Open Journal of Geology, **2013, 3, 66-82**
http://dx.doi.org/10.4236/ojg.2013.32011 Published Online April 2013 (http://www.scirp.org/journal/ojg)

A Review of Carbonatite Occurrences in Italy and Evaluation of Origins

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Received February 22, 2013; revised March 22, 2013; accepted April 22, 2013

ABSTRACT

This review and evaluation seeks to clarify the controversial origins of the Umbria-Latium Ultra-alkaline District (ULUD) and the Vulture carbonatitic occurrence (Intramontane Ultra-alkaline Province, IUP) and their relation to the Roman Comagmatic Province (RCP). Generally, the geochemical and isotopic features of the IUP can be linked to those of the RCP. Hence, the rocks of the ULUD district, together with part of the Tuscan and Roman Province generated in the last 2 Ma can be ascribed to a complex interplay of two subduction events related to magmatism associated with the European and Adria slabs associated with the effect of a slab window below the Italian Peninsular. Carbonate sediments together with pelagic-terrigenous sediment played a major role in the metasomatism of the mantle wedge beneath the IUP, and perhaps all along the transect from southern Italy (Eolian Islands magmatism) to north-central Italy (Tuscan and Umbria magmatism). A diffuse $CO_2 + H_2O$ metasomatic front produced the condition necessary for the formation of carbonatitic magmatism. However, even where carbonatites are related to continental rift system (*i.e.*, OIB), an origin for MORB-sediment convective recycling melting in the mantle has been hypothesized [*i.e.*, 1].

Keywords: Carbonatites; Isotopes; Sediments; Arc System; Roman Comagmatic Province

1. Introduction

Recent work by [2] pointed out that there are more than 500 carbonatitic occurrences worldwide which causes new interest for studying them and understanding the associated genetic processes. To enlighten further the understanding of carbonatite genesis, the differences between extrusive and intrusive carbonatites have to be taken in account [3]. The relationship between the Roman Comagmatic Province and the Pleistocene rocks of the Ultra-alkaline Latium-Umbria District (ULUD) and Vulture volcano carbonatitic outcrops [e.g., 4,5] is investtigated from geochemical, petrological and tectonic points of view in order to better understand the origin of the carbonatitic magmas erupted in Italy. Particular emphasis is given to the petrogenesis of the Italian carbonatites and their links to the Italian tectonic system. An origin for the carbonatites is suggested based on the available literature [*i.e.*, 4]. The origin of carbonatitic rocks is still debated: a deep-seated origin—plume hypothesis [6] versus a shallower origin—lithospheric metasomatised mantle [*i.e.*, 7]. Moreover, Italy seems anomalous to find carbonatitic rocks, and their presence can play a major role 1) to shed light on the Italian tectonic setting [e.g., 8-12], and 2) to contribute to the understanding of the genesis of carbonatitic rocks. There is considerable research that links recycled materials with carbonatitic rocks through metasomatism in the upper mantle. [13] demonstrate that carbonate remains as a refractory phase in rutile eclogite residue in equilibrium with andesite melt in subduction regimes. [14-16] experimentally show that deep global cycling of carbon, with storage in the mantle, can occur. The recycling character of the carbonated eclogite triggers metasomatic processes in the upper mantle. The processes may have a role in metasomatically enriching and carbonating parts of the upper mantle, producing sources suitable for subsequent production of silica undersaturated silicate liquids and carbonatites that are subsequently emplaced in the crust.

The vast literature on the Italian peninsula has focused attention on two conflicting hypothesis differing over the role of recent slab subduction: 1) The origin of the Plio-Pleistocene Quaternary volcanism is a consequence of Neogene subduction of the Adria plate below the Tyrrhenian sea [e.g., 17-20 and references therein]; and 2) The presence of the carbonatitic rocks (ULUD and Vulture, *i.e.* IUP) and their tectonic setting is taken to suggest that the Italian peninsula is associated with postcollisional rifting [e.g., 21-23 and references therein] with the Italian magmas being derived from a deep mantle plume [9,10]. However, the hypothesis of the presence of the European plate dipping southward [e.g., 24-26] and a recent subducted slab dipping westward are supported by geophysical studies [e.g., 20,24,25,27-35].

1.1. A Framework of the Tectonic Setting and Magmatic Activity in the Roman Comagmatic Province

Subduction of the Adria plate started in the Early Oligocene-Early Miocene and developed to the east of the former Alpine Chain. The Apenninic accretionary prism formed at the front of the pre-existing Alpine back-thrust belt. The associated back-arc extension migrated eastward and boudinaged the Alpine nappe stack [36]. Kinematic and geophysical data support the presence of an eastward migrating asthenospheric wedge at the subduction hinge of the roll-back Adriatic plate [37]. The rifting started to the east of Corsica and Sardinia, and generated two major basins in the southern Tyrrhenian, *i.e.*, the Magnaghi-Vavilov basin (7 - 3.5 Ma) and the Marsili basin (1.7 - 1.2 Ma). Thus, the Apennine subduction took place during the last 30 Ma.

Beneath Central Italy, there is clear evidence of lithospheric roots, reaching at least of 130 km deep over a width of 120 km, below the western edge of the thick sedimentary basins (75 km deep) to below the extension-compression transition area (200 km deep). The crust exhibits clear layering and lateral variation in thickness: about 25 km below the Tuscan Metamorphic Complex (TMC), 30 km below the extensional thick sedimentary basins, and 35 km below the Umbria-Marche geological domain (UMD). The lithospheric mantle (lid) is thin (about 30 km) below the TMC, but it is about 70 km thick below UMD. All along the profile a mantle wedge, with thickness of about 20 km, lies between the crust and the lid. The wedge exhibits very low mantle velocities and hence may well decouple the underlying lid from the crust. Young magmatism at the surface and high heat fluxes in the region where this low-velocity upper mantle wedge gets shallower and attains its maximum thickness (TMC) suggest that this layer may represent a partially molten mantle, in agreement with petrological and geochemical data [38]. The subcrustal earthquakes [31,39] seem to cluster in the shallower part of the thick Adriatic lid and in the eastern part of the lithospheric root, consistently with a slab-like geometry, while the part of the lithospheric root and thin lid to the west seems to be almost free of seismic activity. This is seen in many P-wave tomographic images indicating the presence of a high-velocity body of significantly larger volume than that defined by earthquake foci. There are two possible explanations for the existence of a large lithospheric volume with laterally varying mechanical properties under North-Central Italy: 1) the presence of lateral variations in the stiffness of the lithosphere, consistent with the heat flow distribution, and/or 2) the coexistence of the Adria west-dipping remnant slab, with a possible relic of the old Alpine east-dipping slab consistent with geological [36,40] and seismic reflection data [41,42].

Volcanic activity in this region included MORB, island arc tholeiites, calc-alkaline, high-K calc-alkaline and shoshonitic products, Ca-, Na- and K-alkaline rocks [5, 43]. Carbonatitic rocks have been recently suggested to form a new Province (the Intramontane Ultra-alkaline Province [IUP]) formed by the Umbria Latium Ul-traalkaline District and some volcanic deposits of Vulture volcano, east of the Roman Province and Campanian District (**Figure 1**; e.g., [4,5 and references therein]). Particularly, potassic and ultrapotassic magmatism (Roman Comagmatic Province, RCP) represents the most characteristic magmatic feature of the Tyrrhenian area. It spans a time interval between 4 Ma and the present time. Potassic and ultrapotassic rocks have variable petrochemical affinity that range from Roman type potassic series (KS), to Roman type high-potassium series (HKS), lamproites, and kamafugites [e.g., 44]. KS and HKS rocks

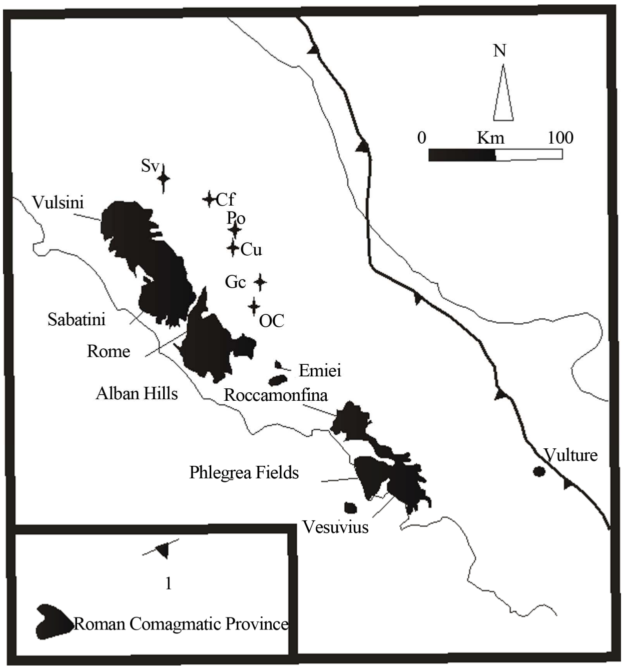

Figure 1. Location map of the Roman Comagmatic Region. Stars represent Umbria Latium Ultralkaline District (ULUD) volcanoes. Symbols: 1: main active compression; Sv, San Venanzo; Cf, Colle Fabbri; Po, Polino; Cu, Cupaello; GC, Grotta del Cervo; OC, Oricola-Camerata Nuova (Modified from [57].

occur in the Roman province, whereas lamproites are present in Tuscany and Corsica, and kamafugites form few centers east of the Roman province [e.g., 45-47]. The KS rocks are similar to shoshonites, whereas the HKS shows a very strong enrichment in potassium and incompatible elements. However, both the KS and HKS have relatively low contents of high field strength elements (*i.e.*, Nb and Ta; HFSE). Kamafugites show similar incompatible element patterns as HKS, but they are more strongly under-saturated in silica and have higher CaO and lower Na contents than the HKS.

1.2. Italian Carbonatitic Magmatism Related to the Roman Comagmatic Province

1.2.1. A Petrographic Outline of ULUD and Vulture Volcanic Deposits

The ages of the ULUD deposits range between 0.53 and 0.265 Ma (*i.e.*, San Venanzo and Polino) (Stoppa and Villa, 1991). Carbonatitic rocks include lithotypes with modal calcite ranging from ~10% to >50% (carbonatitic 20% - 50%, carbonatites >50%). The San Venanzo volcano is composed of three vents: the San Venanzo maar; the Pian di Celle tuff ring, and the Celli tuff cone [48]. The pyroclastic rocks consist of carbonatitic tuffs and tuffisites. These deposits contain spherical and plastically deformed lapilli and bombs. The tuffs may contain up to 50% of fine grained calcite, the other minerals present are melitite, leucite, and olivine with a glassy groundmass. The lapilli are concentric with porphyritic carbonate-rich melilitite material cored with forsteritic olivine. The lapilli are also embedded in fine-grained carbonate rich matrix. There are lava flows characterised as porphiritic kalsilite pholögopite-olivineleucite melilitite (kamafugite). These rocks are composed of olivine phenocrysts within a groundmass composed of leucite, kalsilite, melitite, phlogopite, and clinopyroxene, accessory minerals are perovskite, zeolites, and carbonates [49 and references therein]. Colle Fabbri (**Figure 1**) consists of two vent-opening explosions that formed subaerial breccias with two stages of intrusion: 1) dykelet swarms of melilitic lava, and 2) a massive holocrystalline, medium-grained plug (*i.e.*, leucite-wollastonite melilitolite of [50] or alternatively called euremite from [51]. This outcrop (leucite-wollastonite melilitolite) has been interpreted by [52] as melilite-bearing pyrometamorphic rocks (paralavas) due to coal fires. This interpretation has been challenged by [53], and [54] reaffirming that the Colle Fabbri outcrop is of magmatic origin. The leucite-wollastonite melilitolite is medium grained and equigranular, with fine-grained margins consisting partly of calcite-zeolite filled ocelli. The rock is composed of melilite euhedra, poikilitically enclosing wollastonite and intergranular leucite. Melilite also intergrows with leucite and kalsilite. High temperature, accessory phases are garnet (schorlomite) and apatite. Anorthite is also common and occurs in single crystals. The order of crystallization is wollastonite, melilite, anorthite, Ti-magnetite, schorlomite, and leucite. Quench clinopyroxene is present at the margins. Late-stage zeolites and peculiar carbonate-silicate-sulphate are very abundant in the melilitolite and the host rock [54, 55].

The Polino diatreme is filled by a breccia consisting of calcite-carbonatite lapilli and bombs [56]. The matrix is a calcite-cemented tuffsite composed of concentric layered lapilli (spin lapilli). The massive carbonatite consists of xenocrysts of forsterite that often have a monticellite reaction rims, xenocrysts of phlogopite, and microphenocrysts of Th-perovskite, Zr-schorlomite, Ti-magnetite within a cryptocrystalline calcite matrix. Modal analyses has 53% calcite (10% vesicles plus groundmass), monticellite at 23%, Th-perovskite plus Ti-magnetite at 9%, olivine at 6%, phlogopite at 6%, Zr-schorlomite at 2%, and apatite <1%. Cupaello is formed by a small vent or fracture from which a sequence of carbonatitic and phonolitic pyroclastic rocks and kalsilite melilitite (coppaelite) lava flow erupted. The pyroclastic level is composed of bombs of melilitite with a micritic carbonate matrix. The coppaelite is porphiritic and contains xenocrysts of corroded phlogopite and diopside in a hypocrystalline matrix of diopside, kalsilite, melilite, monticellite, spinel, perovskite, götzenite, khibinskite, apatite, and glass. The coppaelite ranges in composition from kalsilitite to kalsilite melilitite.

The Grotta del Cervo (**Figure 1**) locality is a pyroclastic deposit in the Pietrasecca karst-cave system. The Grotta del Cervo mela-foiditic tuff is composed of lapilli ash tuff, welded lapilli, ultramafic xenoliths, cognate lithics, and pelletal lapilli [57]. The welded lapilli consist of diopside, leucite, haüyne, eastonite, melanitic garnet, LREE-S-apatite, magnetite, kalsilite, and olivine. The chemistry of Grotta del Cervo characterize the rock as kamafugite. The lapilli ash tuff contains more than 10 wt% of carbonate and is therefore a carbonatic kamafugite. The Carsoli-Oricola volcanic field (**Figure 1**) consist of six vents (tuff rings). Oricola carbonatite tuffs consist of plastically moulded lapilli [58]. They are composed of fragments of olivine, diopside, phlogopite and apatite plus leucititic glass shards. Silicate fragments are immersed in a micro-cryptocrystaline matrix of Ca-carbonate. Finally, in the Vulture (**Figure 1**) occurrence, the Monticchio diatremic activity produced several maars (age: 0.13 Ma) which erupted carbonatite-melilitite lapilli in carbonatitic matrix [59]. Melititic lapilli and bombs in carbonatitic ash tuff form the main part of the deposits. Peridotite nodules of spinel wherlites and lherzolites are also present [60]. Some carbonatite concentric strata are preserved around melilitite lapilli. The mineral assemblage of the juvenile fragments (blocks of lapilli) consist of xenocrysts of Al-Cr diopside, residual forsterite, Cr-spinel, and very rare Mg-garnet. The groundmass contains melilite, spinel with magnetite rims, Baphlogopite, olivine, hauyne-lazurite, apatite, calcite, and perovskite and pyrite veins.

1.2.2. Geochemical Outline of the IUP Related to the RMP

The kamafugites of central Italy are ultra-basic, silica undersaturated, peralkaline rocks (K+Na/Al = 1.2 - 1.3) containing a typically plagioclase-free assemblage of kalsilite, leucite±nepheline. They also have high CaO contents (~ 15 wt%), Mg# (75 - 81) and K_2O/Na_2O ratios compared with other volcanic rocks of the Roman Comagmatic Province. The carbonate is high enough to form carbonate minerals, essential calcite and monticellite, plus xenocrysts of phlogopite and olivine [5]. The mafic minerals are melilite, and diopside characterized by high Mg, Ni, Cr contents. Olivine melilitites (SiO_2 <41%) and calciocarbonatites (SiO_2 <12%), although sharing many characteristics with leucitites, have an even more primitive and undersaturated character, including very high Cr+Ni contents (<1000 ppm). They carry phlogopite in the mantle debris suggesting a source of carbonated phlogopite peridotite (the same source is invoked experimentally by [61]). The carbonatitic rocks and associated lithologies (e.g. melilitite, melilitolite, and kamafugite) show a wide range in CaO contents from 37.7 wt%, to ~2.2 wt%. The high values are also present in the melilitolite rocks. Al_2O_3 ranges between 23.3 and 1.82 wt%, and TiO_2 is scattered and ranges between 2.8 and 0.2 wt%. MgO and K_2O show similar features.

Multi-element diagrams normalized to primitive mantle show that kamafugite and carbonatite rocks have overlapping concentrations. In particular, the Polino carbonatite-San Venanzo kamafugite and Grotta del Cervo kamafugite-Oricola carbonatite pairs have similar patterns [58 and references therein]. A petrological association is also confirmed by major and trace element plots, which show an evolutionary trend with a gap between Polino and some Cupaello samples (richer in Ca content; Oricola also get closer to this field) and the rest of the IUP (e.g., San Venanzo; CaO-SiO_2 diagram). As discussed below, this gap may be the result of immiscibility between the most silicic and carbonatitic rock series. Multi-element diagrams also show 1) that the patterns of Melilitite lava, carbonate-rich rock from Cupaello and leucite tephrite from Vulsini (Roman Comagmatic Province) are broadly similar [62], and 2) that the wide compositional ranges observed among carbonatitic, melilititic, kamafugitic and potassic and ultrapotassic rocks, may be due to heterogeneity in the source and/or various extent of melting proportion. Such a source may have been metasomatised by fluid and sediments released by the slab in subduction [63 and references therein], and, indeed there is evidence for a metasomatised mantle beneath Italy [64].

The $^{143}Nd/^{144}Nd$-$^{87}Sr/^{86}Sr$ diagram (**Figure 2**) shows the relationship between most of the Italian volcanic rocks, and the Italian Sr-Nd isotopic array is highlighted, as is the ULUD (Umbria-Latium ultra-alkaline district, [5, 21] (carbonatites, melilitites; [65]). [65] compared the Sr-Nd isotope ratios ($^{87}Sr/^{86}Sr$: 0.70970 - 0.7119, $^{143}Nd/^{144}Nd$: 0.5119 - 0.5122) of the ULUD volcanic rocks to kamafugites, orangeites and lamproites. The Ugandan kamafugites do not overlap with the Italian kamafugites, melilitites and carbonatites. However, on the basis of mineralogy and major elements, [66] classify the Chinese carbonatite-kamafugite association together with associated Polino (Italy) and Fort Portal (Uganda). The ULUD rocks plot between the field of South African orangites and Western Australian lamproites. However, the ULUD carbonatite-melilitite of S. Venanzo, Polino, Colle Fabbri

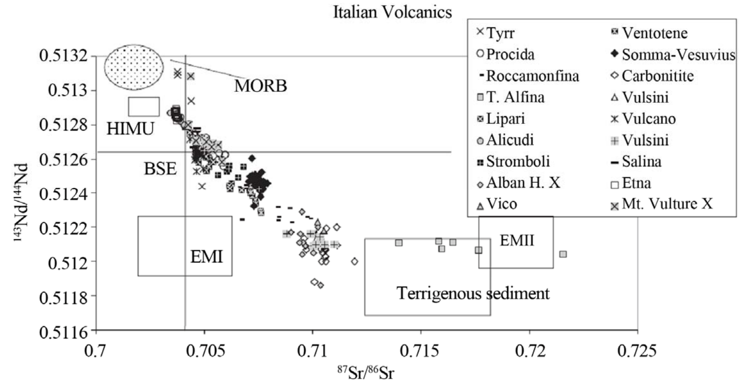

Figure 2. $^{143}Nd/^{144}Nd$-$^{87}Sr/^{86}Sr$ diagram. MORB, HIMU, EMI, EMII and BSE are from [147]. Tyrrhenian platform volcanics, Ventotene, Procida, Somma-Vesuvius, Roccamonfina, Carbonatite (ULUD), T.Alfina, Vulsini, Lipari, Alicudi, Vulcano, Stromboli, Salina, Alban Hills, Etna and Vico are from ([71] and references therein, [65,77] and references therein; Mt. Vulture xenolith are from [70]. Terrigenous sediment field from [148].

(leucite-wollastonite melilitolite) has been interpreted by [52] as melilite-bearing pyrometamorphic rocks (paralavas). This interpretation has been challenged by [53], reaffirming that Colle Fabbri outcrop is of magmatic origin. First, homogenization temperatures of inclusions in wollastonite, anorthite and clinopyroxene show that the studied Colle Fabbri rocks started to crystallize at temperatures greater then 1250˚C which are clearly in the igneous temperature range. Second, the complete melting of clay country rocks would need temperatures higher than 1300˚C which are unreasonable for underground lignite fires [67].

IUP rocks are isotopically off the worldwide car- bonatites array (higher $^{87}\text{Sr}/^{86}\text{Sr}$) [68] and they fall off the Ugandan kamafugites trend [69]. On the other hand, the same rocks fall on the Sr-Nd isotopic Italian array (**Figure 2**), isotopically similar to some of the Roman volcanoes (*i.e.*, Alban Hills, Vulsini, Vico) and other potassic continental rocks such as orangeites and lamproites. In addition, [70] showed that the Sr-Nd isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$: 0.7042 - 0.7058, $^{143}\text{Nd}/^{144}\text{Nd}$: 0.51260 - 0.5131) of the mantle xenoliths from the Mt. Vulture carbonitite-melilitite volcanic rocks have lower Sr and higher Nd isotopic ratios than the ULUD isotopic ratios but they are isotopically similar to the Campanian Volcanic District (*i.e.*, Campi Flegrei and Somma-Vesuvius, [71, 72]). The Pb isotopic data [73] are reported in **Table 1** with the respective petrographic rock types for the carbonatitic occurrences and associate silicate rocks. The $^{87}\text{Sr}/^{86}\text{Sr}$-$^{206}\text{Pb}/^{204}\text{Pb}$ and $^{143}\text{Nd}/^{144}\text{Nd}$-$^{206}\text{Pb}/^{204}\text{Pb}$ diagrams (**Figures 3(a)** and **(b)**) show that the Italian carbonatite field falls on the Italian isotopic array with radiogenic Sr isotopes and unradiogenic Nd isotopes and $^{206}\text{Pb}/^{204}\text{Pb}$ of 17.9 - 18.87. These diagrams also suggest that the Italian isotopic array is made by the following end-members: A) a mixtures of DMM and HIMU, the HIMU is likely because the data points towards the HIMU end-member. This character is clear on the Sr-Nd-Pb isotopic space of [9,10] and B) an upper crustal component characteristic of the Italian enriched upper mantle. Furthermore, the $^{208}\text{Pb}/^{204}\text{Pb}$-$^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$-$^{206}\text{Pb}/^{204}\text{Pb}$ diagrams (**Figure 4**) show a straight line with the Italian carbonatites plotting with lower radiogenic Pb isotope values than the Etna field and overlapping with the oceanic sediments field. The Pb isotopic regional components characterizing the Italian carbonatites overlap the sediments and the Eolian arc fields components. Sardinia trends towards EMI, and Etna plots below the NHRL into the Pietre Nere, and Iblei fields. The carbonatites seem to have an EM2 com- ponent and it is suggested here that it reflects mixing between MORB and oceanic sediments. In other words, they are dominated by sediments as suggested by EM2 for Nd and Sr isotopes. However, further insight can be gained by studying the three isotope Ne diagram ($^{20}\text{Ne}/^{22}\text{Ne}$-$^{21}\text{Ne}/^{22}\text{Ne}$, **Figure 5**). This diagram shows that S. Venanzo, Cupaello, Polino and Vulture trend towards a crustal component as in [74 and references therein] for the Eolian arc and the Somma-Vesuvius volcano [75,76]. Hence, the ULUD falls broadly with the leucite-bearing rocks [77].

The Sr-Nd-Pb isotopic variation for the ULUD [65], included Mt. Vulture mantle xenoliths associated with the carbonatitic-melilitic Monticchio magmas [70], and it is in accordance with the Italian isotopic array. These isotope ratios values vary in parallel to the Roman and Campanian regions from Umbria-Latium region to the

Table 1. Pb isotopic compositions of the carbonatitic occurences in Italy and associate silicate rocks

Samples		$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Vulture				
VUT-106	Phonolitic foidite lava	19.296	15.69	39.301
VUT-255	Malanite phonolite pumice	19.162	15.673	39.119
VUT-1523	Melilite bearing foidite lava	19.28	15.68	39.253
VUT-69	Leucite melilitolite dyke	19.457	15.711	39.509
Polino				
IT120	Ca carbonatite tuff	18.774	15.69	39.003
IT121	massive Ca carbonatite	18.767	15.679	38.978
Oricola				
OR1	Ca carbonatite tuff	18.745	15.681	38.996
OR1b	Ca carbonatite lapillus	18.744	15.68	38.995
San Venanzo				
VEN-5	Kal lc ol melilitite lava	18.742	15.662	38.929
VEN-10	Kal lc ol melilitite lava	18.747	16.667	38.952
Colle Fabbri				
CF-13	Lc woll melilitolite plug	18.747	15.66	38.747
CF-18	Lc woll melilitolite plug	18.868	15.683	38.946
Cuppaello				
COP-4	Melilite kalsilitite lava	18.75	15.676	38.963
COP-8	Melilite kalsilitite lava	18.755	15.68	38.972

The abbriviattion are as follow: Kal, kalsilite; lc, leucite; woll, wollastonite; ol, olivine.

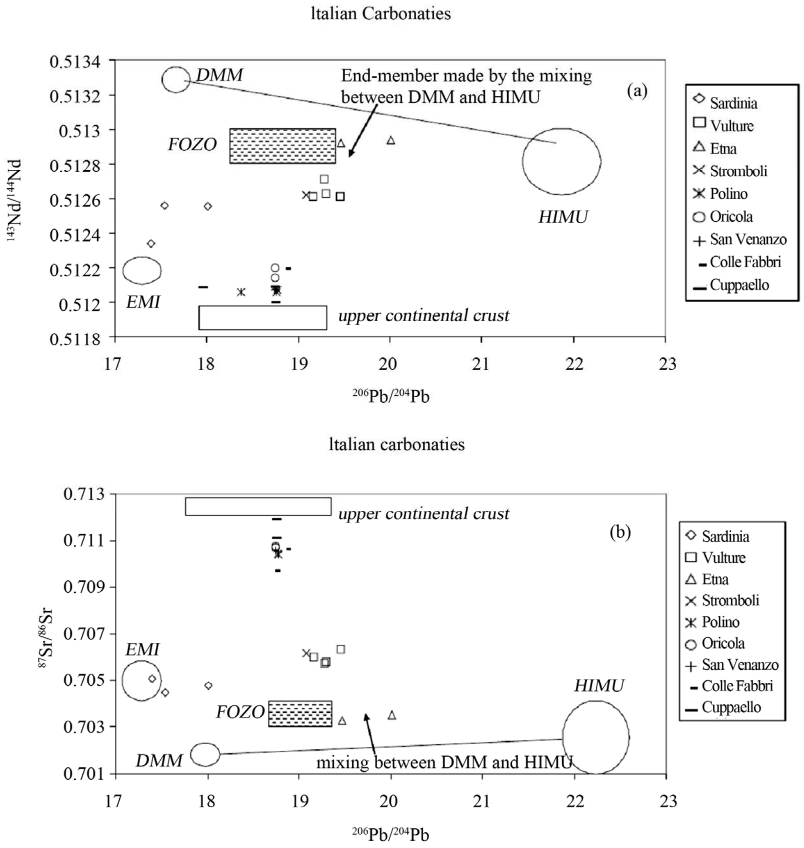

Figure 3. (a) $^{143}Nd/^{144}Nd$-$^{206}Pb/^{204}Pb$ diagram. The carbonatitic, Vulture, Etna, and Sardinia data are unpublished data. The fields of DMM, HIMU, and EMI, are from [147]. The FOZO field is from [93]. (b) $^{87}Sr/^{86}Sr$-$^{206}Pb/^{204}Pb$ diagram. The isotopic data and the fields are as in the Figure 2A. The upper continental crust field is from [77,148 and references therein].

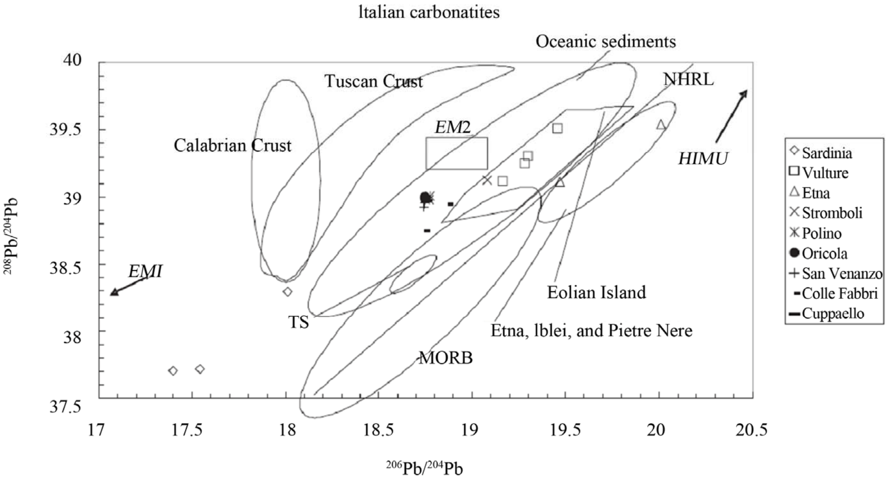

Figure 4. $^{208}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ diagram. The fields of Tuscan and Calabrian crusts, oceanic sediments, MORB, Tyrrhenian Sea floor (TS), Na-alkaline and calc-alkaline volcanic rocks from South Italy, and NHRL are reported. Fields and lines are drawn after [77 and references therein].

Mt. Vulture carbonatitic occurrence [70,78,79]. In addition, calcite in sövite ejecta (O and C isotopes) from Vulture [80] lies close to the "mantle box" and has clearly undergone minimal deuteric-hydrothermal exchange, whereas the Vulture carbonate-rich extrusive tuffs plot within, or close to, the outlined field of carbonatitic tuffs from elsewhere, as do the Cuppaello and San Venanzo tuffs and the Polino tuffisite. Whatever the mechanism

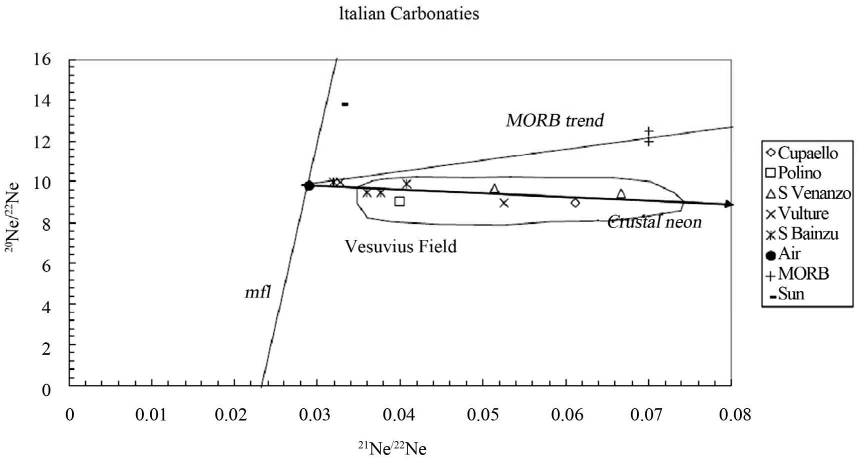

Figure 5. ^{20}Ne/^{22}Ne-^{21}Ne/^{22}Ne diagram. The Neon isotope data are unpublished data.

for these changes, which have been addressed in a number of papers [e.g., 81-84], it is important to note that carbonate in the Italian extrusive carbonatites have similar trends to extrusive carbonatites from other localities. However, The IUP $\delta^{13}C$ (PDB) ranges from −16 to −2 which may also have derived by a mixing between MORB and Marine sediments components whereas O isotopes may have affected by deuteric-hydrothermal exchange ($\delta^{18}O \sim 22$).

Additionally, the chondritic-REE normalised plot of the Italian carbonatites [5] show a characteristic Eu negative anomaly similar to those of the Roman Province [85, 86] and Campanian volcanic District [72]. Such Eu anomalies are attributed to mixing between MORB component and various proportion of clay-shale sediment [72, 85,87,88] at upper mantle levels. More evidence come from the work of [89] on the Betic Cordillera (Southern Spain) where Sr-Eu anomalies together with the Sr-Nd isotope data are interpreted as being due to subduction metasomatism from terrigenous sediments. Moreover, Eu anomalies are not a common feature in the world-wide carbonatites [90,91]. However, Laiwu-Zibo carbonatites from western Shandong Province, China [92] show the presence of a small Eu anomaly similar to the Italian carbonatites. These carbonatites are also characterized by the similar Sr-Nd isotopic composition as the ULUD.

2. Discussion

The controversy identified by [8,65] is focused on the relation between the ULUD and the Roman Magmatic Province origins and the related hypothesed tectonic setting. Particularly, [8] state that the Italian (IUP) and Ugandan (East African Rift Zone) volcanoes have sampled similar mantle conditions. Although the large scale geodynamic regimes are in total contrast, as are the deep mantle tomographic structures, the crucial common factor at the igneous province level is extensional tectonics. Extension, promoting release of volatiles (*i.e.*, H_2O, CO_2). [93] argue for a deep seated origin given the similarity of the isotopic signatures to FOZO (Focal Zone) and HIMU to carbonatites worldwide. [9,10] attempt to model with a geochemical and isotopical approach, the Italian carbonatites to the rest of the Italian magmatism by a large plume centred in the Tyrrhenian Sea and extending from beneath the western Alps through the Italian mainland westwards under the Sardinia and Corsica. The three isotopic end-members involved are FOZO, EMI and an Italian enriched mantle (ITEM as defined by [9,10]). The same trend is observed by [62,94] with different interpretations of the end-members: DMM, HIMU and an upper crust component. [94] envision a slab window below the Italian peninsula which is also supported by slab detachment tomographic data (e.g., [24,95,96]. This structure would have permitted mixing of the HIMU (AOC, altered ocean crust) and DMM (mantle wedge) with and isotopic enriched component derived from the subducted sediments from the European and the Adria plates.

As discussed above, there are some inconsistencies between the general geochemistry of the carbonatites (ULUD) and the Italian tectonics which need some clarification. 1) The geochemical framework of [97] emphasises the role of dolomitic-carbonatitic melt as a predicted vehicle of metasomatism and melt fluxing in the mantle wedge overlying the subducted slab. 2) The geographic position of the carbonatitic occurrences [4,5,98] in relation to the potassic and ultrapotassic magmatism [77 and references therein] and the assumed Italian subducted trench (*i.e.*, [99 and references therein]). 3) The amount of Mesozoic carbonatic sediment apparently subducted below the Italian peninsula [e.g., 100] from which it can be inferred that the carbonatitic occurrences in Italy may be related to subduction processes. However, the radiogenic ($^{87}Sr/^{86}Sr$ ratio) and unradiogenic ($^{143}Nd/^{144}Nd$ ratio) isotopic signature requires a contribution from terrigenous-pelagic sediments probably through a fluid phases separating from the slabs and hydrating the mantles above it [e.g., 101] given the isotope data on Appenine limestones ($^{87}Sr/^{86}Sr$ ~ 0.707460; $^{143}Nd/^{144}Nd$ ~ 0.511824) which are quite different from the Italian (Sr-Nd-Pb) carbonatitic signature. It is argued that the magmas were produced by partial melting of the upper mantle hybridized by melt and fluid derived by the slab in subduction. The evidence comes also from geochemical computations of multi-element patterns for melt in equilibrium with secondary cpx in mantle xenoliths (OIB example; [102]), compared to a carbonatite from Italy [4]. These indicate that rutile-bearing carbonated eclogite (subducted oceanic crust) is the likely source for metasomatic carbonate melts (features inherited by the multi-element patterns are enriched LILE and negative spikes for Nb, Ta, Hf, Zr and Ti, as in subduction related settings). In agreement with experiments and calculations [e.g., 103], the subducted oceanic crust undergoes subsolidus dehydration reactions at depths of <100 km, but does not decarbonate at the same time. Provided that the trace elements signature is not significantly modified by this dehydration, carbonated rutile-bearing eclogite may persist to considerable depths in the mantle. Intersection of this material with the carbonated eclogite solidus provides a ubiquitous deep source of metasomatising carbonate melt. Primary calcitic carbonatite magmas may be from shallower depths according to experiments of [61], [e.g., 104].

[105] demonstrate that low seismic velocities may also be considered as zones of melting without elevated temperatures; the low velocity zone (~70 - 150 km depth) is caused by melting due to the presence of carbonate. Seismic imaging of deep low velocity regions may reveal the locations of old subducted crust. Moreover, [106] show that there is no evidence of deep mantle origin in oceanic volcanism (*i.e.*, Hawaii and Iceland). Car- bonatitic occurrences and/or Ca-rich magmas have also been recognised in Tabar-Lihir-Tanga-Feni arc (Papua New Guinea), in the Northern Tonga arc, and western Shandong Province, China [92,107,108]. In addition, other evidence comes from the ultra-calcic magmas and/or island-arc ankaramites from arc system and experimental geochemical data ([109 and references therein, 110]; **Figure 6**).

The rise of carbonatitic melts has to be linked to the plate spreading processes above the mantle wedge particularly in Italy where the carbonatites post-date the extensional tectonic (late Miocene to Quaternary, [111,112 and references therein]. The carbonatitic melting regime in arc systems is also supported by carbonate recycling variation (higher CO_2 closer to the trench) in volcanic arc ([113], Central American Arc, [114]; evidence in the Italian peninsula, [115]). According to [97] carbonatitic form at P-T conditions between the dense cold slab and the higher T and lower P of the mantle wedge [116,117]. Such environments would produce melt and fluid migration from the subducted slab into the peridotite mantle wedge [118] leading to the reaction and crystallisation at subsolidus conditions of pyroxene, garnet and phlogopite at depths > than 95 km. However, the relative abundances of primary Cr-spinel in xenoliths in carbonate-rich melilitic tuff from Monticchio [60,70] coupled with opx, cpx, phlogopite, amphibole and very rare garnet suggest a shallower origin for the Monticchio carbonatites.

Carbonatite melt may therefore form in the mantle wedge at T > 935˚C and/or coexist with a silicate regime of water-saturated-silicate solidus corresponding to temperatures between 970˚C and 1020˚C and pressures between 70 to 100 Km (rutile-bearing eclogite and garnet lherzolite, [97] and references therein; [119], 2000, Dalton, personal communication). Further, [120] show experimentally that liquids coexisting with orthopyroxene, clinopyroxene, garnet, and carbonate mark the transition between CO_{2-}, dolomite- and magnesite-bearing magmas between two P-T invariant points (A: 2.6 GPa, 1230˚C, B: 4.8 GPa, 1320˚C). However, the [120] lherzolitic model can be used as a broad reference for the Italian carbonatites since the primary conditions of the Italian carbonitite sensu latu ought to be explained within this thermochemical system. In fact, the melting conditions applied to the Italian carbonitites in order to accept a subduction-related environment must be lower and in concordance with the model predicted by ([97], see his **Figure** 7.13a, and b). Such P-T melting conditions are obtained by invoking a $H_2O + CO_2$ excess in the mantle wedge due to the descending slab. If the [97] model is correct in terms of melting conditions, the slab components added to the mantle wedge, and the condition of immiscibility, then a carbonatite melt highly and distinctively enriched in incompatible elements can form in the convergent-margin silicate system. Moreover, I have used the [120] work on CMAS-CO_2 as a guide to possible carbonatite and correctly note that "real" arc mantle melting conditions must be at lower T—because of H_2O, Na_2O, FeO. The task is to consider the melting conditions for Peridotite-H_2O (see **Figure** 7.4 in [97]) noting differences for refractory fertile and enriched mantle and water-saturated vs dehydration-melting (pargasite lherzolite), then adding CO_2 (see **Figure** 7.5 in [97] and applying the phase relations to the inferred Italian arc or back arc environment and using a "high fO_2" assumption.

By "choosing" high fO_2 you avoid CH_4, and graphite and the application of **Figure** 7.5c from [97] and can focus on applying **Figure** 7.5b from [97] to Italian P-T profiles. Note also that **Figure** 7.2 from [97] is equivalent to the [120] CMAS-CO_2 model but the role of Na_2O is

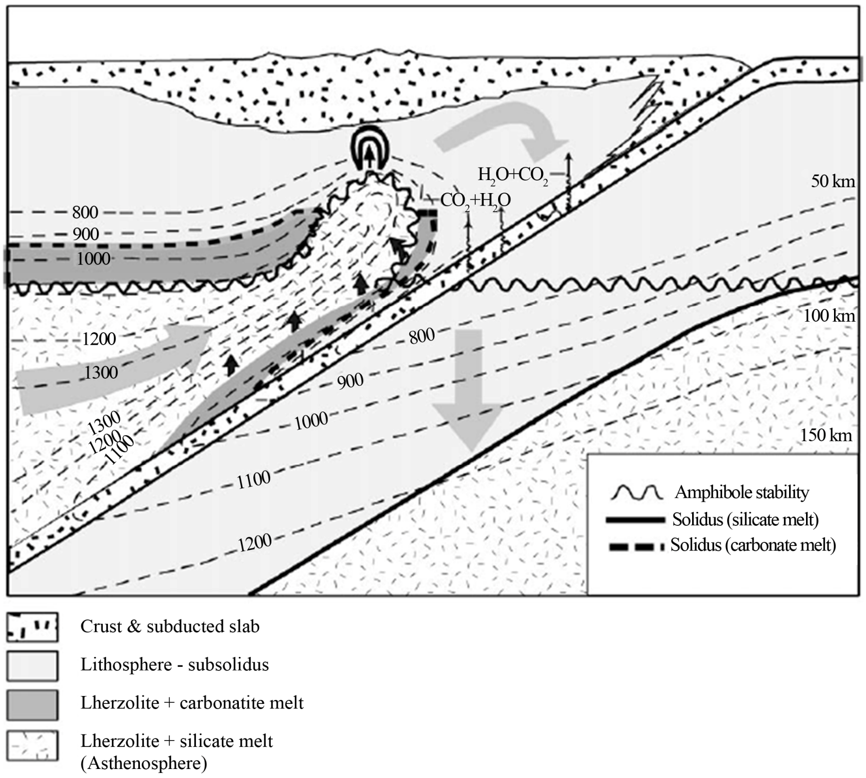

Figure 6. Schematic representation of subducted slab environment showing the (carbonatite-melt + lherzolite) region below the silicate melting region of peridotite + (CO_2 + H_2O). The figure summarizes the combination of frist-stage melting, carbonatite metasomatism and diapirism of partially molten (silicate melt) peridotite suggested for carbonatitic regime (copied with permission from [97], Figure 7.13a).

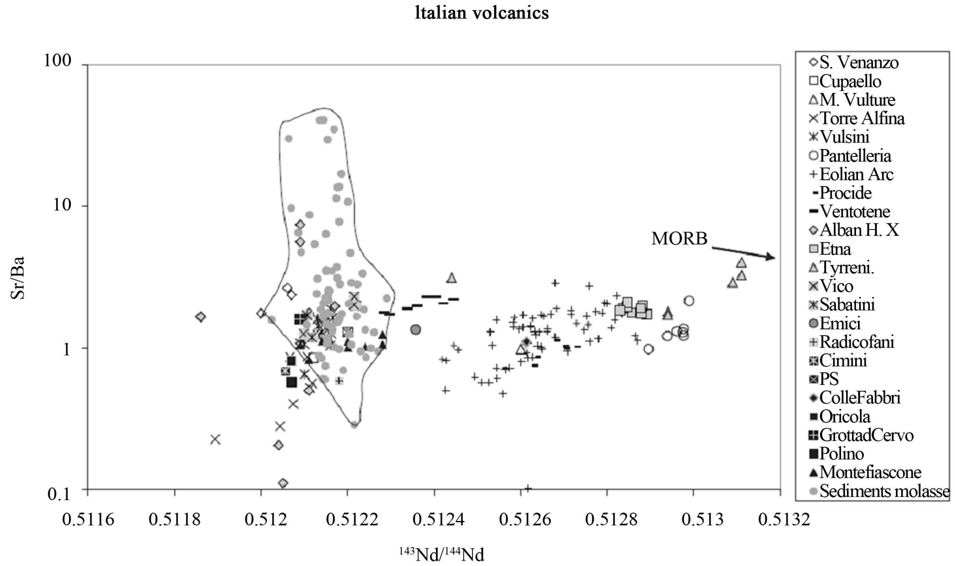

Figure 7. Sr/Ba-^{143}Nd/^{144}Nd diagram. The Italian volcanic rocks are from [12,19,50,58,77,85,87,88,94]. The molasse sediments are from [136].

considerable, moving invariant point I6 to 2 Gpa, 1030 approximately. Note that in the subduction regime profile of **Figure** 7.13a and b from [97] carbonatite magmas have a path to the surface avoiding capture in the silicate melting regime (e.g., the arc ankaramites of the [109] only if they lie either side of the upwelling wedge/silicate melting regime as could be the case in the Italian tectonic situation.

Evidence of immiscibility has been presented in the work of [121]. They show that combined silicate-carbonate melt inclusions in apatite phenocrysts occurred during magma evolution. Inclusions in the phenocrysts from an olivine-leucite phonolitic nephenilite bomb from Monticchio lake formation, record open system magma evolution during its rise towards the surface including crystallization, degassing, oxidation, and liquid immiscibility processes. [122] also point to immiscibility processes both at high T, to form carbonatite and late stage immiscibility at relatevely low P-T (670˚C - 800˚C; <1 kb) to form ocelli in melilitolite groundmass. [49] explain the relationship between the kamafugite with the Ca-carbonatite rocks at Cupaello (Italy) with an origin from primary "kamafugitic" magmas providing evidence of immiscibility processes. [123] show that the immiscibility processes of the two-liquid silicate-carbonate can occur both at low and high pressure and the immiscibility two-liquid space is dependant on the amount of CO_2 present in the system. The carbonate melt can migrate effectively only after separation from the silicate melt within liquid-dominated reservoirs (sills, dikes, or chambers) [124]. This intra-crustal environment may also be envisaged as the interface between upper mantle-lower crust and/or lower-intermediate crust where carbonated mantle derived magma can pond, stagnate, differentiate [125,126] and can start up to the surface (~1 Kb) to undergo to immiscibility processes with the formation of diatremic tuffsite at fast speeds of emplacement [127].

From [4,86], the ITE (incompatible trace elements) patterns of the San Venanzo, Polino, Cupaello and Mt. Vulture carbonatitic occurrences and the related lavas are compared. It is further inferred that upper crustal contamination which would have resulted in dilution of the broad ITE carbonatitic pattern abundances with respect to the correspective lava was not important [62,86]. Other disagreements against Peccerillo hypothesis [e.g., 62] are expressed by [128,129].

An alternative mechanism to explain the carbonatitic ITE abundances is to invoke different partition coefficients for these elements which would have depended on the P-T and the melt chemistry. Such a hypothesis is in agreement with the [130] study which experimentally showed that a carbonatitic melt may broadly correspond to the near-solidus in CMAS-CO_2 at 3 GPa [120], similar to the melting of carbonated mantle lherzolite. Such melts have elevated incompatible trace elements, depletion of Ti and Zr and fractionated REE patterns similar to the broad geochemistry of the Italian carbonatites ([62,86 and references therein]).

From an overview of the major element carbonatitic data [5], the Ca/(Ca + Mg) ratios ranges from 0.72 to 0.90 which provides minimum overlap with the Ca/(Ca + Mg) ratios experimentally produced by [61]. While the high Ca/(Ca + Mg) values can be explained with intra-volcanic suites fractionation processes, the lower values confirm the hypothesis of [61] that calciocarbonatitic melt are generated from lherzolitic, harzburgitic source at a P > 25 kbar through carbonatite-metasomatism.

Further evidence of the connection between carbonatitic melts with subduction-related system have been noted by [131]. They suggest that carbonatitic melts can be an agent of mantle metasomatism producing relatively enriched trace elements (LILE, LREE and some HFSE). Such hypothesis is not in contrast with the general tectonic model of [99] and lately with [20] and [43]. Finally, carbonatitic rocks are formed by the accumulation of sedimentary material which can have a deep (OIB, subducted slab recycling in the upper-lower mantle producing the carbonation of the mantle, [1,113] or shallow origin (IAB, 70 - 100 km melting area; e.g., [92,108] depending on the tectonic system. Similarly, [132] confirmed the circuitous carbon pathways between the crust and some sources of carbonatitic magma in the mantle through the subduction system, involving carbon transport in a variety of phases. The material in the carbonated mantle wedge (eclogite and lherzolite) in the arc system is recycled into the deeper mantle linking hot spot and arc volcanoes erupting carbonatitic magma. Recently, [133] demonstrated experimentally that a hot slab could have produced a carbonatitic regime as it has occurred in Italy. Lately, a slab subduction recycling evidence in OIB may also be inferred from W-Os isotopes [134]. This compelling work rules out a simple core-mantle mixing scenario and suggests that the radiogenic osmium in ocean-island basalts can better be explained by the source of such basalts containing a component of recycled crust. [135] show that isotopic results in peridotite xenoliths in islands of Western Samoa and Austral (OIB) indicate that carbonatite-rich melts were derived from recycled cru- stal components in the convecting mantle.

Another hypothesis to consider is that the mantle wedge and/or upper mantle portion from which the Italian rocks originated underwent complex tectonic events such as the subduction of the European plate [26] before the subduction of the Adria plate in the most recent times. This tectonic succession would have influenced in a complex isotopic way the mantle wedge with an isotopic zonation from north to south. The Sr/Ba-^{143}Nd/^{144}Nd diagram (**Figure 7**) shows that the Alpine molasse sediments [136] have trace (Sr/Ba ratio) elements and unradiogenic Nd isotope ratios similar to the most enriched rocks of the Italian peninsula (Northern-central sector of the RMP). Thus, the source (mantle wedge) of the Italian volcanic rocks may be inferred to have been affected by the geochemical fluxing from the European and the Adria plate; and hence, the northern sector has been influenced by more intense metasomatism compared to the southern sector, where the isotopic trends (Sr-Nd-Pb and noble isotopes) come closer to the MORB-OIB values (Etna volcano-Iblean Plateu). Evidence of Carbonate metasomatism is also present at Finero (Ivrea zone-western Alps) and is shown by [137]. [138,139] link this metasomatism to a subduction setting.

The broad data from literature confirm a subduction related environment linking the ULUD, the Roman and Campanian Province within a unique tectonic system. However, even when the carbonatite are erupted in a distensional regime a component present into the mantle can derive from a residual slab subducted through the mantle [105,132]. Hence, further evidence of slabs recycling deep in the mantle and erupted in OIB is given by [134, 140-142]. The ubiquitous presence of slabs in the mantle which produce OIB magmatism is also supported by geochemical and geophysical studies [105,143 and references therein].

3. Conclusion

In the light of the new carbonatitic findings in Italy [5, 144-146], coupled with recent experimental work and geochemical and isotopic work on carbonatitic magmas, it is concluded that these carbonatitic volcanic rocks are related to the Roman Comagmatic Province. The relationship among the rocks, the rock ages and the distinctive character of the isotopic components in Italy suggest a tectonic structure (slab breakoff-slab window centered in north-central Italy) with the mixing by two mantle domains one above the Adria plate and another above the European plate. The two plates have metasomatised the above mantle by repeated dehydration and have mixed in various proportion the metasomatised mantles. This produced the vast isotopic variety rocks that are present on the Italian peninsula. The tomographic data may support such scenario (see references inside for major detail). The data coming from the OIB sites shows that a component from a recycled crust can be invoked to explain the presence of the carbonatite.

4. Acknowledgements

This work started during the Individual Post-doc Marie Curie Fellowship (EU grant, tutor: Chris Hawkesworth) at Bristol University (2001) as an off-hand project. I continued to work on this discontinuing project with a Postdoctoral Research Grant at the Università degli Studi di Napoli Federico II. Chris Hawkesworth, Dan Barker, David Green, Monica Piochi, Dean Presnall, Gianpiero Venturelli and Robert Ayuso are acknowledged for having perfected part of the manuscript. Any error in the manuscript has to be blamed to the author.

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