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Carbon degassing through volcanoes and active tectonic regions

Outgassing of Mantle Volatiles in Compressional Tectonic Regime Away From Volcanism: The Role of Continental Delamination

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- Mantle-derived volatiles outgas in the continental convergent region without any evidences of volcanism at the surface
- Heat-helium relationship highlights the occurrence of magmatic intrusion at depth in convergent region
- Delamination processes in continental convergent margin can produce magmatism at depth

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antonio.caracausi@ingv.it**Citation:**Caracausi, A., & Sulli, A. (2019). Outgassing of mantle volatiles in compressional tectonic regime away from volcanism: The role of continental delamination. *Geochemistry, Geophysics, Geosystems*, 20, 2007–2020. <https://doi.org/10.1029/2018GC008046>

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Abstract In this study we discuss the occurrence of mantle-derived heat and volatiles (i.e., helium and CO₂) feeding hydrothermal systems in a seismically active margin between two convergent plates (African and European) without any signals of volcanism. The helium (He) isotopes clearly indicate a mantle-derived component in the outgassing volatiles. The estimated mantle-derived He fluxes are up to two to three orders of magnitude greater than those in a stable continental area. Such high He fluxes cannot be provided by a long-lasting diffusion, thereby implying a more efficient transport (i.e., advective transport through faults). He data coupled to heat-He relationship suggest the occurrence of active degassing of magmatic intrusions in this area of continental collisional. Geophysical data indicate the presence of a hot mantle wedge below the outgassing of mantle volatiles and a system of faults cutting the continental crust down to the hot mantle wedge. Here we discuss the hot mantle wedge and possible associated magmatic intrusions as the source of the mantle-derived volatiles outgassing in the region. We also assessed the output of mantle-derived CO₂ from the investigated hydrothermal basins. The possible occurrence of magma at depth as well as the geometry of the thick-skinned deformed wedge unambiguously indicates delamination processes that are related to continental subduction. Hence, we show that delamination processes can really produce magma at depth without evidences of volcanism at the surface. Finally, we have also provided the fault systems that work as a network of pathways and actively sustain the advective transfer of the mantle fluids toward the surface.

Plain Language Summary Volatiles from the Earth's mantle escape into the atmosphere mainly in volcanic districts and in submarine regions where new magma reaches the oceanic bottom. A lesser extent occurs in continental regions undergoing active tectonics. How mantle volatiles degas in continental regions and where evidences of volcanic activity are lacking remain a key challenge, given that in absence of magma the mantle would not lose its volatiles. Here we use the He-heat systematics and recognize the presence of mantle volatiles in a continental region where there is no evidence of volcanism on the surface. This is a rare case of active outgassing of fluids coming from the mantle in a region that is characterized by continental collision. These geochemical evidences support the occurrence of magmatic bodies at depth and an advective flow of volatiles and heat through the crust. Geophysical data corroborate the geochemical evidences demonstrating the occurrence of a portion of hot mantle in between two crustal layers in correspondence of the mantle volatiles at the surface. Geology coupled to geophysics shows the presence of tectonic discontinuities cutting the crust down to the mantle working as a network of pathways through which mantle fluids move to the surface.

1. Introduction

Identification of the transfer of mantle-derived heat and fluids (e.g., CO₂, H₂O, and He) in continental regions is critical for developing exploration strategies and for identifying and quantifying the distribution of economic resources (i.e., Ballentine et al., 2001; Holland & Gilfillan, 2013; Prinzhofer, 2013). Furthermore, quantitative evaluations of fluxes of both mantle-derived heat and volatiles provide new insights into mantle-crust tectonic and on the possible relation between magmatism and geodynamics (i.e., Caracausi et al., 2005; Caracausi et al., 2013; Chiarabba & Chiodini, 2013; Kennedy & Van Soest, 2007; O'Nions & Oxburgh, 1988; Torgersen, 1993). Recently, it has also been shown that magmatic intrusion of dike-like bodies in mountain chains may trigger earthquakes with magnitudes that could be relevant to

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seismic hazard assessment (Di Luccio et al., 2018). Hence, the outgassing of mantle-derived volatiles (e.g., CO₂ and He) in seismic region provides a new perspective for interpreting the seismicity in mountain chains and possibly furnishes new tools for the monitoring of active seismic regions.

Helium (He) is a good tracer for recognizing the outgassing of mantle-derived fluids in continental regions, including where evidences of volcanic activity are lacking (i.e., Burnard et al., 2012; Caracausi et al., 2005; Caracausi et al., 2013; Italiano et al., 2000; O'Nions & Oxburgh, 1988). The Earth's mantle has retained a significant fraction of the primordial He at the time of its formation. In contrast, the continental crust has been extensively reworked over geological time, which has resulted in losing most of its primordial He, and its inventory is predominantly radiogenic, produced by the decay of U and Th content in the crust. Consequently, a relatively high ³He/⁴He ratio (R ; 8 ± 1 times higher the value in atmosphere, R_a) characterizes He degassing in regions of mantle melting, such as at midoceanic ridges (e.g., O'Nions & Oxburgh, 1988). Mantle-derived fluids injected into the crust became progressively diluted by radiogenic He produced in the crust, where the ³He/⁴He ratio is $\sim 0.02R_a$. Hence, ³He/⁴He ratios higher than $0.1R_a$ in natural fluids provide strong evidence for the presence of mantle-derived fluids (Ballentine & Burnard, 2002).

Most durable questions about the outgassing of primordial He in continental regions away from volcanism arise from the localization of its source and from the mechanisms of He transfer through the crust. The occurrence of an outgassing of mantle-derived fluids in continental regions strongly indicates the generation and degassing of magma bodies at depth (i.e., O'Nions & Oxburgh, 1988). In fact, without magma generation and its successive migrations, it would be difficult for the mantle to lose its volatiles (O'Nions & Oxburgh, 1988; Oxburgh et al., 1986; Watson & Brenan, 1987). Mantle-derived volatiles are transferred through the entire crust when the volatiles are able to cross the ductile lower crust, which represents a barrier to the advective transfer of fluids because of its low permeability on long timescales (i.e., Kennedy & Van Soest, 2007, and references therein). In fact, if it is true that faults lead to greater permeability in the region of the tectonic discontinuities, nevertheless, the ductile zone can work as an impermeable boundary because crustal fractures are unable to remain open over long timescales (i.e., Byerle, 1993; Sleep & Blampied, 1992). However, fluid migration in the middle crust cannot be explained in terms of classical concepts, and recent studies highlight that creep cavitation can establish a dynamic granular fluid pump in ductile shear zones (i.e., Fussesis et al., 2009), opening new frontiers in the transfer of fluids in the ductile crust and associated processes (e.g., mantle degassing).

Even if it is well accepted (e.g., O'Nions & Oxburgh, 1988) that volatiles can report the occurrence of magmatic intrusions at depth and the role of faults in the transfer of fluids, it is difficult to recognize the position of the source of mantle-derived volatiles at depth and the network of pathways through which they reach the atmosphere. Recently, seismic tomography is contributing to fill this gap. For instance, in the Apennines, strong CO₂ emission, seismicity, and belt topography, correlated with thermal/fluid anomaly in the mantle, have been associated with extensional faulting and sublithospheric mantle replacement after delamination of the lithosphere (Chiarabba & Chiodini, 2013).

In the Central Mediterranean region, the active tectonic setting is the result of the slow convergence between African and European plates. In the northern Sicily continental margin, it gave rise to the Sicilian Fold and Thrust Belt collisional complex beside the Ionian-Tyrrhenian subduction system, whose complex interaction is responsible for coexisting compressional, extensional, and strike-slip deformation, accompanied by heat flow anomalies and fluid emission in the absence of volcanic evidences.

Here we present new chemical and He isotope data from hydrothermal systems of central Sicily and investigate the relationships between He and heat in order to constrain the origin of the emitted fluids. We also discuss the geochemical data together with the results of the deep seismic profile SiRiPro that arrive to investigate the mantle-crust tectonic features of the region (Catalano et al., 2013) and the main tectonic discontinuities at a regional scale. This multidisciplinary study points to localize the source of the mantle fluids (i.e., He and CO₂) degassing away from volcanism and the tectonic discontinuities through which the fluids move toward the surface. This work gives a new contribution to figure out the crust-mantle tectonic in the central-western Mediterranean that is a key area in the geodynamic evolution of the Mediterranean. Finally, we also furnish a preliminary data of mantle-derived CO₂ output in a compressional tectonic regime.

2. Geological Framework

The central Mediterranean is a complex area constituted by a puzzle of different lithospheric segments, whose geological evolution is constrained by the continuing northward advance of the African plate (Doglioni et al., 2012; Goes et al., 2004) toward Europe. In this geological domain, the northern Sicily continental margin represents a link between the Sicilian-Maghrebian chain and the Tyrrhenian extensional (backarc) area in the north-south direction, while in the east-west direction the collisional complex is replaced by a subduction system (Figures 1 and 2; Catalano et al., 1996; Catalano & Sulli, 2006; Cernobori et al., 1996; Lentini et al., 1994; Roure et al., 1990).

In this area the structure of the lithosphere is strongly a matter of debate (Chiarabba et al., 2008; Doglioni et al., 2007; Faccenna et al., 2005). A high-penetration seismic reflection profile along the central Sicily (SiRiPro) has evidenced the deep structure of the A-subduction system, showing a basement-involved collisional belt (Catalano et al., 2013). The deformed wedge rises from the folding, detachment, and thrusting of sedimentary rocks deposited on both the Mesozoic-Paleogene rifted-passive African continental margin and the Neogene-Quaternary convergent margin. The collisional complex of Sicily, pertaining to the Apenninic-Maghrebian chain, is formed by the following (Figures 1 and 2): (1) the E-to-SE vergent fold and thrust belt. The tectonic history of the Sicily Fold and Thrust Belt (hereafter FTB), started from the early Miocene collision with the Sardinia Block, was a combination of progressive frontal accretion of shallow seated thrust sheets and duplex and underthrusting of deep-seated units (Figure 3), combined with backthrusting and clockwise rotation of the allochthons. Accordingly, two main noncoaxial compressional events, generated and developed at different structural levels (shallow- and deep-seated thrusts) and at different time intervals, formed the present-day tectonic assemblage.

Eastward, along a region developing from southern Tyrrhenian (Marsili basin), through Aeolian Islands and Calabrian Arc (including northeastern Sicily), to the Ionian sea, a B-subduction complex occurs (Figure 2). The forward migration of the accretionary wedge-volcanic arc system was accompanied by rifting episodes. As a consequence, Plio-Pleistocene high-angle extensional to transtensional faults are widespread in northern Sicily continental margin, which dissected also the internal part of the Sicilian collisional system (Bello et al., 2000; Catalano et al., 2000b, 2013; Roure et al., 1990) affecting up to the middle-upper Pleistocene marine and continental deposits. Conversely, some authors (e.g., Giunta et al., 2009) postulated the existence in this area of an E-W trending right-lateral wrenching connected to a crustal discontinuity inherited from the African margin dissection.

The behavior of the subduction beneath Apennines and Maghrebides is explained by different geodynamic models schematized by two endmembers: (1) a continuous laterally bent slab underlying the whole Apenninic-Maghrebian salient (Doglioni et al., 1999); and (2) a seismically active Calabrian slab solely driving the subduction processes being the Southern Apennines and Sicily only lateral rootless belts (Faccenna et al., 2005). Seismic tomography evidenced a continuous 25-km-deep low *P* velocity feature beneath Southern Apennines-Calabria-Sicilian Maghrebides (Chiarabba et al., 2008). Different geometries and shortening between the Apennine-Maghrebide and Calabrian wedges could be explained by tears separating different sectors of a composite continental-oceanic subduction system, producing variable shortening in the upper plate and variable subduction angle in the lower plate.

2.1. Geophysical Constraints

Geophysical data reveal different types of crust (from thin anomalous Tyrrhenian to normal African) across the northern Sicily continental margin. The Moho depth increases southward from 10 km in the Tyrrhenian abyssal plain to about 25 km near the Sicily margin reaching about 37–40 km under the Sicilian FTB (Cassinis et al., 2003; Scarascia et al., 1994); from here it decreases southward until about 27 km beneath the Iblean platform (Chironi et al., 2000) and from 20 to 16 km along the Ionian margin and the abyssal plain, respectively (Catalano et al., 2000a; De Voogd et al., 1992). *S* wave tomography indicates a shallow upper mantle source for the Apennines-Tyrrhenian igneous system, while the asthenosphere is postulated to be very shallow, as deep as 30–40 km (Panza et al., 2007). The map of the magnetic basement (Morelli, 2003) shows depth values of 8–10 km beneath the Iblean domain, 10–12 km in western Sicily, more than 14 km in the Caltanissetta trough, and about 13 km along the northern margin (Bello et al., 2000; Catalano et al., 2000b; Finetti, 2005).

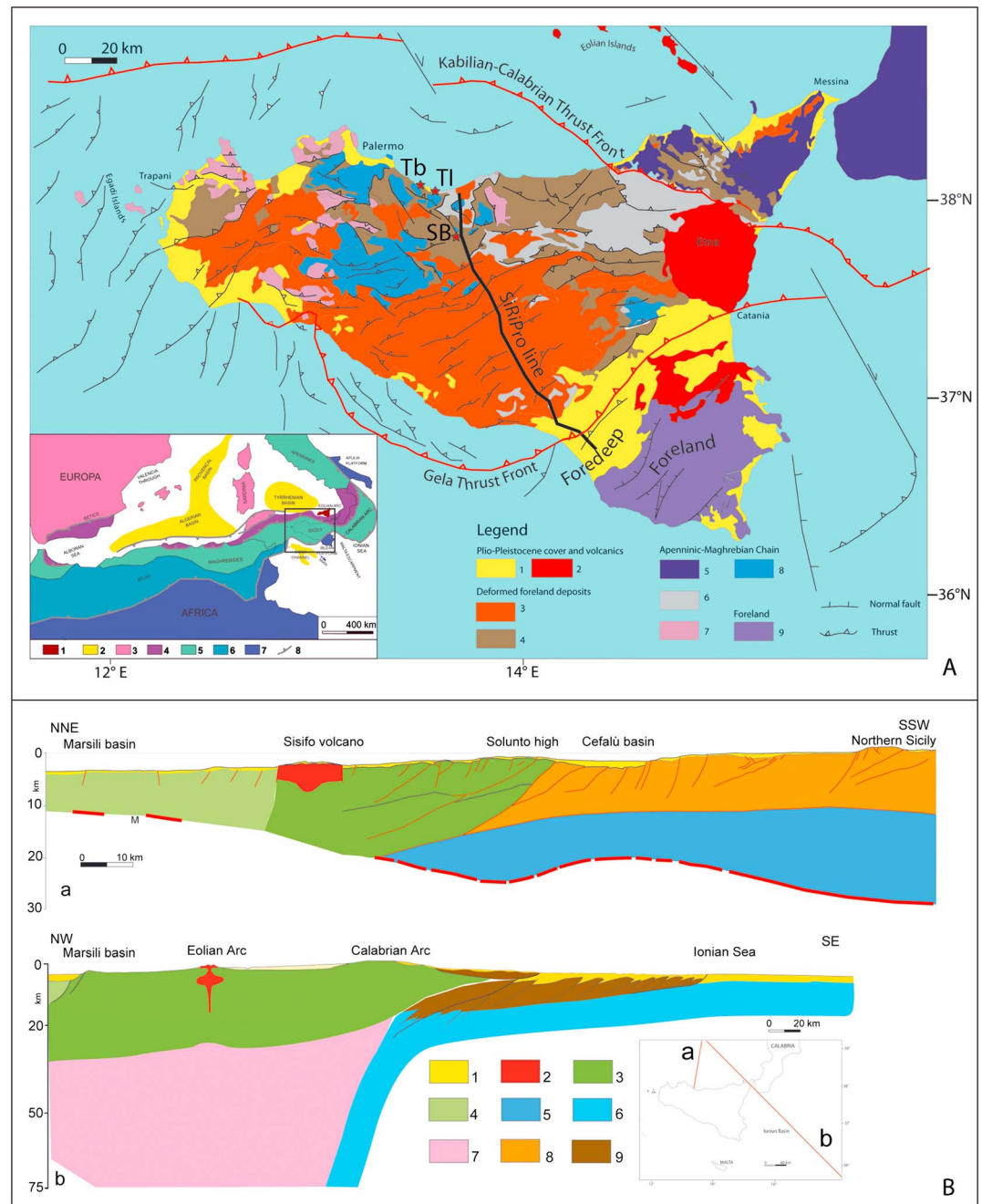


Figure 1. (A) Structural map of Sicily (modified from Catalano et al., 2013). (1) Plio-Pleistocene cover, (2) volcanics, (3) upper Miocene-lower Pliocene deformed foreland deposits, (4) upper Oligocene-lower Miocene deformed foreland deposits, (5) Kabilian-Calabrian crystalline units, (6) Sicilide units, (7) Meso-Cenozoic carbonate platform deformed units (Sicilian-Maghrebian shallow-water units), (8) Meso-Cenozoic slope-to-deep-basin deformed units (Sicilian-Maghrebian deep-water units), and (9) Meso-Cenozoic carbonate platform not-deformed units (Sicilian-Maghrebian foreland). Red stars indicate the sampling points (i.e., TI, Tb, and SB). Inset map shows the main physiographic regions of the central western Mediterranean. (1) Volcanics, (2) extensional basins, (3) European units, (4) Kabilian-Calabrian units, (5) Apenninic-Maghrebian units, (6) Atlas units, (7) African foreland, (8) main thrust fronts (modified from Roure et al., 2012; Catalano et al., 2013). (B) Geological sections showing the Sicilian collisional system in the southern Tyrrhenian Sea (a) and the B-subduction complex, from the Ionian Sea to the southern Tyrrhenian Sea (b). (1) Plio-Pleistocene cover, (2) volcanics, (3) Kabilian-Calabrian (European) units, (4) thinned to oceanic Tyrrhenian crust, (5) African crust, (6) Ionian crust, (7) mantle, (8) Sicilian-Maghrebian units, and (9) Ionian accretionary wedge. The geological sections were obtained from the interpretation of the crustal seismic profile CROP6 (a) and M2 (b), respectively, calibrated by refraction data, well logs, and field geology.

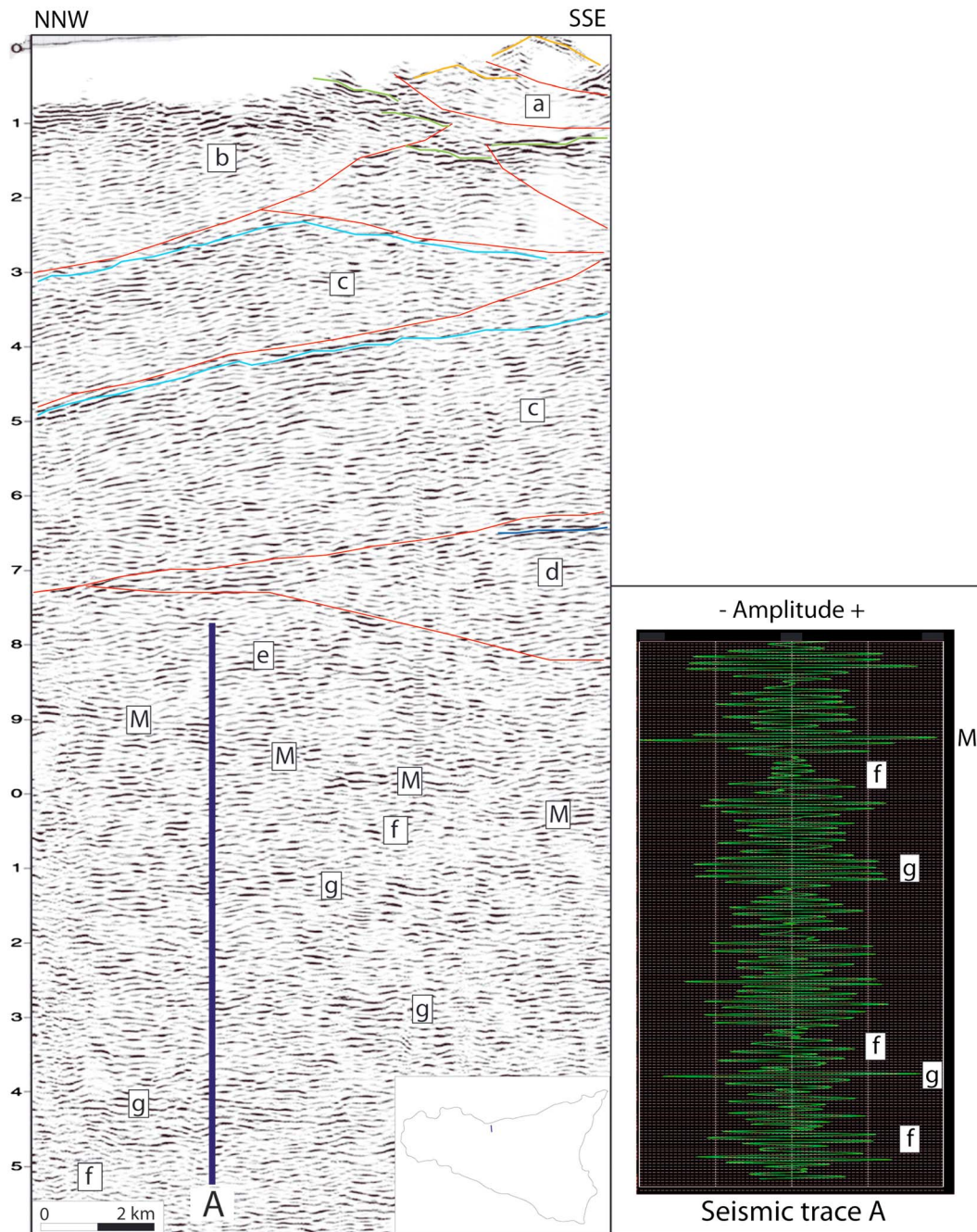


Figure 2. Detail of the northernmost sector of the SiRiPro line (see Figure 1). Seismic units: (a) high-frequency to reflection-free bodies, assembled as tightly deformed thin slices, interpreted as a stack of both detached terrigenous Tertiary cover and Upper Mesozoic-lower Tertiary Sicilide units; (b) high frequency deformed slices, interpreted as Permian-Cenozoic deep water carbonate units; (c) low-to-high frequency deformed bodies, interpreted as pertaining to the Meso-Cenozoic shallow-water carbonate units; (d) low-to-high frequency shallow-water Meso-Cenozoic carbonate unit, derived from the deformed northward prolongation of the Iblean foreland; (e) transparent-to-reflective body, topped by a high-amplitude reflector, interpreted as the continental crust, with a steep ascent in a northward direction. The lower part has an anomalously high reflectivity, which could be linked to stretching extensional processes; (f) transparent layer, interpreted as mantle due to its position below the Moho and its correlation with seismic refraction data; (g) lens/wedge-shaped reflective bodies, which could correspond to delaminated fragments of the lower crust (and possibly part of the lithospheric mantle) inside the mantle. Brown line, top of Numidian Flysch and Sicilide units; green line, top of Meso-Cenozoic Sicilian-Maghrebian deep-water units; light-blue line, top of Meso-Cenozoic Sicilian-Maghrebian shallow-water units; blue line, top of Meso-Cenozoic deformed foreland; M, Moho discontinuity; red lines, faults. On the right, the lower part (from 8 to 15 s/TWT) of the seismic trace is shown.

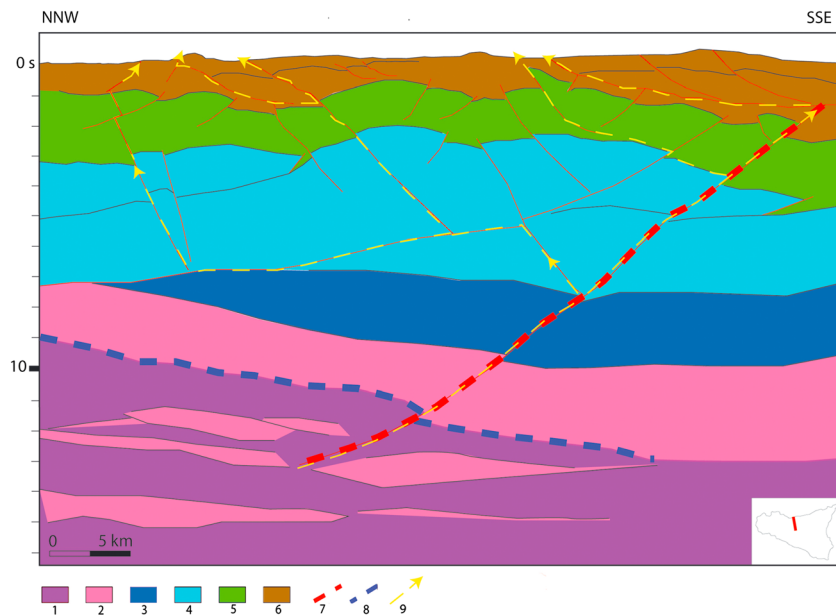


Figure 3. Geoseismic section showing the tectonic stack forming the Sicilian FTB and relationships with the crust-mantle layers. The complex network of faults is shown by red lines. (1) Mantle, (2) African continental crust and delaminated layers, (3) deformed and undeformed Iblean carbonate units, (4) deep-seated, shallow-water Meso-Cenozoic carbonate tectonic units, (5) shallow-seated, deep-water Meso-Cenozoic carbonate tectonic units, (6) shallow-seated, terrigenous Tertiary detached cover, (7) basement-involved main thrust, crossing the crust and penetrating the mantle, (8) delamination surface, and (9) pathways for ascending fluids.

In Sicily, heat flow values vary generally from 40 to 50 mW/m² (Della Vedova et al., 2001). Localized areas of higher values are present in the Iblean foreland (up to 80 mW/m²), in westernmost Sicily (up to 80 mW/m²), in northern Sicily (up to 70 mW/m²), and in the Tyrrhenian Sea (more than 100 mW/m²). The high heat flow in the westernmost sector can be linked to an excess of heat due to accumulations of mantle-derived melts into the crust or at the crust-mantle boundary (Caracausi et al., 2005). The high heat flow of the Tyrrhenian Sea is linked to the Eolian volcanism (Della Vedova et al., 2001), while no detailed studies have been still carried out to investigate the origin of the high heat flow in northern Sicily and in the Iblean foreland.

Sicily and the surrounding areas are characterized by intense recent tectonic activity, testified by a strong seismicity, individuating main seismotectonic zones. In particular, excluding areas located far away from the study area, major earthquakes are concentrated in the following (Billi et al., 2010; Pondrelli et al., 2006): (1) a contractional-transpressional belt in southern Tyrrhenian and western Sicily, passing eastward and southward to (2) an extensional-transtensional belt in the Madonie-Peloritani mountains (e.g., Pollina cluster) and Caltanissetta trough; (3) a transtensional belt in the Iblean foreland, parallel to the Malta Escarpment, separating the Sicily from the Ionian abyssal plain (Catalano et al., 2000a).

In northern central Sicily, clusters of deep earthquakes, concentrated mainly along N-S to NNW-SSE trends, point out an anomalous lithosphere depth that encourages the hypothesis of subduction processes beneath central Sicily (Billi et al., 2010; Chiarabba et al., 2008).

3. Fluids Geochemistry

3.1. Sampling and Analytical Methods

Three hydrothermal systems are localized in the northernmost Sicily (TI, Tb, and SB; Figure 1), just in correspondence of the SiRiPro profile (Catalano et al., 2013). A total of 12 waters were sampled from springs and wells localized in TI, Tb, and SB between 2002 and 2013. The water samples for the analysis of the chemistry of the dissolved gases and the He-isotope ratio were collected in glass bottles according to protocols described by Capasso and Inguaggiato (1998) and analyzed in a few days from their collection in order to prevent any contamination and/or loss of volatiles.

Table 1
Chemical Data

Site	Data	T (°C)	He	N ₂	CH ₄	CO ₂	⁴ He/ ²⁰ Ne	³ He/ ⁴ He
TI 1	Sep 2002	43.4	1.3E−03	1.1E+01	9.4E−03	3.2E+01	9.55	1.33
TI 2	Sep 2002	42.6	1.3E−03	1.2E+01	3.6E−03	2.9E+01	8.83	1.32
TI 3	Apr 2001	41.4	1.1E−03	1.6E+01	3.1E−03	4.8E+01	6.97	1.31
TI 1	Jun 2012	43.1	1.7E−03	1.4E+01	1.6E−02	3.1E+01	6.19	1.31
TI 2	Apr 2012	42.2	2.0E−03	1.3E+01	1.4E−02	3.4E+01	18.15	1.29
TI 1	Feb 2013	42.9	1.7E−03	1.2E+01	1.3E−02	3.1E+01	6.81	1.30
Tb	Sep 2004	27.8	1.2E−03	2.0E+01	1.4E−02	8.5E+00	4.09	0.36
Tb	Dec 2004	27.5	1.2E−03	1.4E+01	3.4E−02	8.5E+00	4.52	0.39
Tb	May 2013	27.5	1.1E−03	1.7E+01	1.2E−02	1.0E+01	3.88	0.36
SB	Dec 2004	33.2	4.4E−04	3.1E+00	1.9E+01	1.9E+01	7.88	0.77
SB	Nov 2004	32.3	6.6E−04	1.9E+00	2.1E+01	3.6E+01	3.78	0.77
SB	May 2013	32.8	6.1E−04	n.a.	n.a.	n.a.	12.1	0.74

Note. Total dissolved inorganic carbon is expressed in mmol/L; He concentrations are in ccSTP/L; ³He/⁴He are expressed as R/R_a values; δ¹³C values are in ‰. n. a. not available data.

The chemical compositions of the dissolved gases were determined with a gas chromatograph (Perkin Elmer 8500) with Ar carrier gas on a 4-m column (Carbosieve SII) and double detector (TCD and FID). The analytical error was about ±3% for all species. The concentrations of the dissolved gases in the waters have been computed on the basis of the solubility data of the gaseous species in water (Capasso & Inguaggiato, 1998).

He isotopes were analyzed using a static vacuum mass spectrometer (GVI Helix SFT) with a double collector in order to detect ³He and ⁴He ion beams simultaneously (isotopic ratio precision within ±0.5%); this method ensured very low errors for the ³He/⁴He measurements. The ³He/⁴He ratio was determined by measuring ³He in an electron multiplier detector and ⁴He in an axial Faraday detector. ⁴He/²⁰Ne ratios were measured with a quadrupole mass spectrometer.

He isotopic ratios are reported as R/R_a values, where R_a is the He-isotope ratio in atmosphere (1.39×10^{-6} ; Ozima & Podosek, 2002). All sampling and analytical devices were provided by the Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo.

3.1.1. Geochemical Data

The chemical and isotopic data of the collected samples are reported in Table 1. The temperature of the emerging waters ranges from 27.5 to 43.4 °C for Tb and TI waters, respectively (Table 1). The temperature of the SB waters is from 32.3 °C to 33.2 °C. Previous investigations (Carapezza et al., 1987; Grassa et al., 2006) highlighted the following: (1) TI and SB waters are chloride-sulfate-alkaline waters, in contrast to the bicarbonate-alkaline-terrigenous waters of Tb; and (2) a meteoric recharge of the hydrological basins with a large contribution from seawater in the TI basin.

Gases dissolved in TI waters are CO₂ dominated (from 29 to 48 ccSTP/L), with an amount higher than in water in equilibrium with the atmosphere (air saturated water). In contrast, N₂ (14–20 ccSTP/L) is the main dissolved gas in Tb waters. SB waters are CH₄- and CO₂-rich, from 19 to 21 ccSTP/L and 19 to 36 ccSTP/L, respectively. He is always in trace and its abundance is up to two orders of magnitude higher than the air saturated water (4.41×10^{-8} ccSTP/g at 25 °C; Ozima & Podosek, 2002).

He-isotope composition in the collected fluids is from 0.36R_a (Tb) to 1.33R_a (TI). He isotope signature at SB site is 0.74–0.77R_a. All of the ⁴He/²⁰Ne ratios are at least one order of magnitude higher than the value for the atmosphere (0.318; Ozima & Podosek, 2002), indicating that air contamination was negligible in all of the investigated fluids (Table 1).

3.1.2. Mantle-Derived He Degassing

In large crustal fluid systems, reasonable sampling “average” crust ³He/⁴He ratios in excess of $1-3 \times 10^{-8}$ (i.e., more than three times the upper crust value; Ballentine & Burnard, 2002) are due to a ³He excess from sources external to the crust (Marty et al., 1993). ³He/⁴He ratios in the study area are from 5.0×10^{-7} (0.4R_a) to 1.8×10^{-6} (1.3R_a), at least one order of magnitude higher than the upper crust value (0.01–0.03R_a), so considering that the He atmospheric contribution is negligible in the North-Central Sicily thermal basins (NCStb), there is a clear contribution of mantle-derived He.

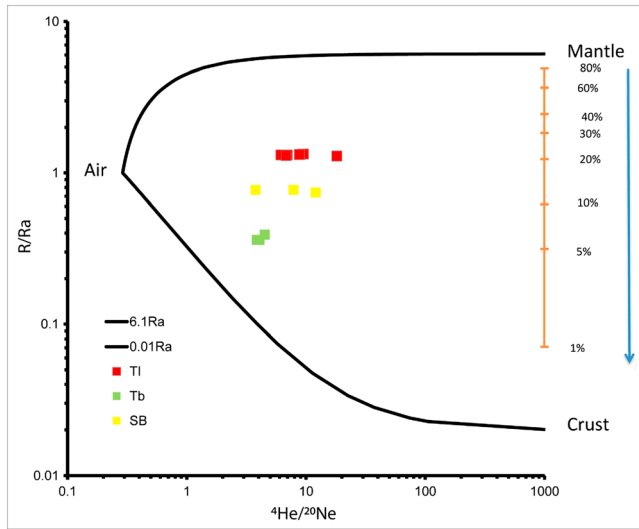


Figure 4. $^3\text{He}/^4\text{He}$ ratios (as R/R_a) plotted against the $^4\text{He}/^{20}\text{Ne}$ ratios. The line shows the mixing between the three possible end-members: air, crust, and mantle.

On the basis of the approach proposed by Sano et al. (1997), it is possible to solve the percentage of mantle-derived He and crustal He (U and Th decay in the crust) in the studied gases by using mixing equations and both the He isotopic ratio and the $^4\text{He}/^{20}\text{Ne}$ ratio of the three possible source of He: atmosphere, mantle, and crust (Figure 4). The typical crustal He endmember, dominated by ^4He production due to U and Th decay in the crust, is $0.01\text{--}0.02R_a$ (Ozima & Podosek, 2002). Because the investigated thermal systems are in a continental region, we made calculations assuming a subcontinental lithospheric mantle, with a He-isotope ratio of $6.1 \pm 0.9R_a$ (Gautheron & Moreira, 2002), as mantle source in the area. Fluids associated with NCSfb are characterized by a very low atmospheric contribution and contain mantle helium contributions from $\sim 5\%$ to $\sim 20\%$ (Figure 4).

Considering that the tectonics in NCSfb acts upon the hydrology of the thermal systems (Carapezza et al., 1987), according to Kennedy et al. (1997), we computed the ^3He flux ($\Phi_{^3\text{He}}$) based on the upward fluid flow rates through faults and the production of radiogenic He in the crust. Mantle He moving through the crust across faults is diluted by radiogenic ^4He produced by the decay of U and Th in the crust. The result is a vertical gradient of He isotopic ratio as a function of the radiogenic He production rate and of the vertical rate of fluid flow (Kennedy et al., 1997). The upward flow rate (q) is as follows:

$$q = \frac{H_c \rho_s P(\text{He})}{\rho_f [\text{He}]_{F,m}} \times \left[\frac{R_s - R_c}{R_m - R_c} \right] \quad (1)$$

where H_c is the crustal thickness, ρ_f and ρ_s are the density of fluids and rocks, respectively, $P(\text{He})$ is the radiogenic He production rate (Ozima & Podosek, 2002), which is computed by using the U and Th contents of the rocks, $[\text{He}]_{F,m}$ is the initial concentration in the mantle fluid and is calculated from the measured ^4He concentration and He isotopic composition of the sampled fluid, R is the $^3\text{He}/^4\text{He}$ of sample (s), mantle (m), and crust (c). Based on crustal thickness below the investigated region (40 km: 3 km shales, 12 km limestone, and 25 km crystalline basement plus mantle wedge; Figures 2 and 3) and computing the ^4He production rate by assuming the U and Th contents in the different lithology of the CWS crust (shale U = 4 ppm and Th = 12 ppm; limestone U = 1.3 ppm and Th = 0.2 ppm; crystalline basement U = 1.4 ppm and Th = 5.6 ppm; data in Rudnick & Fountain, 1995; Schön, 1996; Caracausi et al., 2005), the calculated upward fluids flow rates range from about 30 to ~ 110 mm/year.

On the basis of the upward flow rate of fluids, it is possible to calculate the ^3He flux (Kulongosky et al., 2013):

$$\Phi_{^3\text{He}} = q \times \rho_f \times [\text{He}] \times R \quad (2)$$

where $[\text{He}]$ and R are the concentrations of ^4He and $^3\text{He}/^4\text{He}$ ratio in the sample, respectively. The computed $\Phi_{^3\text{He}}$ in the NCSfb ranges from 1.8×10^4 to 7.7×10^4 atoms $\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ (at Tb and TI, respectively; at SB is 4.3×10^4 atoms $\cdot\text{m}^{-2}\cdot\text{s}^{-1}$); these values are much higher than the ^3He flux from stable continental crust (less than 10^2 atoms $\cdot\text{m}^{-2}\cdot\text{s}^{-1}$; Ozima & Podosek, 2002) and are comparable with flux from continental areas undergoing extensive tectonics (up to 10^5 atoms $\cdot\text{m}^{-2}\cdot\text{s}^{-1}$; Ozima & Podosek, 2002). Furthermore, according to equations (1) and (2), if the radiogenic He production rate is higher than the computed values (U-rich crust: contents of U up to 4 ppm vol. and Th up to 12 ppm vol.; Rudnick & Fountain, 1995), the $\Phi_{^3\text{He}}$ will be higher than 1.5×10^5 atoms $\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. This still supports that the $\Phi_{^3\text{He}}$ are in the range of the values from continental areas undergoing extensive tectonics. Such high He fluxes cannot be sustained by a long-lasting diffusion (Ballentine & Burnard, 2002), thereby implying an efficient He transport (i.e., advective transport through faults). In fact, high mantle He fluxes are typical of continental regions affected by extensional tectonics (e.g., Caracausi et al., 2005; Italiano et al., 2000; O'Nions & Oxburgh, 1988; Ozima & Podosek, 2002), where magmatic intrusions in the crust were inferred (Ballentine & Burnard, 2002).

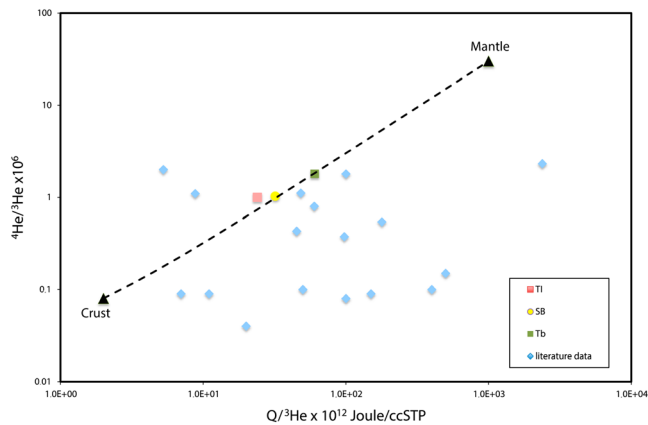


Figure 5. Heat versus He relationship in continental-hosted geothermal systems. Mantle-derived He is associated with heat coming from the mantle in the investigated hydrothermal basins. Heat and He in these basins have not experienced significant $Q/{}^3\text{He}$ fractionation (e.g., magma aging or adiabatic cooling). Data on the crust and mantle endmembers and literature data characteristics are available in Kennedy et al. (2000) and Mutlu et al. (2008).

Cataldi et al., 1995) and the computed ${}^3\text{He}$ flux, from 1.8×10^4 to 7.7×10^4 atoms·m $^{-2}$ ·s $^{-1}$ (Tb and TI, respectively). In geothermal system associated to midoceanic ridge, the He isotopic compositions of plume fluids are indistinguishable from the mantle, and the $Q/{}^3\text{He}$ ratios vary from ~ 1 – 10×10^{12} J/ccSTP (Baker & Lupton, 1990). Moreover, the measured heat/He ratios are remarkably similar to the theoretically predicted value, providing a measure of validity to the theory of heat-He coherence in geothermal systems. In a stable continental crust, He is dominated by radiogenic He production and the $Q/{}^3\text{He}$ ratio is $\sim 1 \times 10^{15}$ J/ccSTP, up to three orders of magnitude larger than the expected mantle value (Kennedy et al., 2000). Because of the large difference between the ratio in volcanic and nonvolcanic systems, the heat/ ${}^3\text{He}$ ratio can allow discriminating possible contributions of mantle heat feeding continental geothermal system. The computed heat/ ${}^3\text{He}$ ratios for the NCStb (TI, SB, and Tb) fall in a narrow range of values, from 25 to 60×10^{12} J/ccSTP, which are lower than the typical values of geothermal systems in continental crust far from volcanoes. Furthermore, the NCStb values are comparable with the same ratio in geothermal systems (Figure 5), which are characterized by deep permeability and fluid circulation along an elevated geothermal gradient partially driven by mantle melting (Kennedy et al., 2000; Kennedy & Van Soest, 2007; Mutlu et al., 2008). This evidence, coupled with (1) structural conditions (active extension in central northern Sicily), (2) localized high heat flow, (3) evidences of a hot mantle wedge embedded into crust (sections 2 and 4), and (4) high ${}^3\text{He}$ flux that are typical of continental region affected by crustal extensional tectonics, strongly supports that the release of mantle-derived He in the NCStb is related to magmatism at depth. In actual fact, mantle volatiles are more efficiently transferred by mantle-derived melt intrusion into the crust (Ballentine & Burnard, 2002), thus showing evidence of a subsurface magmatism when other possible indicators are lacking (i.e., Italiano et al., 2000; O'Nions & Oxburgh, 1988). Release of mantle He is often associated with magmatism, and it seems logical that the mantle must melt in order to liberate He: in fact diffusion through solid mantle would be too slow to account for the observed fluxes (Burnard et al., 2012).

4. Gravity Modeling, Seismic Reflection, and Geological Features

Starting from the hypothesis of magmatic intrusion as source of degassing of mantle-derived fluids, we used geological and geophysical constraints to identify the geodynamic mechanism responsible for the crust-mantle features and behavior.

It is generally agreed that processes as post-orogenic extensional collapse, regional uplift, deep-seated magmatism, elevated heat flow, and subcrustal seismicity could be the tectonic and geodynamic consequences of lithospheric delamination (Bird, 1979; Knapp et al., 2005; Meissner & Mooney, 1998).

Furthermore, assuming that the mantle $\text{CO}_2/{}^3\text{He}$ is 2×10^9 (Marty & Jambon, 1995), we also compute the flux of mantle-derived CO_2 , by using the computed ${}^3\text{He}$ flux, and it is from 1.8×10^3 to 8.2×10^3 mol·km $^{-2}$ ·year $^{-1}$. These values are at least three orders of magnitude lower than the CO_2 flux in active and quiescent worldwide volcanic systems (Caracausi et al., 2015, and reference therein) and one to two orders of magnitude lower than the flux of mantle-derived CO_2 along the African rift system (up to 2.5×10^5 mol·km $^{-2}$ ·year $^{-1}$; Foley & Fischer, 2017). However, the computed mantle- CO_2 flux in the NCStb is comparable with that from the San Andreas Fault (4.0×10^4 mol·km $^{-2}$ ·year; Kulongosky et al., 2013), and these are rare data from a continental region away from volcanism in a compressional tectonic regime.

The three investigated hydrothermal systems fall in a E-W elongated region of high heat flow, up to 70 mW/m 2 , so from 20 to 30 mW/m 2 higher than the heat flow in the surrounding area at regional scale (Cataldi et al., 1995). This evidence supports that in the NCStb the outgassing of mantle-derived He is associated to high heat flux. Hence, in order to investigate a possible relation between heat and mantle-derived volatiles, we computed the heat/ ${}^3\text{He}$ ratios, by dividing the heat flux in the region of the investigated hydrothermal systems (70 mW/m 2 ;

The geometry of the lithosphere down to the mantle-crust interface along the Sicily FTB can be drawn by the high-penetration seismic reflection profile (SiRiPro) that crosses Sicily for more than 100 km from the Tyrrhenian Sea to the Sicily Channel (Catalano et al., 2013). Data related to gravity modeling, seismic refractions, shallower reflections, field geology, and borehole stratigraphy are widely available for the studied region (Gasparo Morticelli et al., 2015; Giustiniani et al., 2018), and they support the interpretation of the seismic data. Just below the area of the outgassing of mantle-derived volatiles degassing coupled to heat flow anomalies in the NCStb, the seismic line provides evidence that the crystalline basement is involved in thrusting and appears to be in a stacked arrangement down to the mantle-crust interface (Figure 2). The sedimentary portion is detached from the basement and more tightly deformed and accreted to form a tectonic edifice with thickness more than 15 km. Still in this region, at a depth of 30–40 km, a wedge-shaped body is interbedded between two crustal segments, the uppermost resting above the wedge, and climbing up toward the north, where it links with the thinned continental crust beneath the Tyrrhenian sea, and the lowermost deepening abruptly beneath it (Figure 3). The resulting feature is a trough-shaped geometry of the deep crust and a dome-shaped geometry of the overlying tectonic edifice. In correspondence of this wedge-shaped body, gravity modeling has provided an anomalous high density of 3.1 g/cm^3 at the base of the crust (supported by a positive Bouguer anomaly of +40 mGal), compared with the mean value of 2.9 g/cm^3 along the profile. This anomalously high density cannot be explained by the typical density of crust, instead of being more similar to the mantle density. Distribution of the refraction seismic velocities (Scarascia et al., 1994) indicates the presence of velocity inversion, which was attributed to a doubling of the crust and a northward subduction of the African plate. If we analyze the geophysical evidences considering the outgassing of mantle-derived volatiles fed by magmatic intrusions at depth, this high-density, wedge-shaped body must be interpreted as a mantle wedge composed of asthenospheric and/or lithospheric mantle, located between two different crustal bodies (Figures 2 and 3).

Wedging generally develops in B-subduction systems, and its high temperatures produce melting and feeding the volcanism of arcs. The peculiarity of the present case is that wedging develops in a collisional system produced by A-subduction.

In the southern Tyrrhenian Sea, a transition zone in the northern Sicilian belt separates the collisional from the subduction system (Figure 1). This area experienced faulting and stretching related to the Tyrrhenian backarc rifting (Malinverno & Ryan, 1986) and consequently is characterized by lithospheric thinning, which could be responsible for the passive up-doming of the asthenosphere in a context of passive rifting, in relation to the role of mantle.

Westward, a cold and dense lithospheric root of the orogen slips into the hotter asthenosphere, creating lateral temperature instability. This drives convective flow that can delaminate the lower portions of the thickened lithosphere. Therefore, a mantle wedge separating two crustal bodies should be the consequence of delamination processes of the continental crust, already invoked as being necessary to explain the continental subduction of the African plate in the framework of southern Apennines orogenesis.

The recent tectonics along the central northern Sicily is well documented by structural and seismological data (Billi et al., 2010), demonstrating that the network of a mainly compressional-transpressional fault system could be negatively inverted in still-active WNW striking extensional-transensional faults, descending to the deep crust. These observations support the existence of the structural condition necessary for delamination processes, as well as the generation and transfer of hot melt material among the upper and lower crust, whose surface evidence is the active degassing of mantle-derived volatiles coupled to a high heat flow.

Examples from the Alps have demonstrated that their late-stage widespread uplift, as in the northern Sicily belt, could be explained by delamination and/or convective removal of a thickened lithosphere and mechanical decoupling between the mantle and crust of the subducted lithosphere, enhanced by erosional unloading (Genser et al., 2007). Beneath the Apennines and Calabria, along the western margin of Adria, as well as in the Aegean Arc and other segments of the Eastern Mediterranean, delamination processes between the Apulian crust and its mantle lithosphere, linked to the back-arc extension and related asthenospheric upwelling, in addition to slab pull, were considered responsible for the progressive retreat of the mantellic slab, giving rise to downflexing and accelerated subsidence of the foreland crust besides areas of rapid uplift (Roure et al., 2012).

5. Delamination and Mantle-Derived Volatiles Degassing

Recognition of delamination-related magma is a key tool to constrain the occurrence of delamination events at depth (Anderson, 2005; Kay & Kay, 1993). Hence, the occurrence of magmatic intrusions at depth in the central part of the Mediterranean—as inferred from geochemical data of mantle-derived fluid outgassing coupled to heat-flow anomalies—together with the geological and geophysical data strongly supports the possible occurrence of delamination processes that are related to the continental subduction as a consequence of the convergence between the European and African plates (e.g., Chiarabba & Chiodini, 2013).

Above the mantle wedge, the SiRiPro data highlight a very complex pattern of faults that are Mesozoic to Tertiary-Quaternary in age and represented by two different systems (Avellone et al., 2010; Bello et al., 2000): (1) the older is quasihorizontal, separating the different structural layers constituting the Sicily Chain, and (2) the younger has a high angle and is from transpressional to transtensional, crossing the whole tectonic edifice and reaching depths from the crust down to the mantle-crust interface (Figure 3). Since it is linked directly to the anomalous wedge, it acts as the escape route for the transfer of mantle volatiles across the entire crust (Figure 3).

Degassing of mantle-derived fluids coupled to active tectonics and seismicity points to a deformation-enhanced permeability in the deep crust. Moreover, the present-day seismicity indicates that the prevailing focal mechanisms are extensional, and the hypocenters of the earthquakes are mainly concentrated at locations deeper than 30 km and shallower than 10 km (Doglioni et al., 2012), supporting that the tectonic is active and the faults are able to transfer fluids through the deep crust toward the surface.

6. Conclusions

Our work demonstrates that outgassing of mantle volatiles can also occur in a compressional geodynamic regime. Here we highlighted that He isotopes are powerful tools to solve the mantle-crust tectonics involving the occurrence of magma without any evidences of volcanism on the surface. The outgassing of mantle-derived He constrains that the investigated region is also affected by mantle CO₂ degassing because it is a major magmatic volatile component and it can be the carrier of mantle He through the crust. On the basis of the CO₂/³He ratio and the ³He fluxes, here we computed the mantle CO₂ flux in this sector of the Mediterranean (from 1.8×10^3 to 8.2×10^3 mol·km⁻²·year⁻¹). These values of CO₂ flux are lower than those from active and quiescent volcanic systems (e.g., Caracausi et al., 2015, and references therein), and they are comparable with those from other seismic regions (e.g., San Andrea Faults, USA) through which an active degassing of mantle-derived volatiles is well recognized. However, our data are from a continental region in a type A subduction system that is tectonically affected by a compressional regime. Results of this study show that a flux of heat and mantle volatiles (i.e., CO₂ and He) are due to magmatic intrusions at depth, highlighting that these can also occur below a tectonic chain. In fact, the geological and geophysical data support the presence of a hot mantle wedge below the area characterized by the outgassing of mantle volatiles. The presence of this mantle wedge that is in between two layers of crust, the African above and the European below, respectively, is the consequence of delamination processes that is well recognized to produce magmatism at a large scale.

Furthermore, our geochemical data support that the transfer of mantle-derived volatiles through the crust is due to advective processes through WNW-ESE trending extensional tectonic discontinuities, still active in central northern Sicily. Finally, we discuss a geological section that highlights the occurrence of a system of deep faults crossing the continental crust and connecting the mantle wedge to the surface in correspondence of the NCStb. These tectonic discontinuities represent the possible structural paths through which volatiles move across the entire crust and reach the surface.

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All the geochemical data of the NCStb that we discussed in this paper are unpublished and are in Table 1. Seismic data were acquired in the frame of the SiRiPro Italian project, funded by MIUR Italian Research Ministry, and are stored at the Department of Earth and Marine Science of the University of Palermo; the data are available at www.siripro.it or by contacting the authors (e.g., attilio.sulli@unipa.it). The geological data discussed in this manuscript are literature data, and all the references are cited in our manuscript.

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