Per. Mineral. (2003), *72*, SPECIAL ISSUE: *Miocene to Recent...*, **183-193** 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 4
The Radicofani volcano

MASSIMO D'ORAZIO*

Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria, 53, Pisa, 56126, Italy

4.1 HISTORICAL PERSPECTIVE

The mighty Rocca of Radicofani rises since before the year 1000 on the top of an imposing basaltic cliff 900 m high, from which it dominates the whole territory between the Mount Cetona, the Orcia Valley and Mount Amiata. The ancient Roman Cassia road, then named Francigena or Romea, ran at the base of the Radicofani hill. Therefore, the Roman Pope and Siena struggled to control the Fortress throughout three centuries. Pope Adriano IV reinforced the castle and in 1198 Innocenzo III started great new works on the fortification. In 1262 the fortress became a haven of Guelphs refugees from Siena; in the following years the Senesi regained and destroyed the walls of Radicofani. In 1295, the castle became the eagle nest of Ghino di Tacco from Siena. His father and brother were executed in 1286 for robberies and bloodshed, and Ghino took refuge in Radicofani, at the border between the possessions of Siena and the Pope. From here, Ghino captured people travelling along the Via Francigena to Rome, then, after collecting information about their wealth, he robbed them, always leaving them enough to keep going and offering them a banquet. Then Ghino left to Rome with four hundred armed followers, went to the tribunal and decapitated the senese judge that condemned his father (Dante reports this episode in the Divina Commedia). Also the abbot of Cluny was captured by Ghino: he recovered from its stomach sickness by the diet (dried fava beans and bread) imposed by Ghino. The abbot was so happy that, once free, he interceded by the Pope Bonifacio VIII: Ghino was given the title of Cavaliere, and Siena forgave him. In 1301-1302 Radicofani was again involved in a war between senese Ghibellines and the Guelphs cities allied with the Pope. In the second half of the 14th century, Siena and the Pope struggled again to control the Radicofani fortress. In 1405, the castle became a possession of Siena, and in 1417 the construction of the new bastionated fortress began around the original medieval nucleus. In the second half the 15th century, the Senesi, to better manage the traffic along the Roman Cassia road, destroyed part of the ancient path and replaced it with a new layout running just under the fortifications. The last siege suffered by the stronghold of Radicofani dates back to 1555, when the introduction of the artillery was changing forever the historical role of fortresses and castles.

4.2 GEOLOGICAL SETTING

The small Pleistocene volcanic centre of Radicofani (12°27' E - 42°53' N) is located in

* E-mail: dorazio@dst.unipi.it

the central portion of the Neogene Radicofani Basin (Liotta and Salvatorini, 1994), about 10 km to the east of the much larger and younger Monte Amiata volcano (Fig. 1). The Radicofani Basin is one of the graben-type tectonic depressions developed in southern Tuscany after the paroxysmal phases of the Apennine orogeny. It has a prevalent NNWSSE direction and is limited to the north by the «Soglia di Pienza», a structural high that separates the Radicofani Basin from Siena Basin; to the south it disappears under the volcanic cover of the Mts. Vulsini, whereas its western and eastern sides are bounded by the Montalcino-Castell'Azzara and Mt. Cetona ridges, respectively.

Seismic, gravimetrical and stratigraphical studies (Liotta and Salvatorini, 1994) showed that the Radicofani Basin is bounded, by both the eastern and western sides, by normal listric faults dipping towards the centre of the basin. It is very likely that one of this faults acted as the pathway for the uprising of Radicofani magmas. Close to the centre of the basin, the Pliocene sediments, constituted by prevailing blue-grey clays with subordinate conglomerates and sandstones, reach a maximum thickness of more than 2500 m. At about 3.3 Ma the Radicofani Basin was almost completely emerged in response to a regional tectonic upwelling of the southern Tuscany - northern Latium area. This upwelling was mainly due to the isostatic re-equilibration of the Apennine Chain, but locally it was greatly enhanced by the uprise of anatectic magmas into upper crust levels.

The remains of the volcanic structure have a truncated conical shape with a basal diameter of about 400 m and a height of about 100 m. They are interpreted as the erosional remnant of a volcanic neck with associated relics of some lava flows (Innocenti, 1967). The contact between the neck and the surrounding Pliocene marine clays is always covered by a large amount of rockfall talus accumulated at the base of the neck itself. The macroscopic features of the rocks that constitute the neck are variable going from its base towards the flat top (during medieval times, the top of the neck was levelled to build a stronghold). At its base, the neck is made of a homogeneous and massive dark-grey rock. It crops out for 50-60 m by thickness and can be easily recognised for its irregular columnar jointing. Towards the top of the neck, lithologic types differing by colour, vesiculation, flow structures and weathering can be found. In some cases their inter-relations are not easy to be interpreted. The outcrop lying just at the south side of the stronghold foundations is particularly problematic. Here, liver-red rocks contain centimetric to decimetric black lava tongues and vice versa; in other parts of the same outcrop dyke-like intrusions of black lava into red massive rocks can be found. The occurrence of this kind of structures was regarded by Innocenti (1967) as an evidence for the past activity of a small lava lake. He interpreted the black tongues of lava as portions of fresh undegassed pyromagma mingling, along the convective currents generated in the lava lake, with the already degassed and oxidised magma. In some sectors of the top of the neck, in particular around its central part, deposits of red scoriae can be found that probably once constituted the external cover of the entire volcanic edifice.

Debris of volcanic rocks can be found in many localities around the central apparatus. They generally constitute scattered masses varying in size and state of preservation; in two cases, Poggio Sasseta and Poggio Casano, it is possible to interpret the more continuous outcrops of volcanic rocks as remnants of lava flows. Four age determinations have been obtained for the Radicofani volcanics (Barberi *et al.*, 1971; Pasquarè *et al.*, 1983; D'Orazio *et al.*, 1991; 1994); two are K-Ar datings of samples from the neck rocks; the other two are the ^{40}Ar-^{39}Ar and K-Ar datings of the same sample from the Poggio Casano lava flow. Although these geochronological data do not allow to establish with reasonable confidence the relative age of the neck and lava flows, they indicate that the Radicofani volcanic centre

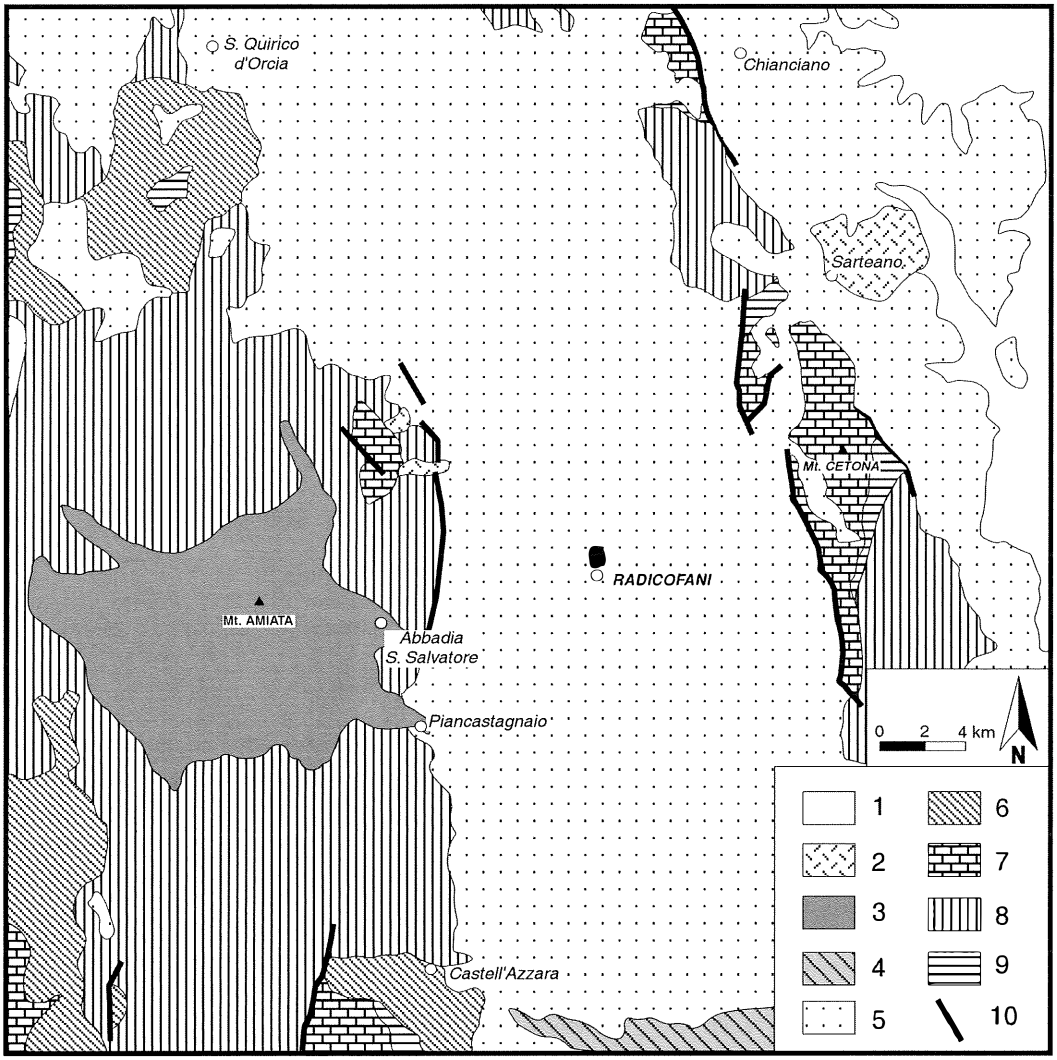

Fig. 1 – Geological sketch map showing the position of the Radicofani volcano within the Radicofani Neogene Basin. 1. Continental, fluvial-lacustrine deposits, Quaternary; 2. Travertine, Pliocene-Quaternary; 3. Mt. Amiata volcanics (0.6-0.4 Ma); 4. Vulsini volcanics (0.6-0.1 Ma); 5. Terrigenous, marine and continental deposits, Miocene Sup.-Pliocene; Tuscan Units; 6. Turbiditic sandstones («Macigno») and Cretaceous-Upper Oligocene; 7. Cherty-limestones, radiolarites, marls, limestones and dolomites, Trias Sup.-Cretaceous Inf.; 8. Ligurian Units; 9. Sub-Ligurian Units; 10. Main normal faults.

was active at around 1.3 Ma. During approximately the same time-span, volcanic activity occurred at Monte Cimino (1.35-0.95 Ma) and Torre Alfina (0.82 Ma).

It is worth noting that the volcanic nature of the Radicofani rocks was recognised as far back as 1722, when the botanist, abbot Pier Antonio Micheli identified the black and red scoriae he found at Radicofani as the products of an extinct volcano (Targioni Tozzetti, 1776); the discovery of Pier Antonio Micheli has to be recorded as one of the first recognition of volcanic formations in an area not volcanically active.

4.3 THE VOLCANIC ROCKS OF RADICOFANI

4.3.1 Major elements, classification and petrography

Radicofani volcanics are Q-normative and subalkaline (Irvine and Baragar, 1971). Both MgO contents (7.1-8.6 wt%) and Mg#'s (71-77) are high. This is particularly striking, considering the high silica content (53.9-56.1 wt%) of these rocks. The K_2O/Na_2O ratios range from 1.5 to 3.7, and nine samples out of twenty fulfil the criteria proposed by Foley *et al.* (1987) to define a rock as ultrapotassic (i.e., $K_2O > 3$ wt%, $K_2O/Na_2O > 2$, $MgO > 3$ wt%). On the whole, Radicofani volcanics exhibit a compositional variation towards lower Al_2O_3, FeO_{tot}, CaO and Na_2O and higher SiO_2, TiO_2, P_2O_5 and Mg# from the less potassic to the extreme ultrapotassic rocks. By virtue of their high Al_2O_3 content, the ultrapotassic rock from Radicofani fall in the Group IV of Foley *et al.* (1987), even if the most potassic samples are transitional towards the Group I lamproite rocks.

Major element composition of Radicofani volcanics, coupled with their mineralogy, allow to attribute them to a shoshonite series. In the K_2O vs. SiO_2 classification diagram of Peccerillo and Taylor (1976) the sample data-points fall in the fields of high-K basaltic andesite, shoshonite and latite (Fig. 2). The high-K basaltic andesites are porphyritic/glomeroporphyritic rocks (Porphyritic Index=16-21) with a phenocryst assemblage consisting of olivine + plagioclase + clinopyroxene. The intersertal groundmass is composed of plagioclase, clinopyroxene, ilmenite, alkali feldspar, interstitial glass, olivine and scarce brown mica flakes. These rocks can be found only in the lower and intermediate levels of the neck. Olivine is the most abundant phenocryst phase (8-10 vol.%; average size ~ 0.5 mm) and frequently hosts small octahedra of Cr-rich spinel. It has rounded shape and it is partially replaced, along the rims and the internal microfractures, by bowlingitic products and/or iddingsite. Olivine compositions cluster around Fo_{75} (Innocenti, 1967; Poli, 1985; D'Orazio *et al.*, 1994). Clinopyroxene phenocrysts are classified as diopside and augite; they appear fresh and almost euhedral, with sizes slightly smaller than that of olivine. They frequently show the polysynthetic twinning (100) and a slight zoning. Clinopyroxene phenocrysts have variable but generally low content of TiO_2 (0.5-0.9%), Al_2O_3 (1.8-5%) and Na_2O (0.1-0.2%).

Compositional variations are restricted in the range $Wo_{39-45}En_{48-55}Fs_{7-11}$. Plagioclase crystals show a continuous range of sizes from the groundmass microlites to the largest phenocrysts (maximum length 2 mm). These latter are zoned with bytownitic cores (An_{88-80}) and more sodic rims up to An_{74}. They usually show very thin rims marking a sharp transition towards alkali feldspar compositions.

Shoshonites (both potassic and ultrapotassic) were found in the upper levels of the neck and constitute the lavas of Poggio Sasseta. They are vesiculated, porphyritic rocks with an intersertal/intergranular groundmass. With respect to the high-K basaltic andesites, the shoshonites are characterised by a decrease of the plagioclase/alkali feldspar ratio and a decrease of the plagioclase phenocrysts content. Concurrently, the content of brown mica in the groundmass increases. Olivine is the most abundant phase of the phenocryst assemblage (8-12 vol.%). Olivine phenocrysts can appear clear and very fresh, crowded with Fe-Ti oxides or extensively replaced by iddingsite. The observed compositions vary between Fo_{84} (cores) and Fo_{69} (rims). Clinopyroxene phenocrysts (~ 3 vol.%) are diopsides and augites; observed compositions fall in the range $Wo_{39-44}En_{49-53}Fs_{7-8}$.The groundmass is composed of labradoritic plagioclase microlites, alkali feldspar, clinopyroxene, olivine, brown mica, ilmenite, apatite and scarce interstitial glass.

Ultrapotassic latites were found exclusively as blocks scattered around the hills surrounding

groundmass is dominated by alkali-feldspar joined by clinopyroxene, brown mica, ilmenite, apatite and moderate quantity of olivine, plagioclase, brown amphibole and interstitial glass. Optical and X-ray diffraction data (Innocenti, 1967) obtained on the alkali feldspars of the Poggio Casano ultrapotassic latite, indicate a high temperature sanidine with about 73 mol.% Or. The volcanic rocks from Radicofani commonly contain millimetre-sized quartz xenocrysts or quartz aggregates that, occasionally, can reach up to several centimetres in size (Lacroix, 1893). Quartz xenocrysts are rounded and mantled by a well developed reaction rim constituted of acicular green clinopyroxene crystals. Less frequently, cordierite xenocrysts and microxenoliths made up of andalusite+sillimanite+green spinel+ anorthite were also found. It is worth to note that the proportion of this xenocrystal material is always well below 0.1% by volume.

4.3.2 Trace elements

Sc, V, Cr, Co, Ni. Radicofani volcanics contain moderately to quite high levels of the 3d transition trace elements. In particular, the concentrations of Cr (404-565 ppm) and Ni (124-264 ppm) are not far from those presumed for primary mantle melts. Ni and, to

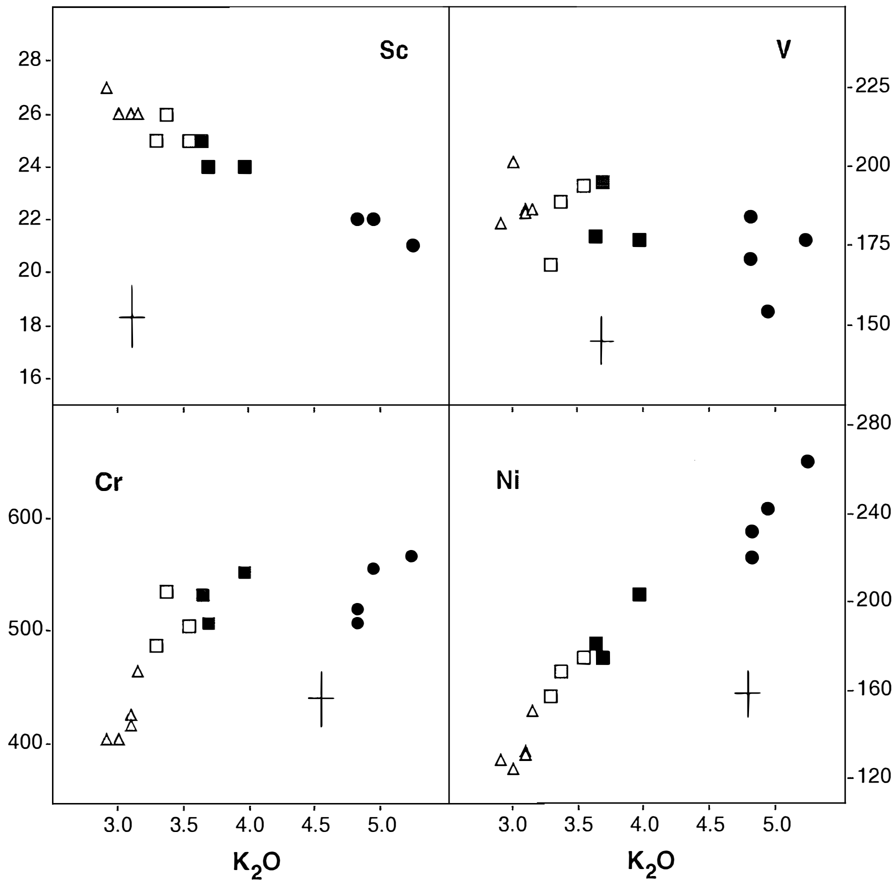

Fig. 3 – K_2O (wt.%) vs. 3d transition elements (Sc, V, Cr, Ni; ppm) for the Radicofani volcanics. Crosses indicate analytical uncertainties (1σ). Same symbols as in figure 2.

a lesser extent, Cr correlates with K_2O and most of the other incompatible trace elements (Fig. 3); the behaviour of Ni, that doubles its concentration from the high-K basaltic andesites to the ultrapotassic latites, is quite striking and poses major constraints to the petrogenesis of Radicofani volcanics. V is present at moderately high levels, but do not show any correlation with K_2O (Fig. 3); by contrast, Sc shows a clear negative correlation with K_2O (Fig. 3). The concentration of Co is strikingly constant (33 ± 1 ppm). Nb, Ta, Zr, Hf. In the mantle-normalised concentration diagrams of Fig. 4, the «twin» HFS elements Nb and Ta form pronounced negative anomalies that, along with the negative spikes of the major elements P and Ti, are a typical features of the northern Apennines mantle-derived rocks. In the same diagram, Zr and Hf do not display any spike in respect to the neighbouring elements, and the Zr/Hf ratio roughly decreases from the high-K basaltic andesite (Zr/Hf ca. 42) to the ultrapotassic latites (Zr/Hf ca. 32). Nb, Ta, Zr and Hf also exhibit very good linear positive correlation with K_2O (Fig. 5).

Rb, Sr, Ba, Pb, Th, U. Rb, Th and U are characterised by high and variable contents and correlate positively with K_2O (Th/U = 5.3 ± 0.3); Sr and Ba are present at relatively lower concentration and form marked negative spikes in the mantle-normalised diagram of fig. 4; also, they exhibit a narrow range of variation. The low Sr levels of Radicofani volcanics, coupled with their relatively high LREE contents, give rise to very high Ce/Sr ratios (>0.3). Within the northern Apennine region, Ce/Sr ratios higher than those characterising Radicofani volcanics, were only found for the Tuscan lamproites (Ce/Sr up to 0.7; Conticelli and Peccerillo, 1992). Pb is present at high levels (it forms a pronounced positive spike in the diagram of fig. 4) but, like Ba and Sr, its variability is considerably low.

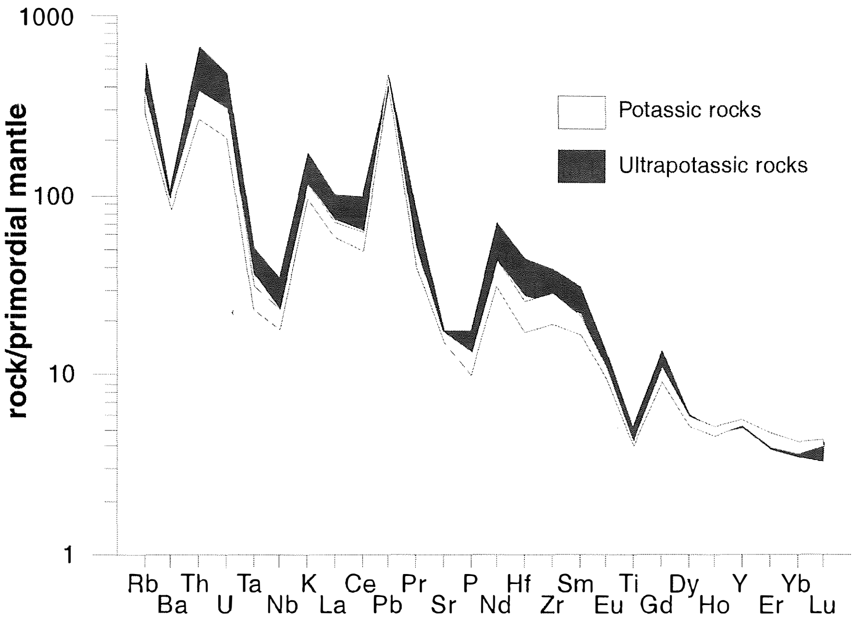

Fig. 4 – Primordial mantle – normalised incompatible element concentrations for Radicofani volcanics. Normalizing values after McDonough and Sun (1995).

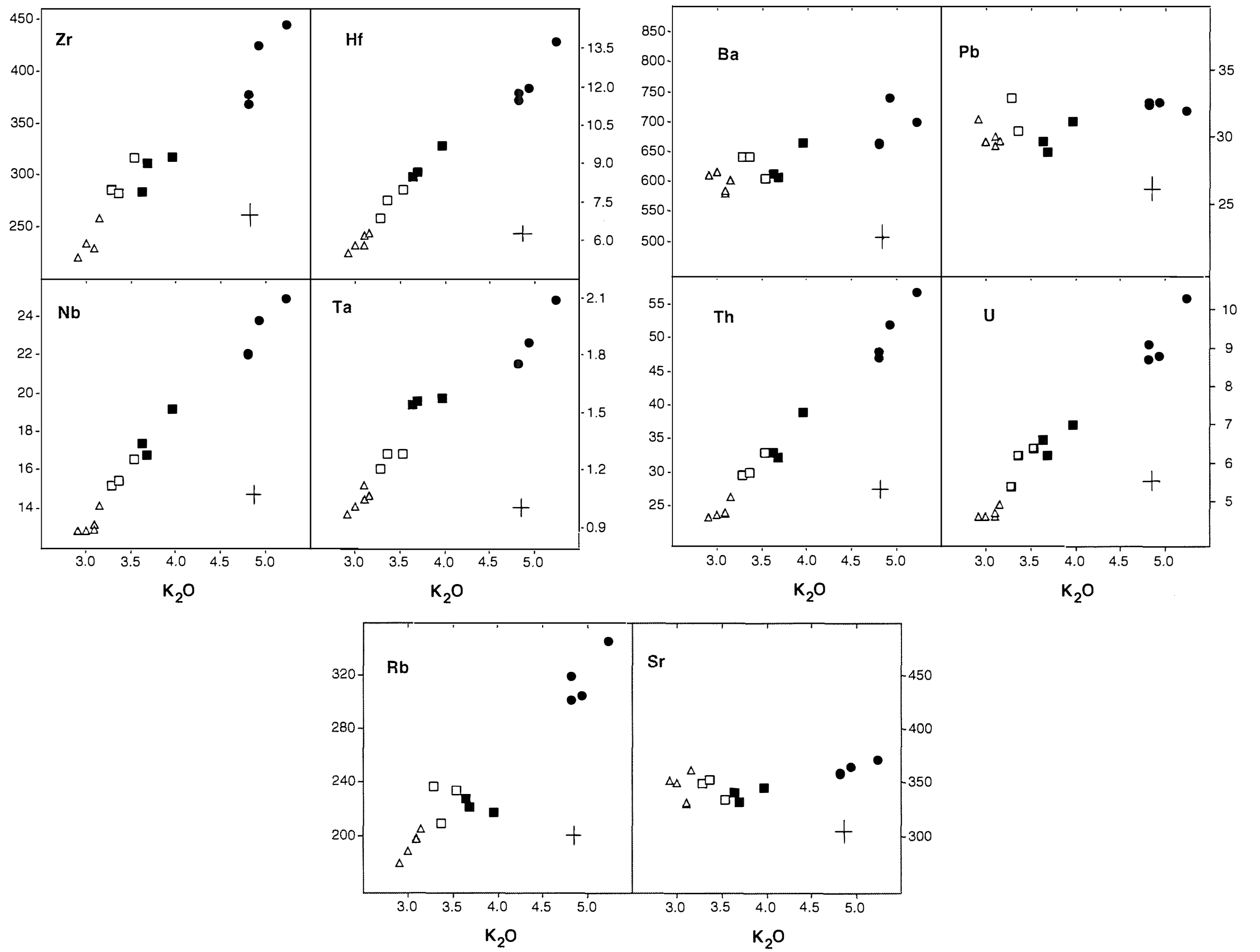

Fig. 5 – K_2O (wt.%) vs. incompatible trace elements (ppm) for the Radicofani volcanics. Crosses indicate analytical uncertainties (1σ). Same symbols as in figure 2.

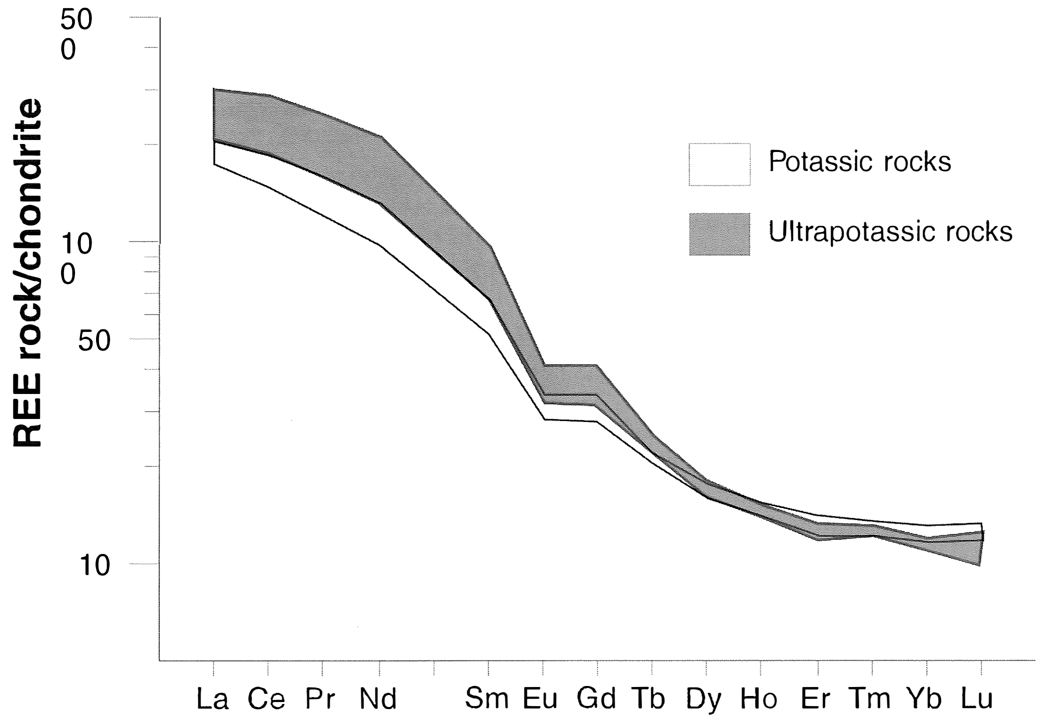

Fig. 6 – Chondrite – normalised REE concentrations for Radicofani volcanics. Normalizing values after McDonough and Sun (1995).

REE. The chondrite-normalised REE patterns of the Radicofani volcanics (Fig. 6) are characterised by the following features: (1) strong LREE/HREE fractionation ($[Ce/Yb]_N$ 11.7-25.4), (2) high LREE concentrations ($[La]_N$ 173-300), (3) low La/Nd ratios ($[La/Nd]_N$ 1.4-1.8), (4) low HREE fractionation ($[Ho/Lu]_N$ 1.1-1.5), (5) negative Eu anomalies (Eu/Eu* 0.60-0.77). Similar chondrite-normalised REE patterns were found for the Tuscan lamproites (Conticelli *et al.*, 1992), and also for the lamproites of southern Spain and Priestley Peak (Antarctica; Foley *et al.*, 1987). The $[La/Nd]_N$ and Eu/Eu* ratios decrease and the $[Ce/Yb]_N$ increase from the high-K basaltic andesites to the ultrapotassic latites. The $[Ho/Lu]_N$ ratios show a limited variation between the ultrapotassic and potassic terms.

4.3.3 Sr-Nd isotopes

The whole range of $^{87}Sr/^{86}Sr$ values is particularly wide (0.71332-0.71632). Sr-isotope compositions are highly radiogenic and correlates with the degree of K and incompatible element enrichment. The $^{143}Nd/^{144}Nd$ ratios of Radicofani volcanics are low (0.51207-0.51220) and less variable than $^{87}Sr/^{86}Sr$ ones.

4.4 Petrogenesis

4.4.1 Comparison with other high MgO, high SiO_2 potassic/ultrapotassic rocks from the northern Apennine

Among the primitive, silica saturated/oversaturated rocks of the northern Apennines, the high-K calcalkaline rocks from the Island of Capraia have major-element compositions quite similar to those of Radicofani but are characterised by K_2O/Na_2O ratios < 1 and by $^{87}Sr/^{86}Sr < 0.710$. Moreover, their incompatible trace-element distributions are distinctly less enriched.

The Montecatini Val di Cecina and Orciatico ultrapotassic rocks (orendites) have a lamproitic affinity even if, according to Mitchell (1991), they are not true lamproites as their Ba contents are too low and they are not peralkaline. Compared to the most K-rich rocks from Radicofani, the Montecatini Val di Cecina and Orciatico orendites are characterised by lower Al_2O_3, CaO, Na_2O, Sc, V and higher TiO_2, K_2O, P_2O_5 and Ni, and by an even more extreme enrichment of incompatible trace elements (particularly Rb, Zr, Nb, Ba, LREE, Hf and Th). Major-element differences between the two groups of rocks are reflected in the abundance of phlogopite + sanidine and the lack of plagioclase in the Montecatini and Orciatico rocks.

The ultrapotassic, olivin-latitic lavas from Torre Alfina have major- and trace-element distributions quite similar to Radicofani volcanics, nonetheless, they are more enriched in incompatible elements. This holds true particularly for Sr, Zr, Nb, Ba, LREE, U and Pb. Among the 3d transition elements, as already observed for the Tuscan lamproites, the Torre Alfina lavas are depleted in Sc and V and enriched in Ti and Ni with respect to Radicofani volcanics. For their abundance of forsteritic olivine phenocrysts and the lack of feldspar phenocrysts, Torre Alfina lavas resemble the ultrapotassic olivin-latite lavas from Radicofani. However, the former bear frequent phlogopite microphenocrysts that are never observed at Radicofani.

The primitive shoshonite lavas erupted during the late activity of the Latera volcano (western sector of the Vulsini volcanic complex), can be distinguished from the Radicofani rocks by virtue of their ol-hy normative compositions, their higher Sr and lower TiO_2, P_2O_5, K_2O/Na_2O and $^{87}Sr/^{86}Sr$ (Conticelli *et al.*, 1992). Moreover, Latera shoshonites contain sanidine phenocrysts, and clinopyroxene prevail over olivine in the phenocryst assemblage.

4.4.2 Crystal fractionation, pneumatolytic differentiation and crustal contamination

The large variability of the $^{87}Sr/^{86}Sr$ and, to a lesser extent, the $^{143}Nd/^{144}Nd$ ratios combined with the covariance of Ni and Cr with the magmaphile elements, rule out the possibility that the chemical variation observed among Radicofani magmas could be exclusively attributed to crystal fractionation processes acting on a unique parental magma. The peculiar geochemical differences between the high-K basaltic andesites, forming the base of the neck, and the ultrapotassic latites of some lava flows, led some authors (Marinelli, 1961; Innocenti, 1967) to speculate that they could result from the magmatic vesiculation inside the volcanic conduit with an effective transport of alkalies in the gas phase. However, the more complete trace element data set now available, indicates that the enrichment in K and Rb is accompanied by a corresponding increase of elements not easily mobilised into the gas phase such as Zr, Hf, Ta, Nb. The involvement of crustal-derived materials in the chemical differentiation of Radicofani magmas is suggested by the occurrence of resorbed quartz and cordierite xenocrysts and the andalusite + sillimanite + green spinel + anorthite microxenoliths, as well as by the high and low values of $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$, respectively. Modelling of assimilation plus fractional crystallisation process (AFC) starting from high-K basaltic andesite and ultrapotassic latite, and using as the crustal contaminant the average composition of the crystalline basement of Tuscany (Gianelli and Puxeddu, 1979) or a mafic lower crust, indicate that the chemical variations that would be produced by AFC are strongly contrasting to those observed for the Radicofani lavas. A process of bulk contamination by the same crustal materials as above, would imply a very large proportion (> 80%) of crustal materials to drive the ultrapotassic latite towards the basaltic andesite composition. Such a large fraction of added felsic materials should have moved the contaminated magmas to very low

MgO and CaO concentrations, in contrast with what is actually observed.

4.4.3 Lamproitic and shoshonitic primary magmas?

The geochemical and isotopic data to date obtained lead to exclude that the compositional variability documented within Radicofani volcanics could primarily result from open or closed system magmatic processes acting on a single parental magma. At least two primary magmas with contrasting composition should have contemporarily concurred to the activity of the Radicofani volcano. A lamproite-type magma, very similar to that originating the orendites found at Montecatini Val di Cecina and Orciatico, could be envisaged as the ultrapotassic end-member, whereas the identification of the less potassic counterpart is more controversial. Any likely candidate for this end-member should have SiO_2 > 54 wt%, Al_2O_3 > 17.5 wt%, K_2O/Na_2O < 2, K_2O < 3 wt%, MgO and CaO > 7.5 wt%, Sr ~ 300 ppm. These chemical characteristics can not be found neither among the primitive lavas of potassic series of the Roman Comagmatic Province, nor among the mafic magmatic enclaves occurring inside the Mt. Amiata trachydacites. All these rocks are in fact characterised by higher K_2O and K_2O/Na_2O ratios and by higher Sr contents. Within the Neogene-Quaternary northern Apennine magmatic province, mafic lavas with composition akin to the Radicofani potassic end-member were found only in the Capraia Island (Punta dello Zenobito).

Whatever the nature of the two end-members, another important question about the petrogenesis of Radicofani rocks concerns the origin of the lavas intervening between the two extreme ones. The two contrasting hypotheses are: (1) they are the mixing products of two end-member magmas (lamproite and shoshonite), and (2) they were originated by the partial melting of a progressively metasomatised mantle source.