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Volcanological implications of crystal-chemical variations in clinopyroxenes from the Aeolian Arc, Southern Tyrrhenian Sea (Italy)

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Abstract Crystal chemistry and structural data for clinopyroxene from the Aeolian islands (Southern Tyrrhenian Sea, Italy) were determined with the aim of obtaining geobarometric information and exploring implications for the structure of volcanic plumbing systems. Cell and M1 site volumes for clinopyroxenes, which are known to decrease with increasing pressure of crystallization, revealed variable values, both within some single islands and along the entire arc, indicating polybaric conditions of crystallization. The lowest cell and M1 volumes were found at Filicudi, plotting close to values of clinopyroxenes from high-pressure ultramafic xenoliths entrained in alkali basalts. Indications of high-pressure crystallization were also found at Salina and, to a lesser extent, at Alicudi, all situated in the western sector of the Aeolian Arc. The central and eastern islands of Lipari, Vulcano, Panarea and Stromboli generally show higher values of cell parameters, suggesting crystallization in shallow magma chambers. These islands are characterized by the occurrence of large calderas, which are apparently lacking at Salina and Filicudi. Time-related variations were observed for cell and M1 volumes of clinopyroxene for some islands. At Salina, the early-erupted products display low values of cell parameters with respect to later activity, thus indicating a decrease in crystallization pressure with time. A similar, although less striking, pattern is observed at Alicudi and Lipari.

An overall increase in cell parameters with time was observed at the scale of the entire arc. The observed variations in clinopyroxene structural parameters highlight the significance of pyroxene crystal chemistry for petrogenetic and volcanological interpretation. Correlation with time and the structural characteristics of volcanoes suggest significant regional and temporal modifications in the plumbing systems of Aeolian volcanoes. Clinopyroxenes from Filicudi and the older Salina crystallized at high pressure in deep magma chambers, in the lower crust or at the mantle–crust boundary. The lower crystallization pressure in the younger Salina is interpreted as evidence of upward migration of magma chambers with time. Similar evolution can be envisaged for Alicudi. Instead, the entire evolutionary history of the central and eastern islands was dominated by low-pressure crystallization, with formation of calderas and generation of abundant acid products that are scarce or absent in the western islands. Evolution of the plumbing system of single volcanoes and of the Aeolian arc in general is probably related to modification of stress regimes and/or thinning of the arc basement, due to the effect of uprising mantle material above the Ionian subduction zone.

Keywords Crystal chemistry · Clinopyroxene · Geobarometry · Magma chambers · Arc volcanism · Aeolian Arc

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Introduction

The Aeolian Archipelago, Southern Tyrrhenian Sea (Fig. 1) consists of seven volcanic islands (Alicudi, Filicudi, Salina, Lipari, Vulcano, Panarea, Stromboli), of which two volcanoes, Stromboli and Vulcano, are still active. The Aeolian rocks have variable magmatic affinities, from calc-alkaline (CA), high-K calc-alkaline (HKCA) and shoshonitic (SHO) to potassic (KS). A general evolution from basic to more evolved products with time in some islands has been recognized, and rhyolites are the typical final products at Lipari, Vulcano, Panarea

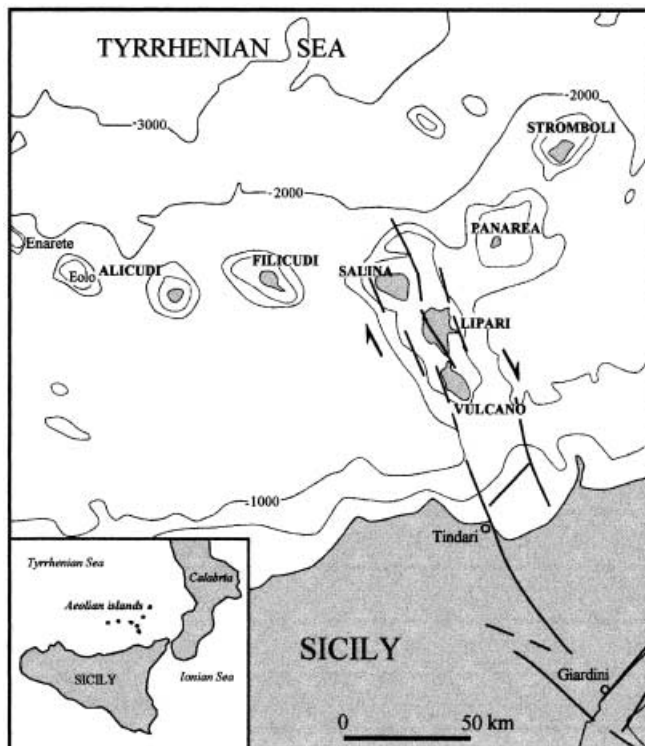


Fig. 1 Regional location of Aeolian volcanic system. Main regional tectonic lines as reported by Falsaperla et al. (1999)

and Salina (Keller 1980; De Rosa et al. 1996; De Astis et al. 1997). This temporal compositional evolution of Aeolian magmas may reflect modifications of the plumbing systems of these volcanoes, with magma chambers migrating from deep crust to shallower levels (De Astis et al. 1997; Nazzareni et al. 1998). According to this hypothesis, magma processes in deep reservoirs are dominated by mixing between mafic magmas and resident liquids, which prevents evolution towards acid compositions, whereas fractional crystallization plays a leading role in shallow magma chambers, allowing evolution towards acid compositions. These models are based mostly on petrological and geochemical data, but geobarometric constraints are lacking.

Since the early 1980s clinopyroxene (cpx) crystal chemistry has been related to pressure of crystallization. Recent studies by Nimis (1995, 1999) and Nimis and Ulmer (1998) attempt to calibrate the changes in clinopyroxene crystal chemistry (e.g. cell volume and polyhedral volumes) with pressure, and thus provide an opportunity to constrain the depth of magma chambers.

In this paper we review crystal-chemical data (single-crystal X-ray diffraction and electron microprobe analyses) of clinopyroxenes present in rocks ranging from basalt to rhyolite of the entire Aeolian arc (Faraone et al. 1988; Malgarotto et al. 1993; Pasqual et al. 1995, 1998; Nazzareni et al. 1998). Clinopyroxenes from the islands of Filicudi, Salina and Alicudi show evidence of high crystallization pressure (ca. 6–8 kbar), whereas those of the eastern islands of Lipari, Vulcano, Panarea and

Stromboli equilibrated at lower pressures (<3 kbar). More importantly, estimated crystallization pressures for the entire arc tend to decrease with time, and are also correlated with increasing proportions of high-silica rocks in the erupted products. We interpret this to reflect modifications of the plumbing system through time, related to changes of stress regimes and crustal thickness, possibly as a consequence of rapid mantle upwelling beneath the Aeolian arc.

Geological and volcanological setting of the Aeolian Arc

The Aeolian arc consists of seven islands and various seamounts (Fig. 1). It is built up on the Calabro-Peloritan continental margin, a complex structure of Paleozoic rocks, with minor Jurassic ophiolites and Mesozoic to Recent sedimentary series. Crustal thickness varies from 40–45 km under Calabria and 15–20 km under the Aeolian Arc, to approximately 10 km under the Tyrrhenian abyssal plain (Morelli et al. 1975).

Several authors (e.g. Keller 1980; Gasparini et al. 1982) consider the Aeolian islands to be a volcanic arc associated with NW-dipping subduction under the Calabria region. A close relationship between regional tectonic structures and volcanism has been recognized in the archipelago. Salina, Lipari and Vulcano rest on the NW–SE Tindari-Giardini dextral transcurrent fault, which separates the NE–SW alignment of Panarea and Stromboli in the east from the E–W segment of Salina, Alicudi and Filicudi in the west (Fig. 1).

The oldest rocks exposed in the arc apparently include Upper Pleistocene (1.2 Ma) volcanics at Filicudi (Santo et al. 1995) and 1.0–0.8 Ma samples dredged from the westernmost seamounts (Sisifo, Eolo, Enarete). Salina is 430 to 32 ka old. Younger activity is concentrated at Alicudi (60–25 ka), the westernmost part of Salina (Pollara, 30 ka), Lipari (<150 ka), Vulcano (<120 ka), Panarea (60 ka) and Stromboli (<90 ka; Gillot 1987).

The petrological and geochemical variability of Aeolian Arc magmas is believed to reflect the occurrence of several compositionally distinct mantle-derived parental magmas, and complex shallow evolutionary histories (Ellam and Harmon 1990; Esperança et al. 1992; De Astis et al. 1997, 2000). Fractional crystallization of different parental magmas seems by far the most important process of magma evolution (Peccerillo and Wu 1992; De Astis et al. 1997; Del Moro et al. 1998; De Astis et al. 2000). The occurrence of abundant metamorphic xenoliths (mainly quartzitic) in all the Aeolian volcanoes suggests that crust plays an important role during magma evolution (e.g. Barker 1987; Esperança 1992; De Astis et al. 1997); however, crustal assimilation does not appear to be a first-order process in the generation of petrological and geochemical variability of mafic magmas (De Astis et al. 2000).

Methods of crystal chemical investigation

Crystal chemical investigation is carried out on selected fragments of clinopyroxene phenocrysts. These are extracted from euhedral crystals that do not show evidence of disequilibrium (e.g. rounded edges, embayments) with the surrounding matrix. Fragments from core and rim are taken whenever crystals show optical zoning. Crystal fragments are taken from a section approximately 150 μm thick, after careful optical selection, and then submitted to X-ray investigation under an automated diffractometer in order to obtain structural parameters. After X-ray data collection, the single fragments are embedded in epoxy resin, polished, coated and analysed by electron microprobe. Up to ten spot analyses (depending on the degree of homogeneity in composition) are then averaged in order to obtain a mean composition of the investigated surface as close as possible to the bulk composition of the crystal fragment. Site partitioning data are then calculated by least-squares minimization of structural and chemical data.

Repeated determinations on various clinopyroxene phenocrysts from a single sample gave reproducible values of structural parameters (VM1 and Vcell), with 2σ around 1%. Moreover, chemical studies of zoned clinopyroxenes from single samples show that chemical variations such as those observed in the Aeolian clinopyroxenes do not affect significantly geometrical parameters (Margarotto et al. 1993; Pasqual et al. 1995). Further details on sampling, clinopyroxene compositions, and experimental procedure and equipment are given by Faraone et al. (1988), Margarotto et al. (1993), Pasqual et al. (1995), Nazzareni et al. (1998), and references therein.

Clinopyroxene host rocks subjected to investigation here include various lithologies which cover the entire compositional spectrum of the Aeolian magmas as well as various activity stages of the individual islands. Representative chemical analyses of the investigated Aeolian clinopyroxenes, and indications of host rock composition and stratigraphic position are given in Table 1.

Geobarometric significance of clinopyroxene crystal chemistry

Dal Negro et al. (1982) observed close relationship between structural site occupancies and geometric modification in site and cell structural parameters, by a systematic study of crystal chemistry of volcanic clinopyroxenes. Further studies carried out on high-pressure natural and synthetic clinopyroxenes (Dal Negro et al. 1984; Dal Negro et al. 1989; Manoli and Molin 1988) pointed out the dependence of M1 site and cell volume on crystallization pressure.

Manoli and Molin (1988) showed that M1 and cell volumes retain a record of crystallization pressure, and they may thus be used to distinguish clinopyroxenes crystallizing in various pressure conditions. For a given composition, Vcell and VM1 decrease linearly as pressure increases, due to a series of substitutions:

- $\text{Ca}(\text{M}2), \text{Mg}(\text{M}1) \leftrightarrow \text{Na}(\text{M}2), \text{Al}(\text{M}1);$
 $\text{Mg}(\text{M}1), \text{Si}(\text{T}) \leftrightarrow \text{Al}(\text{M}1), \text{Al}(\text{T}); \text{Ca}(\text{M}2) \leftrightarrow \text{Mg}(\text{M}2).$

Notwithstanding the chemical complexity of these relations, pressure can be expressed as a simple linear function of Vcell and VM1, making cpx a useful geobarometer able to furnish the pressure equilibrium of magmatic clinopyroxene. More recently, Nimis and Ulmer (1998), and Nimis (1995, 1999), proposed an equation that relates Vcell and VM1 to crystallization pressure of clinopyroxene from basic to acid tholeiitic to mildly alkaline types, allowing a quantitative use of the cpx geobarometer. Nimis (1999) found that standard error on prediction of pressure crystallization values was approximately ± 2 kbar for these magmas; however, errors for calc-alkaline magmas were suggested to be higher, probably as a result of the strong variability of experimental melt compositions on which geobarometric studies were based. However, we point out that petrological and volcanological interpretation of this work is not based on absolute values, but rather on relative time- and space-related variations of crystallization pressures; these are measured on compositionally similar clinopyroxenes, which have been extracted from petrologically similar rocks types. This obviously reduces compositional-dependent systematic errors.

Crystal chemistry of Aeolian Arc clinopyroxene

According to the pyroxene nomenclature of Morimoto et al. (1988), Aeolian cpx range from augite to diopside. Extreme chemical cpx composition for various stages of evolution in each island is reported in Table 1; quadrilateral and non-quadrilateral components are also reported. Composition of host rocks (classification according to the Peccerillo and Taylor 1976) is also given in Table 1.

In the following section we present the cpx crystal-chemical data for the Aeolian islands in the context of chemical and temporal evolution of each volcano.

Alicudi

The island of Alicudi is a well-preserved 60- to 30-ka-old conical volcano, consisting mainly of CA products. Eruptive activity is divided into three main stages. The first two stages are characterized by basalts and basaltic andesite lavas and minor pyroclastics. Andesitic lava flows and domes were emplaced during the third stage. Peccerillo and Wu (1992) and Peccerillo et al. (1993) suggested that early stages were fed by a relatively primitive magma, which underwent significant interaction with wall rocks, whereas fractional crystallization dominated the evolution of the latest emplaced magmas, with little or no interaction with continental crust.

Clinopyroxenes range from diopside to augite (Fig. 2, inset). Cell and M1 volumes are high indicating a moderate to low pressure of crystallization; note, however, that there is a small but systematic increase in the cell and M1 volumes in cpx from the first to the third stages, suggest-

Table 1 Extreme compositions (expressed in weight percent oxides) of clinopyroxenes from the Aeolian islands. Quadrilateral and non-quadrilateral components are reported. Rock compositions for each evolutionary stage of various islands are also reported (classification according to Peccerillo and Taylor 1976). CA calc-alkaline; HKCA high potassium calc-alkaline; SHO shoshonitic; KS potassic series; B basalt; BA basaltic andesite; A andesite; L latite; R rhyolite; RD rhyodacite; D dacite

Stage I	Alicudi			Filicudi			Salina			Lipari			Vulcano			Panarea			Stromboli		
	ALC39	ALC33	F10c	F9c	S18	S22	L4	L10	P123	Pd42	Cc3	Mz16	S2c	S8c	S8r						
SiO ₂	51.42	53.30	52.32	51.89	50.12	51.77	53.88	51.44	50.42	54.06	50.82	52.94	53.17	51.65	50.65						
TiO ₂	0.51	0.20	0.23	0.40	0.4	0.41	0.16	0.46	0.78	0.22	0.57	0.33	0.44	0.45	0.63						
Al ₂ O ₃	4.01	2.11	0.89	2.12	3.5	2.55	1.66	2.55	3.07	0.81	4.03	1.92	1.50	3.90	3.55						
Cr ₂ O ₃	0.19	0.77	0.02	0.01	0.09	0.07	0.77	0.01	0.06	0.34	0.01	0.02	0.05	0.21	0.05						
FeO	6.51	3.84	8.81	8.51	8.24	8.27	4.00	9.92	9.56	4.00	7.86	7.50	8.10	4.78	6.22						
MnO	0.14	0.07	0.75	0.43	0.19	0.19	0.13	0.31	0.20	0.12	0.21	0.24	0.40	0.12	0.16						
MgO	15.44	17.27	14.36	14.82	15.77	15.59	18.07	15.43	14.35	17.75	14.93	16.19	15.93	16.04	15.72						
CaO	21.44	23.31	21.04	21.18	20.25	20.78	21.79	19.45	21.44	22.96	21.58	21.45	21.49	23.00	22.52						
Na ₂ O	0.21	0.16	0.40	0.24	0.20	0.20	0.13	0.18	0.16	0.00	0.15	0.17	0.34	0.27	0.21						
Total	99.87	101.04	98.85	99.60	98.76	99.83	100.59	99.75	100.04	100.26	100.16	100.76	101.42	100.42	99.71						
Quad	89.24	91.76	97.34	92.59	86.58	91.25	94.46	91.31	87.59	96.66	87.48	93.29	92.41	87.27	86.39						
Non-Quad	10.76	8.24	2.66	7.41	13.42	8.75	5.54	8.69	12.41	3.34	12.52	6.71	7.59	12.73	13.61						
Wo	44.74	46.26	43.39	43.40	41.51	42.34	43.44	39.74	43.73	45.13	44.33	42.88	42.71	46.82	45.59						
En	44.74	47.68	41.20	42.27	45.00	44.19	50.13	43.90	40.72	48.56	42.67	45.07	44.09	45.41	44.35						
Fs	10.53	5.967	14.19	13.61	13.19	13.16	6.22	15.85	15.24	6.10	12.63	11.69	12.59	7.57	9.80						
Stage II																					
SiO ₂			F15c	F19c	S2	S7	L16	L17	Lc3	Lb6	Rsb1l	Tr14	S21c	S21r	S28r						
TiO ₂			53.00	50.63	53.02	51.03	51.50	51.48	52.15	51.27	52.04	51.23	50.03	50.95	50.69						
Al ₂ O ₃			0.37	0.21	0.21	0.46	0.43	0.58	0.46	0.50	0.51	0.62	0.57	0.53	0.91						
Cr ₂ O ₃			1.17	3.80	2.05	4.00	1.38	2.25	1.85	2.38	3.32	2.37	4.98	4.65	3.20						
FeO			0.00	0.04	0.27	0.05	0.03	0.03	0.34	0.13	0.53	0.07	0.16	0.07	0.03						
MnO			9.36	7.83	5.07	6.48	12.29	12.51	7.86	14.79	4.97	13.62	5.29	4.87	10.10						
MgO			0.61	0.21	0.15	0.14	0.45	0.42	0.26	0.29	0.10	0.29	0.15	0.10	0.22						
CaO			14.41	14.78	16.61	15.17	13.54	13.29	15.83	14.79	16.41	13.26	15.11	15.56	14.56						
Na ₂ O			20.60	21.76	22.7	22.89	19.34	19.58	21.24	20.47	23.03	18.53	23.43	23.08	19.96						
Total			0.35	0.19	0.10	0.19	0.25	0.28	0.00	0.31	0.13	0.19	0.14	0.14	0.42						
Quad			99.87	99.88	100.18	100.41	99.21	100.42	99.99	99.66	101.04	100.18	99.86	99.95	100.09						
Non-Quad			96.13	87.19	93.64	86.88	94.61	92.51	92.98	89.04	88.57	93.01	83.76	86.57	87.77						
Wo			3.87	12.81	6.36	13.12	5.39	7.49	7.02	10.96	11.43	6.99	16.24	13.43	12.23						
En			42.53	44.78	45.50	46.56	40.17	40.66	42.83	38.77	46.23	38.74	48.12	47.48	41.35						
Fs			41.40	42.30	46.32	42.93	39.15	38.39	44.40	38.96	45.81	38.58	43.16	44.54	41.98						
Total			15.09	12.56	7.93	10.31	19.96	20.28	12.36	21.83	7.81	22.22	8.46	7.82	16.30						
Stage III																					
SiO ₂			F8c	F13r	S12	S30	L22	L25	Fb3	Vd1	Ba12c	Lc9	S32c	S32r	S35c						
TiO ₂			50.94	51.41	51.82	48.94	49.98	52.24	51.51	50.32	53.65	51.91	50.71	52.98	53.88						
Al ₂ O ₃			0.54	0.38	0.33	0.59	0.70	0.36	0.47	0.87	0.16	0.42	1.09	0.39	0.25						
Cr ₂ O ₃			3.77	3.57	1.61	4.29	3.75	2.35	2.49	3.29	0.81	2.54	3.81	2.06	1.68						
FeO			0.02	0.27	0	0.02	0.03	0.04	0.09	0.13	0.03	0.06	0.04	0.43	0.26						
MnO			7.23	5.00	10.32	8	9.08	7.92	9.27	9.85	7.91	8.47	8.15	4.12	3.07						
MgO			0.17	0.11	0.7	0.16	0.40	0.23	0.20	0.41	0.83	0.24	0.24	0.10	0.11						
CaO			14.69	15.80	14.15	14.37	13.17	15.51	14.21	13.62	14.35	15.25	14.43	16.66	17.26						
Na ₂ O			21.39	21.09	20.22	22.25	21.91	21.47	21.64	21.48	22.83	21.41	21.44	23.90	23.71						
Total			0.30	0.27	0.32	0.24	0.45	0.35	0.11	0.04	0.30	0.18	0.29	0.10	0.08						
Quad			100.91	100.18	99.47	98.86	99.47	100.47	99.99	100.01	100.87	100.48	100.20	100.74	100.30						
Non-Quad			88.57	88.43	93.11	82.86	85.79	90.33	91.89	88.23	96.09	91.12	87.61	92.29	95.57						

Table 1 (continued)

	Alicudi	Filicudi	Salina	Lipari	Vulcano	Panarea	Stromboli
Non-Quad	7.62	11.43	6.36	14.21	8.11	3.91	12.39
Wo	42.64	45.67	41.67	46.00	44.35	46.00	44.57
En	42.13	42.56	40.59	38.46	40.50	40.23	41.74
Fs	14.21	11.51	16.61	14.86	14.84	12.44	13.27
Stage I	CA: B (5), BA (2), A (2)	CA: B (4), HKCA: BA (2), A (3)	CA: B (9), BA (2)	CA: B (1), HKCA: BA (4)	SHO: B (5)	CA: A (3), D (4)	CA: BA (2), HKCA: BA(2), A (4)
Stage II		CA: B (2), HKCA: BA (2), A (4)	CA: B (1), BA (4), A (1)	HKCA: A (12), BA (2)	SHO: B (2), KS: L (2), R (2)	CA: D (6), RD (4)	HKCA: B (1), L (3), SHO: B (6), L (1)
Stage III	CA: A (5)	CA: B (5), HKCA: A (1)	CA: BA (3), A (5)	HKCA: R (4)	SHO: L (6)	CA: D (3), R (3)	HKCA: B (2), BA (1), SHO: B (4)

Samples referred with c and r are fragments from core and rim of phenocrysts. The number of samples analyzed for each lithotype is reported in brackets. Data source: Salina and Filicudi, Malgarotto et al. (1996); Stromboli, Pasqual et al. (1995); Lipari, Pasqual et al. (1998); Vulcano, Faraone et al. (1988); Alicudi, Nazzareni et al. (1998); Panarea, S. Nazzareni et al. (in preparation)

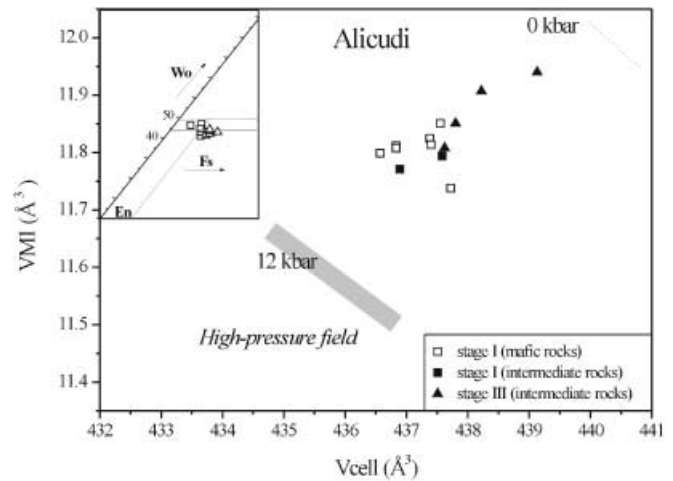


Fig. 2 Cell vs M1 site volumes for Alicudi clinopyroxenes (Nazzareni et al. 1998): Different symbols are used to discriminate cpx from mafic ($\text{SiO}_2 < 53$ wt.%) and intermediate ($\text{SiO}_2 = 53\text{--}63$ wt.%) and acid ($\text{SiO}_2 > 63$ wt.%) volcanics. *Inset*: Wo–En–Fs triangular classification for Alicudi clinopyroxenes. The shaded field for the 12-kbar range, from high-pressure experiments of Manoli and Molin (1988) and the high-pressure field, are reported

ing polybaric crystallization, with early basalts and basaltic andesites formed at higher pressure than late-stage crystals (Nazzareni et al. 1998). Therefore, the various stages of Alicudi activity may have been fed by magma chambers at different depths beneath the volcano.

Filicudi

The volcano of Filicudi is more complex than that of Alicudi, from both structural and volcanological viewpoints. It consists of several centres, mainly aligned W–E. Volcanic activity is much older than at Alicudi (1.1–0.17 Ma; Santo et al. 1995) and consisted of both effusive and explosive eruptions. Rock compositions range from CA basalt to dacite.

According to Francalanci and Santo (1993) and Santo (2000), the evolution of the Filicudi magmas was dominated by fractional crystallization, with large-scale magma mixing and significant crustal assimilation. Francalanci and Santo (1993) suggested high-pressure crystallization for the Filicudi magma, on the basis of the high Al and Sr contents of the Filicudi rocks with respect to those of other Aeolian CA volcanoes. High Al and Sr requires that the phases hosting these elements did not crystallize to any significant degree during the evolutionary history of the magma. Since plagioclase is the only common phase of CA magmas which has partition coefficients higher than one for both Al and Sr, it was concluded that the magma crystallized outside the stability field of plagioclase (Francalanci and Santo 1993). This points to pressure conditions typical of lower crust.

The Filicudi cpxs have compositions similar to those of other Aeolian clinopyroxenes (Fig. 3, inset), i.e. diopside and augitic (Malgarotto et al. 1993). However,

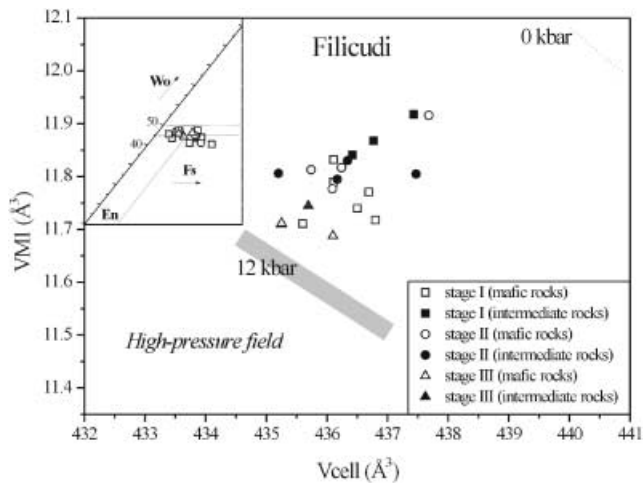


Fig. 3 Cell vs M1 site volumes for Filicudi clinopyroxenes (Malgarotto et al. 1993). For further explanation see legend of Fig. 2 and text

they show the smallest cell and VM1 values among Aeolian samples, ranging, respectively, from 435.20 to 437.68 Å³ and 11.740 to 11.919 Å³ (Fig. 3). These values are close to data from high-pressure residual cpx from spinel lherzolite nodules (Dal Negro et al. 1984). Furthermore, Vcell–VM1 plot does not show systematic variations among samples from the various stages, pointing to a generally high crystallization pressure; therefore, structural data on clinopyroxene from Filicudi provide support for the hypothesis of magma evolution in deep magma chambers, as suggested by geochemical studies.

Salina

The island of Salina was built up during three main stages of CA volcanic activity (Keller 1980; De Rosa et al. 1996). The earliest activity (430–127 ka) was mafic. This was followed by a second stage (100–66 ka) of basaltic to high-K andesitic and dacitic volcanism. The third stage (30–13 ka) consists of basalt to rhyolite, the latter marking the final explosive activity at Pollara, in the western end of the island.

As in the other Aeolian volcanoes, magma evolution at Salina has been the result of fractional crystallization, magma mixing and crustal assimilation. However, trace element data highlight significant time-related modifications of the geochemical signatures of mafic CA magmas (De Rosa et al. 1996; Gertisser and Keller 2000). Moreover, late-stage rhyolites display variable trace element characteristics, which indicate separate genetic processes for various batches of acid magma. Magma mixing played a key role at Salina (Calanchi et al. 1993) and is especially evident in the latest-stage acid rocks.

The Salina cpxs show large variations in Vcell and VM1 (Malgarotto et al. 1993). The smallest values are those of crystals extracted from the early lavas. Cell and M1 volumes increase up to values of 439 and 11.96 Å³

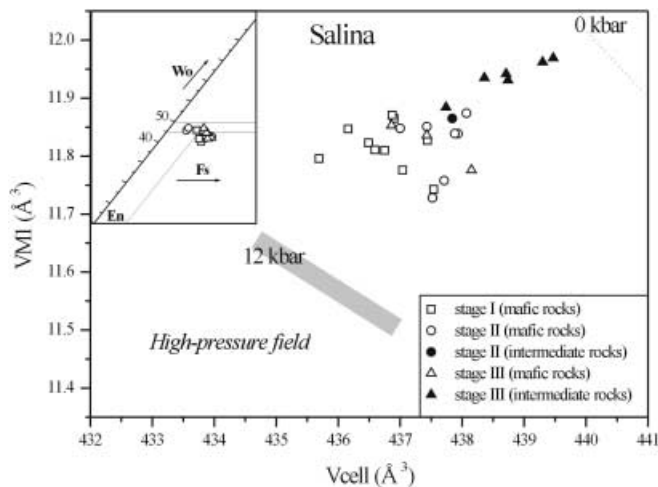


Fig. 4 Cell vs M1 site volumes for Salina clinopyroxenes (Malgarotto et al. 1993). For further explanation see legend of Fig. 2 and text

from second- to third-stage volcanics (Fig. 4). The cell parameters of pyroxenes from the early stages of activity are similar to those of Filicudi; therefore, high-pressure (ca. 6–8 kbar) can be inferred for the magma chamber in which they crystallized. The increase in Vcell and VM1 values in the younger rocks suggests a decrease of crystallization pressure, consistent with upward migration of the magma chambers with time. The increase in the degree of evolution of rocks with time may be an effect of such modifications in the plumbing system, i.e. magma mixing with primary melts may have prevailed during evolution of the deep reservoir, which was closer to the source and therefore more abundantly refilled with mafic magma. This kept the magma composition in the mafic range, which is typical of the first stage of activity. Later, upward migration of magma chambers was accompanied by decreased mafic magma input and increased fractional crystallization, with a consequent increase in the degree of magma evolution.

Vulcano

Vulcano is one of the two active volcanoes in the Aeolian Arc. Rock compositions range from basalt to rhyolite and from HKCA to SHO and KS. Several studies (e.g. Keller 1980; Castellet y Ballarat et al. 1982; De Astis et al. 1997; De Astis et al. 2000) recognize various stages of activity, from 120 ka to present. The oldest rocks (Primordial Vulcano) consist of HKCA basalts, basaltic andesites and andesites; these were followed by HKCA and SHO volcanism, mainly acid, of Lentia volcano. The latest eruptive stages gave rise to the active acid centre of La Fossa and to the historical leucite tephritic to trachytic centre of Vulcanello, which developed at the centre and on the northern margin of the Lentia caldera. Petrological and geochemical data show that potassium increases with time in mafic magma,

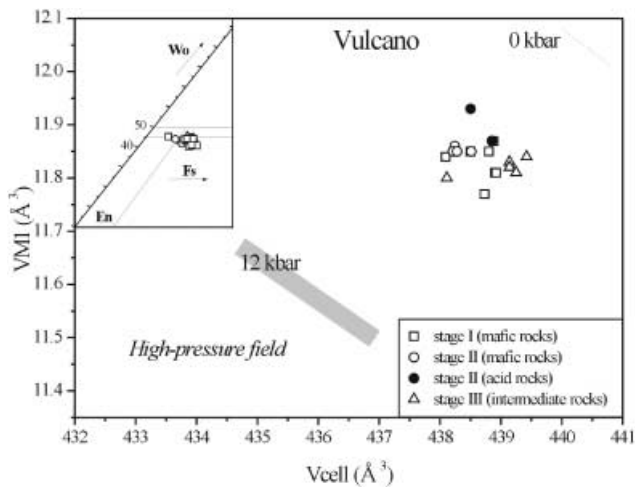


Fig. 5 Cell vs M1 site volumes for Vulcano clinopyroxenes (Faraone et al. 1988). For further explanation see legend of Fig. 2 and text

probably reflecting source characteristics; however, the increase in the degree of rock evolution with time is an effect of low-pressure processes (De Astis et al. 1997). The abundant rhyolitic rocks have been interpreted to derive from shoshonitic mafic and intermediate parents by fractional crystallization and small degrees of crustal assimilation (De Astis et al. 1997).

Structural parameters measured on clinopyroxenes from Vulcano (Faraone et al. 1988) show no significant variations of Vcell and VM1 from the oldest to the most recent volcanics (Fig. 5). A small increase in Vcell for cpx from the younger rocks may be related to the increased alkalinity of the parent rocks. Similar variations have been detected in other cpx extracted from tholeiitic to Na-alkaline rocks from several areas, e.g. East Africa (Dal Negro et al. 1986). Structural data point to relatively similar crystallization pressures throughout the evolution of Vulcano. Therefore, either polybaric crystallization did not occur or it may have taken place, but the differences in crystallization pressure were not large enough to be recorded by significant changes in clinopyroxene structures.

Lipari

Lipari is the largest island in the Aeolian Arc. The lowest exposed rocks are CA basaltic andesites and HKCA andesites. Dacites and rhyolites dominate later activity, which lasted until historical times. Several eruptive cycles have been described in Lipari. Rocks are characterized by a very steep increase in potassium passing from mafic to acid compositions. According to Crisci et al. (1991) and Barker (1987), this increase and the associated geochemical modifications cannot be ascribed entirely to fractional crystallization, but indicate a complex interplay of fractional crystallization, magma mixing and strong interactions with continental crust.

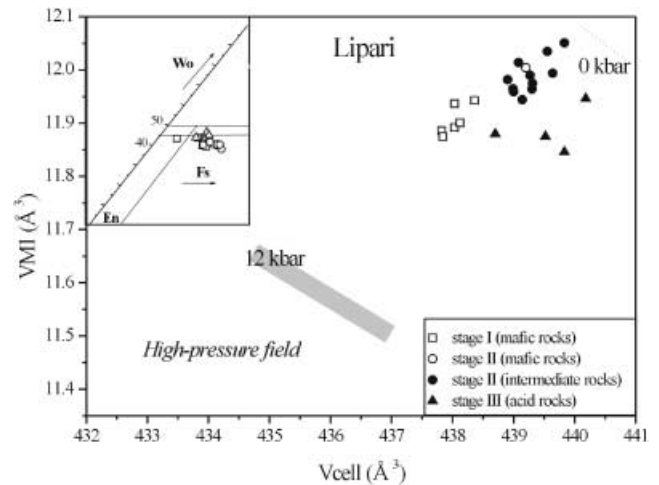


Fig. 6 Cell vs M1 site volumes for Lipari clinopyroxenes (Pasqual et al. 1998). For further explanation see legend of Fig. 2 and text

Structural parameters have been determined for cpx from volcanic rocks of various ages that we reduce to three stages (Pasqual et al. 1998). The Vcell and VM1 values increase with decreasing age (Fig. 6), indicating decreasing crystallization pressure with time. A different feature is typical of the xenocrystic cpx of the third-stage rhyolite, which is enriched in trivalent cations (Fe^{3+} , $^{\text{VI}}\text{Al}$) and Ca, causing a decrease in VM1 and a larger variation in Vcell, as compared with the other Lipari samples. This feature may reflect the complex processes (mixing and crustal assimilation) suggested for the evolution of these magmas.

Panarea

Panarea is the remnant of a larger structure, mostly hidden below sea level. Most of the exposed activity occurred between approximately 150 and 50 ka (Calanchi et al. 1999). Outcropping rocks are generally CA dacites and rhyolites, but a few CA and HKCA basic and intermediate rocks also occur, mainly as inclusions within acid products (Calanchi et al. 1999). The studied cpxs mostly come from dacites and rhyodacites. Geometric parameters increase slightly from oldest rocks to the youngest rhyolites, the latter having the largest cell volumes measured for Aeolian cpx samples (Nazzareni et al. in preparation); however, cell and M1 volumes are typical of low-pressure cpx, suggesting that the exposed Panarea magma evolved in a very shallow magma chamber (Fig. 7).

Stromboli

Stromboli is the northernmost island of the Aeolian Arc. It consists of a large variety of mafic and intermediate volcanic products ranging from CA to KS. Present activity is represented by shoshonitic basaltic lavas and strombolian scoriae. The exposed rocks at Stromboli are younger than 90 ka and were erupted during four main

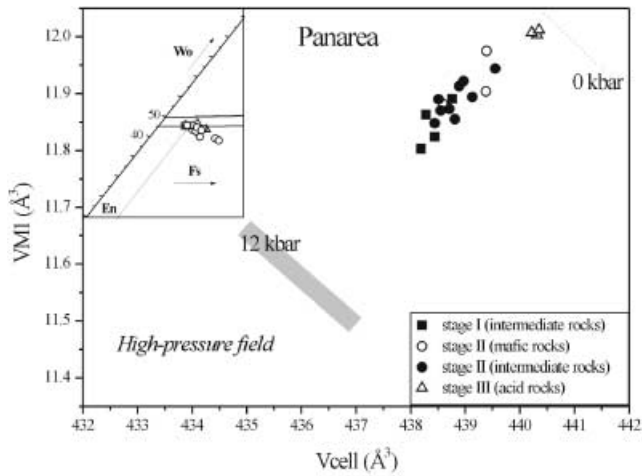


Fig. 7 Cell vs M1 site volumes for Panarea clinopyroxenes (S. Nazzareni et al. in preparation). For further explanation see legend of Fig. 2 and text

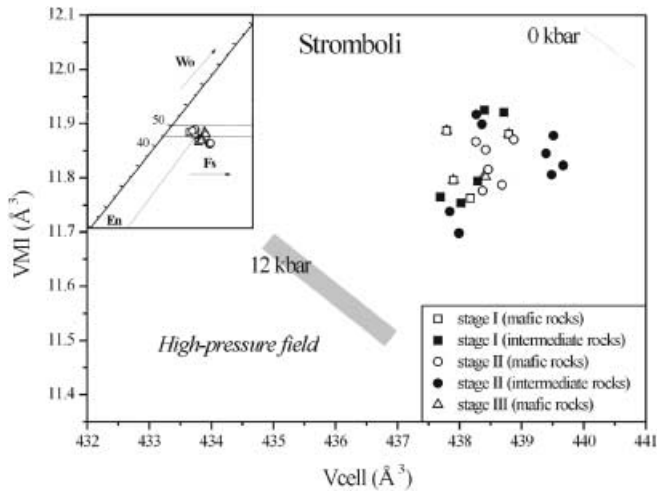


Fig. 8 Cell vs M1 site volumes for Stromboli clinopyroxenes (Pasqual et al. 1995). For further explanation see legend of Fig. 2 and text

stages of activity. The nearby CA neck of Strombolicchio is 204 ka years (Gillot and Keller 1993).

Clinopyroxenes at Stromboli range from diopside to augite (Clocchiatti 1981), and geometric parameters (Pasqual et al. 1995) point to shallow crystallization pressure (Fig. 8). There is no clear relationship between volcanic evolution stages and cpx geometrical parameters, nor have significant variations been found for the cpx from volcanics of different petrochemical affinities (CA–SHO–KS). Francalanci et al. (1989) suggested that the time-related changes in the petrological and geochemical characteristics of the Stromboli magmas are related to evolution in two separate magma chambers at different depths, which underwent different styles and degrees of assimilation and fractional crystallization and mixing with mafic CA magma. Our cpx data argue against a polibarc evolution of magma, supporting instead the alternative hypothesis that the geochemical and

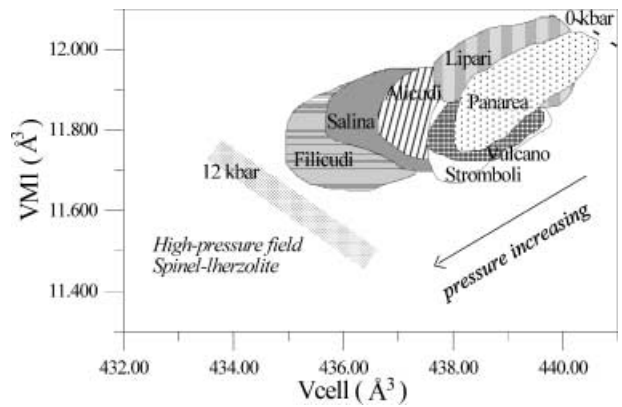


Fig. 9 Cell vs M1 site volumes for Aeolian clinopyroxenes. Geometric parameter variations are reported as *circled fields* for each island (Vulcano: Faraone et al. 1988; Salina and Filicudi: Malgarotto et al. 1993; Stromboli: Pasqual et al. 1995; Lipari: Pasqual et al. 1998; Alicudi: Nazzareni et al. 1998; Panarea: S. Nazzareni et al. in preparation)

petrological variations of Stromboli are related to source characteristics and/or processes.

Implications for evolution of the Aeolian Arc

Previous petrological and volcanological studies have shown that the Aeolian Arc is characterized by large-scale regional variations. The western islands of Alicudi, Filicudi and Salina have CA magmas with variable degrees of evolution but with the prevalence of intermediate and mafic compositions over acid rocks. In this sector, eruptions occurred either from central craters or from centres aligned E–W. No caldera structures have been identified on Salina or Filicudi, whereas two small caldera-forming events occurred at the end of the first and second stages of activity at Alicudi. The central islands of the Arc (Vulcano, Lipari, Panarea) reveal the most complex structures, with the remains of large calderas. Rock compositions range from calc-alkaline to shoshonitic and potassic. The degree of evolution is also very variable, and abundant acid rocks are associated with intermediate and mafic products. Lastly, the island of Stromboli consists of a wide variety of magmatic types, from CA to KS, but acid products are lacking. A caldera structure has been recognized in the older series.

Clinopyroxenes from various Aeolian rocks display comparable, diopside to augite composition; however, crystal chemistry data show important variations on a regional scale. This is shown in Fig. 9. High-pressure cpxs are restricted to the islands of Filicudi and Salina, whereas low-pressure crystals are typical of all the other islands. The absence of caldera structures in the islands with the lowest volumes of cell parameters for clinopyroxenes has important implications for models of the plumbing system of these volcanoes, inasmuch as both data provide evidence for the lack of large shallow-level magma chambers.

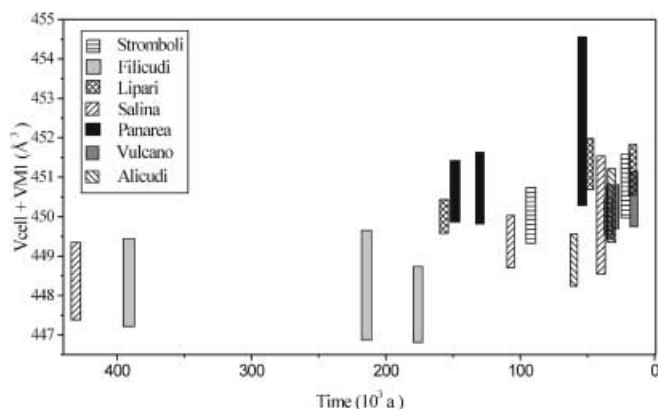


Fig. 10 Sum of V_{cell} and $VM1$ for Aeolian cpx plotted against age of host rocks. Crystallization pressure of cpx is linearly correlated to V_{cell} and $VM1$. The sum of these two parameters indicates pressure variations among Aeolian islands

Falsaperla et al. (1999) emphasize the Aeolian-Tindari Giardini tectonic line as a boundary between two different tectonic domains with distinct seismogenic features. Volcanism is extinct in the western arc, which has only shallow seismicity; instead, the eastern and central sectors host active volcanism and intermediate to deep seismicity. The higher crystallization pressure of Salina and Filicudi may therefore reflect a different stress regime in the western arc with respect to the eastern and central sectors; however, the low-pressure crystallization of the Alicudi cpx does not completely fit this model.

A much better fit is obtained if the time-related variations of cpx structural characteristics are related with the age of magma eruption (Fig. 10). Clinopyroxenes older than approximately 150 ka have cell parameters indicating higher crystallization pressure than younger ones, thus suggesting a relationship with the stage of arc evolution rather than with the areal distribution of its volcanoes. Crystal chemistry data may thus reveal a migration of magma chambers towards shallower levels with time. This may have regional significance, although additional data on old volcanic rocks (e.g. those dragged from seamounts) are necessary to confirm this hypothesis. The decrease in crystallization pressure with time and the shallowing of the magma chambers may be related to the structural evolution of the arc. Wang et al. (1989) suggested dramatic isotherms uprising during the last 6 Ma under the Aeolian Arc at a rate of 10 km/Ma. According to this model Esperança et al. (1992) suggested lithospheric and crustal thinning by uprising of asthenospheric mantle. The suggested regional upward migration of magma chambers is in agreement with such an evolution model. The magma reservoir, sited at any level within the crust, may have migrated upwards as a consequence of changes either in the crustal thickness of the arc basement and/or in the regional stress regime related to mantle doming beneath the arc.

Conclusion

The cell parameters of clinopyroxenes from the Aeolian Arc volcanics show important variations as a consequence of variable crystallization pressure. Crystals from the island of Filicudi show the smallest V_{cell} and $VM1$ values, indicating the highest crystallization pressure over the entire arc. Crystals separated from the lowest exposed rocks at Salina also have high-pressure structural characteristics, but the younger cpx appear to have crystallized at low pressure. Filicudi and lower Salina are the oldest exposed rocks in the Aeolian Arc. Shallow crystallization is inferred for cpx from the other islands, although some polybaric crystallization is recognized at Alicudi and Lipari. Cpx crystal chemistry data show a relation with time, since those with smaller cell and M1 volumes are all older than 150 ka. Low-pressure cpx are all younger than this age and are found in volcanoes with caldera depressions, indicating shallow magma chambers.

Crystal chemistry of clinopyroxenes together with volcanological and petrological data concur in indicating that the Aeolian Arc volcanoes underwent significant variations of their structure over time. Since cpx with the smallest cell and M1 volumes are all from rocks older than 150 ka, low-pressure cpx are all younger than this age and are found in volcanoes with caldera depressions, indicating shallow magma reservoir. Early stages, represented by Filicudi and the older Salina, were fed by deep magma chambers, and cpx geobarometry indicates pressures of 6–8 kbar, corresponding to deep crust. Younger magmas evolved in shallow reservoirs; these underwent collapse and experienced higher degrees of fractionation, with the development of huge amounts of rhyolites. Regional modifications of the plumbing system with time are probably related to mantle dynamics characterized by uprising of hot materials which caused arching, thinning of the arc and were accompanied by changes in the style of magma evolution.

Clinopyroxene structural data have shed light on these changes, providing significant constraints on the evolution of the Aeolian Arc. This emphasizes the importance of clinopyroxene crystal chemistry study for constructing models of the plumbing system of volcanoes.

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References

- Astis G de, La Volpe L, Peccerillo A, Civetta L (1997) Volcanological and petrological evolution of Vulcano island (Aeolian Arc, Southern Tyrrhenian sea). *J Geophys Res* 102:8021–8050
- Astis G de, Peccerillo A, Kempton PD, La Volpe L, Wu TW (2000) Transition from calcalkaline to potassium-rich magmatism in subduction environments: geochemical and Sr, Nd, Pb isotopic constraints from the Island of Vulcano (Aeolian arc). *Contrib Mineral Petrol* 139:684–703

- Barker DS (1987) Rhyolites contaminated with metapelite and gabbro, Lipari, Aeolian islands, Italy: products of lower crustal fusion or of assimilation plus fractional crystallization? *Contrib Mineral Petrol* 97:460–472
- Calanchi N, Rosa R de, Mazzuoli R, Rossi PL, Santacroce R, Ventura G (1993) Silicic magma entering a basaltic magma: eruptive dynamics and magma mixing. An example from Salina (Aeolian Island, Southern Tyrrhenian Sea). *Bull Volcanol* 55:504–522
- Calanchi N, Tranne CA, Lucchini F, Rossi PL, Villa IM (1999) Explanatory notes to the geological map (1:10,000) of Panarea and Basiluzzo islands (Aeolian arc, Italy). *Acta Vulcanol* 11:223–243
- Castellet y Ballarat G, Cresenzi R, Pompili A, Trigila R (1982) A petrological model on magma evolution of Vulcano eruptive complex (Aeolian islands, Italy). In: Reidel D (ed) *Comparative study of the planets*. Norwell, Massachusetts, pp 459–476
- Clocchiatti R (1981) La transition augite-diopside et les liquides silicates intra-cristallins dans les pyroclastes de l'activité actuelle du Stromboli: témoignages de la réinjection et du mélange magmatiques. *Bull Vulcanol* 44:339–357
- Crisci GM, de Rosa R, Esperança S, Mazzuoli R, Sonnino M (1991) Temporal evolution of a three component system: the island of Lipari (Aeolian Arc, southern Italy). *Bull Volcanol* 53:207–221
- Dal Negro A, Carbonin S, Molin GM, Cundari A, Piccirillo EM (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 Heidelberg New York, pp 117–150
- Dal Negro A, Carbonin S, Domeneghetti C, Molin GM, Cundari A, Piccirillo EM (1984) Crystal chemistry and evolution of the clinopyroxenes in a suite of high-pressure ultramafic rocks from the Newer Volcanics of Victoria, Australia. *Contrib Mineral Petrol* 86:221–229
- Dal Negro A, Cundari A, Piccirillo EM, Molin GM, Uliana D (1986) Distinct crystal-chemistry and site configuration of the clinopyroxene from alkali basaltic rocks. The Nyambeni clinopyroxene suite, Kenya. *Contrib Mineral Petrol* 92:35–43
- Dal Negro A, Molin GM, Salviulo G, Secco L, Cundari A, Piccirillo EM (1989) Crystal chemistry of clinopyroxenes and its petrogenetic significance: a new approach. In: Boriani A, Bonafede M, Piccardo GB, Vai GB (ed) *Int Lithosphere Prog Mid Term Conf Accademia Naz Lincei* 80:271–295
- Del Moro A, Gioncada A, Pinarelli L, Sbrana A, Joron JL (1998) Sr, Nd and Pb isotope evidence for open system evolution at Vulcano, Aeolian Arc, Italy. *Lithos* 43:81–106
- Ellam R M, Harmon RS (1990) Oxygen isotope constraints on the crustal contribution to the subduction-related magmatism of the Aeolian islands, Southern Italy. *J Volcanol Geotherm Res* 44:105–122
- Esperança S, Crisci GM, Rosa R de, Mazzuoli R (1992) The role of the crust in the magmatic evolution of the island of Lipari (Aeolian islands, Italy). *Contrib Mineral Petrol* 112:450–462
- Falsaperla S, Lanzafame G, Lomgo V, Spampinato S (1999) Regional stress field in the area of Stromboli (Italy): insights into structural data and crustal tectonic earthquakes. *J Volcanol Geotherm Res* 88:131–207
- Faraone D, Molin GM, Zanazzi PF (1988) Clinopyroxenes from Vulcano (Aeolian islands, Italy): crystal chemistry and cooling history. *Lithos* 22:113–126
- Francalanci L, Santo AP (1993) Magmatological evolution of Filicudi volcanoes, Aeolian Island, Italy: constraints from mineralogical, geochemical and isotopic data. *Acta Vulcanol* 3:203–228
- Francalanci L, Manetti P, Peccerillo A (1989) Volcanological and magmatological evolution of the Stromboli volcano (Aeolian Island): the role of fractional crystallization, magma mixing, crustal contamination and source heterogeneity. *Bull Volcanol* 51:355–378
- Gasparini C, Iannaccone G, Scandone P, Scarpa R (1982) Seismotectonics of the Calabrian Arc. *Tectonophysics* 84:267–286
- Gertisser R, Keller J (2000) From basalt to daeite: origin and evolution of the calc-alkaline series of Salina, Aeolian Arc, Italy. *Contrib Mineral Petrol* 139:607–626
- Gillot P-Y (1987) Histoire volcanique des Iles Eoliennes: arc insulaire ou complexe orogénique annulaire. *Doc Trav IGAL Paris* 11:35–42
- Gillot P-Y, Keller J (1993) Radiochronological dating of Stromboli. *Acta Vulcanol* 3:69–77
- Keller J (1980) The island of Vulcano. *Rend Soc Ital Mineral Petrol* 36:369–414
- Malgarotto C, Molin GM, Zanazzi PF (1993) Crystal chemistry of clinopyroxenes of Filicudi and Salina (Aeolian Island, Italy). *Geothermometry and barometry*. *Eur J Mineral* 5:915–923
- Manoli S, Molin GM (1988) Crystallographic procedures in the study of experimental rocks: X-ray single-crystal structure refinement of C2/c clinopyroxene from Lunar 74275 high-pressure experimental basalt. *Min Petrol* 39:187–200
- Morelli C, Giese P, Cassinis R, Colombi B, Guerra L, Luongo G, Scarascia S, Schutte KG (1975) Crustal structure of southern Italy. A seismic refraction profile between Puglia–Calabria–Sicily. *Boll Geof Teor Appl* 18:183–210
- Morimoto D (1988) Nomenclature of pyroxenes. *Mineral Mag* 52:535–550
- Nazzareni S, Molin GM, Peccerillo A, Zanazzi PF (1998) Structural and chemical variations in clinopyroxenes from the island of Alicudi (Aeolian Arc) and their implications for the conditions 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, Ulmer P (1998) Clinopyroxene geobarometry of magmatic rocks. Part 1. An expanded structural geobarometer for anhydrous and hydrous, basic and ultrabasic systems. *Contrib Mineral Petrol* 133:314–327
- Pasqual D, Molin GM, Zanazzi PF (1995) Crystal chemistry of Stromboli clinopyroxene: a comparison with analogues from other Aeolian islands (Italy). *Eur J Mineral* 7:369–378
- Pasqual D, Molin GM, Zanazzi PF, Crisci GM (1998) Clinopyroxene from Lipari: comparative crystal chemistry with analogues from other Aeolian islands (Italy). *Can Mineral* 36:97–105
- Peccerillo A, Taylor SR (1976) Geochemistry of Eocene calc-alkaline volcanic rocks from Kastamonu area, northern Turkey. *Contrib Mineral Petrol* 58:63–81
- Peccerillo A, Wu TW (1992) Evolution of calc-alkaline magmas in continental arc volcanics: evidence from Alicudi, Aeolian Arc (Southern Tyrrhenian Sea) Italy. *J Petrol* 33:1295–1315
- Peccerillo A, Kempton PD, Harmon RS, Wu TW, Santo AP, Boyce AJ, Tripodo A (1993) Petrological and geochemical characteristics of the Alicudi volcano, Aeolian Island Italy: implications for the magma genesis and evolution. *Acta Vulcanol* 3:235–250
- Rosa R de, Mazzuoli R, Ventura G (1996) Relationships between deformation and mixing processes in lava flows: a case study from Salina (Aeolian islands, Tyrrhenian Sea). *Bull Volcanol* 58:286–297
- Santo AP (2000) Volcanological and geological evolution of Filicudi (Aeolian islands, south Tyrrhenian Sea, Italy). *J Volcanol Geotherm Res* 96:79–101
- Santo AP, Chen Y, Clark AH, Farrar E, Tsegaye A (1995) $^{40}\text{Ar}/^{39}\text{Ar}$ ages of the Filicudi Island volcanics: implications for the volcanological history of the Aeolian Arc, Italy. *Acta Vulcanol* 7:13–18
- Wang CY, Hwang WT, Shi Y (1989) Thermal evolution of a rift basin: the Tyrrhenian Sea. *J Geophys Res* 94:3991–4006