# Petrogenesis of the High-Alumina Basalt-Andesite suite from Sant'Antioco Island, SW Sardinia, Italy 

Aida Maria Contel,*, Danilo Mauro Palladino ${ }^{2}$, Cristina Perinelli ${ }^{3}$ and Emmanuelle Argenti ${ }^{4}$<br>${ }^{1}$ C.N.R.- I.G.G.- U.O.S. di Roma, Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le Aldo Moro 5, 00185 Roma, Italy<br>${ }^{2}$ Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le Aldo Moro 5, 00185 Roma, Italy<br>${ }^{3}$ Dipartimento di Scienze della Terra, Università di Pisa, Via Santa Maria 53, 56126 Pisa, Italy ${ }^{4}$ Parco Naturale Regionale Bracciano Martignano, Via A. Saffi, 4/A, Bracciano, 00062 Roma, Italy

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Abstract - Present-day Sant'Antioco Island (SWSardinia, Italy) hosted one of the southernmost, and youngest, subduction-related, Cenozoic magmatic events of western Sardinia. A high-alumina basaltandesite rock association, the focus of this paper, crops out in the southern portion of the island and represents the mafic end-member of volcanism developed during Miocene. Basaltic andesites and andesites are the dominant rock-types, while basalts and dacites are occasional. Minero-petrographic and geochemical characteristics reveal: $i$ ) a clear calc-alkaline signature for these rocks, in spite of high $\mathrm{FeO}^{*} / \mathrm{MgO}$ ratios that mimic a tholeiitic affinity; ii) a magma evolution mainly controlled by fractional crystallization and iii) some degree of crustal assimilation. Phase relationships and compositions, mass balance calculations and T, $\mathrm{P}, \mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ estimates consistently indicate that fractional crystallization occurred at low pressure ( $\mathrm{P}=100-400 \mathrm{MPa}$ ), under different $\mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}$ conditions, which explain the observed wide shifts in major oxides (e.g., $\mathrm{Al}_{2} \mathrm{O}_{3}$ and MgO ), for comparable $\mathrm{SiO}_{2}$ contents, and the ambiguous tholeiitic character as well. Phase relationships in the least evolved lithotypes point out that higher $\mathrm{H}_{2} \mathrm{O}$ concentrations (estimated at up to $6 \mathrm{wt} \%$ ) in the melts reduced the crystallization of plagioclase and favoured that of

[^0]E-mail: aidamaria.conte@uniroma1.it
olivine, whereas lower $\mathrm{H}_{2} \mathrm{O}$ contents (up to $3 \mathrm{wt} \%$ ) promoted plagioclase fractionation and earlier crystallization of orthopyroxene at the expense of olivine. This $\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ imprint was recorded up to the most evolved compositions. Finally, the study rock suite can be derived from a parental (near-primary) magma matching in composition high- MgO basalts from the Montresta calc-alkaline district in NW Sardinia, in the light of the close compositional similarity between the high- $\mathrm{Al}_{2} \mathrm{O}_{3}$ basaltic andesites in the two districts. Thus, starting from a common parental composition, here we reconstruct liquid lines of descent, where the relative proportions of fractionating plagioclase $v s$ mafic phases, as controlled by $\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ in the melts, may account for the compositional differences of Sant'Antioco rock-types ab initio.

RiAssunto - L'Isola di Sant'Antioco (Sardegna sudoccidentale) ospita una delle più recenti manifestazioni del magmatismo orogenico del margine occidentale della Sardegna connesso alla subduzione cenozoica. Oggetto del presente lavoro sono le vulcaniti affioranti nella porzione meridionale dell'isola, costituite essenzialmente da andesiti basaltiche alte in allumina e da andesiti (più occasionali basalti e daciti), che rappresentano i termini meno differenziati del locale magmatismo di età miocenica. Oltre ad integrare l'ampio
panorama degli studi esistenti sul magmatismo orogenico sardo, la caratterizzazione minero-petrografica e geochimica e la parametrizzazione $\mathrm{P}, \mathrm{T}, \mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ dei litotipi investigati, consente una ricostruzione dei relativi processi petrogenetici, anche alla luce dei recenti sviluppi sperimentali sui sistemi calco-alcalini. I risultati indicano che le vulcaniti in esame rivelano una chiara affinità calco-alcalina, nonostante gli alti rapporti $\mathrm{FeO}^{*} / \mathrm{MgO}$ tipici di rocce di serie tholeiitica, e che la differenziazione magmatica è stata controllata principalmente dalla cristallizzazione frazionata, associata a differenti gradi di assimilazione crostale. Le relazioni di fase e i calcoli di bilancio di massa, in accordo con le stime di Te P di cristallizzazione dei fenocristalli e dei contenuti di $\mathrm{H}_{2} \mathrm{O}$ in soluzione nei magmi, suggeriscono una cristallizzazione a bassa pressione ( $\mathrm{P}=100-400 \mathrm{MPa}$ ) con differenti $\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$. Proprio quest'ultimo parametro spiega sia l'ampia variabilità composizionale di queste rocce (in particolare i differenti contenuti in $\mathrm{Al}_{2} \mathrm{O}_{3}$ e MgO per contenuti in $\mathrm{SiO}_{2}$ simili), sia l'apparente carattere tholeiitico. Le relazioni di fase osservate nei litotipi meno evoluti indicano infatti che alte concentrazioni di $\mathrm{H}_{2} \mathrm{O}$ nei fusi (stimate intorno al $6 \%$ in peso) hanno ridotto l'incidenza del plagioclasio (che tuttavia rappresenta invariabilmente la fase dominante, seguita dal clinopirosseno), favorendo la cristallizzazione dell'olivina fra le fasi femiche. Viceversa, minori contenuti in $\mathrm{H}_{2} \mathrm{O}$ (fino a $\sim 3 \%$ ), oltre a favorire il frazionamento di plagioclasio, hanno comportato la precoce cristallizzazione dell'ortopirosseno a spese dell'olivina. L'evidenza di diversi contenuti in $\mathrm{H}_{2} \mathrm{O}$ quale fattore di controllo determinante del processo di differenziazione dei magmi persiste fino alle composizioni più evolute dell'associazione in esame. Infine, le litologie meno differenziate riscontrate a Sant'Antioco possono essere considerate come direttamente derivanti da un magma più primitivo di composizione simile a quella dei basalti alti in MgO affioranti nel distretto vulcanico di Montresta (Sardegna nord-occidentale), anche sulla base delle significative analogie composizionali fra le andesiti basaltiche alte in $\mathrm{Al}_{2} \mathrm{O}_{3}$ nelle due aree. L'insieme dei dati è compatibile con un modello in cui, a partire da una comune composizione parentale, le differenze riscontrate sin dai termini meno evoluti di Sant'Antioco possono essere ricondotte a percorsi evolutivi caratterizzati da diversi rapporti tra le fasi frazionate (in particolare fra il plagioclasio e le fasi femiche) sotto il controllo cruciale della $\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$.

Key words: Cenozoic orogenic volcanism, highalumina basaltic-andesites, petrology and geochemistry, Sant'Antioco, Sardinia.

## Introduction

Cenozoic, subduction-related, igneous activity in Sardinia has been widely investigated (e.g., Dostal et al., 1982; Beccaluva et al., 1994; Brotzu et al., 1997a, b; Morra et al., 1994, 1997; Mattioli et al., 2000; Downes et al., 2001; Franciosi et al., 2003; Lustrino et al., 2004, 2009). However, information on petrography, mineralogy and chemistry of one of the southernmost volcanic districts, Sant'Antioco, is still scarce and incomplete. Up to now, the few geological and compositional data available on the Sant'Antioco volcanics were reported in Luxoro (1987), in the 1:25,000 geo-petrographic map of Sant'Antioco Island (Maccioni et al., 1990) and in Lecca et al. (1997), who considered the andesitic s.l. rocks from Sant'Antioco Island as part of the orogenic magmatism in the Sulcis area (SW mainland Sardinia).

The Sulcis volcanic district is the southernmost part of the calc-alkaline magmatic belt that developed during late Eocene - middle Miocene time span (Lustrino et al., 2009) along the western side of Sardinia (Fig. 1), as a consequence of subduction acting in the Western Mediterranean Sea beneath the southern European margin (e.g., Doglioni, 1991; Doglioni et al., 1999 and references therein).

This work illustrates the mineralogical, geochemical and petrological aspects of the Sant'Antioco volcanics in order to integrate the large set of studies on Cenozoic orogenic magmatism in Sardinia and to reconstruct petrogenetic processes. In particular, we focus on the influence of $\mathrm{H}_{2} \mathrm{O}$ on the magma liquid lines of descent in the light of recent studies on natural and experimental calc-alkaline systems (Sisson and Grove, 1993a, b; Pichavant and Macdonald, 2007 and references therein; Ulmer, 2007 and


Fig. 1 - a) Geological sketch map of Sardinia, showing the location of Sant'Antioco Island and other subduction-related Cenozoic volcanics (after Cherchi and Montadert, 1982, Savelli et al., 1979 and Morra et al., 1997, modified). (1) PlioceneQuaternary sediments; (2) Middle Miocene-Pleistocene anorogenic volcanics; (3) Late Eocene-Middle Miocene sedimentary and volcanic rocks: (3a) silicic ignimbrites; (3b) andesites s.l.; (4) continental sedimentary rocks of Cixerri Formation; (5) undifferentiated Paleozoic basement and Mesozoic up to Eocenic cover; (6) main Post-Paleozoic regional faults. b) Geological sketch map of Sant'Antioco Island. c) Enlargement of the area shown in b, where the sampling sites are reported. (* lava clasts in Pispisia-M.te Arbus polygenic breccias).
references therein). Furthermore, possible relationships with compositionally analogous, or even less differentiated, Cenozoic orogenic rocktypes of western Sardinia will be considered, aiming at identifying a reliable near-primary parental magma for the studied rock association.

Geological Background

The Sant'Antioco Island, located immediately offshore of southwestern mainland Sardinia (Italy; Fig. 1), extends 17.5 km in a N-S direction, with a maximum W-E width of 10 km . It is part of the calc-alkaline volcanic belt that stretches along the western coast of Sardinia, which developed during late Eocene-middle Miocene (38-12 Ma, Lustrino et al., 2009 and references therein) along the main branches of the "Sardinian Rift System" (Main Branch Volcanic Zone) and in Sulcis (South-Western Volcanic Zone; sensu Lecca et al., 1997). The Sardinian Rift System and related magmatism are interpreted in the frame of the kinematic processes acting in the western Mediterranean, which involved the Hercynian paleo-margin of southern Europe. These processes occurred in connection with the back-arc spreading produced by the eastward roll-back of the westwardsubducting plate related to convergence between Africa and Europe (Doglioni, 1991; Doglioni et al., 1999 and references therein). This caused the separation and counterclockwise (i.e., southeastward) rotation of the Corsica-Sardinia continental microplate up to its present position (upper Oligocene-middle Miocene). In this context, the Cenozoic calc-alkaline magmatism of Sardinia is directly related to the subduction of oceanic crust. The earliest calc-alkaline magmatic events along the present western side of Sardinia predate the rotation of the CorsicaSardinia microplate; then magmatism migrated southeastward following the west-directed, eastward retreating, subduction zone beneath Sardinia until middle Miocene. The Cenozoic
orogenic magmas in Sardinia were emplaced through a variably thinned continental crust (ca. 30 to 20 km thick, from North to South; Egger et al., 1988; Sartori et al., 2004; Sau et al., 2005), which may account for the differences in composition and eruptive style of magmatic activity from North to South along the Sardinian Rift (e.g., Lustrino et al., 2002).

The Sulcis volcanic district, which includes a south-western coastal area of mainland Sardinia and the nearby islands of San Pietro and Sant'Antioco, represents the southernmost expression of orogenic magmatism in Sardinia (Fig. 1) and one of its youngest occurrences as well. Volcanic stratigraphy is characterized by: 1) lava and subordinate pyroclastic successions, including andesites, basaltic andesites and rare basalts, of Oligo-Miocene age, which crop out in Sulcis mainland (i.e., S. Giovanni Suergiu, Narcao, Giba) and in the southern part of Sant'Antioco, and 2) silicic welded ignimbrites and subordinate lava flows and domes, ranging in composition from dacites to comendites, of Miocene age, exposed in mainland Sulcis (Portoscuso area), in the northern and western parts of Sant'Antioco, and throughout the whole San Pietro Island (Assorgia et al., 1990; Morra et al., 1994; Pioli and Rosi, 2005; Pioli et al., 2008).

The pre-volcanic substrate on Sant'Antioco includes biohermal-biostromal and oolitic limestones and silty marls of Cretaceous age, cropping out in the SE part of the island (Maccioni et al., 1990). Almost all of the island is made up of volcanic rocks of Miocene age from both silicic, mainly explosive, and mafic to intermediate, mainly effusive, activities. Published K-Ar age data indicate values clustered at around 16-18 Ma (Araña et al., 1974; Savelli et al., 1979; Montigny et al., 1981; Maccioni et al., 1991). A younger age of about 12 Ma was recently obtained $\mathrm{by}^{40} \mathrm{Ar} /{ }^{39} \mathrm{Ar}$ determinations for the trachytic neck of Isola del Toro, South of Sant'Antioco (Lustrino et al., 2007), which is intermediate between the age of the last products
of the Oligo-Miocene orogenic igneous phase in SW Sardinia and the early volcanism of the late Miocene-Quaternary phase in SE Sardinia (ca. 6.64 Ma , Lustrino et al., 2007).

## FIELD Characteristics

OF THE STUDIED ROCK-TYPES

The present study investigates the mafic to intermediate volcanic rocks that crop out in the southern part of Sant'Antioco Island. These are represented by high- and low-aspect ratio lava flows and small lava domes (typically less than 1 km across), associated with minor pyroclastic
deposits, locally cut by lava dykes. In order to characterize this volcanic activity on Sant'Antioco, a set of sixty-seven representative rock samples has been analyzed, as listed in Table 1 (sample localities are shown in Fig. 1). Table 1 also summarizes relevant field characteristics of the studied volcanics, along with their correlation with the units identified by previous studies (i.e., Luxoro, 1987; Maccioni et al., 1990). Following the stratigraphic scheme of Luxoro (1987), the studied samples include: $i$ ) twenty-two samples from the "Lave iniziali" (early lavas, hereon abbreviated as LI), consisting of thick (up to 10 m ), massive, lava

Table 1
List of the analyzed samples of Cenozoic mafic to intermediate volcanic rocks from Sant'Antioco Island studied in this work (sample locations in Fig. 1), grouped according to unit nomenclatures in Luxoro (1987) and Maccioni et al. (1990). LI: Lave iniziali (Early lavas); P: Pispisia-M.te Arbus polygenic volcanic breccias; LT: Lave terminali (Final lavas); F: lava dykes.

| SAMPLES | FIELD ASPECT | Luxoro (1987) | Maccioni et al. (1990) |
| :---: | :---: | :---: | :---: |
| SA22, SA29-29b, SAV8b | Lava dyke | F | 13a |
| SA21, SA24, SA25 | Lava dyke | F | 13b |
| $\begin{aligned} & \text { SA1, SA2, SA3-3b, SA4, } \\ & \text { SA6, SA7, SA8, SA9, } \\ & \text { SA16, SA35, SA36, SA37, } \\ & \text { SA38, SA39, SA40-40b, } \\ & \text { SAV2, SAV4, } \\ & \text { SAV11, SAV12 } \end{aligned}$ | Thin lava flow interbedded with scoriaceous levels | LT | 14 |
| SAV16, SAV17, <br> SAV19, SAV21 | Lava clasts in polygenic breccias | P | 15a |
| SA19, SA27, SA28, SAV14, SAV15-15b, SAV20 | Lava injections in polygenic breccias | P | 15b |
| SA15-15b, SA23, SAV18 | Thick lava flow or lava dome | LI | 17 a |
| $\begin{aligned} & \text { SA5, SA10, SA11, SA30, } \\ & \text { SA34-34b, SAV7, SAV9, } \\ & \text { SAV10, SAV13 } \end{aligned}$ | Thick lava flow | LI | 18 |
| SA12-12b, SA13, SA14, SA17, SA18, SA31, SA33, SAV5, SAV6, SAV8 | Thick lava flow or lava dome | LI | 19a |
| SA20, SA32-32b | Lava dome | LI | 20 |

flows and lava domes; $i i$ ) eleven samples from lava injections and lava blocks within the Pispisia-M.te Arbus polygenic volcanic breccia deposits (hereon P); iii) twenty-seven samples from thin (usually 1.5 m -thick) lava flows, part of the "Lave terminali" (final lavas, hereon LT); iv) seven samples from lava dykes intersecting the above volcanics (hereon F).

## Petrography

The studied Sant'Antioco volcanics range in composition from basalts to dacites (see Geochemistry section). Basaltic andesites largely prevail within LT rock-types, while andesites are dominant within LI lithologies. Both basaltic andesites and andesites occur in the PispisiaM.te Arbus lava types (P), as well as in lava dykes (F). Hereafter, for the sake of simplicity, the products from P and F units are grouped within either the LI or LT main-types, on the basis of bulk rock composition and of common mafic phenocryst assemblages (plagioclase is invariably the main phase and opaques are ubiquitous, see below).

Lava rocks from both LI and LT mostly show porphyritic or glomeroporphyritic (15-48 vol\% phenocrysts), isotropic to pilotaxitic or seriate, textures and microcrystalline groundmass. Phenocryst and groundmass assemblages, as determined from modal analyses in thin section, are reported in TABLE 2 for a set of representative samples.

LT rocks (also including part of F dykes) consist of basaltic andesites and occasional basalts characterized by the ubiquitous, although relatively scarce, presence of olivine (always $<5$ vol\%) and by the prevalence of clinopyroxene (Cpx) on orthopyroxene (Opx). In a few cases, within the least evolved lavas, which show very low contents of mafic phenocrysts (about 5\%), Opx is lacking and olivine (3-4 vol\%) prevails on Cpx.

LI rocks (also including P lavas and part of F dykes) comprise basaltic andesites and occasional dacites characterized by: $i$ ) the ubiquitous presence of pyroxene phenocrysts, with Opx often prevailing on Cpx ; ii) the lack or occasional presence of scarce amounts of olivine; iii) the occurrence of hornblende in two samples from the

Table 2
Modal analyses of the most representative LT and LI rock-types (at least 1000 points counted for each sample).

| Rock-type | LT | LT | LT | LT | LI | LI | LI | LI |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Sample: | SA7 | SA40 | SA35 | SA3 | SA12 | SA15 | SA31 | SA32 |
|  | HABA | HABA | HABA | HABA | AND | AND | AND | DAC |
| Plg $\left(\right.$ ph ${ }^{\text {a }}$ +mph ${ }^{\text {b }}$ ) | 23.2 | 23.5 | 16.8 | 21.9 | 22.5 | 21.4 | 32.1 | 29.5 |
| Ol (ph +mph$)$ | 3.5 | 5.4 | 3.5 | 0.2 | - | - | - | - |
| Cpx $($ ph +mph$)$ | 6.6 | 4.2 | 0.6 | 9.1 | 0.6 | 2.5 | 3.4 | 2.7 |
| Opx $(\mathrm{ph}+\mathrm{mph})$ | - | - | - | - | 1.6 | 7.6 | 9.7 | 6.5 |
| Opx mph | 0.5 | - | - | 0.8 | - | - | - | - |
| Fe-Ti oxides mph | 1.0 | 1.1 | 0.9 | 1.5 | 1.3 | 2.3 | 2.5 | 1.9 |
| Hbl ph | - | - | - | - | - | - | - | 1.0 |
| P.I. $($ ph +mph$)$ | 34.8 | 34.2 | 21.8 | 33.5 | 26.0 | 33.8 | 47.7 | 41.6 |
| Gdm | 65.2 | 66.8 | 78.2 | 66.5 | 74.0 | 66.2 | 52.3 | 58.4 |

[^1]most evolved andesites and in the dacite sample.
Phenocryst glomeri (mostly Cpx and Opx, associated with coarse-grained $\mathrm{Fe}-\mathrm{Ti}$ oxides, subordinate plagioclase and occasional olivine) are more common in LI than LT and typically occur in two-pyroxene andesites (cfr. "Type a" microinclusions in Brotzu et al., 1997a).
Mineral chemistry and geochemical features of whole rock samples are reported in the following sections. Analytical methods are illustrated in Appendix A.

## Mineralogy

## Plagioclase

Plagioclase is the most abundant phenocryst phase (up to $80 \%$ by volume of total phenocrysts and microphenocrysts) in both LT and LI groups. It usually occurs as individual, variably sized, euhedral grains or, mainly in andesites, in glomerocrystic aggregates. Plagioclase crystals often show continuous zoning and clear surfaces. Dusty or cellular textures may be present, where crystal portions may enclose glassy material. Plagioclase phenocrysts also enclose magnetite and minute plagioclase crystals or, more rarely, fine skeletal Cpx grains.
In LI rock-types, plagioclase crystals show common intracrystalline compositional ranges, with either normal (core: $\mathrm{An}_{75-67}$; rim: $\mathrm{An}_{65-59}$ ) or reverse (core: $\mathrm{An}_{64-68}$; rim: $\mathrm{An}_{72-74}$ ) zoning. Although usually normally zoned, LT plagioclases are characterized by a wider compositional pattern: phenocryst core compositions even $>\mathrm{An}_{90}$ are observed in several examples, while phenocryst rim and microphenocryst mostly range $\mathrm{An}_{60-75}$ in composition (representative analyses are reported in Table 3). As a whole, the compositional ranges of LT plagioclase vary significantly, even within rocks with similar evolution degree. For example, if we consider the least evolved lithotypes, the prevailing
plagioclase compositions vary from $\mathrm{An}_{75-85}$ (SA7), through $\mathrm{An}_{78-90}(\mathrm{SA} 40)$, to $\mathrm{An}_{85-93}(\mathrm{SA} 35)$ (Table 3; Fig. 2), concomitant with increasing $\mathrm{Al}_{2} \mathrm{O}_{3}$ contents in the corresponding whole rocks (cfr. Geochemistry section).

## Pyroxenes

In LT rocks, Cpx is the dominant mafic phenocryst phase ( $5-15 \%$ by volume), while Opx usually does not exceed $5 \mathrm{vol} \%$. With increasing degree of differentiation, the amount of Opx vs Cpx increases to become prevalent in most of the olivine-free LI samples. In these latter, Cpx and Opx phenocrysts are often associated in polycrystalline aggregates (glomeri). As a whole, Cpx may occur as: $i$ ) euhedral pheno- to microphenocryst grains; ii) coarser, rounded grains, sometimes enclosing corroded relics of olivine; iii) microgranular coronas that mantle both Opx and Cpx phenocrysts, mainly in evolved LI andesites; $i v$ ) microliths in the groundmass. Clinopyroxene is always augitic, with a narrow compositional range $\left(\mathrm{Wo}_{37-45} \mathrm{En}_{39}\right.$ ${ }_{45} \mathrm{Fs}_{11-20}$ ). No clear compositional variations are observed as a function of the degree of evolution from basalts to andesites: both $\mathrm{Al}_{2} \mathrm{O}_{3}$ (1.6-6.5 $\mathrm{wt} \%$ ) and $\mathrm{TiO}_{2}$ (0.33-1.10 wt \%) contents do not well correlate with the magnesium number [mg\# $=\mathrm{MgO} /\left(\mathrm{MgO}+\mathrm{FeO}^{*}\right)$ molar $]$, as they show different amounts for comparable mg\# values (e.g., LT in Fig. 3 and Table 4).

Orthopyroxene ( $\mathrm{Wo}_{2-4} \mathrm{En}_{54-72} \mathrm{Fs}_{25-42}$, Table 4) occurs as either euhedral to subhedral phenocrysts or microphenocrysts (either isolated or in polycrystalline glomeri), in some cases mantled by Cpx grains. Solid inclusions, commonly of magnetite and, more rarely, of plagioclase laths, are also found.

## Olivine

Olivine mostly occurs in LT rocks and usually does not exceed 2-3 vol $\%$. In a few, less evolved,
TABLE 3
Representative electron microprobe analyses of plagioclase from the Sant'Antioco study rock-types.

| Unit | SA7 | SA7 | SA7 | SA7 | SA7 | SA7 | SA35 | SA35 | SA35 | SA35 | SA35 | SA35 | SA40 | SA40 | SA40 | SA40 | SA40 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | LT | LT | LT | LT | LT | LT | LT | LT | LT | LT | LT | LT | LT | LT | LT | LT | LT |
|  | 1/c | 1/r | 2/c | 2/r | mph | g | 1/c | 1/r | 2/c | 3/c | mph | g | 1/c | 2/c | 2/r | mph | g |
| $\mathrm{SiO}_{2}$ | 45.45 | 48.78 | 47.43 | 47.54 | 47.73 | 48.99 | 44.89 | 49.64 | 43.61 | 45.89 | 46.44 | 49.21 | 44.42 | 45.50 | 47.65 | 46.82 | 47.86 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 34.88 | 31.26 | 33.05 | 32.92 | 32.38 | 31.65 | 34.05 | 31.19 | 35.92 | 34.68 | 33.30 | 31.92 | 35.55 | 31.74 | 32.97 | 33.71 | 32.59 |
| FeO | 0.84 | 0.63 | 0.85 | 0.64 | 0.90 | 0.76 | 0.54 | 0.97 | 0.62 | 0.64 | 0.81 | 0.93 | 0.58 | 0.66 | 0.61 | 0.67 | 0.83 |
| CaO | 17.77 | 16.18 | 16.62 | 15.85 | 15.70 | 14.97 | 19.70 | 15.73 | 19.25 | 17.87 | 16.91 | 14.99 | 18.68 | 17.71 | 15.80 | 16.83 | 15.57 |
| $\mathrm{Na}_{2} \mathrm{O}$ | 1.56 | 2.88 | 2.19 | 2.73 | 2.77 | 3.27 | 0.87 | 3.03 | 0.74 | 1.53 | 2.18 | 3.25 | 1.14 | 1.71 | 2.87 | 2.21 | 2.86 |
| $\mathrm{K}_{2} \mathrm{O}$ | - | 0.09 | 0.10 | 0.10 | 0.10 | 0.10 | 0.04 | 0.13 | - | - | - | 0.12 | - | - | - | - | 0.18 |
| Total | 100.49 | 99.82 | 100.24 | 99.78 | 99.58 | 99.74 | 100.09 | 100.69 | 100.14 | 100.62 | 99.64 | 100.41 | 100.37 | 97.32 | 99.90 | 100.24 | 99.89 |
| An (mol \%) | 86.32 | 75.26 | 80.28 | 75.80 | 75.37 | 71.26 | 92.39 | 73.62 | 93.50 | 86.57 | 81.08 | 71.35 | 90.05 | 85.13 | 75.26 | 80.80 | 74.28 |
| Ab (mol \%) | 13.68 | 24.24 | 19.14 | 23.63 | 24.06 | 28.17 | 7.38 | 25.66 | 6.50 | 13.43 | 18.92 | 27.99 | 9.95 | 14.87 | 24.74 | 19.20 | 24.69 |
| Or (mol \%) | 0.00 | 0.50 | 0.58 | 0.57 | 0.57 | 0.57 | 0.22 | 0.72 | 0.00 | 0.00 | 0.00 | 0.66 | 0.00 | 0.00 | 0.00 | 0.00 | 1.02 |
| $\mathrm{K}_{\mathrm{D}}$ | 2.40 | 1.18 | 1.59 | 1.22 | 1.19 | 0.96 | 5.12 | 1.17 | 5.88 | 2.63 | 1.75 | 1.04 | 4.12 | 2.60 | 1.38 | 1.91 | 1.37 |
| Unit | $\begin{gathered} \hline \text { SAV1 } \\ \text { LT } \\ 1 / \mathrm{c} \\ \hline \end{gathered}$ | $\begin{aligned} & \text { SAV11 } \\ & \text { LT } \end{aligned}$ | SAV11 | SAV11 | $\begin{gathered} \text { SAV11 } \\ \text { LT } \end{gathered}$ | $\begin{gathered} \text { SAV11 } \\ \text { LT } \end{gathered}$ | SAV15SAV15 |  | 5 SAV15SAV15 SAV15 |  |  | SAV5 | SAV5 | SAV5 | SAV5 | SAV5 | SAV5 |
|  |  |  | LT | LT |  |  | P | P | P | P | P | LI | LI | LI | LI | LI | LI |
|  |  | 1/r | 2/c | 2/r | mph | g | 1/c | 1/r | 2/c | mph | g | 1/c | 1/r | 2/c | 2/r | mph | g |
| $\mathrm{SiO}_{2}$ | 46.54 | 50.87 | 45.18 | 45.32 | 53.86 | 55.24 | 46.15 | 47.36 | 47.42 | 48.70 | 59.11 | 49.32 | 53.02 | 50.32 | 52.43 | 51.31 | 59.31 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 34.12 | 30.80 | 34.73 | 34.53 | 28.42 | 27.33 | 34.23 | 33.12 | 33.33 | 32.38 | 23.92 | 32.22 | 29.62 | 31.40 | 29.94 | 30.51 | 24.36 |
| FeO | 0.42 | 0.74 | 0.56 | 0.81 | 1.28 | 1.51 | 0.72 | 0.61 | 0.69 | 0.78 | 1.03 | 0.33 | 0.44 | 0.52 | 0.30 | 0.64 | 0.86 |
| CaO | 17.07 | 13.51 | 18.14 | 17.98 | 10.88 | 9.66 | 17.25 | 16.53 | 16.41 | 15.12 | 5.94 | 15.15 | 12.10 | 14.13 | 12.47 | 13.19 | 6.26 |
| $\mathrm{Na}_{2} \mathrm{O}$ | 1.72 | 3.79 | 1.06 | 1.28 | 5.09 | 5.45 | 1.54 | 1.97 | 2.04 | 2.72 | 5.53 | 2.84 | 4.49 | 3.40 | 4.31 | 3.97 | 5.31 |
| $\mathrm{K}_{2} \mathrm{O}$ | - | - | - | - | 0.29 | 0.72 | - | - | 0.13 | - | 3.66 | - | 0.22 | 0.13 | 0.20 | - | 3.88 |
| Total | 99.87 | 99.71 | 99.67 | 99.92 | 99.82 | 99.91 | 99.89 | 99.59 | 100.02 | 99.70 | 99.19 | 99.86 | 99.89 | 99.90 | 99.65 | 99.62 | 99.98 |
| An (mol \%) | 84.58 | 66.33 | 90.44 | 88.59 | 53.24 | 47.40 | 86.09 | 82.26 | 81.01 | 75.44 | 29.25 | 74.67 | 59.06 | 69.14 | 60.81 | 64.74 | 30.55 |
| Ab (mol \%) | 15.42 | 33.67 | 9.56 | 11.41 | 45.07 | 48.39 | 13.91 | 17.74 | 18.22 | 24.56 | 49.28 | 25.33 | 39.66 | 30.10 | 38.03 | 35.26 | 46.90 |
| Or (mol \%) | 0.00 | 0.00 | 0.00 | 0.00 | 1.69 | 4.21 | 0.00 | 0.00 | 0.76 | 0.00 | 21.46 | 0.00 | 1.28 | 0.76 | 1.16 | 0.00 | 22.55 |
| $\mathrm{K}_{\mathrm{D}}$ | 2.42 | 0.87 | 4.16 | 3.42 | 0.52 | 0.43 | 2.96 | 2.22 | 2.13 | 1.47 | 0.28 | 1.73 | 0.87 | 1.35 | 0.94 | 1.08 | 0.38 |

Note: c: phenocryst core; r: phenocryst rim (1, 2, 3: phenocryst identification); mph: microphenocryst; g: groundmass. The plagioclase-melt Ca-Na exchange distribution coefficients $\left(\mathrm{K}_{\mathrm{D}}\right)$ are also reported (see text for calculation details).


Fig. 2 - Frequency histograms displaying the variation of An contents in plagioclase of the SA7, SA35 and SA40 highalumina basaltic andesite (HABA) samples from LT unit, which stand for the least evolved Sant'Antioco products (frequency expressed as number of analyses). Note that each sample shows a dominant plagioclase composition related to the $\mathrm{Al}_{2} \mathrm{O}_{3}$ content in the whole rock (cfr. Table 6).
rocks it may attain up to $5 \mathrm{vol} \%$ and represent the main mafic phase. Overall, Fo component ranges $50-59 \mathrm{~mol} \%$; individual crystals are usually normally zoned (Table 5). Generally, olivine crystals are altered to iddingsite, even if they preserve the original habit. In a few cases, fresh olivine relics are observed at the core of altered crystals. Some olivine crystals are bordered by granular Cpx.

## Amphibole

Euhedral to subhedral amphibole phenocrysts, showing opacitic rims, are found in scarce amounts ( $<2$ vol\%) in two LI andesite samples with $\mathrm{SiO}_{2}$ contents $>58 \mathrm{wt} \%$ and in the dacite sample. Representative analyses, reported in Table 5, allow a classification as MgOhornblende, following Leake et al. (2004). Compositional (i.e., low $\mathrm{Al}_{2} \mathrm{O}_{3}$ content, $\sim 8 \mathrm{wt} \%$ on average) and textural relationships testify their late stage crystallization under low pressure conditions.

## Fe-Ti oxides

$\mathrm{Fe}-\mathrm{Ti}$ oxides (Table 5) are present ubiquitously both as microphenocrysts (either dispersed or bordering pyroxene phenocrysts) and, in higher amounts, as groundmass phases. Magnetite-titanomagnetite is common in basaltic andesites, while ilmenite only occurs in andesites.

## Geochemistry

Representative bulk rock compositions from the Sant'Antioco volcanics are reported in Table 6. Essentially they plot in the basaltic andesite and andesite fields of the TAS classification diagram (Le Bas et al., 1986), with quite subordinate basalts and dacites. According to other classification diagrams, i.e. $\mathrm{K}_{2} \mathrm{O}$ vs $\mathrm{SiO}_{2}$ (Peccerillo and Taylor, 1976; Fig. 4a), and MgO vs $\mathrm{Al}_{2} \mathrm{O}_{3}$ (Kersting and Arculus, 1994; Fig. 4b), the studied products are mainly high-alumina basaltic andesites and andesites (with quite subordinate basalts and dacites: only one data point each) of medium-K calc-alkaline affinity. On the other hand, on the mere basis of the $\mathrm{FeO} * / \mathrm{MgO}$ vs $\mathrm{SiO}_{2}$ diagram (Miyashiro, 1974) all the investigated rocks would show a tholeiitic to mildly tholeiitic affinity (Fig. 4c). However, the plot of $\mathrm{FeO}^{*} / \mathrm{MgO}$ vs $\mathrm{FeO}^{*}$ (inset in Fig. 4c) indicates that the relatively high values of FeO*/MgO in the Sant'Antioco rock suite are not accompanied by an iron enrichment trend typical of tholeiitic series. Furthermore, a possible tholeiitic affinity for the Sant'Antioco volcanics conflicts with the lack of pigeonite microphenocrysts (Kuno, 1959) and of Feenrichment in plagioclase (Aramaki and Katsura, 1973), as well as with the observed $\mathrm{TiO}_{2}$ and $\mathrm{Al}_{2} \mathrm{O}_{3}$ contents, which pertain more properly to calc-alkaline rock-series. On these grounds, the relatively high $\mathrm{FeO}^{*} / \mathrm{MgO}$ ratios, which mimic a tholeiitic affinity, may be likely linked to the relative proportions of fractionating plagioclase

| $\stackrel{\infty}{\stackrel{\infty}{i}} \rightrightarrows$ |  | moo min | $\begin{aligned} & 0 \\ & 0 \\ & 0 \end{aligned}$ | ${\underset{\sim}{*}}_{\substack{* \\ \sim \\ \hline}}$ |  $\text { in } \quad \text { i }=0 \mathrm{~m} 20$ |  | $\stackrel{0}{0}$ |
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| $\sum_{i}^{m}=$ |  | $\begin{gathered} n \\ n \\ n \\ n \\ \sim \end{gathered}$ | $\stackrel{\sim}{0}$ | $\frac{n}{\pi} \exists+$ |  |  | $\stackrel{\bigcirc}{\bigcirc}$ |
| $\frac{n}{2} \sum_{i}^{n}$ |  | min | $\begin{aligned} & \infty \\ & 0 \\ & 0 \\ & \hline \end{aligned}$ | $\begin{aligned} & n \\ & \underset{\sim}{ふ} \\ & \vdots \\ & 0 \end{aligned}$ |  | $\begin{aligned} & n \stackrel{n}{N} \stackrel{n}{\infty} \\ & \infty \\ & \sim \end{aligned}$ | $\stackrel{\infty}{\circ}$ |
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c：phenocryst core ；r：phenocryst rim；mph：microphenocryst；g：groundmass； $\mathrm{mg} \mathrm{\#}$ ： $\mathrm{MgO} /(\mathrm{MgO}+\mathrm{FeO})$ molar，with all iron as $\mathrm{Fe}^{2+}$ ．


LT-HAB: $\quad \triangle$ SAV12
LT-HABA: $\diamond$ SA7 ■SA35 O SAV10 ○ SAV15
LI-AND: $\quad \Delta$ SAV8 O SA10 $\circ$ SA15
Fig. 3 - Variation diagrams of magnesium number (mg\#) vs $\mathrm{Al}_{2} \mathrm{O}_{3}$ (a) and $\mathrm{TiO}_{2}$ (b) for clinopyroxenes of representative Sant'Antioco samples. Note the difference in $\mathrm{Al}_{2} \mathrm{O}_{3}$ and $\mathrm{TiO}_{2}$ contents of clinopyroxenes in lavas with similar evolution degree (i.e., SA7 and SA35 considered for petrogenetic modeling). HAB: high-alumina basalt; HABA: high-alumina basaltic andesite; AND: andesite.
and mafic phases during magma evolution, leading to the observed low- MgO and high$\mathrm{Al}_{2} \mathrm{O}_{3}$ compositions (e.g., Pichavant and McDonald, 2007; also see below).
Variation diagrams (Fig. 5) exhibit broad correlations of major oxides with MgO , besides wide scatter (e.g., $\mathrm{Al}_{2} \mathrm{O}_{3}$ and CaO ). As a whole, in spite of distinct field appearance and petrographic features, LI and LT do not define separate compositional trends, whereas both rock groups display correlations consistent with crystallization and removal of the aforementioned phenocryst phases (i.e.,
plagioclase, pyroxenes, Fe -Ti oxides, olivine). In fact, $\mathrm{FeO}_{\mathrm{t}}, \mathrm{TiO}_{2}, \mathrm{CaO}$, and $\mathrm{Al}_{2} \mathrm{O}_{3}$ are positively correlated with MgO , while $\mathrm{SiO}_{2}$ and $\mathrm{Na}_{2} \mathrm{O}$ are negatively correlated with MgO . The extent of $\mathrm{Al}_{2} \mathrm{O}_{3}$ and CaO scattering, however, implies at least different mineral phase proportions and/or compositions during fractional crystallization.

Trace elements depict broad correlations with silica, despite considerable scattering. In particular, $\mathrm{Rb}, \mathrm{Ba}, \mathrm{Zr}, \mathrm{Y}$ and Nb (Table 6, Fig. 6) exhibit an incompatible behaviour, as also evidenced by their mutual positive correlations (not shown). Conversely, V and Sr behave as compatible elements and reflect the progressive removal of $\mathrm{Fe}-\mathrm{Ti}$ oxides and plagioclase. Cr and Ni display low concentrations ( $<100$ and $<60$ ppm , respectively; TABLE 6), a typical feature of low- MgO , high $-\mathrm{Al}_{2} \mathrm{O}_{3}$ arc magmas worldwide, which is related to the prolonged removal of mafic phases during magma differentiation (e.g., Pichavant and Macdonald, 2007 and references therein).

Spider diagrams of trace element concentrations normalized to N-MORB (Sun and Mc Donough, 1989; Fig. 7a), show depletion of HFSE (High Field Strength Elements; with pronounced troughs at Nb and Ti ) with respect to LILE (Large Ion Lithophile Elements) and LREE (Light Rare Earth Elements), as it is typical of arc magmas. The whole set of samples shares very similar patterns, with a general enrichment toward the most differentiated rocks and only slight changes in the incompatible/compatible element ratios. The chondrite-normalized REE patterns are also similar for rocks with different degree of evolution (Fig. 7b) and show a slight increase of $(\mathrm{La} / \mathrm{Yb})_{\mathrm{N}}($ from 3.6 to 5.9 ; subscript N indicates normalized abundances), for near constant $(\mathrm{Sm} / \mathrm{Yb})_{\mathrm{N}}$, in the most differentiated rocks. The latter also show a weak Eu trough $\left(\mathrm{Eu} / \mathrm{Eu}^{*}=0.83-\right.$ 0.88 , where $\mathrm{Eu}^{*}$ is $\left.(\mathrm{Sm}+\mathrm{Gd}) / 2\right)$, which instead is lacking in less differentiated rock types ( $\mathrm{Eu} / \mathrm{Eu}^{*}=0.93-0.97$ ).

Table 5
Representative electron microprobe analyses of olivine, amphibole and Fe-Ti oxides from the Sant'Antioco study rock-types.

Olivine

| Unit | SAV12 | SAV12 | SA7 | SA35 | SA35 | SA40 | SA40 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | LT | LT | LT | LT | LT | LT | LT |
|  | c | mph | c | c | r | c | r |
| $\mathrm{SiO}_{2}$ | 35.73 | 38.70 | 35.53 | 37.56 | 38.58 | 36.7 | 38.13 |
| FeO | 37.82 | 32.27 | 37.86 | 34.76 | 36.1 | 37.7 | 39.047 |
| MnO | 0.64 | 0.68 | 0.75 | 0.52 | 0.24 | 0.64 | 0.50 |
| MgO | 26.37 | 25.94 | 24.99 | 25.91 | 24.18 | 24.94 | 22.06 |
| NiO |  |  |  |  |  |  |  |
| CaO | 0.64 | 0.71 | 0.43 | 0.47 | 0.70 | 0.29 | 0.41 |
| Total | 100.56 | 97.58 | 99.13 | 98.75 | 99.10 | 99.98 | 99.74 |
| Fo (mol\%) | 55.42 | 58.90 | 54.06 | 57.06 | 54.43 | 54.12 | 50.18 |

Amphibole
Fe-Ti oxides

| Unit | $\begin{gathered} \text { SA34 } \\ \text { LI } \end{gathered}$ | $\begin{gathered} \text { SA25 } \\ \mathrm{F} \end{gathered}$ | $\begin{gathered} \text { SA32 } \\ \text { LI } \end{gathered}$ | $\begin{gathered} \text { SAV8 } \\ \text { LI } \end{gathered}$ | $\begin{gathered} \text { SAV8 } \\ \text { LI } \end{gathered}$ | $\begin{gathered} \text { SAV11 } \\ \text { LT } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{SiO}_{2}$ | 47.53 | 47.71 | 47.41 | - | 0.21 | - |
| $\mathrm{TiO}_{2}$ | 1.44 | 1.34 | 1.45 | 1.70 | 45.84 | 3.12 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 8.68 | 8.33 | 8.18 | 1.43 | 0.12 | 1.34 |
| FeO | 14.58 | 13.61 | 13.79 | 89.99 | 50.32 | 88.39 |
| MnO | 0.07 | 0.12 | 0.12 | 0.35 | 2.13 | 0.37 |
| MgO | 13.75 | 14.41 | 14.37 | - | 0.1 | 0.33 |
| CaO | 10.34 | 10.54 | 10.97 |  |  |  |
| $\mathrm{Na}_{2} \mathrm{O}$ | 1.36 | 1.61 | 1.37 |  |  |  |
| $\mathrm{K}_{2} \mathrm{O}$ | 0.21 | 0.31 | 0.36 |  |  |  |
| Total | 97.96 | 97.98 | 98.02 | 93.47 | 98.72 | 93.55 |
| mg\# | 0.63 | 0.65 | 0.65 |  |  |  |

c : phenocryst core ; r : phenocryst rim; mph: microphenocryst; $\mathrm{mg} \#=\mathrm{MgO} /(\mathrm{MgO}+\mathrm{FeO})$ molar, with all iron as $\mathrm{Fe}^{2+}$.

Overall, trace element patterns indicate that magmatic evolution was mostly controlled by fractional crystallization, consistent with evidence from major element variations. The wide data point scatter, however, implies that fractional crystallization cannot fully account for the observed chemical variations in the Sant'Antioco volcanics and that an additional
process, such as crustal contamination, was likely involved in magma evolution (also see below). This seems to be confirmed by the ${ }^{87} \mathrm{Sr} /{ }^{86} \mathrm{Sr}$ initial (i.e. at 15 Ma ) isotopic ratios for Sant'Antioco whole rocks, which range from 0.70698 to $0.70858 \pm 1$ (Table 6). Crustal assimilation is also suggested by the positive correlations of the initial Sr isotope ratios with


Fig. 4 - Classification diagrams of $\mathrm{K}_{2} \mathrm{O}$ vs $\mathrm{SiO}_{2}$ (after Peccerillo and Taylor, 1976) (a), MgO vs $\mathrm{Al}_{2} \mathrm{O}_{3}$ (after Kersting and Arculus, 1994) (b), $\mathrm{FeO}^{*} / \mathrm{MgO} v s \mathrm{SiO}_{2}$ (after Miyashiro, 1974) (c), for the investigated Sant'Antioco volcanics. Inset in (c) shows the plot of $\mathrm{FeO}^{*}$ vs $\mathrm{FeO} * / \mathrm{MgO}^{*}=$ all iron as FeO ). The three samples representative of the least evolved compositions (i.e., SA7, SA35 and SA40) are marked. Solid lines enclose the compositional field of Cenozoic orogenic volcanic rocks of Sardinia (data from literature cited in the text). HMB: high-magnesia basalt; HAB: high-alumina basalt; $\alpha$ : medium-K basalt; $\beta$ : medium- K basaltic andesite; $\gamma$ : medium- K andesite; $\delta$ : medium- K dacite.
$\mathrm{SiO}_{2}$ and with some incompatible trace elements sensitive to crustal contamination (i.e., $\mathrm{Rb}, \mathrm{Ba}$, Zr ), along with the negative correlation with Sr abundance, sensitive to crustal contamination + plagioclase fractionation (Fig. 8).

## Estimates of magma temperatures

 and $\mathrm{H}_{2} \mathrm{O}$ CONCENTRationsGeothermometric determinations based on magnetite/Ti-magnetite and ilmenite pairs (Buddington and Lindsley, 1964) are prevented for the Sant'Antioco suite, due to the rare
occurrence of coexisting, unexsolved crystals of the two opaque phases in the analyzed samples. Therefore, in order to constrain the crystallization temperatures of magmas, the twopyroxenes equilibrium geothermometer of Lindsley (1983) was applied. This approach may provide a general indication of temperature even in the lack of coexisting low-Ca pyroxene, by plotting individual augite phenocryst compositions. The projection onto Lindsley's isotherms for $\mathrm{P}=500 \mathrm{MPa}$ (preferred to the 1 GPa and 1 atm schemes to constrain the maximum crystallization depth at Sant'Antioco,
 $\begin{array}{rrrrrrr}52.68 & 53.18 & 53.91 & 54.51 & 55.55 & 56.00 & 57.22 \\ 1.07 & 1.05 & 0.99 & 0.96 & 0.90 & 0.91 & 0.70 \\ 18.82 & 19.17 & 19.47 & 18.70 & 18.96 & 18.48 & 19.71 \\ 3.43 & 4.42 & 4.56 & 3.69 & 3.82 & 3.63 & 3.39 \\ 5.53 & 4.59 & 4.06 & 4.99 & 4.27 & 4.53 & 3.36 \\ 0.16 & 0.19 & 0.17 & 0.17 & 0.16 & 0.16 & 0.13 \\ 4.41 & 3.76 & 3.19 & 3.07 & 2.58 & 2.59 & 1.78 \\ 9.37 & 9.24 & 9.44 & 8.63 & 8.69 & 8.44 & 8.57 \\ 2.30 & 2.49 & 2.53 & 2.30 & 2.48 & 2.18 & 2.78 \\ 1.00 & 0.72 & 0.97 & 1.11 & 1.07 & 1.42 & 0.95 \\ 0.16 & 0.16 & 0.17 & 0.20 & 0.17 & 0.17 & 0.26 \\ 1.01 & 0.99 & 0.51 & 1.63 & 1.31 & 1.43 & 1.11 \\ 99.94 & 99.96 & 99.97 & 99.96 & 99.96 & 99.94 & 99.96\end{array}$





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$\stackrel{n}{\infty} \underset{\sim}{\dot{\sigma}}$




－чธ்่ч ：VgVH ؛ ؛ alumina basaltic andesite；AND：andesite； ＊lava injection in polygenic breccia； $\mathrm{mg} \#=\mathrm{MgO} /\left(\mathrm{MgO}+\mathrm{FeO}^{*}\right)$ molar，with all $\mathrm{mg} \#=\mathrm{MgO} /\left(\mathrm{MgO}+\mathrm{FeO}^{*}\right)$ molar，with all
iron as FeO ．
Table 6

| FINAL LAVAS（LT） |  |  |  |  |  |  |  |  |  |  | DYKES（F） |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Sample | SAV12 | SA40 | SA7 | SA35 | SAV11 | SA36 | SA3 | SA1 | SA38 | SA9 | SA29 | SA21 | SAV8b | SA25 |
| ${ }^{\text {Rock－type }}$ | HAB | HABA | HABA | HABA | HABA | HABA | HABA | HABA | HABA | HABA | HABA | AND | AND | AND |


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Fig. 5 - Variation diagrams of selected major oxides $v s \mathrm{MgO}$ for the investigated Sant'Antioco volcanic suite. The three samples representative of the least evolved compositions (i.e., SA7, SA35 and SA40) are marked.


Fig. 6 - Variation diagrams of selected trace elements $v s \mathrm{SiO}_{2}$ for the investigated Sant'Antioco volcanic suite. The three samples representative of the least evolved compositions (i.e., SA7, SA35 and SA40) are marked.
according to the observed phase relationships and MELTS modeling; Ghiorso et al., 1994; see below in this Section) indicates that most temperatures fall in the range of $1000-1150^{\circ} \mathrm{C}$.

One of the least evolved basaltic-andesites, SA7 (LT), shows the highest equilibration temperature at $\sim 1200^{\circ} \mathrm{C}$ (Fig. 9).

In addition, crystallization temperatures were


Fig. 7 - Normal MORB-normalized diagram of trace element concentrations (a) and chondrite-normalized REE patterns (b) for representative Sant'Antioco volcanics (HABA: high-alumina basaltic andesite; AND: andesite).
estimated by applying the plagioclase-liquid geothermometer (Putirka, 2008) to the plagioclase cores-whole rock pairs. For these calculations, basaltic andesite and andesite samples characterized by the lowest contents of phenocrysts (either isolated or in glomeri) were selected as the best representative of liquid compositions. The calculated temperature interval of $1100-1165^{\circ} \mathrm{C}$ broadly matches that obtained through Lindsley's (1983) method.
The amount of dissolved $\mathrm{H}_{2} \mathrm{O}$ in the system can be also estimated based on the plagioclasemelt equilibrium equation (Putirka, 2008). Calculations yield $\mathrm{H}_{2} \mathrm{O}$ concentrations in the 2.3$3.9 \mathrm{wt} \%$ range, where the highest value refers to the highest- $\mathrm{Al}_{2} \mathrm{O}_{3}$ lava sample (SA35). A similar range of $\mathrm{H}_{2} \mathrm{O}$ contents (2.0-4.1 wt\%) is derived through the Pichavant and Macdonald (2007) equation (an empirical geohygrometer based on melt compositions for arc basalt melts), using T values obtained from pyroxene geothermometry. Notably, among the least evolved lavas (mg\# $\geq$ 0.4 ), SA35 records both the highest $\mathrm{H}_{2} \mathrm{O}$ content ( $\sim 4 \mathrm{wt} \%$ ) and the lowest crystallization temperature (Table 7).
The obtained $\mathrm{H}_{2} \mathrm{O}$ contents are consistent with the observed plagioclase compositional variations, the $\mathrm{An} / \mathrm{Ab}$ ratio being sensitive to
$\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ in the melt. From experimental evidence (Sisson and Grove, 1993a, b), the $\mathrm{K}_{\mathrm{D}}{ }^{\mathrm{Ca}-\mathrm{Na}}\left(=\mathrm{X}_{\mathrm{Ca}}{ }^{\mathrm{Pl}}\right.$ * $\left.\mathrm{X}_{\mathrm{Na}}{ }^{\text {liq }} / \mathrm{X}_{\mathrm{Na}}{ }^{\mathrm{Pl}} * \mathrm{X}_{\mathrm{Ca}}{ }^{\text {liq }}\right)$ for plagioclase-melt equilibria of high-alumina basalts and basaltic andesites is strongly dependent on $\mathrm{H}_{2} \mathrm{O}$ contents and relatively independent on pressure, as it increases from 1.1 (anhydrous conditions) up to 5.5 ( $\mathrm{H}_{2} \mathrm{O}$-saturated magmas).

On these grounds, the plagioclase-liquid $\mathrm{Ca} / \mathrm{Na}$ (molar) diagram provides constraints on the pre-eruptive $\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ conditions of the studied products (Fig. 10). Concerning high-alumina basaltic andesites, $\mathrm{K}_{\mathrm{D}}^{\mathrm{Ca}-\mathrm{Na}}$ values for microphenocrysts and phenocryst rims vs bulk groundmass compositions range from ca. 1.3 to 2.3, most of the data points plotting between the experimental $\mathrm{K}_{\mathrm{D}}{ }^{\mathrm{Ca}-\mathrm{Na}}$ equilibrium lines for
 hydrated melts ( $\mathrm{K}_{\mathrm{D}}{ }^{\mathrm{Ca}-\mathrm{Na}=1.7 \text {; Fig. 10). }}$ Phenocryst cores $v s$ whole rock equilibria yield higher $\mathrm{K}_{\mathrm{D}}{ }^{\mathrm{Ca}-\mathrm{Na}}$ values (from ca. 2.6 to 4.5 ), corresponding to the interval between $2 \mathrm{wt} \%$ $\mathrm{H}_{2} \mathrm{O} \quad\left(\mathrm{K}_{\mathrm{D}}{ }^{\mathrm{Ca}-\mathrm{Na}=1.7)}\right.$ and the $\mathrm{H}_{2} \mathrm{O}$-saturated conditions ( $6 \quad \mathrm{wt} \% \quad \mathrm{H}_{2} \mathrm{O} ; \quad \mathrm{K}_{\mathrm{D}}{ }^{\mathrm{Ca}-\mathrm{Na}=5.52}$ ). Phenocryst cores $v s$ whole rock data for selected andesites (Fig. 10) reveal lower $\mathrm{H}_{2} \mathrm{O}$ concentrations than in basaltic andesites


Fig. 8 - Variation diagrams of ${ }^{87} \mathrm{Sr} /{ }^{86} \mathrm{Sr} v s \mathrm{SiO}_{2}$ and selected trace elements for representative Sant'Antioco mafic volcanics. Data for volcanic rocks from Montresta (HMB: high- MgO basalt, HAB : high- $\mathrm{Al}_{2} \mathrm{O}_{3}$ basalt, BA : basaltic andesite and AND: andesite) and Sarroch (basaltic andesite and andesite) districts (after Morra et al., 1997 and Conte, 1997) are also reported for comparison.


Fig. 9 - Representative analyses of pyroxenes from the Sant'Antioco study suite, projected onto the Di-En-Fs-Hd quadrilater (following Lindsley, 1983). Isotherms are shown for $\mathrm{P}=500 \mathrm{MPa}$, chosen, in preference to 1 GPa or 1 atm , as the most appropriate pressure conditions for magma crystallization in our case study (see text).

Table 7
Calculated water contents $\left(\mathrm{H}_{2} \mathrm{O}\right.$ wt\%) for selected Sant'Antioco samples, following the methods of Pichavant and McDonald (2007) and Putirka (2008).

| Rock <br> samples | Pichavant and <br> Macdonald <br> $(2007)$ | Putirka <br> $(2008)$ |
| :--- | :---: | :---: |
| SAV12 | 3.8 | - |
| SA7 | 2.6 | 2.4 |
| SA35 | 4.1 | 3.9 |
| SA40 | 2.5 | 2.7 |
| SAV11 | 2.9 | 2.5 |
| SA15 | 3.1 | - |
| SAV15b | 3.4 | 2.6 |
| SAV13 | 3.3 | - |
| SA10 | 2.4 | - |
| SAV10 | 3.1 | - |
| SAV5 | 2.0 | 2.3 |
| SAV8 | 3.5 | - |

(comparable to the values obtained from crystal rims in these latter).

Furthermore, the relationships between the calculated $\mathrm{H}_{2} \mathrm{O}$ contents in the melts and plagioclase compositions for some of the least evolved lavas (i.e., SA7, SA40 and SA35) were checked following silicate melt modeling (Ghiorso et al., 1994) for different amounts of dissolved water in the system ( $1-6 \mathrm{wt} \%$ ), within the load pressure interval of $100-400 \mathrm{MPa}$. Model results broadly confirm the above estimated water contents, the latter being the most critical parameter controlling $\mathrm{K}_{\mathrm{D}}$ values (rather than mere load pressure). For example, a run at $\mathrm{P}=100 \mathrm{MPa}, \mathrm{T}=1110^{\circ} \mathrm{C}$ and $2 \mathrm{wt} \% \mathrm{H}_{2} \mathrm{O}$ fits the calculated $\mathrm{K}_{\mathrm{D}}{ }^{\mathrm{Ca}-\mathrm{Na}}$ for phenocryst cores $v s$ whole rock for sample SA7, while a run at $\mathrm{P}=200 \mathrm{MPa}, \mathrm{T}=1040^{\circ} \mathrm{C}$ and $5 \mathrm{wt} \% \mathrm{H}_{2} \mathrm{O}$ yields a $\mathrm{K}_{\mathrm{D}}{ }^{\mathrm{Ca}-\mathrm{Na}}$ matching that obtained for sample SA35. Finally, from pilot experiments performed on the


Fig. 10 - Comparison of [Ca]/[Na] (molar) in plagioclase and coexisting liquid for selected samples from Sant'Antioco volcanics (HABA: high-alumina basaltic andesite; AND: andesite). The three samples representative of the least evolved compositions (i.e., SA7, SA35 and SA40) are marked. Each bar represents the range of values for a single rock-sample. Crystal-liquid equilibria are referred to either phenocryst cores $v s$ whole rock compositions or phenocryst rims and microphenocrysts $v s$ bulk groundmass compositions. Straight lines represent experimental equilibrium $\mathrm{K}_{\mathrm{D}}{ }^{\mathrm{Ca}-\mathrm{Na}}$ values for


Sant'Antioco least evolved rocks, it has been inferred that SA35 experienced crystallization under significantly higher $\mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}$ with respect to SA40 and SA7 (Conte et al., 2000).

## Petrogenetic inferences

The paucity of primitive magma compositions in subduction-related volcanism worldwide precludes the assessment of the origin of primary magmas, and makes it difficult to distinguish the effects of subcrustal $v s$ crustal processes. Similarly, as concerns the rather differentiated lavas from Sant'Antioco, only low-pressure processes involved in their petrogenesis can be addressed here. Indications on source-related processes can be only tentatively drawn by comparison with less-evolved Cenozoic calcalkaline rocks of Sardinia.
By considering the new set of mineropetrographic and geochemical data, in the light of the huge amount of literature studies on highalumina arc magmatism, it appears that the wide spectrum of low- MgO (and low $\mathrm{Mg} \#, \mathrm{Ni}, \mathrm{Cr}$ ), high-alumina rock-types from Sant'Antioco likely reflects extensive fractional crystallization of a parental basaltic liquid, where changes in the fractionating mineral assemblages occurred in response to variable $\mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}$ conditions (Sisson and Grove, 1993a, b; Pichavant and Macdonald, 2007 and references therein; Ulmer, 2007 and references therein), coupled with crustal interaction at some extent (as suggested by trace element and Sr isotope data; Geochemistry section). On the other hand, the lack of typical disequilibrium textures (i.e., rim resorption, mantling by other phases, reverse or oscillatory zoning) in pyroxene crystals does not support additional low-pressure processes, such as mixing between compositionally different magmas. In this regard, plagioclase dusty textures and zoning patterns are not considered as conclusive evidence of magma mixing and are, instead, thought to be essentially controlled
by $\mathrm{H}_{2} \mathrm{O}$ conditions (also cfr. Lonis et al., 1997). Even if, in some cases, the observed plagioclase disequilibrium textures and the occurrence of polycrystalline aggregates in LI andesites may point out some crystal recycling in the magma reservoir, we exclude that this process may have significantly affected the chemical evolution of the Sant'Antioco magmas. In this regard, the observed wide scattering in $\mathrm{Al}_{2} \mathrm{O}_{3}$ and CaO vs MgO contents (Fig. 5) would imply unlikely high amounts (some tens vol\%) of plagioclase + pyroxenes-bearing glomeri (also cfr. Brotzu et al., 1997a), which do not actually occur in the study volcanics. Moreover, trace element patterns (e.g., the absence of $\mathrm{Sr}, \mathrm{Eu}$ and Cr positive anomalies) provide no evidence of significant cumulitic processes.

In order to constrain in more detail the petrogenetic processes involved in the studied rock suite, we focus now on the least evolved compositions (i.e., SA7, SA40 and SA35, highalumina basaltic andesites), which are characterized by different $\mathrm{MgO}, \mathrm{Al}_{2} \mathrm{O}_{3}, \mathrm{~K}_{2} \mathrm{O}$ and FeO contents, in spite of similar $\mathrm{SiO}_{2}$ contents (around $52 \mathrm{wt} \%$ ). In Fig. 5, the $\mathrm{Al}_{2} \mathrm{O}_{3}$-richest sample, SA35, also displays slightly higher CaO and lower FeO contents with respect to the MgO-richest sample, SA7, while sample SA40 shows intermediate contents. Trace element contents are quite similar, except for higher Sr in SA35 and slightly higher Ni and Cr in SA7 (Table 6).

In addition, the three samples are characterized by distinctive phenocryst assemblages, although all plagioclase-dominated (TABLE 2): the $\mathrm{Al}_{2} \mathrm{O}_{3^{-}}$ richest, phenocryst-poorest, sample SA35 contains the lowest plagioclase amount, and olivine plus rare Cpx as mafic phases; SA 40 , with intermediate $\mathrm{Al}_{2} \mathrm{O}_{3}$ content, shows higher abundances of plagioclase and mafic phases, with olivine again prevailing on Cpx; in SA7, the $\mathrm{Al}_{2} \mathrm{O}_{3}$-poorest and MgO -richest sample, Cpx prevails on olivine, and minor amounts of Opx are also observed.

The three samples also differ in mineral chemistry, being characterized by distinct plagioclase compositions (i.e. $\mathrm{An}_{75-85}, \mathrm{An}_{78-90}$ and $\mathrm{An}_{85-93}$ for SA7, SA40 and SA35, respectively; Fig. 2) and different $\mathrm{Al}_{2} \mathrm{O}_{3}$ contents in Cpx (from $\sim 2 \mathrm{wt} \%$ in SA7 up to $\sim 6 \mathrm{wt} \%$ in SA35), which parallel whole-rock $\mathrm{Al}_{2} \mathrm{O}_{3}$.
These differences likely indicate that corresponding magmas underwent different preeruptive conditions of storage and crystallization, consistent with the above estimated values of temperature, pressure of crystallization and dissolved water content for the three cases. In particular, plagioclase-host liquid equilibria (Fig. 10) provide quantitative information on $\mathrm{H}_{2} \mathrm{O}$ contents in the three magmas at different evolutionary stages (the liquid compositions being roughly represented by either the whole-rock or groundmass bulk compositions with ongoing magma crystallization).
Water content data broadly fit the abovereported mineralogical features of samples. In fact, it has been proven that high dissolved $\mathrm{H}_{2} \mathrm{O}$ concentrations in high-alumina melts, not only favour the early formation of spinel and the crystallization of An-richer plagioclase, but also reduce the total proportion of plagioclase in the crystallizing assemblage, expand the stability field of olivine at the expense of other mafic phases such as Cpx and Opx, and decrease the En-Fs contents of Cpx in favour of CaTs (Kushiro, 1969; Sisson and Grove, 1993a; Pichavant and Macdonald, 2007).

These considerations lead us to conclude that changes in phenocryst proportions and compositions (and consequent changes in bulk rock chemistry) in the least evolved basaltic andesites were determined by different $\mathrm{H}_{2} \mathrm{O}$ concentrations in the melts and by the physical conditions controlling water exsolution from the system during magma ascent. In summary: the $\mathrm{Al}_{2} \mathrm{O}_{3}$-richest, MgO -poorest sample (SA35) displays, consistent with the highest $\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ (up to
ca. $6 \mathrm{wt} \%$, Fig.10), the lowest modal amount of plagioclase, accompanied by the Ca-richest composition, a paucity of Cpx , with the $\mathrm{Ca}-\mathrm{Ts}-$ richest augite composition, and the presence of olivine. Conversely, the MgO -richest, $\mathrm{Al}_{2} \mathrm{O}_{3}$ poorest composition of SA7, may reflect a crystallization path under $\mathrm{H}_{2} \mathrm{O}$-poorer conditions (up to ca. $3 \mathrm{wt} \%$ ), which favoured the crystallization of higher amounts of Ca -poorer plagioclase and $\mathrm{Al}_{2} \mathrm{O}_{3}$-poorer Cpx , as well as the occurrence of Opx at the expense of olivine. SA40, which shows intermediate $\mathrm{Al}_{2} \mathrm{O}_{3}$ and MgO contents, consistently accounts for intermediate $\mathrm{H}_{2} \mathrm{O}$ concentration in the magma (up to ca. $4 \mathrm{wt} \%$ ). In this picture, the Ab-richer plagioclase rims and microphenocrysts in the three samples may testify late $\mathrm{H}_{2} \mathrm{O}$ exsolution.

Moreover, modes of water retention/exsolution in the system influence the amphibole stability field. Notably, amphibole only occurs in two LI samples, which records prolonged $\mathrm{H}_{2} \mathrm{O}$ retention in the corresponding magmas; late-stage processes of decreasing pressure and $\mathrm{H}_{2} \mathrm{O}$ exsolution, causing amphibole break-down, are testified by the presence of opacitic rims.

The effect of $\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ on phase equilibria thus may represent the key factor in determining the observed geochemical differences among the least evolved Sant'Antioco rock-types, as a result of different evolution paths from a possible common parental melt.

## Identification of the parental magma

As it is typical of arc-related magmatism worldwide (e.g., Nye and Reid, 1986; Brophy, 1989; Eggins, 1993; Sisson and Grove, 1993b; Rohrbach et al., 2005; Pichavant et al., 2002; Pichavant and Macdonald, 2007), in Cenozoic orogenic magmatism of Sardinia, high-magnesia basalts (HMBs, MgO >8 wt\%), possibly representative of mantle-derived magmas, are relatively uncommon and limited to a few areas (Mattioli et al., 2000 and references therein). In
particular, HMBs from the Montresta district, NW Sardinia (18.5 Ma, Montigny et al., 1981; Morra et al., 1997; Fig. 1) could match in composition the possible precursor for Sant'Antioco LT basaltic andesites. In fact, the high- $\mathrm{Al}_{2} \mathrm{O}_{3}$ basaltic andesites derived from Montresta HMBs through fractional crystallization $\pm$ assimilation processes (Morra et al., 1997) show major and trace element compositions that closely resemble those from Sant'Antioco (Fig. 11, 12), except for significantly lower Ba contents (e.g., 140-250 vs 300-400 ppm, for Montresta and Sant'Antioco HABA, respectively; Fig. 8).
If a typical Montresta HMB (e.g., sample $\mathrm{KB} 13, \mathrm{MgO}=9.08 \mathrm{wt} \%$, Morra et al., 1997) is chosen as representative of the Sant'Antioco parental magma composition, major element mass balance calculations (following Stormer and Nicholls, 1978) broadly indicate that samples SA7, SA40 and SA35 may be consistently derived by fractional crystallization under different $\mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}$ conditions (Table 8). Notably, the results yield similar fractions of residual liquid for the three cases ( $\sim 45-50 \mathrm{wt} \%$ ), but different proportions of the main crystal phases (especially plagioclase vs mafic phases), i.e.: $\mathrm{Plg} /(\mathrm{Ol}+\mathrm{Cpx})=0.52,0.36$ and 0.24 for SA7, SA40 and SA35, respectively.
The similar fractions of residual liquid may account for the similar contents in the majority of incompatible trace elements in the three cases, whereas the observed differences in the Sr contents can be explained by the different amounts of plagioclase fractionation (Fig. 6; 7a, b).
It is also worth noting that relatively high $\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ conditions ab initio, which determine the fractionation of high proportions of mafic phases (with high $\mathrm{MgO} / \mathrm{FeO}^{*}$ ratios), with respect to plagioclase, may even result in the observed ambiguous tholeiitic character of the Sant'Antioco mafic volcanics (Fig. 4). In our interpretation, this inference could also apply to the "tholeiitic" lavas in the Montresta district
(Morra et al., 1997).

## Magma evolution

From the whole compositional spectrum of the studied Sant'Antioco volcanics it appears that the differences existing in the least evolved compositions also reflect in the differentiation products (Fig. 5, 11). Major-element massbalance calculations (Table 9) show that the latter can be derived through prolonged fractional crystallization of $\mathrm{Plg}+\mathrm{Cpx}+\mathrm{Fe}-\mathrm{Ti}$ oxides $\pm \mathrm{Ol} \pm \mathrm{Opx}$ mineral assemblages. In more detail, if SA35 and SA7 lava-types, which display the most significant differences in terms of oxide concentrations and $\mathrm{H}_{2} \mathrm{O}$ contents, are considered as starting melts, the results of calculations evidence that olivine continues to play a role in the early stages of the $\mathrm{H}_{2} \mathrm{O}$-rich differentiation trend starting from SA35 (Fig. 11), while Opx may replace olivine in the fractionating crystal assemblage along the $\mathrm{H}_{2} \mathrm{O}-$ poor differentiation trend starting from SA7 (Fig. 11, Table 9). These results confirm, also in agreement with experimental evidence (Pichavant and Macdonald, 2007 and references therein), that in mafic to intermediate calcalkaline magmas Opx is stable only under low $\mathrm{H}_{2} \mathrm{O}$ concentrations, while in more hydrous conditions Opx crystallization is delayed and takes place extensively only in $\mathrm{SiO}_{2}$-richer magmas at lower temperatures. Indeed, in the Sant'Antioco volcanics, like in other typical arcrock suites (e.g., Macdonald et al., 2000), Opx is always present in the most differentiated rocks ( $\mathrm{SiO}_{2}>55 \mathrm{wt} \%$; Table 9). In more hydrous melts, Opx crystallization is joined by amphibole during the late differentiation stages.

However, simple fractional crystallization cannot fully explain the whole compositional spectrum of the study rock suite. In this regard, the above reported ${ }^{87} \mathrm{Sr} /{ }^{86} \mathrm{Sr}$ data ( 0.70698 to $0.70858 \pm 1$; TABLE 2; Fig. 8) are in the 0.70398 0.71130 range pertaining to the Cenozoic
Table 8
Modeled fractionation steps (following Stormer and Nicholls, 1978) for the least evolved basaltic andesites from Sant'Antioco, starting from a typical high-magnesia basalt of Montresta, inferred as possible parental magma.

From HMB-KB13 (Montresta district) to HABA's (Sant'Antioco district)

|  |  | from KB13 to SA35 |  | from KB13 to SA40 |  | from KB13 to SA7 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | KB13* | SA35 | residuals | SA40 | residuals | SA7 | residuals |
| $\mathrm{SiO}_{2}$ | 48.88 | 52.54 | 0.02 | 52.06 | 0.00 | 52.34 | 0.04 |
| $\mathrm{TiO}_{2}$ | 0.75 | 1.04 | 0.00 | 1.09 | 0.01 | 1.07 | 0.01 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 15.55 | 21.02 | 0.00 | 20.00 | 0.00 | 19.22 | 0.02 |
| FeO* | 10.16 | 8.27 | 0.02 | 9.27 | 0.04 | 9.38 | 0.05 |
| MnO | 0.12 | 0.16 | 0.00 | 0.18 | 0.02 | 0.18 | 0.01 |
| MgO | 9.08 | 3.14 | 0.00 | 3.63 | 0.02 | 4.72 | 0.00 |
| CaO | 12.90 | 10.63 | 0.01 | 10.08 | 0.01 | 10.11 | 0.01 |
| $\mathrm{Na}_{2} \mathrm{O}$ | 1.81 | 2.40 | 0.14 | 2.53 | 0.05 | 2.12 | 0.26 |
| $\mathrm{K}_{2} \mathrm{O}$ | 0.52 | 0.58 | 0.05 | 0.98 | 0.00 | 0.70 | 0.04 |
| $\mathrm{P}_{2} \mathrm{O}_{5}$ | 0.23 | 0.21 | 0.02 | 0.18 | 0.02 | 0.16 | 0.03 |
|  | 100.00 | 100.00 |  | 100.00 |  | 100.00 |  |
| $\sum^{\text {r }}$ |  | 0.25 |  |  | 0.16 |  | 0.48 |
| Removed crystals (wt\%) |  |  |  |  |  |  |  |
| Ol |  | 11.89 |  | 10.46 |  | 8.17 |  |
| Cpx |  | 28.41 |  | 28.18 |  | 27.51 |  |
| Plg |  | 9.57 |  | 13.74 |  | 18.66 |  |
| $\mathrm{Fe}-\mathrm{Ti}$ oxides |  | 0.10 |  |  |  | 0.75 |  |
| $\mathrm{wt} \%$ of residual liquid |  | 50.03 |  | 47.62 |  | 44.91 |  |
| $\mathrm{Cpx} / \mathrm{Ol}$ |  | 2.39 |  | 2.70 |  | 3.37 |  |
| $\mathrm{Cpx}+\mathrm{Ol}$ |  | 40.30 |  | 38.63 |  | 35.68 |  |
| $\mathrm{Plg} /(\mathrm{Cpx}+\mathrm{Ol})$ |  | 0.24 |  | 0.36 |  | 0.52 |  |

[^2]Table 9
Modeled fractionation steps (following Stormer and Nicholls, 1978) for the basaltic andesites and andesites of the Sant'Antioco suite, starting from SA7 and SA35 compositions, as discussed in the text.

$\sum^{\mathrm{r}}$ : Sum of squared residuals; other abbreviations as in TABLE 2. Additional explanations as in Table 8.


Fig. 11 - Plot of CaO (a) and $\mathrm{Al}_{2} \mathrm{O}_{3}$ (b) vs MgO contents for the investigated Sant'Antioco volcanics, compared with Montresta (data after Morra et al., 1997; rock abbreviations as in Fig. 8). Arrows represent possible differentiation paths, as considered in mass balance calculations (Table 8, 9). Samples marked are discussed in the text.
orogenic rocks of Sardinia (Dupuy et al., 1974, 1979; Coulon, 1977; Brotzu et al., 1997a, b; Conte, 1997; Morra et al., 1997; Downes et al., 2001), for which different degrees of crustal contamination, coupled with variable enrichment of mantle source by subducted sediments, has been proposed. At Sant'Antioco, the observed range of Sr isotope data, the positive correlation of ${ }^{87} \mathrm{Sr} /{ }^{86} \mathrm{Sr} v s$ elements with crustal affinity (e.g., $\mathrm{Si}, \mathrm{Rb}, \mathrm{Ba}$; Fig. 8), as well as the wide scattering of trace elements (Fig. 6), strongly suggest contamination by crustal wall rocks. In particular, the Sant'Antioco ${ }^{87} \mathrm{Sr} /{ }^{86} \mathrm{Sr}$ values are significantly higher with respect to the chemically analogous products of Montresta, whereas they overlap the higher values from the


Fig. 12 - Representative REE patterns for high- $\mathrm{Al}_{2} \mathrm{O}_{3}$ basaltic andesites (HABA) and andesites (AND) from Sant'Antioco and Montresta (shaded field; data after Morra et al., 1997). The pattern for the Montresta high- MgO basaltic sample (HMB, KB13), considered as parental magma in petrogenetic modeling, is also reported (data after Morra et al., 1997).
nearby Sarroch volcanic district (Fig. 8). In the latter, crustal assimilation has been revealed and quantified in about 4-14 wt\% (Conte, 1997), where the assimilated material considered, i.e. an average composition of the granitoid batolith of Sardinia (from Del Moro et al., 1975; Secchi et al., 1991), would account for the observed trace element enrichment (e.g., $\mathrm{Ba}, \mathrm{Rb}$ and Zr ) and depletion (e.g., Sr ) trends. Besides the oversimplified assumption concerning the crustal material involved, considering the similar ${ }^{87} \mathrm{Sr} /{ }^{86} \mathrm{Sr}$ ratios and trace elements behaviour observed for Sant'Antioco and Sarroch volcanics, we infer that crustal contamination affected magma evolution at Sant'Antioco at analogous, or even slightly higher, extent.

## Concluding remarks

The present work integrates the petrological knowledge on the Cenozoic orogenic magmatism of western Sardinia, with focus on mafic to intermediate rock-types. New data on

Sant'Antioco relatively mafic volcanics, mostly represented by basaltic andesites and andesites, reveal a remarkably wide compositional spectrum in terms of $\mathrm{Al}_{2} \mathrm{O}_{3}, \mathrm{MgO}$ and CaO contents, as related to the characterizing mineral assemblages. The observed variability in whole rock and mineral chemistry likely correlates to different liquid lines of descent, controlled by the $\mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}$ histories of magma systems, starting from a common parental magma composition. The latter has been identified as a high- MgO basalt similar in composition to the broadly coeval Montresta primitive lavas. Different from the Montresta district, the Sant'Antioco area is characterized by the lack of primitive terms, possibly indicating different local tectonic regime favouring magma ponding and differentiation at upper crustal levels.
The overall geochemical features of the Sant'Antioco study rock-types evidence a clear calc-alkaline signature, despite relatively high values of $\mathrm{FeO}^{*} / \mathrm{MgO}$ that could mimic a misleading tholeiitic affinity. Starting from the composition of a Montresta HMB, considered as a suitable primitive (possibly near-primary) magma, two end-member differentiation trends are recognized, which lead respectively to the MgO -richest $/ \mathrm{Al}_{2} \mathrm{O}_{3}$-poorest and MgO -poorest/ $\mathrm{Al}_{2} \mathrm{O}_{3}$-richest basaltic andesites, representing the least evolved rock-types at Sant'Antioco. These trends can be respectively explained by higher proportions of plagioclase $v s$ olivine +Cpx in the fractionating assemblage under $\mathrm{H}_{2} \mathrm{O}$-poorer conditions and vice versa in $\mathrm{H}_{2} \mathrm{O}$-richer conditions. Basically, the $\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}$ imprint is recorded up to the most evolved compositions, being also the main controlling factor of incoming Opx crystallization.
Finally, Sr isotope data and the trends of trace elements of "crustal affinity" with increasing degree of magma evolution, indicate that different degrees of crustal contamination also played a significant role in the petrogenesis of Sant'Antioco volcanics, consistent with magma
slow ascent and ponding within a tick crust in multiple reservoirs and/or feeder conduits that behaved independently.

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## Appendix A: Analytical methods

Whole-rock samples were analyzed for major and selected trace elements (V, Cr, Co, Ni, Rb, $\mathrm{Sr}, \mathrm{Y}, \mathrm{Zr}, \mathrm{Nb}, \mathrm{Ba}, \mathrm{Th}$ ) by a Philips PW1480-XRF spectrometer at IGG-CNR, Rome, using fused dishes (major element) and pressed powder pellets (trace elements). Philips X40 software was used for data reduction. Analytical precision is generally better than $3 \%$ and $5 \%$, for major and trace elements, respectively.

LOI was determined after the samples had been kept at $1050^{\circ} \mathrm{C}$ for 2 h ; resulting losses were corrected for FeO oxidation and FeO was measured by titration with KMnO after acid digestion.

REE, Ta, Hf and U were determined by ICPMS at the Activation Laboratories, Ancaster, Canada.

Sr isotope ratios were measured, after sample dissolution and ion exchange separation procedures, on a VG354 double collector mass spectrometer at the University Federico II, Naples. Repeated analyses of NBS-987 international reference standard gave an average value of $0.71027 \pm 0.00001(2 \sigma)$.

Mineral analyses were carried out using a Cameca SX50 electron microprobe with an accelerating voltage of 15 keV and 15 nA beam current at C.N.R.-IGAG, Rome, using the ZAF correction procedure.

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[^0]:    * Corresponding author,

[^1]:    ${ }^{\text {a }}$ phenocrysts ( $>0.5 \mathrm{~mm}$ ); ${ }^{\text {b }}$ microphenocrysts ( $>0.05 \mathrm{~mm}$ ); Plg: plagioclase; Ol: olivine; Cpx:
    clinopyroxene; Opx: orthopyroxene; Hbl: horneblende; P.I.: porphyritic index; Gdm: groundmass; HABA:
    high- $\mathrm{Al}_{2} \mathrm{O}_{3}$ basaltic andesite; AND: andesite; DAC: dacite.

[^2]:    $\sum \mathrm{r}^{2}$ : Sum of squared residuals; other abbreviations as in TABLE 2; * compositions of whole rock and mineral phases from Morra et al. (1997). For each step of mass balance, the compositions of removed crystals are taken from phenocryst phases (usually rim compositions) from the corresponding parent rocks (see TABLE 3, 4, 5).

