Per. Mineral. (2003), *72*, SPECIAL ISSUE: *Miocene to Recent...*, **157-168** http://go.to/permin

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on *Environment, Archaeometry* and *Cultural Heritage*

CHAPTER 2

Roccastrada volcanites

GIAMPIERO POLI[1]* and DIEGO PERUGINI[1]

[1] Department of Earth Sciences, University of Perugia, Piazza Università, 06100, Perugia, Italy

2.1 HISTORICAL PERSPECTIVE

The first important evidence of human presence in the Roccastrada area dates back to the Neolithic Age. After a transition period, around the third millennium starts the Bronze Age, where, thanks to primitive mines exploitation, the first trades took place. The first material to be exploited were copper and bronze found in the whole area (cupreous material in Roccatederighi). After the year one thousand BC the importance of minerals rose and the importance of the area increased. The Etruscan cities of Vetulonia and Roselle became politically and economically powerful as they stood above the lake Prile, a wide basin facing the Tyrrhenian Sea, a strategic point for trading. Consequentially, while near the cost towns were flourishing, inland, in Roccastrada territory, settlements were still very small and depending on Vetulonia and Roselle that were the solely exploiters of the mines. The only change in settlements there was in 294 BC, when Roma conquered Roselle. At that time the iron excavation stopped because the Romans found more convenient importing the raw materials from far colonies then excavating them locally. Starting from the Imperial time, there was a definitive ruin of the old agricultural economy. The Barbaric times was a very bad period for the area and in the early Middle ages the situation grew worse because of the depopulation. The fortunes of the area revived under the feudal organisation of the Counts of Aldobrandeschi; they ruled for three centuries and built many fortified villages and castles. The first recorded documentation mentioning a castle in Roccastrada's territory dates back to 973 AD.

After a period under the Republic of Siena there was a progressive decline and ruralization of the territory becoming economically dependent to Florence. In the second half of the eighteenth century a series of institutional and administrative reforms were introduced together with a scheme of investments and repopulation. Mines re-opened in Roccatederighi around the first half of the nineteenth century and activity continued up to the first half of twentieth century.

2.2 GEOLOGICAL SETTING

In the Roccastrada area (Fig. 1), the formations of the Tuscan nappe are lacking, and a series of Ligurid flyschoid formations is directly in contact with the Paleozoic basement. Volcanites are represented by discontinuous outcrops spreading over an area of about 100

---

* Corresponding author, E-mail: polig@unipg.it

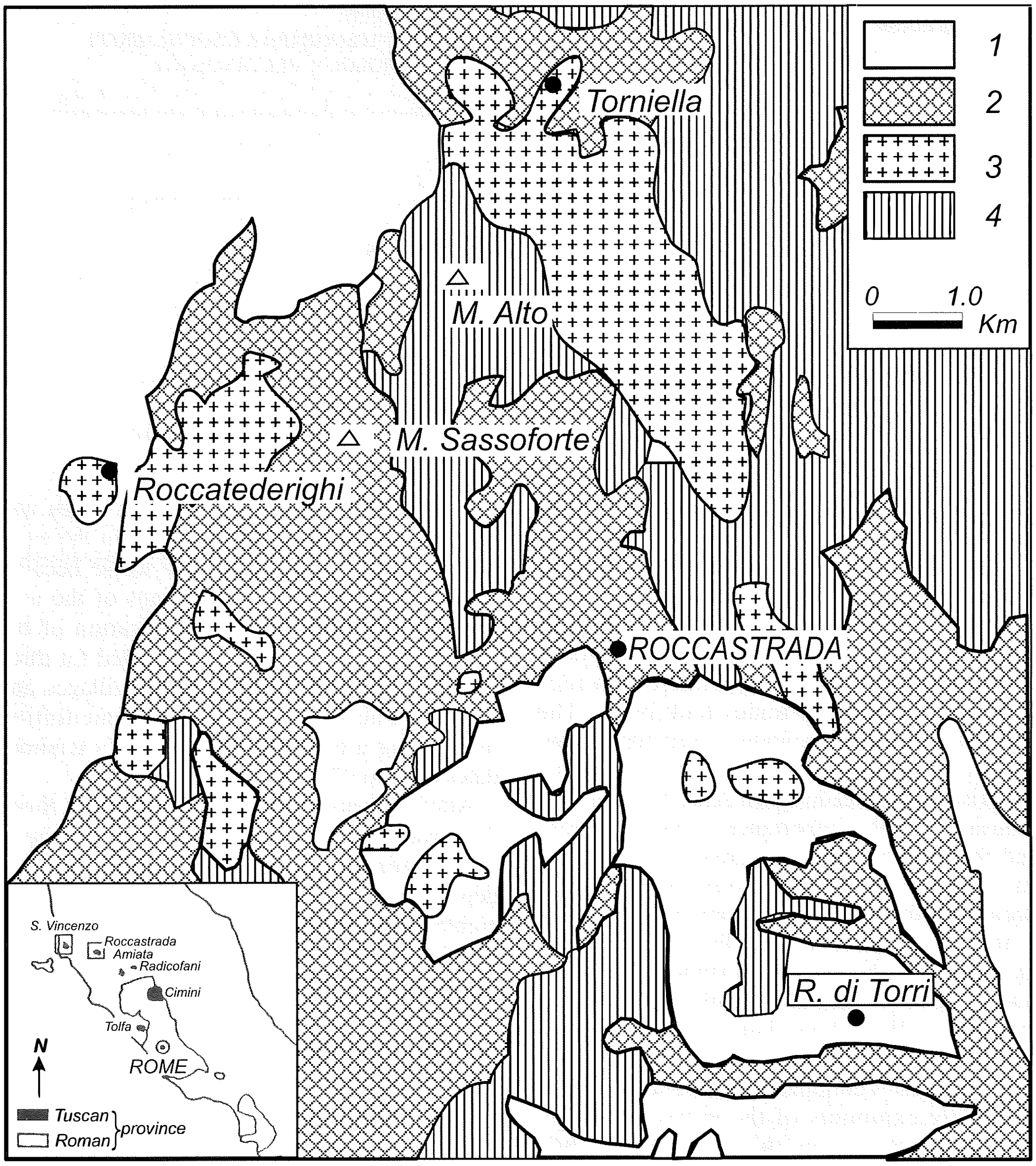


Fig. 1 – Schematic geological map of Roccastrada area.; 1: Lugurids; 2: Neogene deposits; 3: Pliocenic volcanites; 4: Palaeozoic-Triassic Quartzites and phyllites. Modified from Pinarelli *et al.* (1989).

km^2, located on the Western and Eastern flanks of M. Alto. According to Mazzuoli (1967) there are two volcanic vents: one, located north of M. Sassoforte along a SW-NE trending fault, emitted the flows outcropping West of M. Alto; the second vent, located at the intersection of two regional faults south of Torniella village (Fig. 1), emitted the volcanites outcropping

East and South-East of M.Alto and at Roccastrada village.

Volcanites mainly consist of rhyolitic lava flows, but a lava dome is also present near Roccatederighi village. Borsi *et al.* (1965) found a granitic block inside lavas near Torniella village but it is not any more available for sampling

Isotopic age on mineral separates of these volcanites using K/Ar (Borsi *et al.*, 1967; Pinarelli and Villa, 1985) and Rb/Sr (Ferrara *et al.*, 1977) systematics converges around 2.4 Ma, while a single fission track data (Arias *et al.*, 1981) gave an age of 3.23 Ma. A Rb/Sr data on the granite gave 3.5 Ma (Borsi *et al.*, 1965).

Whole rock element compositions have been reported by Giraud *et al.* (1986), and Pinarelli *et al.* (1989). The latter authors report a division into two group of the Roccastrada rhyolites based on Rb contents, whereas no division is reported by Giraud *et al.* (1986). A revision proves that the two groups of rocks exist in all published data and hereafter the division reported by Pinarelli *et al.* (1989) will be used. Note that the two groups reflect also different geographical settings. Noticeably, Roccastrada lavas outcropping east and south-east of M. Alto (Fig. 1) have higher contents of Rb, with respect to the outcrops west of M. Alto. The first group, having higher Rb contents, will be referred to as HRb group, whereas the second (lower Rb contents) as LRb group.

2.3 PETROGRAPHY

Roccastrada volcanites have a porphiritic texture with a glassy or perlitic, sometimes microcrystalline, groundmass, varying between 51 and 67% of rock volume (Table 1). Phenocrysts are two feldspars, biotite, quartz and, in lesser amount, cordierite. Zircon, apatite and magnetite are common accessory phases. In some samples, little fragments of garnet can be also found. Roccastrada lavas sometimes contain metasedimentary enclaves, of microscopic size, mainly consisting of xenomorphic quartz and biotite. Between the two groups of samples defined above little petrographic differences are present, concerning mainly phenocrysts abundances (Table 1).

Samples from the lava dome have a porphiritic texture and their mineralogy is similar to that of lava flows. Nevertheless two

TABLE 1

Average mineralogical modal compositions of Roccastrada volcanites (after Pinarelli et al., 1989).

	Lava Flows						Lava Dome			
	HRb group			*LRb group*			Crystalline			Glassy
Mineral	Average (n=6)		SD %	Average (n=4)		SD %	Average (n=2)		SD %	
Plagioclase	8.0	±	2.5	6.4	±	2	8.0	±	2.5	1.0
K-feldspar	18.1	±	2.8	17.8	±	2.9	19.5	±	2.7	5.1
Quartz	13.2	±	2.4	18.0	±	3.5	14.8	±	3.2	23.5
Biotite	6.3	±	1.4	7.0	±	4.1	3.8	±	0.1	3.4
Cordierite*	1.0			0.3			-			
Accessories*	3.2			1.8			1.0			0.5
Groundmass	53.0	±	5.4	51.0	±	3.5	53.4	±	4.0	67.5

* maximum observed values.

facies can be distinguished on the basis of their textural features: one has a glassy groundamss (Glassy facies) and contains little or no plagioclase as phenocryst; the other has a microcrystalline groundmass (Crystalline facies), contains more plagioclase and is characterized by the presence of K-feldspar megacrysts whose size reach up to 5.0-6.0 cm.

Quartz in lavas from Roccastrada occurs in large crystals, always fractured and sometimes embayed, with inclusions of biotite. Sanidine occurs in large euhedral crystals, sometimes fractured and embayed, with inclusions of biotite, plagioclase and, in the dome, quartz. Its composition varies between Or_{58} and Or_{75}; it is sometimes slightly zoned with the core more orthoclase rich than the rim. This feature is particularly evident in the lava dome. Plagioclase is Albite and Albite-Carlsbad twinned and typically includes biotite. Its composition varies between An_{24} and An_{50}. It is normally zoned with cores containing 34-50% and rims 24-44% of An, rarely mantled by K-feldspar. Microcrysts have the same compositional range of rims. Biotite is euhedral and well preserved, rarely deformed or chloritized, with yellow to dark-brown pleochroism. It has high Al contents, in agreement with the peraluminous character of the rocks. Biotites from the lava dome exhibit the wider spread in tetraedric Al content. The mean Fe/(Fe+Mg) ratio is 0.68 in the biotites of lava flow samples, and 0.50 in those of the lava dome. Cordierite occurs either as euhedral-subhedral rounded crystals with multiple twinning, or as turbid altered fragments. The euhedral type has Fe/(Fe+Mg) ratio about 0.4, while the anhedral type displays higher iron contents, with Fe/(Fe+Mg) ratio of 0.7. The partitioning of Fe and Mg between cordierite (C) and biotite (Bi) can be expressed by the distribution coefficient $KD_{Fe}^{C\text{-}Bi}=[X_{Fe}^{C}/(1-X_{Fe}^{C})]*[(1-X_{Fe}^{Bi})/X_{Fe}^{Bi}]$, where X_{Fe}=Fe/(Fe+Mg). The values of KD for the iron-poor cordierites from Roccastrada samples (0.35-0.39) are in agreement with values reported in literature for equilibrium coexistent cordierite-biotite pairs (Saxena and Hollander, 1969; Hess, 1971). Moreover, Fe/(Fe+Mg) ratio corresponds to cordierites experimentally crystallized by Green (1976) in granitic systems at 700°C and 4.0 Kb. The crystallization of the iron poor cordierites in magmatic conditions is therefore a reliable conclusion, also considering their euhedral habit. Concerning the iron rich cordierites, their occurrence as irregular turbid and altered fragments suggests a restitic origin. In fact, their $KD_{Fe}^{C\text{-}Bi}$ are very high (around 1.0), far from values reported above. They could be, therefore, refractory cordierites coming from the source region, or could derive from refractory garnet, owing the pressure decrease during the magma ascent, by the reaction: Gar = Bio + Cdt + liq.

2.4 THERMOBAROMETRY

Pinarelli *et al.* (1989) used Stormer's (1975) two-feldspar geothermometer to evaluate crystallization temperatures of Roccastrada magmas, as it was applied previously mainly to acidic rocks (Whitney and Stromer, 1976; Czamanske *et al.*, 1981). The presence of embayed grains of plagioclase displaying cores poorer in An than rims, or mantled by k-feldspar, suggests that some feldspars may have not crystallized in equilibrium conditions. To test this possibility, chemographic tests to assess equilibrium crystallization, as suggested by Brown and Parsons (1981), have been applied to Roccastrada feldspars. Twelve sanidine-plagioclase pairs from Roccastrada were selected for temperature calculations. Temperatures obtained for the different pairs are consistent with each other, and indicate crystallization temperatures of 670-700 °C for Roccastrada lava flows and 690 °C for the lava dome.

2.5 GEOCHEMISTRY

Selected major, trace elements and REE analyses of whole rocks and glasses from Roccastrada volcanites are presented in Table 2.

TABLE 2.

Selected chemical analyses of Roccastrada volcanites from Pinarelli et al. (1989) and Giraud et al. (1986).

Sample	*TMR59*	*TMR87*	*TMR88*	*R6*	*R14*	*R3*	*TMR8*	*R12*	*TMR68*	*TMR7*	*TMR81*
Group	***HRb***	***HRb***	***HRb***	***HRb***	***LRb***	***LRb***	***LRb***	***LRb***	***LRb***	***RTDG***	***RTDG***
SiO_2	72.13	73.37	73.64	73.95	72.33	72.48	72.83	73.26	73.97	73.43	74.19
TiO_2	0.25	0.25	0.22	0.21	0.22	0.24	0.29	0.24	0.25	0.27	0.24
Al_2O_3	14.21	13.59	13.44	13.50	13.65	13.56	14.10	13.61	14.33	15.30	14.65
Fe_2O_3	0.88	0.74	0.64	1.63	2.04	2.01	1.51	1.91	0.76	0.76	0.38
FeO	1.12	1.12	1.08	-	-	-	0.80	-	0.90	0.60	0.28
MnO	0.05	0.04	0.04	0.02	0.03	0.03	0.05	0.02	0.03	0.02	0.01
MgO	0.28	0.30	0.28	0.27	0.36	0.36	0.34	0.34	0.30	0.26	0.17
CaO	0.97	0.93	0.89	0.65	1.02	1.02	1.08	0.98	0.97	0.78	0.17
Na_2O	2.50	2.64	2.49	2.42	2.63	2.61	2.24	2.61	2.44	1.94	2.49
K_2O	5.09	5.10	4.84	4.86	4.94	4.86	5.39	5.00	4.91	4.87	4.90
P_2O_5	0.14	0.16	0.15	0.12	0.14	0.14	0.15	0.13	0.14	0.10	0.08
LOI	2.38	1.76	2.30	1.26	1.62	1.56	1.22	1.13	1.00	1.00	2.44
ASI	1.25	1.18	1.23	1.30	1.18	1.19	1.23	1.18	1.29	1.55	1.51
Ni	-	-	-	13	14	12	-	13	-	-	-
Co	-	3.9	2.2	-	3	3	3	3	2.5	1.7	-
Cr	-	11	9.1	-	-	10	14	-	12	13	-
Sc	-	5.2	4.4	-	5	5	4.5	5	4.6	4.7	-
Zn	-	-	-	43	51	52	-	46	-	-	-
Pb	-	-	-	42	47	45	-	45	-	-	-
Ga	-	-	-	21	20	20	-	19	-	-	-
Rb	472	450	443	449	390	395	413	382	384	486	441
Sr	53	54	52	48	70	68	74	70	61	67	71
Ba	89	91	94	110	160	172	200	165	260	130	185
Th	-	19.1	16	20	25	24	21.8	22	22.2	18.8	-
Zr	119	120	124	95	107	113	151	113	125	122	140
Ta	-	2.6	2.5	-	-	-	1.7	-	1.7	1.9	-
Hf	-	3.1	3.2	-	3.9	3.8	3.8	3.5	3.8	3.4	-
Y	37	29	29	26	32	33	57	33	34	28	63
Nb	19	17	18	15	14	14	16	14	17	13	14
La	-	24	21	-	34.1	30.5	34	29.2	34	26	-
Ce	-	42	41	-	71.2	68.1	42	61.6	61	34	-
Nd	-	24	23	-	34	28.8	33	28	33	20	-
Sm	-	6.2	7	-	7.2	6.8	8.7	6.3	7.8	5.2	-
Eu	-	0.45	0.38	-	0.53	0.55	0.69	0.55	0.58	0.36	-
Tb	-	0.8	0.68	-	1.23	1.12	1.2	1.1	0.94	0.61	-
Yb	-	2.7	2.5	-	3.25	3.09	3.4	3.03	2.9	2.1	-
Lu	-	0.39	0.4	-	0.35	0.33	0.53	0.32	0.42	0.37	-
$(Tb/Yb)_n$	-	1.21	1.11	-	1.54	1.48	1.44	1.48	1.32	1.19	-
Eu/Eu*	-	0.27	0.24	-	0.23	0.26	0.28	0.28	0.29	0.27	-
Ree	-	120	113	-	180	166	149	156	164	104	-
$^{87}Sr/^{86}Sr$	-	-	-	0.720	0.718	0.720	-	-	-	-	-

All studied samples are peraluminous, with a quite high peraluminous index (1.15-1.55; Fig. 2) particularly for the Roccatederighi dome. There is no difference between HRb and LRb groups. Samples contain more than 2.5% normative corundum. Whole rock and glass data points are plotted on the Q-Ab-Or diagram in Fig. 3. The whole rock composition of the lava flows (Fig. 3A) is very similar to that of the glasses, indicating a magma composition near the peritectic minimum of the system. The glasses, that represent the residual liquids after crystallization, are enriched in quartz (Q) with respect to the whole rocks, and therefore the first mineral to crystallize in this system was a feldspar. The experimental cotectic line for liquids having the same normative Ab/An ratio of the Roccastrada lavas (4.9-9.2) at 1 and 2 kb (from James and Hamilton, 1968) plots under the whole rock data points, suggesting lower crystallization pressures. For the lava dome samples (Fig. 3B), alteration impeded the analysis of the glass, but the whole rock data points plot in the quartz (Q) field, and the first mineral to crystallize might have been quartz. This interpretation is confirmed by the occurrence of quartz enclosed in the sanidine phenocrysts. In the An-Ab-Or diagrams of figure 3C and D it can be observed that plagioclase was the first feldspar to crystallize in the Roccastrada lava flows (Fig. 3C), while sanidine was the first feldspar to crystallize in the lava dome (Fig. 3D). The crystallization sequences are, thus, recognizable as follows: Roccastrada lava flows: Plg-Kf-Q; Roccastrada lava dome: Q-Kf-Plg.

The ascent of the magma forming the lava dome can be reconstructed also on the basis of

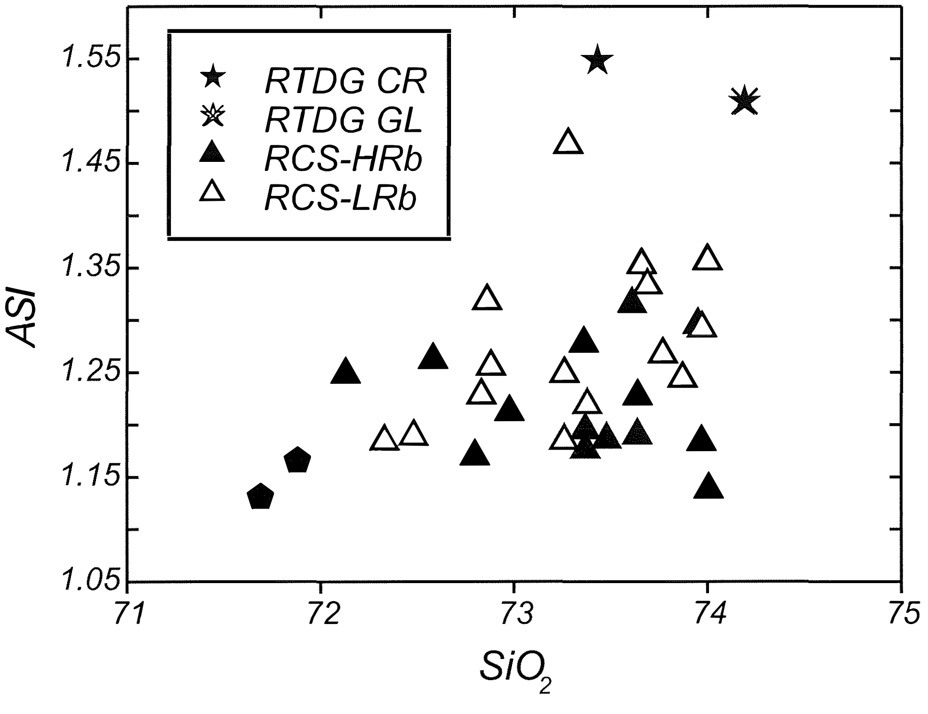


Fig. 2 – SiO_2 vs. ASI (= Aluminium Saturation Index) plot showing the peraluminous character of Roccatsrada rocks. This character is particularly evident for the Roccatederighi dome. No difference exists between HRb and LRb groups. RTDG CR: Roccatederighi dome crystalline facies; RTDG GL: Roccatederighi dome glassy facies; RCS-HRb: High-Rb group; RCS-LRb: Low-Rb group. Data from Giraud *et al.* (1986) and Pinarelli *et al.* (1989).

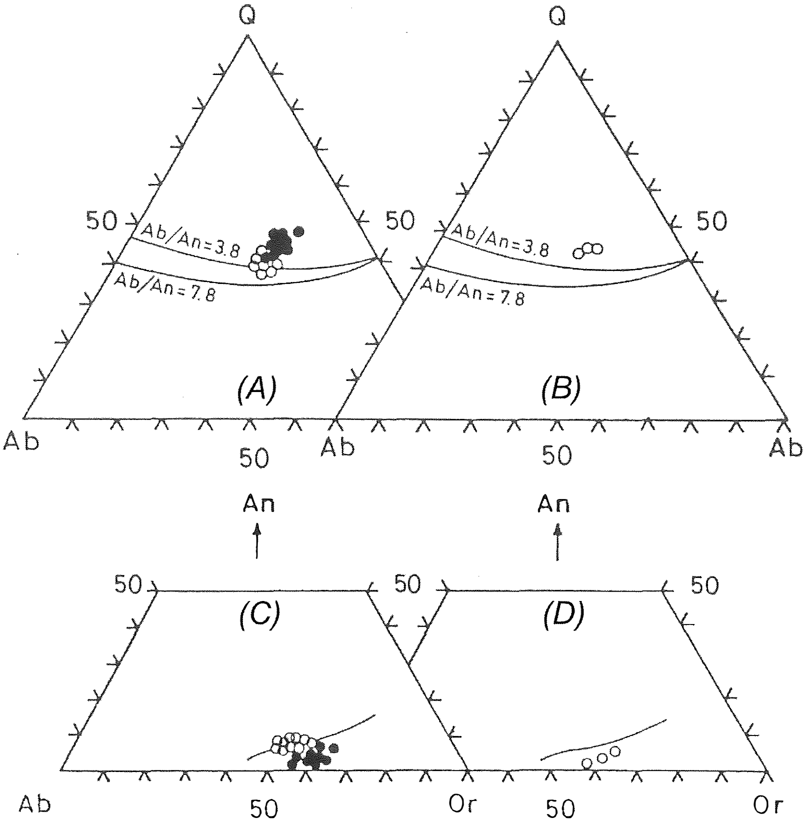


Fig. 3 – Q-Ab-Or diagram for whole rocks and glasses of Roccastrada lava flows (A) and lava dome (B). An-Ab-Or diagram for whole rocks and glasses from Roccastrada lava flows (C) and lava dome (D). Open symbols: whole rocks; closed symbols: glasses. The normative values are computed with the CIPW norm, which produces a slight overestimation of the Or component, with respect to the mesonorm of Mielke-Winkler, because all the K_2O is assigned to the orthoclase. After Pinarelli *et al.* (1989).

mineralogical differences between the glassy and crystalline facies: a first stop of the magma at a shallow depth led to the crystallization of biotite + quartz + alkali feldspar. At this point, part of the crystal mush ascended to the surface and quenched, with little or no crystallization of plagioclase, producing the glassy facies. In the shallow magma chamber the crystallization proceeded along the two-feldspar coetectic line, producing the plagioclase and the alkali-feldspar megacrysts; the intrusion of this crystal mush in the nuclear portion of the dome, gave rise to crystalline facies.

In figures 4, and 5 major and trace elements variation diagrams of Roccastrada rocks are reported. Geochemical characteristics are illustrated hereafter considering also S. Vincenzo rocks for comparison, since such rocks belong to the same type of magmatism (see Part II, Chap. 1). Roccastrada volcanites are more acidic than the S. Vincenzo volcanites (SiO_2 = 72-74% vs. 68-72%), and are characterized by lower contents of TiO_2, Al_2O_3, FeO_{tot}, MgO, CaO, and P_2O_5.With regards to trace elements (Fig. 5), the Roccastrada rhyolites show comparatively

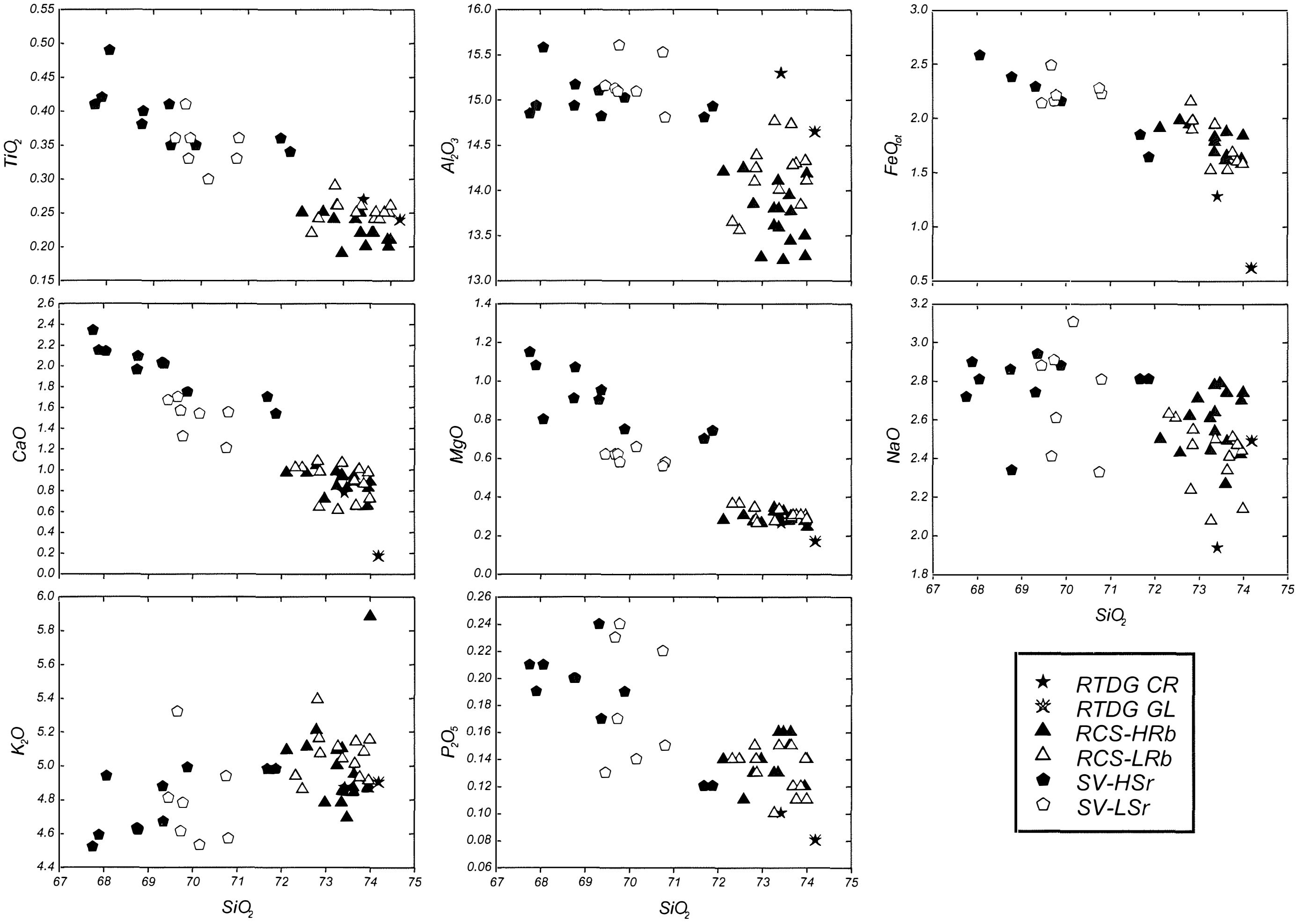


Fig. 4 – Major element Harker diagrams for Roccastrada volcanites. San Vincenzo Volcanites: SV-MG: Mixed Group; SV-NMG: Not Mixing group. Other symbols and acronyms as in figure 2. Data from Giraud *et al.* (1986) and Pinarelli *et al.* (1989).

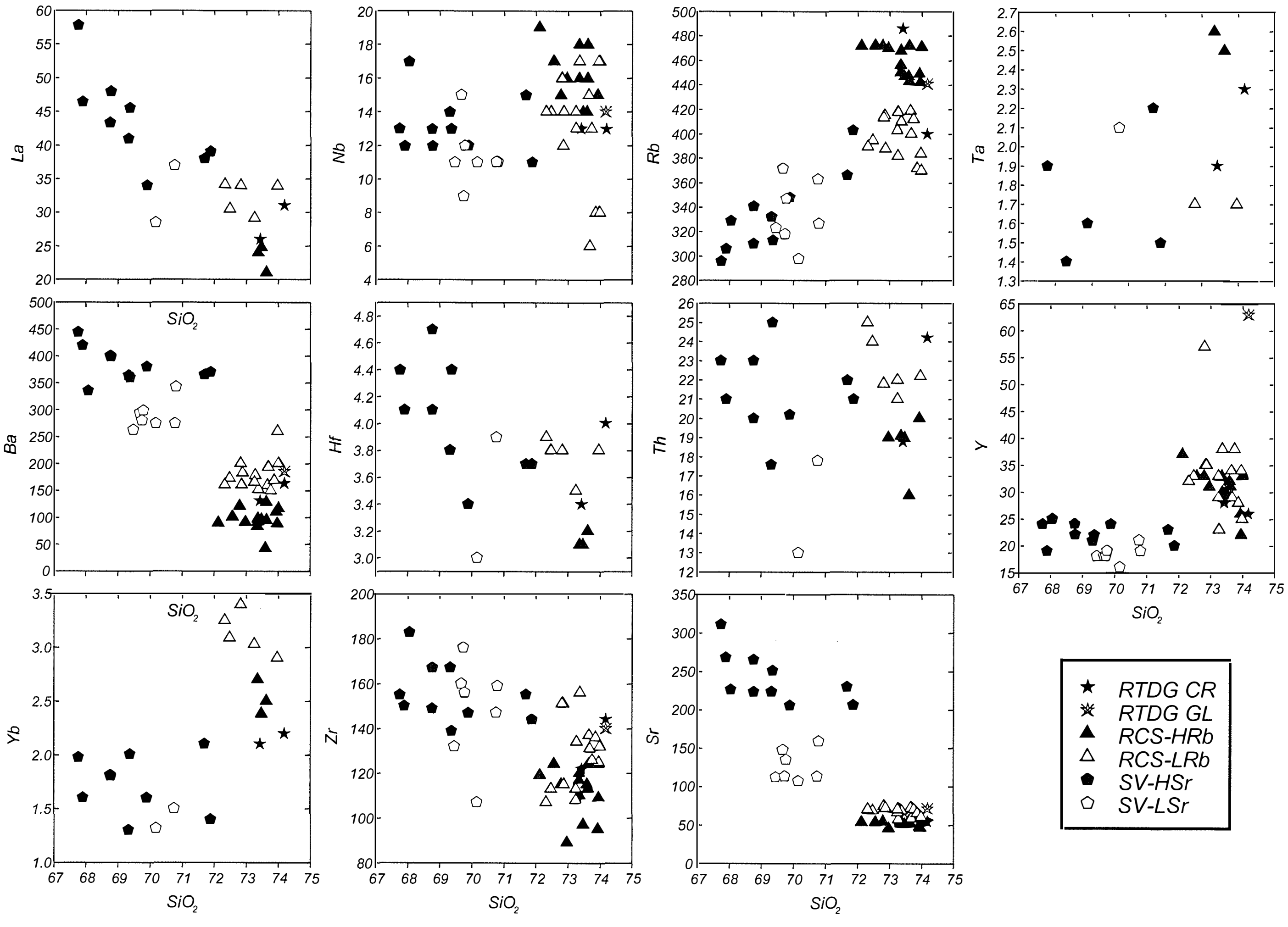


Fig. 5 – Trace element inter-elemental diagrams for Roccastrada volcanites. Symbols and acronyms as in figure 4. Data from Giraud *et al.* (1986) and Pinarelli *et al.* (1989).

higher contents of Rb and Y and lower contents of Sr, Ba, Ce, Zr, Cr, Sc, and Co than S. Vincenzo rhyolites. Th, Ta, and Hf are scattered. The Roccastrada lavas cropping out east and south-east of M. Alto (Fig. 1; HRb group) have noticeably higher contents of Rb (463 vs. 399) and lower contents of Sr (53 vs. 66), Ba (105 vs. 177), Zr (117 vs. 136), Th (17 vs. 22), Hf (3.2 vs. 3.8), and total REE (105 vs. 146), than those cropping out west of M. Alto (LRb group). Samples from Roccatederighi dome is not distinguishable from the Roccastrada rocks on both major and trace element diagrams.

In figure 6 are reported REE patterns for Roccastrada volcanites. All the analyzed samples are relatively enriched in light REE and fractionated for both light and heavy REE. The total REE of the Roccastrada rocks are quit low (100-150), show fractionated patterns [$(Tb/Yb)_n$=1.2-1.6], and have pronounced negative Eu anomalies (Eu/Eu* = 0.22-0.28).

$^{87}Sr/^{86}Sr$ isotope data show that Roccastrada rocks vary form 0.71799 to 0.71971 (Giraud *et al.*, 1986; Volmer, 1976) as a whole, and the two groups have slightly different isotopic signature (Fig. 7).

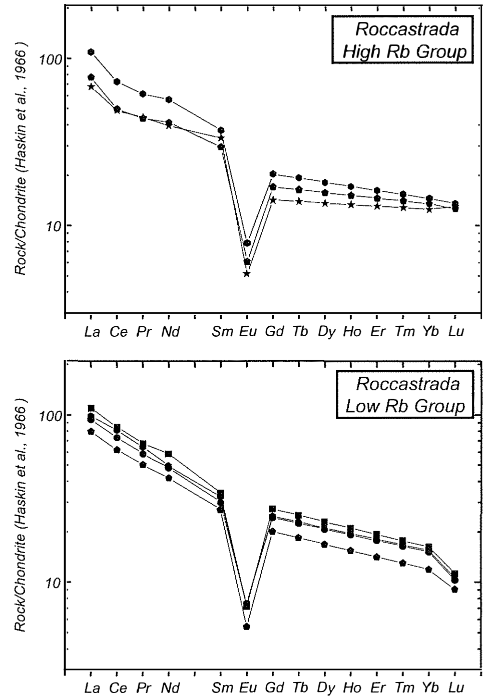


Fig. 6 – Chondrite–normalised REE concentrations for Roccatsrada volcanics. Data from Giraud *et al.* (1986) and Pinarelli *et al.* (1989).

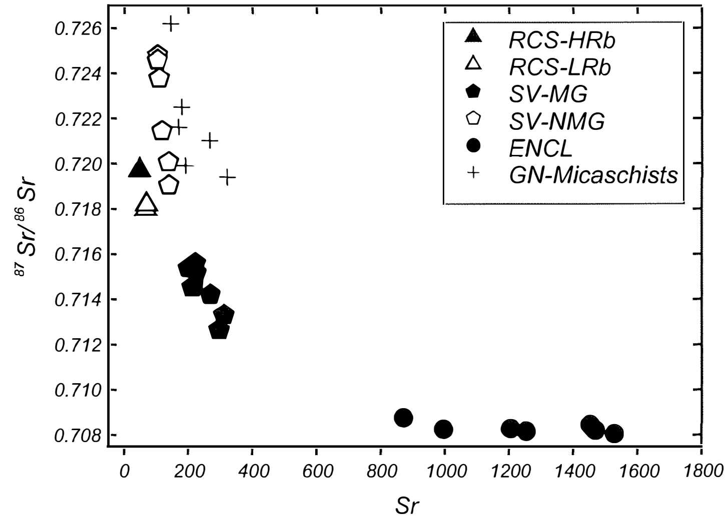


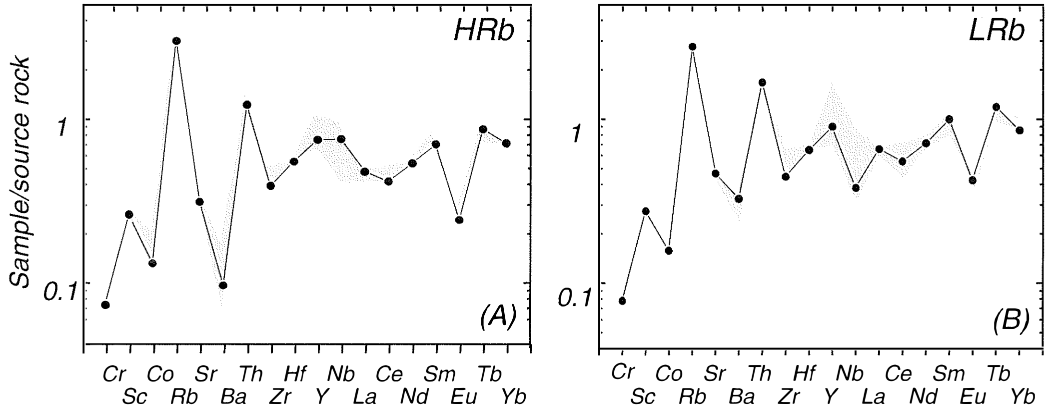
Fig. 7 – $^{87}Sr/^{86}Sr$ vs. Sr plot showing the similarity between Roccastrada rocks (Giraud *et al.*, 1986; Vollmer, 1976) and the garnet micaschists (Pinarelli *et al.*, 1989) found in boreholes in Tuscany.

2.6 PETROGENESIS

Roccastrada rocks exhibit some characteristics typical of crustal derived melts: i) the high values of normative corundum (more than 2.5%), ii) the relatively low Na_2O contents, iii) the high SiO_2 contents with restricted variations, iv) the presence of refractory cordierite ± garnet, and iv) metasedimentary enclaves.

The geochemical differences between rocks cropping out east (HRb) and west (LRb) of M. Alto cannot be due to mineralogical differences, because they have approximately the same mineralogy. Two other possible explanations have to be considered: first, they could be derived from each other by fractional crystallization, second, the two magma batches could be derived through differing degrees of partial melting of the same crustal rocks. The former hypothesis can be excluded on the basis of quantitative fractionation tests, based on Stormer and Nicholls (1978) program. In fact, the very small differences in bulk composition would involve only 3.8% of fractionated solid, constituted by biotite, plagioclase, and K-feldspar. This fractionation would only produce enrichment factors for Ba, Sr and Rb of 1.02, 1.03 and 1.04, values that differ greatly from those observed (0.5, 0.8 and 1.2, respectively).

The high $^{86}Sr/^{87}Sr$ claims 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. 7). To test this second hypothesis, a partial melting process under dry conditions



HRb	Residual phases	LRb
Bio	≅	Bio
Plg	≅	Plg
KF	>	KF
Crd	<	Crd
(Cpx/Opx)	≅	(Cpx/Opx)
Acc	≅	Acc

Fig. 8 – Observed (solid lines plus filled circles) and calculated (shaded areas) trace element contents for Roccastrada volcanites, normalized to the source rock. Observed contents are the mean element abundances in HRb (A) and LRb (B) samples. The calculated ranges (shaded areas) are computed for 40% (A) and 45% (B) 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 (1987b). Residual phases and differences between the two groups are also reported.

was modeled (Shaw, 1970), using the Palaeozoic garnet-bearing micaschists (Bagnoli *et al.*, 1979) as source rocks. The results of the test suggest that the HRb group of volcanites may be derived by 40% partial melting living a residue consisting of quartz, plagioclase, biotite, alkali-feldspar cordierite, garnet and zircon; the LRb group, instead, may be derived by 45% partial melting, with the residue containing less alkali-feldspar and more cordierite (Fig. 8).

These results are in agreement with experimental data (e.g. Clemens and Vielzeuf, 1987) for the anatexis of metapelitic rocks under water deficient conditions. Indeed, if the water is provided by the breakdown of mica (muscovite or biotite), the residue would contain quartz, biotite, alkali-feldspar, plagioclase, and cordierite ± garnet. Moreover, according to Watson (1979), the melting of a rock containing more than 100 ppm Zr will leave zircon in the residue for each degree of melting, thus explaining the negative spike of Zr in figure 8.

2.7 CONCLUSIONS

At Roccastrada only purely anatectic rocks were observed. Rocks cropping out respectively east (HRb) and west (LRb) of M. Alto represent two batches of magma derived from the same source, a rock similar to Paleozoic garnet-bearing micaschists, through different degrees of partial melting and with differing residual mineralogies. The slight isotopic difference observed between the HRb and LRb magma batches could reflect isotopic inhomogeneity of the source. The phenocryst assemblages crystallized at a temperature of around 700°C and a pressure < 1.0 Kb, and were undersaturated with respect to water (2.5% H_2O). The lava dome near Roccatederighi derived through the same anatectic process, though its crystallization sequence and oxygen fugacity differ, suggesting it formed in a separate magma chamber.