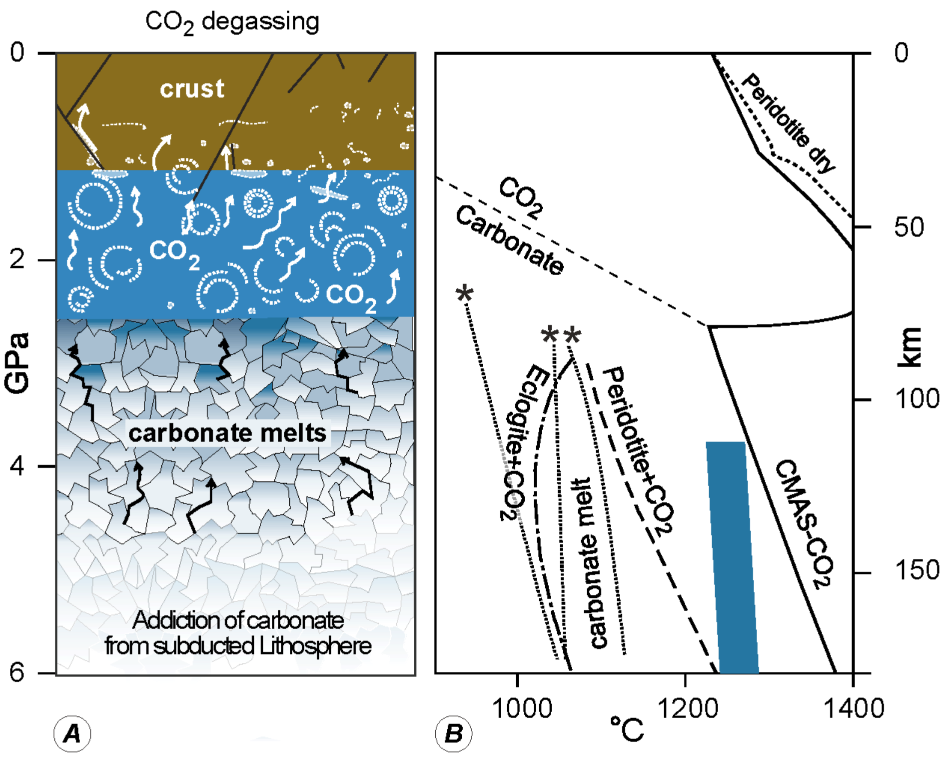
A main question is the identification of the process that generated this layer, i.e. of which components were released from the slab to modify the upper mantle. Also, the occurrence of a low-velocity layer in areas that are not affected by active or recent magmatism, such as the central Tyrrhenian area, needs to be understood. Low V_S waves might be induced by basaltic melts, generated by partial mantle melting processes at elevated temperatures (e.g., Goes and Van der Lee, 2002; Cammarano *et al.*, 2003). Alternatively, the observed low V_S might correspond to a level of C-O-H volatile enrichment (i.e. H_2O bound in mantle mineral's lattice or at grain-boundaries ± carbonates, and/or to free H_2O, CO_2-rich fluids or melts) which may induce composition and density variation in the mantle (Gaetani and Grove, 1998; Jung and Karato, 2001; Presnall and Gudfinnsson, 2005; Dasgupta and Hirschmann, 2006).

The presence of a low velocity layer between 60-70 km to 120-130 km of depth (1.8-4.0 GPa) may be explained by the presence of C-O-H fluid phases (free or mineral-bound) generated by the subducted slab, during the rollback of the west-directed Adriatic-Ionian subduction. It is unlikely that the decrease, with increasing depth, of seismic wave velocities indicates the presence of a 60-km-thick layer with low fractions of basaltic melts, since a continuous supply of more than 1-4% in volume of basaltic melt is required to allow migration through the whole mantle zone (Hyndman and Shearer, 1989). Similar amounts of basaltic melts are highly improbable, since magmatism is not any more active at present. In addition, it would necessarily require considerably high temperatures in the mantle, which are not compatible with the heat flux along the overall trajectory of section 1 (Fig. 3).

CO_2 mantle degassing processes

Frezzotti *et al.* (2009) proposed that the low velocity layer observed between 70 km and 130 km of depth may represent a low viscosity wedge beneath the western Mediterranean, induced by the presence of carbonate-rich melts. The confinement of mantle physical modifications at P > 2 GPa suggests a major role of CO_2 than of H_2O. In the peridotite-CO_2 systems (i.e. CO_2 fluids, carbonate melts, and carbonates), 2 – 2.5 GPa corresponds to the pressure at which the solidus of carbonated-peridotite is considerably depressed (Fig. 5; Dalton and Presnall, 1998; Gudfinnson and Presnall, 2005): peridotite melting would begin generating low fractions of carbonate-rich melts.

Figure 5. Proposed evolution for lithosphere - asthenosphere degassing beneath the Western Mediterranean, modified from Frezzotti *et al.* (2009).



a) Pressure-temperature diagram showing the effects of CO_2 on the solidus of carbonated lithologies in the mantle. Two different estimates of the peridotite - CO_2 solidus are reported: CMSA - CO_2 after Dalton and Presnall (1998), and Gudfinnsson and Presnall (2005), and peridotite - CO_2 (2.5 wt %) from Dasgupta and Hirschmann (2006). Dry peridotite solidus in the CMAS system is from Gudfinnsson and Presnall (2005). Eclogite - CO_2 solidus (dry eclogite + 5 wt % CO_2) from Dasgupta *et al.* (2004). Asterisks (*) corresponds to the KNCFMASH - CO_2 solidus (carbonated pelite + 1.1 wt.% H_2O + 4.8 wt.% CO_2) from Thomson and Schmidt (2008). The effect of carbonates on the composition of melts generated at increasing temperature is reported as wt% CO_2, based on the CMSA – CO_2 system. Gray area = estimated present-day mantle temperatures at the inferred pressures (Carminati *et al.*, 2005). b) Application of the experimentally determined melting relationships for carbonated peridotite, and crustal lithologies to illustrate present mantle processes and metasomatism beneath the Western Mediterranean. Melting of sediments and/or continental crust of the subducted Adriatic-Ionian (African) lithosphere, generates carbonate-rich (hydrous-silicate) melts at pressure > 4 GPa (130 km) and T > 1260°C. Due to their low density and viscosity, such melts can migrate upward through the mantle, forming a 70 km thick carbonated partially molten CO_2-rich mantle layer recorded by tomographic images. Upwelling of carbonate-rich melts to depths less than 60 - 70 km, induces massive outgassing of CO_2 in the lithospheric mantle.. Buoyancy forces, probably favored by fluid overpressures, and tectonics might allow further CO_2 upwelling to the Moho and the lower crust, and, ultimately, outgassing at the surface.

At pressures higher than 2 GPa, carbonates and carbonate-rich melts are stable; at lower pressures, they decompose releasing CO_2 fluids (Canil, 1990; Yaxley and Green, 1996). These properties of CO_2 at depth satisfy the variations of the physical properties of the mantle from 2 GPa to 4 GPa: carbonate-rich melts have very low interfacial energies with respect to mantle minerals. Dihedral angles (θ) are in the range of 25°–30° and allow carbonate melts to rise through and react with mantle minerals, which may well account for the low V_S detected at P > 2 GPa (Hunter and McKenzie, 1989; Watson and Brenan, 1987; Watson *et al.*, 1990). Conversely, the dihedral angles (θ) between CO_2 fluids and mantle minerals are greater than 60° and inhibit the formation of an interconnected fluid network with cessation of V_S reduction (Watson and Brenan, 1987): CO_2 pooling should occur associated to CO_2 outgassing of carbonate melts in the mantle below 2 GPa.

The addition of a carbonate component into the western Mediterranean mantle might have been induced by subduction processes of sediment-bearing old oceanic and/or continental Adria lithosphere either by decarbonation, or by melting reactions. However, decarbonation reactions during subduction represent an uncommon process, since carbonates are very stable phases to very high pressures and temperatures (Kerrick and Connolly, 2001a and b; Connolly, 2005). Fluid-absent partial melting of carbonated-hydrated pelites necessitates of even higher temperatures to generate carbonate ± silicate melts (T=1100 °C- P=2 -5 GPa; Dasgupta etal., 2004; Thomsen and Schmidt, 2008).

Foregoing processes require temperatures that are unrealistic for active subduction mantle geotherms (van Keken *et al.*, 2002). According to Frezzotti *et al.* (2009) decarbonation or melting processes of the Adria lithosphere should have been induced successively, during a progressive rise of mantle temperatures, induced by the combined effect of the strong extensional tectonics affecting this sector of the Tyrrhenian basin and of the eastward mantle flow (Panza *et al.* 2007a), facilitated by the eastward retreating Adriatic-Ionian subducting plates. This hypothesis implies that, in this area, the crust of the retreating subducted slab remained heterogeneously trapped in the mantle at a depth of about 130 km and more.

Lithospheric CO_2 degassing path

Based on a similar model, high amounts of CO_2 can be transported above the deep subducted slab from a depth of about 130 km, in a timescale of a few hundreds of ky. Upwelling of carbonate-rich melts from upper mantle depths is geologically fast, due to their low viscosity and density, and can reach values of the order of tens of cm/y (Hammouda and Laporte, 2000).

At lithospheric depths ≤ 70 km, above the carbonate stability field, massive CO_2 fluxes are produced by outgassing of carbonate melts (Fig. 5). At similar mantle depths, CO_2 fluids have very high density (1.15 – 1.2 g/cm^3 from 60 km to 80 km, at 1000°C; Frezzotti and Peccerillo, 2007), and are very compressible, but virtually immobile (e.g. θ > 60°). Released CO_2 fluids will tend to pool above this pressure threshold to form diffuse and/or concentrated gas-rich regions in the upper mantle (e.g., isolated small pockets confined at mineral grain boundaries). We cannot, however, exclude that CO_2 fluids may coalesce to form larger overpressurized reservoirs, which could facilitate earthquakes.

In Italy, non-volcanic CO_2 degassing is associated with the main crustal geological features, and active tectonics has been proposed as the driving mechanism for CO_2 release from crustal depths (e.g., Miller *et al.*, 2004). The CO_2 migration path from the lithospheric mantle is more complicated. Deep faults, such as the 41° N parallel line, could allow fast upward CO_2 fluxes, and accumulation in the lower crust (Fig. 5; see Mofete d'Ansanto in Table 1). A similar process, however, cannot account for CO_2 mantle rise beneath the Apennines or Tuscany.

The very recent GPS measurements and the unusual subcrustal seismicity distribution have revealed the role of buoyancy forces with respect to the ongoing slow and complex lithospheric deformations in the uppermost mantle along central Italy (Audia *et al.*,2007; Panza and Raykova, 2008; Ismail-Zadeh *et al.*, 2010) . These authors proposed that buoyancy forces, resulting from the heterogeneous density distribution in the lithosphere govern the present-day deformation within Central Italy. Upper mantle buoyancy may explain the upwelling, towards the base of the crust, of otherwise immobile CO_2.

Etna CO_2 emission

CO_2-magma degassing is a normal feature of many OIB-type volcanoes worldwide. However, Etna emits about 1-2 orders of magnitude more CO_2 than most measured OIB volcanoes (see Table 2). Interaction between magma and carbonate wall rocks (Grasso, 2001) seems to be a minor process at mount Etna (Marty *et al.*, 1994), where the anomalous CO_2 emission appears to be mantle-related (Allard *et al.*, 1997; D'Alessandro *et al.*, 1997).

Geochemical studies of present magmatic activity have highlighted the presence of a subduction fluid-component in Etna magmas, testified by enrichments in K, Rb and variation in Sr, B, and Ne-isotope ratios (Condomines *et al.*, 1995; Tanguy *et al.*, 1996; Nakai *et al.*, 1997; Schiano et al 2001; Tonarini *et al.*, 2001; Allard *et al.*, 2006). Gvirtzman and Nur (1999) and Doglioni *et al.* (2001) pointed out that Etna is located along a main lithospheric fault zone running from Lipari and Vulcano (Aeolian arc) to the Malta escarpment. According to these Authors, magmatism is generated at a window along this fault, at the boundary between the border of the African plate and the southeastward retreating Ionian slab. This would allow contemporaneous OIB-type mantle decompression and melting, and CO_2-rich fluid inflow from the undergoing slab in the Etna magmatic system.

An alternative explanation for the origin of deep CO_2 is that the enriched mantle source is represented by the carbonate sequences of the subducted Iblean foreland. The low dipping angle of the Iblean foreland (Doglioni *et al.*, 2001, and references therein) and the absence of deep seismicity beneath the western Aeolian arc suggest sinking and foundering of Iblean slab within the upper mantle, which could release large amounts of CO_2 when conditions of carbonate stability have been reached.

Conclusions

Earth's CO_2 emission in Italy includes both volcanic and non-volcanic emissions, present along Central-Southern peninsular Italy, and in Sicily. Measured CO_2 fluxes totals to 35 - 60 Mt/y, including volcanic degassing (e.g., Etna, Stromboli, Vulcano, Vesuvio, Campi Flegrei, Ischia) and non-volcanic soil emission.

Deep carbon cycling in Italy depends on both degassing of a deep anomalous layer left by the Adria-Ionian slab retreat during Oligocene-Present times and on the formation of CO_2-rich magmas. Slab rollback left a layer of anomalous, low-velocity mantle material at a depth of about 70-120 km, generated by melting of carbonate-rich sediments such as marls. Continuous loss of carbonate components from the retreating slab induced carbonate metasomatism and generated low melt fractions of carbonate-rich melts reflected by the low-velocity layer. This variation in mantle rheology has been preserved long after the end of volcanism possibly as a result of the increase of carbonate melting at higher temperatures, due to heating and decompression. Carbonate-rich melts are unable to reach the surface, since they degas to produce CO_2 at depths shallower than 70 km. CO_2 fluids are substantially immobile at these depths and tend to accumulate in the mantle. Deep lithospheric faults, such as the 41° Parallel Line are able to reach this layer provoking degassing and/or migration of CO_2. This may rise to accumulate to the Moho or to be released to the surface.

The CO_2 storage capability of the mantle reservoir beneath the western Mediterranean has been tentatively calculated by Frezzotti *et al.* (2009) at about 1.35 Mt of CO_2 (equal to 5 Mt carbon) for each km3 of metasomatized mantle. Based on the extension of the low velocity wedge, and assuming a time scale of 30 Ma, CO_2 mantle degassing beneath Italy would conservatively lead to a CO_2 flux of about 70 Mt/y, which exceeds yearly natural CO_2 emission in Italy.

The low velocity wedge beneath the western Mediterranean region represents an important natural cycled C reservoir which stores CO_2 amounts in the order of 100 Gt. Since present day atmospheric CO_2 reservoir is estimated at about 3000 Gt, recycling of carbon through CO_2-mantle degassing in Italy represents a relevant process, which could be a noteworthy source of CO_2 to the atmosphere.

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