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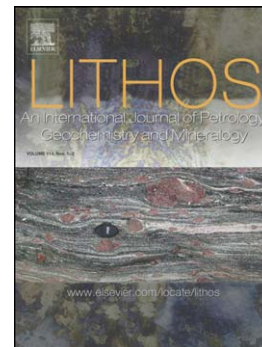
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Carbon elemental and isotopic composition in mantle xenoliths from Spain: insights on sources and petrogenetic processes

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Abstract

The carbon elemental concentration (C wt%) and isotopic (δ^{13}C ‰) composition of mantle xenoliths from the Tallante and Calatrava volcanic occurrences (in South-East and Central Spain, respectively) have been investigated to identify carbon sources and processes occurring in distinct geodynamic settings of the Iberian Peninsula. The peridotitic mantle xenoliths from Calatrava show elemental C ranging from 0.11 and 2.87 wt% which is coupled with a continuous isotopic variation from very negative values (δ^{13}C -26.1 ‰) to typical mantle values (δ^{13}C -5.9 ‰). On the other hand, the Tallante mantle xenolith suite display lower C contents (0.06-0.15 wt%) showing a tighter variation with ^{13}C-depleted values ranging between -20.1 and -23.7 ‰; higher elemental C up to 0.41 wt% displaying distinctly less negative isotopic values (δ^{13}C between -13.8 and -11.9 ‰) have been recorded in veins crosscutting Tallante peridotites, plausibly representing the product of metasomatic reactions. The data from the two investigated xenolith suites invariably display a good correlation between elemental and isotopic composition, suggesting a mantle origin for carbon and Rayleigh-type fractionation as the process responsible for the observed C-δ^{13}C variation. However, the correlation between the carbon isotopic data with other isotopic tracers (e.g. ^{87}Sr/^{86}Sr, ^{3}He/^{4}He) used to identify distinct mantle components and metasomatic reactions, indicate systematic differences between the two xenolith suites suggesting that beneath the Betic Cordillera (where Tallante is located) the deep C-cycle involves recycling, via subduction preceding/accompanying continental collision, of crustal components back in the mantle. Coherently, geochemical trends observed in the Tallante xenoliths seem to be influenced by metasomatic agents generated by

melting of crustal lithologies that according to the analysis of a metasedimentary xenolith can contain C up to 1.2 wt% having $\delta^{13}C$ of ca. -18.0 ‰.

1. Introduction

The deep carbon cycle is extremely complex, interpreted both in terms of sources (primordial vs recycled) and processes (e.g. devolatilization, melting, re-crystallization) that are mediated by multiple phase transitions (Hammouda and Keshav, 2015). Valuable information on juvenile carbon occurrences are provided by deep carbon-bearing rocks and minerals (e.g. carbonatites, diamonds) as well as by volcanic emissions, but the related interpretation which is mainly based on their $^{13}C/^{12}C$ isotopic composition remains controversial (Shirey et al., 2013). In this debate petrological studies on Cenozoic volcanic rocks from the Iberian peninsula represent a suitable case study recording the existence of juvenile carbonate components, that although subordinate, accompany the prevalent silicate magmatism in many Spanish occurrences (Venturelli et al., 1991; Contini et al., 1993; Bailey et al., 2005; Humphreys et al., 2008a; 2010; Conticelli et al., 2009; Puga et al., 2010; Stoppa et al., 2012). However, the evidence which would imply the presence of carbon in the related mantle sources has been debated and criticized (Lustrino et al., 2016). In this contribution, we present new carbon elemental and isotopic analyses of mantle xenoliths carried out in volcanic occurrences at Calatrava (Central Spain) and Tallante (Betic Cordillera), previously studied by Bianchini et al. (2010; 2011; 2015) in order to provide fresh insights on the ongoing debate. These volcanic provinces occur in distinct geodynamic environments, with the former in a foreland unaffected by Cenozoic subduction processes and the latter emplaced in suprasubduction conditions. The obtained data are discussed both in terms of origin of the carbon components and of processes affecting the carbon reservoirs during mantle evolution in differing geodynamic settings and are also useful to discuss the existing hypotheses concerning the cycle of this fundamental element in the deep earth.

2. Geological background

The Tertiary-to-Quaternary volcanism within the Iberian Peninsula (Fig. 1a) is spatially and temporally associated with the formation of the Betic collisional belt, including both orogenic (i.e. subduction-related) and anorogenic (intraplate) volcanic series (Wilson and Bianchini, 1999). This volcanic activity is characterized by an extremely variable compositional spectrum of anorogenic basalts (*s.l.*) in the foreland region represented by Calatrava (CLV) in central Spain, to subduction-related calcalkaline, high-K calcalkaline, shoshonitic and ultrapotassic products in the Betic Cordillera.

The Late Miocene-Quaternary CLV volcanism comprises a series of scattered monogenetic vents consisting of mafic lava flows and pyroclastic deposits over an area of ~5500 km^2. The volcanic products erupted onto a Palaeozoic basement and are mainly associated with north-east-to-south-west and east-to-west extensional and transtensional faults. In this volcanic region, a minor Late Miocene event (8.7–6.4 Ma) was characterized by eruption of leucitites, whereas the main Pliocene-Quaternary magmatic phases (3.7–0.7 Ma) were characterized by the eruption of alkali basalts, basanites, olivine nephelinites and melilitites (Cebriá and López-Ruiz, 1995) and by the emplacement of diatremes and maars filled by carbonate-rich pyroclastics (Bailey et al., 2005; Stoppa et al., 2012). Mantle xenoliths are frequently found in these diatremes.

Volcanic activity also occurred in the south-east corner of the Iberian peninsula along the eastern domain of the Betic cordillera, which is an orogenic belt formed by a series of Cenozoic compressional episodes leading to nappe emplacement and low- to high-grade metamorphism. Volcanism mainly occurred during the post-orogenic extensional phase in which low-angle faulting induced the formation of Neogene-to-Quaternary sedimentary basins (Benito et al., 1999; Cebria et al., 2009). The volcanic events included calcalkaline (e.g. at Cabo de Gata) and high-K calc-alkaline (e.g. at El Hoyazo, Mazarron and Mar Menor) products that erupted between 15 and 6 Ma, as well as shoshonite (e.g. at Cartagena, Vera and Mazarron) and ultrapotassic lamproites (e.g. at Cartagena, Fortuna, Vera and Jumilla) that erupted between 12 and 6 Ma (Benito et al., 1999; Duggen et al., 2005; Conticelli et al., 2009). The geological framework and the evolution of the erupted magmas indicate progressive evolution of the related mantle sources induced by a long and complex history involving subduction of oceanic crust (probably since the Eocene) followed by collision and recycling of continental crustal components back

into the mantle (Beccaluva et al,. 2004; Conticelli et al., 2009; Bianchini et al., 2011; 2013; 2015). After a gap of ~ 4 Ma, in the Early-Pliocene a new volcanic phase consisted of totally distinct Na-alkaline basalts, which exhumed the studied mantle xenoliths from the volcano of Cabezo Negro, Tallante (TL). Evidence of juvenile carbonate-bearing volcanic rocks were provided by Venturelli et al. (1991) and Barbero et al. (2000), and also observed in the volcano of Tallante, where xenoliths are entrained in a whitish volcanic breccia with a carbonate matrix (Fig. 1b, c).

3. Petrology of Mantle xenoliths at Tallante and Calatrava

Petrographic and geochemical characteristics of the studied xenoliths are reported in Supplementary Figures 1-4 and Supplementary Table 1, respectively. Calatrava (CLV) mantle xenoliths consist of protogranular spinel lherzolites, wehrlites, olivine-websterites and olivine-clinopyroxenites characterized by protogranular to porphyroclastic textures (Anchocea and Nixon, 1987; Bianchini et al., 2010; Villaseca et al., 2010). A typical petrographic feature of the CLV suite of ultramafic xenoliths is the presence of "spongy" textured clinopyroxene that often overgrows on olivine and/or orthopyroxene (Supplementary Fig. 1). Reaction patches characterized by sub-graining, with development of "secondary" microcrysts of olivine, clinopyroxene, feldspar, sometimes phlogopite, amphibole, apatite, glassy blebs and carbonate ocelli/patches are widespread. These reaction textures do not show evidence of interaction with the host basalts, and were plausibly formed at mantle depths before exhumation of the xenoliths. SEM back-scattered images (Fig. 2a, b, c) show that ocelli/patches of carbonate are not related to the filling of voids by low-temperature fluids as demonstrated by textures showing co-crystallizing microliths of feldspar and phlogopite (Humphreys et al., 2008b; Bianchini et al., 2010). Moreover, within our collection, an extreme sample, olivine-clinopyroxenitic in composition is characterized by a network of carbonate veins that appear to engulf the pre-existing mineral assemblage. The bulk rock compositions of CLV xenoliths (Supplementary Table 1) are characterized by anomalous CaO (especially in wehrlites) and high FeO_{tot} and TiO_2 contents despite Al_2O_3 and MgO concentrations comparable with other mantle xenolith suites and closely approximating theoretical residual compositions, suggesting that melt extraction was not the only process

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to affect the mantle beneath Calatrava. Coherently, as observed by Villaseca et al. (2010), CLV ultramafic rocks are richer in clinopyroxene (and poorer in olivine) respect to other Spanish mantle xenolith suites. Iron enrichment of these mantle rocks is reflected in the comparatively low Mg# of the constituent mineral phases (e.g. olivine characterized by Mg# down to 88). Cryptic metasomatic processes are confirmed by the trace element distribution which reveal enrichments in the most incompatible elements (LREE, Th, U) and by a relatively homogeneous Sr- and Nd-isotope composition, with $^{87}Sr/^{86}Sr = 0.70312–0.70435$ and $^{143}Nd/^{144}Nd = 0.51278–0.51307$ (Bianchini et al., 2010; Villaseca et al., 2010) that overprinted previous heterogeneities, as also emphasized by a relatively restricted compositional range of the helium isotopes (Martelli et al., 2011) showing values between 4.8-6.5 Ra (with the exception of one sample displaying a value of 3.6 Ra).

Mantle xenoliths from Tallante (TL) are more heterogeneous (Arai et al., 2003; Beccaluva et al., 2004; Shimizu et al., 2004; Bianchini et al., 2011); they consist of protogranular anhydrous spinel (sp)-peridotites, including clinopyroxene (cpx)-rich lherzolites that often contain plagioclase (up to 5%) and more refractory cpx-poor lherzolites and harzburgites (Supplementary Table 1). A typical petrographic feature of the TL suite of ultramafic xenoliths is the presence of orthopyroxene that often overgrows on olivine (Supplementary Fig. 2). In these xenoliths, the content of elements classically considered indicators of mantle depletion by melt extraction, such as CaO, Al_2O_3, TiO_2 decrease with increasing MgO and Ni in the most refractory parageneses. Depletion processes were followed by cryptic metasomatic enrichments that induced enrichments in the most incompatible elements, especially in cpx-poor lherzolites and harzburgites. Sr and Nd isotope composition, show a wide compositional spectrum with $^{87}Sr/^{86}Sr = 0.70213–0.70476$ and $^{143}Nd/^{144}Nd = 0.51250–0.51339$, showing the more radiogenic Sr (and the more unradiogenic Nd) isotope compositions in cpx-poor lherzolites and harzburgites (Beccaluva et al., 2004). The Sr-Nd isotopic heterogeneities, coupled with the wide spectrum of helium isotopic composition (1.4 - 5.7 Ra) recorded in TL mantle xenoliths have been interpreted as the result of interactions between mantle and crustal components (Bianchini et al., 2011; Martelli et al., 2011). The TL suite also include xenoliths characterized by extreme enrichment of orthopyroxene (olivine-orthopyroxenite) and by the presence of amphibole and phlogopite, sometimes cross-cut by felsic veins (Supplementary Fig. 3 and 4); the latter are generally formed by variable amounts of plagioclase, orthopyroxene, quartz and accessory phases such

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as amphibole, phlogopite, apatite, zircon, rutile and huttonite (Arai et al., 2003; Beccaluva et al., 2004; Shimizu et al., 2004; Bianchini et al., 2015); this group of TL xenoliths display variable trace-element enrichment with patterns usually characterized by Eu (and Sr) negative anomalies and extreme Sr and Nd isotope compositions, with $^{87}Sr/^{86}Sr$ values up to 0.70856 and $^{143}Nd/^{144}Nd$ values down to 0.51211 (Beccaluva et al., 2004; Bianchini et al., 2011). The TL suite also includes crustal meta-sedimentary xenoliths (e.g. TL29) equilibrated at pressure of 0.7–0.8 GPa overlapping that recorded in mantle-derived peridotite xenoliths. These crustal lithologies were probably juxtaposed and interlayered to peridotite mantle rock at the MOHO discontinuity, which in orogenic areas is not sharp as commonly assumed and characterized by a gradational nature showing inter-fingering of heterogeneous lithologies (Bianchini et al., 2013; 2015). As concerns the carbon budget of the TL xenoliths, SEM investigation revealed the presence of graphite in the deep crustal lithologies (Fig. 2d), as already reported by Vielzeuf (1983) on analogue TL meta-sedimentary xenoliths. Graphite has been observed also in felsic veins crosscutting peridotite in composite xenoliths, and/or in the orthopyroxene-rich reaction zone between the felsic veins and the surrounding peridotite matrix (Fig. 2e, f), as also reported by Shimizu and Arai (2011) on analogue TL composite xenoliths. On the whole, for the TL suite of xenoliths an important role in the genesis of metasomatic agents is ascribed to the Cenozoic subduction processes that occurred during the collisional stage and recycled a significant amount of continental crustal components in the mantle (Arai et al., 2003; Beccaluva et al., 2004; Shimizu et al., 2004; Conticelli et al., 2009; Martelli et al., 2011; Bianchini et al., 2011; 2013; 2015). This means that in orogenic areas, as result of continental collision, terrigenous sediments (and their metamorphic analogue) or also chunks of continental crust are forced back in the mantle. Partial melting of these continental crustal components generates metasomatic agents that metasomatize the overlying mantle wedge.

4. Analytical methods

Conventional analysis of the carbon isotopic composition in peridotite rocks usually involves several extraction steps (by crushing, or by heating) to ensure that all the carbon has been extracted. Unfortunately, these methods require significant time and sometimes give non-definitive results about the origin and processes of the studied

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matrices. For this reason, continuous-flow (CF) techniques employing an elemental analyzer (EA) that combusts (at furnace temperature as high as possible) and delivers the total gas for isotope ratio mass spectrometry (IRMS) are more appropriate. In this paper, carbon elemental (C) and isotopic analyses ($^{13}C/^{12}C$) were performed on bulk rocks powders using a Vario MICRO CUBE Elemental Analyzer coupled to a Continuous Flow ISOPRIME100 Isotope Ratio Mass Spectrometer (EA-CF-IRMS). Elemental concentration has been expressed in wt%, whereas the isotopic ratio has been reported as $\delta^{13}C$ (‰) respect to the Vienna Pee Dee Belemnite (V-PDB) international standard. The analyses have been conducted at furnace combustion temperature of 950°C, i.e. a temperature at which the main carbon-bearing repositories of spinel-peridotite rocks (carbonate and graphite) destabilize, using the Total Carbon (TC) analytical setting described by Natali and Bianchini (2015). According to these authors, normal earth-sciences samples such as sediments and soils can be analyzed obtaining $\delta^{13}C$ values characterized by accuracy and precision of ±0.1 ‰, as also indicated by the analysis of standards covering a wide range of carbon isotopic compositions ($\delta^{13}C$ from -28 and +2 ‰, Supplementary Table 2). Dealing with peridotite samples characterized by extremely low carbon content is by no means trivial and requires additional scrutiny. Therefore, careful laboratory tests have been performed in order to cross-check the reliability of the obtained EA-CF-IRMS results for very low-carbon matrices (Fig. 3); in this light, some samples have been re-analyzed loading on the instrument different weight of powder (thus obtaining different signals) and verifying the reproducibility of the isotopic data that was generally better than 1 ‰. This method obviously provides information about the bulk carbon composition, but doesn't provide information for the internal isotopic variability of a given sample that could be obtained either by the analysis of separate mineral fractions or by step heating procedures (*cfr.* Mikhail et al., 2014). The carbon speciation in CLV and TL xenoliths will be the focus of our research in the foreseeable future.

5. Results

The obtained carbon elemental and isotopic analyses are reported in Supplementary Table 2 and in Fig. 4. The bulk C content of CLV ultramafic xenoliths ranges between 0.11 and 2.87 wt%. Concentration is positively

correlated with the isotopic composition ($\delta^{13}C$) which displays a continuous variation between -26.1 and -5.9 ‰, with the less negative values conforming to typical mantle signatures defined by Deines (2002) and Wilson et al. (2007). The sample population is characterized by a bimodal distribution with lherzolitic samples generally showing low carbon content associated with more negative $\delta^{13}C$ values and wehrlite, olivine-websterite/clinopyroxenite samples (where modal carbonate is observed) showing the higher C content associated with less negative $\delta^{13}C$ values. In particular, the olivine-clinopyroxenite where carbonate veins were observed at the microscope contain a notable amount of carbon (2.9 wt%), which corresponds to 24 wt% of stoichiometric calcite.

The C content of TL xenoliths varies from 0.06 to 0.10 wt% in anhydrous peridotites, rising up to 0.15 wt% in an amphibole bearing peridotite; higher C content up to 0.41 wt% have been recorded in the felsic veins crosscutting peridotite composite xenoliths. The associated isotopic composition ($\delta^{13}C$) varies between -20.1 to -23.7 ‰ in peridotites, whereas the aforementioned felsic veins display less negative values between -13.8 and -11.9‰ that never reach typical mantle values. Carbon elemental and isotopic composition has been also carried out on a meta-sedimentary crustal xenolith (TL29; Bianchini et al., 2013) belonging to the Tallante suite which displays distinctly higher C content (1.19 wt%) associated with a $\delta^{13}C$ value of -17.7 ‰.

In both xenolith suites a correlation is observed between the carbon contents and the respective $\delta^{13}C$ values suggesting that an analogous process affected vast domains of the Iberian lithospheric mantle. Importantly, in the Tallante xenolith suite $\delta^{13}C$ values that are less negative than those of the Calatrava are never recorded. The heavier isotopic composition recorded by Tallante xenoliths approaches that of the carbonate matrix of the xenolith-bearing volcanoclastic deposit ($\delta^{13}C$ -9.8‰), as well as that of an analogous carbonate-bearing volcanic deposit recorded in another locality of the Betic area described by Puga et al. 2010 (Cerro Prieto; $\delta^{13}C$=-9.0‰); on the other hand, the least negative carbon isotopic composition recorded in Calatrava xenoliths ($\delta^{13}C$=-5.5‰) conforms to the main mantle range and is decidedly less negative than that of carbonatitic tuffs recorded at Calatrava (ca. -9.5‰, Bailey et al., 2005).

The record of ^{13}C depleted compositions appears to be a common feature of vast domains of the continental lithosphere, as evidenced by data carried out in our laboratory on alpine-type peridotites from the Italian eastern Alps ($\delta^{13}C$ between -17 and -11‰), that have been cross-checked with those obtained at the Leigh University (USA) using alternative analytical methods ($\delta^{13}C$ down to -14‰; Förster et al., 2016).

6. Discussion

The understanding of the carbon elemental and isotopic composition in distinct sub-crustal lithospheric domains is a fundamental challenge to define the associated geochemical budget and fluxes that characterize different geodynamic settings on Earth.

The carbon isotope composition of mantle xenoliths investigated in this study is "light" (average of $\delta^{13}C = -15.0$ ‰ in CLV samples, −17.7 in TL xenoliths) compared with the main mantle carbon range ($\delta^{13}C$ from −3.5 to − 8‰) exemplified by Mid Ocean Ridge Basalt (MORB, Coltice et al., 2004; Javoy et al., 1986), carbonatites (e.g. Deines, 1989), carbonate assemblages from hypabyssal kimberlites (Wilson et al., 2007) or diamonds from peridotites (Cartigny, 2005 and references therein). However, similar isotopic compositions have been observed in eclogitic diamonds ($\delta^{13}C$ from −39 to + 5‰, Shirey et al., 2013 and references therein) and in peridotites from the neighboring Alpine-type ultramafic massifs of Ronda and Beni Bousera, where flakes of graphite, sometimes interpreted as pseudomorphs after diamond, have been observed ($\delta^{13}C \sim$ –15.2‰; Crespo et al., 2006), although the relative interpretation is controversial (Luque et al., 2012 and references therein).

Findings of extremely negative $\delta^{13}C$ composition in eclogitic diamonds have been interpreted as evidence for the presence of recycled light carbon derived from subducted material, which has perturbed the homogeneous distribution of carbon isotopes in the upper mantle (Crespo et al., 2006). In this hypothesis, the light carbon isotopic composition results from fractionation processes occurring during the subduction of sediments associated with oceanic metabasalts that are affected by a $\delta^{13}C$ decrease during decarbonation of the subducted slab. More extreme negative isotopic compositions could be ascribed to the involvement of ^{13}C-depleted,

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continental crust components, possibly in the form of terrigenous sediments containing organic matter (and their metamorphic counterparts) in addition to more common pelagic sediments that are widespread in the oceanic environments (Kook-Collars et al., 2014). Unfortunately, a more precise interpretation is hampered because the deep carbon cycle includes phase transformations in an open system that also involves fugitive fluids, and each of these re-equilibrations can induce significant isotopic fractionation. Carbon speciation in the mantle therefore depends on its origin (pristine in the mantle or recycled?) but also on mobilization processes strictly dependent on pressure, temperature, and oxygen fugacity as summarized by Frost and Wood (1997), Luth (1999) and more recently by Stagno et al. (2013). For example, oxidizing conditions will favor formation of carbonates, or molten carbonatite melt or gaseous CO_2, whereas reducing conditions will stabilize graphite, carbides and C-H phases (Hammouda and Keshav, 2015; Horita et al., 2015).

It is important to note that in both CLV and TL suites we observe a direct relationship between carbon content and isotopic composition, i.e. the lower the elemental C concentration, the more negative the associated $\delta^{13}C$, as also observed in other suites of mantle rocks (Förster et al., 2015a; 2015b; 2016). This effect is better represented in the CLV mantle xenolith suite, where the highest carbon contents are coupled with a carbon isotopic signature overlapping that of the mean mantle range and continued depletion in terms of ^{13}C ($\delta^{13}C$ down to -25.7‰) and C content (down to 0.10 wt%) is observed. Moreover, it is interesting to note that in CLV xenoliths the C concentration is inversely correlated with the bulk rock magnesium number (mg# = [(MgO)/(MgO+FeO)]mol; r^2 ca. 0.75) and positively correlated with the Cpx/(Ol+Opx) ratio (r^2 ca. 0.85). The samples characterized by high C concentration and less negative $\delta^{13}C$ value are not common lherzolites, but cpx-rich ultramafic rocks such as wehrlites, olivine-websterites and olivine-clinopyroxenites containing modal calcite in their parageneses. These evidences suggest that the carbon concentration of these rocks is not attributable to low-temperature (secondary) processes, but related to high-temperature metasomatism, preceding the xenoliths exhumation.

Mantle xenoliths from Tallante never record isotopic composition in the mean mantle range and unveined peridotites are invariably characterized by low C content and very negative $\delta^{13}C$ values (-19.3 to -23.7‰),

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whereas higher C content (up to 0.41 wt%) is observed only in felsic veins crosscutting peridotites displaying distinctly less negative $\delta^{13}C$ values between -13.8 and -11.4‰, possibly resulting from metasomatic processes. The increase of C concentration in the felsic veins is plausibly related to the observed presence of graphite (Fig. 2), which indicates that the causative silica-oversaturated melt that crosscut the TL mantle domain contained a significant carbon fraction that was stabilized under reducing conditions, as sometimes observed in granites generated by anatexis of meta-sedimentary protholits (Milord et al., 2001; Zeng et al., 2001) and also recorded in granites from the Iberian peninsula (Bea et al., 2014). Coherently, meta-sedimentary xenoliths that are associated to the ultrafemic xenoliths at Tallante (e,.g. sample TL29) and interpreted as deep crustal rock juxtaposed to mantle domain at the MOHO discontinuity (Bianchini et al., 2013; 2015) contain significant amount of carbon in the form of graphite. This rock has a restitic character compatible with the genesis of the above mentioned graphite-bearing felsic veins crosscutting the composite TL xenoliths.

In our view, both CLV and TL lithospheric sections seem to be affected by multiple processes and the observed C-$\delta^{13}C$ distribution indicates partial melting as a first order process responsible for the observed Rayleigh-type carbon fractionation that has been tentatively modeled in Supplementary Fig. 5. This, in accordance with experimental evidence (Mizutani et al., 2014), suggests that melting generates fugitive fluids with relatively heavier C isotopic composition (with respect to the source material) and the residual compositions have progressively more negative $\delta^{13}C$ values. In other words, it appears that ^{13}C is partitioned preferentially in escaping fluid phases as generally recorded in fluid inclusions hosted in peridotite rocks and diamonds (Mattey et al., 1989; Gurney, 1989; Maruoka et al., 2004), as also observed in magmatic systems where exsolved gases have less negative $\delta^{13}C$ values with respect to the relative magmas (Javoy et al., 1978; Mattey et al., 1990).

Metasomatic processes followed partial melting in both CLV and TL mantle domains, but metasomatic agents were significantly different due to their specific geodynamic settings; CLV metasomatic agents originated from deeper mantle domains and were represented by CO_2-bearing silica-undersaturated melts (Bianchini et al., 2010; Villaseca et al., 2010), or even carbonatites (Bailey et al., 2005; Humphreys et al., 2008a; 2008b; 2010), whereas TL metasomatic agents mainly generated by partial melting of graphite-bearing crustal lithologies that were

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juxtaposed to mantle domains by subduction and collisional processes during the Betic orogenesis. Our hypothesis is corroborated comparing the carbon systematics with the Sr isotopic distribution (Fig. 4), as the $^{87}Sr/^{86}Sr$ is a parameter that is not influenced by fractionation processes and therefore represents a suitable proxy to identify the nature of mantle components and metasomatic agents. The CLV xenolith suite is characterized by restricted $^{87}Sr/^{86}Sr$ range which is coupled with an extreme carbon elemental and isotopic variability. This suggests a relatively homogeneous mantle source where the carbon systematics are mainly controlled by Rayleigh-type fractionation processes. On the contrary, the TL xenolith suite is characterized by an extreme $^{87}Sr/^{86}Sr$ variation that favours metasomatic enrichment related to recycling of crustal components, plausibly occurring via subduction beneath the Betic Cordillera. The scenario is also compatible with He isotopic data that show a limited range around 4.8-6.5 Ra for CLV xenoliths and an extreme variation 1.6-5.75 Ra for TL xenoliths, which plausibly reflect interaction with U-rich crustal lithologies recycled in the mantle (Martelli et al., 2011).

On the whole, the available data suggest that the carbon of the studied xenoliths, originated deep in the mantle, and its isotopic composition results from multiple episodes of degassing and subsequent metasomatic processes.

7. Conclusions

The Iberian lithospheric mantle beneath the Betic Cordillera and the relative foreland in central Spain includes significant amount of carbon as revealed by widespread CO_2-rich emissions, predominantly associated with fracture/fault systems that allow the upwelling of mantle derived gases (García-Aguilar et al., 2014; Elío et al., 2015), and by carbon components recorded in volcanic occurrences (Venturelli et al., 1991; Contini et al., 1993; Bailey et al., 2005; Humphreys et al., 2008a; 2010; Conticelli et al., 2009; Puga et al., 2010; Stoppa et al., 2012). This is corroborated by the presence of carbon in the studied CLV and TL suites of mantle xenoliths. Its ultimate origin is difficult to define due the reasons discussed in the previous chapter. Although we aware of the many factors (including original sources and mobilization processes) that influence the carbon isotopic composition of

mantle rocks we emphasize significant statistical differences between the isotopic values recorded in CLV (average -15.0 ‰, median -15.1 ‰) and TL (average -17.7 ‰, median -20.2 ‰) xenoliths. In our view, this difference is significant and can be ascribed to the distinct Cenozoic geodynamic settings of the volcanic provinces in which xenoliths have been exhumed (Beccaluva et al., 2011; Martelli et al., 2011). In Fig. 5 the new data presented in this paper are plotted against $^{87}Sr/^{86}Sr$ which is a parameter unaffected by fractionation processes, therefore identifying the nature of mantle components and metasomatic agents. The CLV lherzolites are characterized by restricted $^{87}Sr/^{86}Sr$ range, which is coupled with an extreme carbon elemental and isotopic variability. This favours a homogeneous mantle source where the carbon systematics are controlled by Rayleigh-type fractionation processes. Effective fractionation is favoured by progressive redox melting that is in turn influenced by the ability of the mantle with which C-bearing fluids equilibrate to act as an oxidizing or reducing agent. The iron-rich nature of CLV mantle provides a significant buffering capacity, which moderates these processes (Rohrbach and Schmidt, 2011). Within the CLV suite of xenoliths, decidedly higher C concentration (up to 2.9 wt%) and less negative $\delta^{13}C$ values (up to -5.9‰) are observed only in peculiar lithologies such as wehrlites, olivine-websterites and olivine-clinopyroxenites that appear to be representative of discrete mantle domain interested by metasomatic processes occurred before the xenolith exhumation.

Rayleigh-type fractionation processes could be advocated also to explain the more negative $\delta^{13}C$ values observed at Tallante, but in this case the geochemical signature appears to be subsequently overprinted by metasomatic processes characteristic of recycling –via subduction– of continental crust components. This hypothesis is compatible with both geological, petrographic and geochemical data testifying that TL xenoliths are representative of a supra-subduction mantle region active during the Cenozoic, where graphite-bearing continental crust lithologies (possibly including biogenic derived components) have been directly recycled in the mantle wedge overlying the downgoing slab. The same Cenozoic subduction processes could have induced mantle upwelling in the foreland region remobilizing deep carbon-bearing mantle domains (carbonated eclogites from oceanic lithosphere stagnating at the base of the upper mantle?) thus explaining the carbonate components envisaged in the CLV volcanics and associated xenoliths (Bianchini et al., 2010; Beccaluva et al., 2011).

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Figure Captions

Fig. 1 – (a) Simplified geological outlines of the Iberian Peninsula reporting the distribution of Tertiary volcanism and the location of studied mantle xenoliths occurrences, as well as the outcrops of peridotite massifs; (b) mantle xenoliths entrained in a whitish carbonate-bearing volcanic breccia in the Cabezo Negro de Tallante volcano; (c) microphotograph of a mantle xenolith from Calatrava showing ocelli including carbonate (carb), phlogopite (ph), olivine (ol) and feldspar (Plane Polarized Light - PPL).

Fig. 2 – Scanning Electron Microscopy (SEM) Back Scattered Electrons (BSE) images, obtained using a CamScan MX 2500 at the Department of Earth Sciences of the University of Padova, showing the carbon bearing phases occurring in Calatrava (a, b, c) and Tallante (d, e, f) xenoliths. In the Calatrava xenoliths suite carbonate (Cc, Mg-calcite) has been observed in reaction patches of olivine-websterites (a, b) and olivine-clinopyroxenites (c), often in association with alkaline-silicate glass (Gl), feldspar (Fd), phlogopite (Ph) and apatite (Ap). In the Tallante xenoliths suite graphite (Gr) has been observed in meta-sedimentary xenoliths (d) and in felsic vein that crosscut peridotite in composite xenoliths (e, f).

Fig. 3 - Reliability tests to verify the precision and accuracy of the EA-IRMS analytical system for low-carbon matrices: (a) relationship between signal (nA) and isotopic ratio (δ^{13}C), where selected samples have been

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analyzed in standard and high-loading modes; (b) variation of C content and δ^{13}C in samples duplicated in standard and high-loading modes; (c) calibration of standards in normal and low signal regions. Δ^{13}C represents the isotopic difference (‰) observed between the replicated analyses.

Fig. 4 - Carbon elemental and isotopic composition of Calatrava and Tallante xenoliths. The more negative δ^{13}C (‰) values are associated with a decrease in C (wt%) and could be related to fractionation processes occurring during partial melting and melt extraction, whereas the higher C concentrations are representative of metasomatized samples in which carbon-bearing phases (carbonate in CLV xenoliths; graphite in Tallante xenoliths) have been stabilized. Bars are representative of the observed δ^{13}C variability (Δ^{13}C) in replicated samples.

Fig. 5 – (a) δ^{13}C (‰) and (b) C (wt%) vs ^{87}Sr/^{86}Sr of Calatrava and Tallante xenoliths. The lower C-δ^{13}C-^{87}Sr/^{86}Sr values are attributed to depleted mantle domains that suffered melt extraction and were relatively unaffected by metasomatism. Trends toward higher C and δ^{13}C (at relatively low ^{87}Sr/^{86}Sr) values characterize CLV samples metasomatized by CO_2-bearing silica-undersaturated melts. Trends toward higher C and ^{87}Sr/^{86}Sr (at relatively low δ^{13}C) values characterize TL samples metasomatized by subduction-related silica-oversaturated melts.
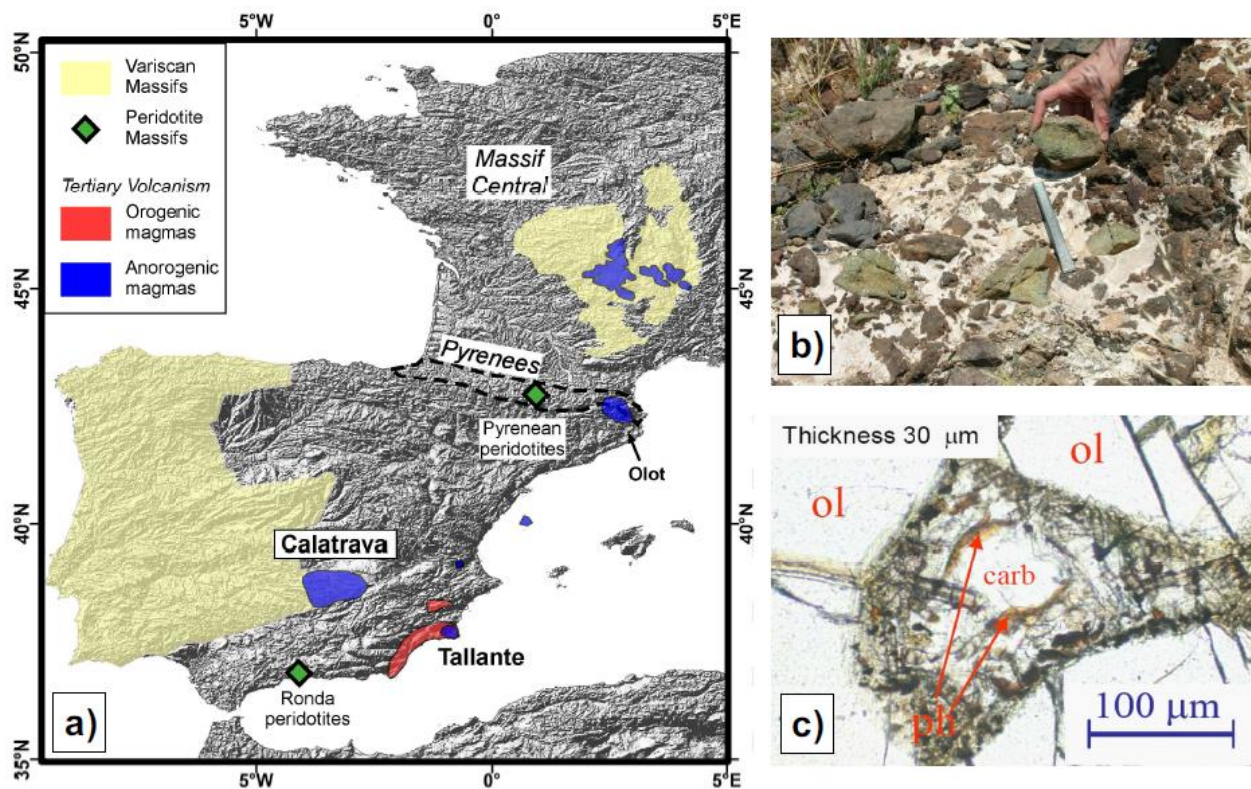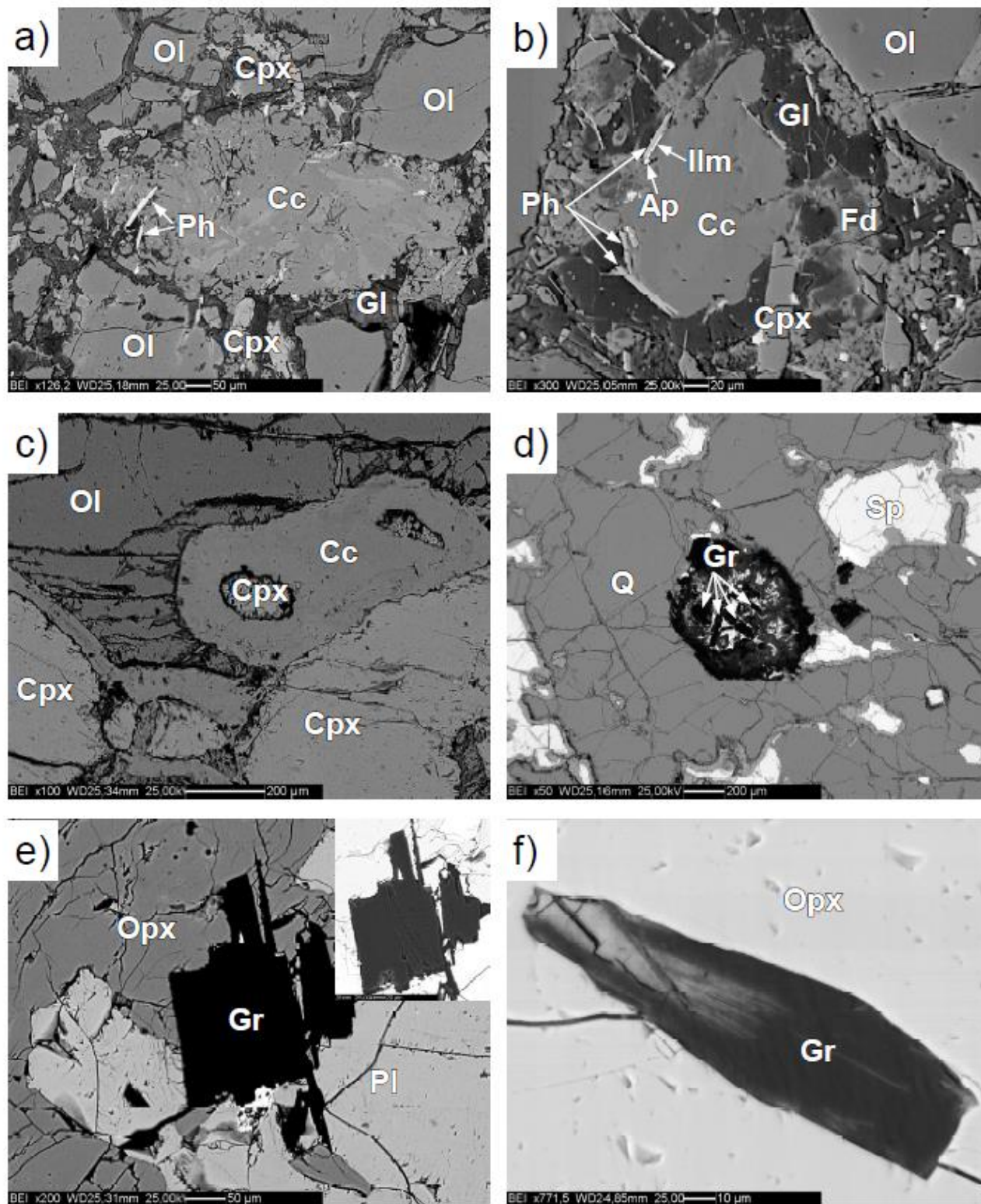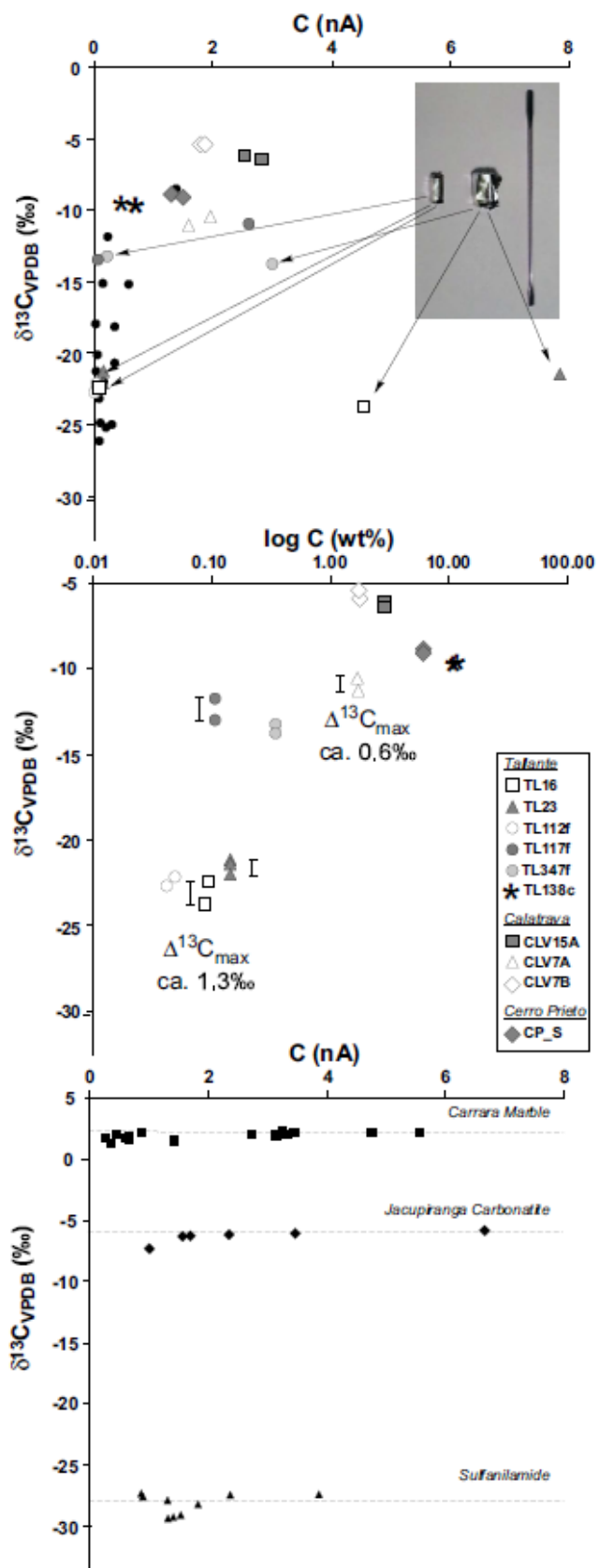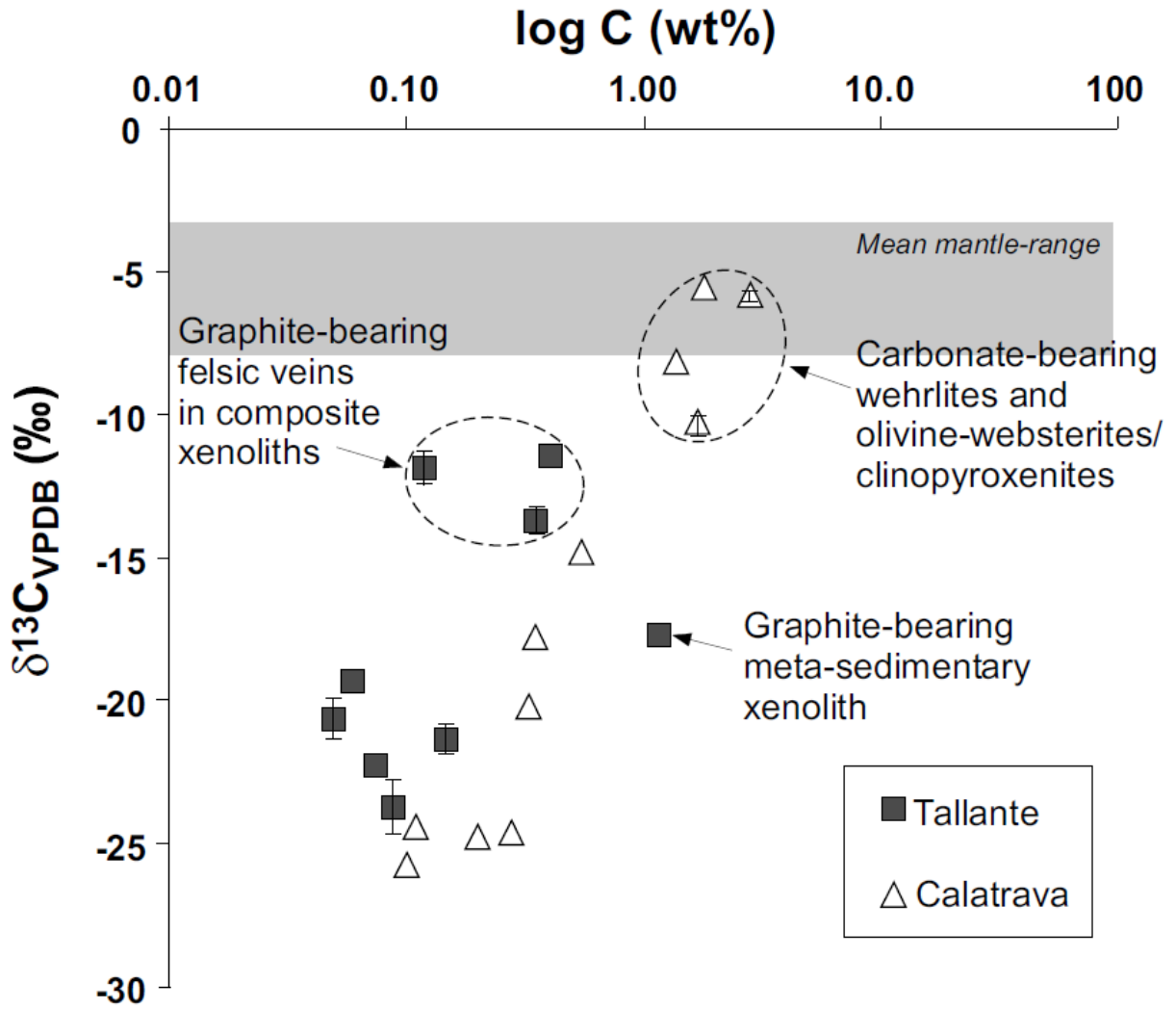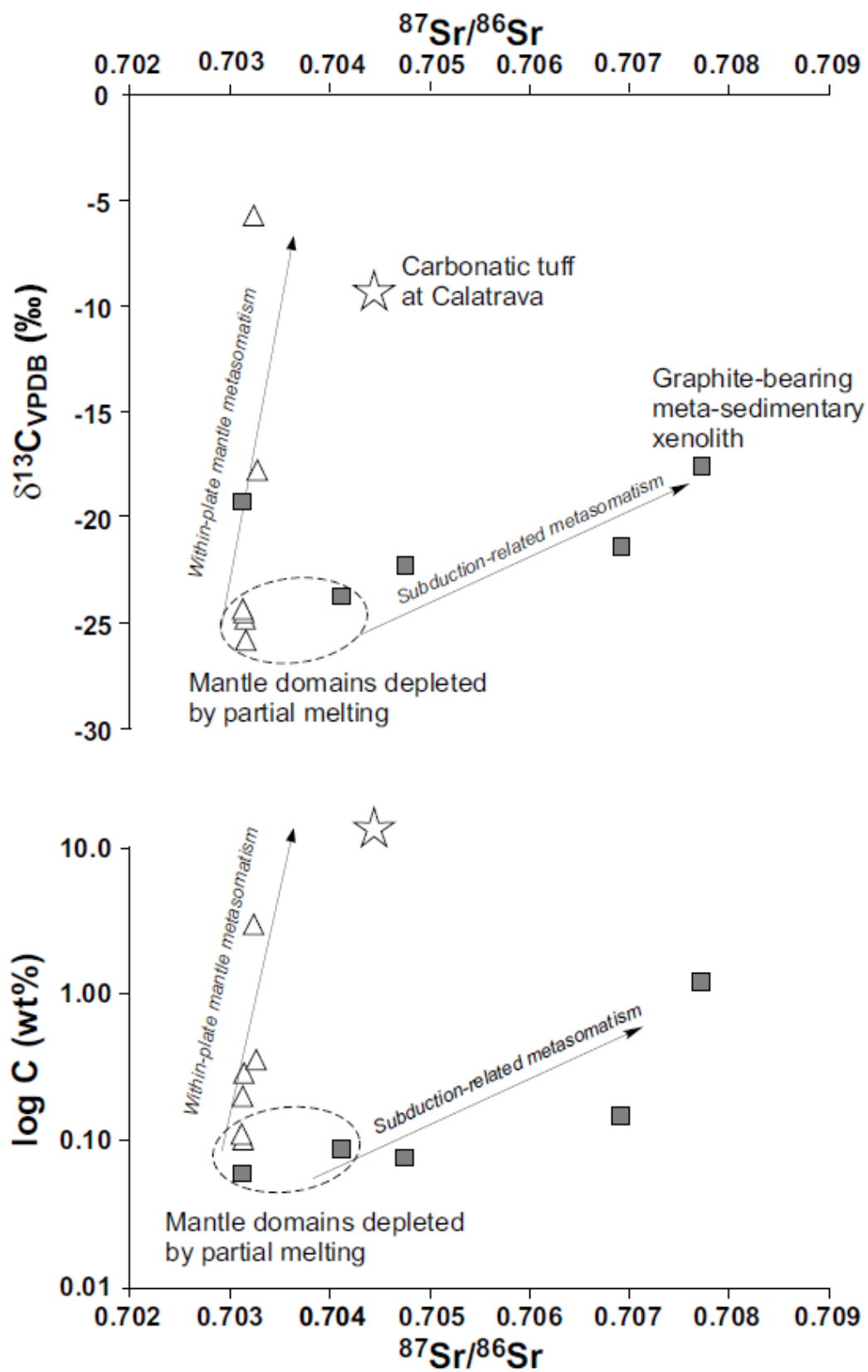
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Research Highlights:

- Carbon elemental and isotopic composition of mantle xenoliths from Iberian Peninsula

- C-δ^{13}C suggests juvenile carbon origin and Rayleigh-type fractionation

- δ^{13}C-^{87}Sr/^{86}Sr correlation indicates metasomatic components

- Evidence of carbon recycling via subduction in the mantle beneath Betic Cordillera