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CARBONATE METASOMATISM AND CO_2 LITHOSPHERE-ASTENOSPHERE DEGASSING BENEATH THE WESTERN MEDITERRANEAN: AN INTEGRATED MODEL ARISING FROM PETROLOGICAL AND GEOPHYSICAL DATA

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Abstract

We present an integrated petrological, geochemical, and geophysical model that offers an explanation for the present-day anomalously high non-volcanic deep (mantle derived) CO_2 emission in the Tyrrhenian region. We investigate how decarbonation or melting of carbonate-rich lithologies from a subducted lithosphere may affect the efficiency of carbon release in the lithosphere-asthenosphere system. We propose that melting of sediments and/or continental crust of the subducted Adriatic-Ionian (African) lithosphere at pressure greater than 4 GPa (130 km) may represent an efficient mean for 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, generates low fractions of carbonate-rich (hydrous-silicate) melts. Due to their low density and viscosity, such melts can migrate upward through the mantle, forming a carbonated partially molten CO_2-rich mantle recorded by tomographic images in the depth range from 130 to 60 km. Upwelling in the mantle of carbonate-rich melts to depths less than 60 - 70 km, 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. The present model may also explain CO_2 enrichment of the Etna active volcano. Deep CO_2 cycling is tentatively quantified in terms of conservative carbon mantle flux in the investigated area.

1. Introduction

The role of Earth degassing in present-day global carbon budget and consequent climate effects has been focused chiefly on volcanic emissions (e.g. Gerlach, 1991a; Varekamp and Thomas, 1998, Kerrick, 2001). The non-volcanic[1] escape of CO_2 from the upper mantle, from crustal carbonate rocks, from hydrocarbon accumulations, and from geothermal fields is not considered in the budgets of natural release processes (cf. IPCC reports). However, the impact of these processes on atmospheric CO_2 budget is relevant if considered at the regional scale.

Italy constitutes an extraordinary example of massive CO_2 subaerial fluxes in the Western Mediterranean region (e.g. Chiodini et al., 1999, 2004; Rogie et al., 2000; Chiodini and Frondini 2001; Minissale, 2004). In Italy, CO_2 emissions occur both in those areas of young or active volcanism (e.g. the Tyrrhenian border of Central Italy; Fig. 1), and at zones in which there is no evidence of magmatic activity, such as Central and Southern Apennines (Fig. 1).

Interactions between magmas and carbonate rocks at walls of magma chambers locally contribute CO_2 in some recent and active volcanic zones (e.g., Alban Hills, Mt. Ernici, Vesuvius; Federico and Peccerillo, 2002; Frezzotti et al., 2007; Iacono Marziano et al., 2007a, b). However, the bulk of present-day soil degassing in Italy is a regional feature affecting both volcanic areas and zones where volcanism is unknown (e.g. Apennines). This suggests that the non-volcanic "cold" CO_2 degassing in Italy has a deep origin (i.e., upper mantle), mainly based on isotope data (e.g. $^{12}C/^{13}C$ and $^{3}He/^{4}He$; Minissale, 2004; Chiodini et al., 1999; 2004; Italiano et al., 2001, 2007).

In this paper, we integrate the V_S tomography of the lithosphere-asthenosphere system along some key sections in the Western Mediterranean region, the geodynamic evolution of the study area, the properties of mantle rocks, and the timing and the nature of the magmatism to discuss a model of mantle metasomatism, which can account for deep carbon cycling and CO_2 degassing to the exosphere.

2. Nature of geologic CO_2 emission in Italy

A summary of recent CO_2 emission measurements in Italy is reported in Fig. 1 and Table 1, based on literature data. Active volcanoes represent a prominent natural source of CO_2 to the pre-industrial atmosphere in Italy, possibly since they started to build up (> 0.1 Ma). At Etna (Fig. 1), CO_2 fluxes ranging from 13 to 43.8 Mt/year (average 25 Mt/year) were measured from 1976 to 1984 (Gerlach, 1991; Allard et al., 1991). Lower values, between 4 and 13 Mt/year, were obtained from 1993 to 1997, due to a decrease of the CO_2 emission rate after the 1991-1993 eruption (Allard et al., 1997). At Etna, further CO_2 degassing occurs from the summit area and the lower S-SW and E flanks (1-5 Mt/year), and from ground waters (0.4 Mt/year). On average, Etna emits more CO_2 than many other volcanoes worldwide (e.g. 3.1 Mt CO_2/year from Kilauea; Gerlach et al., 2002; Table 1) and contributes about 5-10 % of the total estimated global CO_2 emissions by subaerial volcanism (cf. Mörner and Etiope, 2002). Other active volcanoes (e.g., Vesuvius, Phlegrean Fields, Stromboli, Vulcano) contribute substantially to the overall atmospheric CO_2

[1] CO_2 that is not released from the craters and flanks of volcanoes. Although non-volcanic degassing can be associated with recent volcanism, CO_2 does not originate in magma chambers, and it is not discharged through the volcanic systems (Kerrick, 2001).

budget in the Western Mediterranean region, which is conservatively (lower bound) estimated at about 30 Mt CO_2/year (see references in Table 1).

Degassing of “cold” CO_2 in areas where volcanism is not active anymore or is absent occurs via diffuse soil emission, dry gas vents, and from thermal and cold springs associated with fault and fractures often of deep origin (e.g., Chiodini et al., 1998; 1999; 2000; 2004; Etiope, 1999; Italiano et al., 2000; Rogie et al., 2000; Mörner and Etiope, 2002; Minissale, 2004; Gambardella et al., 2004) (see also Fig. 1). Regional CO_2 flux mapping for Central Italy indicates emissions of about 9.7 - 17 Mt CO_2/year in an area of 45.000 km^2 (Tuscany, Northern Latium geothermal fields, and Central Apennine chain; Gambardella et al., 2004, Table 1). The total budget of ground CO_2 degassing is comparable with the volcanic output (from > 4 to 30 Mt/year; cf. Mörner and Etiope, 2002).

A close association between CO_2 escape and the main geological structures is evident: a CO_2 flux of 4-13 Mt /year has been estimated in the axial zones of the Apennines chain (Chiodini et al., 2004 and references therein; see also Table 1). Some 0.1 to 0.3 Mt CO_2/year are emitted from gas vents at the Mefite of the Ansanto valley (Irpinia), located in the external parts of the Apennines, right over the hypocenter of the 1980 earthquake along the deep so called *41° N parallel line* (Fig. 1; Italiano et al., 2000; Rogie et al., 2000). Focused high CO_2 fluxes are also measured in the Siena-Radicofani Graben (Tuscany), and in Sicily from mofetes distributed along two directions, corresponding to major fault systems that cut Eastern Sicily (De Gregorio et al., 2002). In Sardinia, CO_2 fluid degassing occurs, in the northern part of the Campidano Graben, from faults in the Logudoro basin (Minissale et al., 1999).

Carbon and helium isotope compositions have been used to constrain the origin of CO_2 in non-volcanic soil emissions. $^3He/^4He$ ratios from gases, summarized in Fig. 2 (R/Ra up to 4.48; Minissale, 2004), indicate an important mantle component, and are similar to R/Ra measured in lavas of Plio-Quaternary volcanoes. Chiodini et al. (2000) report that about 40 % of the inorganic carbon in non-volcanic CO_2 derive from a source characterized by a $\delta^{13}C$ of -3 ‰, compatible with a mantle metasomatized by crustal fluids, and/or with mixed crust + mantle.

Isotope data have led most authors (e.g., Chiodini et al., 2004; Minissale, 2004, and references therein) to propose that mantle CO_2 contributes significantly to present-day degassing processes in Central-Southern Italy. CO_2 rising from the mantle would accumulate at the Moho or within the lower crust. Namely, direct degassing of CO_2 at the surface in the zones of thinned continental crust would occur through extensional fault systems, typical of such a context. Conversely, in those areas (like some sectors of the Apennines) characterized by a thickened continental crust and little extension, mantle-derived CO_2 would remain confined in structural traps. Crustal CO_2 confinement might result in over-pressurized reservoirs, which would facilitate seismogenesis, like the Colfiorito 1997 earthquake (Chimera et al., 2003; Miller et al., 2004).

3. Overview of the geodynamic evolution

The Oligocene to present evolution of the Western-Central Mediterranean region has been characterized by the separation of the Corsica-Sardinia block from the southern European margin, the opening of the Ligurian-Provençal, Algerian, and Valencia basins, and by the opening of the Tyrrhenian Sea and counter-clockwise rotation of the Italian peninsula (e.g., Doglioni et al. 1997, 1999; Carminati et al. 1998; Faccenna et al., 2001; Peresan et al., 2007). There is a general consensus that these structural modifications are related to Oligocene to present west-dipping subduction of the African plate beneath the southern European margin, which migrated from west to east, up to its present position in the southern Tyrrhenian Sea. The Balearic-Provençal Sea opened as a back arc basin between approximately 32 to 15 Ma ago, contemporaneously with orogenic (mainly calcalkaline) magmatism, which migrated eastward with time from Provence and Balearic Sea to Sardinia (see Lustrino et al. 2004, 2007a, b for a review). The Tyrrhenian Sea opened behind the west-dipping Adriatic-Ionian sectors of the African plate between about 15 Ma and the present, and was accompanied by the eastward migration of the orogenic magmatic activity (Savelli and Gasparotto, 1994). The average lithospheric models proposed for the two basins by Panza and Calcagnile (1979) agree with these age estimates. Parallel zones of compression (at the front) and extension (in the back arc basins) migrated towards the east, in the same direction of the magmatism (Pauselli et al., 2006).

The opening of the Tyrrhenian Sea and the counterclockwise rotation of the Italian peninsula resulted in the longitudinal stretching and fragmentation of the Apennine chain, with formation of several arc sectors separated by important transverse tectonic lines (e.g., the so-called *41° N parallel line*, the Sangineto fault, the Tindari-Letojanni fault; Locardi, 1988; Turco and Zuppetta 1998; Rosenbaum et al., 2008). These structures separate crustal blocks characterized by different drifting velocity, structure of the lithosphere, and degrees of block rotation (Peresan et al., 2007), and by different compositions of the volcanism (Turco and Zuppetta 1998; Peccerillo, 1999; Peccerillo and Panza, 1999). Extensional tectonics affected the margin of the African foreland (Corti et al., 2006) where Oceanic Island Basalt (OIB)-type magmatism occurred, starting from the Miocene.

4. Overview of the magmatism

A wide variety of magma types occur in the Western Mediterranean (Fig. 3). These have been divided into two broad groups, showing distinct geological setting, incompatible element, and radiogenic isotope signatures (Peccerillo, 2005; Peccerillo and Lustrino, 2005; Lustrino and Wilson, 2007). The first group of magmas, generally referred to as “orogenic”, has been erupted in Provence, Balearic Sea, Sardinia, the Southern Tyrrhenian Sea and the Italian peninsula, i.e. in zones which were affected by the Oligocene to present subduction of the African plate beneath the southern European margin. The petrochemical affinity of these magmas is mainly calcalkaline with some arc tholeiites in Sardinia, Balearic Sea, and Provence (Lustrino et al., 2004), whereas it is calcalkaline to shoshonitic and ultrapotassic in the Aeolian arc and in Central Italy (e.g. Francalanci et al., 1993; Peccerillo, 2003; Fig. 1). Orogenic magmas show high LILE/HFSE ratios, with negative Nb, Ta and Ti anomalies, and positive spikes of Pb in their mantle-normalized patterns, features that are typical of volcanic rocks erupted at converging plate margins.

Ages of orogenic magmas are variable. Oldest rocks occur in Provence, Balearic Sea and Sardinia (Oligo-Miocene; Fig. 3) and become younger in the Tyrrhenian Sea floor, in the Italian peninsula and the Aeolian arc (Miocene to present). The decrease in age from west to east would be related to the slab rollback and migration of the subduction zone in the same direction (Carminati et al., 1998; Doglioni et al., 1999 and references therein).

Calcalkaline to ultrapotassic orogenic magmas along the Italian peninsula and in the Aeolian arc have variable degrees of evolution, from mafic to felsic. The most mafic rocks possess high Mg# (Mg/(Mg+Fe^{2+}) atomic ratios > 70), Ni (> 100-200 ppm) and Cr (> 500 ppm), and low

$\delta^{18}O$ (~ +5.5 to +6.0). These are typical of mantle-derived magmas, which have suffered little or no crustal contamination during emplacement. However, these rocks also have Sr-Nd-Pb-Hf isotope compositions that are intermediate between mantle and upper crust, with crustal-like isotopic signatures increasing northward, where some K-alkaline basalts have radiogenic isotope ratios closer to crustal than to mantle compositions. Helium isotope composition determined on fluid inclusions in olivine and clinopyroxene phenocrysts (Martelli et al., 2008) shows a general decrease in $^{3}He/^{4}He$ moving northward (Fig. 2), which correlates with the whole rock radiogenic isotopes increase in $^{87}Sr/^{86}Sr$, and decrease in $^{143}Nd/^{144}Nd$, $^{176}Hf/^{177}Hf$, and $^{206}Pb/^{204}Pb$ (Peccerillo, 2005; Martelli et al., 2008, and references therein).

These data have led several authors (e.g., Peccerillo, 1985; Rogers et al., 1985; Conticelli et al., 2002; Peccerillo, 2005 and references therein) to conclude that mixing between upper crust and mantle components played a key role in the genesis of magmatism along the Italian peninsula and that such interaction occurred within the upper mantle. Melting of such a heterogeneously contaminated mantle generated various types of mafic melts exhibiting hybrid isotopic signatures between crust and mantle. Based on trace element and radiogenic isotope modeling, Peccerillo (1985) and Peccerillo et al. (1988) proposed that marly sediments were introduced by subduction processes into the upper mantle beneath Central-Southern Italy, generating a variably metasomatized source. The involvement of marly sediments in the mantle contamination during the latest stages of Adria plate subduction is able to account for several petrological, geochemical and isotopic characteristics of ultrapotassic magmas in Central Italy (Conticelli and Peccerillo, 1992; Conticelli et al., 2002; Schmidt, 2007).

A second group of magmas, generally referred to as "anorogenic", has been erupted in back arc position and along the northern margin of the African foreland (Fig. 3). These have low LILE/HFSE ratios, generally with positive spikes of Ta and Nb, and no Pb anomalies. Sr-isotope signatures are poorly to moderately radiogenic, whereas Nd, and especially Pb isotopes are variable, and cover almost entirely the range of values shown by OIB-, and MORB-type magmas at global scale (see, Peccerillo, 2005; Stracke et al., 2005). Anorogenic magmas in the study area have been mainly erupted from 5 to 0.1 Ma ago in Sardinia, with incipient activity recently detected at about 12 Ma (Lustrino et al., 2007b), contemporaneously with the opening of the Tyrrhenian Sea (Lustrino et al., 2004), at several places in the Tyrrhenian basin (e.g., Ustica and several seamounts; Fig. 3), along the Sicily Channel (Miocene to present: Pantelleria, Linosa, and several seamounts; Calanchi et al., 1989; Rotolo et al., 2007; Di Bella et al., 2008), at Hyblei, and Etna (0.5 M.y. to present). Etna, overall showing OIB-type composition, also possesses some geochemical and isotopic signatures (e.g., relatively low Ti, high fluid-mobile element contents, relatively high $\delta^{11}B$ ~ -3 to -5) that are close to arc magmas (see Schiano et al., 2001; Tonarini et al., 2001). The Tyrrhenian Sea anorogenic magmatism includes abundant MORB-type magmas forming new oceanic crust and some weakly Na-alkaline centers with an age ranging from 7 to 0.1 Ma (Peccerillo, 2005, and references therein).

5. Mantle structure beneath the Western Mediterranean

5.1 Present-day imaging: V_S tomography

Sample profiles of the three dimensional S-wave model obtained by the non-linear inversion of surface wave (Panza, 1981) tomography data in the Western Mediterranean and the Tyrrhenian Sea area are shown in Fig. 4. The complete description of the data coverage is given in Fig. 2 of Panza, et al. (2007b). The detailed discussion of the lateral resolution and of the uncertainty in the models is given by Panza, et al. (2007b) and Pontevivo and Panza (2006). The vertical resolution is controlled according to the results of Knopoff and Panza (1977) and Panza (1981). As a rule, the three dimensional variations evidenced satisfy the principle of maximum smoothness (Boyadzhiev et al., 2008) and are consistent with the resolving power of the used data. In Fig. 4, the central values of the Vs models are given for simplicity; details about uncertainties are given by Panza et al. (2007a, b).

Section 1 (Fig. 3, and 4a) goes from Provence to Central Sardinia and to the Campanian area, running along the *41° parallel line* in its Central and Eastern segment (Panza et al., 2007a). This section crosses the Balearic and the Tyrrhenian basins, the main extensional features in the Western Mediterranean area. Section 2 (Fig. 5b) runs from offshore southern Sardinia to the Aeolian arc and Calabria following an E-W and then NW-SE trend (Boyadzhiev et al., 2008; Peccerillo et al., 2008), along the direction of maximum extension of the Tyrrhenian basin during the last 5 M.a. (Sartori, 2003). Section 3 (Fig. 4b) is located in the Central-Northern Tyrrhenian Sea and goes through the Tuscany and Roman magmatic provinces (Panza et al., 2007b), where the abundant mantle-derived ultrapotassic magmatism with crustal-like radiogenic isotope signatures reveals extremely anomalous geochemical compositions for upper mantle sources.

Section 1 (Fig. 4a) shows that the upper mantle beneath continental South-Eastern France exhibits rather homogeneous S-wave velocities (V_S ~ 4.3-4.5 km/s) down to 250 km of depth. Starting from the coast of Provence, the upper mantle structure changes significantly. In spite of the non-uniqueness of the inverse problem of seismological data the occurrence of a low S-wave velocity layer (V_S = 4-4.1 km/s) at a depth of about 60-130 km is a clear-cut feature. Such a layer is enclosed inside high-velocity material (V_S ~ 4.3-4.55 km/s) and extends eastward to Sardinia and the Tyrrhenian Sea, with an almost constant thickness. The low-velocity layer raises to a shallower level beneath the Campania volcanoes of Ischia, Phlegrean Fields and Vesuvius, showing a decrease of V_S to about 3.4-4.2 km/s. Note that the low-velocity layer is not limited to the underwater part of the section where young oceanic or thinned continental lithosphere is very likely present (Panza and Calcagnile, 1979), but it is also present beneath the Corsica-Sardinia block which is a fragment of the old European continental lithosphere, rotated to the East during opening of the Balearic Sea.

Section 2 (Fig. 4b), that goes from Sardinia to the Aeolian Arc and Calabria, also exhibits a low-velocity layer but it is at a much shallower depth of 30 to 70 km and rises to 0-30 km beneath the active Aeolian volcanoes. An almost vertical seismically active body with high V_S from 4.5 to 4.8 km/s likely representing the descending Ionian slab (Panza et al., 2003), cuts the low-velocity layer beneath Calabria.

Finally, section 3 (Fig. 4b) crosses the Central Tyrrhenian Sea and 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 60-130 km of depth, that becomes shallower in the Roman Province (about 30-50 km).

5.2 Geochemical features: xenoliths

Spinel peridotites are present in the orogenic carbonatitic-melilitic pyroclastics of Vulture (0.2 M.y.), in the orogenic lamproitic lavas of Torre Alfina (0.9 M.y.), and in the anorogenic Miocene - Quaternary volcanics of Mt. Hyblei (South-Eastern Sicily), and of Sardinia (Fig. 1; Conticelli and Peccerillo, 1990; Jones et al., 2000; Sapienza and Scribano, 2000 and references therein).

At Vulture (Fig. 1), spinel peridotites consist of lherzolites and harzburgites, with subordinate dunites and wehrlites, which may contain phlogopite, amphibole, and carbonate. Downes et al. (2002) measured enriched LILE and LREE trace element patterns in clinopyroxene, associated with low HFSE contents, and proposed that metasomatic processes occurred by interaction of mantle rocks with silicate melts. Furthermore, peridotites show $^{87}Sr/^{86}Sr$ enrichment (0.7042–0.7058), higher than in most of the European continental lithosphere, and suggest that silicate-melts might have been subduction related. In these rocks, Rosatelli et al. (2007) described the existence of carbonate and silicate glasses, present as inclusions and microveins, formed by immiscibility processes from an original carbonate-rich silicate melt at pressures, P, of 1.8 - 2.2 GPa (about 50-80 km of depth). The $^{87}Sr/^{86}Sr$ ratios in metasomatic calcite are equal to 0.705816 ± $4 \cdot 10^{-6}$, in the same range as rock $^{87}Sr/^{86}Sr$ data from Downes et al. (2002).

Torre Alfina xenoliths (Tuscany; Fig. 1) consist of spinel lherzolites and harzburgites (up to 3-4 cm in diameter) that sometimes contain phlogopite. Rare phlogopite-rich xenoliths have been found and interpreted as remnants of metasomatic veins in the upper mantle. 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).

Protogranular spinel lherzolites and harzburgites from Hyblei (Fig. 1) show whole-rock selective LREE and incompatible elements enrichments (i.e., U, La, Sr, and P; Sapienza and Scribano, 2000). They contain extremely abundant CO_2 inclusions, whose He isotope composition indicates mixing of two sources: a MORB-type mantle, and a radiogenic He enriched reservoir (Sapienza et al., 2005). He isotope data from Hyblei peridotites correlate with the He signature of Etna lavas (cf. Fig. 2).

Taken collectively, mantle xenoliths geochemical and petrological features indicate pervasive metasomatic processes in the Western Mediterranean lithosphere. Carbonate-, and hydrous-silicate melts are recognized as possible metasomatic agents. Sr isotope data in mantle rocks from Vulture further suggest a subduction related origin of metasomatic melts, and the radiogenic isotopes in peridotites at Torre Alfina point to an upper crustal component in their source.

6. Carbon-cycling through subduction, mantle anomalies, and CO_2 degassing in the Western Mediterranean

The data summarized in sections 4 and 5 highlight some remarkable relationships between the structure of the lithosphere-asthenosphere system, as indicated by V_S structural models (Fig. 4), and the main geochemical features of magmas and of mantle peridotites. The occurrence of a continuous 60-130 km deep low-velocity layer, stretching from Southern Provence to the South-

Eastern Tyrrhenian Sea area and running continuously beneath both oceanic-type (e.g., Central Tyrrhenian Sea) and continental-type lithosphere (e.g., Sardinia), coincides with the zone of Oligocene to present slab rollback, and it is associated with orogenic magmatism that migrates in the same direction (Panza et al., 2007a,b; Peccerillo et al., 2008). The low-velocity layer has been interpreted as a geochemically anomalous mantle, modified by the release of "material" (i.e. fluids and/or melts of variable composition) from the retreating lithosphere, leaving a wake of physical anomalies (Peccerillo et al., 2008).

6.1 The low-velocity mantle layer: CO_2-rich fluids/melts at depth

The understanding of the nature of the low-velocity layer is crucial to have an insight into the lithosphere/asthenosphere evolution in the Western Mediterranean and to explain ongoing processes of mantle metasomatism and ultimately CO_2 degassing. Theoretically, a low-velocity layer might be induced by basaltic magmas, generated by partial mantle melting processes at high temperatures (e.g., Goes and van der Lee, 2002; Cammarano et al., 2003). Alternatively, it might correspond to a level of "fluid" enrichment (i.e., free H_2O-, CO_2-rich fluids or melts, and/or H_2O bound in mantle mineral's lattice or at grain-boundaries) which may well induce composition and density variations in the mantle (Gaetani and Grove, 1998; Jung and Karato, 2001; Presnall and Gudfinnsson, 2005; Dasgupta and Hirschmann, 2006).

It is unlikely that the low-velocity layer is related to the presence of a 70-km-thick front of basaltic magma. This would require a sustained supply of significant amounts of melt (more than 1-4% in volume) through the whole mantle zone to allow migration (Hyndman and Shearer, 1989). Upward melt migration is, in fact, controlled by the supply rate from mantle melting at high temperature, and solidification of the partial melts is expected on cooling. Such a thick magma front is improbable, especially in some regions along Section 1 (Fig. 4a), such as the Provençal basin, where magmatism is not any more active at present. In addition, it would necessarily require considerably high temperatures in the mantle, which conflicts with the heat flux along the overall trajectory of Section 1 (Fig. 5).

The considerable thickness of this shallow low-velocity layer may be better justified by the presence of low fractions of volatile-rich melts, or by fluids (free or mineral-bound). Its presence in zones affected by the Oligocene to present subduction strongly suggests that volatiles were likely released during the Eastward rollback of the West-directed Adriatic-Ionian plate. Slab dehydration, with consequent development of mantle wedge structures and volcanic fronts, has been modeled as a continuous process starting from low-grade conditions (10-20 km depth) to more than 200 km (e.g., Schmidt and Poli, 1998). However, if water-rich fluids or melts were the dominant mantle modifiers, there is no explanation for the confinement of the physical modifications at $P > 2$ GPa. Hydrous minerals (e.g., amphibole) are stable at $P \leq 2$ GPa in peridotites that have reacted with subduction released hydrous fluids, like in the Ulten Zone in the Eastern Alps (Scambelluri et al., 2006).

In a carbonated mantle (i.e. presence of CO_2 fluids, carbonate melts, and/or carbonates), 2 GPa represents a well recognized threshold, which corresponds to the carbonated peridotite decrease of the *solidus*, experimentally determined at 2 - 2.5 GPa (Fig. 6a; Falloon and Green, 1990). When $P > 2$ GPa, carbonates are stable phases and peridotite (± hydrous phases) *solidus* is considerably depressed: melting is supposed to commence with low fractions of carbonate-rich melts. When $P < 2$ GPa, both carbonate-rich melts and carbonates decompose releasing CO_2 fluids (Canil, 1990; Frezzotti et al., 2002a, b).

These properties of CO_2 at depth are able to account for the variations of the physical properties of the mantle beneath the Western Mediterranean region. Carbonate melts have the lowest viscosity of any other magma type, and very low interfacial energies with respect to mantle minerals. Dihedral angles (θ) are in the range of 25-30° and depend only weakly on temperature or pressure (Hunter and McKenzie, 1989; Watson and Brenan, 1987; Watson et al., 1990). These properties allow very low fractions of carbonate melts to rise through an interconnected network at very low porosities (0.1 %) and react with mantle minerals, which may well account for the low V_S detected at P > 2 GPa (Dobson et al., 1996; Presnall and Gudfinnsson, 2005). Conversely, at P < 2 GPa, the dihedral angles (θ) between CO_2 and matrix mantle minerals are greater than 60° and inhibit the formation of a porous fluid flow (Watson and Brenan, 1987): CO_2 pooling should occur associated to decarbonation in the mantle above 2 GPa, with cessation of Vs attenuation (Canil, 1990; Frezzotti and Peccerillo, 2007).

Therefore, we propose that the low-velocity layer between 60 and 130 km of depth beneath the Western Mediterranean represents a low viscosity wedge induced by the presence of carbonate-rich melts. Starting from below, the onset of the Vs attenuation at 130 km indicates the onset of mantle melting, while the level at about 60 km is the upward limit for the carbonate melt ascent. Such an interpretation does not signify that (hydrous) silicate melts are absent during mantle modifications at the considered pressures, but only that mantle processes are CO_2 mediated.

6.2 Carbonate-rich melts in the upper mantle beneath the Western Mediterranean

The generation of carbonate-rich melts or fluids via subduction is a two-step process. The first step consists in “removing” carbonates (e.g., by devolatilization or melting) from the subducting lithosphere, and introducing them into the overlying upper mantle. Once carbonates are expelled from the slab and fluxed into the overlying mantle, they might freeze in mantle rocks giving rise to carbonated peridotites. However, if temperatures are sufficiently high, they might be preserved at the liquid state and migrate through porous or reactive flow (Presnall and Gudfinnsson, 2005).

The addition of a carbonate component into the Western Mediterranean mantle may have been induced by two alternative processes: either decarbonation, or melting of sediment-bearing old oceanic and/or continental Adriatic-Ionian lithosphere. Carbonates, however, are stable to very high pressures and temperatures, and remain as refractory phases as lithosphere dehydrates. At depths between 90 and 150 km, marls do not undergo any devolatilization along subduction low-temperature geotherms (400 - 600°C), and decarbonation commences only if temperatures exceed 700 - 950°C (hot subduction; Kerrick and Connolly, 2001; Connolly, 2005). Further, decarbonation at high pressures requires fluxes of H_2O from the marl sediments and/or the underlying lithosphere (Kerrick and Connolly, 2001).

In order to free substantial amounts of CO_2, melting of carbonated crustal lithologies is necessary, which requires even higher temperatures (above 1000 - 1100 °C at 4 GPa; Dasgupta et al., 2004; Thomsen and Schmidt, 2008; Fig. 6a). At P > 3.7 GPa, melting of the assemblage phengite + quartz/coesite + clinopyroxene + kyanite + garnet + calcite (9–10 wt.%) generates immiscible silicate and carbonate liquids at 1100°C, and, at higher temperatures, a homogeneous carbonate-rich hydrous-silicate melt (Thomsen and Schmidt, 2008). At these (P, T) conditions high-degrees of melt are produced: about 9 wt. % carbonate-, and 30-47 wt.% silicate melt. The composition of the silicate melt varies from rhyolitic to phonolitic (K_2O > 10 wt %) at increasing pressures (Thomsen and Schmidt, 2008).

The foregoing processes call for temperatures that are too high for subduction zones with a convergence rate (about 3 cm/year) as the Adriatic-Ionian plate (van Keken et al., 2002; Carminati et al., 2005). Thus, it is improbable that decarbonation of crustal rocks at depth occurred during active subduction in the investigated region. Decarbonation or melting should have initiated successively, during a progressive rise of mantle temperatures, resulting from 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) behind the retreating Adriatic-Ionian subducting plate. This implies that, in this area, crustal lithologies from the retreating Adriatic-Ionian lithosphere remained trapped in the mantle wedge at depths exceeding about 130 km before being melted as a consequence of back arc isotherm uprise. Present-day mantle temperatures beneath the Western Mediterranean, away from the active subducting Ionian plate, are estimated at 1260-1320°C at depths greater than 105 km (Carminati et al., 2005), and such a thermal regime would favor melting of subducted crustal lithologies with respect to decarbonation reactions, generating carbonate and (hydrous) silicate melts (cf. Fig. 6a).

Possible mantle evolution can be evaluated by experimental models in the peridotite-CO_2 system, reported in Fig. 6, which indicate CO_2 as the most important controlling compound on both the temperature of melting of peridotite, and on the composition of the produced melt (Fig. 6a; Dalton and Presnall, 1998; Dasgupta and Hirschmann, 2006; 2007a, b; Dasgupta et al., 2007). Since nominally volatile-free mantle minerals can dissolve only a few ppm CO_2 (Keppler et al., 2003), carbonate phases may form at very low CO_2 concentrations, and abruptly induce a sharp decrease in peridotite partial melting temperatures (Fig. 6a); peridotite melting would commence with low fractions of carbonate-rich melts. At 3 GPa and 1300°C, 0.1 wt % of carbonate melt is in equilibrium with the peridotite mantle, while transition to carbonate-rich silicate melts (> 2 wt % of melt), requires temperature up to 1450°C (Dasgupta et al., 2007).

Therefore, the amount and composition of mantle melts in the enriched mantle zone (i.e. low-velocity wedge) would depend, among other parameters, on temperature. Theoretically, on a further temperature increase, mantle melting enhancement might generate dominantly silicate-rich melts with a carbonate component, promote channeling, and ultimately volcanism. At the inferred present-day temperatures of 1260-1320°C, the mantle beneath Western Mediterranean away from active orogenic volcanism can preserve low fractions of molten carbonates (Fig. 6a). Conversely, in those zones not far away or above the subducting plate, higher temperature fluxes might induce the highest degrees of partial melting, generating CO_2-rich magmas (i.e., the low-velocity ledge beneath the Campania volcanoes and the Aeolian arc; Fig. 4a and b).

6.3 Proposed Regional evolution

According to our model, the tomographic images of the shallow low-velocity-layer represent carbonated partially molten, subducted crustal material mixed with mantle rocks at depths above 130 km (Fig. 6b). Metasomatic melts, would be constituted by a carbonate, and a hydrous silicate component, via melting of carbonated crustal lithologies, as experimentally determined (see section 6.2). The silicate component of this melt represents an important metasomatic agent adding SiO_2, LREE, and LILE to the mantle; progressive crystallization of silicate minerals from the metasomatic silicate component may result in an increasing carbonate-rich fraction in melts, which might induce extensive dissolution and oriented recrystallization of olivine (Dasgupta and Hirschmann, 2006). We might speculate that silicate and carbonate melts preserved as inclusions in spinel peridotites from Vulture illustrate the ongoing mantle refertilization, started more than 200.000 year ago.

Carbonate addition to the mantle via subduction should be considered as a "one-shot" event, whose longevity depends on the timing of the geodynamic evolution in the investigated area. Mantle upwelling for low fractions of carbonate melt is "fast", and estimated between 100 - 1000 m in 0.1-1 M.y. (Hammouda and Laporte, 2000). Resulting ascent times are compatible with the timescale of the Adriatic-Ionian subduction retreat and may account for the persistence of the low-velocity layer also in those zones were subduction ceased around 30 M.y. ago (Balearic Sea).

While carbonate melts accumulate and persist in the shallow low-velocity mantle zone because of present day temperatures, part would outgas at 2 GPa (Fig. 6b). Degassing of CO_2 would result in stiffening of the more viscous silicate melt component, with consequent cessation of the processes, if temperatures are not further increased. Released CO_2 will temporarily halt (and tend to pool) above this pressure threshold to form diffuse and/or restricted gas-rich regions in the upper mantle (Fig. 6b). CO_2 could spread in the subcontinental lithosphere as isolated small bubbles confined at mineral grain boundaries, although we cannot exclude that CO_2 may coalesce to form larger (over pressurized?) reservoirs.

In Italy, non-volcanic high CO_2 flux is associated with the main crustal geological features, thus it is very likely that active tectonics represent the driving mechanism for mantle CO_2 release from crustal depths (Miller et al., 2004; Ventura et al., 2007). Deep strike-slip faults, such as the *41° N parallel line*, would constitute a possible fast way for upward CO_2 mantle rise and accumulation in the lower crust (see Mofete d'Ansanto, in Table 1). Upper mantle buoyancy could also allow mantle CO_2 upwelling towards the Moho and the lower crust. Aoudia et al. (2007) and Panza and Raykova (2008) investigated the role of buoyancy forces with respect to the ongoing slow and complex lithospheric deformations in the uppermost mantle along Central Italy, revealed by the very recent GPS measurements and by the unusual subcrustal seismicity distribution. 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 Moho and the lower crust, of otherwise inert CO_2. Deep CO_2 is indeed a fluid phase with peculiar characteristics: it is very compressible and practically immobile (e.g., $\theta > 60°$), but at the same time it is highly volatile ($d = 1.15 – 1.2$ g/cm^3 in the depth range from 60 to 80 km). For these reasons, CO_2 could not migrate until the porosity reaches high values (> 8 %).It is then likely to ascend "explosively", facilitating earthquakes, not only at 4-8 km from the surface, but also at mantle depths, close to the Moho.

6.4 Aeolian arc and Etna CO_2 emission

In the Western Mediterranean, further massive CO_2 degassing occurs from active volcanoes, which contributes significantly to the total budget of geological emissions (Fig. 1; Table 1). Aeolian volcanoes, do not show any anomalous CO_2 flux with respect to typical magmas generated in a mantle modified by active subduction (see CO_2 output from Stromboli in Table 1). Conversely, Etna volcano alone constitutes an outstanding CO_2 emission anomaly in the centre of Mediterranean (Table 1). Etna is away from low-velocity mantle zones (Fig. 4; Panza et al., 2007b; Peccerillo et al., 2008) and, therefore, the explanation offered for the subduction-related volcanic areas of the Italian peninsula cannot be extended to this volcano.

In principle, CO_2 emission at Etna may reveal some interaction between magma and carbonate wall rocks, since the thick carbonate sequences of the Hyblean foreland are believed to be present beneath Etna (e.g. Grasso, 2001). Oxygen isotope data reported by Viccaro and Cristofolini (2008) are higher than mantle values ($\delta^{18}O \sim +6.1$ to $+ 7.1$), which would support magma contamination. However, Frezzotti et al. (1991) report evidence for deep CO_2 degassing at Etna volcano by mixed CO_2 + basaltic melt inclusions. Measured CO_2 densities indicate pressures of 0.7 GPa (about 25 km of depth) at 1300°C, which correspond to more than 7,000 ppm CO_2 in the magma (Armienti et al., 1996). Allard et al. (1997) determined even higher CO_2 contents in Etna magmas (1.23 wt. % CO_2, based on S/C ratios in the magma), consistent with deep degassing (50 km). According to Allard et al. (1997; 2006), CO_2 degassing from volatile-rich Etna basalts is related to the shallow mantle diapiring at the African-European plate boundary.

All these lines of evidence lead to the conclusion that the anomalous CO_2 emission appears to be a mantle-related process (Allard et al., 1997; D'Alessandro et al., 1997). We propose two possible models of carbonate recycling to explain the anomalous CO_2 emission at Etna. They both lean on the particular geodynamic setting of the Etna volcano. There is a growing evidence that Etna, although being a typical OIB-type volcano, bears geochemical evidence (e.g. enrichment in K and Rb, and B-isotopes) for the presence of subduction components, as discussed earlier (Condomines et al., 1995; 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) highlight the particular position of Etna, which is located along a main lithospheric dextral transform fault system which runs from Lipari and Vulcano (Aeolian arc) to the Malta escarpment (the so-called Tindari-Letojanni fault; Fig. 3), and separates the foreland Hyblean block at the west from the subducting Ionian plate at the east. According to these Authors, the magmatism in this particular geodynamic setting is generated at a window along this fault, at the boundary between the foreland and a subducting slab. This would allow in the Etna magmatic system contemporaneous OIB-type mantle decompression and melting, and CO_2-rich fluids inflow from the undergoing slab. The Ionian subduction zone is very steep, almost vertical, which favors the channeling of slab-derived fluids along the subduction zone and their ascent from very high depth where decarbonation occurs, to shallow levels (Abers, 2005).

An alternative possibility is that the CO_2 source is provided by the carbonate sequences of the subducted Hyblean foreland. The low dipping angle of the Hyblean foreland (Doglioni et al., 2001 and references therein) and the absence of deep seismicity beneath the Western Aeolian arc (Caputo et al., 1970; 1972) suggest slab breakoff on the west of the Tindari-Letoianni fault. This implies detachment and foundering into the mantle of the Hyblean slab beneath the Etna volcanic zone. Sinking carbonate sequences of the foreland could release large amounts of CO_2 when conditions of decarbonation or melting are reached.

Therefore, present-day CO_2 degassing beneath the Western Mediterranean appears to be related to carbon-cycling from the crustal portion of subducted slabs into the upper mantle. However, whereas along zones directly affected by Oligocene to Present subduction, CO_2 emission is related to the temperature regimes and dynamic conditions that develop behind the retreating slab, at Etna the CO_2 emission would be generated either by fluid inflow from the Ionian subducting plate or from decarbonation of carbonate sequences of the detached foreland sinking into the upper mantle.

7. Concluding remarks

Present-day massive "cold" CO_2 soil degassing, occurring in tectonically active areas located above the subduction-enriched mantle wedge (e.g. Tuscany, Northern Latium, Apennines, North Sardinia, *41° N parallel line*), supports efficient cycling of carbon and its return to the atmosphere in the western Mediterranean area.

We propose that the slab retreat during Oligocene to Present times left in front of itself a shallow layer, at a depth of 60-130 km, of very low-velocity mantle material that sits on top of a relatively faster low-velocity layer, which is standard for oceanic structures (e.g. Stixrude and Lithgow-Bertelloni, 2005). The very low velocities can be indeed associated to attenuation, but attenuation affects amplitudes rather than phases and we measure dispersion relations (phase and group velocities) at periods of 10 s and larger. The Vs values we get in the uppermost part (60-130 km of depth) of the mantle low-velocity zone remain very low with respect to the values reported for low-velocity zone of oceanic regions at global scale (Stixrude and Lithgow-Bertelloni, 2005), even when the upper bound of the Vs range is considered (see Panza et al., 2007a, b), and some increment is allowed to account for the attenuation effect through body-waves dispersion (Futtermann, 1962; Panza, 1985).

This layer of very low-velocity mantle material was generated by melting of carbonated crustal lithologies, at temperature above 1100 °C. The result is a chemically and physically heterogeneous upper mantle beneath the Western Mediterranean. The anomalous non-volcanic CO_2 flux, which has been detected in Italy in those regions where volcanism is not active or absent, would derive from mantle degassing, providing a geological CO_2 source, additional to the rise of CO_2-rich magmas, in this active volcanic region.

Upper mantle carbonate Earth recycling via subduction and melting of crustal lithologies at depths > 130 km, as observed In Western Mediterranean, represents a relevant process in the overall Earth deep carbon cycle. The flux of cycled CO_2 can be tentatively calculated based on the extension of the low-velocity wedge beneath the Western Mediterranean. Typical carbonate-rich melts in experimental melting of carbonated lherzolite (Dalton and Wood, 1993) contain about 45% CO_2 by weight. Accepting 0.1 wt% of carbonate melt concentration (cf. Section 6.2), and assuming as convenient (but certainly high) 100% degassing, approximately 1.35 Mt of CO_2 (equal to 0.4 Mt carbon) could be released for each km^3 of metasomatized mantle. Assuming a time scale of 30 M.y., CO_2 degassing of the low-velocity wedge beneath the Western Mediterranean would conservatively lead to lithosphere-asthenosphere CO_2 flux of about 70 Mt/year, which exceeds yearly CO_2 degassing in Italy.

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Table 1 - Geologic CO_2 degassing in Italy

Volcanic	**Output (Mt/y)**
Crater emission	
Etna (1976 - 1985)[1, 2]	25.5
Etna (1993 - 1997)[3]	4 - 13
Stromboli[4]	1 - 2
Vulcano[5]	0.066
Ground emission	
Vulcano Fossa crater[6]	0.073
Vulcano plains[7]	0.027
Vulcano fumaroles[8]	0.088
Stromboli[9]	0.07 - 0.09
Vesuvius[10]	0.5
Solfatara, Phl. Fields[11]	1.8
Ischia[12]	0.14

non-Volcanic	**Output (Mt/y)**
Regional	
Central Italy[13]	> 4
Central Italy[14]	9.7 - 17
Central Apennines[15]	4 - 13.2
Tuscany and N Latium[16]	6
Campania[16]	3
Soil degassing	
Latera, Vulsini[13]	> 0.07
Alban Hills[16]	0.2
Siena graben[17]	> 0.5
Ustica[18]	0.02
Gas vents	
Mefite d'Ansanto[13]	0.3
Rapolano, Tuscany[15]	0.035
Mofeta dei Palici, Sicily[19]	0.091
Geothermal Fields	
Mt. Amiata, Tuscany[20]	0.5

1) Allard et al., 1991; 2) Gerlach, 1991; 3) Allard, et al., 1997; 4) Allard et al., 1994; 5) Baubron et al., 1990
6) Chiodini et al., 1996; 7) Chiodini et al., 1998; 8) Italiano et al., 1998; 9; Carapezza and Federico, 2000
10) Frondini et al., 2004; 11) Caliro et al., 2008; 12); Aiuppa et al., 2007; 13) Rogie et al., 2000;
14) Gambardella et al., 2004; 15) Chiodini et al., 2000; 16) Chiodini et al., 2004; 17) Etiope, 1996;
18) Etiope, 1999; 19) Di Gregorio et al., 2002; 20) Frondini et al., 2008

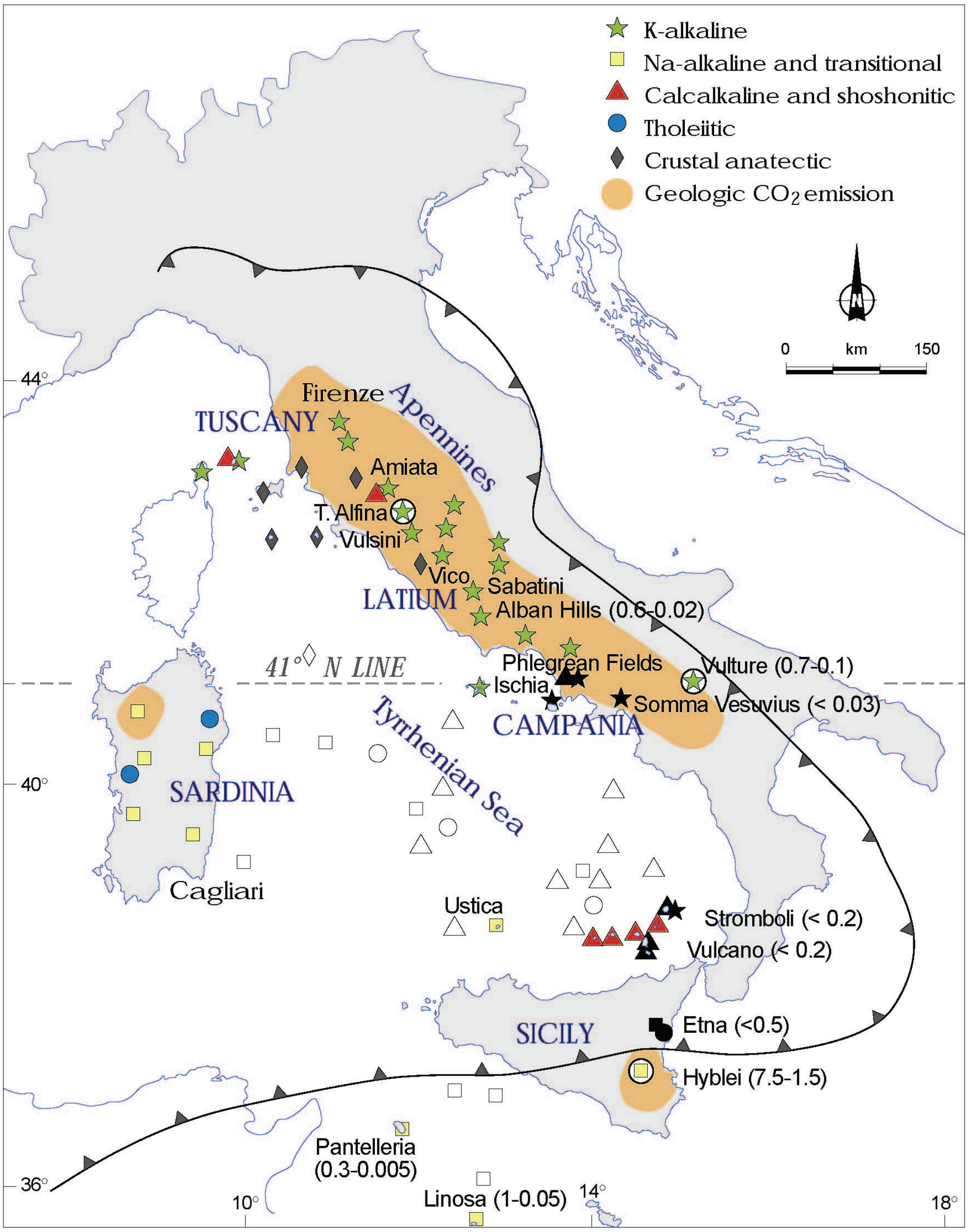


Fig. 1 - Distribution of main geological CO_2 emission in Italy (gray area), as derived from the on-line catalogue of Italian gas emissions, INGV-DPCV5 project (http://googas.ov.ingv.it), and of petrochemical affinities and ages of the main Plio-Quaternary magmatic centers in Italy, modified from Peccerillo (2005). Volcanic centers marked by white circle bear peridotites. Active volcanoes are marked in black. Open symbols refer to outcrops below the sea level. Ages in parenthesis.

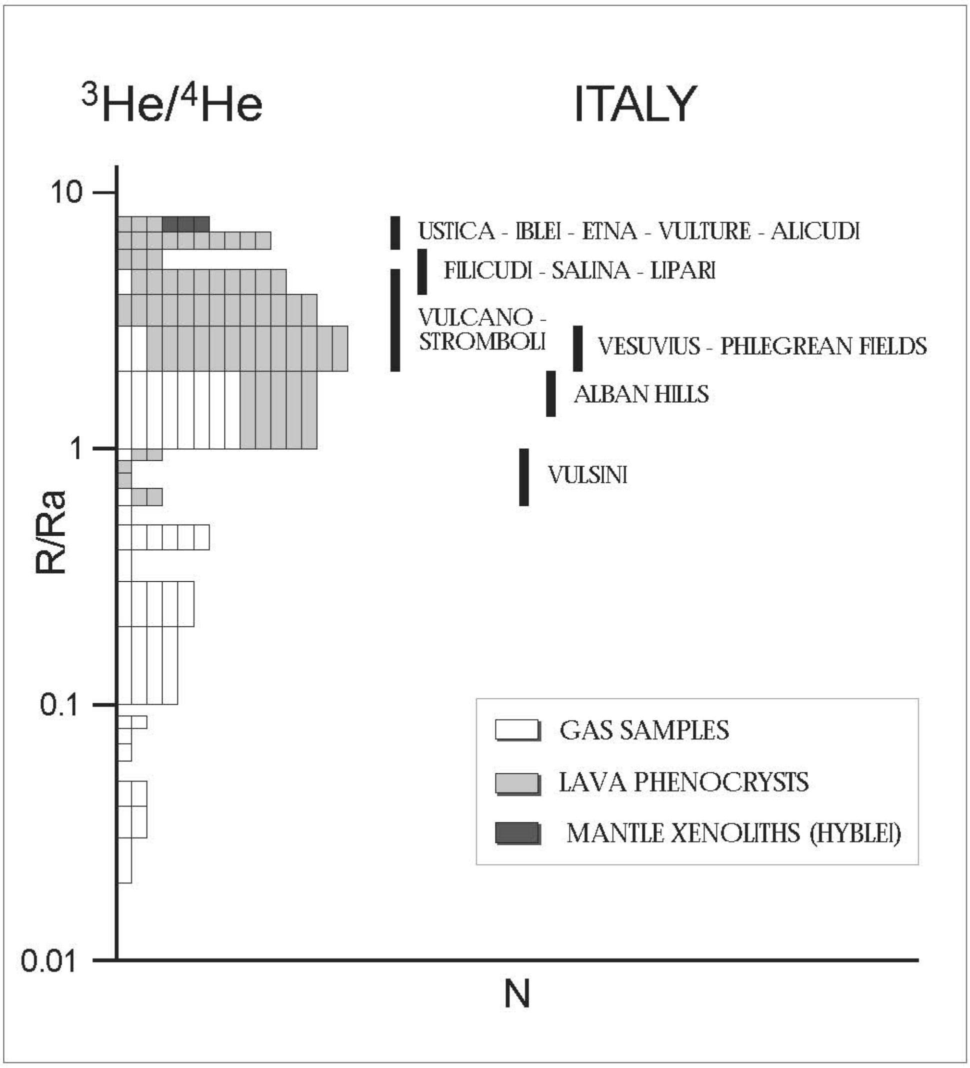


Fig. 2 - Compilation of $^3He/^4He$ ratios (R/Ra), and distribution of helium isotopes in Italy, measured in gas sampled at surface, and in fluid inclusions from Plio-Quaternary magma phenocrysts (olivine and clinopyroxene) and from mantle xenoliths (Minissale, 2004; Martelli et al., 2004; 2008). N = number of measurements.

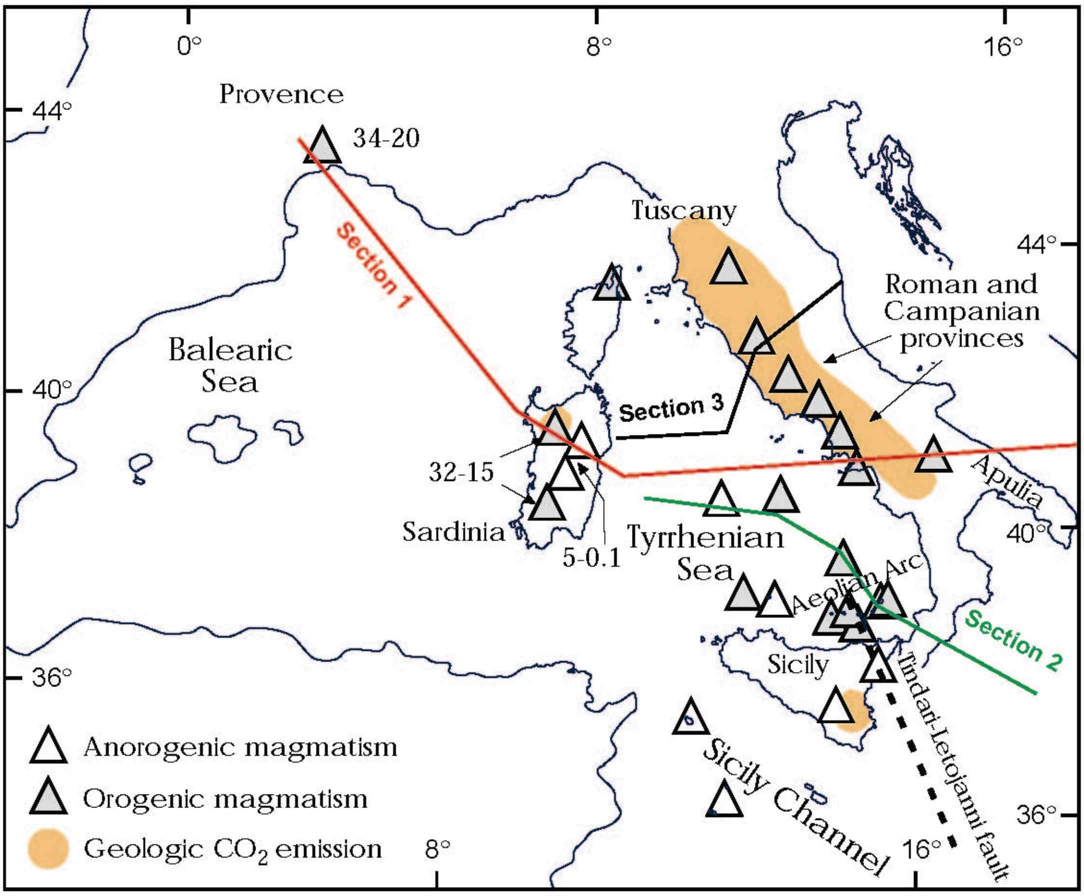
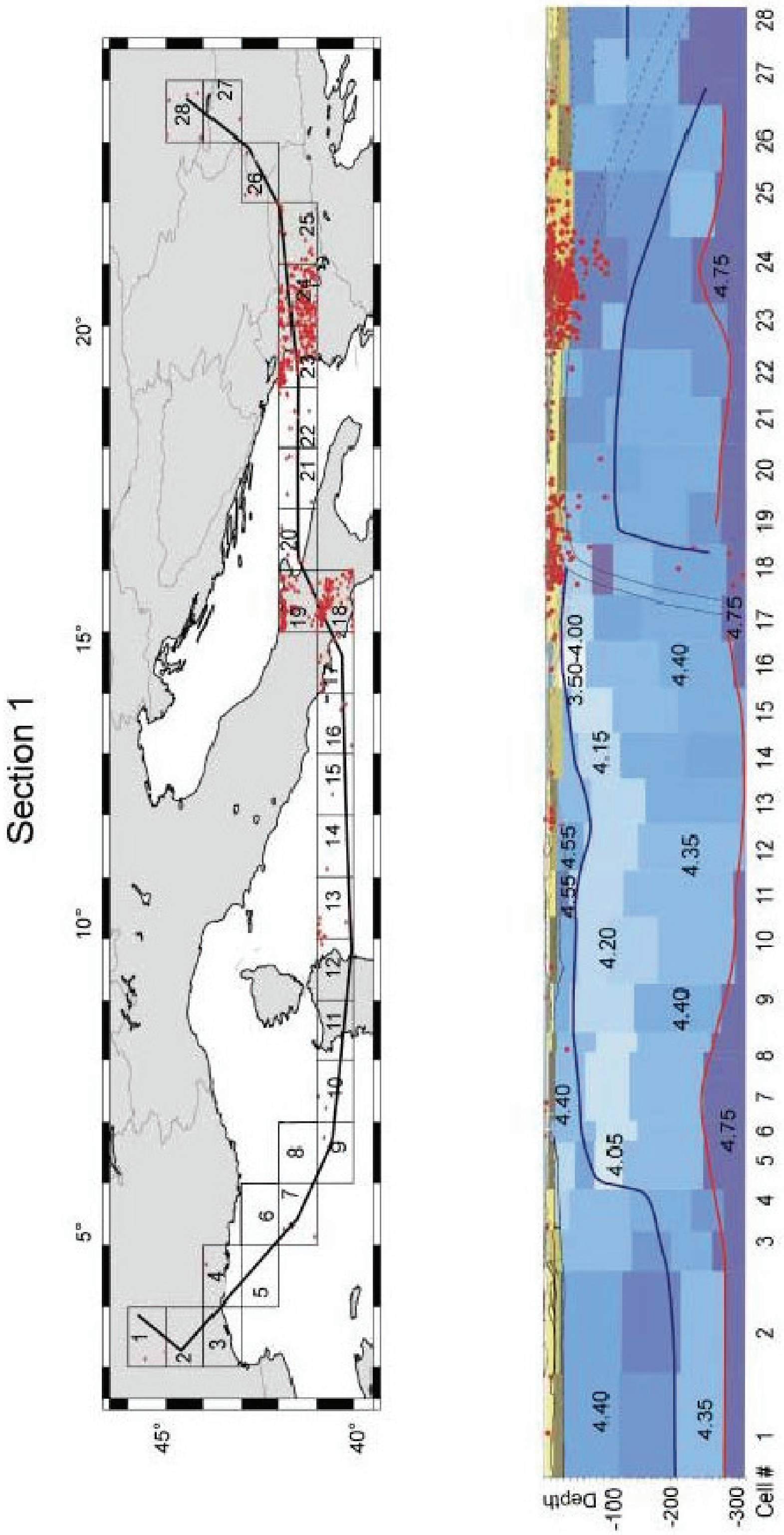


Fig. 3 - Location of the orogenic and anorogenic Plio-Quaternary volcanism in the Western Mediterranean (from Peccerillo, 2003), with respect to geological CO_2 emission areas. Numbered lines represent the pathway of sections illustrated in Figure 4.



Section 1
45°
40°
5°
10°
15°
20°
Depth
-100
-200
-300
Cell #
4.40
4.35
4.05
4.75
4.40
4.20
4.55
4.55
4.35
4.15
3.50-4.00
4.40
4.75
4.75

Figure 4a

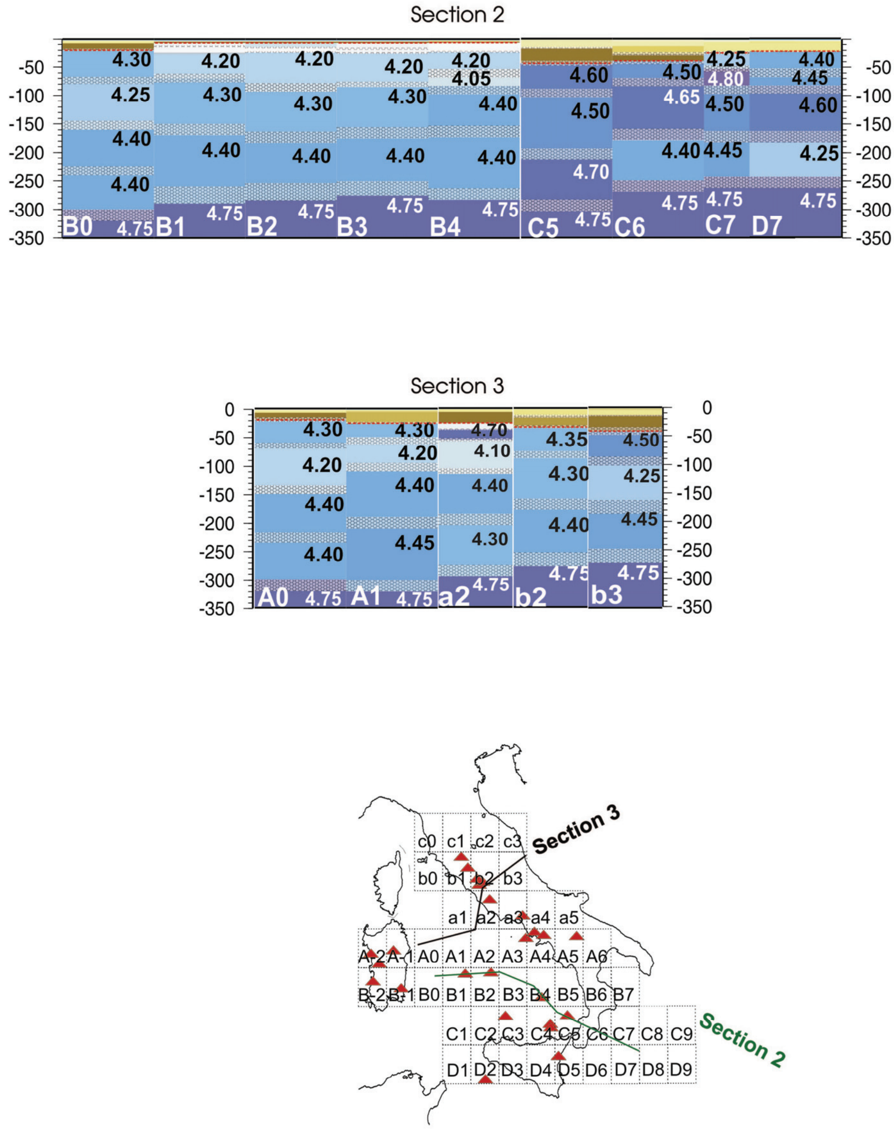


Figure 4b

Fig. 4 - Vs models of the lithosphere-asthenosphere system along three representative sections in the Western Mediterranean. a) Section 1 - 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). b) Sections 2 and 3, are built from the cellular Vs model of the Tyrrhenian Sea and surroundings given by Panza et al. (2007b). 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 Vs ranges of variability are given in Panza et al. (2007a). Red triangles indicate recent and active volcanoes.

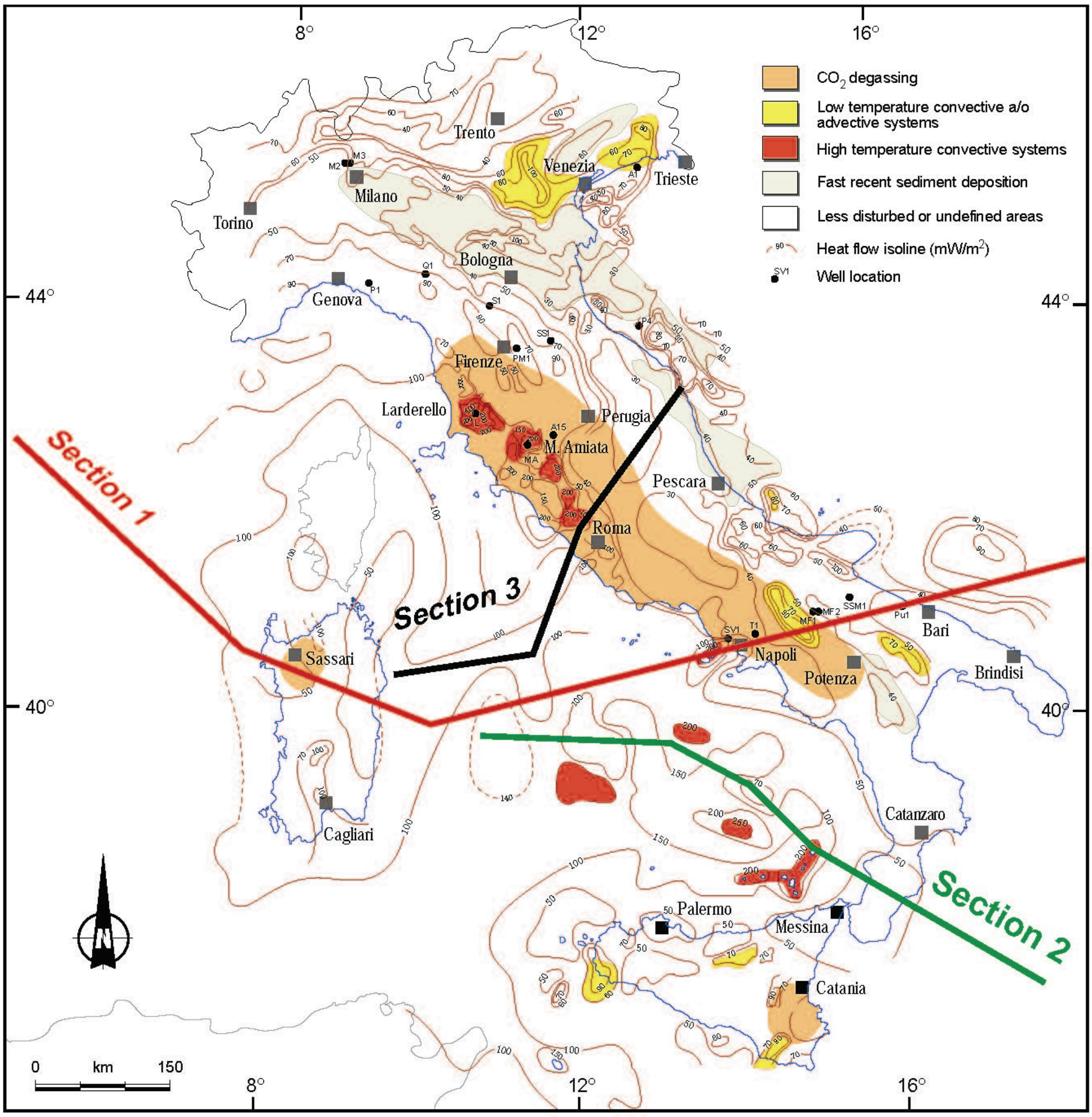


Fig. 5 - Heat flow map of Italy modified after Della Vedova et al. (2001), reporting the location of major CO_2 degassing areas. Most non-volcanic CO_2 emission occurs in areas of normal heat flow. Local high heat flow is associated with subsurface magmas and includes CO_2 fluxes from major geothermal systems (Larderello and Monte Amiata, in Tuscany). Numbered lines represent the pathway of sections illustrated in Figure 4.

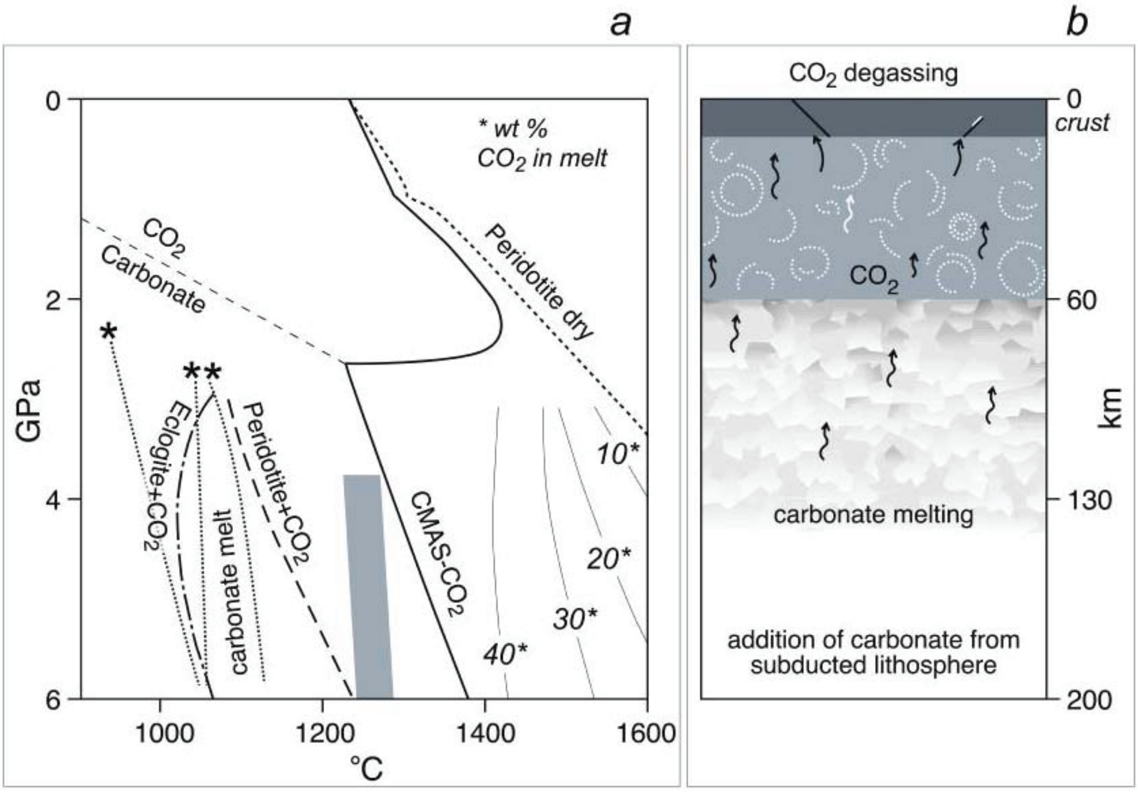


Fig. 6 - Proposed evolution for lithosphere - asthenosphere degassing beneath the Western Mediterranean. a) Pressure-temperature diagram showing the effects of CO_2 on the *solidus* of carbonated lithologies in the mantle. Two different estimates of the peridotite - CO_2 *solidus* are reported: CMSA - 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 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.% H2O + 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, with cessation of Vs attenuation. 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.