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Geochronology and Geochemical Trends of Volcanic Rocks from Campania, S. Italy

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ABSTRACT

K-Ar dating has allowed us to gather the volcanic rocks outcropping in Campania into three age groups: 1) about 6 m.y. old (Ischia green tuff), 2) from 1.2 to 0.4 m.y. (Roccamonfina first cycle), 3) from about 0.35 m.y. to the present (Roccamonfina and Ischia second cycles, Phlegraean Fields, Somma-Vesuvius, "Campanian grey tuff"). Age data, trace-element distributions and strontium isotopic ratios suggest a comagmatic origin for all of the youngest activity. The age relationship between the volcanic activity in the Campanian area and that in other regions of central and southern Italy indicates a shifting of the volcanic activity toward the long axis of the peninsula. Trace-element distributions suggest different degrees of crustal contamination for the three age groups. A strong Ra^{226} excess has been found in rocks younger than 2,000 years from Mt. Vesuvius. It appears to be due to a preferential removal of Ra relative to U and Th from the carbonate rocks surrounding the Vesuvius magmatic conduit.

Introduction

The Campania volcanic area, Southern Italy (Fig. 1), is a field of Tertiary and Quaternary volcanic activity, about 4000 km² in area. It is surrounded by sedimentary rocks (mostly Mesozoic carbonates) to the NW, E and SE. The Campania volcanic area includes four volcanic complexes (Roccamonfina, the island of Ischia, Phlegraean Fields and Somma-Vesuvius), each of them characterized by individual volcanological and petrochemical features. Somma-Vesuvius, Phlegraean Fields and Ischia have been active in the last thousand years, and can still be considered as active volcanoes (IMBÒ, 1965).

The shallow foci of volcanic earthquakes, the absence of any recognizable relationship of activity among the three active volcanoes, the individual petrological trend of each volcano, support the hypothesis of the emplacement of separate magma reservoirs for each volcano and differentiation along individual patterns.

Roccamonfina is the northernmost volcano. It has had two major cycles of activity. During the first cycle, a stratovolcano was formed by leucite-bearing rocks (phonolites, leucitites, leucite-tephrites). A caldera formed at its top, and a second cycle of activity occurred within the caldera and along the eastern slope of the strato-volcano. Two latitic domes (Mt. Lattani and Mt. S. Croce) were formed inside the terminal caldera. This new activity gave rise to rocks from trachytic to basaltic in composition (AREVALO CARRETTERO et al., 1962).

The bulk of the island of Ischia consists of a faulted alkali-trachytic green tuff

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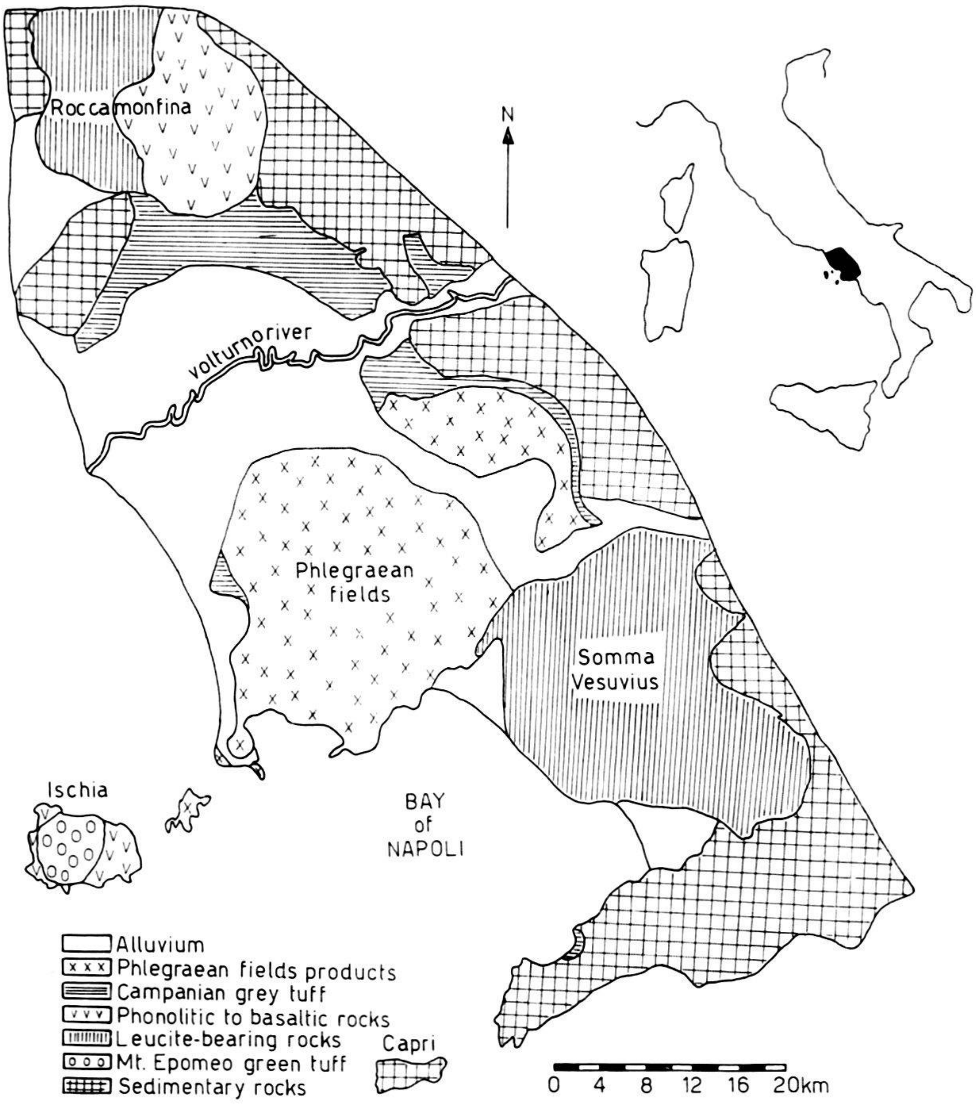

Fig. 1. Schematical geological map of the Campania volcanic area. For the sake of clarity, Campanian grey tuff and Phlegraean Fields products have been distinguished from other phonolitic to basaltic rocks.

block (Mt. Epomeo green tuff), whose top is at about 800 metres above sea level. According to RITTMANN (1948,) the green tuff is the product of a subaereal eruption, and was subsequently submerged and then raised again above sea level. RITTMANN (1948), on paleontological basis, assigns the emergence to lower Pliocene. A second cycle of activity occurred at the edges of the uplifted block. Many lavas and pyroclastic formations (sodalite-phonolites, trachytes, latites, trachybasalts) were erupted. The latest eruption (Arso) occurred in 1302.

Phlegraean Fields is a volcano, largely pyroclastic, on which the city of Napoli has been built. Its oldest outcropping rocks have been assigned to Pleistocene (SEGRÉ, 1965). The most characteristic formations of Phlegraean Fields are (from the oldest to the newest ones): a welded tuff locally known as "piperno", a "chaotic yellow tuff" (Neapolitan yellow tuff) and many layers of ashes, pumices and scoriae erupted by small vents (the most recent being Astroni, Fossa Lupara and Mt. Nuovo). The latest eruption (Mt. Nuovo) occurred in 1538. The composition of the erupted products ranges from phonolites to trachybasalts.

Early Somma-Vesuvius activities produced trachytic rocks. They occur both as ejecta and as distant pumice outcroppings (DI GIROLAMO, 1968). Later, the petrochemistry of erupted products changed into leucite phonolites and leucite tephrites. These rocks formed a regular-shaped strato-volcano (Mt. Somma). A caldera was then formed at the top of Somma and a new cone (Mt. Vesuvius) grew up inside. Mt. Vesuvius erupted mainly leucititic rocks. It has been very active in the last 300 years, the latest eruption being in 1944.

The most widespread formation in the Campania area is, however, an alkali-trachytic ignimbrite, locally known as "Campanian grey tuff". It was probably erupted either through the faults at the borders of the Mesozoic blocks surrounding the volcanic field, or by an unknown vent inside the volcanic area. Field evidence indicates that it is older than Phlegraean Fields "Neapolitan yellow tuff" and younger than most of the products from Roccamonfina (Istituto di Mineralogia, Univ. Napoli, 1968). Ischia green tuff is believed to be the oldest volcanic formation outcropping in the southern part of the Campania volcanic area. The early activities of Phlegraean Fields and Somma-Vesuvius are believed to be roughly contemporaneous.

Geochronology

K-Ar dating has been carried out at the Department of Geology, Rice University, Houston, Texas. Several mineral separates and whole rocks from stratigraphically well-known formations have been dated.

A major problem in dealing with Plio-Pleistocene rocks can be the occurrence of excess ^{40}Ar which, because of the low radiogenic ^{40}Ar content, can frequently be a significant fraction of the total non-atmospheric ^{40}Ar in the system (see DAMON, 1968; DALRYMPLE, 1969).

Mineral separates and a whole rock sample from each sample were analyzed whenever possible on the assumption that the excess ^{40}Ar is unlikely to affect each age determination equally. Hence consistent ages obtained on structurally different minerals or even on a mineral separate and the whole rock can reasonably be thought to represent the actual age of eruption.

The analytical and age data are reported in Table 1. Details on the techniques have already been published (GASPARINI and ADAMS, 1969).

Leucite and whole rock ages are consistent in both cases. Additional consistent pairs of leucite and whole rock ages are reported by GASPARINI and ADAMS, (1969). Feldspar and whole rock ages are consistent in two cases only. All these ages are also coherent from a stratigraphic standpoint. These data stress once again the suitability of leucite in K-Ar dating of very young rocks. Furthermore, they show the feasibility of whole rock dating of samples as young as a few hundred thousand years with a K content as low as 5%.

All M. Lattani (Roccamonfina second cycle) ages are too old relative to its stratigraphic position and the consistent ages of the first cycle products. These ages are too old because of the excess ^{40}Ar contained in the plagioclase and biotite separates.

Table 1. K-Ar analytical and age data.

Volcano Formation	Mineral	K %	$\frac{^{40}Ar_{rad}}{^{40}Ar}$ %	Moles $^{40}Ar_{rad}$ per gr sample. 10^{12}	K-Ar age (m.y.)
ROCCAMONFINA					
S. Maria di Mortola flow	Leucite	11.12 (± 0.10)	19.7	25.53 (± 0.65)	1.26 (± 0.05)
			18.9	25.40 (± 0.80)	
	Whole Rock	5.55 (± 0.07)	6.7	10.33 (± 0.34)	1.07 (± 0.08)
			7.2	11.18 (± 0.42)	
S. Carlo flow	Leucite	17.41 (± 0.27)	14.9	15.20 (± 0.64)	0.46 (± 0.03)
			16.2	14.67 (± 0.24)	
	Whole Rock	8.47 (± 0.11)	5.5	7.07 (± 0.69)	0.46 (± 0.05)
			11.4	7.25 (± 0.25)	
Mt. Lattani dome	Plagioclase	0.83 (± 0.02)	4.8	7.06 (± 0.28)	5.00 (± 0.40)
			6.3	7.77 (± 0.62)	
	Biotite	6.36 (± 0.10)	4.2	72.55 (± 0.84)	4.12 (± 0.42)
	Whole Rock	4.04 (± 0.03)	3.7	5.41 (± 0.31)	0.77 (± 0.06)
			4.3	5.86 (± 0.20)	
ISCHIA					
Green tuff from the very top of	Sanidine	8.68 (± 0.02)	14.0	13.87 (± 0.67)	0.84 (± 0.09)
			12.1	12.48 (± 0.80)	
Mt. Epomeo	Biotite	4.36 (± 0.06)	41.7	46.61 (± 0.58)	6.00 (± 0.14)
Mt. Vico dome	Feldspars	6.31 (± 0.03)	9.1	3.71 (± 0.15)	0.32 (± 0.02)
			6.9	3.56 (± 0.15)	
	Whole Rock	5.84 (± 0.02)	7.0	3.44 (± 0.26)	0.31 (± 0.04)
			6.2	3.36 (± 0.34)	
PHLEGRAEAN FIELDS					
Piperno (Torre dei Franchi)	Sanidine	8.40 (± 0.03)	8.2	2.52 (± 0.30)	0.19 (± 0.05)
			7.3	3.58 (± 0.68)	
	Whole Rock (black flames)	6.41 (± 0.07)	5.0	2.92 (± 0.32)	0.22 (± 0.06)
			4.2	2.40 (± 0.36)	
SOMMA-VESUVIUS					
Drill at Scafati (LUONGO and	Whole Rock	4.63 (± 0.08)	2.6	1.81 (± 0.16)	0.25 (± 0.08)
RAPOLLA, 1964)			4.8	2.50 (± 0.50)	

Similar ^{40}Ar excesses in biotites and plagioclases have been reported in the literature (e.g. DAMON et al., 1967; FUNKHOUSER et al., 1966). The occurrence of excess ^{40}Ar in Mt. Lattani phenocrysts can be due to the high viscosity of a dome-forming magma, which may prevent complete degassing. A striking coincidence is that the ^{40}Ar excess in the biotite and the plagioclase separates is nearly equal. This could mean that both fractions were derived from remelting of an older rock.

The biotite and the sanidine ages of the green tuff from the top of Mt. Epomeo are largely inconsistent. The biotite age is consistent with the paleontological evidence for the time of uplift of the island. A green tuff sanidine age of 0.08 m.y. was reported by EVERNDEN and CURTIS (1965) for a sample collected near Forio, i.e. close to sea level. This age is too young as compared to the internally consistent ages of Mt. Vico (0.3 m.y.), one of the oldest post-Epomeo formations. This suggests that green tuff sanidine ages are too young. The biotite age is believed to be the closest to the actual eruption age. The green tuff age pattern may be a consequence of the different duration of submersion for the Forio and the top of the mountain sample. Ground water alteration of biotite reproduced under laboratory conditions has little affected K-Ar ages (KULP and ENGELS, 1963). A much higher Ar retentivity in biotites than in feldspars from lavas dredged from Pacific Ocean seamounts has been reported by DYMOND and WINDOM (1968).

All the available radiometric ages of Campania volcanics whose stratigraphic position is well known are summarized stratigraphically in Figure 2. The most uncertain date is the Scafati lava (Somma-Vesuvius) age, which is based upon whole rock determinations only. Although it is consistent with the stratigraphic evidence (within

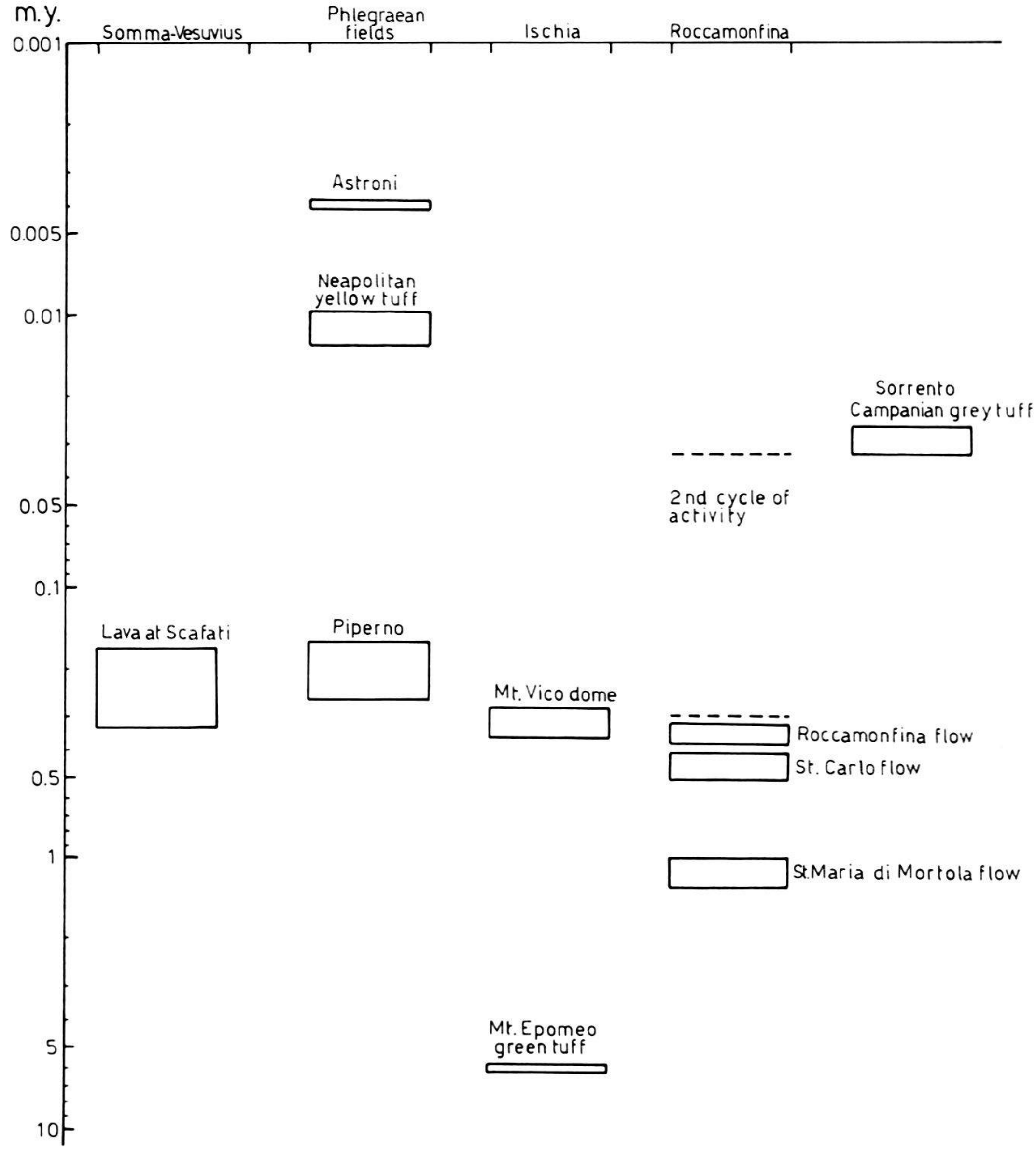

Fig. 2. Stratigraphic summary of the available radiometric ages of Campania volcanic rocks (Data not from this paper are: Astroni, ^{14}C dating from DELIBRIAS et al., 1969, Neaplitan yellow tuff, ^{14}C dating from LUCINI and TONGIORGI, 1959; Roccamonfina lava flow, K-Ar dating, EVERNDEN and CURTIS, 1965; Campanian grey tuff, ^{14}C and K-Ar dating quoted by CURTIS, 1966).

the errors), the slight inconsistency of the two ^{40}Ar determinations adversely affects the reliability of this age. DALRYMPLE (1969) reports no finding of appreciable $^{40}Ar_{rad}$ in a Vesuvius whole rock sample from the lava flow of 1944. The Scafati rock was classified as trachyandesite upon a microscopic study, but the chemical analysis has resulted in a leucite-phonolite composition (DI GIROLAMO P., pers. comm.).

The available radiometric ages and the petrochemistry of the erupted rocks allow us to divide the outcropping volcanic formations into three age groups:

1) about 6 m.y. old (Ischia alkali-trachytic green tuff)
2) from 1.2 to 0.35 m.y. old (Roccamonfina first cycle leucite-bearing rocks)
3) younger than 0.35 m.y. (phonolitic to basaltic rocks from Ischia and Roccamonfina second cycles, Phlegraean Fields and the "Campania grey tuff". Trachytic to leucititic rocks from Somma-Vesuvius).

The oldest available radiometric ages for each central and southern Italy volcano are summarized in Figure 3. Ischia green tuff age is close to the oldest ages of Pontine islands (about 5 m.y.) and the intrusion of the islands of Elba (7 m.y.), Giglio (5 m.y.) and Montecristo (5 m.y.). Most ages from peninsular Italy are significantly younger. The late Tertiary magmatic activity in central and southern Italy apparently began along a line nearly parallel to the present coast and then moved toward the long axis of the peninsula. Roccamonfina first cycle of activity was contemporaneous with Mt. Amiata and the volcanoes of Northern and central Latium.

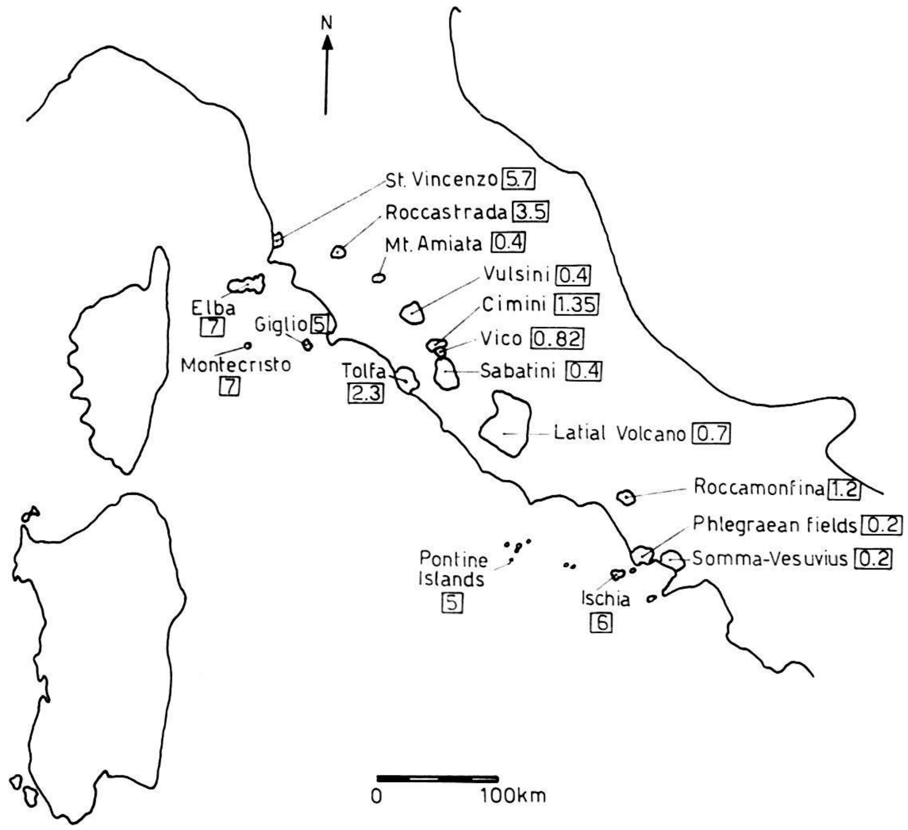

Fig. 3. Post-Mesozoic volcanoes and intrusives in central and southern Italy, for which radiometric ages are available. The oldest available radiometric ages for each volcano are reported within squares. (Data from: EVERNDEN and CURTIS, 1965; BARBERI et al., 1967; BORSI et al., 1967; NICOLETTI, 1969 and this paper).

Geochemical Trends

Scintillation gamma-ray spectrometry determinations of U and Th have been carried out on the Ischia green tuff and the volcanics from Phlegraean Fields and the island of Ponza. The data are reported in Table 2. Other pertinent data relative to many volcanics from Campania are reported in IMBO' et al. (1967). Hereafter the distribution of Th in the volcanics from Campania will be discussed. U follows the same general trend as Th, but with a larger spread. This can be a consequence of the lower precision of U determination by scintillation gamma-ray spectrometry on samples younger than 0.5 m.y. In this case, because the assumption of secular equilibrium through ^{226}Ra is not likely to be valid, U was determined from the low energy part of the spectrum where both ^{234}Th and ^{235}U series contribute. The high contributions by X-rays and scattered gamma-rays make the precision of these U determinations low (see Table 4 and ADAMS and GASPARINI, 1969).

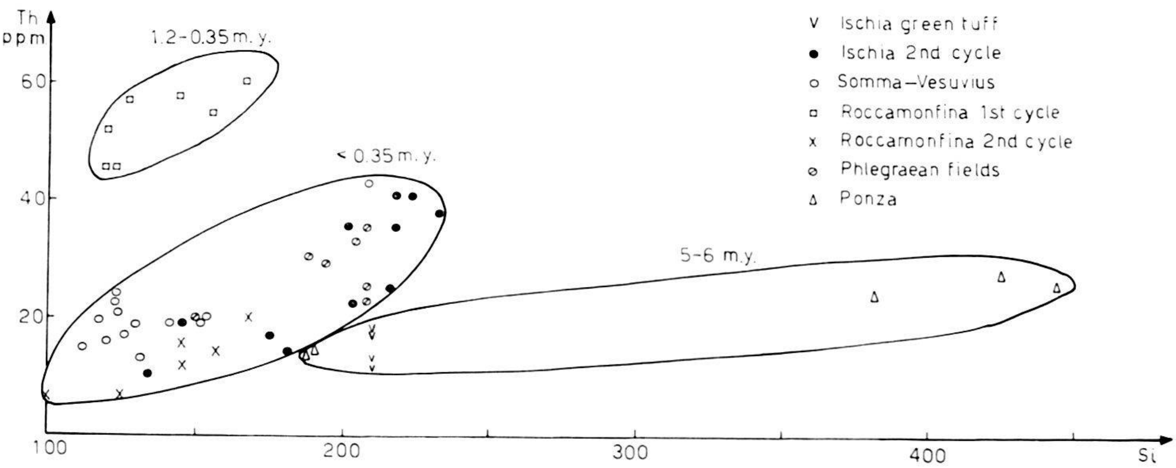

Fig. 4. Variation of the Th content as a function of Niggli's si for volcanics from Campania and Ponza island.

When the Th contents are plotted against any differentiation index, e.g. Niggli's si, a division into three groups, corresponding well to the age groups, is apparent (Fig. 4). Rocks of similar bulk composition but belonging to different age groups have different Th contents. This can be clearly seen when one compares 1.2–0.35 m.y. old leucitites from Roccamonfina with younger than 0.25 m.y. leucitites from Vesuvius or the alkalitrachytic green tuff and the similar Phlegraean Fields tuffs. The only exception are the Ponza dykes (about 2 m.y. old) and the Mt. La Guardia (Ponza) trachyte, which have a comparatively low Th content, although being 1.2–2.0 m.y. old (BARBERI et al., 1967). Figure 5 summarizes the ranges of variation of Th content and $^{87}Sr/^{86}Sr$ ratio for volcanics from Campania and Latium. Th (and U) contents are generally higher than crustal averages. $^{87}Sr/^{86}Sr$ ratios are often lower than typical crustal values, hence suggesting only a partial upper crust contamination. The high Th and U contents are therefore not fully consistent with the $^{87}Sr/^{86}Sr$ ratios. A possible explanation could be that the crust of this region is enriched in Th and U as compared to

Rb and/or that U and Th are preferentially removed from the crust during syntexis. The few available Pb isotopic ratios are consistent with a crustal contamination and high U and Th in the crust (Houtermans et al., 1963; Oversby and Gast, 1968).

Table 2. U and Th contents of some volcanic rocks from Campania volcanic area and the island of Ponza.

Volcano	Formation	Th (ppm)	U (ppm)	Th/U
ISCHIA	Green tuff. Panza	11.5 (± 0.5)	2.2 (± 0.2)	5.2
	Green tuff. Serrara	12.9 (± 0.3)	2.7 (± 0.2)	4.8
	Green tuff. Cetaro	17.2 (± 0.3)	5.4 (± 0.5)	3.2
	Green tuff. Fontana	18.3 (± 0.3)	3.2 (± 0.3)	5.7
PHLEGRAEAN FIELDS	Neapolitan yellow tuff. Lucrino	25.4 (± 0.1)	9.1 (± 1.8)	2.8
	Neapolitan yellow tuff. Lucrino	36.0 (± 0.2)	4.1 (± 1.0)	8.8
	Neapolitan yellow tuff. St. Martino	25.3 (± 0.6)	4.8 (± 0.4)	5.3
	Neapolitan yellow tuff. Posillipo	23.4 (± 0.1)	4.0 (± 0.1)	5.9
	Piperno. (Torre dei Franchi)	29.6 (± 0.4)	5.0 (± 2.0)	5.9
	Trachytic flow. St. Gennaro.	30.9 (± 0.6)	10.0 (± 1.5)	3.1
	Trachyte. Astroni	25.4 (± 1.2)	17.3 (± 1.7)	1.5
PONZA	Oldest Rhyolite (Mt. Schiavone)	25.9 (± 0.5)	8.6 (± 1.3)	3.0
	Oldest Rhyolite (Chiaia di Luna)	24.5 (± 0.6)	7.8 (± 0.5)	3.3
	Rhyolitic Dyke (Chiaia di Luna)	28.3 (± 0.2)	7.9 (± 0.5)	3.6
	Rhyolitic Dyke (Mt. Pagliaro)	27.7 (± 0.2)	8.4 (± 0.5)	3.3
	Trachyte. Mt. La Guardia	15.7 (± 0.3)	5.4 (± 0.4)	2.9
	Trachyte. Mt. La Guardia (Pt. Faro)	15.9 (± 0.3)	7.1 (± 0.1)	2.2

The Th pattern of Campania and Pontine islands volcanics (Fig. 4) suggests a higher upper crust contamination for the 1.2–0.35 m.y. age group as compared to the other age group. The few available $^{87}Sr/^{86}Sr$ ratios (Fig. 5; see also Fig. 3) are also consistent with this interpretation. The higher crustal contamination of 1.2–0.35 m.y. old volcanics as compared to 5–6 m.y. old rocks may be a consequence of the shifting of the volcanic activity from offshore to the continent. Geophysical data indicate a crustal thickness of about 22–24 km around Ischia and the Pontine islands. Moho depth increases steeply to about 30 km on the eastern border of Campania volcanic area (Morelli et al., 1967). The dependence of the degree of crustal contamination on the location of volcanic activity is also supported by the relatively low U and Th contents of 2.0–1.2 m.y. old rocks from Ponza. The decrease

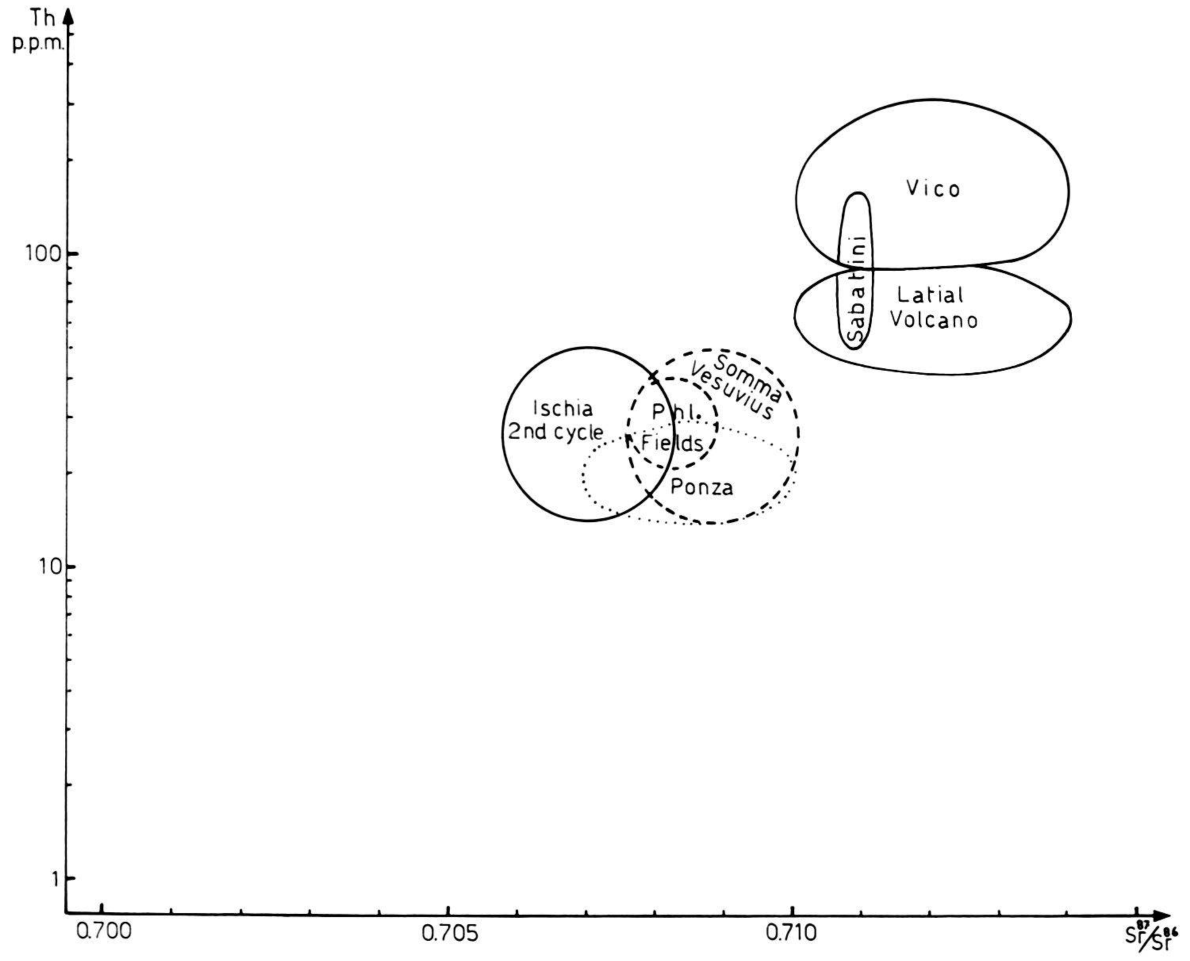

Fig. 5. Ranges of variations of the Th contents and the $^{87}Sr/^{86}Sr$ ratios of volcanoes from Campania and Latium (Sr isotopic data from: HURLEY et al., 1966; BARBERI et al., 1967. Th contents of Latium volcanoes from LOCARDI and SIRCANA, 1967; IMBO et al., 1967).

of Th, and U contents of the youngest Campania volcanics cannot be easily explained. No significant shifting of the activity is apparent. Two possible explanations are:

1) given the steep increase of the Moho depth, remarkable lateral inhomogenities over comparatively small distances have to be expected. Therefore, the youngest volcanic activity in Campania may be due to a lateral intrusion of a magma, which has been formed in a thinner crust region and has been little contaminated from the upper crust;
2) a decrease of heat flow occurred about 0.3–0.4 m.y. ago. This caused an increase of the depth of magma formation and a lower temperature existing in the crust may have decreased the possibility of crustal syntexis by the magma.

The volcanics from the youngest activities of Roccamonfina and Ischia and those from Somma-Vesuvius and Phlegraean Fields have a consistent pattern of their U and Th (Fig. 4). Rb contents (Table 3) are similar. K/Rb ratios are quite low indicating a strong differentiation of the original magma.

The widespread occurrence of trachytic type rocks younger than 0.35 m.y. and the petrochemical nature of the early products erupted from the youngest volcanoes

Table 3. Contents (ppm) of some trace elements in the youngest volcanics from Campania.

Volcano	Th	U	Th/U	Rb	K/Rb	Ba
Roccamonfina (2nd cycle)	7–20[a])	3–17[a])	2.1–3.2	—	—	—
Ischia (Post-Epomeo activity)	11–55[a])	7–33[a])	2.0–4.0	290–300[b])	170–240[b])	<640[c])
Phlegraean fields	23–33[a])	3–17[a])	2.8–8.8	220–390[b])	180–210[b])	250–480[b])
Somma-Vesuvius	14–23[a])	7–30[a])	1.5–3.5	210–350[b])	140–240[b])	1700–2200[b])

[a]) Extremely high contents of very minor pneumatolytic differentiates have been omitted.
[b]) Data from SAVELLI, 1967; and HURLEY et al., 1966.
[c]) KHALIL, 1966, quoted from BERLIN and HENDERSON, 1969.

Table 4. U, Th and U (eq. Ra) contents of carbonate rocks near Mt. Vesuvius and carbonate ejecta from 79 A.D. eruption of Mt. Vesuvius.

Sample	Th (ppm)	U (ppm)	U (eq. Ra) (ppm)
Cretaceous limestones from Sorrento peninsula.	1.0 (± 0.1)	4.5 (± 2.0)	2.8 (± 0.3)
Unmetamorphosed limestones in pumices from 79 A.D. eruption of Mt. Vesuvius (S. Michele at Ottaviano)	1.3 (± 0.1)	8.9 (± 2.0)	0.4 (± 0.1)

suggest that the original magma is trachytic in composition (see also MARINELLI, 1968). The subsequent individual evolutive trends followed by each volcano may be a consequence of very local conditions.

Trachytic rocks from the Phlegraean Fields and Ischia have a much lower Ba content than leucite-bearing rocks from Somma-Vesuvius (Ba contents of trachytes from Somma-Vesuvius are not available). Furthermore, average Ba contents of Somma-Vesuvius leucitite-bearing rocks increase from older leucite tephrites (1700 ppm) to younger tephritic leucitites (2200 ppm).

^{226}Ra Excess in Mt. Vesuvius Lavas

A ^{226}Ra excess above the equilibrium content with the measured ^{238}U has been found in lavas from Mt. Vesuvius, which are younger than 2,000 years (VITTOZZI and GASPARINI, 1963; OVERSBY and GAST, 1968). When the logarithm of the ^{226}Ra excess is plotted against the age of the respective lavas the points are found to fit a straight line closely. This relationship is close enough to suggest its use for dating purposes. The first attempts have been encouraging (VITTOZZI and GASPARINI, 1965; RAPOLLA and VITTOZZI, 1967). The experimental decay constant is of the order of 10^{-11} sec^{-1}, i.e. it is of the same order as that of ^{226}Ra (1.36×10^{-11} sec^{-1}). No dependence on any characteristic of the lava or the eruption has been observed. This indicate that:

1) the unsupported member of the ^{238}U series is actually ^{226}Ra rather than ^{234}U or ^{230}Th. This has been also confirmed by mass and alpha spectrometric determinations (OVERBY and GAST, 1968).
2) either the removal of ^{238}U along with its missing long-lived daughters occurs practically at the same moment of the history of each lava, or Ra is continuously

supplied to the magma so that an equilibrium condition is reached and no variation of ^{226}Ra occurs within the magma.

A removal of ^{238}U, ^{234}U and ^{230}Th from the magma would imply the repetition of a very special process for each eruption of Mt. Vesuvius. It would also imply a Th/U ratio of about 0.5 for the Vesuvian magma. This is not consistent with the Th/U ratio of the coeval lavas from the other volcanoes, which have Th/U ratios always higher than 1.5. However, no appreciable ^{226}Ra excess has been found in the youngest products from Ischia (Arso flow) and Phlegraean Field (Mt. Nuovo eruption).

The high Ba content of Somma-Vesuvius lavas and its increase from older to younger products are very significant with regard to the origin of the ^{226}Ra excess, given the strong chemical affinity of the two elements. The Ba and Ra trends in Somma-Vesuvius products are consistent with the hypothesis of a continuous supply from an external source. In this case, in fact, the radioactive Ra isotopes would reach an equilibrium concentration in the magma, whereas stable Ba would continuously increase[3]).

A possible source of Ba and Ra may be the carbonate rocks surrounding the Somma-Vesuvius conduit. Th, U[4]) and U (eq. Ra) contents determined by gamma-ray spectrometry on carbonate rocks outcropping near Somma-Vesuvius and on carbonate ejecta included in the pumices of the eruption which overcame Pompei (79 A.D.) are reported in Table 4. Carbonate rocks of this area are enriched in U as compared to Th and therefore are a possible source of Ra. Carbonate ejecta younger than 2,000 years have a significant deficiency of ^{226}Ra. Both results suggest a preferential removal of Ra with respect of Th and U from carbonate rocks and a relative enrichment in the magma.

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