GEOCHEMISTRY AND GEOCHRONOLOGY OF THE CALEDONIAN « PORPHYROIDS » FROM CENTRAL SARDINIA (ITALY)

GILBERTO CALDERONI, UMBERTO MASI

Istituto di Geochimica dell'Università, piazza Aldo Moro, 00185 Roma (Italia)

LUCIANO MACCIONI

Dipartimento Scienze della Terra dell'Università, via Trentino 51, 09100 Cagliari (Italia)

MASSIMO NICOLETTI, CLAUDIO PETRUCCIANI

Centro di Studio per la Geochimica e la Geocronologia delle Formazioni Recenti del CNR, c/o Istituto di Geochimica dell'Università, piazza Aldo Moro, 00185 Roma (Italia)

GIORGIO PADALINO

Ist. di Giac. Min., Geofisica e Scienze Geologiche dell'Univ., p.za d'Armi, 09100 Cagliari (Italia)

ABSTRACT. — K-Ar ages of 25 whole-rock samples of « Porphyroids » from 8 outcrops in Central Sardinia have been determined. The radiometric ages, ranging from 246 to 367 m.y., are younger than the ages inferred from stratigraphy, indicating that the volcanites have been altered by post-magmatic event (s).

Geochemical data point out that the « Porphyroids » have kept most of their original features, which allow volcanites to be identified as rhyolites and rhyodacites. Comparison of chemical features between the « Porphyroids » and rocks of other Sardinian calc-alkaline suites such as the Hercynian granitoids and Tertiary ignimbrites, points out a close similarity among the three groups of rocks, indicating that the chemical features of igneous activity in the island have changed little throughout the Phanerozoic. An origin of the « Porphyroids » by crustal anatexis is suggested. Finally, comparison of chemistry between the « Porphyroids » and acidic rock-types of pre-Hercynian time from other areas of the Italian region shows that acidic magmatism with features similar to those of the Sardinian « Porphyroids » occurred in the whole Italian region in Lower Palaeozoic.

RIASSUNTO. — I « Porfiroidi » costituiscono una serie di vulcaniti acide caratteristiche di ignimbrite molto diffuse nella Sardegna meridionale, dove costituiscono i più antichi terreni affioranti.

Le età K-Ar dei « Porfiroidi » sono risultate comprese tra 246 e 367 milioni di anni; questa collocazione cronologica è in netto contrasto con la stratigrafia, in base alla quale la messa in posto sarebbe avvenuta durante l'orogenesi Caledoniana. Tale discrepanza. talora assai accentuata, viene spiegata ammettendo che l'originale K/Ar delle rocce è stato modificato da eventi post-magmatici come un certo grado di metamorfismo o, più verosimilmente, una estesa alterazione esogena.

La geochimica dei « Porfiroidi » mentre da un lato conferma un notevole grado di weathering, dall'altro permette di ricostruire le loro caratteristiche originali e di classificarli come rioliti e riodaciti.

Il confronto tra il chimismo dei « Porfiroidi » e quello di rocce di altre serie calco alcaline sarde (ignimbriti terziarie e granitoidi ercinici) mette in luce una notevole omogeneità indicante limitate variazioni nell'imponente attività vulcanica susseguitasi nell'isola durante il Fanerozoico. Poichè anche altre rocce acide di età pre-Ercinica provenienti da diverse località italiane mostrano un chimismo spesso confrontabile a quello dei « Porfiroidi » vi sono elementi per affermare che durante il Paleozoico inferiore un vulcanismo acido alquanto uniforme ha interessato l'intero territorio italiano.

I risultati ottenuti consentono di formulare un'origine dei « Porfiroidi » per anatessi crostale.

Introduction

The « Porphyroids » are major igneous rocks, which are widespread throughout the southern half of the island of Sardinia where they often represent the oldest outcropping formation. In particular, as according to NAUD (1979) their emplacement occurred
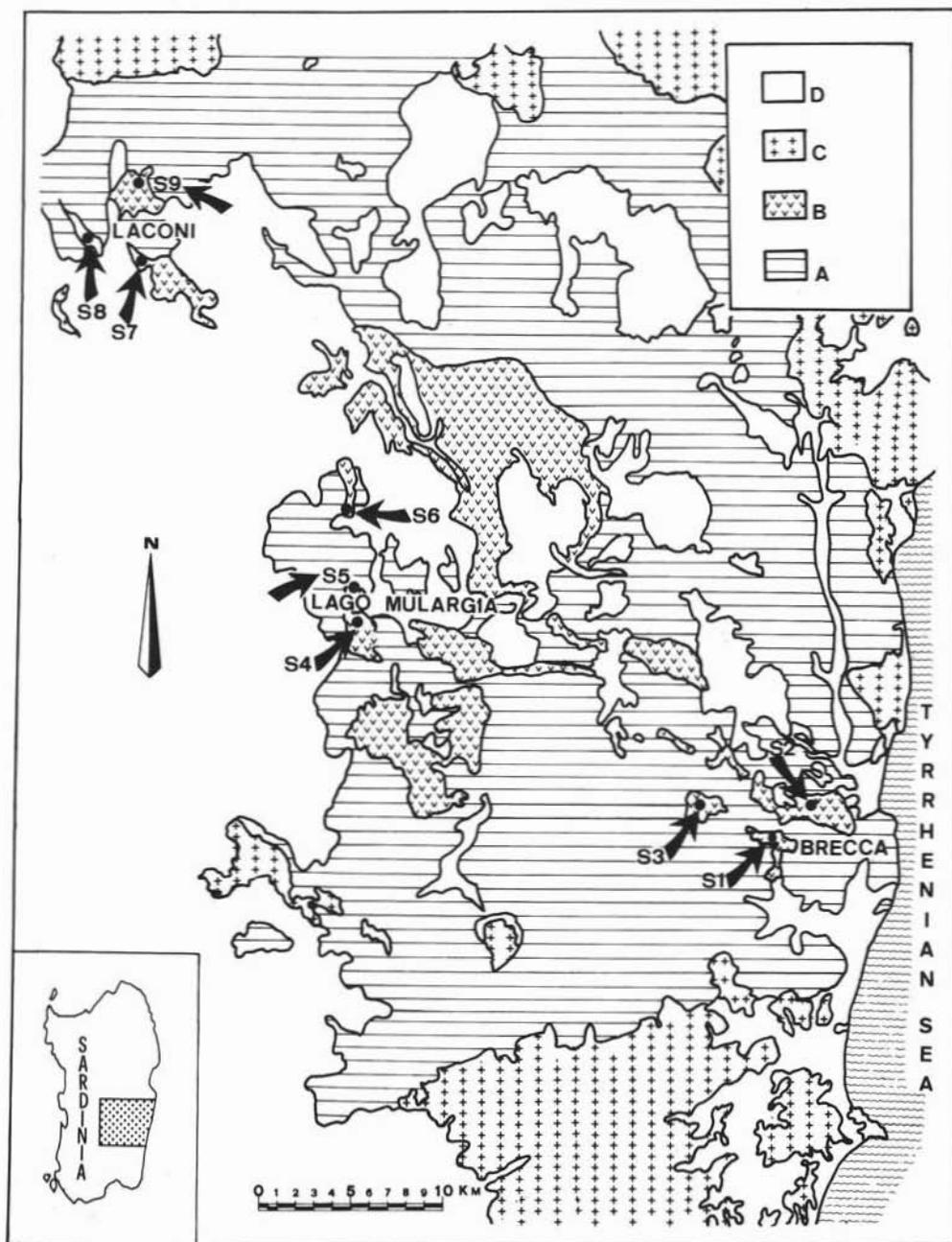
Fig. 1. — Geologic sketch of central Cardinia showing locations of the outcrops studied. The inlet map shows the area investigated. A = Ordovician-Silurian metasediments; B = porphyroids; C = Hercynian terranes.

during the Caledonian orogenesis, they would represent interesting relicts of that old magmatic cycle which seems to be poorly represented in southern Europe. Despite their importance, however, there is no radiometric age and geochemical information on these rocks, apart from a few petrochemical data (DI SIMPLICIO et al., 1974).

Thus in this paper we have carried out a detailed geochemical study and radiometric age determinations of 25 samples of these rocks from 8 outcrops in central Sardinia (fig. 1). The radiometric age obtained, however, have resulted to be younger than the ages inferred from stratigraphy because of alteration of the rocks and, therefore, they have no geological meaning. On the contrary, the geochemical investigations has allowed to recognize the chemical features of these igneous rocks, thus providing a contribution to knowledge of Caledonian magmas of southern Europe. In this view it has been made a comparison between the « Porphyroids » and other similar rocks of Lower Palaeozoic acidic magmatism in this area. The data obtained from the « Porphyroids » have also been compared with those of calc-alkaline rocks of two other magmatic cycles which largely affected Sardinia during the Phanerozoic, such as the Hercynian granitoids and Tertiary ignimbrites, with the aim of outlining the chemical features of the magmatic activity in Sardinia after the Cambrian. Finally, because of the inferred close geological relations between this island and the franco-hyberian continent during Paleozoic (ALVAREZ, 1972), and on the basis of a review (MONTIGNY et al., 1981), the data reported in this paper may be of interest also for geological studies of broader scale on the western Mediterranean area.

Geologic and petrographic features

The « Porphyroids » are acidic effusive rocks, which were emplaced mostly as ignimbrites (DI SIMPLICIO et al., 1975; GARBARINO et al., 1980). According to NAUD (1979) only the megacryst-bearing porphyroids would be of plutonic origin. The «Porphyroids» were metamorphosed to low-grade during the Hercynian orogenesis, which in Sardinia was characterized by the emplacement of a huge batholith through Palaeozoic terranes.

The occurrence of the « Porphyroids » is: a) massive, often dome-shaped with scarce grains size; b) stratoid, in conformity with the metasedimentary formations which they are interbedded with, with a pronounced schistosity and a grain size ranging from fine to medium-large.

Field evidence (NAUD, 1979) indicates the massive porphyroids represent the bottom of the S. Vito formation, and therefore they would have been emplaced during Middle Cambrian in the course of the Caledonian orogenesis. On the contrary, the stratoid porphyroids would be related to the « Sardinian phase » (Lower Ordovician?) of the Caledonian orogenesis, being interbedded with metasedimentary rocks whose upper member is represented by the Caradocian-Ashgillian limestones. According to MEMMI et alii (1982) large part of the porphyroids occurrences should be connected to the Middle-Upper Ordovician magmatic cycle.

Both the stratoid and massive porphyroids are typically characterized by « ocelli » made up by pink K-feldspar and hyaline quartz spread in a greenish schistose matrix. The size of the « ocelli », which are always flattened along the schistosity, is extremely variable, ranging from some millimeters to several tenths of millimeters. In thin section the « Porphyroids » show a typically porphyroclastic fabric. Quartz and feldspar are the most common minerals. The former, always dominant, exhibits well-corroded rims and is always cataclastic. It has an ondulate extinction and anomalous biaxicity. K-feldspar ($\sim 55\%$ Or) is often opaque and twined after Karlsbad. It is often replaced by neogenic albite which developed according to a check pattern. The plagioclase ($\sim 20\%$ An) is not infrequent in the «Porphyroids» from the outcrops near Laconi and Monte Parredis. The matrix, which represents on average 80-90 % of the volume rocks, is essentially made up by quartz and feldspar or, more rarely, by mica. It has a typically anisotropic texture because of the preferential orientation of the sericite microblasts. Apatite, zircon and some opaque mineral are common accessories.

At Brecca the massive porphyroids have a typically isotropic fabric and mineralogical paragenesis which is made up, besides quartz and feldspar, also by biotite. This latter mineral is however often altered to sericite and hosts opaque grains along cleavage lines.

Analytical methods

All the samples have been studied for major, minor and trace elements, except Li,

TABLE 1

Average major element concentrations (weight %) in the Sardinian porphyroids.
Standard deviation in brackets

	S1	S2	S3	S4	S5	S6	S7	S8	S9
SiO_2	74.80(1.04)	73.31(1.56)	71.12(1.35)	70.55(1.64)	76.49(1.15)	77.95(2.97)	69.63(2.07)	68.81(0.27)	73.66(1.32)
TiO_2	0.27(0.03)	0.34(0.02)	0.43(0.09)	0.37(0.01)	0.40(0.09)	0.05(0.00)	0.45(0.03)	0.40(0.04)	0.08(0.06)
Al_2O_3	14.40(1.22)	14.39(0.72)	14.74(0.54)	16.63(1.53)	15.44(1.05)	13.93(2.12)	15.56(0.82)	17.08(0.29)	15.49(0.53)
Fe_2O_3	0.97(0.51)	0.67(0.23)	2.19(0.58)	1.76(0.74)	0.95(0.40)	0.59(0.18)	2.40(1.56)	2.35(0.73)	1.30(0.91)
FeO	0.14(0.12)	0.21(0.26)	0.24(0.32)	0.61(0.45)	0.07(0.01)	0.07(0.03)	0.96(0.19)	0.48(0.40)	0.52(0.41)
MnO	0.01(0.00)	0.01(0.00)	0.01(0.00)	0.04(0.01)	0.01(0.00)	0.01(0.00)	0.03(0.00)	0.01(0.00)	0.04(0.01)
MgO	0.44(0.11)	0.41(0.06)	0.78(0.19)	0.85(0.20)	0.43(0.14)	0.29(0.08)	1.29(0.44)	1.09(0.10)	0.66(0.32)
CaO	0.14(0.05)	0.27(0.02)	0.30(0.05)	0.50(0.39)	0.20(0.04)	0.04(0.02)	0.48(0.13)	0.28(0.00)	0.11(0.16)
Na_2O	0.36(0.02)	1.72(0.31)	2.35(0.04)	0.47(0.16)	1.19(0.10)	0.32(0.06)	2.31(1.13)	2.09(0.38)	0.97(0.49)
K_2O	6.85(0.79)	7.19(0.43)	6.30(0.74)	6.12(0.49)	3.22(0.39)	5.12(2.36)	5.27(1.16)	5.03(0.18)	5.23(0.63)
P_2O_5	0.11(0.04)	0.18(0.01)	0.18(0.01)	0.22(0.01)	0.10(0.03)	0.03(0.00)	0.23(0.00)	0.21(0.01)	0.11(0.10)
H_2O^+	1.50(0.21)	1.32(0.40)	1.34(0.14)	1.87(0.47)	1.52(0.14)	1.59(0.65)	1.39(0.77)	2.18(0.05)	1.84(0.49)

TABLE 2

Average trace element abunandces in ppm except for Tl (PPB) in the
Sardinian porphyroids. Standard deviation in brackets

	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9
Li	23(10)	12(4)	35(20)	42(6)	32(9)	10(4)	40(12)	25(4)	//
Rb	276(14)	254(21)	219(21)	202(28)	86(18)	136(48)	186(63)	184(13)	177(26)
Sr	47(7)	84(5)	89(25)	45(5)	55(4)	13(7)	57(18)	44(6)	67(10)
Ba	597(162)	730(90)	1,261(430)	795(18)	1,223(214)	926(534)	782(103)	683(38)	1,116(424)
La	14(6)	15(3)	21(1)	29(2)	21(7)	23(2)	29(4)	22(4)	18(6)
Ce	24(14)	33(4)	53(21)	50(3)	39(11)	48(6)	54(9)	46(12)	35(6)
Y	55(7)	57(2)	55(6)	52(5)	23(7)	45(8)	52(10)	54(5)	33(12)
Zr	114(16)	139(3)	167(35)	163(19)	100(52)	86(17)	164(31)	170(14)	164(89)
Nb	8(2)	7(3)	9(3)	6(4)	5(4)	9(3)	9(4)	10(2)	13(5)
V	19(4)	18(3)	31(7)	31(2)	48(9)	3(2)	35(2)	32(4)	5(7)
Cr	9(2)	13(1)	17(3)	17(5)	17(2)	2(1)	20(4)	15(2)	< 2
Ni	3(1)	5(2)	8(2)	9(2)	13(12)	2(1)	10(1)	9(1)	8(1)
Cu	16(1)	15(1)	17(3)	18(2)	13(1)	16(2)	16(4)	11(9)	5(1)
Tl	1,940(491)	2,053(390)	1,036(268)	1,483(522)	1,760(891)	1,086(466)	1,253(535)	1,026(281)	//
Zn	24(10)	22(4)	45(11)	154(162)	46(39)	45(47)	59(11)	47(7)	47(16)
Pb	34(14)	11(3)	21(9)	22(2)	16(1)	253(349)	30(16)	26(4)	12(2)

Pb (pro parte), Tl and Fe^{2+}, by means of XRF analysis following the procedure of FRANZINI et al. (1972) for major and minor elements, and LEONI and SAITTA (1976) for trace elements, respectively. The precision and accuracy of measurements have been calculated against several international standards, and they were better than 10 %. Fe^{2+} has been determined by titration with $KMnO_4$, ignition loss by gravimetric method, Li by atomic-absorption. Tl and Pb (p.p.) have been measured by polarographic methodologies as described by CALDERONI (1981) and CALDERONI and FERRI (1982), respectively.

K-Ar ages have been performed following the method proposed by NICOLETTI and PETRUCCIANI (1977). Repeated measurements against international laboratory standards have yielded the following values: muscovite P 207 80.2 ± 1 (81 ± 1); muscovite BERNE 4M 18.1 ± 0.8 (18.7 ± 0.5); biotite LP6 123 ± 3 (125 ± 2). The conventional ages has been calculated by using the following decay constants:

$$\lambda_\varepsilon = 0.581 \cdot 10^{-10} \ y^{-1};$$
$$\lambda_\beta = 4.962 \cdot 10^{-10} \ y^{-1}.$$

The error was calculated according to
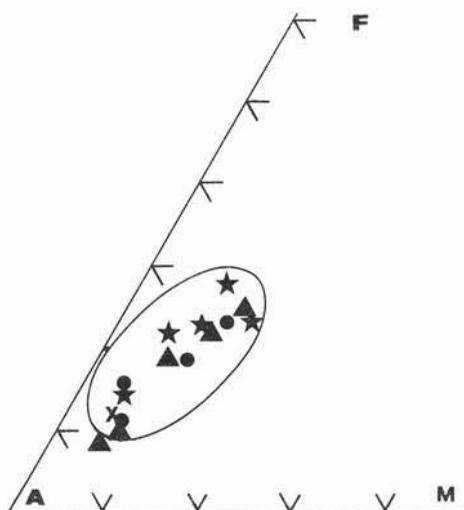
Fig. 2. — *AFM* plot for the Sardinian (▲ massive, ● stratoid) porphyroids. The solid line contours the field of Sardinian porphyroids (Di SIMPLICIO et al., 1974), (x) indicates the average for the Sicilian porphyroids (ATZORI et al., 1978), while (★) indicates the averages for 5 different outcrops of porfiroids from the south-Alpine region (BELLIENI and SASSI, 1981).

DALRYMPLE and LANPHERE's formula (1969). Following the methodology suggested by MELLOR and MUSSET (1975), three samples have been collected along a distance of several meters from each outcrop, except from S-1, which 4 samples have been collected from.

No age determinations have been made for samples from outcrop S-9.

The ages have been calculated following the method of isochrons of the isotopic ratios as suggested by HAYATSU and CARMICHAEL (1970, 1977). The justification of this choice has been discussed by NICOLETTI and PETRUCCIANI (1978).

Geochemistry

The average abundance of major, minor and trace elements in the « Porphyroids » are given in tab. 1 and 2.

Major elements

The volcanic rocks show some variation in major element composition with the SiO_2 content ranging ([1]) from 68.77 to 74.80, excepting S-5 and S-6, which have slightly
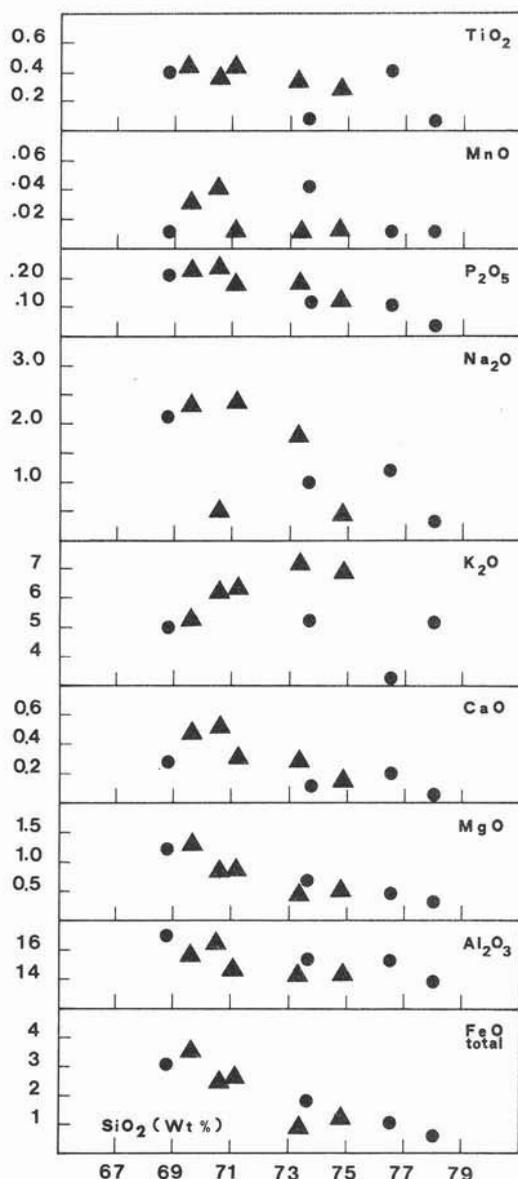
Fig. 3. — Major and minor oxides vs. silica variation diagrams for the Sardinian porphyroids. Abundances are given in weight percent. Symbols as in fig. 2.

higher SiO_2 because of secondary silification. The content of major elements, and their variation trends such as those on the AFM diagram (fig. 2), $(Na_2O + K_2O)$ vs. SiO_2,

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([1]) Hereafter we discuss chemistry of the « Porphyroids » considering these rocks as a whole, because they show close features.
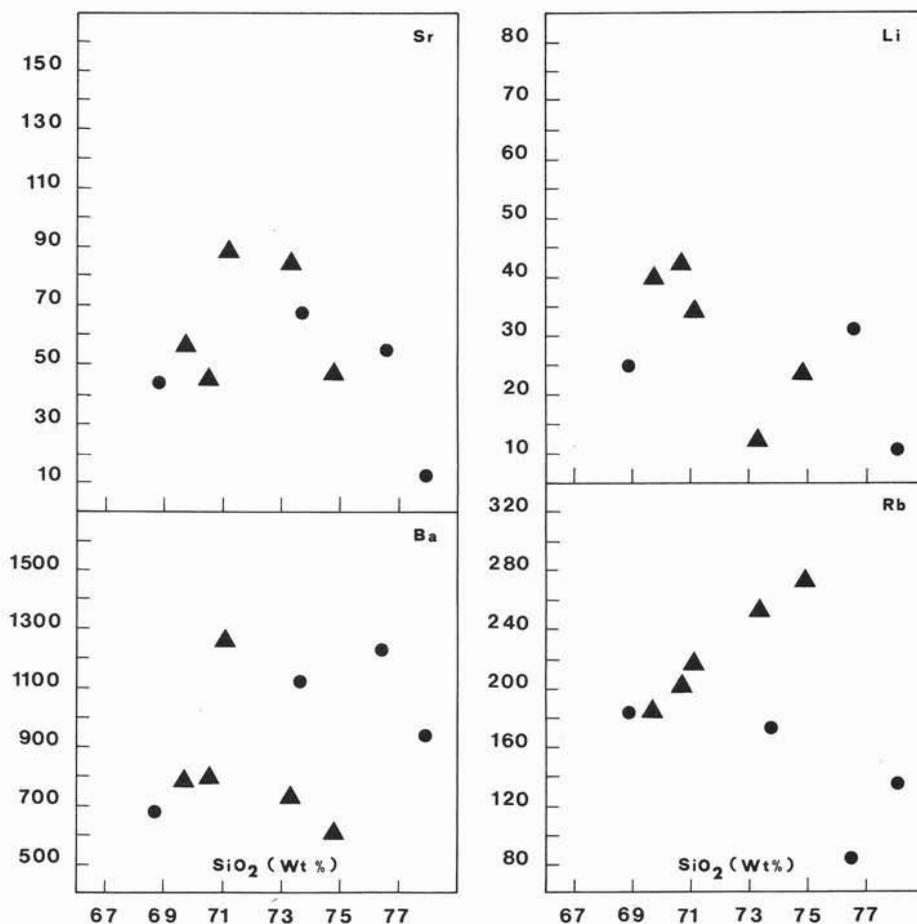
Fig. 4. — Trace elements vs. silica variation diagrams for the Sardinian porphyroids. Abundances are given in ppm, except for Ti which are expressed in ppb. Symbols as in fig. 2.

are typical of Calc-alkaline suites, in agreement with the conclusions of DI SIMPLICIO et al. (1975) and GARBARINO et al. (1980).

Plots of major oxides against SiO_2 are shown in fig. 3. It is apparent that Na_2O, CaO, MgO, FeO tot., Al_2O_3 generally decrease with increasing SiO_2, while K_2O increases except in three outcrops, two of which are represented by silicified rocks. All these trends, except that of Na_2O, can be considered «normal», as usually observed in magmatic differentiation of calc-alkaline volcanic rocks. The «anomalous» trend of Na_2O can be explained admitting that some Na_2O has been lost because of secondary processes particularly from more acidic rocks where glassy matrix is expected be more abundant. This is reasonable as Na_2O content

in the «Porphyroids» is lower than in volcanic rocks of similar SiO_2 content.

Despite the «normal» trends shown by CaO and K_2O, however, there is evidence that also the contents of these two elements have been altered by secondary processes. This is because CaO and K_2O are lower and higher, respectively, than in volcanic rocks of similar SiO_2. Residual CaO appears to be combined mainly with P_2O_5 in the apatite (see later).

Oxidation is very high, the Fe_2O_3/FeO ratio being largely more than 1 in all the samples, in agreement with the low-grade hydrous metamorphism (cf. FLOYD, 1976) which affected the rocks. Finally, ignition loss has to be identified with H_2O^+, as no CO_2 has been detected.
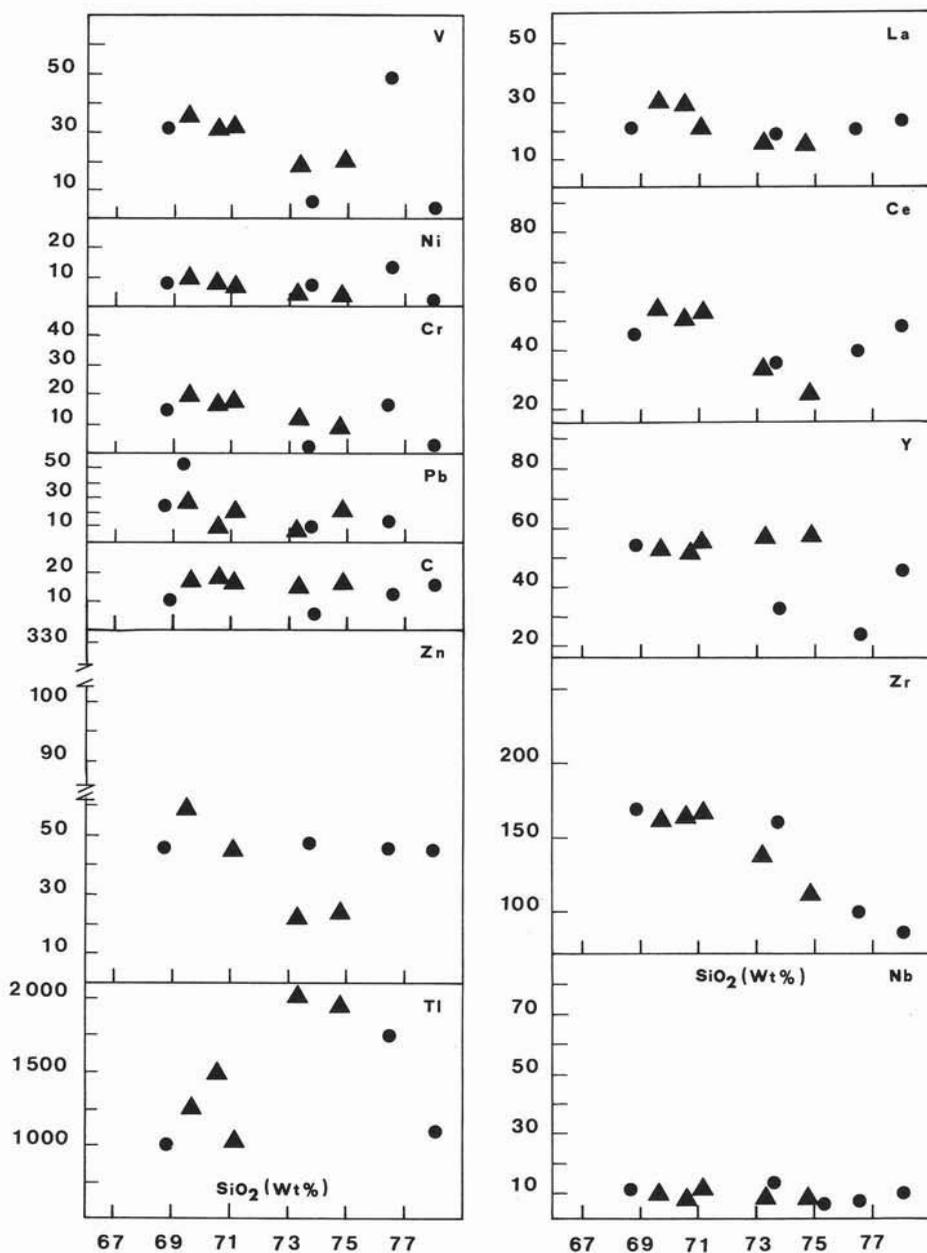
Fig. 4. — Trace elements vs. silica variation diagrams for the Sardinian porphyroids. Abundances are given in ppm, except for Ti which are expressed in ppb. Symbols as in fig. 2.

In conclusion, relative to major element abundances the Sardinian porphyroids have not significantly changed their original features because of transformations occurred after their emplacement, only Na, Ca and K being lost and added respectively, to some extent, during alteration of the rocks.

Minor and trace elements

The variation diagrams of TiO_2, MnO, P_2O_5 vs. SiO_2 are shown in fig. 3. TiO_2 and P_2O_5, which are regarded immobile elements during low-grade metamorphism (cf. PEARCE, 1975; FLOYD and WINCHESTER, 1975; WIN-
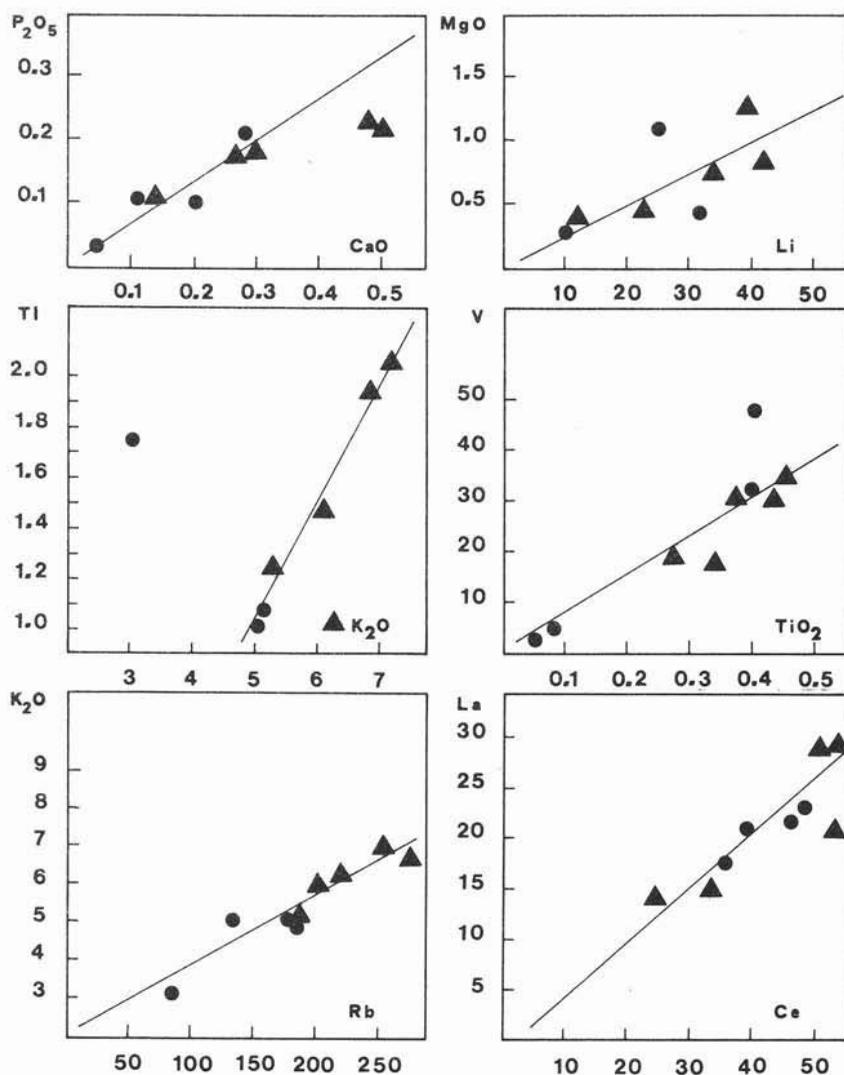
Fig. 5. — Selected interelement relationships in the Sardinian porphyroids. Symbols as in fig. 2. Abundances in weight percent and in ppm for major-minor oxides and trace elements, respectively. Tl abundances are expressed in ppb.

CHESTER and FLOYD, 1976) and weathering, decrease with increasing SiO_2, the former in agreement with magmatic differentiation, and the latter suggesting apatite fractionation. The low content of TiO_2 and P_2O_5 is consistent with the calc-alkaline character of the rocks. Overall MnO decreases with increasing SiO_2, being constant in samples with $SiO_2 > 69\%$.

Plots of trace elements against SiO_2 (fig. 4) show a uniform distribution of Y, Nb, Cu, Zn, no pattern for Ba and Sr, increase

of Rb and Ti, decrease of all the other elements with increasing SiO_2.

The uniform distribution of Y and Nb, as they are regarded typically immobile elements in metavolcanites of greenschist facies (cf. PEARCE, 1975; FLOYD and WINCHESTER, 1975; WINCHESTER and FLOYD, 1976) or in altered rocks, suggests an indifferent behavior of these elements between magmas and crystallizing minerals. This feature seems to be characteristic of intermediate and acidic rocks of many calc-

Fig. 6. — Immobile element plots (WINCHester and FLOYD, 1977) for the Sardinian porphyroids. Symbols as in fig. 2.

be due either to alteration or magmatic differentiation. The anomalous high content of Zn shown by outcrop S-4 indicates major mobilization of this element due to a post-magmatic event. This outcrop, actually, occurs in the vicinity of a mineralization area.

V, Ni, Cr, which are regarded as slightly mobile or immobile during low temperature and pressure processes (WEDEPHOL, 1974), decrease with increasing SiO_2 in agreement with differentiation.

Decrease of Pb can be due to secondary processes, as this element is generally incompatible during magmatic differentiation (LEEMAN, 1979). In particular, the anomalous high Pb content of outcrop S-8, which comes from an area where small mineralizations occur, is certainly related to the circulation of mineralizing fluids.

Tl, whose behavior during low-grade metamorphism and weathering is unknown (WEDEPHOL, 1974), and Rb, a rather mobile element, during alteration shows increase with SiO_2, in agreement with the character of incompatible element during differentiation of calc-alkaline rock suites.

Li, despite a large scatter, decreases with increasing SiO_2, in contrast to its usual behavior during differentiation. This suggests that some Li has been mobilized in more acidic rocks.

Sr and Ba show no definite trend, likely reflecting secondary mobilization.

Decrease of La and Ce with increasing SiO_2 suggests apatite fractionation, in agreement with the parallel decrease of P_2O_5.

Finally, decrease of Zr, a typically immobile element (PEARCE, 1975; FLOYD and WINCHESTER, 1975; WINCHESTER and FLOYD, 1976) indicates that zircon was a crystallizing phase in the porphyroidic magmas.

In conclusion, relative to minor and trace element abundance the more acidic Sardinian porphyroids may have lost some Li, Pb because of alteration. Silicified rocks (outcrops S-5 and S-6) show less Rb, Tl, Zr, Y, and more La, Ce, Ba, Zn, the other elements showing no definite trends.

Interelement relationships

The main interelement relationships are

alkaline suites (cf. TARNEY and SAUNDERS, 1980). On the contrary, the uniform distribution of Cu, whose behavior during low-grade metamorphism and weathering is controversial (WEDEPOHL, 1974), suggests some mobilization, as Cu is a compatible element in magmatic suites. Finally, the uniform distribution of Zn, which is a somewhat mobile element in both metamorphic and weathering processes (WEDEPOHL, 1974) can

Fig. 7. — Major and minor element abundance ranges for the Sardinian calc-alkaline rocks (P = porphyroids, G = Hercynian granitoids, T = Tertiary ignimbrites). Data of the Tertiary ignimbrites after COULON et al. (1977). Data of the Hercynian granitoids after GARBARINO and MASI (in progress).

graphically shown in fig. 5.

There is no relation between K_2O and Na_2O, just as to be expected because of the post-magmatic processes which mobilized Na_2O in most rocks. K and Rb show a close coherence, their ratio being between 200 and 250, i.e. in the range of acidic rocks from many calc-alkaline suites. A good positive correlation is also shown by K (and Rb) and Tl in most samples. This feature is interesting as it shows both these elements behave coherently even in samples affected by secondary processes. The Rb/Tl ratios fall into the range for igneous rocks (WEDE-POHL, 1974). There is a negative correlation between K (and associated elements) and Ba, the K/Ba ratio ranging, similarly to that of the other acidic calc-alkaline rocks. A negative correlation is also observed between K (and associated elements) and Pb, and between Pb and Ba.

CaO and P_2O_5 show a good positive correlation in all the samples except those with higher CaO content, indicating that residual CaO is mostly tied to P_2O_5 in the apatite. Ca and La show some positive correlation, while Ca-Sr and La-Sr show no correlation. La and Ce positively correlate, while there is no correlation between La and Zr.

Rb-Sr and Ba-Sr show some positive correlation. Unlike Rb and Li which do not correlate, Li and Mg show a fairly good positive correlation in contrast to their usual pattern in calc-alkaline suites.

MgO-TiO_2 and $FeO_{tot.}$-TiO_2 show positive correlation, and the three elements to V, Ni, Cr, Zn, respectively. In particular, the TiO_2-V correlation is characteristic of Cenozoic calc-alkaline volcanic rocks (AN-DRIAMBOLONA, 1976).

Finally, Nb, Y and Cu show no relation to other elements.

Nomenclature of the rocks

DI SIMPLICIO et al. (1974) classified the

TABLE 3
K-Ar data of whole-rocks from central Sardinia

SAMPLE	^{40}Ar rad CCSTP/g·10^{-5}	^{40}Ar rad%	K%	Na%	t±ε
S1A	7.852	87.75	6.24	0.25	301± 9
S1B	6.203	85.22	5.15	0.12	290± 9
S1C	6.147	90.38	4.92	0.08	300± 9
S1D	7.876	95.27	5.68	0.00	330±10
S2A	6.476	87.54	5.62	1.45	278± 8
S2B	6.812	93.87	5.89	1.18	279± 8
S2C	7.768	88.96	6.17	1.27	302± 9
S3A	7.696	95.14	5.57	1.69	329±10
S3B	7.060	95.25	5.35	1.62	315±10
S3C	6.236	95.21	6.16	2.23	246± 7
S4A	7.155	93.10	4.59	0.19	367±10
S4B	6.939	84.94	4.66	0.26	352±10
S4C	8.523	93.17	5.79	0.02	352±10
S5A	3.894	88.73	2.66	0.54	344±10
S5B	3.979	85.87	2.95	0.67	321±10
S5C	3.292	73.37	2.11	0.54	367±11
S6A	5.442	88.41	3.64	0.03	353±10
S6B	8.347	92.64	6.91	0.16	290± 9
S6C	3.509	71.99	2.50	0.05	333±10
S7A	5.545	88.72	3.74	2.46	350±10
S7B	7.888	93.65	5.29	0.59	346±10
S7C	6.411	89.26	4.65	2.00	328±10
S8A	6.270	81.25	4.52	1.01	330±10
S8B	6.299	80.22	4.27	1.36	349±10
S8C	5.706	82.60	4.24	1.72	321±10

TABLE 4
K-Ar isotope isochroms of Sardinian porphyroids

SAMPLE	r	$(^{40}Ar/^{36}Ar)_o$	t±ε
S1	.9996	−116±62	378±5
S2	.9975	475±134	288±12
S3	.5494	6316±585	31±27
S4	.9979	190±136	404±15
S5	.9944	390±108	349±21
S6	.9891	609±206	294±25
S7	.9966	185±170	386±19
S8	.9948	765±52	234±14

TABLE 5
Harper isochroms of Sardinian porphyroids

SAMPLE	r	$(^{40}Ar)_o$	t±ε
S1	.9074	$-1.23 \times 10^{-5} \pm 1.92 \times 10^{-5}$	354±88
S2	.9689	$-6.95 \times 10^{-5} \pm 2.06 \times 10^{-5}$	532±89
S3	neg.		neg.
S4	.9842	$8.81 \times 10^{-6} \pm 0.95 \times 10^{-6}$	318±46
S5	.9805	$1.52 \times 10^{-5} \pm 2.50 \times 10^{-6}$	210±26
S6	.9876	$1.21 \times 10^{-5} \pm 4.50 \times 10^{-6}$	254±25
S7	.9780	$1.52 \times 10^{-6} \pm 7.96 \times 10^{-6}$	334±44
S8	.5451	$9.39 \times 10^{-6} \pm 4.58 \times 10^{-5}$	286±256

Sardinian porphyroids as rhyolites and rhyodacites on the basis of a few petrochemical data. The data of this paper, in particular those relative to immobile elements (fig. 6) confirm such classification.

Geochronology

In tab. 3 are given the conventional ages of the samples analysed and in tab. 4 and 5 are reported the overall isochron ages of the outcrops, according to the isochrons of both MELLOR and MUSSETT (1975) and HARPER (1970), respectively. Most of outcrops exhibits isochron ages which are different except S-3, which gives no isochron age, and S-6, which gives an isochron age with a low coefficient of linear correlation. It is known that the isochron ages of effusive suites represent either the age of the emplacement or the age of a post-magmatic event which altered the rocks (MELLOR and MUSSET, 1975). In this respect, as the isochron ages

of the « Porphyroids » from the various outcrops are all lower than the inferred stratigraphic ages, and in many cases unrealistic like those which suggest younger ages than the Hercynian orogenesis, there is evidence that post-magmatic events have systematically altered the original K-Ar ratios of the rocks. As possible causes it can be suggested either metamorphism, which affected the « Porphyroids » during the Hercynian orogenesis, or weathering. This latter cause is more reasonable as the variability of isochrone ages on closeby formations seems too large whether due to a metamorphic event. Finally, it is observed that there is no relation between radiometric age and K₂O content of the rocks.

Concluding remarks

Acidic rocks of pre-Hercynian time showing physiographic features similar to those of the Sardinian porphyroids are known outside Sardinia in a few areas of the Italian region such as Sicily (ATZORI et al., 1979) and the Eastern Alps (D'AMICO, 1962;
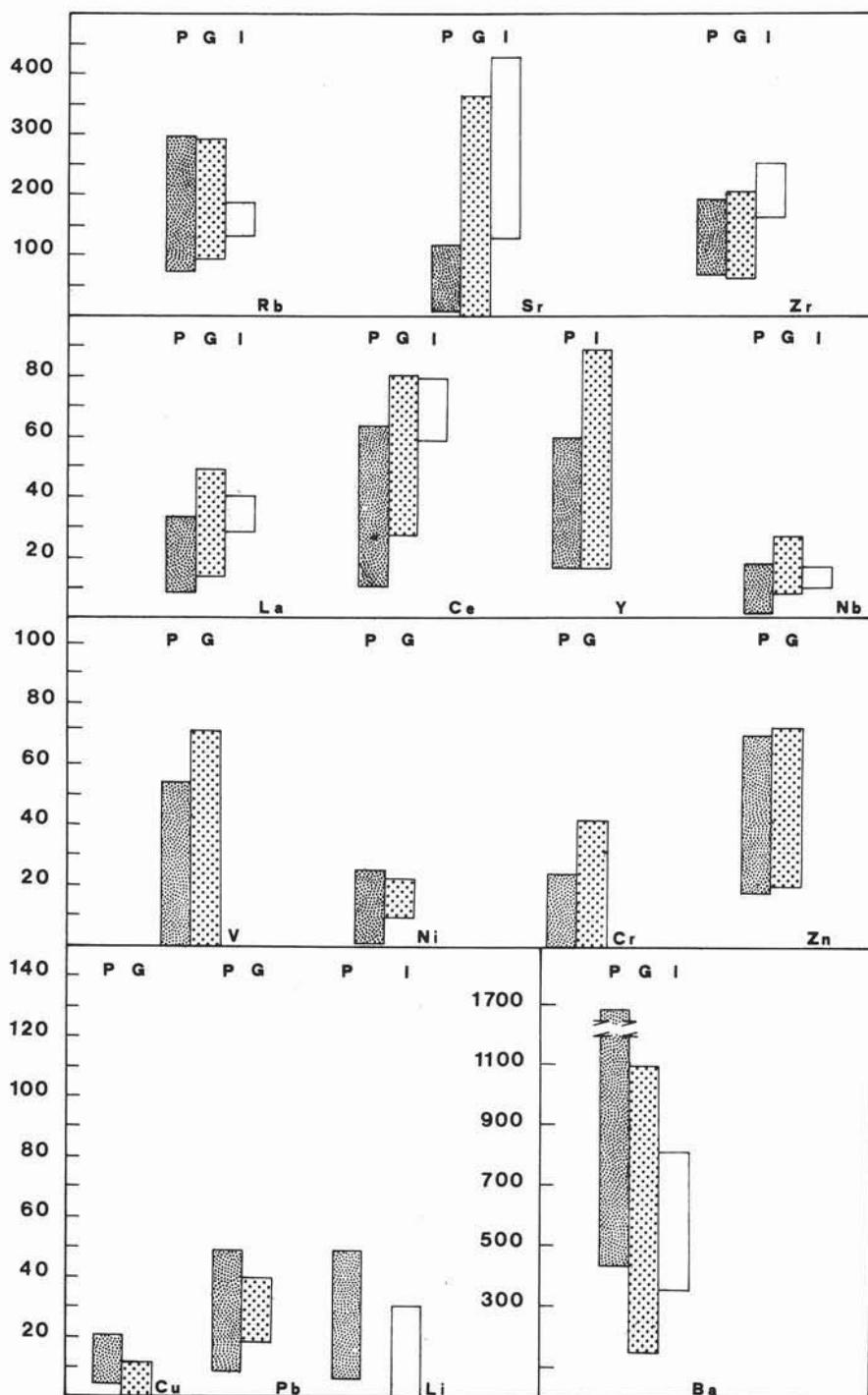
Fig. 8. — Trace element abundance ranges for the Sardinian clac-alkaline rocks. Symbols and source of the data as in fig. 7.

SASSI et al., 1979; BELLIENI and SASSI, 1981). From a comparison of the chemical features of the two groups of rocks it is apparent that there are overall no great differences for most elements, thus suggesting that acidic magmatism with characteristic similar to that of the Sardinian porphyroids occurred in the whole Italiana region in lower Paleozoic. However, further investigation is required in particular on the non-Sardinian rocks, in order to get a comprehensive picture of that.

Comparison of chemistry of the Sardinian porphyroids and other Sardinian calc-alkaline rocks such as the Hercynian granitoids (GARBARINO and MASI, in progress) and Tertiary ignimbrites (COULON et al., 1977) shows that as concerns major and minor elements (fig. 7) there are no great differences except the obvious depletion of Na_2O, CaO, MnO and the moderate increase in K_2O observed in the « Porphyroids » because of alteration. Taking into account trace element abundances it is apparent (fig. 8) that a) Nb and Sr are lower in the « Porphyroids » with respect to the other two groups of rocks, b) Ba and Li are on average higher in the « Porphyroids », c) Sr, La and Ce increase from the « Porphyroids » through the granitoids to the Tertiary ignimbrites. The depletion in Sr and, conversely, the increase in Ba content observed in the « Porphyroids » may be partly explained as due to the same causes which determined the depletion in CaO and the increase in K_2O, respectively, in these rocks, in agreement with the known relations between Sr-Ca and Ba-K in magmatic roscks.

The overall good chemical similarity shown by the rocks of the three Sardinian calc-alkaline suites indicates that the chemical features of igneous activity in this island have changed little throughout the Phanerozoic. This unique fact, in turn, suggests that the magma sources of the three different groups of igneous rocks had close chemical features. Thus the petrological calculations made by COULON et al. (1977) to explain the origin of the Tertiary ignimbrites can apply also to the Sardinian porphyroids, whose origin has thus been likely due to anatexis of granitic rocks or their metamorphic equivalents.

Finally, comparison of chemical features between the Sardinian porphyroids and other calc-alkaline ignimbritic suites from New Zealand (EWART et al., 1969), Chile (ELHINNAWI, 1969), and Mexico (CAMERON et al., 1980) shows fairly good resemblance between the Sardinian and New Zealandan rocks for most elements. However, it is questionable whether this means any tectonic significance.

REFERENCES

ALVAREZ W. (1972) - *Rotation of the Corsica-Sardinia microplate.* Nature, 235, 103-105.

ADRIAMBOLONA R.D. (1976) - *Les éléments de transition dans les suites andésitiques et shoshonitiques du Sud de Pérou.* Thèse 3° cycle, Montpellier, 88 pp.

ATZORI P., LO GIUDICE A., PEZZINO A., PUGLISI G. and BATTAGLIA M. (1978) - *I porfiroidi di Taormina (Sicilia).* Boll. Soc. Geol. IIt., 97, 337-352.

ATZORI P., BATTAGLIA M. and LO GIUDICE A. (1979) - *Distribuzione di alcuni elementi minori nei porfiroidi di Taormina (Sicilia).* Miner. Petrogr. Acta, 23, 257-263.

BARCA S., CARMIGNANI L., COCOZZA T., GHEZZO C., MINZONI N., PERTUSATI P.C. and RICCI C.A. (1981) - *Geotraverse B in Sardinia: Stratigraphic correlation forms.* IGCP Project n. 5, Newsletter, 3, 7-22.

BELLIENI G. and SASSI F.P. (1981) - *New chemical data and a review on the South-Alpine « Pre Hercynian rhyolitic plateau » in the Eastern Alps.* IGCP Project n. 5, Newsletter, 3, 22-28.

CALDERONI G. (1981) - *Determination of lead in igneous rocks by differential pulse anodic stripping voltammetry at Hmde.* Talanta, 28, 65-67.

CALDERONI G. and FERRI T. (1982) - *Determination of thallium at subtrace level in rocks and minerals by coupling differential pulse anodic stripping voltammetry with suitable enrichment methods.* Talanta, 29, 371-375.

CAMERON M., BAGBY W. and CAMERON K. (1980) - *Petrogenesis of voluminous mid-Tertiary ignimbrites of the Sierra Madre Occidental, Chihuahua, Mexico.* Contrib. Miner. Petr., 74, 271-284.

COULON C., DOSTAL J. and DUPUY C. (1978) - *Petrology and geochemistry of the ignimbrites and associated lava domes from N.W. Sardinia.* Contrib. Mineral. Petrol., 68, 89-98.

DALRYMPLE G.B. and LANPHERE M. (1969) - *K-Ar datin.* Ed. W.H. Freeman and Company, San Francisco.

D'AMICO C. (1962) - *La zona cristallina Agordo-Cereda.* Mem. Ist. Geol. Miner. Univ. Padova, 23.

DI SIMPLICIO P., FERRARA G., GHEZZO G., GUASPARRI G., PELLIZZER R., RICCI C.A., RITA F. and SABATINI G. (1974) - *Il metamorfismo ed il magmatismo paleozoico nella Sardegna.* Rend. Soc. It. Mineral. Petrol., 30, 979-1068.

EL-HINNAWI E.E., PICHLER H. and ZEIL W. (1969) - *Trace element distribution in Chilean ignimbrites.* Contrib. Mineral. Petrol., 24, 50-62.

EWART A., TAYLOR S.R. and CAPP A.C. (1968) - *Trace and minor element geochemistry of the rhyolitic volcanic rocks, central North Island, New Zealand.* Contrib. Mineral. Petrol., 18, 76-104.

FLOYD P.A. and WINCHESTER J.A. (1975) - *Magma type and tectonic setting discrimination using immobile elements.* Earth Planet. Sci. Lett., 27, 211-218.

FLOYD P.A. (1976) - *Geochemical variation in the greenstones of S.W. England.* J. Petrol., 17, 522-545.

FRANZINI M., LEONI L. and SAITTA M. (1972) - *A simple method to evaluate the matrix effects in X-ray fluorescence analysis.* X-ray Spectrometry, 1, 151-154.

GARBARINO C., MACCIONI L., MINZONI N., PADALINO G., TOCCO S. and VIOLO M. (1980) - *The strata-bound copper-lead-zinc mineralization of the Sardinian microplate (Italy).* In European Copper Deposits Symposium, Belgrade 1980, 251-260.

GARBARINO C. and MASI U. - *Chemical features of the Hercynian granitoids from Sardinia (Italy)* (in progress).

HARPER C.T. (1970) - *Graphical solutions to the problem of radiogenic Argon-40 loss from metamorphic minerals.* Ecl. geol. Helv., 63/1, 119-140.

HAYATSU A. and CARMICHAEL C.M. (1970) - *K-Ar isochron method and initial argon ratios.* Earth Planet. Sci. Lett., 8, 71-76.

HAYATSU A. and CARMICHAEL C.M. (1977) - *Removal of atmospheric argon contamination and the use and the misuse of the K-Ar isochron method.* Can. J. of Earth Sci., 14, 337-345.

KUNO I. (1967) - *Differentiation of basalt magmas.* Basalts, vol. 2, Intersciences Ed.

LEEMAN W.P. (1979) - *Partitioning of Pb between volcanic glass and coexisting sanidine and plagioclase feldspars.* Geochim. Cosmochim. Acta, 43, 43, 171-175.

LEONI L. and SAITTA M. (1976) - *X-ray fluorescence analysis of 29 trace elements in rock and mineral standards.* Rend. Soc. It. Miner. Petrol., 32, 479-510.

MELLOR D.W. and MUSSETT A.E. (1975) - *Evidence of initial ^{36}Ar in volcanic rocks.* Earth Planet. Sci. Lett., 26, 312-318.

MEMMI I., BARCA S., CARMIGNANI L., COCOZZA T., FRANCESCHELLI M., GATTIGLIO M., GHEZZO C., MINZONI N., NAUD G., PERTUSATI P.C., RICCI C.A. (1982) - *Il magmatismo pre-Ercinico della Sardegna.* In Guida alla Geologia del Paleozoico Sardo, Soc. Geol. It., 157-164.

MINZONI N. (1980) - *Precambriano el Sulcis meridionale (Sardegna).* Miner. Petrogr. Acta, 24, 51-56.

MONTIGNY R., EDEE J.B. and THUIZAT R. (1981) - *Oligo-Miocene rotation of Sardinia: K-Ar ages paleomagnetic data of Tertiary volcanics.* Earth Planet. Sci. Lett., 14, 261-271.

NAUD G. (1979) - *Tentative de synthèse sur l'évolution géodynamique de la Sardaigne antépermienne.* Mem. Soc. Geol. It., 20, 83-96.

NICOLETTI M. and PETRUCCIANI C. (1977) - *Il metodo K-Ar: modifiche metodologiche al processo di estrazione dell'argon.* Rend. Soc. It. Miner. Petrol., 33, 45-48.

NICOLETTI M. and PETRUCCIANI C. (1978) - *Contributo all'analisi critica dei metodi dell'isocrona nella cronologia assoluta con il metodo K-Ar.* Rend. Soc. It. Miner. Petrol., 34, 549-557.

PEARCE J.A. (1975) - *Basalt geochemistry used to investigate past tectonic environments on Cyprus.* Tectonophysics, 25, 41-67.

SASSI F.P., ZANFERRARI A. and ZIRPOLI G. (1979) - *Nuovi dati sulla stratigrafia e i caratteri chimico-petrografici dei porfiroidi del Comelico (Alpi orientali).* Mem. Soc. Geol. It., 20, 425-434.

TARNEY J. and SAUNDERS A.D. (1980) - *Trace element cotraints on the origin of cordilleran batholiths.* In Origin of granitic batholiths, Shiva Publishing Ed.

WEDEPHOL K.H. (1974) - *Handbook of geochemistry.* Ed. Springer-Verlag, Berlin.

WINCHESTER J.A. and FLOYD P.A. (1975) - *Geochemical magma type discrimination: application to altered and metamorphosed basic igneous rocks.* Earth Planet. Sci. Lett., 28, 459-469.

WINCHESTER J.A. and FLOYD P.A. (1977) - *Geochemical discrimination of different magma series and their differentiation products using immobile elements.* Chem. Geol., 20, 325-343.