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Sr-isotope and micro-isotope analyses of minerals: examples from some mafic alkaline potassic rocks

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ABSTRACT. — Evidence suggests that most silicic and mafic magmas evolve through open-system processes in which magma mixing and crustal contamination play an important role. In-situ Srisotope analyses help to decode the evolutionary history of silicic and mafic magmas that have been variously modified from their primary compositions.

In-situ Sr isotope data on single minerals and separated bulk-minerals and rocks were acquired from two mafic alkaline potassic rocks erupted from the Pleistocene Vico volcano, central Italy. The rocks belong to high-potassium rock series (tephriphonolite) and transitional series (olivine-latite).

The higher ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ of the clinopyroxene phenocrysts (${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.71093$) with respect to sanidine core (${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.71063$) enclosed in the tephri-phonolite may be explained by magma mixing between a less Sr radiogenic liquid (${}^{87}\text{Sr}/{}^{86}\text{Sr} \sim 0.7106$), from which the sanidine megacryst crystallised, and a more radiogenic melt (${}^{87}\text{Sr}/{}^{86}\text{Sr} \sim 0.7109$) from which the clinopyroxene crystallised. Before magma mixing the Sr isotope composition of the sanidine megacryst-bearing liquid changed, due to crustal contamination, as recorded by core-rim

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⁸⁷Sr/⁸⁶Sr variation (⁸⁷Sr/⁸⁶Sr from 0.71063 to 0.71077). Magma mixing of more distinct radiogenic Sr end-members is also possible.

The olivine-latite primitive magma (${}^{87}Sr/{}^{86}Sr \sim 0.7101$) increased its Sr-isotope composition (${}^{87}Sr/{}^{86}Sr \sim 0.7103-0.7107$) by crustal contamination and then decreased it by recharge with a similar Sr radiogenic mafic magma (${}^{87}Sr/{}^{86}Sr \sim 0.7101$). This model accounts for the higher ${}^{87}Sr/{}^{86}Sr = 0.7101$). This model accounts for the higher ${}^{87}Sr/{}^{86}Sr = 0.71067-0.71065$) than the clinopyroxene (${}^{87}Sr/{}^{86}Sr = 0.71032$) and for the less Sr radiogenic composition of the bulk rock (${}^{87}Sr/{}^{86}Sr = 0.71014$). However, both sanidine megacrysts and clinopyroxene may have crystallised from different magmas, implying a further mixing event.

The solid-liquid partition coefficient of Sr for sanidine suggests that the sanidine megacrysts crystallised from a mafic latitic melt. The similarity of Sr-isotope ratios in the cores of sanidine megacrysts ($core^{87}Sr/^{86}Sr$ in tephri-phonolite = 0.71063, core $^{87}Sr/^{86}Sr$ in olivine-latite = 0.71067) entrained in mafic and primitive potassic rocks belonging to distinct rock series suggests that they are co-genetic.

RIASSUNTO. — La maggior parte dei magmi subisce, nella camera magmatica, processi di evoluzione in un «sistema aperto» attraverso il mescolamento tra magmi e l'assimilazione crostale. G. PERINI

Di recente sono state messe a punto tecniche che consentono la misura dei rapporti isotopici dello Sr in-situ nei minerali. Grazie a queste tecniche, unitamente alle analisi isotopiche sulle rocce totali, è possibile decodificare con dettaglio i processi di differenziazione dei magmi che modificano la loro composizione rispetto a quella dei fusi magmatici iniziali.

Determinazioni in-situ del rapporto ⁸⁷Sr/⁸⁶Sr su singoli minerali (megacristalli di sanidino), dello stesso rapporto su minerali separati (clinopirosseni) e sulla roccia totale sono stati effetuati su due rocce femiche alcalino potassiche provenienti dal vulcano di Vico (Italia centrale) di età Pleistocenica. Le rocce appartengono a due distinte serie evolutive: una fonolitica (tefrite) a quella denominata alta in potassio, l'altra (olivin-latite) a quella denominata transizionale.

Il più alto valore del rapporto ⁸⁷Sr/⁸⁶Sr nei clinopirosseni separati (87Sr/86Sr = 0.71093) rispetto quello nel nucleo del sanidino (${}^{87}Sr/{}^{86}Sr = 0.71063$) presenti nella tefri-fonolite può essere spiegato attraverso un mescolamento tra un liquido meno radiogenico (87Sr/86Sr~0,7106), dal quale il megacristallo di sanidino proviene, ed uno più radiogenico (87Sr/86Sr~0,7109), dal quale i clinopirosseni hanno cristallizzato. Prima del mescolamento tra questi due liquidi, il magma dal quale il megacristallo di sanidino cristallizzava ha cambiato la sua composizione isotopica mediante assimilazione crostale come è indicato dall'aumento dal nucleo al bordo del 87Sr/86Sr (87Sr/86Sr da 0,71063 a 0,71077). Tuttavia, un modello che prevede il mescolamento tra più componenti non può essere escluso.

In un magma primitivo olivin-latitico (⁸⁷Sr/⁸⁶Sr ~0,7101) il rapporto isotopico dello Sr è aumentato (⁸⁷Sr/⁸⁶Sr~0,7107) per assimilazione crostale e, successivamente è diminuito a seguito dell'arrivo nella camera magmatica di nuovo magma femico (⁸⁷Sr/⁸⁶Sr ~0,7101). Questo modello può spiegare il più alto rapporto ⁸⁷Sr/⁸⁶Sr del megacristallo di sanidino (⁸⁷Sr/⁸⁶Sr = 0,71067-0,71065) rispetto a quello dei clinopirosseni (⁸⁷Sr/⁸⁶Sr = 0,71032) e la più bassa concentrazione di Sr radiogenico nella roccia totale (⁸⁷Sr/⁸⁶Sr = 0,71014). Tuttavia il megacristallo di sanidino e i clinopirosseni possono aver cristallizzato da magmi distinti e quindi non è da escludere un'ulteriore processo di mescolamento.

Il coefficiente di ripartizione solido-liquido dello Sr per il sanidino suggerisce che questo può aver cristallizzato da un magma latitico.

La similitudine dei rapporti isotopici dello Sr determinati al nucleo dei megacristalli di sanidino (nucleo 87 Sr/ 86 Sr per la tefri-phonolite = 0,71063, nucleo 87 Sr/ 86 Sr per l'olivin-latite = 0,71067) inclusi nelle due rocce femiche vicane appartenenti a distinte serie magmatiche suggerisce che questi siano co-genetici.

KEY WORDS: Sr-isotope data, in-situ isotope data, sanidine meagcryst, magma differentiation.

INTRODUCTION

The differentiation of primary magmas generally involves open-system processes in which magma mixing and crustal contamination play a role. These high level processes have been identified in mafic (Arndt and Jenner, 1986; Devey and Cox, 1987; Tepley et al., 1999) and silicic magmas (Feldstein et al., 1994; Umino and Horio, 1998; Knesel et al., 1999) from their chemical and isotopic variations. A combination of these differentiation processes have been documented in rock series (Francalanci et al., 1989; Cioni et al., 1996; Cribb and Barton, 1996) and also in single rock samples (Knesel et al., 1999; Tepley et al., 1999), indicating that, during storage in crustal reservoirs, the chemical and isotopic compositions of magmas vary considerably with time. Recent studies on decoding the evolution of magmatic systems have focused on isotopic variations within single minerals (in-situ data), together with bulk rock and bulk mineral isotopic compositions (Davies et al., 1994; Feldstein et al., 1994; Davidson and Tepley, 1997; Valley et al., 1998; Knesel et al., 1999; Tepley et al., 1999). Generally, the single mineral grains record the history of the magma where they grew and the processes (e.g. crustal contamination, magma mixing) that occurred at different stages of magma evolution. Perturbations of pressure, temperature and volatile content can generate crystals with disequilibrium textures. Textural relationships between minerals and their host melt are not conclusive in recognising an open-system magmatic evolution. Furthermore, the traditional geochemical approach of bulk-rock analyses only gives the geochemical state (major, trace elements and isotope compositions) of the magma at the time of eruption.

In situ Sr-isotope data have been used to constrain the evolutionary history of silicic magmas (Davies *et al.*, 1994; Feldstein *et al.*, 1994; Davidson and Tepley, 1997; Knesel *et al.*, 1999; Tepley *et al.*, 1999) in which minerals (plagioclase and sanidine) with detectable Sr isotope ratios are abundant. However, when a spread of liquid compositions is lacking, the history of a batch of primitive magma is better unravelled by Sr isotope analyses of single mineral phases and in-situ Sr-isotope data.

In Italy, Neogene-Quaternary volcanoes have erupted large volumes of alkaline potassic magmas with different end-member affinities (Conticelli and Peccerillo, 1992). The genesis of the various potassic parental magma series remains controversial. Mantle heterogeneity has been recognised by several authors (Rogers et al., 1985; Conticelli and Peccerillo, 1992; D'Antonio et al., 1996; Peccerillo, 1999, and references therein), and «low pressure processes» have also been invoked (Conticelli, 1998). For this reason, decoding the processes which affected primitive potassic magmas is of primary importance to constrain the petrogenesis of Italian Neogene-Quaternary magmatism.

Sanidine megacrysts have been observed in a number of Italian mafic (and primitive) potassic rocks belonging to distinct series wich do not seem to be genetically related by any «low pressure processes» (Mattias and Ventriglia, 1970; Holm, 1982; Poli *et al.*, 1984; Conticelli *et al.*, 1991; Perini *et al.*, 1997). Rocks containing sanidine megacrysts have been erupted from many volcanoes (Vulsini volcanic complex, Vico volcano, Monte Cimino volcanic complex) in central Italy (fig. 1).

The aim of this paper is to give examples of how Sr-isotope data on minerals, obtained both on whole separated crystals and in-situ, may help to elucidate problems regarding the origin of primitive potassic rocks. These data help to track the differentiation of the magmas in which sanidine megacrysts occur and to a possible genetic link between sanidine megacrysts incorporated by different rock types.

Sr-isotope data were collected from two mafic potassic alkaline rocks, representative of the magmas from the Vico volcano, central Italy (fig. 1). The rocks belong to distinct rock series (high-potassium and transitional series) with tephri-phonolite and olivine-latite compositions respectively. Sr-isotope ratios were determined on bulk rock and separated clinopyroxene phenocrysts, and Sr-microisotope data were also recorded from sanidine megacrysts.

PETROLOGICAL BACKGROUND

The primitive magmas of each series are distinguished on the basis of their mineralogy, degree of silica saturation, enrichment in incompatible elements, and radiogenic Sr contents (Peccerillo and Manetti, 1985; Conticelli and Peccerillo, 1992; D'Antonio et al., 1996 and references therein). In several volcanoes, silica-saturated (potassium, transitional and lamproite) and silicaundersaturated (high-potassium) magma series erupted together over a short time span (Civetta et al., 1984; Peccerillo and Manetti, 1985; Conticelli et al., 1991, 1997; Di Battistini et al., 1998). The parental magmas of each series are inferred to have been generated in the upper mantle, which was variably enriched in incompatible trace elements and radiogenic Sr (Rogers et al., 1985; Civetta et al., 1989; Conticelli and Peccerillo, 1992; D'Antonio et al., 1999; Peccerillo, 1999). However, it has recently been pointed out that there is also evidence for «low pressure processes», as the lamproites have been related to transitional suites via crustal contamination (Conticelli, 1998). Generally, geochemical modeling indicates that primitive rocks of the silicasaturated series are not genetically linked by



Fig. 1 - Sketch map, with location of Vico volcano.

crustal contamination associated with fractional crystallisation (AFC), magma mixing, or other more complex processes with primitive rocks of the silica-undersaturated rock series (Civetta *et al.*, 1984; Conticelli *et al.*, 1991). Mantle heterogeneity explains most of the geochemical variability of primitive potassic rocks, although questions remain regarding the differentiation processes affecting the most primitive end-members of each suite.

Vico is a relatively small volcano, which discharged mafic magma of the high-potassium series and primitive magma of the transitional series (Perini *et al.*, 1997). Generally, primitive rocks of the high-potassium series contain clinopyroxene and olivine, with leucite and plagioclase in the intermediate members, and sanidine and phlogopite in the most evolved rocks (Peccerillo and Manetti, 1985). Abundant olivine phenocrysts together with clinopyroxene, plagioclase and sanidine represent the main mineral assemblage of the primitive rocks of the transitional series (Conticelli and Peccerillo, 1992). The highpotassium rock series vary in composition from phono-tephrite to phonolite, whereas the rocks of the transitional series vary from shoshonite to latite (Le Bas et al., 1992). The Mg-value $(Mg-v = 100*Mg/(Mg + 0.85*Fe_{tot})$. Frey et al., 1978) >65, generally indicates the primitive character of potassic rocks (Peccerillo et al., 1988; Conticelli and Peccerillo, 1992; Foley, 1992), sometimes associated with high silica contents (e.g. >55 wt% SiO₂).

The ⁸⁷Sr/⁸⁶Sr isotope ratios of the primitive rocks of the high-potassium series lie in the range 0.709-0.711 (Conticelli and Peccerillo, 1992; D'Antonio *et al.*, 1996; Conticelli *et al.*, 1997; Di Battistini *et al.*, 1998); those of transitional primitive rocks are more variable ⁸⁷Sr/⁸⁶Sr: 0.710-0714 (Conticelli and Peccerillo, 1992, and references therein).

HOST ROCK PETROGRAPHY AND CHEMISTRY

Clinopyroxene phenocrysts and sanidine megacrysts were sampled from two lava flows of Vico volcano. Based on the IUGS classification (Le Bas et al., 1992) and on mineralogical and chemical data (Perini, 1997), these rock samples are classified as tephriphonolite (VCO 99) and olivine-latite (VCO 155) (fig. 2). The tephri-phonolite is a mafic rock (Mg-v = 59) belonging to the highpotassium series; the olivine-latite is more primitive (Mg-v = 72) and belongs to the transitional series (fig. 2; Perini, 1997). These lavas represent some of the least evolved rocks which erupted from Vico. There is no age determination on the samples, but stratigraphic reconstruction suggests that the tephriphonolite erupted between 0.305 and 0.250 Ma and the olivine-latite between 0.138 and 0.095 Ma (Perini et al., 1997, and references therein).



Fig. 2 – Total alkali - silica classification diagram (LE BAS *et al.*, 1992) for analysed samples from Vico volcano. Vico rock data are from PERINI (1997). Analyses are reported on water-free basis.

The tephri-phonolite is highly porphyritic, with a seriate texture (porphyritic index = P.I.=30 vol.%; all modal abundances are reported in vol.%). The phenocryst assemblage is composed of clinopyroxene (36%), leucite (33%), plagioclase (6%) and olivine (1%). Groundmass phases include sanidine and phlogopite in addition to the minerals present as phenocrysts. Ti-magnetite and apatite are present as accessory minerals. The phenocrysts generally occur as euhedral to subhedral crystals. Clinopyroxene and plagioclase crystals are frequently enclosed in leucite, suggesting that they crystallised before this mineral phase. A similar crystallisation sequence has been observed in intermediate rocks of the high-potassium series elsewhere (Peccerillo and Manetti, 1985). Evidence of magma mixing in the studied rocks, and in other tephri-phonolites from Vico, is suggested by the presence of some olivine crystals not in equilibrium with the host rock and reverse zoning of clinopyroxene phenocrysts (Perini, 1997).

The olivine-latite is less porphyritic, with a seriate texture (P.I. = 13%), containing clinopyroxene (44%), olivine (40%) and plagioclase (12%) phenocrysts, which are present also in the groundmass together with sanidine crystals. Ti-magnetite and apatite are accessory phases. The olivine and clinopyroxene phenocrysts are euhedral, but the plagioclase is anhedral.

The sanidine megacrysts occurring in the tephri-phonolite and olivine-latite are 20 to 25 mm in length and 5 to 6 mm in width. They are zoned, and always subhedral in shape; none have fragmented edges (fig. 3a, b). No sanidine megacryst-bearing xenoliths have been observed in the studied samples or in other similar rocks from Vico.

ANALYTICAL TECHNIQUES

Sr-isotope analyses on the two selected rock samples where carried out on bulk-rock, whole separated minerals (clinopyroxene) and on



Fig. 3a, b – Microphotographs of tephri-phonolite (a) and olivine-latite (b) samples, showing textural characteristics of sanidine megacrysts.

different sectors of single megacryst grains (sanidine). Chemical analyses of the various mineral phases were also carried out.

Mineral separation was carried out using conventional magnetic techniques. Individual crystals were handpicked under a binocular microscope. To remove glass and inclusions from the surface of the grains, these were cleaned for 30 minutes in a 2.5N HCl ultrasonic bath and then rinsed with ultra high quality water. Some of the separated mineral grains were then embedded in polyester resin and polished for microprobe analyses. Polished chips of rocks with sanidine megacrysts were also obtained for microdrilling and microprobe analyses.

Chemical analyses were performed by a JEOL JXA-8600 electron microprobe at the «Centro Studi Minerogenesi e Geochimica Applicata» of the C.N.R. at the Dipartimento di Scienze della Terra (University of Florence), equipped with four WDS spectrometers integrated with an EDS system. Operating conditions were 15 kV accelerating voltage and 10 nA beam current. Variable counting times (see Vaggelli et al., 1999) were used in order to avoid alkali loss during the analytical routine and to improve statistics for minor and trace elements. Data were corrected using Bence and Albee's (1968) method. Precision and accuracy for major and minor elements in mineral phases agree with those reported by Vaggelli et al. (1999).

Diamond-plated tips with a diameter of 0.51 mm were used to drill the cores and rims of the sanidine megacrysts, following the procedure described by Tepley *et al.* (1994) and Davidson *et al.* (1998). Sr concentrations, in the sanidine crystals from potassic alkaline rocks, are generally greater than 100 ppm (Cundari, 1979; Baldridge *et al.*, 1981; Conticelli *et al.*, 1997) therefore drilling was done to ensure that a minimum amount of Sr (>5 ng) was recovered. This amount was required for precise isotope analyses. The amount of Sr effectively loaded on the filament was always equal to or greater than 40 ng.

Drops of ultra high quality water were added to the samples to ease drilling and crystal powder collection by creating a slurry. Samples were collected by a pipette and put an aluminium container to dry down on a hot plate. The amount of powder produced by the micro-drilling was always <0.25 mg. After drilling, the polished rock chips were cleaned in ultra high quality water in an ultrasonic shaker and then rinsed in a stream of water. Subsequently, the drilled holes were inspected under a binocular microscope for drilling residue and the presence of mineral inclusions. None of the megacryst drills contained mineral inclusions in their walls.

Microsamples were dissolved, and Rb and Sr separated in small chromatographic columns using Eichrom Sr-specific resin (Sr.SpecTM). Sr-isotope analyses were performed at the Department of Earth and Space Sciences of the University of California (Los Angeles) on a multicollector VG Sector mass spectrometer. 87Sr/86Sr ratios for separated crystals and micro drilling samples were measured in a dynamic peak switching mode at 3V (88Sr). 86Sr/88Sr ratios were normalised to 0.1194 for mass fractionation. All errors reported for within run precision are 2 SE (2 standard error). During the period of analyses NBS 987 standard vielded an 87Sr/86Sr value of 0.710240 ±15 (N = 2). Rb isotopic composition was measured in a static mode at 0.2V (87Rb).

Rb and Sr concentrations on mineral phases were measured by isotope dilution techniques. A mixed ⁸⁷Rb(>99%)-⁸⁴Sr(>99%) spike with an Rb/Sr ratio <1 was added to sample aliquots. Accuracy on Rb and Sr concentrations was 1% and 0.5% respectively. During sample measurements, blanks were ≤0.31 ng for Sr and ≤14.0 ng for Rb; no blank corrections were made.

RESULTS

Separated clinopyroxene crystals from the tephri-phonolite and olivine-latite are mainly diopside, but some augitic compositions were also analysed in the tephri-phonolite (fig. 4). Crystals from the tephri-phonolite have slightly

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variable Mg# (Mg/[Mg + Fe²⁺]) ranging from 0.85 to 0.72, whereas those from the olivinelatite have homogeneous values between 0.89 and 0.84 (Table 1). Fig. 4 also shows compositional fields for clinopyroxene from Vico rocks with similar tephri-phonolitic and olivine-latitic compositions and common zoning trends. The analysed clinopyroxene crystals are not zoned, althrough, in other tephri-phonolites and olivine-latites from Vico volcano normal, inverse and reverse zonings have been detected (fig. 4; Perini, 1997).

The compositions of the sanidine megacrysts hosted in the two rock samples are shown in fig. 5 and Table 2. They record limited core-torim compositional variations in terms of orthoclase contents (mol%), which are within the ranges of 76 (core)-75 (rim) in the megacrysts from the tephri-phonolite and 77 (core)-76 (rim) in the megacrysts from the



Fig. 4 – Wo - En - Fs classification diagram (MORIMOTO, 1989) of clinopyroxene crystals separated from tephriphonolite (VCO 99) and olivine-latite (VCO 155) from Vico volcano. Shaded area: composition of clinopyroxene crystals from a sanidine-meagacryst-bearing tephriphonolite, similar in composition to VCO 99, and from other olivine-latitic samples similar to VCO 155. Clinopyroxene data from other Vico samples are from PERINI (1997). Arrows: main enstatite and wollastonite variations observed in other samples.

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Analyses of separated clinopyroxene crystals in tephri-phonolite (VCO 99) and olivine-latite (VCO 155) samples from Vico volcano.

Sample			VCO 99)				VCO 15	5	
Analysis	4	5	6	8	9	1	2	3	4	5
SiO ₂	50.4	51.5	49.0	50.0	50.5	53.1	52.7	53.1	51.8	52.0
TiO ₂	0.52	0.53	0.71	0.86	0.71	0.35	0.41	0.40	0.53	0.41
Al_2O_3	4.15	3.26	4.80	3.89	4.57	2.74	2.40	3.06	4.08	3.59
Cr_2O_3	bdl	0.11	0.02	0.04	0.12	0.12	0.03	0.74	0.55	0.32
Fe ₂ O ₃	3.94	3.11	4.38	3.94	2.84	0.93	3.37	1.13	2.35	3.22
FeO	2.37	2.15	4.85	5.91	2.51	3.63	0.97	2.61	2.06	2.42
MnO	0.11	0.15	0.23	0.22	0.10	0.12	0.03	0.09	0.10	0.10
MgO	15.2	16.1	13.1	14.1	15.6	16.4	17.0	17.2	16.4	16.1
CaO	23.7	23.9	22.9	21.7	23.8	23.5	24.2	23.0	23.3	23.7
Na ₂ O	0.15	0.11	0.33	0.32	0.02	0.15	0.25	0.21	0.26	0.23
Total	100.5	100.8	100.3	100.9	100.8	101.1	101.4	101.5	101.5	102.0
En	32.7	44.5	37.8	40.1	43.9	45.7	46.3	48.0	46.1	44.5
Wo	47.8	47.5	47.6	44.4	48.0	47.1	47.5	46.2	47.2	47.1
Fe	9.5	7.9	14.6	15.5	8.1	7.2	6.2	5.8	6.7	8.4
Mg#	0.82	0.85	0.72	0.72	0.84	0.86	0.88	0.89	0.87	0.84
En = enstat	ite, Wo = w	vollastonite;	Fe = ferros	silite; Mg# =	= Mg/(Mg+)	Fe2+). Fe3+ is	s evaluated	on stoichio	metry.	

TABLE 2

Analyses of sanidine megacrysts in tephri-phonolite (VCO 99) and olivine-latite (VCO 155) from Vico volcano.

Sample	V	CO 99	VC	VCO 155		
Analysis	1	2	1	2		
	core	rim	core	rim		
SiO ₂	64.2	63.3	64.1	65.6		
TiO ₂	0.12	0.10	bdl	bdl		
$Al_2 \tilde{O}_3$	18.9	19.4	18.2	18.8		
Fe ₂ O ₃	0.29	0.17	0.28	0.21		
CaO	0.54	0.76	0.43	0.45		
Na ₂ O	2.34	2.34	2.27	2.27		
K ₂ Ō	13.0	12.8	13.0	12.6		
SrO	0.20	0.31	0.14	0.27		
BaO	0.10	0.34	0.15	0.35		
Total	99.7	99.5	98.6	100.6		
Or	76.3	74.9	77.2	76.2		
Cn	0.2	0.6	0.3	0.7		

bdl = below detection limit; Or = orthoclase, Cn = celsian. Analyses from cores and rims performed close to microdrillings.

olivine-latite (Table 2; fig. 5). Consistent BaO and SrO core-to-rim variations (wt%) were detected in both sanidine megacrysts (Table 2). Fig. 5 shows the compositional field of feldspars from Vico rocks similar to the tephriphonolite and olivine-latite. Only sanidine compositions mantling the plagioclase in the sanidine-megacryst-bearing tephri-phonolite are shown in fig. 5 (Perini, 1997).

Mineral chemistry data on all mineral phases in tephri-phonolite and olivine-latite rocks from Vico are presented elsewhere (Perini and Conticelli, submitted).

The bulk-rock Sr-isotope composition of the tephri-phonolite (87 Sr/ 86 Sr = 0.711158±10) reveals that the separated clinopyroxene phenocrysts and sanidine megacryst are not in isotopic equilibrium with their host, being less radiogenic than the bulk rock (fig. 6*a*; Table 3). The drilled megacryst shows, significant isotopic heterogeneity from core to rim, the core is less radiogenic (87 Sr/ 86 Sr = 0.710629±12) than the rim (87 Sr/ 86 Sr = 0.710771±12). The Sr-isotope ratio of



Fig. 5 – Ab - An - Or classification diagram of sanidine megacrysts of tephri-phonolite (VCO 99) and olivine-latite (VCO 155) from Vico volcano. Shaded area: the composition of feldspar crystals from a sanidine-meagacryst-bearing tephriphonolite, similar in composition to VCO 99, and from other olivine-latitic samples similar to VCO 155. Feldspar data from other Vico samples are from PERINI (1997).



Fig. 6*a*, b - Sr contents *vs* age-corrected ⁸⁷Sr/⁸⁶Sr ratios (Sr_i) of bulk rocks, separated clinopyroxene crystals and sanidine megacrysts of *a*) tephri-phonolite and *b*) olivine-latite. Sr_i data of tephri-phonolite are calculated back to 0.3 Ma, those of olivine-latite to 0.1 Ma. Sr data of bulk rock are from PERINI (1997).

TABLE 3

Measured Sr isotope ratios of bulk rock, separated clinopyroxene and sanidine megacrysts collected by micro-drilling.

		⁸⁷ Sr/ ⁸⁶ Sr	Sr _i	Rb	Sr	Rb/Sr
Tephri-phonolite (VCO 99)	bulk rock	0.711158±10	0.71158	493	1339	0.37
Separated minerals:	clinopyroxene crystals	0.710933±9	0.71093	11	227	0.05
Micro-drilling:	sanidine core sanidine rim	0.710629±12 0.710771±12	0.71062 0.71077	171 172	542 1236	0.32 0.14
Olivine-latite (VCO 155)	bulk rock	0.710136±9	0.71013	423	601	0.70
Separated minerals:	clinopyroxene crystals	0.710321±14	0.71032	4	199	0.02
Micro-drilling:	sanidine core	0.710665±10	0.71066	449	1644	0.27
Aicro-drilling: san	sanidine rim	0.710650±12	0.71065	439	1877	0.23

 Sr_i = Initial ⁸⁷Sr/⁸⁶Sr adjusted to 0.3 Ma for tephri-phonolite and to 0.1 Ma for olivine-latite. Rb and Sr concentrations of mineral phases have been analysed by isotope dilution. Rb and Sr data of bulk rock are from Perini, 1997.

clinopyroxene crystals $({}^{87}Sr/{}^{86}Sr = 0.710933 \pm 9)$ is higher than that of the sanidine megacryst rim and significantly lower than that of the bulk rock.

Similarly the mineral phases from the olivine-latite are not in isotopic equilibrium with their host rock. Which is less radiogenic (87 Sr/ 86 Sr = 0.710136±9) than the separated clinopyroxene phenocrysts (87 Sr/ 86 Sr = 0.710321±14) and sanidine megacryst, which is isotopically homogeneous (core 87 Sr/ 86 Sr = 0.710665±10, rim 87 Sr/ 86 Sr = 0.710650±12) (Table 3; fig. 6).

DISCUSSION

Some general observations on sanidine megacrysts must be made before discussing the isotope data and their inferences on the evolutionary history of the studied mafic alkaline potassic magmas.

Sanidine phenocrysts in phonolites of the high-potassium series and in primitive latitic rocks of the transitional series are in equilibrium (Peccerilllo and Manetti, 1985; Conticelli and Peccerillo, 1992). In tephriphonolitic rocks of the high-potassium series, sanidine is present only in the groundmass phases thus indicating that it is not a nearliquidus phase (Peccerillo and Manetti, 1985). Using the Sr composition from the core of the sanidine megacrysts enclosed in the tephriphonolite and olivine-latite, and a range of solid-liquid partition coefficients (K_D) for Sr from the literature (K_{DSr} = 2.3-5.3, Larsen, 1979; Francalanci et al., 1987), the Sr content of the liquids were calculated (Table 2). According to this calculation, the parental magma of the megacryst enclosed in the tephriphonolite should have Sr varying from 223 to 515 ppm, and the megacryst enclosed in the olivine-latite from 319 to 735 ppm (fig. 7). Considering the Sr concentration of all Vico rocks, the melt source of the sanidine megacrysts should have a latitic, trachytic or phonolitic composition (fig. 7).

Petrological and geochemical evidence

suggests that the sanidine megacrysts in the tephri-phonolite did not crystallise from a tephri-phonolitic liquid, but that their presence is due to mixing/mingling processes. Interaction between various magmas in tephriphonolite evolutionary history is supported by mineral chemistry data (see HOST ROCK PETROGRAPHY and CHEMISTRY). The sanidine megacryst enclosed in the olivine-latite may have crystallised from a latitic liquid.

Sanidine megacrysts in the tephri-phonolite and olivine-latite from Vico volcano are zoned with respect to K, Ba and Sr contents (Table 2). Megacrysts are commonly found in mafic alkaline rocks from continental volcanic provinces and are often associated with mantle or cumulitic xenoliths. In some cases, they are interpreted as fragments of high-pressure xenoliths (Larsen, 1981; Righter and Carmichael, 1993, and references therein). The absence of xenoliths in the studied samples, the morphology (unbroken edges), and the nonhomogeneous compositions of the megacrysts of the Vico rocks all suggest that they do not



Fig. 7 – Mg-v values vs Sr contents (ppm) for Vico rocks. Light shaded area indicates range of Sr composition for parental magma of sanidine megacrysts in tephri-phonolite; dark shaded coloured area indicates range of Sr composition for parental magma of sanidine megacrysts in olivine-latite. Data from PERINI (1997).

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come from the disaggregation of xenoliths, but were crystallised in a melt before being trapped in a magma en route to the surface.

Evolution of tephri-phonolite

The Sr isotopic disequilibrium between clinopyroxene phenocrysts and tephriphonolite, together with the less radiogenic Sr compositions of the sanidine megacryst (fig. 6*a*; Table 3) provides evidence for open-system magmatic processes. The higher Sr-radiogenic composition of the clinopyroxene crystals with respect to the sanidine records magma mixing between isotopically different liquids. In the high-potassium magma series, sanidine follows the crystallisation of clinopyroxene (Peccerillo and Manetti, 1985): therefore, if a highpotassium liquid differentiates by AFC, the sanidine would record higher Sr-isotope ratios than the clinopyroxene phenocrysts.

Three processes may explain the recorded increase from core to rim of the ⁸⁷Sr/⁸⁶Sr across the sanidine megacryst of the tephri-phonolite: 1) diffusive equilibration; 2) crustal contamination; 3) magma mixing.

The first process envisages diffusive equilibration of the sanidine megacryst with the



Fig. 8 – Calculated percent diffusive equilibration curves for Sr diffusion in sanidine with radii variations from 10 mm (solid line) to 20 mm (dotted line) at 1075°C and 975°C. Diffusion coefficient for sanidine is 6.03×10^{-17} (m²/s) at 1075°C and 2.22×10^{-18} (m²/s) at 975°C (CHERNIAK, 1996).

liquid when it was incorporated in a more Sr radiogenic melt (like that from which the clinopyroxene crystallised) by magma mixing, thus increasing the 87Sr/86Sr ratio. Using the equation of Crank (1975) for a sphere having an initially uniform Sr isotopic ratio and immersed in an infinite reservoir with a different Sr isotopic ratio, it is possible to calculate the degree of isotopic equilibration. Temperatures calculated for primitive alkaline potassic liquids range from 1286 to 1161°C (Kamenetsky et al., 1995; Conticelli et al., 1997), which represents a maximum crystallisation temperature for the more evolved tephri-phonolitic liquid. The diffusion coefficient of Sr in sanidine at 1075°C is $6.03 \times$ 10^{-17} (m²/s) and at 975 °C is 2.22×10^{-18} (m²/s) (Cherniak, 1996). Fig. 8 shows the degree of equilibration for sanidine with radius variations from 10 to 20 mm. The residence time of a magma in a small chamber is between days and 10⁴ years (Huppert and Sparks, 1988; Francalanci et al., 1999). During this time, a sanidine xenocryst with a radius of 20 mm at 1075°C would achieve isotopic equilibration with a host liquid between 0% and 66% (fig. 8). Thus, in 10⁴ years, a 10 mm (radius) sanidine xenocryst having a 87Sr/86Sr ratio of 0.7106 (sanidine core) immersed in a melt with a ⁸⁷Sr/⁸⁶Sr ratio of 0.7109 (like that recorded in the clinopyroxene crystals) would reach a value of 0.7108, like to that recorded in the sanidine megacryst rim of the tephri-phonolite (Table 3). A residence time of 10⁴ years, however, is extremely long for a small mafic magma system, suggesting that diffusive equilibration did not play an important role in the production of the Sr isotope inhomogeneity in the sanidine megacryst enclosed in the tephri-phonolite. Therefore, its core probably retains the original Sr isotope ratio of the liquid from which it grew. The initial value of the ⁸⁷Sr/⁸⁶Sr ratio (Sr_i) of the megacryst core, 0.3 Ma (same age as the host rock) is 0.71063, similar to the measured value, which represents that of its inequilibrium liquid.

The second process envisages that an increase of the ⁸⁷Sr/⁸⁶Sr ratio in the sanidine

megacryst reflects contamination of the parent magma with high-⁸⁷Sr/⁸⁶Sr country rock. The sanidine megacryst growth occurred in a melt of increasing ⁸⁷Sr/⁸⁶Sr, and was in isotopic equilibrium with the parent magma at all stages of its evolution. The parental magmas of Vico rocks have an Sr isotopic composition in the range from 0.708 to 0.710 (Perini, 1997). High ⁸⁷Sr/⁸⁶Sr ratios (0.714-0.738) have been found locally in crustal-derived rocks (Civetta *et al.*, 1989; Conticelli, 1998) and the potential crustal contaminant of Vico magmas.

The third process able to explain the inhomogeneous Sr-isotope composition of the sanidine megacryst entrained in the tephriphonolitic magma is that the magma from which the sanidine core grew was a hybrid liquid. In this case, the high ⁸⁷Sr/⁸⁶Sr ratio of the sanidine rim reflects overgrowth after injection into a more radiogenic Sr melt. A less

radiogenic magma having an Sr_i similar to that of the megacryst core (Sr_i ~0.7106) may have been incorporated in a more radiogenic melt (Sr_i ~ 0.7108), with K-feldspar on the liquidus.

In the hypothesis that the Sr-isotope variation across the sanidine megacryst is generated by crustal contamination, a two end-member magma mixing scenario must be envisaged to form the tephri-phonolite liquid, because of the crystallisation sequence of clinopyroxene and sanidine (fig. 9*a*). One end-member would have an Sr_i similar to that of the clinopyroxene phenocrysts (Magma 2 of fig. 9*a*, Sr_i~0.7109) and the other one a less radiogenic composition with an Sr_i similar to the sanidine megacryst core (Magma 1 of fig. 9*a*, Sr_i~0.7106) (fig. 9*a*).

In the hypothesis that the core-rim Sr isotope variation of the sanidine megacryst is generated by magma mixing, the tephri-phonolite liquid would have differentiated by magma mixing of



Fig. 9*a*, *b* – Two feasible models illustrating differentiation of tephri-phonolite. *a*) Magma 1 assimilated country rocks built up its Sr_i to 0.7108, and then mixed with Magma 2. *b*) Magma mixing of three different liquids: Magma 1 has Sr_i similar to sanidine megacryst core, Magma 2 similar to megacryst rim, and Magma 3 similar to clinopyroxene crystals. Magma mixing with Magma 4, which has Sr_i similar to bulk rock, or contamination by country rock (up to $Sr_i = 0.7112$) may be envisaged as final event for both models a and b.

three different end-members (fig. 9*b*). These would have respectively Sr_i similar to the sanidine megacryst core (Magma 1 of fig. 9*b*, $Sr_i \sim 0.7106$), its rim (Magma 2, $Sr_i \sim 0.7108$) and the clinopyroxene phenocrysts (Magma 3 $Sr_i \sim 0.7109$).

In both hypotheses, contamination by crustal rocks after magma mixing would not be excluded, as suggested by the increase in Sr_i from clinopyroxene crystals to bulk rock tephri-phonolite (Sr_i = 0.71116) (fig. 9a, b). This increase in radiogenic Sr may also have been generated by magma mixing with a further end-member with an ⁸⁷Sr/⁸⁶Sr similar to the bulk-rock value (Magma 4 of fig. 9a, b, Sr_i \geq 0.7112). In fact, old radiogenic Sr magmas $(Sr_i = 0.7113 - 0.7115)$ did erupt from Vico volcano (Perini et al., 2000). Tephri-phonolite is a porphyritic rock mainly composed of clinopyroxene and leucite phenocrysts. Bulk rock Sr isotope data would not reflect only the ⁸⁷Sr/⁸⁶Sr of the liquid, but also that of these mineral phases. No Sr isotope data are available for the leucite phenocrysts although, on the basis of the tephri-phonolite crystallisation sequence, leucite should have crystallised together with clinopyroxene. Indeed, leucite might have a lower 87Sr/86Sr than the bulk rock, and so the final tephriphonolite liquid value would be higher than the analysed bulk-rock (Sr_i \ge 0.7112).

Evolution of olivine-latite

The inhomogeneity of Sr_i observed in the separated clinopyroxene crystals, sanidine megacryst and host olivine-latite bulk rock (fig. 6b) does not record Sr ingrowth by radioactive decay in a closed magma system. The increase in the Sr isotope value from bulk rock to the mineral phases is not coupled with an increase in Rb/Sr (or ⁸⁷Rb/⁸⁶Sr) ratios (Table 3).

Chemical composition and mineral chemistry data reveal that this olivine-latite is a primitive rock (Perini, 1997). The lower Sr-isotope ratio of the bulk rock with respect to the mineral phases (clinopyroxene crystals and sanidine megacryst) reveals that its evolutionary history occurred in an open system. Olivine-latite is a low porphyritic rock and the ⁸⁷Sr/⁸⁶Sr ratio of the bulk rock reflects that of final olivine-latitic liquid.

A feasible model for the evolutionary history of the olivine-latite, able to account for the different Sr-isotope ratios measured in mineral grains and bulk-rock, would combine magma mixing and crustal contamination. Progressive fractional crystallisation of clinopyroxene (and olivine) and sanidine megacryst from a magma with an isotopic signature similar to that of the bulk rock (Magma 1 of fig. 10a, Sr_i~0.7101) reflects an increase in the ⁸⁷Sr/⁸⁶Sr ratio (up to $Sr_i \sim 0.7107$, as recorded in the sanidine megacryst), which is linked to contamination by radiogenic crust. Injection into the magma chamber of a new batch of hot mafic magma lowered the Sr isotope ratio to the value recorded in the olivine-latite bulk rock $(Sr_i \sim 0.7101)$ (fig. 10*a*). This model may explain the increase in ⁸⁷Sr/⁸⁶Sr from clinopyroxene to sanidine megacryst and the lower bulk rock ratio. Recharge of the magma system with hot mafic magma is consistent with the abrupt reverse zonings recorded by the clinopyroxene phenocrysts from other olivinelatites (fig. 4; Perini, 1997).

A second model proposes that the sanidine megacryst and the clinopyroxene did not crystallise from the same liquid. A more radiogenic magma (Magma 2 of fig. 10b, $Sr_i \sim 0.7107$), in which where the sanidine megacryst was growing mixed with a less radiogenic liquid (Magma 1 of fig. 10b, $Sr_i \sim 0.7101$), which was crystallising clinopyroxene and assimilating crustal rocks (up to $Sr_i \sim 0.7103$, as recorded in the clinopyroxene; fig. 10b). A final recharge with less radiogenic magma (Magma 1 of fig. 10b, $Sr_i \sim 0.7101$) must be envisaged (fig. 10b).

The magma history of the olivine-latite would not have involved any evolved sanidinemegacryst-bearing liquid, because this would have strongly affected its primitive chemical and petrographic characteristics. Any magmamixing event would have involved mafic liquids or, if any evolved end-member were involved,



Fig. 10 *a*, *b* – Two feasible models illustrating the differentiation of the olivine-latite. *a*) Magma 1, having Sr_i similar to that of the whole rock, was contaminated by country rock reaching a Sr_i value of 0.7107 similar to that recorded in the sanidine megacryst while it crystallised clinopyroxene and sanidine. A recharge of the magma chamber with Magma 1 occurred subsequently. b) Magma 1, having Sr_i similar to that of the whole rock, assimilated country rock reaching a Sr_i value of 0.7103 similar to that recorded in the clinopyroxene crystals. This magma mixed with Magma 2, which have Sr_i similar to that recorded in the sanidine megacryst (0.7107). A recharge of the magma chamber with Magma 1 occurred subsequently.

its amount must have been minute compared to with that of the mafic end-member.

Common petrogenesis of sanidine megacryst core

In spite of the distinct petrologic affinity of the bulk rock (high-potassium rock series and transitional series) and bulk-rock isotope compositions (Table 3), the measured Srisotope ratios of sanidine cores are similar in the two mafic rocks from Vico volcano (87 Sr/ 86 Sr = 0.71067 and 0.71063). This suggests that the sanidine megacrysts originated from a common parental magma, of probable latitic, trachytic or phonolitic composition. None of the phonolites at Vico contain sanidine > 10 mm in length, but some trachytic magmas with euhedral sanidine megacrysts were erupted at the beginning of Vico magmatic history (Perini *et al.*, 1997). However, these trachytes are characterised by higher radiogenic Sr contents than the sanidine megacryst cores (Sr_i of bulk-rock calculated back to the age of the studied samples = 0.71126; Perini *et al.*, 2000). Evidence to date suggests that a latitic liquid is the parental magma of the sanidine megacrysts.

CONCLUDING REMARKS

Understanding the magmatic processes that affected the evolution of primitive magmas is of particular importance in areas where mantle heterogeneity is implicated in the genesis of magmatism. Differentiation processes may overshadow the geochemical characteristics of the primary magma and thus of the source region.

Sr isotopic systematics recorded in separated mineral phases and in single crystals gives insights into the evolution of magmas during their storage in a magmatic reservoir. This is particularly useful for identifying differentiation processes in primitive magmas when major and trace elements and bulk-rock isotope variations may be masked.

Sr-isotope data on separated clinopyroxene phenocrysts and in-situ Sr-isotope data on single sanidine megacrysts in primitive rocks from the potassic Vico volcano indicate that these mineral phases are not in equilibrium with their host rocks. Therefore, the most mafic magma of the high-potassium series and the primitive magma of the transitional series of Vico volcano evolved through open-system processes. Crustal contamination associated with mixing among end-members with different Sr-radiogenic compositions seems to be the dominant process in changing the composition of these magmas, but magma mixing between several end-members having distinct ⁸⁷Sr/⁸⁶Sr cannot be ruled out.

A co-genetic origin is proposed for the sanidine megacrysts in the tephri-phonolite (high-potassium series), and olivine-latite (transitional series), on the basis of micro Srisotope analyses. Since the sanidine megacrysts from Vico volcano are co-genetic, it is possible to highlight interactions between petrologically different magmas.

Sanidine megacrysts 10-50 mm in size are common in alkaline potassic primitive rocks from central Italy (Mattias and Ventriglia, 1970; Holm, 1982; Poli *et al.*, 1984; Perini *et al.*, 1997) and observations on Vico rocks may be extended to products from other volcanoes. Therefore, a micro Sr-isotope study on sanidine megacrysts may also help to elucidate problems related to the genesis of potassic alkaline magmas in Italy.

Micro Sr- isotope data is particularly useful to establish whether or not there is equilibrium between phenocrysts and their host magma. It is also possible to obtain the Sr-isotope composition of the end-members implicated in differentiation processes. Isotopic diffusion processes do not seem to affect the internal part of these sanidine megacrysts even at high temperatures, because of the short residence time of small, mafic magma systems.

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