

PETROGENESIS OF ORENDITIC AND KAMAFUGITIC ROCKS FROM CENTRAL ITALY

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ABSTRACT

In central Italy, ultrapotassic rocks having an orenditic or lamproitic and kamafulugitic affinity are found associated with potassic (KS) and highly potassic (HKS) volcanic rocks of the Roman Province. Orenditic rocks (OREN) are silica-oversaturated, intermediate in composition and have a high (71–80) value of $Mg\#$ [$100 \text{ Mg}/(\text{Mg} + \text{Fe}^{2+})$], high K/Na, and high abundances of incompatible elements, Cr and Ni. Kamafulugitic rocks (KAM) are ultrabasic, strongly silica-undersaturated, and show the highest Ca(%), $Mg\#$ (75–81) and K/Na in the Roman province; incompatible elements are highly enriched; Ni and Cr range from 79 to 153 and from 40 to 830 ppm, respectively. Orenditic rocks have higher Sr-isotope ratio (0.71256–0.71715) and lower abundance of Sr (402–847 ppm) with respect to KAM ($^{87}\text{Sr}/^{86}\text{Sr}$ 0.71037–0.71120; 1724–3704 ppm Sr). Derivation of OREN from KAM or HKS magmas by assimilation of crustal material, although consistent with Sr isotopic variations, is ruled out by the high $Mg\#$, Ni and Cr of OREN, as well as by a large number of other geochemical and petrological data. The genetic model proposed suggests that KAM and OREN were generated by melting at different depths of a residual, phlogopite-bearing upper mantle enriched in LILE and radiogenic Sr. Enrichment was provided by addition of liquids derived by melting of sediments carried down by subduction processes that were active under the Appennines during Tertiary times. The strong degree of silica undersaturation and the very high $Mg\#$ exclude significant interaction of KAM magmas with crustal rocks. Contamination of OREN magma with significant amounts of crustal material is possible only if parental magma had extremely high Mg, Ni, and Cr, as found in kimberlites and some high-Mg lamproites which, however, are not observed in the Italian peninsula.

Keywords: ultrapotassic rocks, orendite, lamproite, madupite, kamafulugitic rocks, lamprophyres, Roman Province, Italy.

SOMMAIRE

On trouve, dans la partie centrale de l'Italie, des roches ultrapotassiques ayant une affinité soit orenditique ou lamproitique, soit kamafulugitique; elles sont associées aux laves potassiques (KS) et très potassiques (HKS) de la province romaine. Les roches orenditiques sont sursaturées en silice,

intermédiaires en composition, relativement magnésiennes [rapport $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$] ou $Mg\#$ (entre 71 et 80), à K/Na élevé, et enrichies en K, Cr, Ni et éléments incompatibles. Les roches kamafulugitiques (KAM) sont ultrabasiques et fortement sous-saturées en silice; elles possèdent les valeurs de Ca(%), $Mg\#$ (75–81) et K/Na les plus élevées de la province romaine. De plus, ces roches sont fortement enrichies en éléments incompatibles; les teneurs en Ni et en Cr se situent entre 79 et 153 et entre 40 et 830 ppm, respectivement. La suite orenditique possède un rapport des isotopes de strontium plus élevé (0.71256–0.71715) et une concentration de Sr plus faible (402–847 ppm) que la suite KAM ($^{87}\text{Sr}/^{86}\text{Sr}$ entre 0.71037 et 0.71120; entre 1724 et 3704 ppm Sr). On ne pourrait dériver la suite OREN à partir des magmas KAM et HKS par assimilation de matériaux crustaux, malgré les variations des isotopes de Sr, vu le $Mg\#$ et la teneur élevée en Ni et en Cr de la suite OREN, et compte tenu d'un grand nombre de données géochimiques et pétrologiques. Selon le modèle pétrogénétique préféré, les magmas KAM et OREN ont été formés par fusion à des profondeurs différentes d'un manteau supérieur résiduel, mais porteur de phlogopite et enrichi en éléments incompatibles à large rayon et en strontium radiogénique. L'enrichissement serait dû à des liquides formés par la fusion de sédiments arrivés à ces profondeurs par processus de subduction sous la chaîne des Appennins à l'époque Tertiaire. La forte sous-saturation en silice et le $Mg\#$ très élevé font penser que les magmas KAM n'auraient pas pu être modifiés par des roches crustales. Une contamination des magmas OREN par des quantités importantes de roches crustales serait permise dans le seul cas où le magma aurait, au départ, des teneurs en Mg, Ni et Cr extrêmes, comme dans les kimberlites et quelques lamproïtes magnésiennes, roches qui n'ont toutefois pas été repérées dans la péninsule italienne.

(Traduit par la Rédaction)

Mots-clés: roches ultrapotassiques, orendite, lamproïte, madupite, roches kamafulugitiques, lamprophyres, province romaine, Italie.

INTRODUCTION

Ultrapotassic rocks from the Roman province, in Central Italy, have been the subject of many petrological, geochemical and isotopic investigations that

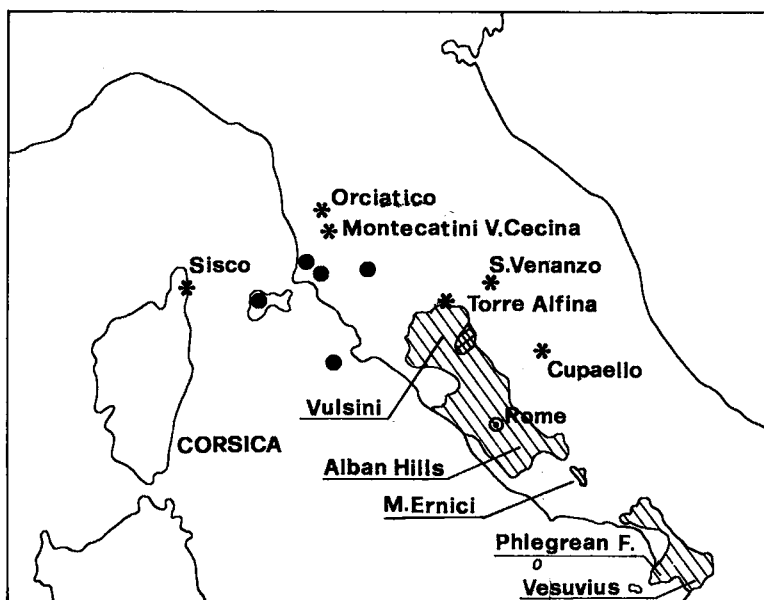


FIG. 1. Location map of orenditic and kamaufugitic rocks in central Italy (asterisks). Black dots: South Tuscany crustal anatectic rocks; ruled area: Roman Comagmatic Province.

have contributed to a clarification of many of their petrogenetic and geodynamic aspects; see Peccerillo & Manetti (1985) for a review and references. Detailed investigations carried out on different sectors of the Roman province (e.g., Civetta 1981, Rogers *et al.* 1985) have shown that volcanic rocks display significant compositional differences across the Italian peninsula, as already stated some time ago by Turi & Taylor (1976). Whether these differences reflect heterogeneity in the source of magmas or result from different degree of interaction of magmas with upper crust is still a matter of debate (Turi *et al.* 1986, Holm & Munksgaard 1986).

In order to shed light on these problems we have undertaken a petrological and geochemical investigation of some of the least-studied ultrapotassic rocks of central Italy, *i.e.*, the melilitites from San Venanzo and Cupaello (venanzite and coppaellite of former authors, see Sahama 1974) and minettes (mica-rich lamprophyres, locally known as selagititi) from Montecatini val di Cecina and Orciatico, southern Tuscany (Fig. 1). Our investigation was also extended to the Sisco lamprophyre (Corsica) which, although older, is similar in composition to Tuscan minettes. Despite their rarity, these rocks are relevant to an understanding of the potassic magmatism because 1) they have the highest $Mg\#$ [$Mg/(Mg + Fe^{2+})$ atomic ratio] and abundance of ferromagnesian elements among Italian potassic rocks, and, thus, they may be the most likely candi-

dates to represent primary magmas; and 2) they are exposed near the northernmost portion of the Roman province, *i.e.*, in a zone where, according to some authors (Turi & Taylor 1976, Ferrara *et al.* 1986, Turi *et al.*, 1986) the potassic rocks show the strongest effects of crustal contamination; some of the investigated rocks are closely associated with the Tuscan anatectic province (Fig. 1).

The data obtained in the present work also will be used to address a number of other topics of current interest in the study of Italian potassic volcanism, such as 1) the nature of the mantle contamination event; 2) the geochemical evolution of the mantle source prior to generation of potassic magma; and 3) the composition of the mantle prior to contamination.

GEOLOGICAL SETTING AND PETROGRAPHY

The rocks from Sisco (SIS), Montecatini val di Cecina (MVC), Orciatico (ORC), S. Venanzo (SVEN) and Cupaello (CUP) have been studied by several authors who report detailed information on the geology and volcanology as well as data on petrology and phase composition (e.g., Mitterperger 1965, Barberi & Innocenti 1967, Gragnani 1972, Poli 1985, Wagner & Velde 1986). The following descriptions partly lean on these studies. The Sisco lamprophyre crops out as a sill, 2 to 4 m thick, intruded into crystalline rocks of the so-called "Schistes Lus-

tre's" Formation, which was affected by alpine folding and metamorphism. The K/Ar ages reported by Civetta *et al.* (1978) are in the range 14–15 Ma. The texture of the sill is variable, from microgranular to porphyritic, and both these rock types have been analyzed in the present work. Porphyritic rocks occur at the border of the sill and contain phenocrysts of brown mica and altered olivine set in a matrix of fine-grained brown mica, olivine, amphibole and sanidine. The same phases occur in the microgranular lithologies. The brown mica is phlogopite, and the amphibole is a K richterite (Velde 1967, Wagner & Velde 1986). Accessory phases consist of apatite,

titanite, chromite, ilmenite, priderite and rutile (Wagner & Velde 1986). Calcite is present as a secondary phase, together with alteration products of olivine. Quartz crystals, more or less extensively resorbed, are found.

The rocks from Montecatini and Orciatico crop out as two associated subvolcanic bodies intruded into Lower Pliocene argillaceous sediments that show evidence of contact metamorphism. One single K/Ar age determination, performed by Borsi *et al.* (1967) on a MVC sample, gave a value of 4.1 Ma. The MVC and ORC minettes are variable in texture and composition (Barberi & Innocenti 1967) and all the lithol-

TABLE 1. MAJOR-ELEMENT COMPOSITION (wt.%) AND CIPW NORMS OF ORENDITES FROM CENTRAL ITALY AND CORSICA

Slaco	Montecatini Val di Cecina									
	SIS-10	SIS-11	SIS-8	SIS-7	SIS-4	SIS-2	MVC-22	MVC-10A	MVC-24	MVC-20A
SiO ₂	56.73	57.83	57.89	58.29	58.50	58.63	56.61	56.63	64.14	64.18
TiO ₂	2.27	2.15	2.37	2.31	2.27	2.35	1.62	1.52	0.95	0.79
Al ₂ O ₃	10.60	10.65	10.47	10.82	10.84	10.86	12.12	12.27	14.69	14.64
Fe ₂ O ₃	2.00	1.81	2.17	1.74	0.81	1.84	3.66	3.19	2.31	1.86
FeO	2.40	2.56	2.52	3.26	2.42	2.96	3.20	3.20	1.02	1.04
MnO	0.07	0.07	0.08	0.07	0.06	0.08	0.07	0.07	0.07	0.05
MgO	7.13	6.88	6.38	7.05	6.63	6.47	7.21	7.71	3.34	1.82
CaO	3.65	3.53	3.64	2.93	3.12	3.15	3.48	3.55	1.33	1.84
Na ₂ O	1.10	1.30	1.06	1.01	1.02	0.88	1.50	1.30	1.78	2.00
K ₂ O	10.46	10.15	10.49	10.35	10.73	10.70	7.87	7.84	9.99	9.83
P ₂ O ₅	0.64	0.66	0.82	0.76	0.67	0.71	1.18	1.18	0.37	0.32
L.O.I.	2.96	2.69	2.07	2.14	2.09	1.91	2.71	1.55	0.81	1.43
Mg # *	78.1	77.5	74.8	78.4	77.8	77.0	70.8	72.7	61.3	58.5
Qz	1.99	3.72	4.73	4.26	4.51	4.97	0.42	1.64	9.27	9.07
Or	57.80	57.97	57.09	59.00	59.11	59.22	46.45	46.27	58.96	58.02
Ab	0.0	0.0	0.0	0.0	0.0	0.0	12.68	10.99	15.05	16.91
An	0.0	0.0	0.0	0.0	0.0	0.0	3.09	4.49	2.59	1.94
Ns	1.62	1.49	1.51	1.46	1.49	1.21	0.0	0.0	0.0	0.0
Ks	1.09	0.54	1.34	0.58	1.17	1.09	0.0	0.0	0.0	0.0
Ac	2.05	2.05	2.20	2.00	1.97	2.00	0.0	0.0	0.0	0.0
Di	10.99	10.44	10.06	7.54	8.76	8.67	5.18	4.33	3.66	4.14
Hy	15.43	15.24	14.32	16.60	14.89	14.56	21.72	23.26	8.10	4.13
Mt	0.0	0.0	0.0	0.0	0.0	0.0	1.54	1.50	0.77	0.67
Il	4.32	4.09	4.51	4.39	4.32	4.47	3.08	2.89	1.81	1.50
Ap	1.52	1.56	1.94	1.80	1.59	1.68	2.79	2.79	0.88	0.76

Orciatico	Torre Alfina						
	OR-2E	OR-2I	OR-7	OR-4	OR-10	OR-12	OR-1
SiO ₂	56.74	57.18	57.61	57.69	58.11	58.11	58.11
TiO ₂	1.42	1.42	1.43	1.43	1.43	1.42	1.60
Al ₂ O ₃	11.25	11.15	11.51	11.18	11.18	11.82	10.95
Fe ₂ O ₃	2.00	2.09	2.05	2.61	1.74	1.52	1.77
FeO	2.92	2.88	2.96	2.52	3.32	3.38	3.32
MnO	0.08	0.08	0.08	0.08	0.08	0.07	0.06
MgO	8.29	8.20	8.95	8.20	8.78	8.70	6.96
CaO	4.40	4.47	3.42	3.64	3.60	3.56	3.84
Na ₂ O	1.36	1.34	1.32	1.50	1.56	1.35	1.49
K ₂ O	7.68	7.84	7.82	7.42	7.43	7.92	7.35
P ₂ O ₅	0.70	0.69	0.69	0.75	0.70	0.69	0.76
L.O.I.	3.16	2.66	2.17	2.67	2.07	1.46	2.26
Mg # *	78.7	78.4	79.4	78.0	79.1	79.4	74.9
Qz	0.90	1.00	1.36	3.24	1.85	1.48	7.09
Or	45.33	46.27	46.16	43.80	43.85	46.75	43.38
Ab	11.50	11.33	11.16	12.68	13.19	11.41	12.60
An	1.91	1.28	2.38	1.86	1.56	2.80	1.48
Ns	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ks	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ac	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Di	12.16	12.99	7.98	8.97	9.52	8.20	10.02
Hy	12.29	18.71	23.03	20.77	22.74	22.21	16.92
Mt	1.16	1.18	1.18	1.21	1.32	1.16	1.21
Il	2.70	2.70	2.72	2.72	2.70	3.04	1.89
Ap	1.66	1.63	1.63	1.78	1.66	1.63	1.80

* Mg/(Mg + Fe²⁺) atomic ratio calculated assuming Fe₂O₃/FeO value of 0.2, multiplied by 100.

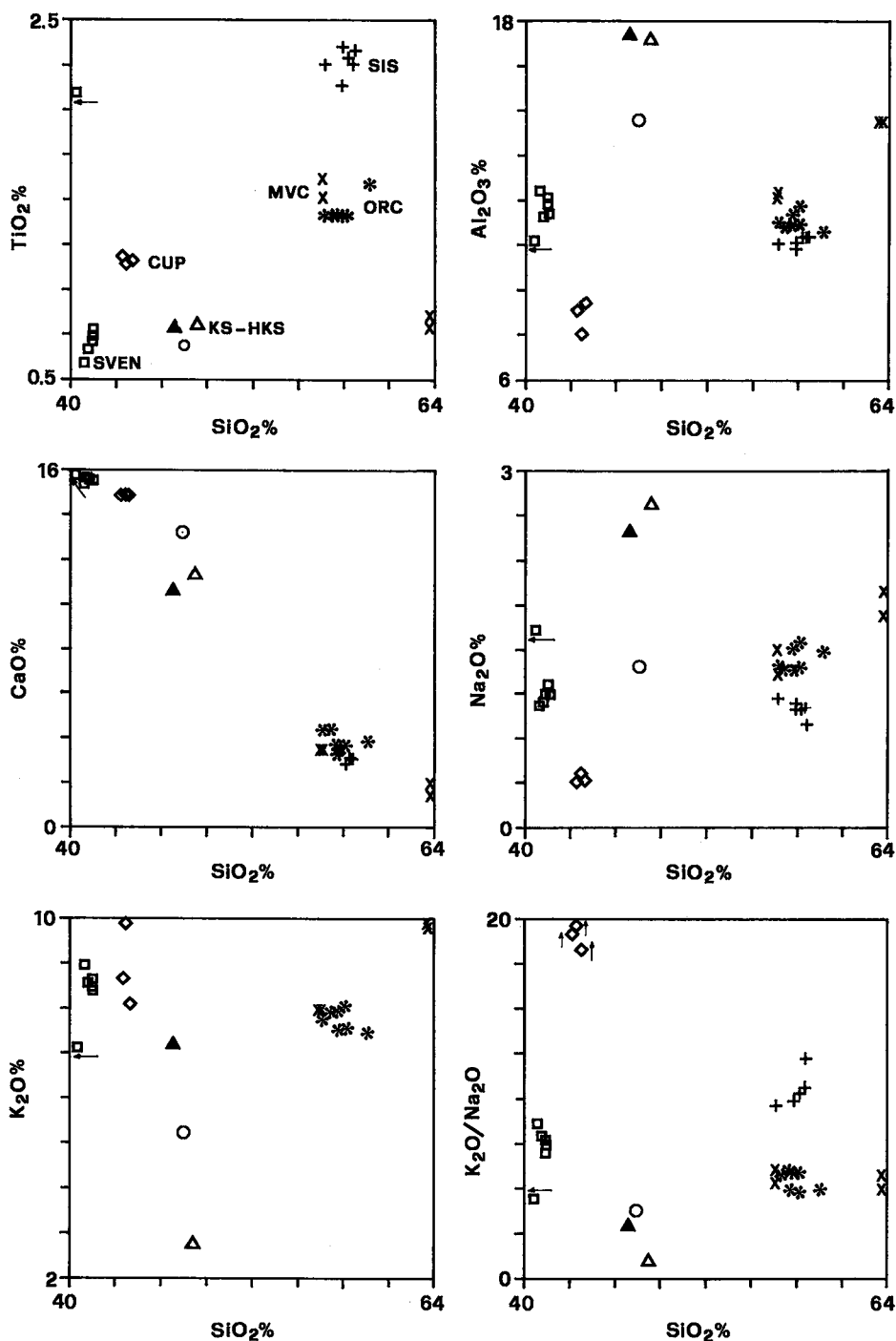
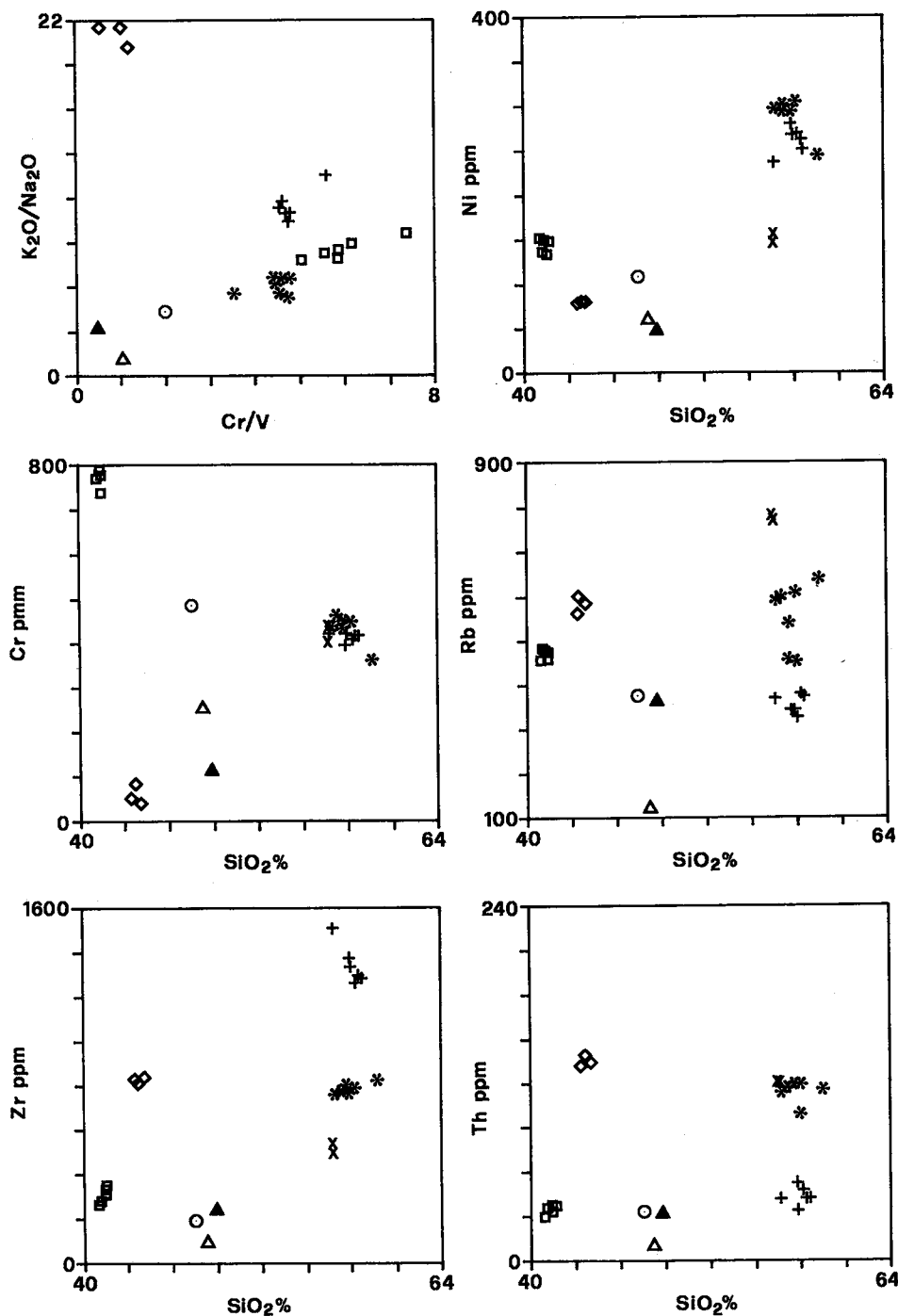


FIG. 2. Variation diagrams of some major and trace elements. Squares: SanVenzano; diamonds: Cupaello; asterisks: Ociatico; St. Andrea's crosses: Montecatini val di Cecina; crosses: Sisco. Differentiated rocks from MVC and SVEN are not represented on trace-element diagrams. Open circle, open triangle and full triangle represent average values of mafic HKS rocks from Vulsini (data from Civetta *et al.* 1984), of mafic KS and HKS rocks from Monti Ernici (data from Civetta *et al.* 1981).



ogies have been sampled and analyzed. The ORC rocks range from porphyritic to microgranular. The porphyritic rocks contain phenocrysts of olivine, brown mica and clinopyroxene set in a groundmass

containing the same phases plus sanidine, variable amounts of glass, and some K-rich amphibole (Wagner & Velde 1986). Apatite, ilmenite, chromite and rutile are accessories. The brown mica is phlo-

pite (Poli 1985, Wagner & Velde 1986). The olivine (up to 90% Fo) is more or less extensively resorbed and altered. A few olivine phenocrysts have kink banding and may represent mantle-derived xenocrysts. The clinopyroxene ranges from Fe-poor diopside to augite (Poli 1985). Microgranular varieties consist of the same phases as the porphyritic ones. MVC minettes have generally a granular texture with a poorly porphyritic tendency. They are composed of sanidine, brown mica and minor clinopyroxene. Altered phenocrysts of partly resorbed olivine, and a few intergranular quartz grains are also present. Apatite and Ti-Fe oxides are the main accessories. The phlogopite shows color zoning (pale brown core, dark brown margin) which reflects a rimward increase of Fe and Ti (Poli 1985). The MVC minettes are cut by felsic veins up to a few cm across. These have a granular texture and consist of sanidine, minor quartz, and some brown mica. The last is present as thin elongate crystals that still preserve a pale brown core. Apatite is the main accessory phase.

The Cupaello (CUP) volcanic center consists of one single lava flow 500 m long that rests on Cretaceous limestone and on Upper Pliocene lacustrine deposits. The rock exhibits clinopyroxene and a few phlogopite phenocrysts set in a matrix composed of clinopyroxene, phlogopite, kalsilite, melilite, Fe-Ti oxides, perovskite, monticellite and glass. Pyroxene is diopsidic in composition and has very low Al contents typical of clinopyroxene from melilite-bearing rocks; phlogopite has a high Mg (MgO about 21 wt. %), and is extensively transformed into opaque oxides (Graggani 1972, Gallo *et al.* 1984).

The San Venanzo (SVEN) volcanic complex consists of two centers: San Venanzo and Pian di Celle (Mitterpergher 1965). Radiometric dating indicates an age of 0.5 Ma (Fornaseri 1985). The Pian di Celle volcano is a tephra cone with welded scoria and a lava flow at its top. San Venanzo is a cinder cone. The lava flow consists of a weakly porphyritic rock containing olivine phenocrysts with chromite inclusions set in a holocrystalline groundmass of olivine, leucite, melilite, clinopyroxene and kalsilite with accessory apatite, Fe-Ti oxides and perovskite. Zeolites and carbonate minerals are present as secondary phases. The lava flow contains pegmatitic veins of kalsilite, melilite, leucite and phlogopite, with abundant pneumatolitic minerals. These veins were considered by Mitterpergher (1965) as late-stage differentiates of the SVEN magma.

ANALYTICAL METHODS

The major elements have been determined by X-ray fluorescence, Mg and Na by atomic absorption, Fe^{2+} by titrimetric technique, and LOI by classical gravimetric methods. The concentrations of Ni, Cr,

V, Th, Rb, Sr, Zr, Nb, Y and Ba have been determined by X-ray fluorescence (Franzini *et al.* 1972) and Th, Hf, Ta, Co, Sc and REE by INAA following the method of Poli *et al.* (1977). Precision is better than 5% for all the elements determined by X-ray fluorescence and for Th, Ta, Co, Sc, Sm and Eu, better than 10% for La, Ce and Hf, and better than 15% for Lu, Tb and Nd.

The isotopic composition of Sr has been determined on one sample from each of the Sisco, Montecatini, and Orciatino outcrops. Analyses were performed at the Department of Earth Sciences, University of Rome, by a VG Micromass 54E spectrometer. Values were recalculated to the SrCO_3 standard value of 0.71011. For San Venanzo and Cupaello we have used the data already available in the literature (Holm & Munksgaard 1982, Holm *et al.* 1982, Taylor *et al.* 1984). In view of the small volume of the rock masses and of their rather constant composition, demonstrated by major and trace-element data, we believe that the $^{87}\text{Sr}/^{86}\text{Sr}$ data available are representative of the rocks under investigation.

RESULTS: THE SISCO-MONTECATINI VAL DI CECINA-ORCIATINO ROCKS

Major, trace-element and Sr-isotopic data are reported in Tables 1 and 3 together with the CIPW norms. Except for the MVC felsic veins, the single magmatic bodies show a rather homogeneous composition for major and most trace elements.

Major elements and classification

The rocks from the three localities have many petrological characteristics in common; they have intermediate silica content, high Mg# (71–80), K, K/Na and K/Al. All are silica-oversaturated; only the SIS minette is peralkaline. Compared with typical Roman intermediate volcanics, these rocks have higher Mg, Ti, K/Na, K/Al, and lower Al and Na (Fig. 2). All these characteristics make the investigated minettes distinct from typical rocks of the Roman province and result in their classification as ultrapotassic rocks with an *orenditic* or *lamproitic affinity* (Sahama 1974, Mitchell 1985, Foley *et al.* 1986, 1987). These rocks also differ from the minettes found by Van Bergen *et al.* (1983) as inclusions in the Monte Amiata lavas. Comparison with rocks from other ultrapotassic provinces indicates a close compositional similarity with orendites from Spain (Venturelli *et al.* 1984) and Leucite Hills (Carmichael 1967, Kuehner *et al.* 1981). Preliminary major- and trace-element data indicate that other rocks with a similar composition also crop out at Torre Alfina (Fig. 1), on the northern edge of the Vulsinian complex. Detailed investigations of Torre

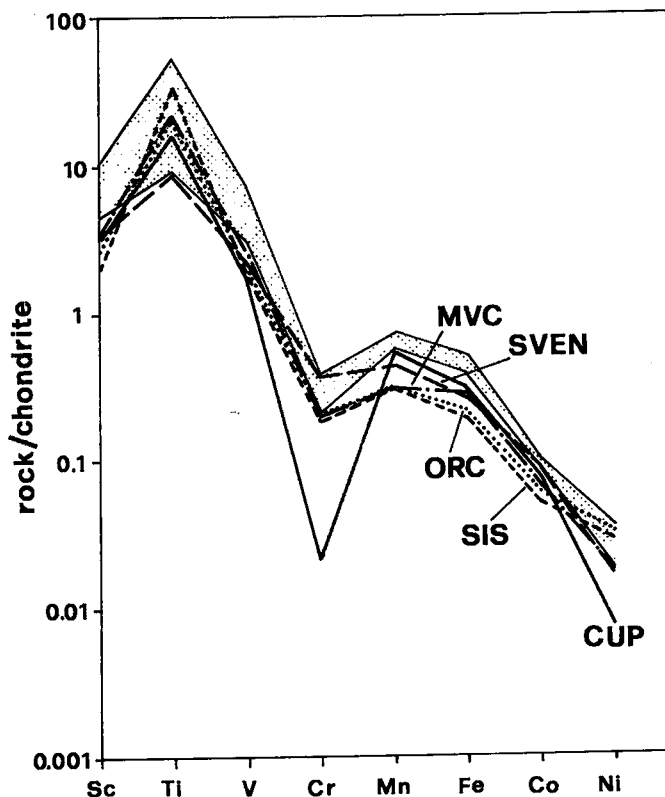


FIG. 3. Chondrite-normalized patterns of transition-group elements for average OREN and KAM rocks. The dotted area represents ranges of values of basalts from different environments (from Langmuir *et al.* 1977).

Alfina volcanics are still in progress and only two representative analyses are reported in Tables 1 and 3. The acidic veins that cut the MVC minette have higher Si, Al, Na, K, and lower Fe, Mg, Ti and P than the host rock.

Trace elements

The transition-group elements all have high values, especially if one considers the SiO_2 level of the analyzed rocks. Ni and Cr are particularly enriched and show values that fall within the range of primary basalts from different tectonic environments (Fig. 3). Co, Sc and V are less abundant than in basalts and increase from SIS to MVC and ORC minettes; on the contrary, Cr and to a lesser degree Ni, are almost constant. Consequently, Cr/V (Fig. 2), Cr/Sc, Ni/V, and Ni/Sc are higher in SIS than in Tuscan minettes. The incompatible elements display a high enrichment. The REE patterns are strongly fractionated for both LREE and HREE (Fig. 4a,b). Th, Rb and Cs increase from SIS to MVC and ORC, whereas Ta, Hf, Nb, Zr, LREE and Sr have an oppo-

site trend. Accordingly, LILE/HFSE is higher in Tuscan minettes; note, however, that LILE/HFSE values are invariably higher than those of ultrapotassic rocks from intracratonic areas (Mitchell & Bell 1976) and are within the field of arc-related volcanic rocks (Pearce 1982). The same has been found true for all volcanic rocks from Central Italy (Peccerillo 1985), indicating a close genetic relationship of OREN with typical Roman volcanics. The patterns of hygromagmatophile elements for the analyzed orendites (Fig. 5a) all show strong fractionation, with negative anomalies of Ba, Ta, Nb and Ti, as found in all Roman volcanic rocks (*e.g.*, Peccerillo *et al.* 1984). Tuscan minettes, however, also have a strongly negative anomaly in Sr content that is not seen in mafic rocks from the Roman province. The MVC felsic veins have lower concentrations of the ferromagnesian trace elements, Ba, and LREE, and have higher Rb, Zr, Th, Ta and Nb than the host minette. These variations are qualitatively consistent with a derivation from the host minette by crystal fractionation, as suggested by Barberi & Innocenti (1967).

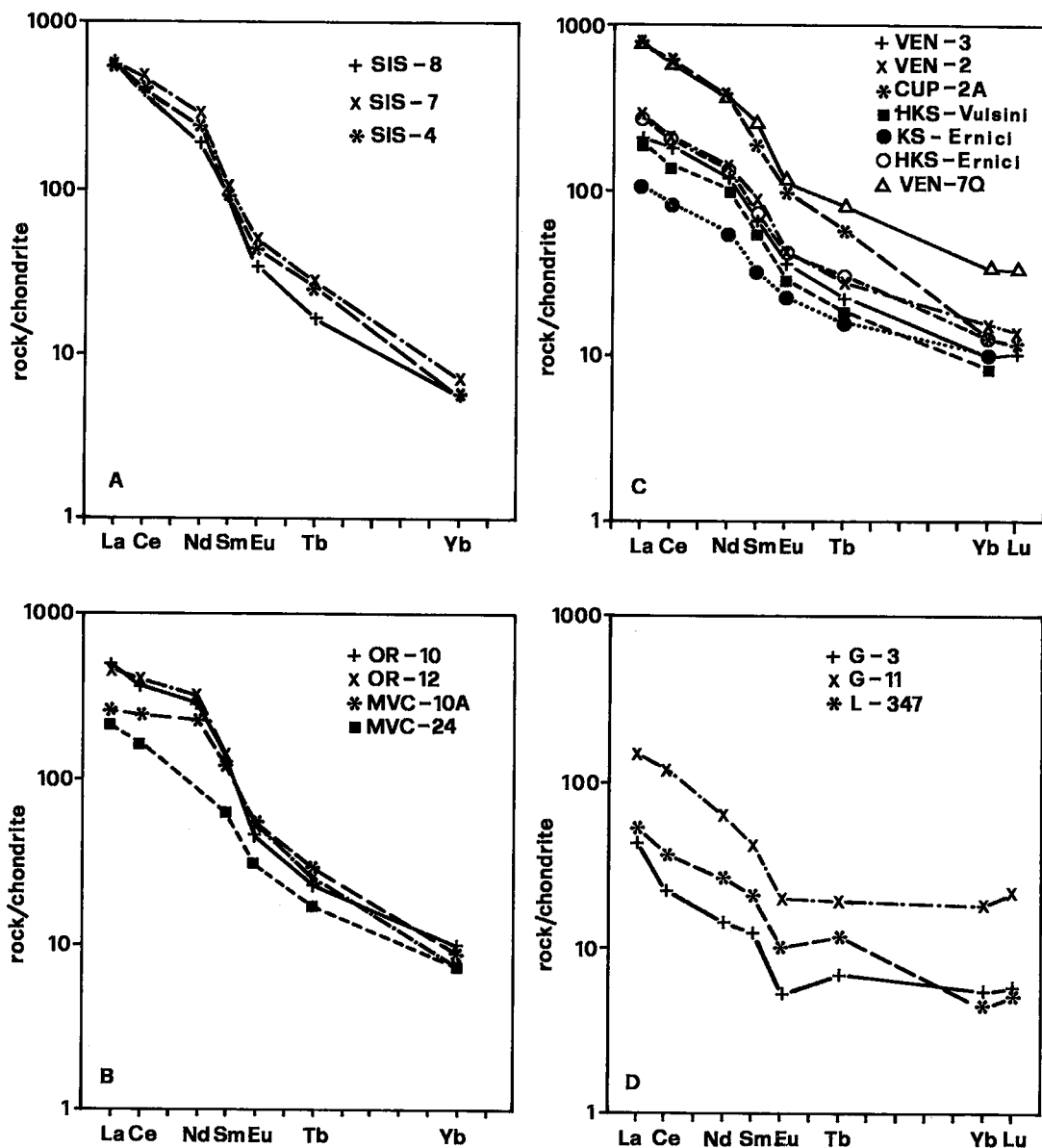


FIG. 4. Chondrite-normalized REE patterns for the analyzed rocks, for average KS and HKS mafic rocks from Monti Ernici and Vulsini (A,B,C), and for three selected siliceous rocks from Northern Apennines (D).

Sr-isotope ratios

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ value ranges from 0.71256 to 0.71715 and increases from SIS to ORC and MVC, in which they reach values that are within the range of crustal anatectic acidic rocks from the same area (Vollmer 1977).

RESULTS: THE SAN VENANZO AND CUPAELLO ROCKS

Major- and trace-element data, together with CIPW norms, are reported in Tables 2 and 4. Except for sample Ven-7Q, the San Venanzo and Cupaello volcanics have a homogeneous composition both for

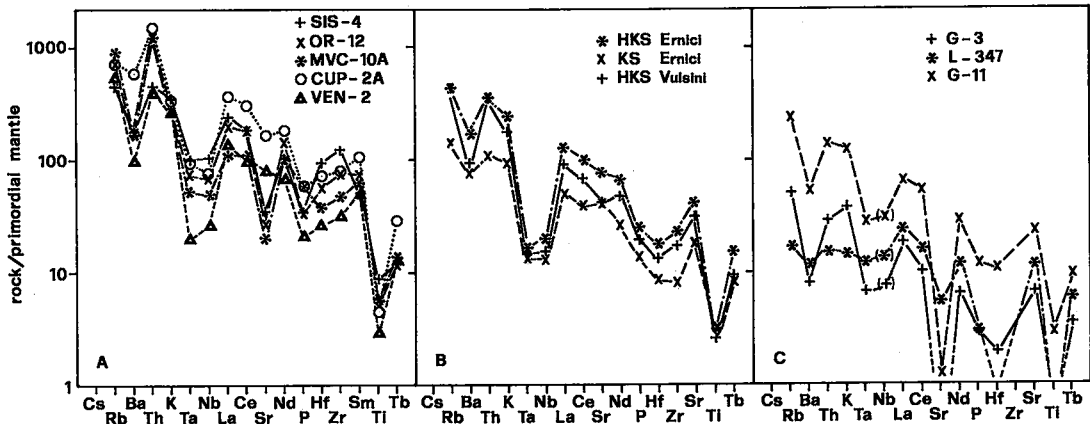


FIG. 5. Patterns of hygromagmatophile elements (Wood 1979) for some of the analyzed rocks (A), for average KS and HKS mafic rocks from Monti Ernici and Vulsini (B), and for three Northern Apennine siliceous sedimentary rocks (C).

TABLE 2. MAJOR-ELEMENT COMPOSITION (wt.%) AND CIPW NORMS OF MADUPITES FROM CENTRAL ITALY AND WESTERN USA

	San Venzano							Cupaello			Leucite Hills (USA)	
	VEN-7Q	VEN-3	VEN-8	VEN-5	VEN-2	VEN-4	VEN-11	CUP-2A	CUP-1A	CUP-1B	MAD-7	MAD-1
SiO ₂	38.96	41.03	41.20	41.46	41.52	41.55	41.46	43.68	43.43	43.98	43.10	44.65
TiO ₂	2.14	0.59	0.67	0.72	0.76	0.71	0.78	1.15	1.19	1.16	2.32	2.25
Al ₂ O ₃	10.44	12.39	11.51	12.00	12.05	12.17	11.62	7.53	8.40	8.55	8.58	8.16
Fe ₂ O ₃	3.14	2.09	1.39	1.69	1.68	1.84	1.82	5.47	5.33	5.30	5.34	6.38
FeO	7.10	4.08	4.88	4.76	4.88	4.56	4.80	2.20	2.56	2.55	0.80	—
MnO	0.18	0.10	0.11	0.11	0.11	0.11	0.11	0.12	0.12	0.12	0.13	0.12
MgO	7.30	13.09	12.76	12.93	12.76	12.76	12.70	10.52	10.50	10.86	11.60	12.30
CaO	18.85	15.50	15.73	15.61	15.67	15.62	15.64	14.97	14.98	14.91	10.71	14.06
Na ₂ O	1.65	1.04	1.07	1.13	1.20	1.20	1.13	0.45	0.40	0.40	0.93	0.93
K ₂ O	7.03	8.86	8.43	8.50	8.36	8.53	8.31	9.88	8.56	8.01	8.53	7.18
P ₂ O ₅	1.49	0.36	0.39	0.41	0.43	0.42	0.42	1.14	1.26	1.24	2.13	3.04
L.O.I.	1.72	0.86	1.86	0.68	0.57	0.55	1.11	2.90	3.27	2.74	—	—
M# *	60.7	82.2	81.4	81.2	80.8	81.2	80.6	75.6	75.0	75.7	81.3	81.8
An	0.32	2.97	1.71	2.57	2.80	2.63	2.09	0.0	0.0	0.0	0.0	0.0
Ne	7.56	4.77	4.90	5.18	5.50	5.50	5.18	0.0	0.0	0.0	0.0	1.08
Lc	32.54	26.14	30.43	29.34	29.71	29.48	31.62	32.20	35.92	36.56	36.69	33.23
Kp	0.0	10.78	6.22	7.25	6.51	7.24	4.96	0.0	0.0	0.0	0.0	0.0
Ns	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.10	0.62
Ks	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.78	1.31	0.18	0.99	0.0
Ac	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.35	2.98	2.98	2.75	2.81
Cs	24.71	22.12	22.81	22.32	22.30	22.29	22.49	13.31	14.07	13.47	2.87	3.53
Di	2.87	0.0	0.0	0.0	0.0	0.0	0.0	19.04	16.39	17.90	24.67	30.41
Ol	20.05	28.64	28.18	28.56	28.33	28.22	28.27	18.95	19.80	20.05	16.16	15.36
Mt	2.44	1.47	1.51	1.54	1.57	1.53	1.58	0.07	0.32	0.30	0.0	0.0
Il	4.07	1.12	1.27	1.37	1.45	1.35	1.48	2.19	2.26	2.21	4.41	4.28
Ap	3.53	0.85	0.92	0.97	1.02	0.99	0.99	2.70	2.98	2.94	5.04	7.20

* calculated with Fe₂O₃/FeO ratio of 0.2, MAD-7 and MAD-1, madupites from Leucite Hills respectively from Kuehner et al. (1981) and from Thompson et al. (1984).

major and trace elements.

Major elements and classification

Lavas from the two volcanoes are ultrabasic and strongly silica-undersaturated; they have very high Mg# and Ca. The CUP rocks are peralkaline and

have higher Ti, Si, P, K and K/Na than SVEN lavas, whereas Na and Al are lower and reach the lowest values among potassic rocks from central-southern Italy (Fig. 2). The LOI is relatively high in CUP, testifying to some degree of alteration. Compared with literature data for the same rocks (Gallo *et al.* 1984, Taylor *et al.* 1984), however, our samples have lower

TABLE 3. TRACE-ELEMENT CONCENTRATIONS (ppm) IN ORENDITIC ROCKS FROM CENTRAL ITALY AND CORSICA

	Sisico						Montecatini Val di Cecina			
	SIS-10	SIS-11	SIS-8	SIS-7	SIS-4	SIS-2	MVC-22	MVC-10A	MVC-24	MVC-20A
V	89	85	89	90	91	93	123	124	58	48
Cr	425	400	425	411	420	421	404	435	99	68
Sc			9.8	13	11.5			20	7.8	
Ni	239	283	271	272	264	254	148	156	50	34
Co			19	27	23			32	9	
Rb	370	342	343	327	380	376	781	770	977	948
Sr	839	847	812	738	803	847	469	454	451	436
Ba	1235	1230	1267	1022	1310	1329	1167	1202	693	635
La	188	188	183	176	172	193	76	78	62	86
Ce	337	333	302	400	347	344	182	206	135	151
Nd			111	165	139				140	
Sm			19	21	19				25	13
Eu			2.5	3.6	3.2				3.8	2.2
Tb			0.8	1.3	1.2				1.4	0.8
Yb			1.1	1.4	1.1				1.7	1.4
Y	28	25	26	25	27	27	37	40	39	37
Th	43	53	41	46	43	43	122	118	139	153
Hf			25	35	33			14	15	
Zr	1257	1384	1351	1274	1309	1302	536	502	708	706
Ta			3	5	4.3			2.2	2.3	
Nb	61	66	66	63	63	64	32	31	38	37
$^{87}\text{Sr}/^{86}\text{Sr}$					0.71256			0.71715		

	Orciatice							Torre Alfina	
	OR-2E	OR-2I	OR-7	OR-4	OR-10	OR-12	OR-1	TA-1	TA-2
V	98	98	96	97	97	100	103	125	142
Cr	439	463	449	442	455	449	364	842	552
Sc					15	17			
Ni	292	299	300	297	307	274	247	321	259
Co					28	31			
Rb	591	597	536	455	449	609	637	458	334
Sr	638	641	628	649	646	613	594	737	606
Ba	1154	1185	1198	1177	1175	1224	911	1292	1145
La	143	143	145	141	149	141	154		100
Ce	310	321	319	309	315	338	332	257	212
Nd					165	184			
Sm					29	28			
Eu					3.3	3.8			
Tb					1.1	1.2			
Yb					1.9	1.4			
Y	30	30	30	29	29	32	32		35
Th	115	118	119	120	109	121	116		
Hf					18	20			
Zr	764	777	796	787	787	797	830	655	581
Ta					2.6	3.1			
Nb	40	40	41	40	41	41	42	35	37
$^{87}\text{Sr}/^{86}\text{Sr}$					0.71588			0.7165 - 0.7168*	

* data from Ferrara et al. (1986).

LOI, Si, and Ca, and much higher K; we conclude that the lower degree of alteration in our samples may account for the observed discrepancy. The CIPW norms show that CUP and SVEN lavas are more strongly silica-undersaturated than other Roman rocks and contain larnite. Large amounts of kalsilite appear in the norm of CUP. Many of the above petrological characteristics (especially the degree of silica undersaturation, abundance of Na and Al, alkali/silica, K/Na and Fe/Mg values) are peculiar to the SVEN and CUP rocks and are not found in the typical Roman volcanic rocks. Because of the extreme degree of silica undersaturation, leading to the occurrence of modal melilite, leucite and kalsilite, the SVEN and CUP rocks have been considered by Sahama (1974) and Gallo *et al.* (1984) to belong to ultrapotassic rocks with a *kamafugitic*

affinity. The same affinity has been recognized by Foley *et al.* (1987). Accordingly, the olivine melilitite of SVEN is mineralogically comparable to katungites (Sahama 1974), whereas the Toro-Ankole biotite mafurite would be the closest equivalent to the phlogopite melilitite of CUP. As stated by Sahama (1974), however, the latter rock "is chemically not too different from the madupites of Leucite Hills and in this sense is intermediate between the rocks of orenditic and kamafugitic affinity" possessing the strong undersaturation of kamafugites and the Fe and Mg abundance of orendites. In our opinion the CUP and SVEN significantly differ from typical kamafugitic rocks from central Africa and should simply be called madupites in view of their chemical equivalence with Leucite Hills madupites as well as of their association both in the western United

TABLE 4. TRACE-ELEMENT CONCENTRATIONS (ppm) IN MADUPITES FROM CENTRAL ITALY

	San Venanzo							Cupaello		
	VEN-7Q	VEN-3	VEN-8	VEN-5	VEN-2	VEN-4	VEN-11	CUP-2A	CUP-1A	CUP-1B
V	430	112	126	135	147	134	146	83	49	41
Cr	75	830	780	793	746	787	812	50	52	51
Sc	58	19			23			18		
Ni	40	153	139	149	136	150	139	80	79	80
Co	38	40			39			36		
Rb	277	458	483	475	462	480	477	596	563	581
Sr	2330	1727	1724	1778	1819	1781	1784	3704	3649	3611
Ba	2044	617	642	670	720	690	698	4390	4388	4557
La	236	65	86	87	95	90	93	254	295	296
Ce	482	156	177	186	191	185	198	578	483	481
Nd	214	71			88			232		
Sm	52	14			20			41		
Eu	8.1	2.7			3.3			7.6		
Tb	3.9	1.1			1.4			2.9		
Yb	6.7	2.0			3.1			2.6		
Lu	1.0	0.33			0.43			0.36		
Y	95	35	37	39	41	39	41	59	60	59
Th	112	30	36	38	38	36	38	137	134	135
Hf	25	7.4			9.2			25		
Zr	952	264	283	312	341	317	335	825	835	842
Ta	2.3				0.84			3.9		
Nb	39	13	13	15	16	15	15	46	46	47
$^{87}\text{Sr}/^{86}\text{Sr}$		0.71037*							0.71120*	

* Data from Holm & Munksgaard (1982)

States and Italy with ultrapotassic rocks of orenditic affinity. In order to avoid confusion with previous nomenclature, however, we will continue to consider the SVEN and CUP volcanics as ultrapotassic rocks with a kamafugitic affinity.

Sample Ven-7Q has lower Si, Al, Mg, and ferromagnesian trace elements, and has higher Fe, P and incompatible trace elements as the main facies of the SVEN lavas. This composition, which will not be discussed further, may represent a typical example of differentiation of a madupitic melt.

Trace elements

Both SVEN and CUP show high enrichment in incompatible elements, but this feature is extreme in CUP. The hygromagmatophile element patterns (Fig. 5a) are similar to those of typical KS and HKS Roman rocks (Fig. 5b) and exhibit a strong fractionation, negative anomalies of Ba, Ta, Nb, and Ti, and a small or negligible Sr anomaly. This clearly indicates a close genetic relationship of KAM with typical Roman potassic volcanics. The CUP samples are distinctive in the higher absolute abundance of incompatible elements and in the small negative anomaly of Sr and Ba. The REE are strongly fractionated (both *LREE* and *HREE*) and have a small Eu anomaly (Fig. 4c). The ferromagnesian elements, especially Cr, are very abundant in SVEN, but not so much in CUP (Fig. 3).

Sr and oxygen isotope ratios

The $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ in SVEN and CUP lavas have been reported by Holm & Munksgaard (1982, 1986), Holm *et al.* (1982) and Taylor *et al.*

(1984). CUP rocks have a higher Sr-isotopic ratio (0.7112) and $\delta^{18}\text{O}$ (+12.1, Holm & Munksgaard 1986) than the SVEN lavas, which have $^{87}\text{Sr}/^{86}\text{Sr}$ 0.71037 and $\delta^{18}\text{O}$ +11 to +12.

DISCUSSION

Peccerillo & Manetti (1985) reviewed the petrological and geochemical characteristics of Italian potassic rocks and concluded that, at least four different types of ultrapotassic rocks occur in the Italian peninsula: the potassic series (KS), high-potassium series (HKS), orenditic (OREN), and kamafugitic (KAM) rocks. The distinct degree of silica undersaturation, K/Na ratio, K, Na, Al, and trace-element abundances (see also Fig. 2) led Peccerillo & Manetti to conclude that these magmas cannot be related to each other by any common evolutionary processes. Accordingly, it was suggested that the magmas were formed independently within an anomalous upper mantle heterogeneously enriched in incompatible elements. On the basis of evidence emerging from experimental petrology (*e.g.*, Arima & Edgar 1983, Wendlandt & Eggler 1980a,b), Peccerillo & Manetti (1985) suggested that the strongly undersaturated to oversaturated potassic rocks from central Italy formed by a low degree of partial melting of a phlogopite-bearing olivine pyroxenite or phlogopite peridotite at upper-mantle depth. The pressure of melting, however, was thought to be different for the various potassic magmas, namely, the silica-oversaturated OREN were formed at relatively low pressures (<15 kbar) in the uppermost mantle, where phlogopite melts incongruently to give olivine and oversaturated potassic liquids as reaction products

(Wendlandt & Eggler 1980a,b). A genesis at relatively low P has been hypothesized also by Foley *et al.* (1986) for high-silica lamproites on the basis of experimental data. On the contrary, KS, HKS and KAM were attributed to melting at progressively greater depths. Variable H_2O/CO_2 in the source is thought to have played an important role in determining the petrological variations between CUP and SVEN. A similar petrogenetic model was put forward by Kuehner *et al.* (1981) to explain the genesis of associated madupites and orendites at Leucite Hills. A deeper source for HKS than for the KS was also suggested by Civetta *et al.* (1981) on the basis of trace-element evidence.

The new data do not fully agree with the above model. The strong *HREE* fractionation in OREN indicates a genesis by melting of a garnet-bearing rock, with garnet left in the residue. Because garnet is stable at high P (> 15 – 20 kbar) in the mantle, the hypothesis that OREN were formed in the uppermost mantle conflicts with geochemical evidence. As will be discussed later, the derivation of OREN magma from a source with fractionated *HREE*, resulting from enrichment processes, overcomes this problem.

If there is a consensus on the mantle origin of Italian potassic magmas, there is still debate on the relative role played by crustal contamination and enrichment in the mantle in determining the geochemical peculiarities of Italian potassic rocks.

Interaction with crustal material

Italian potassic rocks are characterized by high enrichment in incompatible elements and high $^{87}Sr/^{86}Sr$ (typically in the range 0.705–0.711) and high $\delta^{18}O$ values. These observations led several authors to suggest that primary potassic magmas were generated in an anomalous upper mantle (*e.g.*, Holm *et al.* 1982). Others have stressed the role of interaction with continental crust in determining anomalous Sr and O isotopic compositions (*e.g.*, Turi & Taylor 1976).

Recently, integrated geochemical and isotopic investigations (*e.g.*, Civetta *et al.* 1981, 1984, Rogers *et al.* 1985) have shown that the most primitive members of KS and HKS have an abundance of ferromagnesian trace elements that are close to those thought to be typical of poorly evolved mantle-derived magmas. This characteristic has been interpreted as evidence that the most primitive magmas of the potassic series have undergone moderate crystal fractionation with little interaction with continental crust (*e.g.*, Peccerillo 1985, Rogers *et al.* 1985).

We believe that the same conclusion holds true for SVEN rocks as well. In fact, these have similar $^{87}Sr/^{86}Sr$ ratios and comparable or higher Ni and Cr abundances than mafic HKS rocks from Alban Hills, Vico, Vulsini and Ernici. In addition, the Mg and

Ca abundances are the highest in the Roman province. In spite of this, Taylor *et al.* (1984) suggested, chiefly on the basis of oxygen-isotopic evidence, that the SVEN magma may have assimilated significant amounts of crustal material (about 20% of the initial magma's volume). Such a process, together with the concomitant crystal fractionation, should have raised the silica content of the magma. Taylor *et al.* (1984) suggested that the original composition of the magma had a carbonatitic affinity. It must be pointed out, however, that the similarity between the patterns of hygromagmatophile elements of SVEN and HKS mafic rocks (Fig. 5) contrasts with a hypothetical carbonatitic affinity of SVEN volcanic suite. Accordingly, we believe that the San Venanzo rocks represent barely evolved or primary mantle melts that have not suffered important fractionation and interaction with crustal material. If so, the high enrichment in incompatible elements and the high $^{87}Sr/^{86}Sr$ and, possibly $\delta^{18}O$ values, are inherited from the source, as also suggested by Holm & Munksgaard (1982, 1986), Civetta *et al.* (1981), Holm *et al.* (1982), Rogers *et al.* (1985), and Peccerillo (1985) for mafic rocks from several Roman volcanoes. An alternative process that may explain the high $\delta^{18}O$ could be that referred to by Taylor *et al.* (1984), when they state that in narrow conduits strong $^{18}O/^{16}O$ interaction between magma and country rocks may occur without significant changes in the chemical composition of the magma. In this case, however, the relevance for petrogenetic interpretation of oxygen-isotope values is dubious and may lead to invalid conclusions.

Turning to CUP rocks, these have higher abundances of Si, incompatible elements, Sr, and oxygen-isotope ratios, together with lower ferromagnesian-element abundance with respect to the SVEN lavas. Therefore, it is tempting to suggest that the CUP rocks were derived from SVEN magma by processes of crustal assimilation. However, the CUP rocks have higher Sr abundance than SVEN rocks, and this is the opposite to what is expected from assimilation processes. Combined assimilation and crystal fractionation (AFC) increase both Sr and $^{87}Sr/^{86}Sr$ values if partition coefficients ($K_{d/l}$) of Sr for the crystals that separated are lower than unity (De Paolo 1981). Olivine phenocrysts in the SVEN volcanics have K^{Sr} much less than 1; their separation, concomitantly with crustal contamination, could produce an increase of both Sr-isotope ratio and Sr abundance. In order to model the Sr increase, however, we must assume a large amount of olivine separation. In addition, we also need a high ratio between mass of assimilated material *versus* that of crystallized magma (Ma/Mc) in order to obtain the necessary increase in Sr-isotope ratio. Assuming a Ma/Mc value of 0.8, we need a separation of about 40% solid in order to get the Sr and $^{87}Sr/^{86}Sr$ values

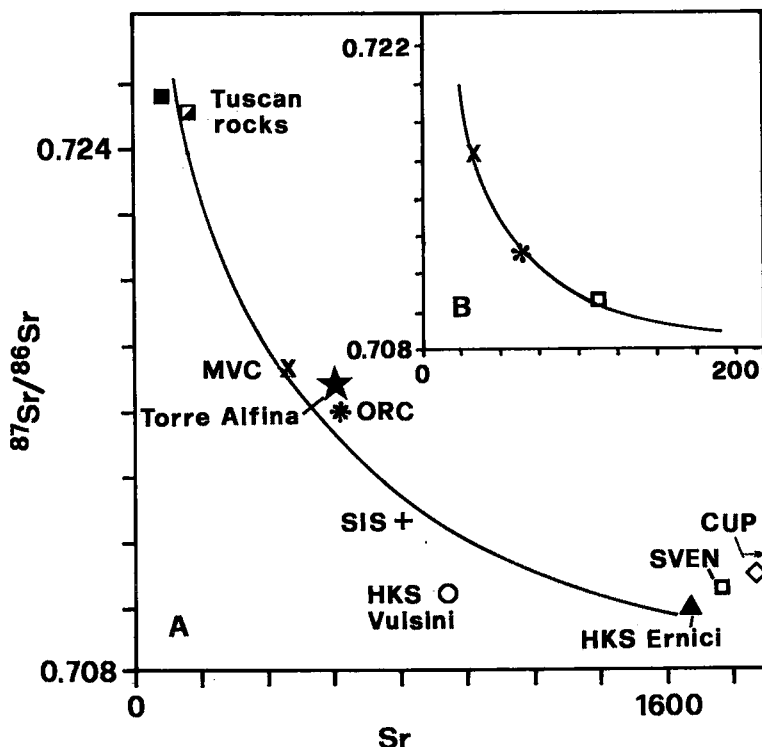


FIG. 6. A) Sr-isotope ratio versus Sr abundance for the analyzed rocks, for average HKS mafic volcanics from Vulsini and Ernici, Torre Alfina lavas, a gneiss from Tuscany (half-filled square), and a South Tuscany rhyolite (filled square). Inset diagram (Fig. 6B) represents $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr relationship of a mantle peridotite contaminated with 20% of a liquid generated by 40% melting of a sedimentary rock containing different proportions of siliceous and carbonate components. St. Andrea's cross represents a peridotite contaminated with a liquid derived from an almost pure siliceous sediment and mimics the source-rock composition of Tuscan orrendites; asterisk and open square represent a mantle contaminated with marly sediments containing increasing amounts of carbonate fraction and mimic the source composition of SIS and HKS-KAM rocks, respectively. For further explanation see text.

of CUP. Because olivine has K^{Ni} between 15 and 40 in Italian potassic rocks (Holm 1982, Francalanci *et al.* 1987), such extensive separation of olivine should produce a decrease of Ni to less than one ppm, even with the conservative assumption of K^{Ni} in the range 10–15. The element Ni does decrease, but not as sharply as expected. More complex evolutionary processes, such as repeated injection of new magma contemporaneously with AFC, could account for the lack of a sharp decrease in the abundance of ferromagnesian-elements abundance (O'Hara 1977). However, these processes are likely to occur in volcanic systems with well-developed magma chambers. On the contrary, Cupaello volcano consists of one single lava flow. Accordingly, we believe that SVEN and CUP magmas cannot be related by evolution-

ary processes; rather, they indicate distinct types of magmas generated independently in the source. The same conclusion has been drawn by Holm & Munksgaard (1986) on the basis of O and Sr isotopic evidence.

Data on OREN rocks are even more intriguing. These have lower Sr contents than KAM or HKS rocks and higher values of Sr-isotope ratio. These observations hold true even for Torre Alfina lavas which, as previously mentioned, have similar petrological characteristics as MVC and ORC rocks (see Table 1).

Figure 6a illustrates $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr relationships for all the rocks investigated and for some HKS lavas from Monti Ernici, Mts. Vulsini and Torre Alfina (Ferrara *et al.* 1986). A Tuscan metamorphic

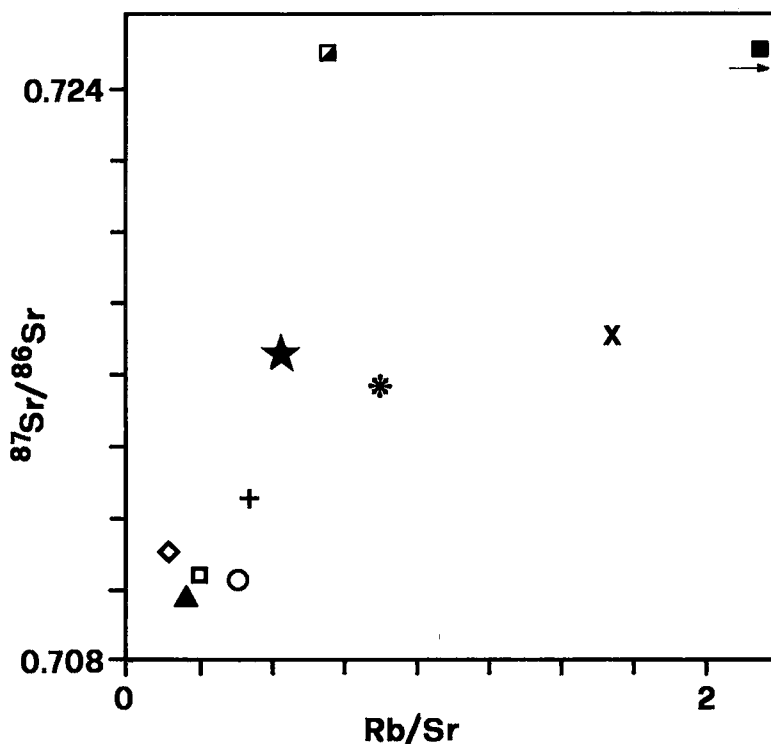


FIG. 7. Rb/Sr versus Sr-isotope ratios. Symbols as in Figure 6A.

gneiss (Ferrara *et al.* 1986) and a Plio-Quaternary felsic volcanic rock from the same area (Vollmer 1977) are also plotted. It is evident that the OREN suite plots along a hyperbolic curve having at its extremes KAM-HKS and Tuscan rocks. The $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr relationship becomes linear on a Sr-isotope ratio versus $1/\text{Sr}$ plot. These relationships are strongly indicative of mixing and suggest that OREN may have been formed by interaction of HKS or KAM with the metamorphic basement or with acidic anatectic rocks of Plio-Quaternary age that occur in several different places in southern Tuscany (Fig. 1). The positive relationship of $^{87}\text{Sr}/^{86}\text{Sr}$ versus Rb/Sr (Fig. 7) also points to the same conclusion. This hypothesis was proposed by Ferrara *et al.* (1986) and Turi *et al.* (1986) for Torre Alfina lavas. However, if we consider the volumes of end-member material involved in such a process, at least 70% of crustal end-member must be assimilated by HKS or KAM magma to reach the $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr ppm values of Tuscan OREN. The abundance of crustal end-member becomes even higher if one invokes AFC instead of simple two-end-member mixing with either acidic volcanic rocks or metamorphic basement. These values are in strong disagreement with a large number of geochemical data. For instance, Rb, Th, REE and other incompatible elements are

much higher in OREN than in KAM, HKS, metamorphic basement, and Tuscan rhyolites and rhyodacites (Gianelli & Puxeddu 1979, Giraud *et al.* 1987). More significantly, Cr and Ni abundances in OREN are similar to or higher than those of KAM and HKS mafic rocks. The same holds true for Torre Alfina lavas, which have Mg#, Cr and Ni similar to the analyzed orendites (see Tables 1,3). One may suspect that the high Ni and Cr abundance of the investigated OREN results from mafic-mineral accumulation. This possibility, however, is ruled out by the fact that the analyzed rocks have a variable texture which ranges from porphyritic to microgranular, but have a constant major and trace-element composition within each single magmatic body. On the basis of this evidence, we conclude that the OREN rocks (Torre Alfina included) are not produced by interaction of HKS or KAM magma with crustal material.

If this conclusion is accepted, one must explain the high values of $^{87}\text{Sr}/^{86}\text{Sr}$ of OREN as well as the mixing relationship (Figs. 6,7). In general terms two possibilities exist: 1) OREN rocks are produced by interaction of subcrustal magma with upper crust; in this case the mantle end-member is not akin to HKS or KAM but must have a very high ferromagnesian-element abundance, resembling kimberlites or some high-Mg lamproites; 2) OREN are

primary or poorly modified mantle-derived melts, and the high Sr-isotope values are inherited from the source. Hypothesis (1) is not unlikely because high-Mg, -Ni, -Cr, ultrabasic to basic lamproites are found associated with intermediate, Mg-, Cr-, Ni-rich rocks in several areas, *e.g.*, in western Australia (Jaques *et al.* 1984); however, there is no evidence for the occurrence of ultrabasic lamproitic rocks in Italy. Hypothesis (2), which implies that the mantle source-rocks of OREN were more strongly contaminated with crustal material than KAM, is explored in detail below.

Nature of the enrichment process

Both petrological and geochemical data indicate that the mantle source of OREN and KAM was affected by contamination. The process increased the abundance of incompatible elements and the $^{87}\text{Sr}/^{86}\text{Sr}$ value of peridotite, and stabilized phlogopite which, according to experimental petrology, is a key mineral in the source rocks of potassic magmas. Such a hypothesis has been proposed for many K-rich rocks from different areas (*e.g.*, Bachinski & Scott 1979, 1980, Barton & Hamilton 1979, Kuehner *et al.* 1981, Cullers *et al.* 1985).

For Italian potassic magmatism, however, there is no agreement on the nature of the enrichment process. According to some authors (*e.g.*, Cundari 1980), the enrichment was provided by fluids from the lower mantle, as suggested for other potassic magmatic provinces (Eifel and East Africa). On the other hand, other authors (*e.g.*, Thompson 1977, Di Girolamo 1978, Edgar 1980, Peccerillo *et al.* 1984, Peccerillo 1985) used discriminant-element abundances to suggest that enrichment was provided by introduction into the mantle of crustal material carried down by subduction processes that were active under the Apennines in Tertiary times (Civetta *et al.* 1978). A suitable crustal contaminant could be sedimentary rocks or their metamorphic equivalents which make up the Tuscan basement (Peccerillo 1985). Trace elements of Jurassic siliceous sedimentary rocks from various zones of Northern Apennines were determined by Manetti *et al.* (1979). These rocks have variable trace-element contents; data for three representative samples are shown in Table 5. The patterns of incompatible elements and REE of these rocks are shown in Figures 4d and 5c. The few available data (Gianelli & Puxeddu 1979) indicate that Tuscan gneiss has a similar distribution pattern of incompatible elements as that of Northern Apennines sedimentary rocks. Inspection of incompatible-element patterns (Fig. 5c) reveals a number of interesting features. The absolute abundance of the elements in the sedimentary rocks considered here have a fractionated incompatible-element pattern with high values of LILE/HFSE, and negative

TABLE 5. CONCENTRATIONS OF SOME MAJOR AND TRACE ELEMENTS IN THREE REPRESENTATIVE SILICEOUS - PELITIC SEDIMENTS FROM THE NORTHERN APENNINES

		G-3	G-11	L-347
K ₂ O	wt. %	1.12	3.65	0.42
TiO ₂		0.17	0.72	0.08
P ₂ O ₅		0.06	0.24	0.07
Rb	ppm	43	195	14
Sr		44	28	122
Ba		60	390	83
La		13	45	16
Ce		18.5	99.5	30.5
Nd		8.3	36.4	15.1
Sm		2.6	8.7	4.3
Eu		0.39	1.47	0.74
Tb		0.35	0.93	0.57
Yb		1.10	3.57	0.89
Lu		0.18	0.67	0.16
Th		2.7	12.7	1.4
Hf		0.69	3.66	0.28
Ta		0.29	1.15	0.5

All the data except for K₂O, TiO₂, P₂O₅, Rb and Sr are from Manetti *et al.* (1979).

anomalies of Ta, Nb, Ba, Sr and Ti which mimic those observed in Roman potassic rocks. The REE patterns are fractionated and show small but significant negative Eu anomalies. This latter characteristic is common in many Roman potassic rocks (see Fig. 4c), even the most primitive ones, in which plagioclase is absent as a liquidus phase.

The role of these sediments as possible subduction-related mantle contaminants is also consistent with a Sr-isotope determination on one siliceous rock sample from the same outcrop as the samples reported in Table 5, which give a present-day $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7235 (M. Barbieri, pers. comm. 1987) and with preliminary data of a systematic Sr-isotope investigation of Northern Apennine sediments, which gave values ranging between 0.714–0.744 (authors' unpublished data). This range encompasses the values of metamorphic rocks of the Tuscan basement (0.725–0.733) reported by Ferrara *et al.* (1986). We adopt a value of 0.724 for average sedimentary rock in the following calculations. For the absolute abundance of Sr we will use a value of 50 ppm, which is the mean of the three samples reported in Table 5. Under the assumption of a simple two-end-member mixing, Sr-isotope ratios as those of KAM can be obtained by interaction of a primitive mantle having $^{87}\text{Sr}/^{86}\text{Sr}$ 0.704 and Sr absolute abundance at chondritic levels (say 10–15 ppm) with about 5–15% of sediment. In contrast, to model the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of OREN one must mix primordial mantle material with 15% to 30% sediment.

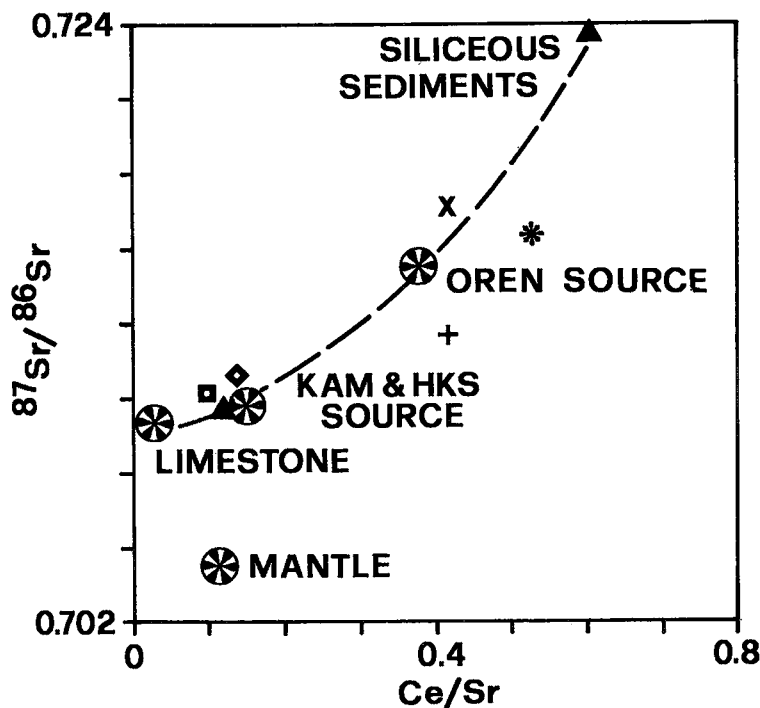


FIG. 8. Ce/Sr versus $^{87}\text{Sr}/^{86}\text{Sr}$ diagram for the analyzed rocks and for HKS from Vulcini and Ernici. Large asterisks represent values of mantle, limestones, HKS-KAM and OREN source rocks, and siliceous sediments. For other symbols see Figures 2 and 6A. OREN and HKS-KAM sources have been modelled assuming that primordial mantle interacted with 20% of a liquid formed by 40% melting of sedimentary rocks containing variable amounts of carbonate component. The dotted line represents compositional variation of sediments containing siliceous and carbonate components in different proportions. For further explanation see text.

Some geochemical characteristics are not explained by a process of simple two-end-member mixing between mantle and bulk sediments. These include: 1) the very high Th/Ta values of OREN and KAM (10–50), which are higher than those of the analyzed sediments (3–11); 2) the strong fractionation of HREE in OREN and KAM (Tbn/Ybn 3–5) which is less strong in sediments (Tbn/Ybn 1.3–2.6); and 3) the absence of Sr negative anomalies in KAM (Ce/Sr 0.1–0.15), which are present in OREN (Ce/Sr 0.3–0.5) and in sediments (Ce/Sr 0.25–0.4) (see Fig. 8).

Additional problems arise from the difficulty in mechanical mixing between solid sediments with mantle, and from the rather high amount of crustal material that should be involved in mantle contamination to attain $^{87}\text{Sr}/^{86}\text{Sr}$ values of MVC orendites. Many of these problems become less severe if one considers more complex but also more realistic models for sediment involvement in mantle contami-

nation. It is unlikely that sediments carried down by subduction can mix with upper mantle without undergoing any modification prior to mixing. More realistically, sediments are first dehydrated and then metamorphosed; successively they melt partially, producing acidic liquids. These rise through the mantle wedge and, because of the compositional contrast, react with the peridotite (Nicholls & Ringwood 1973). Such reaction leads to the formation of phlogopite (Wyllie & Sekine 1982) and generates an enrichment in incompatible elements and radiogenic Sr. Later, melting of phlogopite-bearing rocks produces potassic liquids (Wyllie & Sekine 1982, Wendlandt & Eggler 1980a,b). Accordingly, the concentration of the incompatible elements of potassic liquids depends on several factors that include: 1) the elemental abundances in the original sediments, 2) the elemental abundances in sediment-derived melts which, in turn, depend on the degree of sediment melting and the residual mineralogy, 3) the

elemental abundance in the upper mantle prior to reaction, and 4) the degree of melting of phlogopite pyroxenite or peridotite and the residual mineralogy. Obviously, in order to model satisfactorily the concentration of incompatible-element contents in potassic rocks, one must reconstruct the possible residual mineralogy and degree of partial melting of sediments along the subduction zone and of the anomalous mantle. Problems connected with uncertainty about the degree of partial melting can be partly overcome by using evidence from experimental petrology, and by considering ratios of incompatible elements with a similar degree of incompatibility for the main rock-forming minerals, instead of absolute abundances of elements.

The melting temperatures of sedimentary rocks involved in subduction are variable and depend on the amount of water present. Accordingly, the degrees of melting can be variable also. We assume a degree of melting of 40% in the following calculations. As for the residual phases, garnet is a liquidus mineral during melting of siliceous sediments at high P (Green 1976). Accessory minerals also can be present and can have important effects on the behavior of some trace elements. The occurrence of Ti-, Nb-, Ta-bearing minerals as residual phases during magma formation is often invoked to explain the high Th/Ta ratios of arc-related rocks. This hypothesis may even apply to our rocks. The presence, in the residue, of magnetite and ilmenite is by itself sufficient to produce a large increase in Th/Ta and $LREE/Ta$ values in the liquids. In fact, during sediment melting, residual minerals are in equilibrium with acidic liquids. Nash & Crecraft (1985) reported $K_{s/l}$ in magnetite and ilmenite coexisting with acidic magmas. These data indicate that K^{Ta} is much higher than K^{Th} and K^{LREE} . It is obvious that a small but significant amount of these minerals left in the residue after sediment melting can produce felsic liquids with much higher Th/Ta than the original solid. The presence in the residue of 4% magnetite and 2% ilmenite is able to produce a liquid with Th/Ta ~ 40 , close to the highest values found in the rocks investigated. Higher Th/Ta values can be obtained by decreasing the degree of melting. Finally, the presence of 10% garnet in the residue brings $HREE$ fractionation of melted sediments to values higher than those of the most $HREE$ -fractionated rocks under investigation. Reaction of these melts with the upper mantle generates a rock which has a strong $HREE$ fractionation. The melting of this rock is able to produce potassic liquids with high Tb/Yb values as that of OREN even if garnet is not left in the residue.

Consider now the absence of negative Sr anomalies in KAM and all HKS rocks. It is impossible to work out a melting model that gives liquids with no Sr depletion, starting with an average sediment. Any

liquid formed from these sediments should show a negative Sr anomaly, independently of the amount and type of phases left in the residue. Accordingly, the only possible alternative is that a second component took part in mantle contamination. This component should have a high abundance of Sr, but a low concentration of other incompatible elements, so that the final sedimentary end-member retains the same pattern as the analyzed siliceous rocks, but contains more Sr. This additional component could be a rather pure carbonate rock (Beccaluva *et al.* 1985). In this view the differences in Ce/Sr among OREN and KAM can be explained simply by differences in the amount of carbonate material mixed with siliceous sedimentary rocks involved in subduction, melting and contamination. Assuming a carbonate component with 500 ppm Sr (values commonly found in Apennine carbonate rocks), $^{87}Sr/^{86}Sr$ 0.709 (similar to current seawater values) with negligible abundances of other incompatible elements, we should mix about 40% of carbonate with 60% of average siliceous rock in order to reach Ce/Sr values equivalent to those of KAM and HKS rocks. Such a mixture contains about 230 ppm Sr and has a $^{87}Sr/^{86}Sr$ value of 0.711. A liquid formed by 40% melting of this mixture has Sr = 500 ppm, if $K^{Sr} = 0.1$ for residual minerals. A mixture of 20% of this liquid with 80% primitive mantle (two times chondritic abundance of Ce and Sr) gives a Sr-isotope ratio of 0.7103 and Ce/Sr 0.15 (Fig. 8), similar to those in SVEN and HKS rocks.

As for OREN, which have a sharp negative Sr anomaly, the amount of carbonate component involved in source contamination must have been either much lower or absent. In order to model the Sr isotope and Ce/Sr values of the OREN source rock, we shall again mix 80% mantle and 20% melted sediment; however, in this case the original sedimentary rock must contain less than 10–15% of carbonate component (Fig. 8).

In conclusion, an interaction between mantle and felsic liquids generated by partial melting of sediments of variable composition, *i.e.*, containing a variable amount of carbonate fraction, is considered a possible explanation for the high and variable $^{87}Sr/^{86}Sr$ and Ce/Sr values of OREN and KAM. In other words, the source rocks of minettes were probably affected by contamination with partial melts derived from a siliceous sediment containing low amounts of a carbonate component. In contrast, the HKS and KAM source rocks were contaminated with felsic liquids derived by melting of a marly sediment containing comparable amounts of a carbonate and siliceous components. This model is also consistent with the variation of Rb/Sr versus $^{87}Sr/^{86}Sr$. The lamprophyres studied have higher Rb/Sr values and Sr-isotope ratios than KAM in accordance with the higher Rb/Sr and $^{87}Sr/^{86}Sr$ of siliceous sediments

with respect to marly rocks.

The proposed model also explains the puzzle of the hyperbolic mixing line from KAM and HKS to Tuscan metamorphic rocks through OREN (Fig. 6a). In fact, primordial mantle-rocks contaminated with a fixed amount of melt derived from sediment of different composition show a hyperbolic relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr absolute abundance, that mimics that displayed by OREN, KAM and HKS (Fig. 6b). Accordingly, the observed hyperbolic relationship could simply reflect the different proportions of siliceous sediments and limestones added to the mantle source-zone of OREN, KAM and HKS.

Constraints on mantle composition

Both OREN and KAM rocks show some petrological and geochemical characteristics that are not found in other potassic Roman volcanic rocks. These include the low to very low Na, very high K/Na and Mg#, high Ni, and Cr, and variable but moderate Sc, V and Co. Cr/V (Fig. 3), Ni/V, and Ti/Ca are also high in OREN, whereas KAM volcanics have high Ca/Al. Some of these characteristics are found in other ultrapotassic rocks (e.g., Jaques *et al.* 1984) and have been attributed to several processes that include: 1) preferential melting of some phases (e.g., phlogopite) that produce liquids with a composition similar to that of the phases being melted; 2) some sort of metasomatism or gaseous transfer in the magma after formation that may lead to depletion in mobile elements; and 3) melting of residual peridotite.

Possibilities (1) and (2) can explain only some of the above characteristics. For instance, preferential melting of phlogopite can give liquids with low Na, high K/Na and high Mg#. The preferential melting of phlogopite has been invoked by several authors (e.g., Van Kooten 1980, Cullers *et al.* 1985, Wagner & Velde 1986) to explain the major-element chemistry of ultrapotassic rocks from different areas. This hypothesis, however, does not explain the high Cr/V and Ni/V of OREN. In fact, if the process occurred under equilibrium conditions, the trace-element contents in the liquid were not affected by the phases that entered the melt but only by the residual mineralogy (Consolmagno & Drake 1976). Residual garnet during mantle melting may be responsible for the low Sc in the liquid, but not the low V. Residual spinel would preferentially retain Cr instead of V. Gaseous transfer is able to change the contents of mobile elements such as alkali elements, but should not affect other elements such as Ti. Accordingly, the possibility that the mantle material successively affected by contamination was represented by residual peridotite seems a suitable explanation for many of the above characteristics. Experimental investigations (e.g., Mysen & Kushiro 1977) indicate that silicate phases of a peridotite that suffered partial

melting with extraction of basaltic liquid become enriched in Mg, Cr and Ni, and depleted in Al, Na and Ca with respect to unmodified lherzolite. If residual peridotite undergoes a further melting event, the newly formed liquids have higher Mg#, Ni and Cr, and lower Na, Al and Ca than normal basalts. If residual peridotite is affected by contamination before melting, additional changes may occur as a function of the composition of the added material. We have shown that contamination with sediments of variable composition affected the source rocks of OREN and KAM, the contaminant in the case of OREN being less carbonate-rich than that added to the source rocks of the KAM suite. Accordingly, we suggest that the presence of a residual mantle in the source zone of both OREN and KAM is responsible for the high Mg#, Ni, Cr and Na contents of the investigated rocks, whereas the high Ca of KAM reflects the higher amount of this element present in the sedimentary contaminant. In this view, the variation of Cr/V, Ni/V, and Ti/Al observed in the investigated OREN may indicate that the source rocks of these magmas underwent different degrees of partial melting prior to contamination, and that the source peridotite of SIS minettes had a stronger residual character than that of MVC and ORC rocks.

The hypothesis of a residual mantle does not change significantly the results of previous calculations, but only leads to a lowering of the amounts of crustal material that must be added to the peridotite in order to model the Sr-isotope ratio.

CONCLUSIONS

Ultrapotassic rocks having a kamafugitic and orenditic affinity are minor but important components of the Roman comagmatic province. These represent distinct magma types with respect to the prevailing HKS and KS rocks. The OREN types are silica-oversaturated, intermediate in composition, and have high Mg#, Ni and Cr together with extreme enrichment in LILE. KAM also have a high Mg#, Cr, Ni, and LILE, but are ultrabasic in composition and are strongly silica-undersaturated. Geochemical, isotopic, and experimental evidence suggest that both OREN and KAM can be derived by melting of an anomalous mantle that was affected by contamination with crustal (probably sedimentary) material dragged down by subduction processes which were active under the Italian peninsula during Late Tertiary times (Civetta *et al.* 1978). According to the model proposed, the sediments involved in subduction were first dehydrated and then partially melted. Partial melting generated acidic liquids with higher HREE fractionation and higher LILE/HFSE than the parent rocks owing to the presence in the residue of garnet and some accessory phases such as magnetite and ilmenite, which have $K_{s/1}$ much lower for

LILE than for HFSE when they coexist with acidic melts. Melted sediments rose through the upper mantle, reacted with peridotite, and stabilized phlogopite, as suggested by Wyllie & Sekine (1982). Successive partial melting of phlogopite-peridotite or phlogopite-olivine-pyroxenite at different pressures gave potassic liquids whose petrological characteristics in terms of silica saturation were determined by the reaction products of phlogopite which change with pressure (Wendlandt & Eggler 1980a,b). Some compositional peculiarities, such as high Mg#, Ni, Cr and low Al in KAM, and high Ni, Cr, Mg# and low Ca and Na in OREN are probably connected to the residual nature of the mantle peridotite which could have suffered a previous melting event before contamination with sediments. The different Sr-isotope, Ce/Sr and Rb/Sr values between OREN and KAM are explained by the different relative amounts of silicate and carbonate sediments involved in subduction and mixing with the upper mantle.

The proposed model assumes that the OREN and KAM samples studied represent primary or poorly evolved mantle-derived melts. This assumption is supported by the strong silica undersaturation of KAM and by the high ferromagnesian-element abundance and Mg# in both KAM and OREN. This latter evidence positively excludes the possibility that OREN are formed by interaction of KAM or HKS with crustal rocks.

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