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A lamproitic component in the high-K calc-alkaline volcanic rocks of the Capraia Island, Tuscan Magmatic Province: evidence from clinopyroxene crystal chemical data

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Abstract. — The Island of Capraia (Tuscan Archipelago) is the westernmost volcanic centre of the Tuscan Magmatic Province. It is made by the overlap of two volcanoes: the Capraia and the Zenobito ones. The Capraia Volcano is a large composite apparatus dominated by lava flows and lava domes with a high-K calc-alkalic affinity built up over the period between 7.5 and 6.9 Ma at its top. The Zenobito Volcano is a small monogenetic apparatus that produced a cinder cone associated to a very small plateau-like lava structure in a short time spanning at 4.6 Ma, overlapping the south-westernmost edge of the Capraia Volcano. Outcropping rocks of the older volcano are high-K calc-alkalic (HKCA) rocks ranging in composition from dominant andesite and dacite to rare rhyolite, straddling latite and trachyte fields. Volcanic rocks from the Zenobito Volcano are much more uniform in composition ranging from potassic trachybasalt to shoshonite, but some sub-alkalic samples falling within the andesite basaltic field have been also found.

To explore the relationships between clinopyroxene structural and chemical parameters and the physico-chemical conditions of their crystallisation, selected clinopyroxene crystals from the older high-K calc-alkalic rocks (10 crystals) and from the younger shoshonitic rocks (2 crystals) of the Capraia and Zenobito Volcanoes, respectively, have been studied. Single-crystal X-ray diffraction measurements and microprobe analyses have been carried out.

The clinopyroxene from Capraia Volcano has augitic composition whereas clinopyroxene from Zenobito Volcano is enriched in the diopsidic component. Structural parameters show significant variations, in particular in the V_{M1} and V_{cell}. These volumes are larger for clinopyroxene crystals from Capraia volcanic rocks than those of clinopyroxene crystals from shoshonitic rocks of the Zenobito Volcano. It is unlikely that the increase of V_{M1} and V_{cell} observed in the clinopyroxene crystals from HKCA rocks can be simply referred to a different chemical composition of the host magmas. More likely, it could reflect different pressure of crystallisation suggesting that the magma chamber of the Capraia Volcano HKCA volcanic rocks was sited at shallower depth than that of shoshonitic volcanic rocks of the Zenobito Volcano. On the other hand, comparison between clinopyroxene diopsidic crystals from Zenobito Volcano and those from Radicofani volcanoes highlights a close structural and chemical similarity. By contrast, clinopyroxene crystals from HKCA rocks show significant differences with respect to those of other calc-alkaline volcanic rocks from volcanic arcs, such as the Aeolian Arc. In particular, the deficiency in Al found in the clinopyroxene crystals from Capraia Volcano recalls a similar characteristic observed in clinopyroxene from lamproites. This possibly

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suggests that the Capraia high-K calc-alkalic magmas might be related in some ways to lamproitic magmas and that clinopyroxene crystals record this petrologic characteristic, which is not anymore observed in the bulk rock compositions. The occurrence of lamproitic component in the genesis of HKCA magmas of the Capraia Volcano may also explain the large variation in the K_2O contents of the Capraia volcanic rocks, which is not easily explained by any common evolution process. It also agrees with the hypothesis that calc-alkalic, shoshonitic and lamproitic magmas in the Tuscany Magmatic Province are cogenetic, and that the lower incompatible element contents of calc-alkalic and shoshonitic rocks reflect a dilution effect generated by a larger degrees of partial melting in a veined mantle source. Finally, Capraia Volcano and Zenobito Volcano magmas are considered to represent different episodes of partial melting of different mantle sources.

Key Words: *clinopyroxene, EPMA analyses, structure refinement, magmatic plumbing system.*

Riassunto. — L'isola di Capraia (Arcipelago Toscano) rappresenta il centro vulcanico più a ovest della Provincia Magmatica Toscana. Essa è costituita da due vulcani: il vulcano Capraia e il vulcano Zenobito. Il vulcano Capraia, emerso in un periodo compreso tra 7,5 e 6,9 milioni di anni fa, è costituto da un grande apparato composito dominato da colate laviche e duomi ad affinità calcalcalina alta in potassio; il vulcano Zenobito, edificato 4,6 milioni di anni fa nella parte sud-occidentale dell'isola, è costituito da un piccolo apparato monogenico formato da un cono di scorie e alcune sottili colate laviche. La composizione delle rocce del vulcano Capraia va da andesitica a riolitica mentre quella dello Zenobito è molto più uniforme passando da trachibasalti potassici a shoshoniti.

Per esplorare le relazioni intercorrenti tra i parametri chimico-strutturali dei clinopirosseni e le condizioni fisico-chimiche di cristallizzazione dei magmi, abbiamo selezionato cristalli di clinopirosseno da rocce appartenenti ai due differenti vulcani (10 cristalli per il vulcano Capraia e 2 per lo Zenobito), e su questi è stato intrapreso uno studio combinato diffrazione-X a cristallo singolo e microsonda elettronica.

I clinopirosseni estratti dalle rocce del vulcano Capraia presentano composizione augitica mentre quelli dello Zenobito mostrano una maggiore componente diopsidica. I parametri strutturali ottenuti hanno messo in evidenza significative variazioni specialmente nei valore di V_{M1} e V_{cell}. Infatti, questi volumi sono risultati più grandi per i cristalli estratti dalle rocce di Capraia rispetto a quelli dello Zenobito. Riteniamo che l'aumento di volumi osservato per i cristalli del vulcano Capraia non possa essere semplicemente riferito ad una differente composizione chimica dei magmi ma possa indicare una diversa pressione di cristallizzazione, ovvero, che la camera magmatica del vulcano Capraia sia situata ad una profondità minore rispetto a quella del vulcano Zenobito. Inoltre, tutti i clinopirosseni analizzati presentano una caratteristica deficienza di Al, che non si riscontra nelle rocce calco-alcaline e shoshonitiche di archi insulari, quali l'Arco Eoliano, tipica delle rocce lamproitiche toscane. Tale caratteristica indica che le rocce dell'Isola di Capraia presentano una affinità lamproitica che non è evidenziata dal chimismo delle rocce ma che emerge con chiarezza dallo studio dei clinopirosseni. Tale affinità costituisce un'evidenza a favore dell'ipotesi che i magmi calcalcalini, shoshonitici e lamproitici toscani sono cogenetici e che il minore arricchimento di elementi incompatibili dei primi sia dovuto a un maggior grado di fusione parziale di una sorgente mantellica attraversata da vene flogopitiche di origine metasomatica. D'altra parte le rocce del Vulcano dello Zenobito mostrano caratteristiche petrologiche diverse dalle altre rocce shoshonitiche della Provincia magmatica Toscana e potrebbero rappresentare un nuovo evento di fusione parziale di un mantello di differente natura rispetto a quello dei magmi del più antico Vulcano di Capraia e della restante Provincia Magmatica Toscana.

INTRODUCTION

The relationships between crystal chemistry of clinopyroxene and petrologic affinity of the rocks from which they crystallize have been investigated for a wide spectrum of igneous associations (e.g., Dal Negro *et al.* 1982, 1989; Carbonin *et al.* 1984, 1991; Faraone *et al.* 1988; Malgarotto *et al.* 1993; Cellai *et al.* 1994; Pasqual *et al.* 1995; Nazzareni *et al.* 1998; Bindi *et al.* 1999, 2002; Princivalle *et al.* 2000; Salviulo *et al.* 2000; Avanzinelli *et al.* 2004). These studies have shown that cation substitutions in clinopyroxene are controlled by either the physical conditions of crystallisation (e.g., pressure and temperature) and/or by compositional characteristics of parent magmas. Consequently, clinopyroxene chemistry should be supplemented with structural data in order to investigate the relationships between geometric (and chemical) variations and the conditions of formation.

The present study has been undertaken to investigate the crystal chemistry of clinopyroxene from a peculiar magmatic setting and association, which is found in westernmost sector of the Tuscan Magmatic Province (e.g., Washington, 1906; Conticelli *et al.* 2004) at the Capraia island, where high-potassium calc-alkalic volcanic rocks of the Capraia Volcano and shoshonitic volcanic rocks are associated in space but not in time (e.g., Barberi *et al.* 1986; Peccerillo *et al.* 1987; Poli *et al.* 1995, 2006; Conticelli *et al.* 2002; Aldighieri *et al.* 2004). Crystal chemical investigations have been carried out combining single-crystal X-ray diffraction data with electron microprobe analysis on the same crystal fragment with the aim of elucidating possible relationships between clinopyroxene crystallization and petrologic affinities of magmas, which have been outpoured using the same plumbing system, and possibly generated in similar mantle sources.

GEOLOGICAL AND PETROLOGIC OUTLINE

The Island of Capraia is the westernmost island in the Tuscan Archipelago, and then, the nearest volcanic outcrop to Corsica lamproite (i.e., Sisco; Fig. 1). It is the third in size, after Elba and Giglio islands, both characterized by the presence of considerable sized granitoid intrusions (e.g., Innocenti *et al.* 1992; Westermann *et al.* 1993). The Capraia Island is formed by the coalescence of two volcanic structures: the Capraia and the Zenobito Volcanoes (e.g., Rodolico 1938; Franzini

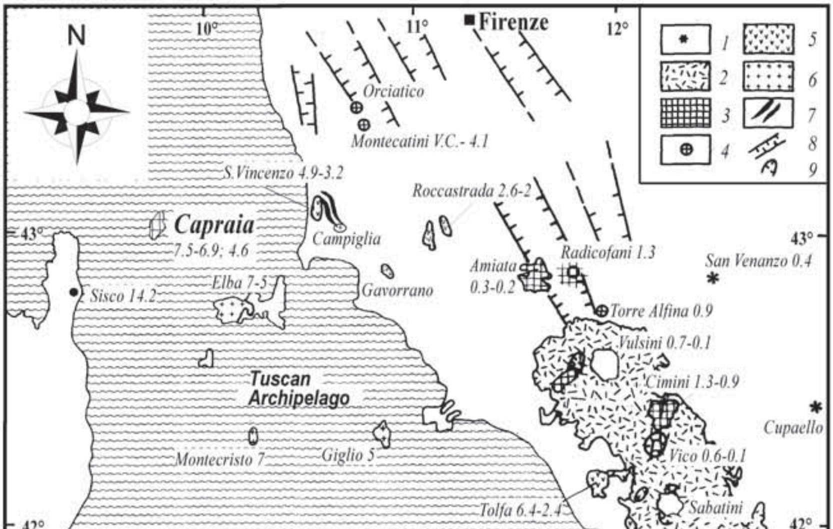

Fig. 1 – Geological sketch map of the Northern Tyrrhenian Sea and adjoining areas (redrawn after Conticelli and Peccerillo 1992), ages are from Ferrara and Tonarini (1985), Barberi *et al.* (1986), d'Orazio *et al.* (1991), Conticelli *et al.* (1992), Barberi *et al.* (1994), Conticelli *et al.* (2001), Aldighieri *et al.* (2004). Legend: 1 = kamafugites of the Roman Magmatic Province; 2 = plagio-leucitites and leucitites (HKS) of the Roman Magmatic Province; 3 = High-K calc-alkalic, shoshonitic, and transitional rocks of the Tuscan and Roman Magmatic Provinces; 4 = lamproites of the Tuscan Magmatic Province; 5 = effusive rhyolites of anatectic origin; 6 = intrusive granitoid of anatectic origin; 7 = dikes; 8 = main extensional faults with Apennine direction; 9 = calderas.

1964; Barberi *et al.* 1986; Poli *et al.* 1995, 2006; Poli and Perugini 2003; Aldighieri *et al.* 2004).

The Capraia Volcano is a large asymmetric composite volcano, strongly dissected by recent tectonic activity accompanied to flank collapse and sea-driven erosion. It is made up by the coalescence of several domes and volcanic centers, which produced predominant massive lava flows and ash and block flows with only subordinate pyroclastic flows. The exposed magmatic activity has been dated at a very restricted range from 7.5 to 6.9 Ma using both K/Ar and ^{40}Ar/^{39}Ar methods (e.g., Barberi *et al.* 1986; Aldighieri *et al.* 2004), although older ages have been found by early studies using K/Ar methods (i.e., 9.5-8.3 Ma; Ferrara and Tonarini 1985). Domes and volcanic centers are aligned along NNE-SSW trends, which are also followed by the main tectonic structures that brought to the subsidence of the western portion of the volcano.

The Zenobito Volcano renewed volcanic activity in the area after a *hiatus* of about 2.5 Ma. It is a small monogenetic center characterized by a sub-aerial cinder cone, overlain by a small sequence of thin lava flows embedded in scoria layers. It crops out on the south-westernmost edge of the Capraia Volcano, and strong marine erosion has brought to rapid destruction of the volcanic apparatus, leaving nowadays only the feeding neck and the northernmost portion of the monogenetic volcano overlain the epiclastic deposits of the Capraia Volcano. On the basis of the volume of magma emitted it can be considered as a monogenetic volcano, which has been lived for a very short time. Dating of Zenobito volcanic rocks with different methods has provided slightly different ages of 4.9 (K/Ar) and 4.6 (^{40}Ar/^{39}Ar) Ma (e.g., Ferrara and Tonarini 1985; Barberi *et al.* 1986; Aldighieri *et al.* 2004).

Volcanic activity of the Capraia Island can be considered as the oldest volcanic event of the Tuscan Magmatic Province (e.g., Peccerillo *et al.* 1987; Innocenti *et al.* 1992; Conticelli *et al.* 2004). In addition, by considering that Capraia Volcano elevated of some hundred meters above sea-floor and that dating refers only to activity exposed at the surface, it can be safely hypothesized that volcanism started much earlier than indicated by available radiometric dating.

On the other hand, the Zenobito Volcano renewed volcanism using probably the same feeding system of the Capraia one, but it developed totally above sea-level for a short time span. Its radiometric age of 4.6 Ma is slightly younger than the emplacement age of the shoshonitic dyke of Monte Castello at Elba island (i.e., 5.8 Ma, Conticelli *et al.* 2001). Moreover, it occurred when volcanic activity of Tuscan Magmatic Province has already migrated eastward, on the mainland of Tuscany (e.g., Civetta *et al.* 1978; Ferrara and Tonarini 1985; Conticelli *et al.* 1992).

Volcanic rocks of the Capraia Volcano outcropping above sea level can be divided into two main groups on the basis of their stratigraphy: an old series, grouping the *Punta del Trattoio*, *Monte Rosso*, *Monte Campanile*, *Monte Castello* Synthems (7.6 Ma; Alderighi *et al.* 2004); a young series, corresponding to the *Monte Ruscitello* Synthem (7.2 Ma, Alderighi *et al.* 2004; 6.9 Ma, Barberi *et al.* 1986). With respect to the other volcanic rocks of the Tuscan Magmatic Province, those of the Capraia Volcano fall well within the field of high-K calc-alkalic rocks (HKCA), and they are mostly high-silica two-pyroxene rocks, with high-Mg# mafic rocks missing (e.g., Peccerillo *et al.* 1987; Poli *et al.* 1995, 2006; Poli 2004). Plagioclase, clinopyroxene, amphibole, and biotite are the most abundant phenocryst phases set in a groundmass made up also by K-feldspar, opaque minerals, apatite, and zircon. Rare olivine phenocrysts are also found in the less evolved rocks of the most mafic rocks found at *Punta del Ferraione*. Trace element distribution of Capraia volcanic rocks resembles closely that observed for other volcanic rocks of Tuscan Magmatic Province and of Sisco lamproite (Corsica), with characteristics depletion of HFS elements with respect to LIL elements (Poli *et al.* 1995, 2006; Poli and Perugini 2003; Poli 2004; authors' unpublished data). Initial ^{87}Sr/^{86}Sr (0.70872-0.71020; Conticelli *et al.* 2002) and ^{143}Nd/^{144}Nd (0.512234-0.51228; Conticelli *et al.* 2002) for Capraia Volcano rocks are significantly lower and higher, respectively, to the values of the Tuscan Magmatic Province, but close to the values of Corsica lamproite (i.e., ^{87}Sr/^{86}Sr$_i$ = 0.71229, ^{143}Nd/^{144}Nd = 0.51215; Conticelli *et al.* 2002).

Volcanic rocks of the Zenobito Volcano are more uniform in composition than those of the Capraia Volcano. They are represented by high-Mg#

mafic lavas and scoriae exhibiting phenocrysts of clinopyroxene and euhedral olivine dotted by minute spinel, set in an intersertal groundmass made up by clinopyroxene and plagioclase (e.g., Poli *et al.* 1995, 2006). Fractionation between HFS and LIL elements is much less prominent in the volcanic mafic rocks of the Zenobito Volcano (authors' unpublished data). On the other hand, Zenobito volcano shows less radiogenic initial ^{87}Sr/^{86}Sr (0.70812) and higher ^{143}Nd/^{144}Nd (0.51226) values of Capraia HKCA and Tuscan Magmatic Province mafic rocks (Conticelli *et al.* 2002).

SAMPLING AND ANALYTICAL TECHNIQUES

Samples from both Capraia and Zenobito Volcanoes have been collected and studied. Samples from Capraia Volcano are from both the old series and the young series, whereas those from the Zenobito Volcanoes are from the Neck, the Cinder Cone, and the thin lava flows (Tables 1 and 2). Major and trace elements on bulk rocks have been performed by integrated XRF and AAS method following the Franzini *et al.* (1972) procedure. ICP-MS replicate analyses have been also performed on selected samples, and bias was found to be within the analytical error. Trace elements have been performed using XRF, and matrix effect has been corrected following De Vriers and Jenkins (1971) method.

Clinopyroxene crystals selected are both from two-pyroxene rocks of the Capraia Volcano (old series: CP101, CP114 and CP108; young series: CP102, CP103) and single-pyroxene rocks of the Zenobito Volcano (CP116). They have been separated under optical polarised transmission and binocular microscopes, after rock chip crushing rejecting those crystals showing twinning, crystal defect or zoning.

X-ray diffraction data (Table 3) have been obtained using an automated diffractometer Bruker-P4 with Mo$K\alpha$ radiation monochromatized by a flat graphite crystal. The unit cell parameters have been determined by the least-square methods using 25 high-θ reflections. The intensities of the reflections with $\theta \leq 35°$ were recorded using a ω-scan technique and they have been corrected for absorption following the semi-empirical method of North *et al.* (1968). Only reflections with $Fo > 4\sigma$ (Fo) were employed for the structure refinement, which has been performed using the program SHELXL-93 (Sheldrick 1993), in the space group *C2/c*. The scattering curves for neutral atoms – Ca vs. Na (M2 site), Mg vs. Fe (M1 site), Si, O – have been taken from *International Tables for X-ray Crystallography*, volume IV (Ibers and Hamilton 1974). In all the crystals studied the difference Fourier map showed significant residual density at about 0.7 Å from the M2 position, suggesting the presence of the M2' site (Rossi *et al.* 1987). Further least-squares refinement using the Fe^{2+} atomic scattering factor for M2' has been performed. The temperature factor of M2' was fixed equal to the equivalent isotropic temperature factor of M2. The introduction of M2' significantly improved the *R* index according to the Hamilton's test (Hamilton 1965). Bond distances and angles are reported in Table 3.

EPM analyses have been performed on the same crystals used for the X-ray study, using a "JEOL JXA 8600" electron microprobe operating at 15 kV and 10 nA, with variable counting times: 10 seconds for Na, 15 seconds for other major elements, and 40 seconds for Ti, Cr, and Mn. Matrix effect correction has been performed using the Bence and Albee (1968) and Albee and Ray (1970) methods. Replicate analyses on different spots of the same crystal (five for each crystal) have been performed, showing that the studied crystals were homogeneous within analytical error (Vaggelli *et al.* 1999); the estimated analytical precision was ± 0.02 for CaO, FeO and MgO, ± 0.03 for SiO_2 and TiO_2, ± 0.05 for Cr_2O_3, ± 0.06 for Na_2O, ± 0.07 for MnO and ± 0.1 for Al_2O_3. The clinopyroxene crystal labelled CP114-2 was lost during polishing.

The chemical formula has been calculated on the basis of 4 cations (Cameron and Papike 1981) and Fe^{3+} was evaluated on both the charge-balance and the experimental M1-O mean bond distance (best fit between observed and calculated M1-O mean bond lengths). The distribution of Mg^{2+}-Fe^{2+} between M1 e M2 sites was done following the procedure suggested by Dal Negro *et al.* (1982), which is based on the comparison between electron microprobe analyses (EPMA) and X-ray structure refinement (X-ray). The population M2+M2' has been obtained using the total amount of Ca, Na and Mn derived from EPMA adding an

TABLE 1 – *Major and trace elements of studied samples from Capraia Volcano.*

	Capraia Volcano											
Series:	Old	Young	Old	Old	Young	Old	Young	Old	Young	Old	Young	Young
Locality:	*Arpagna*	*San Rocco*	*Colombaia*	*Colombaia*	*San Rocco*	*Cala Ceppo*	*Ferraione*	*Frontone*	*San Rocco*	*Porto*	*Castle*	*Garitta*
Latitude:	43°01'09"N	43°02'40"N	43°01'18"N	43°01'28"N	43°02'31"N	43°02'03"N	43°03'02"N	43°01'52"N	43°02'12"N	43°02'53"N	43°03'51"N	43°02'44"N
Longitude:	09°48'22"E	09°50'27"E	09°48'25"E	09°48'22"E	09°50'17"E	09°49'25"E	09°50'35"E	09°48'24"E	09°49'57"E	09°50'16"E	09°50'37"E	09°50'39"E
Sample:	**CP 108**	**CP 115**	**CP 107**	**CP 109**	**CP 114**	**CP 111**	**CP 101**	**CP 110**	**CP 112**	**CP 100**	**CP 102**	**CP 103**
type:	lava	lava	lava	lava	lava	lava	lava	lava	lava	lava	lava	pumice
Age (Ma):	7.55	7.15	7.55	7.55	7.15	7.55	7.15	7.55	7.15	7.55	7.15	7.15
SiO_2	60.5	61.0	61.4	61.7	61.8	61.9	61.9	62.3	62.4	62.9	66.6	67.2
TiO_2	0.86	0.74	0.83	0.78	0.68	0.72	0.69	0.68	0.74	0.80	0.50	0.47
Al_2O_3	16.0	15.5	15.7	16.1	15.3	15.2	15.3	15.2	15.3	16.1	14.9	14.0
Fe_2O_3	1.97	1.48	2.69	1.13	2.19	2.27	2.67	3.27	3.01	3.58	0.55	1.55
FeO	3.45	3.73	2.64	3.45	2.82	2.91	2.45	1.45	2.36	1.09	2.45	1.45
MnO	0.08	0.08	0.08	0.07	0.08	0.06	0.07	0.07	0.07	0.07	0.05	0.05
MgO	3.42	3.91	3.49	3.53	3.75	3.45	3.48	2.88	2.73	2.35	1.38	1.56
CaO	5.12	5.56	4.77	4.79	5.45	5.16	5.48	4.59	5.23	4.24	3.09	2.53
Na_2O	3.64	3.17	3.00	3.51	2.99	3.14	3.14	3.14	2.90	3.86	3.40	3.76
K_2O	3.32	2.98	3.61	3.58	3.30	3.24	3.33	3.90	3.32	4.07	4.38	4.29
P_2O_5	0.21	0.18	0.22	0.22	0.17	0.18	0.18	0.29	0.18	0.26	0.16	0.13
LOI	1.38	1.64	1.49	1.10	1.42	1.74	1.36	2.19	1.71	0.63	2.50	3.02
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Mg#	0.579	0.619	0.591	0.624	0.621	0.594	0.601	0.579	0.531	0.533	0.496	0.535
V	96	114	95	96	126	111	128	137	108	81	40	34
Cr	115	132	112	122	173	135	177	132	141	57	25	29
Co	*15.8*	*14.0*	16	14	16	14	*11.9*	*15.2*	11	*11.7*	*6.3*	*6.0*
Ni	28	15	20	14	19	15	29	bdl	10	bdl	bdl	bdl
Cu	16	bdl	-	-	-	-	12	11	-	12	bdl	bdl
Zn	68	62	67	63	76	63	73	79	68	76	46	37
Rb	147	132	160	162	115	134	116	161	136	178	185	205
Sr	447	620	481	526	824	678	733	933	689	431	344	356
Y	*24.5*	*21.7*	30	27	29	30	*19.3*	*30.9*	23	*21.0*	*18.3*	*19.1*
Zr	211	183	220	218	162	174	185	234	170	251	166	233
Nb	*16.1*	*12.5*	16	16	10	12	*11.9*	*14.3*	12	*20.1*	*13.6*	*14.0*
Ba	*620*	*721*	714	705	770	737	*711*	*1410*	757	*751*	*731*	*673*
Th	*35.5*	*26.3*	46	48	26	31	*23.1*	*49.4*	31	*43.6*	*36.4*	*36.4*

Legend: *Mg#* = [MgO]/([MgO]+[0.85*FeO_{tot}]); bdl = below detection limit; data performed by ICP-MS are reported in italic; ages are from Alderighi *et al.* (2004).

TABLE 2 – *Major and trace elements of studied samples from Zenobito Volcano compared to Radicofani and Elba Shoshonites.*

	Elba		**Zenobito Volcano**						**Radicofani**	
Occurrence:	*dyke*	*dyke*	*Cinder Cone*	*Cinder Cone*	*Plateau*	*Plateau*	*Neck*	*Neck*	*Flow*	*Bottom*
Locality:	*Monte*	*Castello*	W. Beach	Cala Rossa	*Piana*	*Piana*	*Tower*	*Tower*	*South*	*Neck*
Latitude:	–	–	43°00'21"N	43°00'16"N	43°00'11"N	43°00'12"N	43°00'08"N	43°00'09"N	–	–
Longitude:	–	–	09°48'50"E	09°48'35"E	09°48'44"E	09°48'44"E	09°48'40"E	09°48'40"E	–	–
Sample:	**ST 135/3**	**ST 135/9**	**CP 54**	**CP 106**	**CP 104**	**CP 105**	**CP 119**	**CP 116**	**VS 184**	**VS 129**
type:	dyke	dyke	scoria	scoria	lava	lava	neck	neck	lava	neck
Age (Ma):	5,83	5,83	4,63	4,63	4,63	4,63	4,63	4,63	1,28	1,28
SiO_2	50,8	51,2	*50,56*	*50,61*	50,7	51,5	*52,61*	*54,01*	56,4	54,3
TiO_2	0,80	0,82	*1,650*	*1,918*	1,37	1,52	*1,493*	*1,519*	1,17	0,85
Al_2O_3	14,9	13,4	*15,49*	*15,89*	15,0	15,4	*14,84*	*14,88*	14,9	17,4
Fe_2O_3	2,34	2,68	*9,31*	*10,93*	6,18	3,97	*9,35*	*8,46*	1,26	1,68
FeO	4,86	4,45	0,80	0,045	2,64	5,18	n.d.	n.d.	4,25	4,44
MnO	0,14	0,19	*0,125*	*0,178*	0,11	0,14	*0,116*	*0,126*	0,11	0,11
MgO	6,33	5,22	*6,41*	*6,25*	7,13	8,18	*6,74*	*6,30*	9,48	7,82
CaO	6,31	10,1	*7,92*	*7,38*	8,41	7,33	*7,57*	*7,52*	5,37	7,60
Na_2O	2,31	1,47	*2,83*	*3,36*	3,22	2,99	*2,76*	*3,16*	1,44	2,05
K_2O	3,01	1,94	*2,42*	*2,16*	2,48	2,57	*2,36*	*2,20*	4,96	3,09
P_2O_5	0,16	0,14	*0,48*	*0,47*	0,40	0,37	*0,47*	*0,33*	0,29	0,22
LOI	7,76	8,04	*1,13*	*1,31*	2,33	0,87	*1,25*	*0,46*	0,41	0,46
Sum	99,72	99,60	*99,10*	*100,49*	100,00	100,00	*99,56*	*98,97*	100,01	100,00
Mg#	0,656	0,615	0,594	0,570	0,646	0,662	0,627	0,635	0,787	0,734
V	178	191	166	118	170	168	161	144	131	154
Cr	352	416	400	438	391	428	373	355	554	429
Co	27	21	*30,0*	*39,7*	37	*40,6*	*31,8*	*29,0*	36	–
Ni	33	28	69	63	68	88	67	63	267	135
Cu	5	9	25	26	–	30	23	17	34	29
Zn	97	74	87	91	92	88	128	47	77	59
Rb	161	89	115	172	137	148	130	126	379	193
Sr	460	468	399	414	403	343	424	385	401	350
Y	17	14	20	*27,8*	27	*22,1*	*28,4*	*24,3*	27	24
Zr	135	133	221	210	197	209	179	156	495	268
Nb	6	6	15	*21,3*	17	*19,9*	*17,6*	*15,6*	26	14
Ba	515	395	540	*609*	504	*484*	*536*	*446*	839	–
Th	13	12	24	*27,5*	28	*22,1*	*18,2*	*17,1*	58	29,7

Legend: *Mg#* = [MgO]/([MgO]+[0.85*FeO_{tot}]); bdl = below detection limit; data performed by ICP-MS are reported in italic. Data of Elba dyke are from Conticelli *et al.* (2001), those of Radicofani are Conticelli's unpublished data. Ages are from Conticelli *et al.* (2001) [Elba dyke], Alderighi *et al.* (2004) [Zenobito volcano], and D'Orazio *et al.* (1991) [Radicofani neck].

Table 3 – *Crystal data and selected bond distances for the studied clinopyroxene crystals. Standard deviation is reported in parenthesis.*

	Zenobito		**Capraia**										
	Punta dello Zenobito		**Punta del Ferraione**			**Capraia Castle**		**La Garitta**		**San Rocco**		**Arpagna**	
	cp116-1	**cp116-2**	**cp101-1**	**cp101-2**	**cp101-5**	**cp102-1**	**cp102-2**	**cp103-1**	**cp103-2**	**cp114-1**	**cp114-2**	**cp108-1**	**cp108-2**
a	9.736(2)	9.744(1)	9.770(2)	9.769(1)	9.777(1)	9.780(1)	9.780(2)	9.777(1)	9.776(1)	9.770(1)	9.769(1)	9.769(1)	9.768(1)
b	8.913(2)	8.905(1)	8.960(2)	8.957(1)	8.959(2)	8.960(1)	8.963(2)	8.961(1)	8.961(1)	8.953(2)	8.951(1)	8.955(1)	8.955(1)
c	5.263(1)	5.268(1)	5.260(1)	5.257(1)	5.257(1)	5.258(1)	5.258(2)	5.257(1)	5.257(1)	5.259(1)	5.257(1)	5.258(1)	5.259(1)
β	106.28 (1)	106.35(1)	106.00(1)	106.02(1)	105.93(1)	105.90(1)	105.86(1)	105.90(1)	105.87(1)	106.03(1)	106.01(1)	106.05(1)	106.07(1)
V_{cell}	438.39(10)	438.62(8)	442.62(8)	442.13(11)	442.79(12)	443.12(6)	443.36(8)	442.95(10)	443.01(11)	442.12(11)	441.84(8)	442.06(5)	442.04(8)
N.obs.refl.	902	929	748	919	912	899	816	841	857	852	844	916	918
R obs.	2.42	3.11	7.98	2.74	3.21	3.07	5.76	8.2	3.19	3.67	3.1	5.07	3.21
θ max	35	35	35	35	35	35	35	35	35	35	35	35	35
M2 site													
M2-O2	2.309(1)	2.308(1)	2.312(3)	2.308(2)	2.313(1)	2.316(1)	2.316(2)	2.309(2)	2.317(1)	2.309(2)	2.308(2)	2.306(2)	2.305(2)
M2-O1	2.360(1)	2.360(1)	2.345(2)	2.342(2)	2.345(1)	2.349(1)	2.349(2)	2.344(1)	2.347(1)	2.340(2)	2.339(1)	2.340(1)	2.339(1)
M2-O3C1	2.565(1)	2.563(1)	2.604(3)	2.602(2)	2.599(1)	2.595(1)	2.595(2)	2.599(1)	2.597(1)	2.601(2)	2.603(1)	2.602(1)	2.602(1)
M2-O3C2	2.720(1)	2.721(1)	2.752(3)	2.747(2)	2.744(1)	2.744(1)	2.744(2)	2.744(1)	2.743(1)	2.749(2)	2.747(1)	2.747(1)	2.749(1)
mean	2.488	2.488	2.503	2.499	2.500	2.501	2.501	2.499	2.501	2.500	2.499	2.499	2.499
V_{M2}	25.45	25.45	25.82	25.70	25.74	25.76	25.76	25.70	25.77	25.71	25.70	25.68	25.67
Δ(M2)	0.309	0.311	0.332	0.330	0.325	0.324	0.324	0.327	0.323	0.332	0.330	0.331	0.334
M1site													
M1-O2	2.041(1)	2.040(1)	2.053(3)	2.060(2)	2.062(1)	2.063(1)	2.061(2)	2.062(1)	2.061(1)	2.059(2)	2.059(1)	2.057(1)	2.059(1)
M1-O1A1	2.055(1)	2.056(1)	2.074(3)	2.074(2)	2.077(1)	2.079(1)	2.078(2)	2.077(1)	2.079(1)	2.074(2)	2.073(1)	2.073(1)	2.073(1)
M1-O1A2	2.129(1)	2.130(1)	2.141(3)	2.143(2)	2.142(1)	2.142(1)	2.142(2)	2.143(1)	2.142(1)	2.141(2)	2.140(1)	2.142(1)	2.141(1)
mean	2.075	2.075	2.090	2.092	2.094	2.095	2.094	2.094	2.094	2.091	2.091	2.091	2.091
V_{M1}	11.82	11.82	12.08	12.12	12.16	12.17	12.15	12.16	12.16	12.11	12.1	12.1	12.11
σ^2 θ (oct.)	17.83	17.68	15.52	15.76	15.66	15.7	16.01	15.79	15.82	15.99	15.93	16.08	16.08
λ (oct.)	1.0057	1.0057	1.0049	1.005	1.0049	1.0049	1.005	1.0049	1.0049	1.005	1.005	1.0051	1.0051
T site													
T-O2	1.596(1)	1.597(1)	1.595(3)	1.590(2)	1.590(1)	1.589(1)	1.591(2)	1.591(1)	1.591(1)	1.591(2)	1.590(1)	1.592(1)	1.591(1)
T-O1	1.612(1)	1.614(1)	1.605(3)	1.604(2)	1.605(1)	1.605(1)	1.606(2)	1.606(1)	1.605(1)	1.606(2)	1.606(1)	1.607(1)	1.608(1)
T-O3A1	1.666(1)	1.667(1)	1.660(3)	1.666(2)	1.668(1)	1.668(1)	1.669(2)	1.670(1)	1.669(1)	1.666(1)	1.667(1)	1.668(1)	1.667(1)
T-O3A2	1.683(1)	1.682(1)	1.688(3)	1.684(2)	1.683(1)	1.683(1)	1.683(2)	1.681(1)	1.681(1)	1.682(1)	1.681(1)	1.681(1)	1.681(1)
$T-O_{nbr}$	1.604	1.605	1.600	1.597	1.598	1.597	1.599	1.599	1.598	1.599	1.598	1.600	1.600
$T-O_{br}$	1.674	1.674	1.674	1.675	1.676	1.676	1.676	1.676	1.675	1.674	1.674	1.675	1.674
mean	1.639	1.640	1.637	1.636	1.637	1.636	1.637	1.637	1.636	1.636	1.636	1.637	1.637
V_T	2.244	2.247	2.234	2.230	2.232	2.231	2.234	2.233	2.231	2.232	2.231	2.234	2.233
σ^2 θ (tet.)	24.43	23.87	24.68	24.74	24.99	24.89	26.08	25.36	24.8	24.18	24.32	24.11	24.07
λ (tet.)	1.0057	1.0056	1.0057	1.0058	1.0059	1.0059	1.0062	1.006	1.0059	1.0057	1.0057	1.0057	1.0057

appropriate amount of Fe^{2+} and Mg, which has been partitioned taking into account e^{-}(M2+M2')$_{X\text{-}ray}$ derived from the occupancy refinement. The M1 site was considered filled by the residual Fe^{2+}, Mg, Al and Fe^{3+} and by Cr and Ti from the analysis. The chemical compositions of the investigated crystals are reported in Table 4.

The proposed site population is thought to be reliable, since there is a good agreement between: (1) the electron number derived from microprobe analyses (e$^{-}_{EPMA}$) and that computed by M1+M2+M2' site occupancy refinement (e$^{-}_{x\text{-}ray}$); (2) the observed and calculated mean M1-O bond lengths. The calculated mean M1-O distance has been obtained assuming the following linear combination: <M1-O> = $X(i)D(i)$, where $X(i)$ is the fraction of the i^{th} cation and $D(i)$ is the pure mean cation-oxygen distance for the site M1. The $D(i)$ values used were: 2.081Å for <Mg-O> (Bruno *et al.* 1982); 2.126Å and 2.031Å for <Fe^{2+}-O> and <Fe^{3+}-O> respectively; 1.93Å for <Al-O>; 1.96Å for <Ti-O>; 2.02Å for <Cr-O> (Ungaretti *et al.* 1981; Dal Negro *et al.* 1982) and 2.173Å for <Mn-O> (Freed and Peacor 1967).

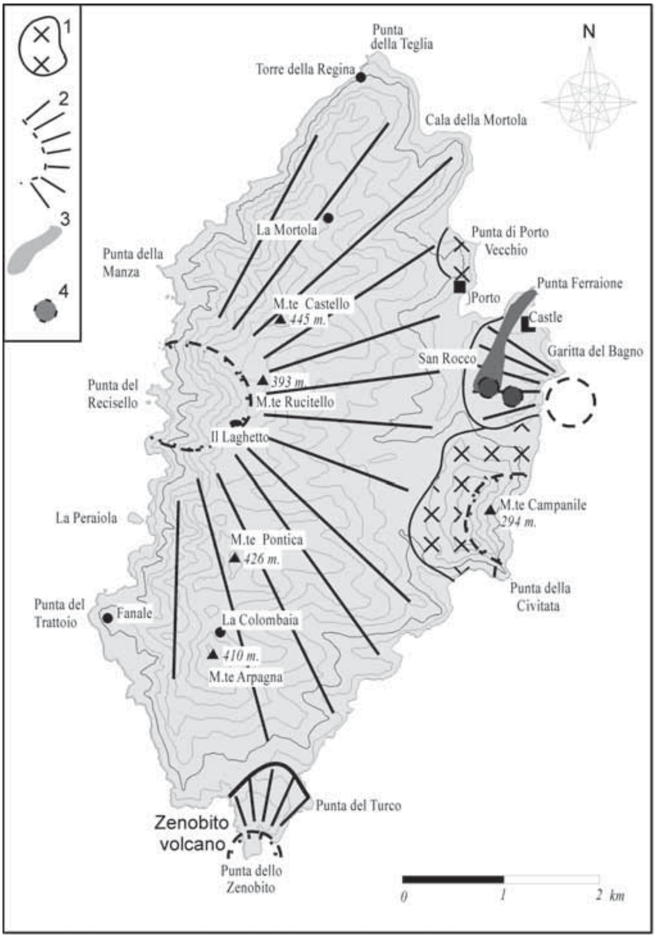

Fig. 2 – Geological sketch map of the Capraia Island drawn on the basis of data from Prosperini (1993), Ogna (1994), Poli *et al.* (1995, 2006). Legend: 1 = domes; 2 = volcanic apparata; 3 = volcanic centre; 4 = recent lava flow.

Table 4 – *Electron microprobe analyses for the studied clinopyroxene crystals.*

	Zenobito		Capraia									
	Punta dello Zenobito		Punta del Ferraione			Capraia Castle		Punta della Garitta		San Rocco	Arpagna	
	cp116-1	**cp116-2**	**cp101-1**	**cp101-2**	**cp101-5**	**cp102-1**	**cp102-2**	**cp103-1**	**cp103-2**	**cp114-1**	**cp108-1**	**cp108-2**
SiO_2	51,0	50,7	52,3	52,1	51,7	51,9	51,9	51,9	51,2	52,2	51,9	51,6
TiO_2	0,86	1,08	0,12	0,21	0,11	0,05	0,05	0,06	0,04	0,12	0,17	0,22
Al_2O_3	3,54	3,92	0,58	0,71	0,48	0,47	0,47	0,55	0,36	0,69	0,89	1,12
Cr_2O_3	1,03	0,68	bdl	bdl	bdl	0,02	0,03	0,02	0,02	0,02	bdl	bdl
Fe_2O_3	0,50	1,26	1,13	0,81	2,31	1,96	1,71	1,50	2,61	2,56	2,37	2,43
FeO	4,76	5,00	11,2	10,6	10,5	10,6	10,4	11,2	9,89	9,97	10,5	10,7
MnO	0,17	0,18	0,58	0,42	0,58	0,63	0,64	0,61	0,76	0,50	0,45	0,49
MgO	16,1	16,3	13,0	13,1	12,6	12,4	12,4	12,2	12,0	13,2	13,0	13,0
CaO	21,0	20,2	21,1	21,0	21,4	21,8	21,7	21,3	22,4	21,2	21,1	20,6
Na_2O	0,26	0,33	0,15	0,26	0,19	0,16	0,24	0,24	0,13	0,29	0,23	0,25
Total	99,23	99,57	100,08	99,11	99,82	99,82	99,51	99,67	99,42	100,78	100,57	100,3
T site												
Si	1,886	1,869	1,973	1,976	1,960	1,966	1,972	1,973	1,958	1,956	1,950	1,944
Al	0,114	0,131	0,026	0,024	0,021	0,021	0,021	0,025	0,016	0,030	0,039	0,050
Fe^{3+}	0,000	0,000	0,001	0,000	0,019	0,013	0,007	0,002	0,026	0,014	0,011	0,006
M1 site												
Mg	0,854	0,854	0,713	0,741	0,713	0,701	0,705	0,692	0,681	0,737	0,728	0,728
Fe^{2+}	0,038	0,022	0,252	0,222	0,237	0,254	0,251	0,264	0,268	0,201	0,211	0,203
Fe^{3+}	0,014	0,035	0,032	0,023	0,047	0,043	0,042	0,041	0,049	0,058	0,056	0,063
Al	0,040	0,039	0,000	0,008	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Cr	0,030	0,020	0,000	0,000	0,000	0,001	0,001	0,001	0,001	0,001	0,000	0,000
Ti	0,024	0,030	0,003	0,006	0,003	0,001	0,001	0,002	0,001	0,003	0,005	0,006
M2 site												
Ca	0,831	0,796	0,851	0,854	0,871	0,886	0,882	0,869	0,918	0,852	0,849	0,833
Na	0,019	0,024	0,011	0,019	0,014	0,012	0,018	0,018	0,010	0,021	0,017	0,018
Mn	0,005	0,006	0,019	0,014	0,019	0,020	0,021	0,020	0,025	0,016	0,014	0,016
Fe^{2+}	0,109	0,132	0,100	0,113	0,096	0,082	0,079	0,093	0,047	0,111	0,120	0,133
Mg	0,036	0,042	0,019	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
e^- $M1_{EPMA}$	13,48	13,38	16,01	15,50	16,01	16,18	16,12	16,30	16,46	15,69	15,79	15,78
e^- $M1_{X\text{-ray}}$	13,57	13,51	15,58	15,70	15,88	16,07	16,10	16,31	16,12	15,54	15,62	15,75
$M1\text{-}O_{obs}$	2,076	2,069	2,091	2,088	2,089	2,090	2,090	2,090	2,091	2,087	2,088	2,087
$M1\text{-}O_{calc}$	2,075	2,075	2,090	2,092	2,094	2,095	2,094	2,094	2,094	2,091	2,091	2,091
Mg#	0,858	0,853	0,675	0,689	0,682	0,676	0,681	0,660	0,683	0,703	0,687	0,684

RESULTS

Samples studied cover the entire range of compositions of both Capraia and Zenobito Volcanoes (Tables 1 and 2; Fig. 3 and 4). Samples from Capraia volcano range in composition from andesite, through dacite and latite, to trachyte and rhyolite (Fig. 4). The Capraia Volcano rocks are among the least rich in potassium and alkalis among Tuscany mafic-intermediate rocks (Fig. 3). No differences can be observed between volcanic rocks of the old and young series of Capraia Volcano, if exception is made for the Garitta pyroclastic flows and for the rhyolitic lava flow of the Capraia Castle, which are the most silica-rich rocks of the volcano (Fig. 4).

Samples from Zenobito Volcano are rather uniform ranging from potassic trachybasalt (scoria of cinder cone), through shoshonite (plateau lavas), to basaltic andesite (neck). These are slightly sub-alkaline and are particularly enriched in Na_2O with respect to K_2O contrarily to typical subduction related shoshonite. In comparison, with other shoshonites from Tuscan Magmatic Province, the Zenobito ones show higher TiO_2 (1.4-2.0 wt.%; Table 2), and Na_2O (2.8-3.4 wt.%; Table 2), but lower SiO_2 (50.6-54.3 wt.%; Table 2).

Comparison with shoshonitic rocks from Elba Island (Fig. 5) shows that Zenobito, Elba, and Capraia volcanic rocks form an unique trend with MgO and other ferromagnesian major and trace elements; differences, however, between Elba shoshonite and Capraia rocks appear significant when Na_2O, TiO_2 and Rb/Sr values are taken in consideration (Fig. 5). Among Capraia rocks a larger compositional range is observed for the rocks of the young series with respect to those of the old series.

Clinopyroxene crystals studied are representative of the overall group of rocks above described (Tables 3 and 4). Clinopyroxene crystals from Capraia Volcano do not display significant compositional

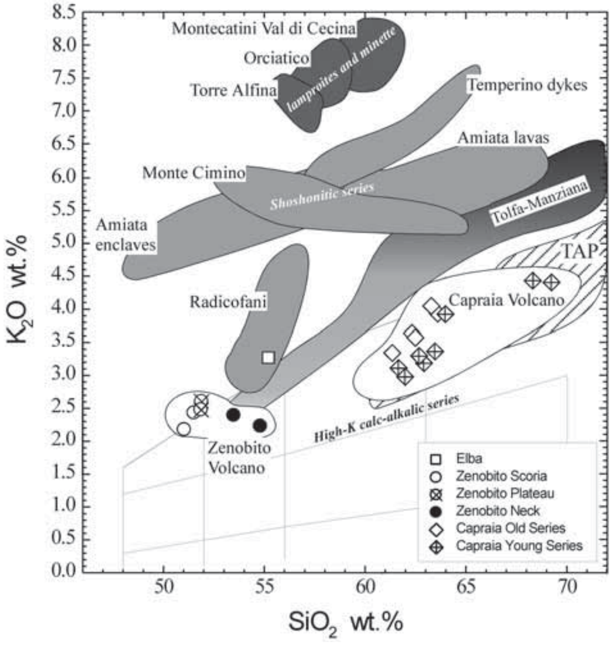

Fig. 3 – Volcanic rocks of Capraia and Zenobito Volcanoes plotted in the K_2O vs. SiO_2 classification diagram suggested to be used for orogenic volcanic series by Peccerillo and Taylor (1976). For data source of fields of other volcanic rocks of Tuscan Magmatic Province see references in Conticelli *et al.* (1992, 2002). TAP field encircles the overall intrusive anatectic rocks of the Tuscan region (Tuscan Anatectic Province).

differences between those of the young and old series. They have augitic to diopsidic compositions (Fig. 6A) with low Al and Ti contents (Fig. 6B). It is worth noticing that clinopyroxene from Zenobito rocks has still augitic compositions close to the boundary with diopside (Fig. 6A) with variable Ti and Al contents (Fig. 6B). Zenobito clinopyroxene has higher MgO/(MgO+FeO) value than Capraia clinopyroxene. Note that the two studied Zenobito crystals show slightly higher Al contents than those observed in literature (Fig. 6B).

An interesting compositional feature of Capraia pyroxene is represented by the sum of Si+Al that is not sufficient to fill completely the tetrahedral site. In these cases a Si substitution by Fe^{3+} and/or Ti is required. In the crystals investigated in the present work, the sum of Si+Al+Ti is in some case lower than 2.00 a.f.u. On this basis we assumed that Fe^{3+} fills the tetrahedral site.

Discussion

The structural parameters of the examined clinopyroxene crystals (Table 3) show significant variations, in particular in the V_{cell} and V_{M1}. As pointed out by several authors (Dal Negro *et al.* 1982; Nimis and Ulmer 1998), variation of both V_{cell} and V_{M1} can be related to a progressive crystal-chemical response to compositional variations of the parent melt, to a pressure decrease (increase), and, to a minor extent, to variation in crystallization temperature. V_{cell} and V_{M1} volumes are larger for the clinopyroxene crystals from the Capraia Volcano with respect to those extracted from Zenobito volcanic rocks. It is unlikely that the decrease of V_{M1} and V_{cell} observed for the clinopyroxene crystals from Zenobito is simply an effect of different chemical composition of the host magmas. The above observed structural feature could reflect a different pressure of crystallisation: the magma chamber of Capraia Volcano magmas might be situated at shallower depth, as also testified by the intense evolution processes that brought to extreme magmatic differentiation (Gagnevin *et al.* 2006). On the other hand, clinopyroxene from Zenobito volcanic rocks crystallized at pressures significantly higher than those of Capraia. Indeed, if we investigate the Mg-Fe exchange ratios between whole rocks (Mg# =

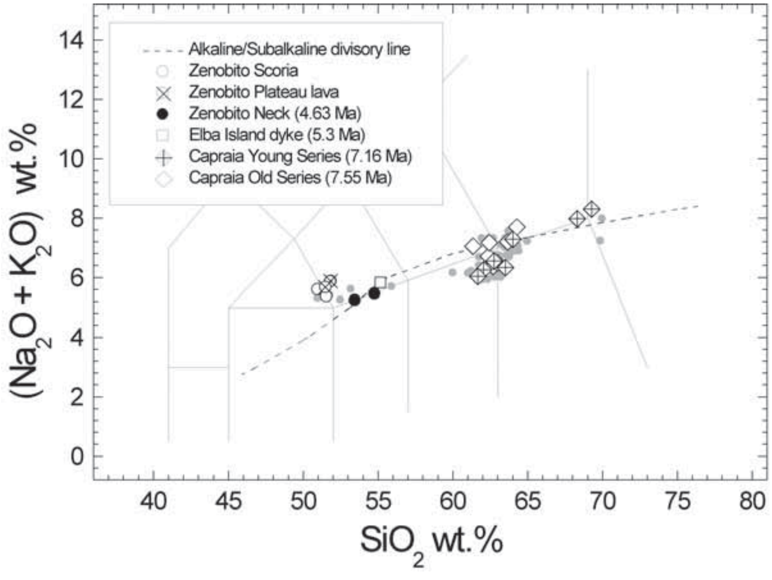

Fig. 4 – Total Alkali - Silica (TAS) classification diagram (Le Maitre 1989) for samples of Capraia and Zenobito Volcanoes. Small solid grey circles in background are Capraia data from literature (e.g., Poli *et al.* 1995, 2006, Gagnevin *et al.* 2006). Data are plotted on water free-basis.

[MgO]/([MgO]+0.85*[FeO_{tot}]; Rhodes 1981) and clinopyroxene crystals [MgO/(FeO+MgO)] (Fig. 7), it appears evident that Mg# does not change significantly for all the analyzed rocks from which crystals have been separated (0.49-0.62, Capraia Volcano; 0.64, Zenobito Volcano); conversely the [MgO/(FeO+MgO)] ratio varies significantly in the different clinopyroxene crystals (0.521-0.570, Capraia Volcano; 0.765-0.772, Zenobito Volcano). Therefore, it sounds well-funded to assume that the variation of structural parameters of the analysed clinopyroxene crystals reflects a variation (increase) of the crystallisation pressure between Capraia magmas and those erupted during the Zenobito stage. An important restriction for the application of structural geobarometers (Nimis 1995, 1999; Nimis and Ulmer 1998) is their sensitivity with respect to temperature of crystallisation and to the alkalinity of the parent magma; as a consequence, putting values on pressure variation is a difficult

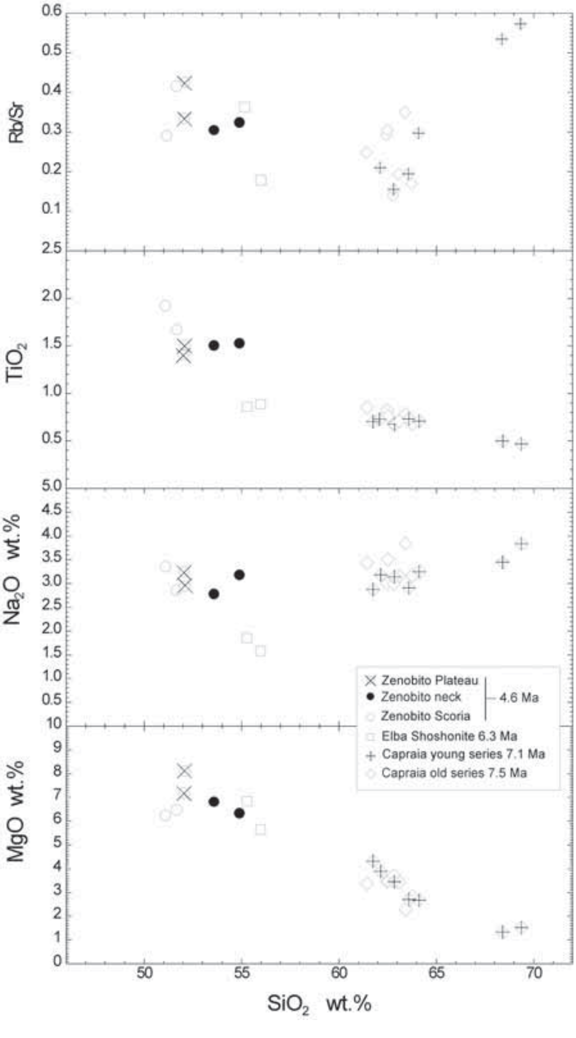

Fig. 5 – Representative Harker variation diagrams for Capraia and Zenobito Volcanoes. Data are plotted on water free-basis.

task. The consistency of crystal chemical variations among various stages, however, provides support to the hypothesis of a different crystallisation depth of clinopyroxene crystals, with the Capraia stage being characterized by lower pressures with respect to the Zenobito stage.

Previous studies have emphasised that HKCA rocks of Capraia Volcano show significant petrologic and geochemical differences with respect to the typical HKCA rocks from the Italian peninsula (Conticelli *et al.* 2002, 2004; Peccerillo and Martinotti 2006). We have compared the structural and chemical characteristics of Capraia clinopyroxene crystals with those from calc-alkalic and high-K calc-alkalic rocks of the Aeolian Arc (e.g., Francalanci 1993; Francalanci and Santo 1993; Malgarotto *et al.* 1993; Nazzareni *et al.* 1998) and those from shoshonite and lamproite from Tuscan Magmatic Province (e.g., Conticelli and Peccerillo 1992; Conticelli *et al.* 1991, 1992; Cellai *et al.* 1994; Conticelli 1994, 1998). Clinopyroxene from Capraia HKCA rocks (Fig. 8) shows significant differences with respect to the clinopyroxene from other calc-alkalic Italian rocks

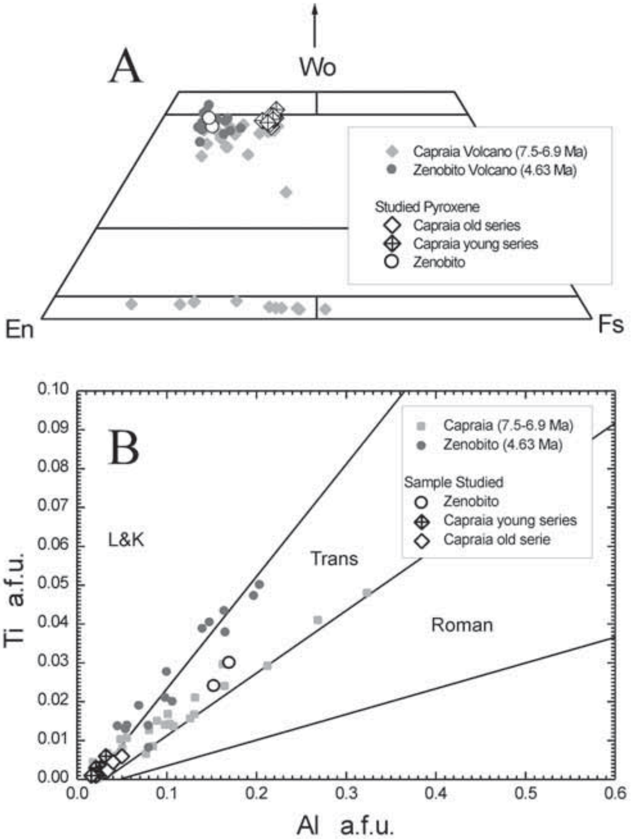

Fig. 6 – Classification diagrams for pyroxene: A) based on quadrilateral components after Morimoto (1988); note that calc-alkalic rocks of Capraia volcano are two pyroxene-bearing rocks, whereas in shoshonitic rocks from Zenobito volcano orthopyroxene is missing; B) based on Ti versus Al contents in clinopyroxene (Conticelli 1994, 1998); L&K = field of clinopyroxene from lamproite and kamafugite; Trans = field of clinopyroxene from transitional shoshonitic rocks; Roman = field of clinopyroxene from Roman-type leucite-bearing rocks. Small solid grey symbols (diamonds and circles) in background are Capraia data from literature (e.g., Prosperini, 1993, Ogna 1994, and Poli *et al.* 1995, 2006).

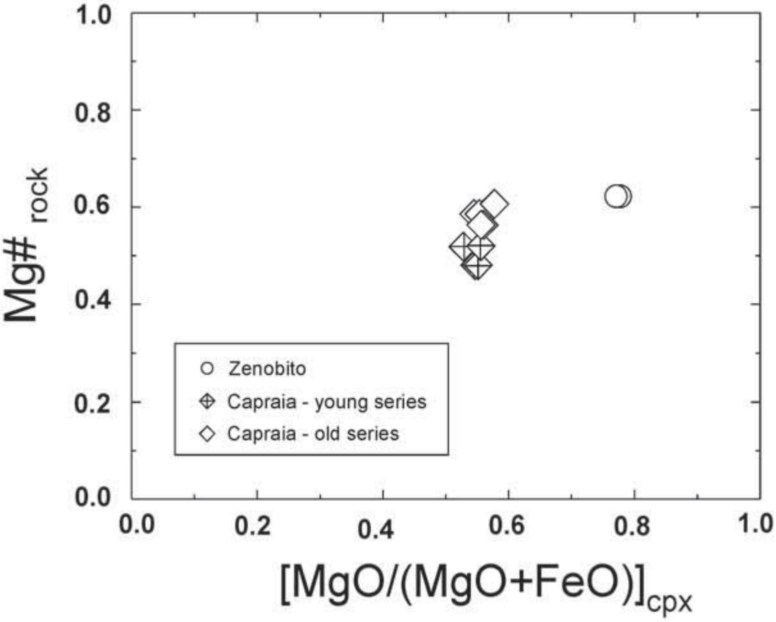

Fig. 7 – Relationship between the MgO/(FeO+MgO)$_{cpx}$ and Mg#$_{rock}$ for the analysed samples.

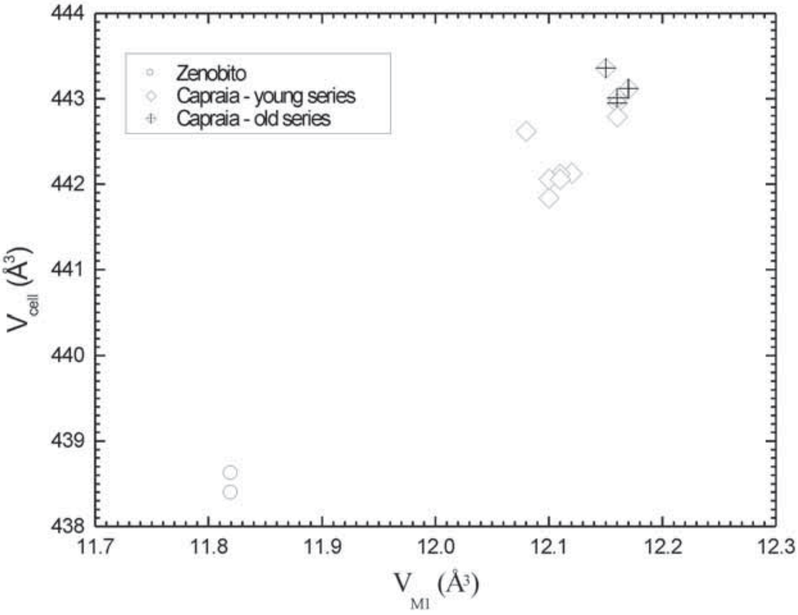

Fig. 8 – Relationship between the octahedral volume (V_{M1}) and the unit-cell volume (V_{cell}).

highlighted in the previous studies. In addition, the Si+Al deficiency in the tetrahedral site of Capraia clinopyroxene recalls closely the crystal chemical characteristics of lamproites, and in particular those from Tuscany (Fig. 9) and Corsica (e.g., Wagner and Velde 1986; Conticelli *et al.* 1992; Conticelli 1998). Clinopyroxene from Capraia displays similarities with that from lamproites: high-silica contents (1.92-2.00 a.f.u.), low Al_2O_3 contents (0.32-1.39 wt. %), and Ca^{2+} varying from 0.76 to 0.89 a.f.u. (Cellai *et al.* 1994). This reinforces the hypothesis that Capraia high-K calc-alkalic rocks are compositionally akin to lamproites indicating a possible role for a lamproitic component in their genesis. A role of a lamproitic component in the genesis of HKCA rocks explains large variation in the K_2O content in the HKCA andesites at Capraia. Such a variation is not easily explained by any common evolution process. A lamproitic affinity for Capraia rocks is also supported by their incompatible element patterns that are very similar to those of lamproites, and are distinct from those of calc-alkalic and shoshonitc rocks of the Aeolian Arc (see Francalanci *et al.* 1993; Peccerillo 2005; Peccerillo and Martinotti 2006).

On the other hand, we have also compared clinopyroxene crystals from Zenobito Volcano with those of similar volcanic rocks from the Tuscan Magmatic Province. For this purpose we have compared the crystal chemical characteristics of clinopyroxene from Radicofani (Cellai *et al.* 1994) and Elba Island shoshonites. Although, Zenobito trachybasalt, on one hand, and Radicofani and Elba Island shoshonites, on the other ones, display slight but significant differences on the major element compositions (Table 2), close structural and compositional similarities in clinopyroxene are shown (Fig. 8).

The lamproitic affinity of Capraia magmatism has some important implication for the genesis of calc-alkalic to ultrapotassic lamproitic mafic magmatism in Tuscany and possibly in other areas in the Western Mediterranean, such as the Western Alps and the Betic Cordillera, where similar rock types occur (Venturelli *et al.* 1984a, b; Peccerillo 2005; Peccerillo and Martinotti 2006). It has been suggested that the variable petrologic and geochemical signatures of rocks with various enrichments in potassium were the effect of variable degrees of partial melting of a lithospheric

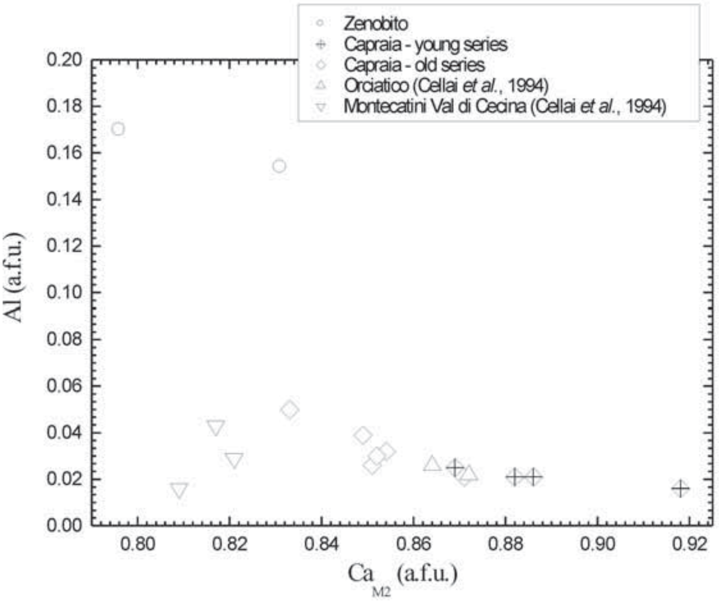

Fig. 9 – Relationship between Ca_{M2} and Al for the studied clinopyroxenes. Data for the crystals from Orciatico and Montecatini Val di Cecina were taken from Cellai *et al.* (1994).

mantle cut by metasomatic vein rich in phlogopite (Conticelli *et al.* 2002). Lamproitic rocks would represent almost pure vein melts, whereas the less potassic calc-alkaline and shoshonitic magmas would represent melts formed by a contribution from both the veins and the host lithospheric mantle (Conticelli *et al.* 2006). In other words, calc-alkalic and shoshonitic magmas would represent lamproitic melts diluted by melting of peridotite rocks depleted in trace elements. The affinity between the Capraia magma and Tuscany lamproites highlighted by the present study supports the above hypothesis.

SUMMARY AND CONCLUSION

Crystal chemical and structural data from clinopyroxene from Capraia Volcano and Zenobito Volcano are significantly different to each others. The observed crystal-chemical variations cannot derive from compositional modifications of host magmas, but rather reflects changes in the pressure conditions of magma storage and crystallisation, thus providing information on depth of magma reservoirs.

The Capraia Volcano clinopyroxene crystals analyzed in this work display close similarities with those from the nearby lamproites. This claims for a common component in the genesis of these magmas. Lamproitic, shoshonitic, and high-K calc-alkalic magmas of the Tuscan Magmatic Province are genetically related to different degrees of partial melting of a common litospheric source modified by subduction-derived metasomatic agents (e.g., Peccerillo *et al.* 1988; Conticelli *et al.* 2006). Lamproitic magmatism could be the product of metasomatic phlogopitic veins, whose melting generated magmas very enriched in potassium and incompatible elements. The less potassic calc-alkaline and shoshonitic magmas could reflect higher degrees of partial melting, with participation in the melt of both phlogopitic veins and peridotitic rocks.

Zenobito Volcano clinopyroxene, on the other hand, are distinctively different from those of the Capraia Volcano, and particularly from those of shoshonites from Tuscan Magmatic Province, speaking for a different genetic link. In addition, Zenobito Volcano rocks have geochemical and petrologic characteristics significantly different from those of shoshonites and HKCA from Tuscan Magmatic Province, suggesting an increasing role of an astenospheric component in their mantle source.

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REFERENCES

ALBEE, A.L. and RAY, L. (1970) – *Correction factors for electron probe analysis of silicate, oxides, carbonates, phosphates, and sulfates.* Anal. Chem., **48**, 1408-1414.

ALDIGHIERI B., GROPPELLI G., NORINI G., TESTA B. (2004) – *Capraia Island: Morphology and Geology of a Complex Volcanic activity during the Miocene and Pliocene.* In: Morini D. & Bruni P. (edts.), The Regione Toscana project of Geological Mapping, case histories and data acquisition, 51-59.

AVANZINELLI R., BINDI L., MENCHETTI S. and CONTICELLI S. (2004) – *Crystallisation and genesis of peralkaline magmas from Pantelleria Volcano, Italy: an integrated petrological and crystal-chemical study*. Lithos, **73**, 41-69.

BARBERI F, FERRARA G., FRANCHI F., SERRI G., TONARINI S. and TREUIL M. (1986) – *Geochemistry and geochronology of the Capraia Island volcanic Complex (North Tyrrhenian Sea, Italy).* Terra Cognita, **6**, 185.

BENCE, A.E. and ALBEE, A.L. (1968) – *Empirical correction factors for the electron microanalysis of silicate and oxides.* J. Geol., **76**, 382-403.

BINDI L., CELLAI D., MELLUSO L., CONTICELLI S., MORRA V. and MENCHETTI S. (1999) – *Crystal Chemistry of Clinopyroxene from Alkaline undersaturated rocks of the Monte Vulture Volcano, Italy.* Lithos, **46**, 259-274.

BINDI L., TASSELLI F., OLMI F., PECCERILLO A. and MENCHETTI S. (2002) – *Crystal chemistry of clinopyroxenes from Linosa Volcano, Sicily Channel, Italy: implications for modelling the* *magmatic plumbing system.* Min. Mag., **66**, 953-968.

Bruno E., Carbonin S. and Molin G. (1982) – *Crystal structure of Ca-rich clinopyroxenes on the* $CaMgSi_2O_6$-$Mg_2Si_2O_6$ *join*. Tsch. Mineral. Petrogr. Mitt., **29**, 223-240.

Cameron M. and Papike J. J. (1981) – *Structural and chemical variations in pyroxenes.* Am. Mineral., **66**, 1-50.

Carbonin C., Dal Negro A., Ganeo S. and Piccirillo E.M. (1991) – *Influence of magma composition and oxigen fugacity on the crystal structureof C2/c clinopyroxenes from a basalt-pantellerite suite*. Contrib. Mineral. Petrol., **108**, 34-42.

Carbonin S., Dal Negro A., Molin G.M., Munno R., Rossi G., Lirer L. and Piccirillo E.M. (1984) – *Crystal chemistry of Ca-rich pyroxenes from undersatured to oversatured trachytic rocks, and their relationships with pyroxenes from basalts.* Lithos, **17**, 191-202.

Cellai D., Conticelli S. and Menchetti S. (1994) – *Crystal- chemistry of clinopyroxenes in Italian Lamproites and Kamafugites: Implications on their genesis.* Contrib. Mineral. Petrol., **116**, 301-315.

Civetta L., Orsi G., Scandone P. and Pece R. (1978) – *Eastward migration of the Tuscan Anatectic magmatism due to anticlockwise rotation of the Apennines.* Nature, **276**, 604-606.

Conticelli S. (1994) – *Relationships among lamproitic, kamafugitic and Roman Type magmas: mineralogical, petrological and experimental data.* In: “Proceedings of the International Mineralogical Association”, 16th General Meeting, Pisa, 82.

Conticelli S. (1998) – *Effects of Crustal Contamination on Ultrapotassic Magmas with Lamproitic Affinity: Mineralogical, Geochemical and Isotope data from the Torre Alfina Lavas and Xenoliths, Central Italy.* Chem. Geol., **149**, 51-81.

Conticelli S., Bortolotti V., Principi G., Laurenzi M.A., Vaggelli G. and D’Antonio M. (2001) – *Petrology, mineralogy and geochemistry of a mafic dyke from Monte Castello, Elba Island, Italy.* Ofioliti, **26**, 249-262.

Conticelli S., Carlson R.W., Widow E. and Serri G. (2006) – *Chemical and isotopic composition (Os, Pb, Nd, and Sr) of Neogene to Quaternary Calc-alkalic, shoshonitic and Ultrapotassic mafic rocks from the Italian Peninsula: inferences on the nature of their mantle sources.* In: “Cenozoic volcanism in the Mediterranean area”, L. Beccaluva, G. Bianchini, M. Wilson (eds), Geological Society of America, Special Paper, **418**, in press.

Conticelli S., D’Antonio M., Pinarelli L. and Civetta L. (2002) – *Source contamination and mantle heterogeneity in the genesis of Italian potassic and ultrapotassic volcanic Rocks: Sr-Nd-Pb Isotope data from Roman Province and Southern Tuscany.* Mineral. Petrol., **74**, 189-222.

Conticelli S., Francalanci L. and Santo A.P. (1991) – *Petrology of final stage Latera lavas, Vulsini Mts.: Mineralogical, Geochemical and Sr-isotopic data and their bearing on the genesis of some potassic magmas in Central Italy*. J. Volcanol. Geotherm. Res., **46**, 187-212.

Conticelli S., Manetti P. and Menichetti S. (1992) – *Petrology, Chemistry, Mineralogy and Sr-isotopic features of Pliocenic Orendites from South Tuscany: implications on their genesis and evolutions.* Eur. J. Mineral., **4**, 1359-1375.

Conticelli S., Melluso L., Perini G., Avanzinelli R. and Boari E. (2004) – *Petrologic, Geochemical and Isotopic characteristics of potassic and ultrapotassic magmatism in Central-Southern Italy: inferences on its genesis and on the nature of mantle sources.* Per. Mineral., **73**, 135-164.

Conticelli S. and Peccerillo A. (1992) – *Petrology and geochemistry of potassic and ultrapotassic volcanism in central Italy: petrogenesis and inferences on the evolution of the mantle sources.* Lithos, **28**, 221-240.

Dal Negro A., Carbonin S., Molin G.M., Cundari A. and Piccirillo E.M. (1982) – *Intracrystalline cation distribution in natural clinopyroxenes of tholeiitic, transitional, and alkaline basaltic rocks.* In: Saxena SK (ed) Advances in physical geochemistry, Vol. 2. Springer, Berlin Heilderberg New York, pp. 117-150.

Dal Negro A., Molin G.M., Secco L., Cundari A. and Piccirillo E.M. (1989) – *Crystal-chemistry of clinopyroxene and its genetic significance: a new approach.* In: Boriani A. Bonafede M. Piccardo G.B. Vai G.B. (eds) The lithosphere in Italy: advances in Earth sciences research. Atti dei Convegni Lincei 80, pp. 271-295.

De Vries J.L. and Jenkins R. (1971) – *Spettrometria a raggi X in pratica.* Biblioteca Tecnica Philips, Milano 154 pp.

D’Orazio M., Laurenzi L.A. and Villa I.M. (1991) – *$^{40}Ar/^{39}Ar$ dating of a shoshonitic lava flow of the Radicofani volcanic center (Southern Tuscany).* Acta Vulcanol., **1**, 63-67.

Faraone D., Molin G.M. and Zanazzi P.F. (1988) – *Clinopyroxenes from Vulcano (Aeolian Island, Italy): Crystal chemisty and cooling history.* Lithos, **22**,113-126

Ferrara G. and Tonarini S. (1985) – *Radiometric geochronology in Tuscany: results and problems.* Rend. Soc. Ital. Mineral. Petrol., **40**, 110-124.

Francalanci L. (1993) – *Mineral chemistry of Stromboli volcanics as indicator of magmatic processes.* Acta Vulcanol., **3**, 99-113.

Francalanci L. and Santo A.P. (1993) – *Magmatological evolution of Filicudi volcanoes, Aeolian Island, Italy: constraints from mineralogical, geochemical and isotopic data.* Acta Vulcanol., **4**, 203-227.

Francalanci L., Taylor S.R., McCulloch M.T. and Woodhead J. (1993) – *Geochemical and isotopic variations in calc-alkaline rocks of the Aeolian Arc (Southern Tyrrhenian Sea, Italy): constraints on the magma genesis.* Contrib. Mineral. Petrol., **113**, 300-313.

Franzini M. (1964) – *Studio mineralogico e litologico dell'isola di Capraia.* Atti della Società Toscana di Scienze Naturali, Memorie, Serie A, **71**, 326-386.

Franzini M., Leoni L. and Saitta M. (1972) – *A simple method to evaluate the matrix effect in X-Ray fluorescence analysis.* X-Ray Spectr., **1**, 151-154.

Freed R.L. and Peacor D.R. (1967) – *Refinement of the crystal structure of johannsenite*. Am. Mineral., **52**, 709-720.

Gagnevin D., Daly J.S., Poli G., and Conticelli S. (2006) – Plagioclase chemical zoning in the Capraia Volcano (Italy): record of a complex magma recharge history. Mineral. Mag., submitted.

Hamilton W.C. (1965) – *Significance tests on the crystallographic R factors.* Acta Crystallogr., **18**, 502-510.

Ibers J.A. and Hamilton W.C. Eds. (1974) – *International Tables for X-ray Crystallography*, Vol. **IV**, 366 p., Kynock, Dordrecht, The Netherlands.

Innocenti F., Serri G., Ferrara P., Manetti P. and Tonarini S. (1992) – *Genesis and classification of the rocks of the Tuscan Magmatic Province: thirty years after Marinelli's model.* In: "*Marinelli Volume*", Acta Vulcanol., **2**, 247-265.

Le Maitre R.W. (ed.) (1989) – *A Classification of igneous rocks and glossary of terms.* Blackwell, Oxford, 193 pp.

Malgarotto C., Molin G.M. and Zanazzi P.F. (1993) – *Crystal chemistry of clinopyroxenes from Filicudi and Salina (Aeolian Islands, Italy). Geothermometry and barometry.* Eur. J. Mineral, **5**, 915-923.

Morimoto N. (1989) – *Nomenclature of pyroxenes.* Can. Mineral., **27**, 143-156

Nazzareni S., Molin G.M., Peccerillo A. and Zanazzi P.F. (1998) – *Structural and chemical variations in clinopyroxenes from the island of Alicudi (Aeolian arc) and their implications for contitions of crystallization.* Eur. J. Mineral, **10**, 291-300.

Nimis P. (1995) – *A clinopyroxene geobarometer for basaltic systems based on crystal structure modeling.* Contrib. Mineral. Petrol., **121**, 115-125.

Nimis P. (1999) – *Clinopyroxene geobarometry of magmatic rocks, Part 2. Structural geobarometers for basic to acid, tholeiitic and mildly alkaline magmatic systems.* Contrib. Mineral. Petrol., **135**, 62-74.

Nimis P. and Ulmer P. (1998) – *Clinopyroxene geobarometry of magmatic rocks, Part 1. An expanded structural geobarometer for anhydrous and hydrous, basic and ultrabasic system.* Contrib. Mineral. Petrol., **133**, 122-135.

North A.C.T., Phillips D.C. and Mathews F.S. (1968) – *A semi-empirical method of absorbation correction.* Acta Crystallogr., **A24**, 351-359.

Ogna M. (1994) – *Studio magmatologico e petrografico dell'isola di Capraia (Arcipelago Toscano, Italia).* Università degli Studi di Perugia, Tesi di Laurea.

Pasqual D., Molin G.M. and Zanazzi P.F. (1995) – *Crystal chemistry of Stromboli clinopyroxene: a comparison with analogues from the other Aeolian Island (Italy).* Eur. J. Mineral., **7**, 369-378.

Peccerillo A. (2005) – *Plio-Quaternary volcanism in Italy. Petrology, Geochemistry, geodynamics.* Springer, Heidelberg, 365 pp.

Peccerillo A., Conticelli S. and Manetti P. (1987) – *Petrological characteristics and the genesis of the recent magmatism of South Tuscany and North Latium.* Per. Mineral., **56**, 167-183.

Peccerillo A. and Martinotti G. (2006) – *The Western Mediterranean lamproitic magmatism: origin and geodynamic significance.* Terra Nova, **18**, 109-117.

Peccerillo A., Poli G. and Serri G. (1988) – *Petrogenesis of orenditic and kamafugitic rocks from Central Italy.* Can. Mineral., **26**, 45-65.

Peccerillo A. and Taylor S.R. (1976) – *Geochemistry of Eocene calc-alkaline rocks from Kastamonu area, Northern Turkey.* Contrib. Mineral. Petrol., **58**, 63-81.

Poli G. (2004) – *Genesis and evolution of Miocene-Quaternary intermediate-acid rocks from the Tuscan Magmatic Province.* Per. Mineral., **73**, 187-214.

Poli G. and Perugini D. (2003) – *The island of Capraia.* Per. Mineral., **72**, 195-201.

Poli G., Prosperini N. and Conticelli S. (2006) – *Petrology and Geochemistry of Capraia and Zenobito volcanoes, Tuscan Archipelago – Italy: Complex origin of an High-K calc-alkalic volcano.* In prep.

Poli G., Prosperini N., Conticelli S. and Ogna M. (1995) – *Petrology and Geochemistry of Capraia Island (Tuscan Archipelago - Italy): Complex Origin of a Calc-alkaline Volcano.* In: Atti del 75° Congresso SIMP, Venezia, Plinius, **14**, 121-122.

Principalle F., Tirone M. and Comin-Chiaramonti P. (2000) – *Clinopyroxenes from metasomatized spinel-peridotite mantle xenoliths from Nemby (Paraguay): crystal chemistry and petrological implications*. Mineral. Petrol., **70**, 25-35.

Prosperini N. (1993) – *Petrologia e geochimica delle rocce dell'isola di Capraia (Arcipelago Toscano, Italia): un vulcano calcalcalino di origine complessa*. B.Sc. Thesis, University of Perugia, 149 pp.

Rhodes J.M. (1981) – *Characteristics of primary basaltic magmas*. In: "Basaltic Volcanism Study Project. Basaltic Volcanism on the Terrestrial Planet.", Pergamon Press, New York, U.S.A., p. 409-432.

Rodolico F. (1938) – *Le rocce dell'isola di Capraia. Ricerche sulle rocce eruttive recenti della Toscana.* Atti Società Toscana Scienze naturali, **47**, 125-136.

Rossi G., Oberti R., Dal Negro A., Molin G.M. and Mellini M. (1987) – *Residual Electron Density at the M2 Site in C2/c Clinopyroxenes: Relationships with Bulk Chemistry and Sub-solidus Evolution.* Phys. Chem. Min., **14**, 514-520.

Salviulo G., Secco L., Marzoli A., Piccirillo E.M. and Nyobe J.B. (2000) – *Ca-rich pyroxene from basic and silicic volcanic rocks from the Cameroon Volcanic Line (West-Africa): crysta chemistry and petrological relationships.* Mineral. Petrol., **70**, 73-88.

Sheldrick G.M. (1993) – SHELXL-93: A new structure refinement program. University of Göttingen, Germany.

Ungaretti L., Smith D.C. and Rossi G. (1981) – *Crystal-chemistry by X-ray structure refinement and electron microprobe analysis of a series of sodic-calcic to alkali-amphiboles from the Nybö eclogite pod, Norway.* Bull. Mineral., **104**, 400-412.

Vaggelli G., Olmi F. and Conticelli S. (1999) – *Quantitative electron micriprobe analysis of reference silicate mineral and glass samples.* Acta Vulcanol., **11**, 297-303.

Venturelli G., Capedri S., Di Battistini G., Crawford A., Kogarko L.N. and Celestini S. (1984a) – *Ultrapotassic rocks from South-Eastern Spain*. Lithos, **17**, 37-54.

Venturelli G., Thorpe R.S., Dal Piaz G.V., Dal Moro A., and Potts P.J., (1984b) – *Petrogenesis of calc-alkaline, shoshonitic and associated ultrapotassic Oligocene volcanic rocks from the North Western Alps*. Contrib. Mineral. Petrol., **86**, 234-254.

Wagner C. and Velde D. (1986) – *The mineralogy of K-richterite bearing lamproite.* Am. Mineral., **71**, 17-37.

Washington H.S. (1906) – *The Roman Comagmatic Region.* Carnegie Inst. Washington Yearbook, **36**, 1-220.

Westerman D.S., Innocenti F., Tonarini S. and Ferrara G. (1993) – *The pliocene intrusions of the island of Giglio.* Mem. Soc. Geol. Ital., **49**, 345-363.