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Evidence of Early Oligocene submarine volcanism in the Caltanissetta Basin (Central-Southern Sicily)

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Abstract - Petrological and geochemical data of volcanic rocks from several sites of the Caltanissetta Basin (central-southern Sicily) are discussed to provide information about volcanism in the northern portion of the African plate. Volcanics occur as large isolated blocks, mainly as pillows and subordinate lava flows, enclosing sedimentary levels of marly limestones. They are packed in several Paleogene and Neogene clayey lithologies, which are correlated to the sedimentation into the Miocenic Foredeep. The age of volcanism is referable to Early Oligocene (Rupelian), as revealed relative dating of the interpillow calcareous sediments. The studied samples are transitional and poorly evolved alkali basalts. Petrographic study highlights a discrete uniformity for the most samples, with porphyritic texture characterized by olivine, clinopyroxene and plagioclase phenocrysts in a microcrystalline groundmass, composed of the same phases plus opaque minerals. Major and trace element data are poorly variable and the trends show low degree of fractional crystallization with some contribution of mineral accumulation. Abundance and ratios of incompatible elements resemble OIB-type volcanics from intraplate environment. A slightly different garnet lherzolite sources that underwent a low partial melting degree can be hypothesized for the studied rocks. The Oligocene volcanism of the Caltanissetta Basin results as different magmatic pulses intruded along lithospheric fractures originated in response to flexure and uplift of the African paleomargin, in the pre-subduction stage and then incorporated in the future Sicilian accretionary prism.

Riassunto - Dati petrologici e geochimici delle rocce vulcaniche provenienti da vari siti del bacino di Caltanissetta (Sicilia centro-meridionale) sono discussi allo scopo di fornire informazioni sul vulcanismo della porzione settentrionale della placca africana. Le vulcaniti si rinvengono in grandi blocchi isolati, in subordinate colate e prevalenti pillows nei quali sono intercalati livelli sedimentari di calcari marnosi. Dal punto di vista stratigrafico i corpi vulcanici sono inclusi in litologie argillose del Paleogene e Neogene, che sono correlate alla sedimentazione nella zona di avanfossa Miocenica. L'età del vulcanismo è riferibile all'Oligocene (Rupeliano), come è stato rivelato dalle datazione relative effettuate sui sedimenti calcarei interpillow. I prodotti vulcanici analizzati hanno mostrato un'affinità alcalina transizionale, risultando poco evoluti con prevalenti composizioni basaltiche. L'analisi petrografica ha messo in evidenza una discreta omogeneità tessiturale e composizionale per la maggior parte dei campioni, che sono caratterizzati da una tessitura porfirica con fenocristalli di olivina,

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clinopirosseno e minore plagioclasio in una massa di fondo microcristallina composta dalle stesse fasi più variabili quantità di minerali opachi. I trend osservati sui diagrammi di variazione degli elementi maggiori ed in tracce hanno indicato uno scarso frazionamento con il contributo di fenomeni di cumulo. Le abbondanze e i rapporti degli elementi incompatibili sono comparabili con quelle di magmi tipo OIB e riconducibili dal punto di vista geodinamico a vulcaniti originatesi in un ambiente di tipo intraplacca. I magmi coinvolti deriverebbero da una sorgente mantellica lherzolitica a granato interessata da differenti gradi di fusione parziale. I risultati ottenuti ci consentono di dire che il vulcanismo Oligocenico del Bacino di Caltanissetta si sarebbe originato in seguito alla risalita di pulsi magmatici provenienti da fratture litosferiche sviluppatesi come conseguenza della flessura e dell'uplift del paleomargine africano, nella fase di pre-subduzione. Gli edifici o corpi vulcanici sarebbero stati poi incorporati nel prisma di accrezione siciliano.

KEY WORDS: *Caltanissetta basin; Oligocenic intraplate volcanism; biostratigraphic characterization; trace element geochemistry; garnet-lherzolite source*.

INTRODUCTION

Sicily represents a significant area on the volcanological point of view, because of the occurrence of various episodes of magmatic activity from Mesozoic to Present (Lucido *et al.*, 1978; Tanguy, 1978; Bianchini *et al.*, 1998; Trua *et al.*, 1998; Beccaluva *et al.*, 1998; Civetta *et al.*, 1998; Armienti *et al.*, 2004; Di Bella, 2007; Di Bella *et al.*, 2008b; 2009). During Triassic and mainly in the Jurassic times, the Sicilian area was interested by distensive tectonics leading to opening of the Tethys Ocean, with formation of various rift basins, along which volcanism took place. Discontinuous magmatic activity also occurred during closure of Tethys basin, from Eocene to Present (Peccerillo and Lustrino, 2005; Peccerillo, 2005).

The Plio-Pleistocene magmatism of Sicily has been so far intensively studied and much has been understood about its petrological features and magma sources (Beccaluva *et al.*, 1998; Trua *et al.*, 1998). In contrast, few information is available on the more ancient Sicilian magmatism (Lucido *et al.*, 1978; Di Bella, 2007; Di Bella *et al*, in progress). As regards the western-central Sicily volcanism, only preliminary petrological studies on the Caltanissetta Basin lavas have been carried out (Di Bella *et al.*, 2006; 2008a; 2009). All the above volcanic sites, in particular the Plio-Pleistocenic volcanics from Linosa, Pantelleria, some Sicily Channel Seamounts, Etna, Hyblean Hills and the Cretaceous volcanics of Capo Passero, Augusta and Siracusa, are situated in a similar geodynamic setting along the northern sector of the African plate. They show OIB-type affinity, but are different in age and for some geochemical-isotopic signatures (Beccaluva *et al.*, 1998; Trua *et al.*, 1998; Di Bella *et al.*, 2008b and references therein).

In this work we focus on the undated and poorly studied isolated volcanic outcrops in the Caltanissetta basin (central-southern Sicily) (Fig. 1), reported in several geological maps and papers (Behrmann, 1938; Beneo, 1955; 1956; Decima, 1972; Schmidt Di Friedberg, 1967a; 1967b). The volcanic bodies are mainly pillows and subordinate lava flows packed in several clayey deposits correlated to the sedimentation into the Foredeep Basins. The aim is to constrain their origin and geodynamic significance, through petrological study of four well-preserved representative volcanic outcrops (Cattolica Eraclea, Siculiana Marina, Pietranera, and Xirbi), and to discuss their genesis and evolution. The relative age of these volcanic events is indirectly provided using the calcareous nannofossils and foraminifers present into the sedimentary levels inserted in a few pillow lavas.

GEOLOGICAL SETTING

Central Sicily is part of the Maghrebian Sicilian

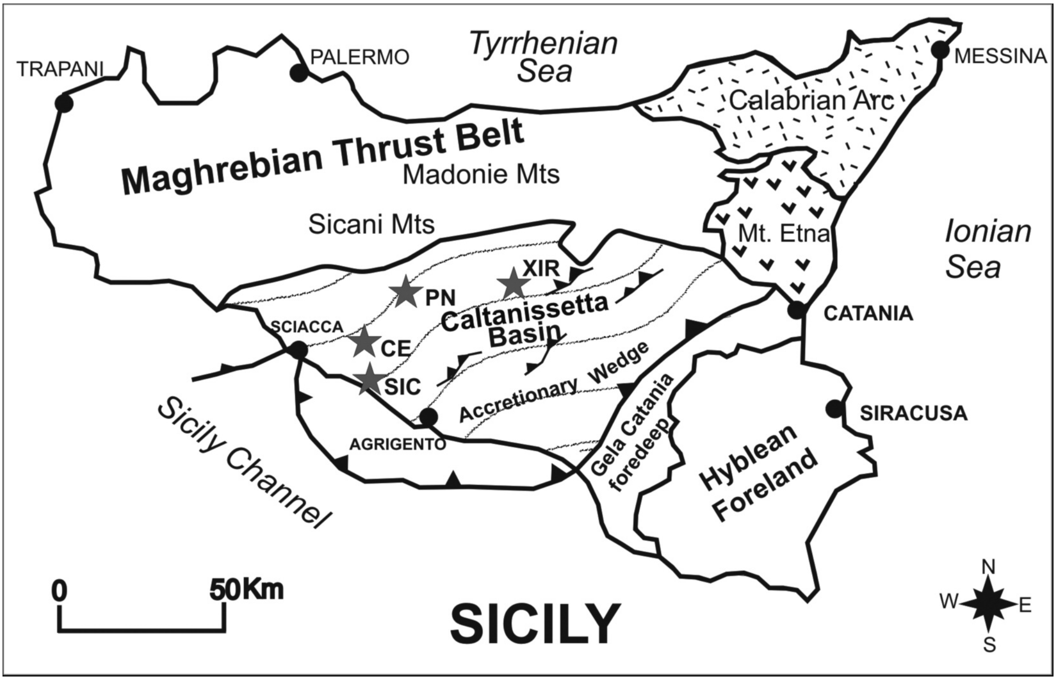

Fig. 1 - Geological sketch map of Sicily with localization of the studied volcanic sites (Grey stars): CE = Cattolica Eraclea; SIC = Siculiana Marina; PN = Pietranera; XIR = Xirbi.

Front Thrusts Belt, a segment of the Alpine collisional belt, described as a result of both post-collisional convergence between Africa and Europe and roll-back of the subduction hinge of the Ionian lithosphere (Grasso *et al.*, 1991). The volcanic bodies here examined are situated in the central-southern Sicily, where a Neogene-Quaternary accretionary wedge, the so-called Caltanissetta Basin or Gela Nappe, widely crops out (Ogniben, 1957; 1960; 1969; Argnani, 1987; Grasso *et al.*, 1991; Butler *et al.*, 1993). The wedge, up to 6 km thick, incorporates faulted and folded materials including Cretaceous-Eocene to Lower Miocene Variegated Clays, Late Oligocene marls and marly limestones, Lower Miocene Numidian Flysch, covered by Neogene to Pleistocene glauconitic and quartz-rich sandstones, marly clays, sandstones, conglomerates, evaporites, marls and calcarenites. Moreover, several large bodies of chaotic lenses of mud breccia, including large heterogeneous exotic Meso-Cenozoic sedimentary and volcanic blocks, extensively crop out interlayered with different stratigraphic levels. They overlie pre-Burdigalian beds in the north, and Tortonian-Pliocene beds in the south (Roure *at al.*, 1990). These chaotic clayey assemblages, consisting of brecciated clays (Ogniben, 1957) or olistostromes related to gravitative trasport on the instable clayey basin slopes (Rigo De Righi, 1957; Schmidt Di Friedberg, 1967), have been reinterpreted as tectonic melanges (Roure *et al.*, 1988) and more recently as the result of different manifestations of mud diapirism (Monaco and Tortorici, 1996). Such structural setting is the result of continental collision, after the closure of Tethys Ocean, during progressive growing and southward advancing Maghrebian-Sicilian thrust belt, involving the sedimentary cover of subducting African continental margin (Roure *at al.*, 1990).

The four volcanic bodies studied in this paper are located, from north-east to south-west, near Caltanissetta Xirbi railway station (XIR), to the east of Alessandria della Rocca village (PN), near Cattolica Eraclea old railway station (CE) and between Siculiana and Montallegro villages (SIC). They occur as large isolated blocks 5-20 m in thickness and up to 50 m in width, disseminated within Cretaceous to Lower Miocene dark-brown to grey-light mud breccias, that always underlie Messinian evaporites. The volcanic blocks are mainly represented by pillow lavas and subordinate lava flows, enclosing, except for the Siculiana outcrop, cm/dm-thick sedimentary levels of white-yellowish marly limestones (Fig. 2). The relationships between volcanic blocks and the surrounding associated clayey assemblages are not clear, consequently it is difficult to understand whether they are part of tectonically emplaced bodies within melanges or simply represent reworked material inside the basin by sliding phenomena. However, the stratigraphic setting of levels (pillows and interbedded sediments), often gently dipping, supports the first hypothesis.

BIOSTRATIGRAPHIC CHARACTERIZATION

To best define the relative age of these

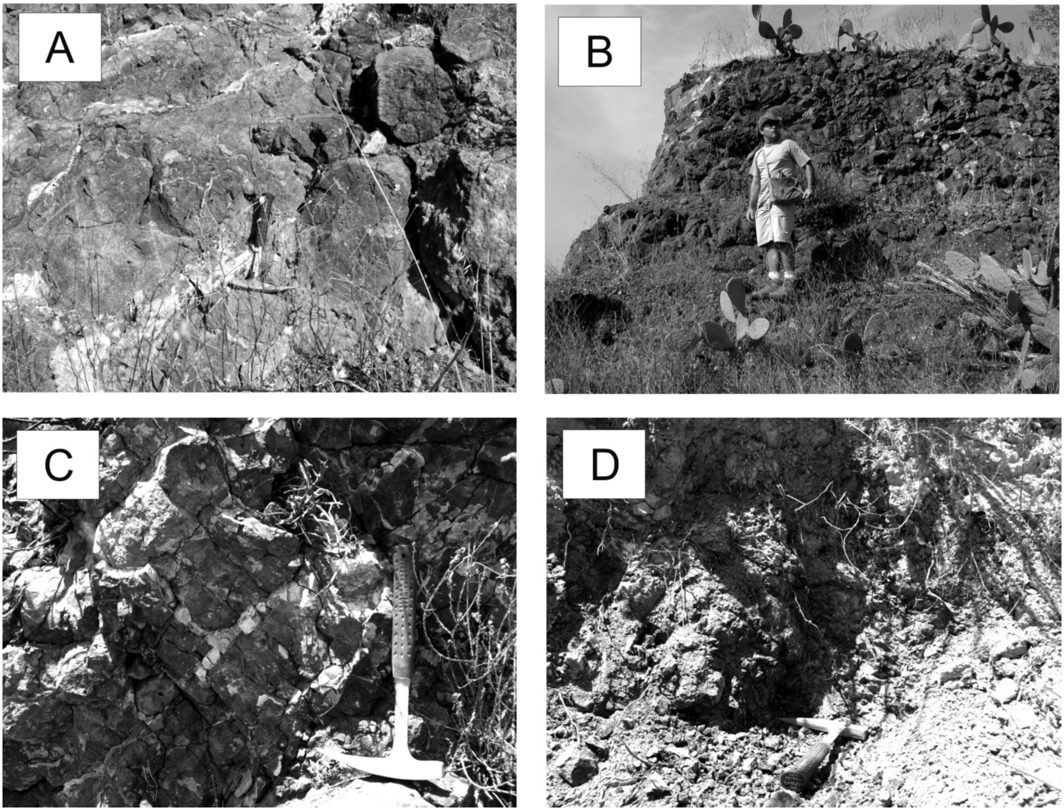

Fig. 2 - Volcanic outcrops of the studied sites: A) Cattolica Eraclea; B) Siculiana Marina; C) Pietranera; D) Xirbi.

volcanic materials, the microbiofacies and the calcareous nannofossils of interlayered sedimentary rocks have been investigated.

The Pietranera and Xirbi samples are wackestone with common foraminifers: the assemblages are rich and dominated by large Globigerinids and *Catapsidrax dissimilis*. The presence of *Chiloguembelina cubensis* allows to identify the P21a subzone of the Early Oligocene. Moreover the calcareous nannofossil assemblages, generally in a medium to poor preservation state, are characterized by common *Dictyococcites bisectus, Cyclicargolithus floridanus*, *Cyclicargolithus abisectus* and rare *Sphenolithus moriformis* and *Reticulofenestra* spp. The presence of *C. abisectus* confirms the Early Oligocene (Rupelian, NP23 Nannofossil Zone) age.

The Cattolica Eraclea samples vary from mudstone to wackestone, the foraminifer assemblages are poor whereas the calcareous nannofossil content is comparable to previous outcrops and still referable to Early Oligocene (Rupelian).

ANALYTICAL METHODS

Mineral composition of selected samples has been determined at the Earth Sciences SEM-EDS Laboratory of the Messina University. Analyses have been carried out using a LEO S420 electron microscope coupled to an Oxford Link ISIS series 3000 EDX spectrometer and Si(Li) detector with resolution of 156 eV at MnKα. The spectral data were acquired at 1500 to 2000 counts/s with dead time below 25%, using the ZAF correction. Analyses have performed operating at working distance of 19 mm, at acceleration voltage of 20 kV and 550 pA (PROBE).

Major (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, K_2O, P_2O_5) and some trace elements (Nb, Zr, Y, Sr, Rb, Ba, Co, Cr, V, Ce, La, Ni) have been determined by X-ray fluorescence (XRF) on powder pellets. The Cattolica Eraclea, Pietranera and Xirbi samples were analysed at Department of Geological Sciences of the Catania University using an automated wavelength-dispersive Philips PW 1400 spectrometer. The Siculiana M. samples were analysed at Department of Earth Science of the Calabria University using a PANalytical PW1480 spectrometer. Both laboratories followed the analytical procedures of Franzini *et al.* (1975). Na_2O and MgO concentrations were determined by atomic absorption procedures. Loss on ignition (L.O.I.) was gravimetrically estimated after overnight heating at 950 °C. The precision was monitored by routinely running a well-investigated house standard (obsidian). Finally, the accuracy was evaluated using an international standard whose composition is similar to that of the analyzed samples. The lava samples used for chemical analyses have been accurately selected, avoiding the rocks affected by secondary alteration phenomena and/or rich of carbonate vacuoles. For the last reasons, the coarse dust of all samples has previously submitted to acid attack (HCl 5%).

The X-ray powder diffraction analyses were performed at "Diffractometric Laboratory" of Messina University. Data were carried out using a BRUKER D8ADVANCE Diffractometer with Cu Kα radiation on a Bragg-Brentano theta-theta goniometer, equipped with a SiLi solid-state detector, Sol-X. Acquisition conditions are 40 kV and 40 mA. Scans are obtained typically from 2 to 80 degrees 2theta, with step size of 0.02 degrees 2theta, with a count time of 1 second. Raw diffraction scans are stripped of ka2 component, background corrected with a digital filter (or fourier filter). Observed peak positions are matched against the ICDD JCPDS database.

PETROGRAPHIC FEATURES

Twenty volcanic samples, after Cattolica Eraclea (CE), Siculiana Marina (SIC), Pietranera (PN), and Xirbi (XIR) have been petrographically studied. The rocks from Cattolica Eraclea and Siculiana Marina sites show common features, whereas those from Xirbi and Pietranera are both different showing distinct textures and parageneses. Some samples, mainly those from Cattolica Eraclea and Xirbi are affected by significant secondary alteration.

In order to characterize the petrographic features and to verify the alteration state of all samples, the mineral phases (both primary and secondary) and the various textures, veins, and vesicles were examined. All minerals were distinguished on the basis of the optical characteristics. The primary minerals are olivine, plagioclase, clinopyroxene, opaques. Secondary minerals include clay minerals, carbonates, iron oxy-hydroxides, zeolites, alkali feldspars. Carbonates frequently replace primary minerals and occur as vesicle filling and veins.

Cattolica Eraclea and Siculiana Marina

The lava samples (Fig. 3 A-B) are characterized by porphyritic texture (P.I. = 30-40%) with clinopyroxene, olivine and minor plagioclase phenocrysts in a microcrystalline intersertal groundmass, consisting of prevalent clinopyroxene and feldspar plus opaque minerals. *Clinopyroxene* phenocrysts are both euhedral and subhedral and frequently partially resorbed. They show a light green to light pink chromatic zonations, and are characterized by common sieve and spongy cellular textures; other crystals are in glomeroporphiric aggregates. The groundmass grains are completely light pink. *Olivine* is a common phenocrystic euhedral to subhedral phase, even subordinate to clinopyroxene, frequently replaced by secondary minerals and absent in the groundmass. Some subhedral crystals, showing resorbed rims, can be interpreted as xenocrysts. In some samples olivine is totally or partially altered and transformed to iddingsite or bowlingite; sometimes alteration is localized along the rims and crystal fractures. *Plagioclase* is rare as phenocryst but becomes the prevalent mineral of the groundmass, together with clinopyroxene. Plagioclase phenocrysts show sieve texture and resorbed rims. The anomalous greenish colour frequently shown by feldspar microlites indicates the probable occurrence of alteration processes. *Opaque minerals* (Magnetite and Ulvo-spinel) are present both as microphenocrysts and microlites, with a skeletal texture in the most samples.

Pietranera

Volcanic rocks from Pietranera (Fig. 3 C) are poorly porphyritic (P.I. = 5-10%) with phenocrysts of olivine, clinopyroxene and minor plagioclase set in an intersertal microcrystalline groundmass consisting of plagioclase and clinopyroxene plus opaque minerals. *Olivine* is the prevalent phenocrystic phase in the most samples. It is totally or partially altered and transformed to iddingsite, serpentine or to a mixture of limonite and chlorite. Rare resorbed crystals are observed. *Clinopyroxene* occurs as subhedral phenocrysts and is the prevalent phase in the groundmass. It shows an evident light pink to light yellow chromatic zonation. *Plagioclase* is present in rare unzoned and twinned phenocrysts, which commonly include glass and opaque grains.

The Pietranera basalts show ultramafic enclaves and a banded texture, both representing peculiar features of this site volcanics. The enclaves, up to centimetre-sized, are olivine-orthopyroxenites consisting of prevalent granular aggregates, with cumulitic texture, of orthopyroxene megacrysts and Cr-spinel with minor olivine and rare Ca-plagioclase. Resorbed xenocrysts of all the above phases are also present. The banded texture, recognizable under the microscope in the most samples, is given by layers containing different amount of opaque grains.

Xirbi

The samples from Xirbi (Fig. 3 D) are highly crystalline and characterised by subophitic-intersertal texture. The primary paragenesis consists of equigranular clinopyroxene, plagioclase and amphibole. Abundant opaque grains of variable size are observed. *Clinopyroxene* shows from euhedral to subhedral habitus and exhibits a pink colour typical of Ti-augite. Brown-orange kaersutitic *amphibole* is present in abundant euhedral crystals. Generally, the observed samples are pervasively affected by deuteric alteration, evidenced by the presence of secondary minerals as analcime and grains of clay minerals replacing feldspars.

MINERAL CHEMISTRY

Primary minerals of volcanics from all the studied sites have been investigated through SEM-EDS, with the aim of characterizing their chemical composition and variability. Analytical results are almost homogeneous for all the common mineral phases, despite the different textures shown by various samples. Representative phase analyses are presented in TABLE 1.

All the *clinopyroxene* phenocrysts, microphenocrysts and microlites have been

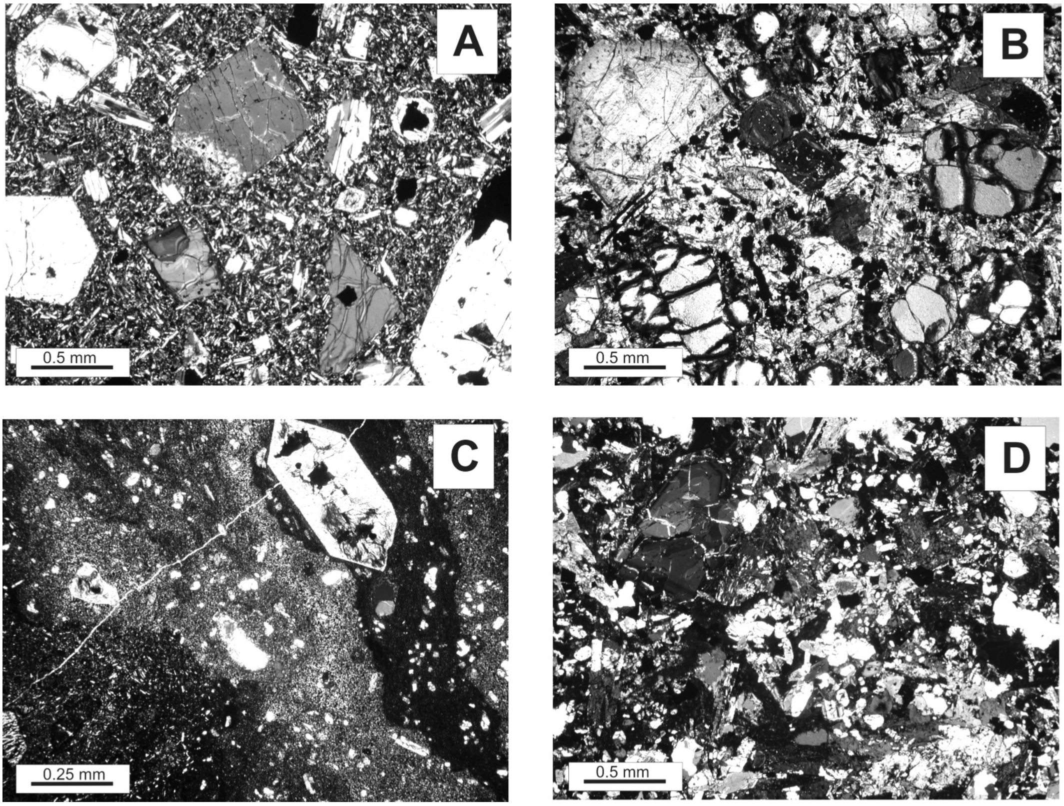

Fig. 3 - Microphotographs (crossed polars) of the studied volcanics: A) Cattolica Eraclea; B) Siculiana Marina; C) Pietranera; D) Xirbi.

TABLE 1

Representative composition (wt%) of mineral phases from Caltanissetta basin volcanics.

OLIVINE

	CE		SIC		PN	
	core	rim	core	rim	micro-phx	enclave
SiO_2	41.10	40.71	42.42	41.45	41.49	42.90
MgO	23.12	24.26	18.40	22.46	38.54	41.89
FeO	36.70	35.03	38.78	35.04	19.45	15.24
CaO	0.22	0.28	0.28	0.32	-	-
Total	101.14	100.28	99.87	99.27	99.48	100.03
Fo	73.89	72.02	78.98	73.56	77.94	82.60
Fa	26.11	27.98	21.02	26.44	22.06	16.85

Ti-Fe-KAERSUTITE

	XIR	
SiO_2	41.32	40.51
TiO_2	6.35	5.98
Al_2O_3	10.26	10.50
FeO	15.95	19.11
MgO	8.26	6.34
CaO	11.88	11.56
Na_2O	1.83	1.74
K_2O	1.03	1.30
Total	96.88	97.04

PYROXENE

	CE			SIC			PN			XIR		
	core	rim	grm	core	rim	grm	micro-phx		enclave	core	rim	grm
SiO_2	50.77	46.39	47.34	53.01	49.99	49.51	45.46	46.60	61.09	50.78	48.20	42.45
Al_2O_3	4.78	9.50	5.80	3.43	4.96	4.99	6.92	6.30	6.99	4.40	4.67	10.84
TiO_2	1.83	3.89	3.05	0.44	2.33	3.38	5.92	3.62	3.06	2.21	3.05	6.88
Cr_2O_3	-	-	-	-	-	-	-	-	0.93	-	-	-
FeO	7.55	6.90	10.72	5.10	8.77	8.41	9.62	13.06	6.44	8.19	13.22	16.78
MgO	12.44	11.10	10.17	14.23	12.66	11.57	10.12	7.83	30.47	11.56	7.73	8.88
CaO	23.43	22.95	22.22	22.76	21.87	21.88	21.90	21.75	1.51	23.24	22.42	12.58
Total	100.80	100.73	99.30	98.97	100.58	99.74	99.94	99.16	100.44	100.38	99.29	98.41
En	37.12	35.28	31.63	42.55	38.02	36.14	32.38	25.43	86.64	35.19	24.73	32.49
Fs	12.64	12.30	18.70	8.55	14.77	14.74	17.26	23.79	10.27	13.98	23.72	34.43
Wo	50.24	52.42	49.67	48.90	47.20	49.12	50.36	50.77	3.09	50.83	51.55	33.08

FELDSPAR

	CE			SIC			PN		XIR		
	core	rim	grm	core	rim	grm	micro-phx	enclave	micro-phx		grm
SiO_2	49.71	50.99	56.18	53.50	54.10	61.25	55.54	50.31	56.53	67.30	68.31
Al_2O_3	31.34	31.22	27.13	28.10	29.80	24.51	26.73	31.83	27.92	19.26	19.25
FeO	0.60	0.74	1.08	-	-	-	0.94	-	0.37	0.58	-
CaO	15.89	15.45	10.84	12.60	13.80	7.43	11.43	16.67	11.69	0.79	-
Na_2O	2.11	2.12	3.68	3.50	2.90	5.45	3.67	1.84	3.59	5.19	4.70
K_2O	-	-	0.69	0.40	0.30	0.94	0.89	0.35	0.45	7.11	8.36
Total	99.65	100.52	99.60	98.10	100.9	99.58	99.20	101.00	100.55	100.23	100.62
Ab	19.37	19.89	36.35	32.51	26.94	53.57	34.71	16.31	34.70	50.36	46.08
An	80.63	80.11	59.17	65.15	71.04	40.36	59.75	81.65	62.44	4.24	0.00
Or	-	-	4.48	2.34	2.02	6.08	5.54	2.04	2.86	45.40	53.92

OPAQUE MINERALS

	CE		SIC		PN	
						enclave
MgO	5.33	5.18	3.56	2.52	17.78	5.62
Al_2O_3	5.69	6.55	4.89	2.44	53.26	8.83
SiO_2	2.46	0.50	0.64	1.03	-	-
TiO_2	20.65	17.64	24.12	28.03	-	2.75
V_2O_5	0.91	-	0.82	-	-	-
Cr_2O_3	0.55	1.40	-	-	15.57	50.48
MnO	0.43	-	0.56	0.60	-	-
FeO	63.89	68.60	64.70	63.27	13.48	35.52
CaO	-	-	0.55	0.32	-	-
Total	99.91	99.87	99.29	97.89	100.09	100.19

CE = Cattolica Eraclea; SIC = Siculiana Marina; PN = Pietranera; XIR = Xirbi analysed. According to IMA pyroxene classification, phenocrysts and microphenocrysts of all the analysed samples are mainly characterized by prevalent diopside with minor augite; microlites from the groundmass show a slightly Fe-rich composition. A compositional zonation is observed in the phenocrysts, with rimward enrichment in FeO and TiO_2 and depletion in MgO, SiO_2 and Al_2O_3. The CaO content is rather constant, except for a few analyses which show an anomalous CaO enrichment and fall outside the diopside field. Cr_2O_3 has been detected only in the subhedral phenocrysts. In the pyroxenes with sieve texture, Ca-plagioclase and Cr-rich magnetite inclusions have been recognized. The observed clinopyroxene compositions are closely related to alkaline basalts from intraplate environment (Leterrier *et al.*, 1982; Peccerillo, 2005).

Unaltered portions of *olivine*, both in phenocrysts and microphenocrysts, have been analysed. Generally the composition ranges from Fo_{68} to Fo_{82} with a slight enrichment in fayalitic component towards the rim. All the phenocryst types, both euhedral and subhedral, are similar in composition, displaying only small differences in the CaO content. Indeed, in the euhedral crystals CaO is not present, whereas the subhedral types show significant CaO concentrations (0.23-0.77 wt%). Variable CaO content may depend either on pressure conditions of crystallisation or on CaO activity of melts from which different olivines crystallised (Simkin and Smith, 1970; Di Bella *et al.*, 2008b). Microanalytical investigations have not revealed olivine microlites.

Phenocrysts and microlites of *feldspars* have been analysed. All the analysed phenocrysts are plagioclase and range in composition from An_{60} to An_{75}, falling in the labradorite and bytownite fields. Each phenocryst shows a homogeneous composition, except for a thin rim slightly enriched in the anorthite component observed in the Pietranera samples. This Ca-enrichment can be interpreted as a result of interaction with a more primitive or H_2O-enriched magma, which induced growth of a CaO-rich rim around the crystals. Generally, the microlite composition is variable from bytownitic to andesinic plagioclase (Cattolica E., Siculiana M., Pietranera) to anorthoclase (Siculiana M.) and sanidine (Or > 45%) (Siculiana M., Xirbi). Sanidine prevails in the Xirbi studied volcanics. Some of the feldspar microlites, which appear greenish in colour in thin section, result Na-zeolites (natrolite group or analcime) indicating an alteration process.

Opaque mineral phases, both as microphenocrysts and microlites, have been analysed. The main composition is Ti-magnetite characterized by high Ti content ranging from 23 to 28%. Abundant ilmenite is widespread in all the analysed samples.

Apatite, both as microlites and microphenocrysts, has been found in all samples.

The analysed a*mphibole*, present only in the Xirbi volcanics, results an Fe-enriched kaersutite.

Ortopyroxene megacrysts in mafic enclaves of Pietranera samples have been also analysed. They are composed of prevalent enstatite-rich (87%) orthopyroxene, Cr-spinel, partially resorbed olivine (Fo 83%) and minor bytownitic plagioclase. Significant disequilibrium textures not optically resolved, such as reaction rims around phenocrysts, have been observed during the SEM-BSE investigations.

WHOLE ROCK GEOCHEMISTRY

Analyses of representative samples are reported in TABLE 2. Some samples were found extensively altered and characterised by high L.O.I. values, and, therefore, were excluded from geochemical study. For the same reason, particular emphasis during illustration and discussion of geochemical data will be given to some elements such as Zr, Y, Nb and Ti, considered geochemically immobile during secondary processes. On the contrary the alkaline elements (Na and K) are highly mobile during alteration processes, consequently the

Table 2

XRF bulk chemical analyses of major (wt%) and trace (ppm) elements of representative samples from Caltanissetta Basin volcanics.

SAMPLE	CE1	CE2	SIC1	SIC2	SIC3	SIC4	PN1	PN2	PN3	PN4	XIR1	XIR2
SiO_2 %	41.94	48.47	43.76	48.42	48.98	49.77	52.10	48.36	48.44	47.40	48.52	48.33
TiO_2	2.55	2.99	2.68	2.28	2.24	2.28	3.37	3.08	3.17	3.18	2.67	2.67
Al_2O_3	9.77	12.92	12.85	9.97	11.16	12.78	13.21	11.71	12.36	11.86	14.86	14.75
Fe_2O_3	12.97	12.40	14.28	11.83	11.32	10.40	9.85	12.64	12.56	13.29	12.02	11.96
MnO	0.15	0.17	0.17	0.16	0.16	0.14	0.11	0.15	0.16	0.18	0.17	0.16
MgO	8.89	7.09	7.10	13.64	12.50	10.74	5.06	9.46	9.17	10.13	4.60	4.57
CaO	13.80	9.30	11.48	7.48	7.20	8.03	10.02	9.21	9.58	9.68	4.89	4.90
Na_2O	1.15	2.32	2.16	1.95	2.32	2.71	2.74	2.44	2.47	2.42	2.94	2.92
K_2O	0.84	1.60	1.72	1.21	1.33	1.06	1.36	1.19	1.26	1.04	2.94	2.95
P_2O_5	0.74	0.44	0.77	0.21	0.19	0.11	0.16	0.27	0.23	0.27	0.93	0.91
L.O.I.	7.20	2.30	3.02	2.85	2.61	1.98	2.58	2.17	1.51	1.48	5.46	5.88
Total	100.00	100.00	99.99	100.00	100.01	100.00	100.56	100.68	100.90	100.92	100.00	100.00
Sr ppm	578	694	645	270	359	433	501	452	497	494	786	789
V	154	143	273	235	216	258	309	269	282	270	50	52
Cr	482	294	669	678	625	420	643	582	512	538	0	0
Co	92	90	55	51	50	45	44	65	64	67	48	51
Ni	276	195	332	306	295	213	168	340	305	320	18	17
Rb	11	19	39	29	30	26	18	14	13	9	48	48
Y	22	17	28	12	12	11	12	15	14	17	37	37
Zr	190	290	238	227	236	196	272	245	254	256	368	366
Nb	46	60	58	54	58	43	42	38	40	39	97	97
Ba	513	651	460	353	401	376	370	327	363	363	1790	1781
La	43	25	50	13	9	5	14	13	16	11	68	75
Ce	104	66	102	13	25	13	52	73	54	78	135	148
Nb/Y	2.05	3.46	2.07	4.50	4.83	3.91	3.49	2.50	2.95	2.38	2.66	2.63
Ba/Nb	11.14	10.88	7.93	6.54	6.91	8.74	8.90	8.50	9.01	9.21	18.41	18.39
Zr/Nb	4.14	4.84	4.10	4.20	4.07	4.56	6.55	6.37	6.31	6.49	3.79	3.78
La/Nb	0.94	0.41	0.86	0.24	0.16	0.12	0.33	0.33	0.41	0.28	0.70	0.77
Ti/Zr	86.40	63.33	69.61	61.98	58.42	71.14	76.13	76.92	76.07	75.50	45.96	46.36

TAS classification (Le Bas *et al.*, 1986; Fig. 4) is slightly rough. In such diagram, the most studied rocks are basalts which show a transitional affinity straddling the Irvine and Baragar line. The weakly alkaline character is potassic according to Le Maitre (2002) classification ($Na_2O - 2 < K_2O$), sodic if the K_2O/Na_2O ratio < 1 is considered. Only the Xirbi volcanics are most evolved falling in the trachy-andesite basalt or mugearite field. It is important to highlight that the secondary processes may be in part responsible for the obtained compositions.

Representative diffractometric analyses of altered samples (LOI > 4%) put in evidence the presence of secondary minerals as prevalent saponite, rare haloysite and calcite replacing primary phases of the groundmass (Fig. 5a). To test the alteration effects on the bulk chemistry, incompatible element patterns of representative altered (LOI ~ 6%) and preserved (LOI ~ 2%)

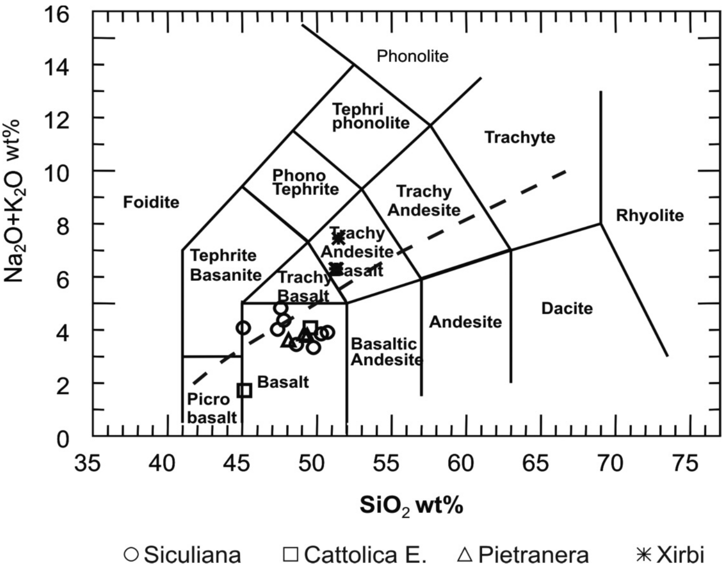

Fig. 4 - Total Alkali vs. silica (TAS) classification diagram (Le Bas, 1986) for the Caltanissetta basin rocks. The dashed line separates the alkaline from sub-alkaline field (Irvine and Baragar, 1971). Data are plotted on water free-basis.

samples from the same volcanic site have been compared (Fig. 5b). In both samples the HFSE abundances are similar, whereas the LILE concentrations increase with increasing LOI values.

Variation diagrams of major elements *vs.* MgO (Fig. 6), though a bit scattered, show a decrease in TiO_2, Al_2O_3, and CaO with increasing MgO, and poorly variable values for the other oxides. The Pietranera samples show high TiO_2 content, as a consequence of the abundance in opaque phases. Overall, major element trends suggest an evolution through a low degree of fractional crystallization, dominated by olivine separation with some clinopyroxene. A role of clinopyroxene fractionation is indicated by decrease of CaO/Al_2O_3 with decreasing MgO (not shown). However, the high values of MgO (up to 15%), and of related trace elements (Cr and Ni) can be interpreted as mineral accumulation effects.

With regard to trace element geochemistry (Fig. 7), among the compatible elements, Cr and Ni are positively correlated with MgO, Co is rather constant with higher values for the Cattolica Eraclea basalts, V (not shown) is scattered. LILE show different trends against MgO; Sr is negatively correlated, Rb is scattered and Ba is constant with increasing MgO. Most of the studied basalts show almost constant concentrations of HFSE (Zr, Nb) and REE (La, Ce) vs. MgO, except the Xirbi volcanics, which are characterised by higher values.

Incompatible element variation is shown by mantle-normalised (McDonough *et al.*, 1989) diagrams (Fig. 8) . Although many trace elements are lacking, the patterns of the analysed samples resemble OIB, with a relative enrichment of HFSE over LILE and a particular depletion in LREE.

DISCUSSION AND CONCLUSIONS

The main scope of the present paper is to show

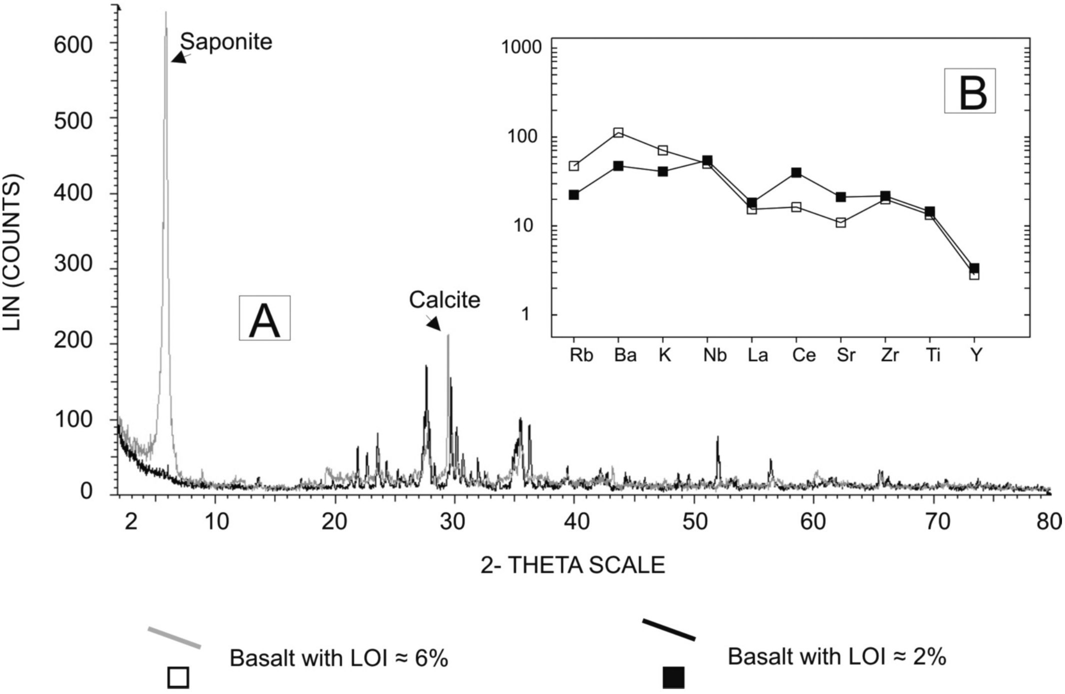

Fig. 5 - A) Representative X-ray powder diffraction patterns of two samples characterized by different LOI values (altered ~ 6 % and preserved ~ 2 %). B) Patterns of incompatible elements relative to XRDP analysed samples.

the first geochemical data on the volcanic rocks from the Caltanissetta basin, which can prompt further investigation. However, a few conclusion can be drawn regarding the genesis, evolution processes and geodynamic setting of its emplacement. As discussed below, the composition of studied volcanics is probably controlled by three important factors: 1) noticeable geochemical homogeneity of the involved magmas; 2) slightly different partial melting degree from similar source regions; 3) scarce fractionation with contribution of mineral accumulation and local mixing processes.

Using relatively immobile trace elements, the studied basalts show high abundances of incompatible elements (e.g., Nb = 40÷100), high Nb/Y (1.5÷5) and low Ba/Nb (6÷12), low Zr/Nb (4÷6.5), La/Nb (0.12÷0.95) and Ti/Zr (60÷90) ratios (Winchester and Floyd, 1977). All these values are typical of alkaline basalts (Table 2). Overall, the incompatible element abundances and their ratios indicate that the basalts exhibit an alkaline chemistry, similar to oceanic island basalts (OIB), typically erupted in within plate tectonic setting. The studied volcanics could represent the products of an intra-plate hot spot as evidenced in the Ti vs. V diagram (Fig. 9; Shervais, 1982). This diagram is usually used to distinguish MORB from island-arc volcanic rocks. The above author demonstrated that the fractionation of V and Ti during partial melting and fractional crystallization is a function of oxygen fugacity, and that Ti/V ratio increases from island-arc to MORB to OIB basalts. All the volcanic rocks from the Caltanissetta Basin show 50 < Ti/V < 100, similar to that of ocean island

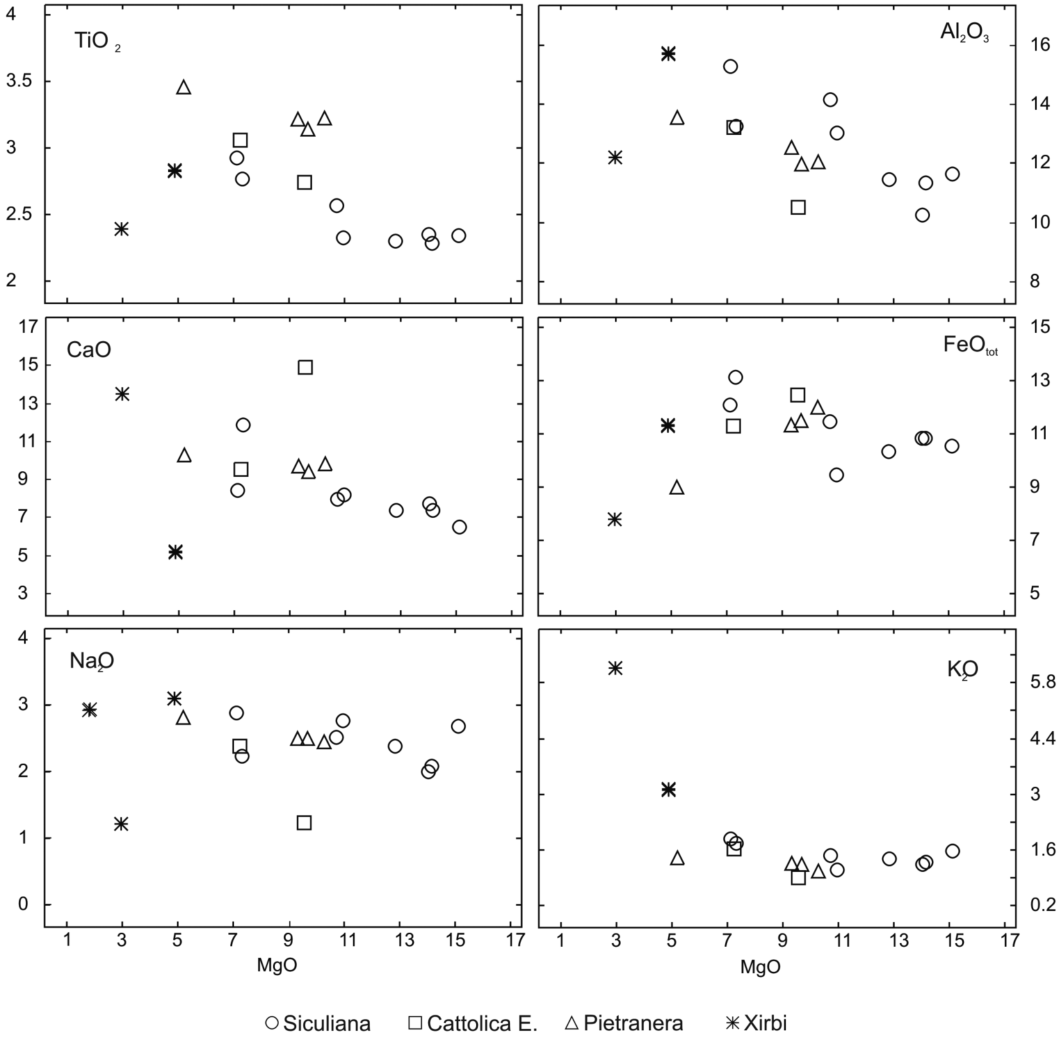

Fig. 6 - Variation diagrams of major elements vs. MgO (wt%).

basalts. Effectively, the normalised trace element pattern of the studied basalts is similar to that of the modern OIB, characterised by relative enrichment of HFSE (*e.g.*, Ta and Nb) over LILE (*e.g.,* Rb and Sr). Comparison with the different types of Italian modern OIB indicates that the studied basalts may have derived by an enriched magma source respect to MORB. Although isotopic data are lacking, the Ba/Nb vs. Zr/Nb plot (Fig. 10) is used to tentatively discriminate the probable source composition, which results intermediate between HIMU- and EM-type reservoirs (Weaver, 1991; Jung, 1999). The high incompatible trace element ratios in alkaline volcanics are usually explained as originated from recycled oceanic lithosphere plus sediments or from sub-continental lithosphere (Weaver, 1991; Liu *et al.*, 1994; Zhi *et al.*, 1990).

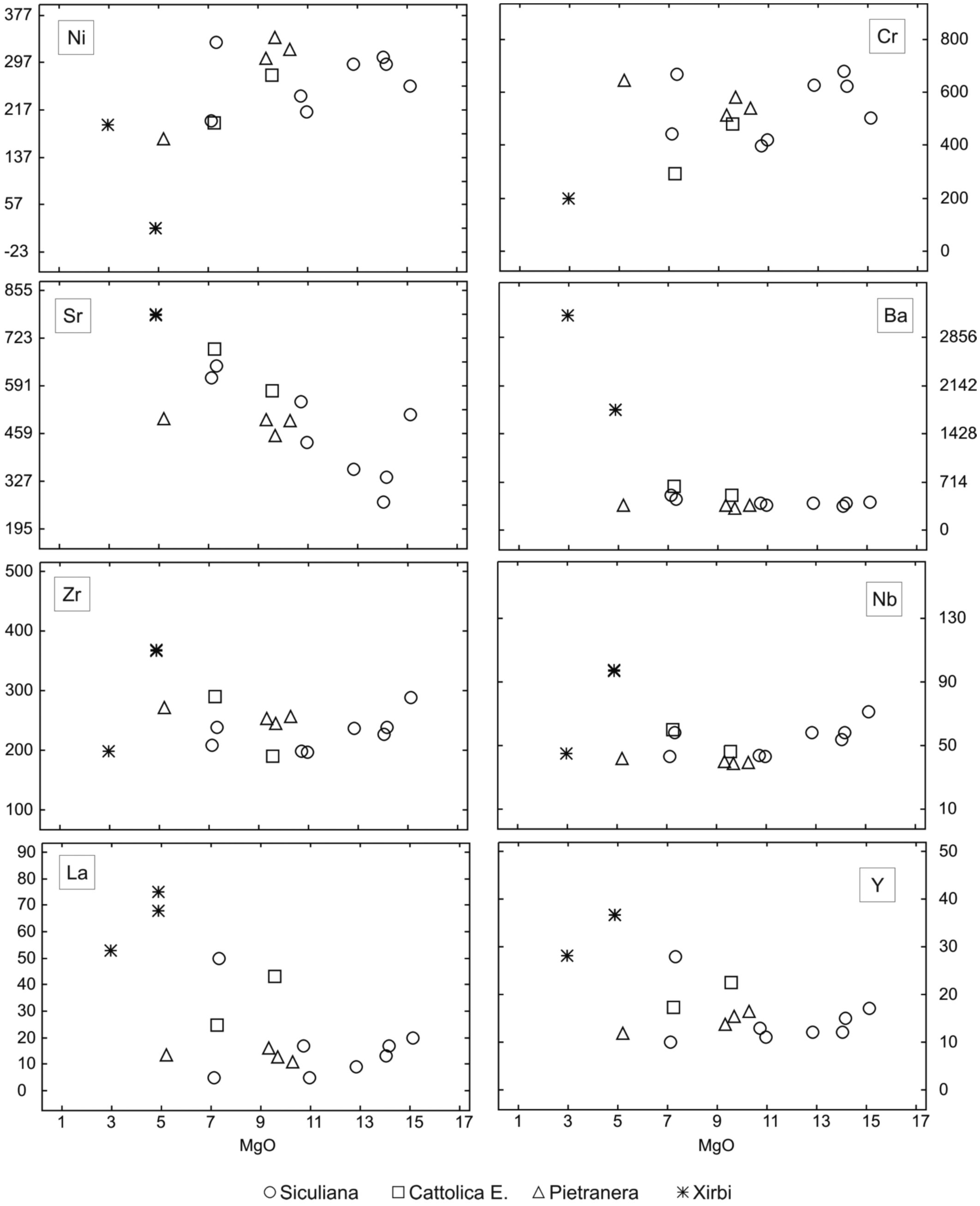

Fig. 7 - Variation diagrams of some trace elements (ppm) vs. MgO (wt%).

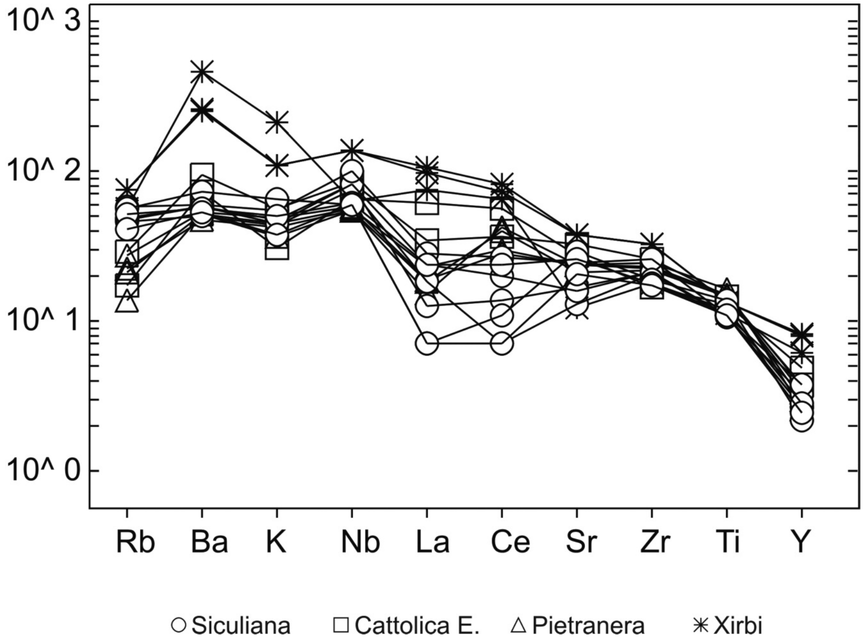

Fig. 8 - Patterns of incompatible elements normalized to primordial mantle composition (Sun and McDonough, 1992) for mafic (MgO > 5 wt%) rock from Caltanissetta basin.

The involvement of crustal contamination and/or sediment assimilation during the magma genesis of the studied rocks is strongly probable.

To test the magma source type and its partial melting degree, Nb/Y versus Zr/Nb diagram of Wilson and Downes (1991; Fig. 11) is used. The studied volcanics display along two different trends, the first outlined by Siculiana M. + Cattolica E. with about 1% of partial melting degree, the second, outlined by Pietranera volcanics, with about 2.5% of partial melting degree. The trends are representative of two partial melt batches from slightly different mantle garnet lherzolite sources. Quantitative model (Harangi, 2001) indicates for a similar garnet lherzolite source an assemblage of ol 59.9% - opx 25.5% - cpx 8.8% - gt 5.8%. The other OIB-type Sicilian volcanics (Peccerillo, 2005 and references therein; Di Bella *et al.*, 2008b), plotted in the same diagram (grey area), show different source compositions.

Integrated petrographic and geochemical results allow us to hypothesize that magmas, originated from slightly different garnet lherzolite sources, underwent low degrees of fractional crystallization. The variation trends of major and trace elements indicate that prevalent olivine and minor clinopyroxene were the first separated phases. The negative correlation shown by Al_2O_3 against increasing MgO suggests that no alumina-rich phases, such as plagioclase, had a significant role during the first stage of magma crystallization. This is also supported by increase in Sr with decreasing MgO. Furthermore, TiO_2 and P_2O_5 (not shown) increase with decreasing MgO, indicating late fractionation of Fe-Ti oxides and apatite respectively. The low variation in LREE contents and the incompatible trace element ratios, as Ce/Y (1÷4), Zr/Nb (4÷6.5) and Nb/Y (2÷4.5),

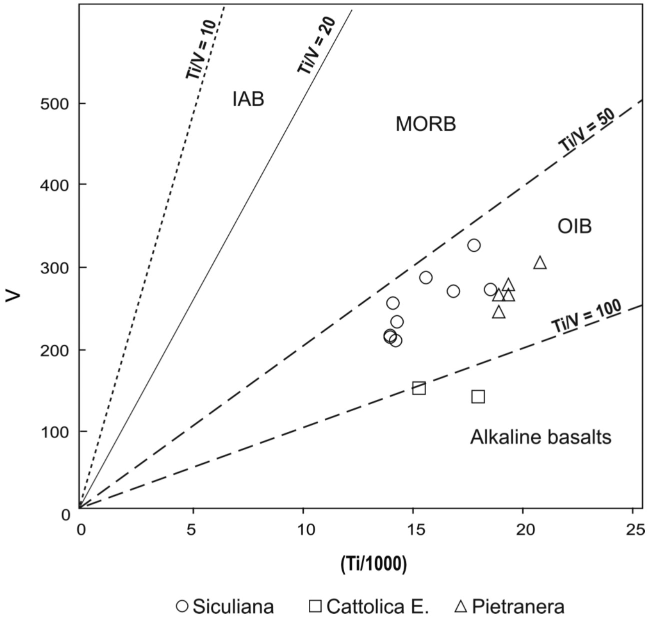

Fig. 9 - Ti vs. V plot from Shervais (1982).

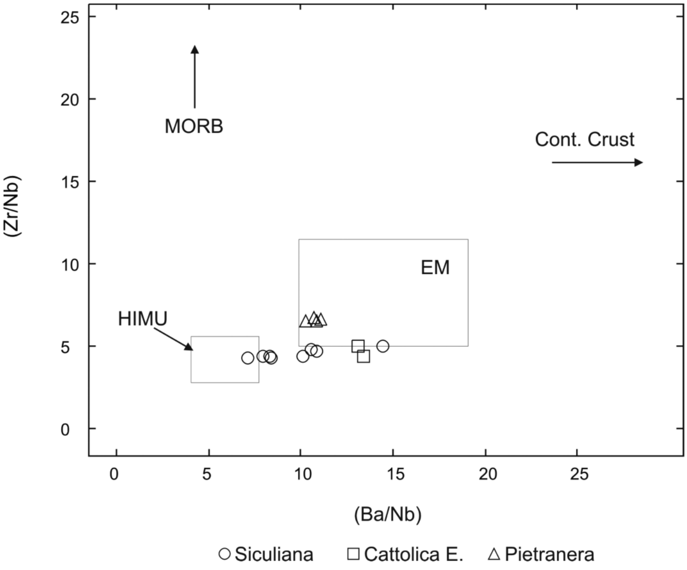

Fig. 10 - Zr/Nb vs Ba/Nb classification diagram. Composition of HIMU-OIB, EM-OIB, MORB and Continental Crust according to Weaver (1991).

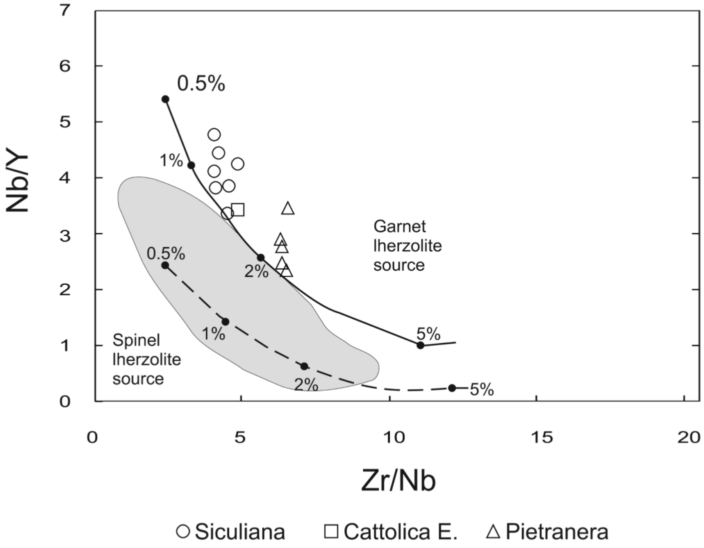

Fig. 11 - Variation of Nb/Y versus Zr/Nb (after Wilson and Downes, 1991). Model melting curves for 0.5-5 % partial melting of spinel- and garnet-peridotite facies mantle from Harangi (2001).

suggest that the involved magmas underwent scarce fractionation during ascent to the surface. In any case, the high concentrations of MgO (5 to 15 wt%), Ni (190 to 350 ppm) and Cr (295 to 700 ppm) indicate a contribution of mineral accumulation. Local mixing events, due to input of less evolved magmas also occurred, as testified by the presence of banded texture in the Pietranera volcanics.

The occurrence of Rupelian pelagic carbonate deposits inserted into volcanic materials testifies for a contemporaneous or slightly successive sedimentation occurred on the sea floor. Therefore, pillow lavas indicate the existence of an early Oligocene submarine magmatism in this sector of Sicily region. This age is more recent respect to multiple levels of basalts, not younger than Eocene, that occur within the Mesozoic-Paleocene sedimentary successions, lying to north in the Sicani and Madonie Mountains. This excludes a reworking of volcanic blocks coming from north during growing of orogenic chain. The Early Oligocene alkaline magmatic activity could be associated with early rifting episodes then aborted, occurred along lithospheric fractures originated in response to flexure and uplift of the African paleomargin, during the pre-subduction stage. Having dated the volcanic activity helps to constrain the timing of the last extensional phase involving the African foreland prior to first foredeep related to Numidian Basin (Giunta, 1985) and to the subsequent arrival of Maghrebian Orogenic Belt Front. Finally, as a result of the tectonic collision, portions of volcanic districts were detached and then incorporated, jumbled together with associated pelagic sediments and other rocks, accreting the future sicilian accretionary prism.

In conclusion, the obtained data suggest that the studied Sicilian alkaline volcanics are genetically linked and are evidently formed in an intraplate environment showing a OIB signature. Slightly different garnet lherzolite sources that underwent low degrees of fractional crystallization, with variable mineral accumulation processes, can be hypothesized for the involved magmas. The studied volcanism could result as product of delocalized magmatic pulses risen during Oligocene along lithospheric fractures of the African paleomargin, in the first stage of continental collision deriving from south verging front of the Maghrebian Thrust Belt.

Further studies on these rocks will furnish important information on the nature of upper mantle beneath the northern margin of the African plate. Such a knowledge is crucial in order to better understand the nature and geodynamic significance of the extensive magmatic activity which have been coming on from Mesozoic to Present in this area.

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