

## CHAPTER 1

### San Vincenzo volcanites

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#### 1.1 HISTORICAL PERSPECTIVE

The area near the town of S. Vincenzo is placed where the Metal Hills reach the sea, forming a trait that links the plain of the river Cecina with the plain of the river Cornia. The first traces of human presence date back to the upper paleolithic age. During Etruscan times this area was densely populated, both for the proximity of Populonia, that was the very powerful Lucumonia at that time, and for the presence of minerals (see Part II, Chap. 2, Fig. 1), large forests and foundries that almost certainly made this an industrial area.

The Romans, once they had conquered the area, made the Aurelia road passing through the actual town of S. Vincenzo and probably built a village and a harbour. In 1406 the Republic of Pisa built the coastal tower, thus stating the new community of S. Vincenzo. This tower is part of a series of coastal fortifications that are scattered along the coast to defend the beaches and the villages from the attack of pirates. Next to the tower evolved the first centre, consisting mainly of small houses of fishermen and farmers. In 1406 S. Vincenzo «passed» under Florentine domination and became part of Campiglia's territory. Then it followed the destiny of the Grand Dukedom of Tuscany until the unification of Italy.

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#### 1.2 GEOLOGICAL SETTING

The Campiglia mounts consist of a series of Cretaceous-Triassic calcareous formations belonging to the Tuscan nappe, overlaid by the Liguride formations and neogene deposits. In this area are present not only the S.Vincenzo volcanites, but also the Botro ai Marmi granite and some quartz- monzonitic veins between Valle S.Maria and Valle del Temperino (see Part III, Chap. 5).

The volcanites (Fig. 1) cover an area of about 10 km<sup>2</sup> north of the town of S.Vincenzo, and consist of both fissural lava flows and lava domes, the latter aligned along a N-S direction from Torre Donoratico to Valle delle Rozze. All outcropping rocks are rhyolites in which are dispersed variable amounts of magmatic enclaves with latitic composition.

Age data on these volcanites are quite scattered: 3.26 Ma (Rb/Sr, Ferrara *et al.*, 1977), 3.7 Ma (fission tracks, Bigazzi and Ferrara, 1971), 4.7 Ma (K/Ar, Borsi and Ferrara, 1971) and 4.96 Ma (fission tracks, Arias *et al.*, 1981). Feldstein *et al.* (1994) obtained 4.38-4.67 Ma by <sup>40</sup>Ar-<sup>39</sup>Ar method, and the younger age can be considered the eruption age.

Whole rock major element compositions have been analysed by Giraud *et al.* (1986), Ferrara *et al.* (1989) and Pinarelli *et al.* (1989). All the authors report a division of the

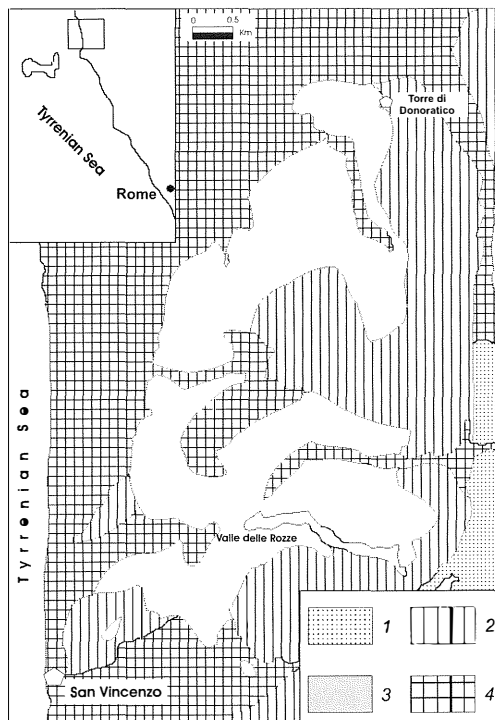


Fig. 1 – Schematic geologic map of S. Vincenzo area. 1: Cretaceous-Triassic limestones; 2: «Monteverdi Marittimo» ligurides units (ophiolites s.l.); 3: volcanites; 4: Neogene deposits. After Pinarelli *et al.* (1989).

S.Vincenzo rhyolites into two groups: group I and II on the basis of major elements (Giraud *et al.*, 1986), group A and B on the basis of MgO contents (Ferrara *et al.*, 1989), and high-Sr and low-Sr groups (Pinarelli *et al.*, 1989). Feldstein *et al.* (1994) used the classification of Ferrara *et al.* (1989) to study isotopic systematic on whole rocks and minerals.

A revision of all the published data proves that the two groups, even if distinguished with different criteria, are exactly the same. In this paper we use Not-Mixed Group (Hereafter NMG; formerly groups I, A, and low-Sr) and Mixed Group (hereafter MG; formerly groups II, B, and high-Sr). It is to note that the two groups reflect different geographical settings as also evidenced by Pinarelli *et al.* (1989). In fact, MG and NMG samples represent the NNE

and the SSW part, respectively, of the area covered by the volcanites (Fig. 2).

### 1.3 PETROGRAPHY

S. Vincenzo volcanites have a porphyritic texture with glassy, cripto- or micro-crystalline groundmass. The phenocryst assemblage is dominated by quartz, alkali feldspar, plagioclase, and biotite with lesser amounts of cordierite; apatite, epidote, monazite, ilmenite, and zircon are present as accessory phases. Groundmass phases include plagioclase, biotite, apatite, zircon, and ilmenite. MG lavas also contain clinopyroxene megacrysts, clots of

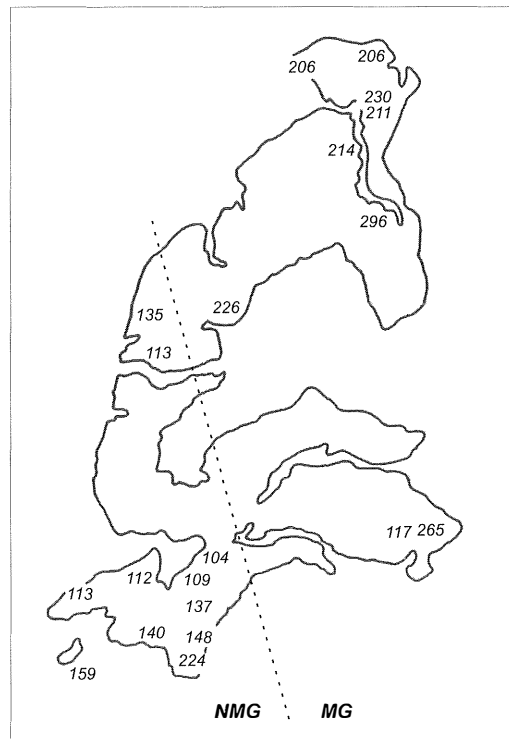


Fig. 2 – Sketch map of S. Vincenzo volcanites showing the Sr content of samples, indicated by the numbers on the map. The dashed line divides the area in two parts. Samples west and east of the line belong to NMG and MG group, respectively. Modified from Pinarelli *et al.* (1989).

clinopyroxene-orthopyroxene and orthopyroxene-plagioclase, as well as magmatic enclaves with latitic composition.

Modal analyses, reported in table 1, show an average crystallinity of 46% and 41% for the MG and NMG group, respectively, even if it is possible to recognize a large variability within single samples. Both groups of rocks are constituted by a glassy matrix, although samples from MG have considerable groundmass crystallization.

### Plagioclase

Plagioclase is most commonly observed as euhedral to subhedral crystals up to 2.0 mm in diameter, although cumulus clots of euhedral grains are also present. The composition of plagioclase from the MG spans a wide range, with very calcic core compositions ( $An_{80}$ ) and rims and groundmass crystals in the range  $An_{30-60}$ . Plagioclase grains in the NMG are generally less calcic, with core compositions up to  $An_{68}$  and rims and groundmass crystals in the range  $An_{27-34}$ . Resorption surfaces are common in the MG but rarer in the NMG.

Disequilibrium textures such as sieve rims or cores (also referred to as honeycomb, fingerprint, spongy, and mottled textures; see Hibbard, 1991 for details) are observed in approximately 30% of the plagioclase in the MG samples but only 10% in the samples from NMG. Plagioclase immediately adjacent to sieve cores is commonly very calcic, up to  $An_{83}$ . Plagioclase is also found as euhedral crystals in the mafic enclaves and associated with pyroxene clots (MG only) and crystals are normally zoned from  $An_{85}$  at the core to  $An_{46}$  at the rims.

### Alkali Feldspar

Alkali feldspar occurs as euhedral to anhedral crystals, commonly embayed, up to 2.0 mm in diameter in both MG and NMG samples. Crystals commonly display granophyric intergrowths with quartz and contain inclusions of biotite and plagioclase oriented parallel to the crystal faces. These textures support a magmatic origin (e.g. Wall *et al.*, 1987). The alkali feldspars vary significantly in composition ( $Or_{56-78}$ ), with rim and groundmass compositions spanning the entire range.

### Biotite

Two populations of biotite are recognized. Ferric biotite is found as individual grains or inclusions in plagioclase, cordierite, and alkali feldspar and as a groundmass phase. Groundmass crystals have Mg# [ $Mg/(Mg + Fe)$ ] ranging from 0.38 to 0.56,  $Al^{VI}$  from 0.46 to 0.74, and  $F/(F + OH)$  from 0.17 to 0.42. Magnesian biotite constitutes a small percentage of the total biotite population. It is found as phenocrysts within the mafic enclaves and is associated with clinopyroxene-orthopyroxene glomerocrysts and plagioclase with extensive sieve zones. Their Mg# ranges from 0.56 to 0.78,  $Al^{VI}$  from 0.17 to 0.33, and  $F/(F + OH)$  from 0.15 to 0.35. Disequilibrium textures, characterized by several titanian magnetite inclusions surrounded by a zone of plagioclase ( $An_{47}$ ) or glass, is frequently observed in the magnesian biotites.

TABLE 1

Average mineralogical modal compositions of *S. Vincenzo rhyolites* (modified from Pinarelli *et al.*, 1989).

Mineral	MG		NMG	
	Average (n=4)	SD %	Average (n=5)	SD %
Plagioclase	16.3 ± 5.1		14.3 ± 7.2	
K-feldspar	13 ± 5.1		12.6 ± 6.9	
Quartz	6.9 ± 3.2		6.6 ± 4.1	
Biotite	9.2 ± 0.7		6.7 ± 4.3	
Cordierite*	1.1		0.8	
Accessories*	0.2		0.4	
Groundmass	53.8 ± 4.9		59.4 ± 15.3	

\* maximum observed values



chemographic tests to assess equilibrium crystallization suggested by Brown and Parsons (1981), have been applied to S. Vincenzo feldspars. In agreement with petrographic evidence, many feldspar pairs resulted not in equilibrium. Only four feldspar couples from NMG were selected for temperature calculations. Temperatures obtained from different pairs are consistent with each other, and indicate crystallization temperatures of 740-790 °C for S. Vincenzo NMG volcanites.

The ternary feldspar thermometer of Fuhrman and Lindsley (1988) was used with the revised parameters of Lindsley and Nekvasil (1989) to determine temperatures of coexisting alkali feldspar and plagioclase in the rhyolites. However, two feldspars exhibiting textural unequivocal evidence for equilibration are rare. An equilibrium temperature of 780 °C at 2.0 Kb was obtained for a pair of feldspars in a clot ( $An_{35}Or_4$  and  $Or_{75}An_1$ ), in agreement with the temperatures above reported. Temperatures calculated from plagioclase crystals mantled by alkali feldspar are not concordant, suggesting that the mantling process was due to disequilibrium conditions (e.g. Hibbard, 1981). Crystallization experiments on peraluminous magmas of compositions similar to those of S. Vincenzo provided an upper limit temperature of 825-870 °C by the presence of biotite (Clemens and Wall, 1981). Two-oxide thermometry could not be used to obtain temperatures in the rhyolite since only one oxide (magnetite) is present. The two-pyroxenes thermometer of Lindsley (1983) was used to determine temperatures of coexisting clinopyroxene and orthopyroxene found as clots in the MG lavas. A temperature of 1100°C at low pressures (2.0 Kb) was obtained from cores of adjacent clinopyroxene and orthopyroxene crystals. The mineralogy of the latitic enclaves is considered to be, for its peculiar texture, the result of quenching, and, therefore, cannot be used to determine the temperature of the melt prior to the interaction process with the rhyolitic liquid.

## 1.6 GEOCHEMISTRY

Whole rock major and trace element compositions have been analysed by Giraud *et al.* (1986), Ferrara *et al.* (1989) and Pinarelli *et al.* (1989). Selected analyses are reported in Table 2.

All samples are peraluminous, with high peraluminous index (1.1-1.4; Fig. 3), and more than 2.5% of normative corundum. NMG rocks are distinctively higher in peraluminous index (Fig. 3). In figure 4A, whole rock and glass data are plotted in the Q-Ab-Or diagram. The whole rock compositions plot well into the stability field of feldspars with the first mineral being a feldspar. In the An-Ab-Or diagrams of figure 4B, it can be seen that the plagioclase is the first crystallized feldspar; accordingly crystallization sequences can be recognized as follows: plagioclase, K-feldspar, quartz.

In figures 5, 6, and 7 major and trace elements variation diagrams of S. Vincenzo lavas are reported. Geochemical characteristics are illustrated hereafter considering also Roccastrada (RCS) and Roccatederighi (RTDG) rocks for comparison, since these rocks belong to the same type of magmatism (see Part IV, Chap. 2).

S. Vincenzo volcanites have high silica contents, slightly variable (68-72%), but lower than Roccastrada rocks (72-74%) and are characterized by higher contents of  $TiO_2$ ,  $Al_2O_3$ ,  $FeO_{tot}$ ,  $MgO$ ,  $CaO$  and  $P_2O_5$ , and slightly lower contents of  $K_2O$  with respect to Roccastrada. MG samples show more scattered patterns of major elements than NMG samples.

S. Vincenzo rocks contain low abundances of compatible elements as expected for so evolved rocks (Fig. 6), but slightly higher than Roccastrada rocks. Generally speaking none of the trace elements (Fig. 7) has good correlation with  $SiO_2$ . Sr is variable and, as evidenced above, two groups of rocks are recognisable having an average Sr content of 250 and 140 ppm, respectively. Such differences can be recognized also for Ba, whereas all the other elements do not discriminate the two groups.



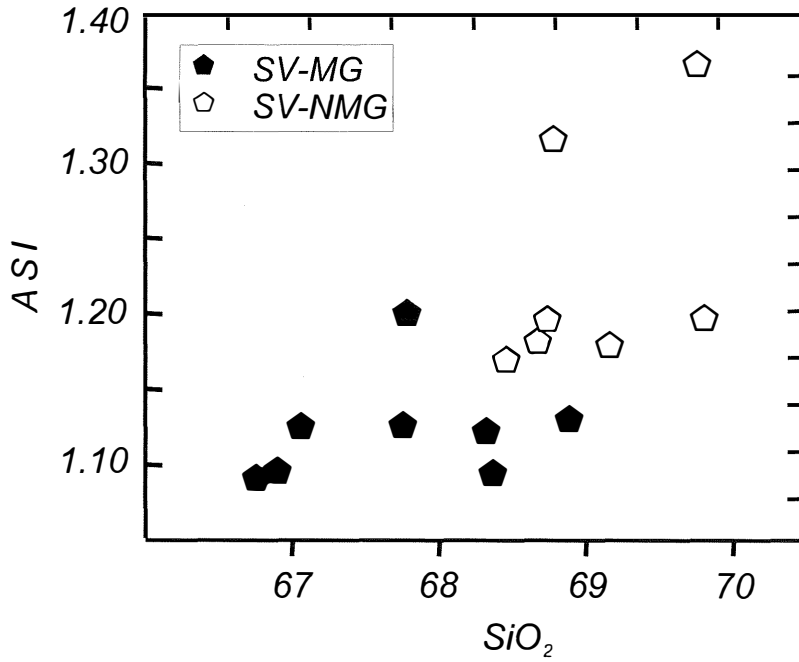


Fig. 3 – SiO<sub>2</sub> vs. ASI (=Aluminium Saturation Index) diagram showing the peraluminous character of S. Vincenzo rocks. This character is particularly evident for the NMG group.

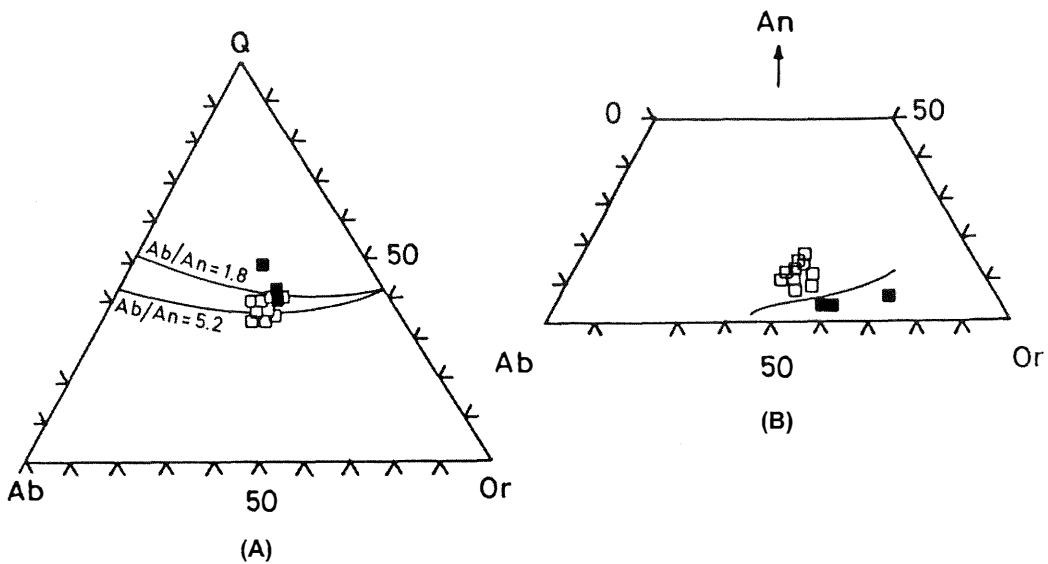


Fig. 4 – Q-Ab-An (A) and An-Ab-Or (B) ternary plots reporting whole rock (open squares) and glass (filled squares) data. Modified from Pinarelli *et al.* (1989).

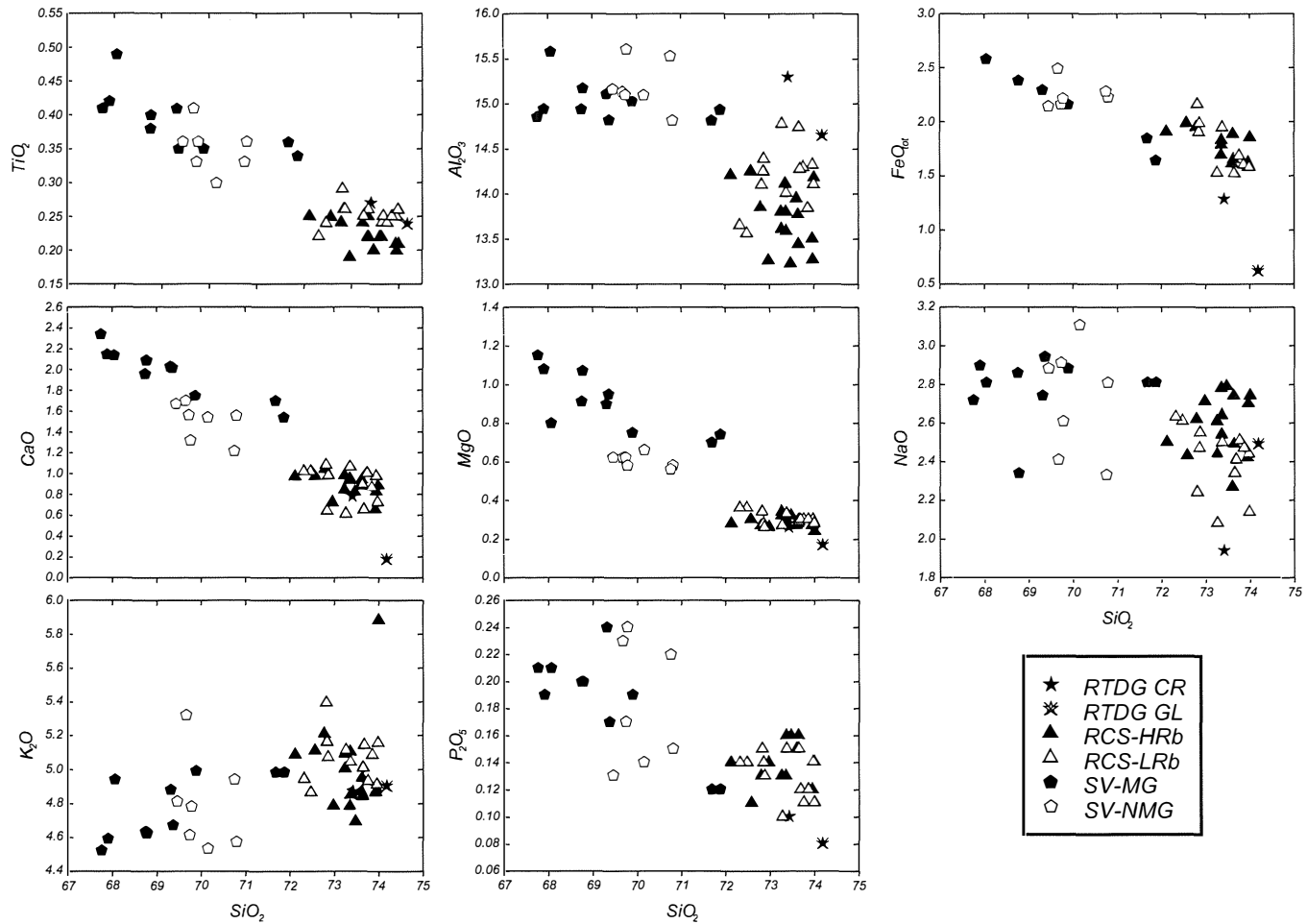


Fig. 5 – Major element Harker diagrams for Roccastrada volcanites. San Vincenzo Volcanites: SV-MG: Mixed Group; SV-NMG: Not Mixing group. Roccastrada volcanites: RTDG CR: Roccatederighi dome crystalline facies; RTDG GL: Roccatederighi dome glassy facies; RCS-HRb: High-Rb group; RCS-LRb: Low-Rb group. Data from Giraud *et al.* (1986) and Pinarelli *et al.* (1989).



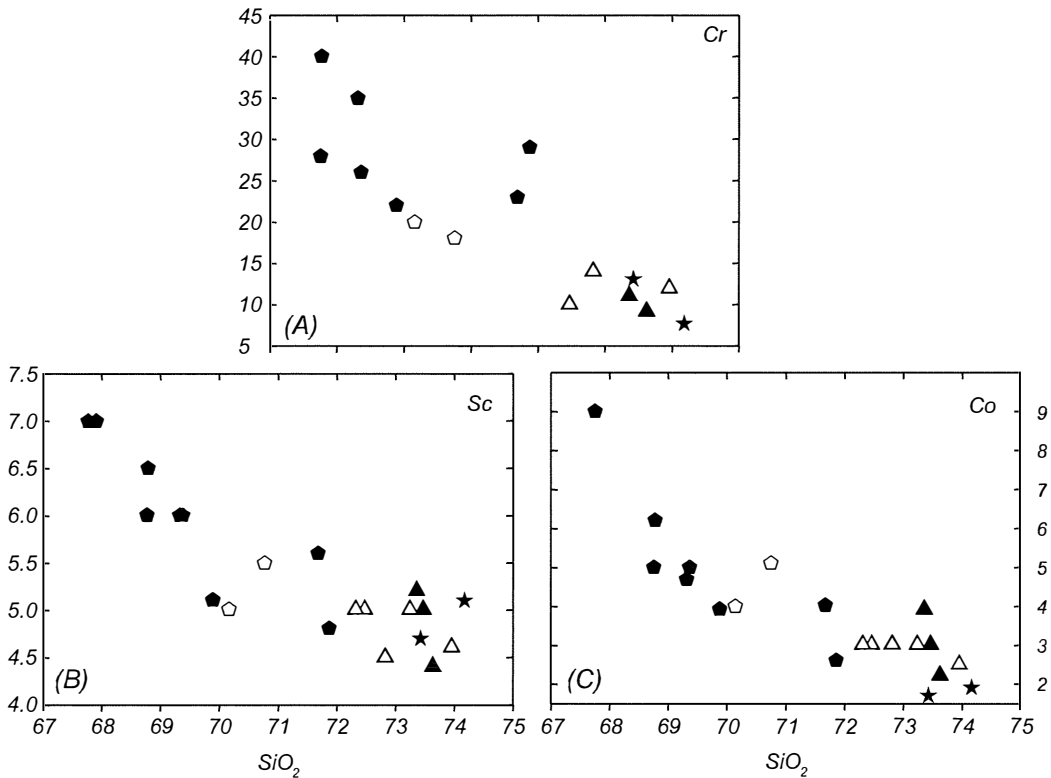


Fig. 6 – Selected inter-elemental diagrams for S. Vincenzo volcanites showing the variation of some compatible elements [Cr (A), Sc (B) and Co (C)] against SiO<sub>2</sub>. Symbols and data as in figure 5.

The samples having different Sr and Ba also reflect different geographical settings (Fig. 2).

In figure 8 are reported REE patterns for S. Vincenzo volcanites. All the analyzed samples are relatively enriched in light REE and fractionated for both light and heavy REE.  $(Tb/Yb)_n$  decrease with silica whereas  $(La/Sm)_n$  is quite scattered around 3.3. Eu anomaly is quite constant at 0.55. Sum of REE decrease strongly with increasing of SiO<sub>2</sub>.

<sup>87</sup>Sr/<sup>86</sup>Sr isotope data show that S. Vincenzo rocks vary from 0.72478 to 0.71263 as a whole and the two groups, MG and NMG, have different isotopic signature: 0.71263-0.71558 and 0.71904 - 0.72478, respectively. Enclaves have the lowest values for Sr isotopes: 0.70806-0.70828.

### 1.7 PETROGENESIS

A petrogenetic model explaining differentiation processes leading to the genesis and evolution of the different rocks outcropping in S. Vincenzo, must take into account for the petrographic and geochemical data above illustrated. Namely, the most striking features can be resumed as it follows: i) petrographic evidence of normal, reverse and patchy zoning in plagioclases, together with sieved plagioclases; ii) presence of magmatic enclaves at least in the MG samples; iii) variability of isotopic ratios.

According to this evidence, a single closed system evolution process starting from a parental basic magma (e.g. crystal

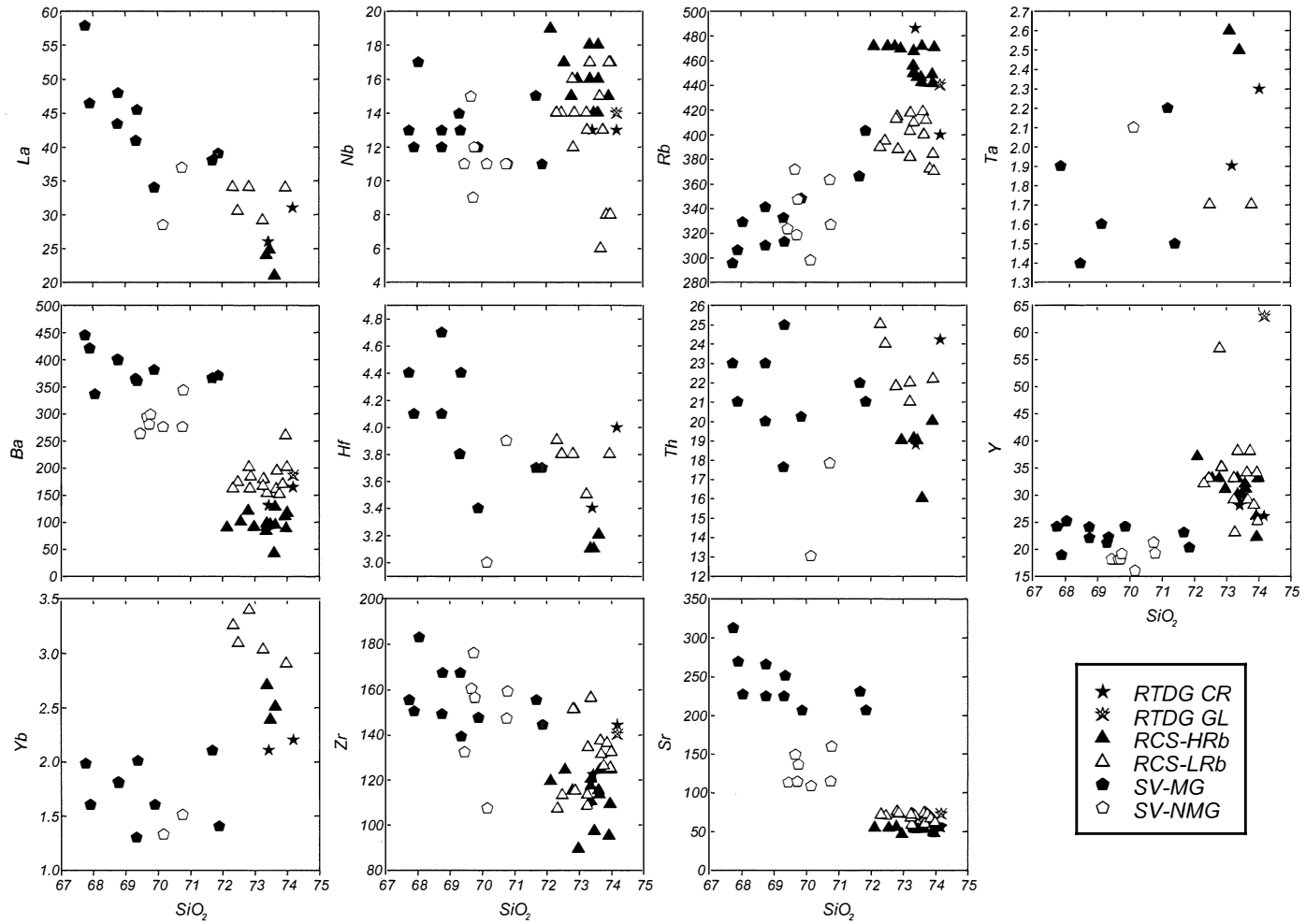


Fig. 7 – Trace elements inter-elemental diagrams for S. Vincenzo volcanites. Symbols and data as in figure 5.

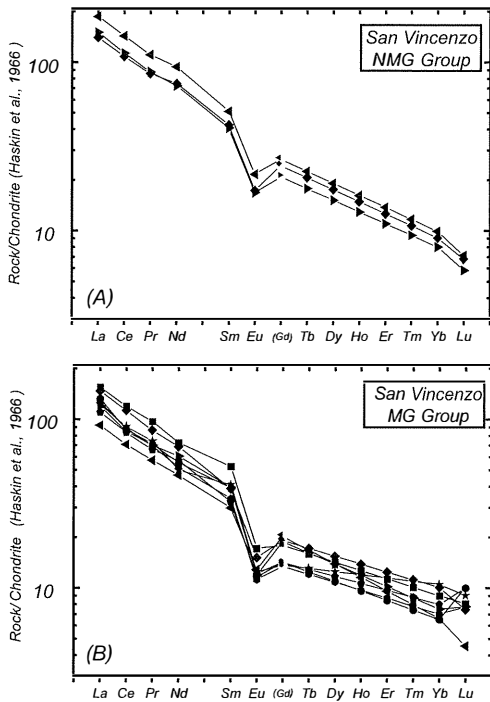


Fig. 8 – Chondrite-normalised REE concentrations for San Vincenzo volcanics. Data from Giraud *et al.* (1986) and Pinarelli *et al.* (1989).

fractionation) is not amenable to explain the genesis of S. Vincenzo volcanites as a whole and the presence of two groups of rocks (NMG and MG). Such features, on the contrary, lead to think that the history of these magmas was characterized by a more complex evolution, often with the lack of equilibrium between mineralogical phases and melt (Feldstein *et al.*, 1994; Ferrara *et al.*, 1989). Moreover, mass balance arguments also rule out a process of assimilation of solid material coupled with fractional crystallization (AFC) starting from a single parental magma. This process would require unreasonably high amounts of basic rocks, and this is in contrast with the limited amount of mafic facies that crop out on the area (< 1%) with respect to the rhyolitic facies.

In figure 9A is reported the variation of Sr against  $^{87}\text{Sr}/^{86}\text{Sr}$ . The plot reveals that data

points plot along hyperbolic curves typical of rock series deriving from a mixing process. This is confirmed by the companion plot (Langmuir *et al.*, 1978) in figure 9B reporting  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $1/\text{Sr}$  showing that S. Vincenzo samples plot along a linear array passing from enclaves to NMG through the MG.

Therefore, a process of mixing of different batches of magmas coupled with minimal, if any, fractional crystallization (MFC) can be proposed for the evolution of S. Vincenzo lavas. Stated the process, the next problem is to find the possible end-members involved in mixing process. From figure 9 it is clear that a simple MFC process could be reasonable starting from the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  enclave as the mafic end-member and using the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  sample belonging to the NMG as the felsic end-member.

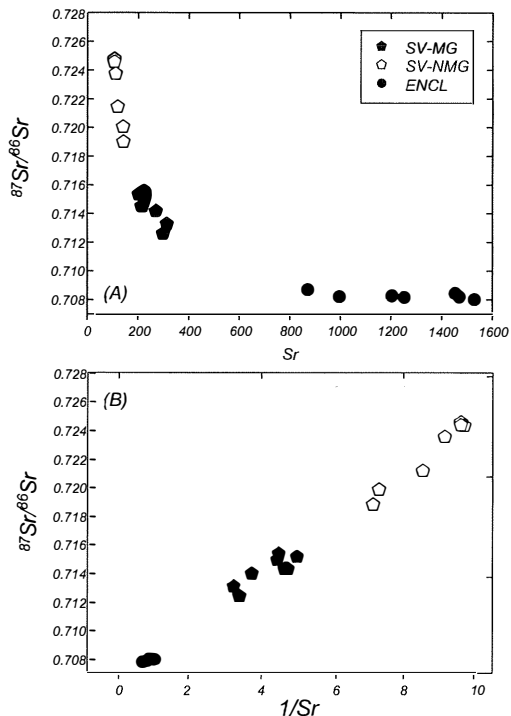


Fig. 9 –  $^{87}\text{Sr}/^{86}\text{Sr}$  vs. Sr (A), and  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $1/\text{Sr}$  (B) plot for S. Vincenzo rocks and enclaves. Data from Giraud *et al.* (1986) and Pinarelli *et al.* (1989).

Enclaves are particularly important to decipher the basic end-member. Chemical and field features strongly suggest that there was interaction between two crystal-mush systems and rule out the possibility that the enclaves might have been totally solid at the time of interaction. This suggests that enclaves underwent partial re-equilibration with host rocks (Feldstein *et al.*, 1994). This is a crucial point, because any process of re-equilibration is geologically reasonable only if the two systems have a Newtonian rheology. For instance, re-equilibration by chemical diffusion processes would require a geologically unreasonable times among systems having a solid rheology. The evidence above outlined supports the hypothesis that the enclaves can be considered as blobs of basic or intermediate, high-temperature magma chilled against a cooler, more silicic host, as it has also been suggested

for other effusive and intrusive associations (e.g. Didier and Barbarin, 1991; Bacon, 1986).

In order to better characterize the interaction process between mafic and felsic magmas and to constrain the nature of felsic and mafic end-members, published Sr isotopic data of Tuscany basic rocks are reported in figure 10 together with S. Vincenzo rocks. The data clearly indicate that lamproites, Cimini, and Radicofani mafic magmas cannot be the end-members of the mixing process responsible for the evolution of S. Vincenzo lavas. On the contrary Capraia, Campiglia mafic dykes and Tolfa enclaves have  $^{86}\text{Sr}/^{87}\text{Sr}$  ratios similar to those of S.Vincenzo enclaves. Campiglia mafic dykes can be excluded on the basis of Nd isotopes (Conticelli *et al.*, 2002). Younger products belonging to the Roman Province have been proposed by Giraud *et al.* (1986) and Pinarelli *et al.* (1989) but, as basic magmatism

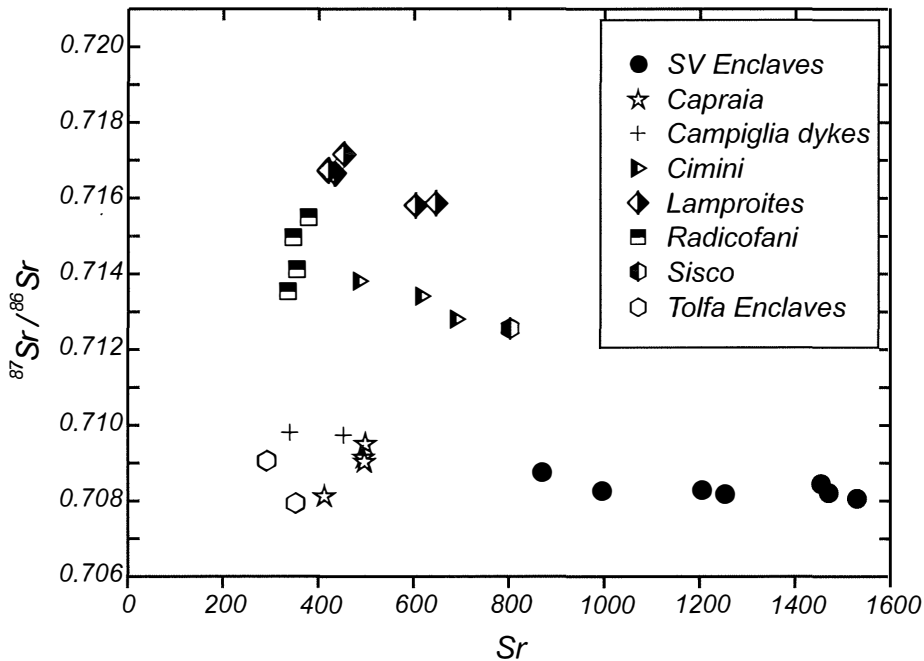


Fig. 10 –  $^{87}\text{Sr}/^{86}\text{Sr}$  vs. Sr plot reporting enclave samples from S. Vincenzo together with mafic products outcropping in the Tuscan Province. Data from Giraud *et al.* (1986), Pinarelli *et al.* (1989) and Peccerillo *et al.* (1987).

changes with age in South Tuscany, basic products of almost the same age should be used. Accordingly, Roman Province products can be safely discarded. It is to note that the same consideration are also valid for the basic magmas associated with the plutonic bodies of the Tuscan Province (see the other chapters of this issue).

Then a basic magma similar to Capraia can be claimed to have acted as basic end-member around 4.0 Ma in South Tuscany. Unfortunately, trace elements are not available for enclaves belonging to S. Vincenzo volcanics, and therefore comparisons on trace element basis are not possible.

Regarding the genesis of the acid end-member, volcanites belonging to the NMG exhibit characteristics typical of crustal derived melts and, in particular: i) the high values of normative corundum (more than 2.5%), ii) the

relatively low  $\text{Na}_2\text{O}$  contents, iii) the high contents of  $\text{SiO}_2$  with restricted variations, iv) the presence of refractory cordierite, v) the high  $^{86}\text{Sr}/^{87}\text{Sr}$  and low  $^{143}\text{Nd}/^{144}\text{Nd}$ . Pinarelli *et al.* (1989) claimed for a genesis of these rocks by partial melting of the tuscan basement and in particular for a source belonging to the garnet bearing micashists group (Fig. 11).

Figure 12 shows a trace element model of batch partial melting starting from average composition of garnet micashists found in boreholes from the Southern Tuscany geothermal field (Gianelli and Puxeddu, 1979). The matching between modelled melt and NMG of S. Vincenzo is striking. In addition, residual phases predicted by the geochemical model agree with experimental petrology data obtained for the same type of sources (e.g., Montel and Vielzeuf, 1997; Pickering and Johnston, 1998). Notably, such residual

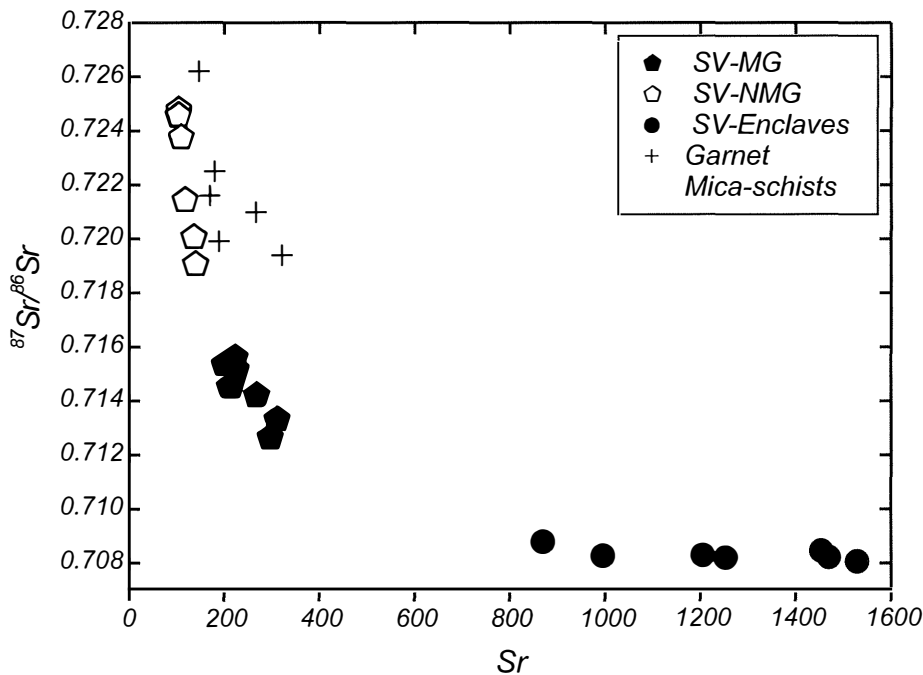


Fig. 11 –  $^{87}\text{Sr}/^{86}\text{Sr}$  vs. Sr plot showing the similarity between S. Vincenzo most evolved rocks (NMG) and the garnet micashists found in boreholes in Tuscany. Data from Giraud *et al.* (1986) and Pinarelli *et al.* (1989).

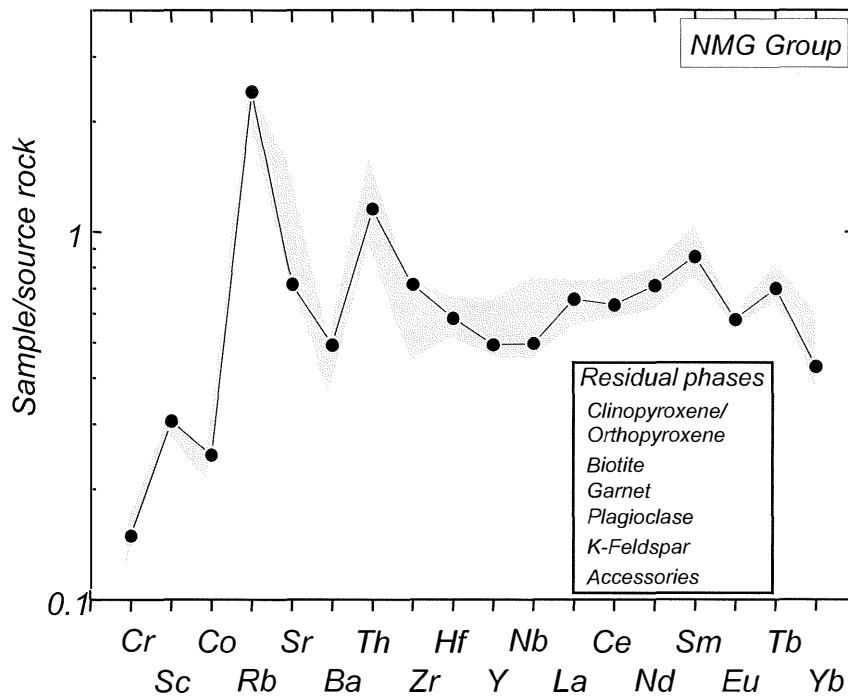


Fig. 12 – Observed (solid lines plus filled circles) and calculated (dashed areas) trace element contents for most evolved rocks from San Vincenzo (NMG), normalized to the source rock. Observed contents are the mean element abundances in NMG group. The calculated ranges (dashed areas) are computed for 40% partial melting, using the range of chemical compositions found in garnet micaschists (Bagnoli *et al.*, 1979) as source rock composition. The used partition coefficients are from Pinarelli (1987). In the inset, residual phases are also reported.

assemblage claims for a pressure greater of 4.0-6.0 Kb. It is to note that models using other basement rocks as phyllites or gneisses (not shown), as sometime suggested as source of S. Vincenzo rocks, do not match the actual rocks, independently on the degree of partial melting. Discrepancies arise mainly for LIL elements that are too depleted in the phyllite source to match the enrichment levels observed in the leucocratic facies of S. Vincenzo.

### 1.8 CONCLUSIONS

At San Vincenzo pure anatectic rocks and rocks derived by interaction among pure anatectic and mantle derived melts were observed. Rocks cropping out east (MG) and

west (NMG) of the main body (Fig. 2) represent the mixed and the pure anatectic products, respectively; emplacement ages are the same within the analytical errors. The anatectic rocks, represented by the NMG, derived from a source similar to Paleozoic garnet-bearing micaschists, through ~40% of partial melting with a residual mineralogy pointing to a pressure greater than 4.0-6.0 Kb. Ranges of Sr isotope ratios of Paleozoic garnet-bearing micaschists and NMG are consistent. The mixed rocks derived by a two end-member mixing process, with scarce, if any, fractional crystallization, between a felsic end-member similar to the NMG rocks and a mafic end-member presumably similar to Capraia magmas. Evolution of S.Vincenzo volcanism can be envisaged as follow. Mafic magmas

were injected into a magma chamber filled by anatectic felsic melts. The chamber became stratified with the upper part constituted by felsic magmas and the lower part constituted by mixed magmas. The repeated injection of the mafic magma triggered sequential extrusions of

the felsic magmas and of the mixed magmas. The first volcanic event filled the west part of the area, and, forming a structural high, prevented the second volcanic event to outpour on the same part. Consequently the MG magmas filled the east part of the area.

