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GEOCHEMISTRY AND STRATIGRAPHIC CORRELATIONS — APPLICATION TO THE INVESTIGATION OF GEOTHERMAL AND MINERAL RESOURCES OF TUSCANY, ITALY*
(Contribution to the Knowledge of the Ore Deposits of Tuscany, II)

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ABSTRACT

Puxeddu, M., Saupé, F., Déchomets, R., Gianelli, G. and Moine, B., 1984. Geochemistry and stratigraphic correlations — Application to the investigation of geothermal and mineral resources of Tuscany, Italy (Contribution to the knowledge of the ore deposits of Tuscany, II). Chem. Geol., 43: 77—113.

Major-element geochemistry (364 analyses) is used to obtain quantitative information on the initial mineralogical composition and the depositional environment of Paleozoic, more or less metamorphic, rocks from Tuscany and Elba. Furthermore, this method can be used to improve stratigraphic correlations by comparing the chemical compositions of the metamorphic rocks and their possible non-metamorphic counterparts of known stratigraphic position. The stratigraphic units were divided into two sets. The first includes the units of known stratigraphic or tectonic position, taken as reference groups: Permian Red Porphyries, Carboniferous rocks, Buti Group l.s., Porphyritic Schists, Porphyroids, Lower Phyllites and metabasites from the Apuan Alps and Elba. The second set comprises the units of uncertain position: metapelites and metapsammites from outcrops, mines and boreholes from the Boccheggiano—Niccioleta area, Calamita Schists and metabasites associated with these two units, Micaschists, Gneisses and associated amphibolites.

The main results are:

(1) The Porphyroids and Porphyritic Schists differ strongly from the Permian Red Porphyries, thus confirming that they belong to two different volcanic episodes.

(2) All the reference units consist of shales, sandstones s.s. or graywackes, differing by their degree of maturity (increasing from the Lower Phyllites to the Buti Group and to the Carboniferous formations).

(3) The Carboniferous rocks, the Buti Group and the Lower Phyllites have distinct chemical compositions.

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(4) The Boccheggiano Formation l.s. and the Calamita Schists are similar and include rocks chemically equivalent to the Lower Phyllites, the Buti Group and the Carboniferous formations.

(5) The Micaschists and Gneisses derive from shales and graywackes respectively, and chemically recall the Lower Phyllites.

(6) The metabasites from the Apuan Alps and from Niccioleta are "within-plate basalts", whereas the amphibolites interlayered within the Micaschists and Gneisses seem "ocean-floor basalts".

1. INTRODUCTION

1.1. Aim and scope

Since the beginning of this century, the production of geothermal energy at Larderello has been inducing a slow decrease of the average pressure in the presently worked reservoirs. The latter are located at a depth of a few hundreds of metres. Wells were drilled to a depth of up to 4 km to search for deeper productive horizons. Thrusts, well known in the cover, are also present in the basement (Gianelli et al., 1978, 1981). Furthermore, the rocks situated at a few kilometres depth below Larderello underwent contact and hydrothermal metamorphism (Marinelli, 1969; Cavarretta et al., 1980, 1982; Puxeddu, 1981), both due to a recent cooling intrusion. Comparison of these metamorphic formations with their outcropping and less metamorphic counterparts can be validly done only on the basis of their chemical compositions (Gianelli and Puxeddu, 1979). The same holds true for the geothermal field of Mount Amiata (Fig. 1) where the rocks found at depth are metamorphosed to a lesser degree.

The iron deposits of Elba and of Tuscany were recently interpreted as belonging to a horizon of syngenetic strata-bound bodies located immediately underneath the Calcare Cavernoso. The deposits of Elba, together with their host-rocks, were said to have undergone a low-grade metamorphism (e.g., Valle Giove) or a high-grade metamorphism (e.g., Ginevro). The metamorphic grade was supposed to depend upon the distance from the hypothetical extension of the intrusion of the Porto Azzurro quartz—monzonite under the Calamita Peninsula (Bodechtel, 1965; Arnold, 1976). Comparison of the chemical composition of the host-rock of Ginevro (Calamita Schists = Scisti di Calamita) and of the host-rock of Valle Giove (= Verrucano) demonstrated the dissimilarity of these two formations (Deschamps et al., 1979, 1983; Deschamps, 1980). Meanwhile, a Middle Paleozoic age was proposed for the Calamita Schists (Bagnoli et al., 1978, 1979) and indirectly corroborated by geochronological data (Saupé et al., 1982). Thus, the host-rocks of the Fe deposit of Ginevro are probably Middle Paleozoic. The host-rocks of the Fe deposit of Niccioleta (Déchomets, 1983) are schists and evaporites, locally transformed into skarns, also considered Paleozoic without fossil evidence.

A more detailed knowledge of the stratigraphy of the Tuscan Paleozoic will, therefore, contribute to the search for geothermal and mineral resources.

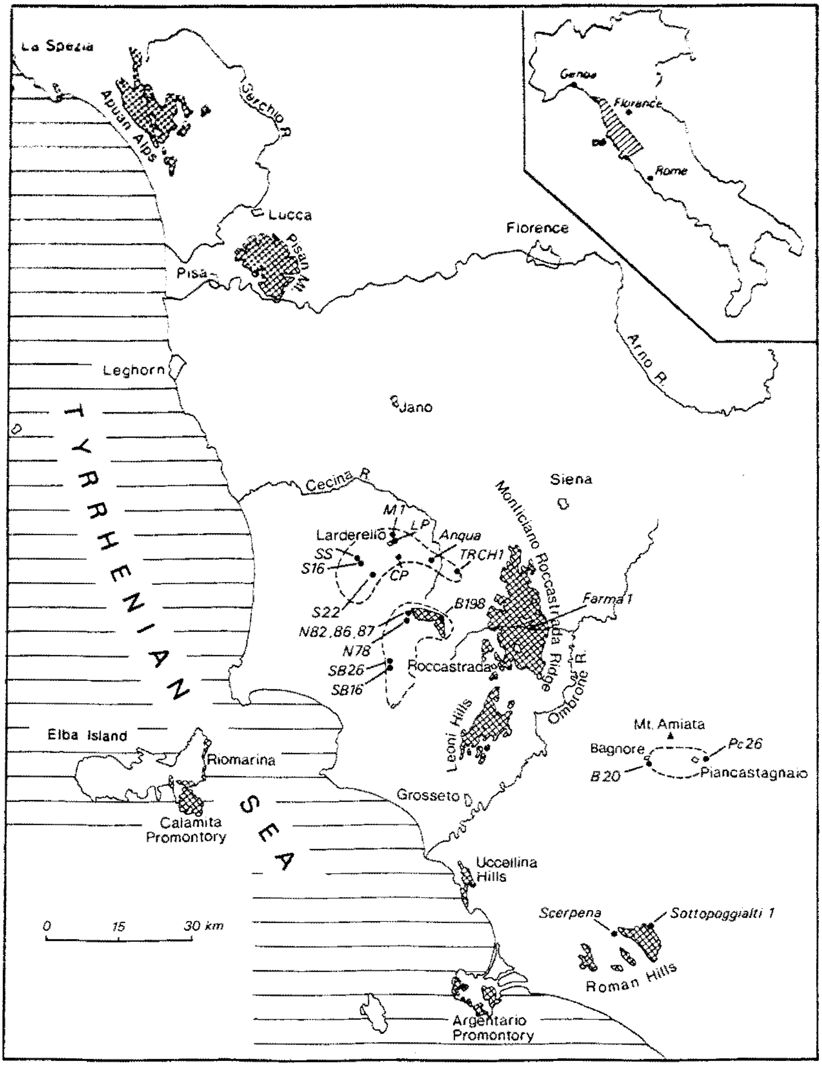


Fig. 1. Position of the analyzed samples and of the quoted localities (*dots*: geothermal wells (ENEL), exploration drillholes (Solmine) and geothermal drillhole (Farma *1*, C.N.R.); *dashed contours*: geothermal and mining areas).

1.2. Geotectonic setting

The Northern Apennines consist of the Umbrian and Tuscan zones lying between the Abruzzi Platform and the Ligurian zone. The subdivision into three zones is mainly based on the Cenozoic flysch formations overlying the different stratigraphic sequences, and not on the Paleozoic formations dealt with below.

The autochthonous, *Umbrian* zone outcrops east of our study region and will not be considered here. The *Tuscan* zone consists of three epimetamorphic tectonic units:

(1) The *Apuan metamorphic sequence* (Carmignani et al., 1978b) present in the Apuan Alps and perhaps in the Island of Elba and in the wells of southern Tuscany.

(2) The *Massa Unit*, west of the first unit, known in the Apuan Alps, in the Pisan Mounts and in southern Tuscany.

(3) The *Tuscan External Unit*, coming from an area east of the Apuan Alps (Boccaletti et al., 1980). The Mesozoic cover of this unit split off from its basement and provided the origin of the Tuscan nappe, which overrode the other units (Reutter et al., 1980).

The *Ligurian* formations are thrust over all the other formations (for more details see Abbate et al., 1970; Decandia et al., 1980; Elter, 1980).

This work deals exclusively with Paleozoic and/or metamorphic formations of the Apuan Unit, Massa Unit, basement of Larderello and Mount Amiata, as well as a few Paleozoic outcrops of uncertain tectonic position (Fig. 1). All these units have a great structural complexity (see, for example, Gianelli et al., 1978, 1981; Deschamps, 1980; Deschamps et al., 1983).

1.3. Stratigraphic setting

The discussion is based on the stratigraphic synopsis elaborated by Bagnoli et al. (1979) and Tongiorgi and Bagnoli (1981), condensed and modified in Table I. Fig. 2 is a correlation diagram which takes into account the improvements derived from the present study.

1.4. Interpretation of chemical diagrams

The chemical composition of predominantly detrital sedimentary rocks provides quantitative information on their mineralogical composition and on their environment of deposition. After metamorphism, chemical data are often the only clues to their origin. Thus, these data are essential to any tentative sedimentological reconstruction and to a correlation between nonmetamorphic and metamorphic sequences (see, e.g., Neugebauer and Kleinschmidt, 1971; Lambert et al., 1981). The compositions are assumed a priori to have undergone only slight changes during metamorphism. This assumption is valid in most cases, but the possibility of metasomatic reactions should be kept in mind for particular conditions (alternating sequences of carbonate rocks with shales and/or sandstones, hydrothermal metamorphism, etc.). The conditions of formation of a sedimentary rock can be derived from its chemical composition (major elements) only through the mineralogical composition that it represents. The processing of the data should therefore be aimed at establishing the connection between the chemical and mineralogical compositions (de La Roche, 1978). Four complementary diagrams were chosen to plot the data in this paper.

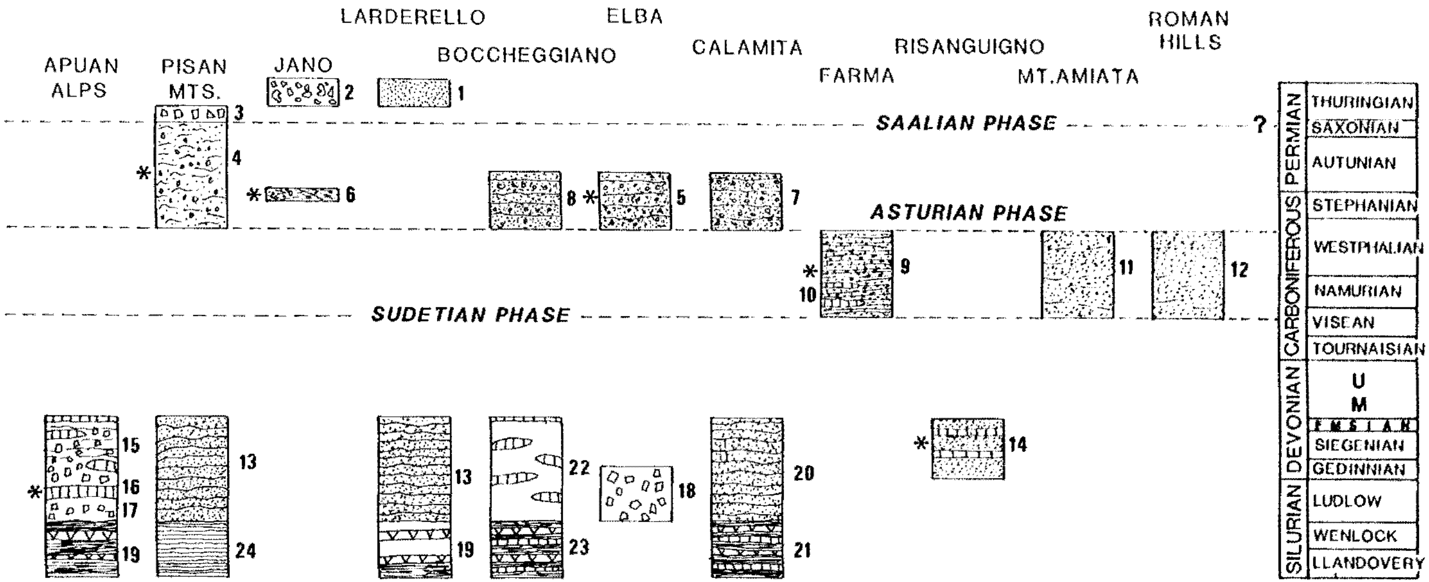
TABLE I

Pre-Mesozoic stratigraphic sequence of Tuscany

Position with respect to orogenic events Associated magmatisms	Stratigraphic groups and units
SUPERGROUP1 *Tuscan Permo-Carboniferous* Post-Saalian or Saalian Rhyolites	Group *1 Asciano* Castelnuovo Red Sandstones Red Porphyries Jano Porphyric Schists Asciano Breccias and Conglomerates
Post-Asturian none	Group *2 San Lorenzo* San Lorenzo Schists Jano Shales and Sandstones Le Cetine Shales and Conglomerates Rio Marina Formation Spirifer-bearing Schists Argentario Sandstone
Pre-Asturian Post-Sudetian none	Group *3 Farma* Farma Formation Carpineta Formation
SUPERGROUP 2 *Tuscan Crystalline Basement* Pre-Sudetian Rhyolites	Group *1 Buti l.s.* Risanguigno Formation Upper Phyllites Orthoceras Dolostone (= "Dolomie scistose a Orthoceras") Graptolite Schists (= "Scisti grafitici a graptoliti") Porphyroids and Porphyritic Schists Buti Group s.s. (Buti phyllites)
Pre-Sudetian WIP basalts	Group *2 Filladi Inferiori* Lower Phyllites Valle del Giardino Metabasites
Pre-Sudetian WIP basalts	Group *3 Incertae sedis* Boccheggiano Formation
Metamorphism of undetermined age OFB tholeiitic basalts	Group *4 Micaschists* Micaschists Gneisses (sequence undetermined)

For explanation see the Appendix.

The diagram (Al/3–K) vs. (Al/3–Na) (de La Roche, 1978; Figs. 3, 6 and 10) integrates all the chemical constituents (since the variables are expressed as quantities, not as ratios) but emphasizes the behavior of Al and the alkalis. It clearly distinguishes a sedimentary and an igneous domain and thus permits us, at a glance, to control the *maturity* of a sedimentary rock.



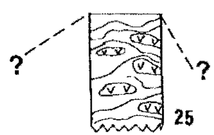


Fig. 2. Correlation diagram for the Pre-Mesozoic units of Tuscany: *1* = Castelnuovo Red Sandstone; *2* = Jano Porphyric Schist; *3* = Asciano Formation; *4* = San Lorenzo Schist; *5* = Rio Marina Formation; *6* = Jano Shale and Sandstone; *7* = Calamita Schist p.p.; *8* = Boccheggiano Formation l.s., outcrops of Boccheggiano and Serrabottini; *9* = Farma Formation; *10* = Carpineta Formation; *11* = Carboniferous of the Mount Amiata boreholes; *12* = Carboniferous of the metamorphic outcrops of the Roman Hills; *13* = Buti Phyllite (Pisan Mount and Larderello boreholes); *14* = Risanguigno Formation; *15* = Upper Phyllite; *16* = Orthoceras Dolostone and Graptolite-bearing Black Schist; *17* = Porphyroid and Porphyritic Schist, Na_2O-rich; *18* = Porphyroid and Porphyritic Schist, K_2O-rich; *19* = Lower Phyllite and Valle del Giardino Metabasite; *20* and *21* = Calamita Schist p.p., possibly forming a thermometamorphic sequence comparable to that of Boccheggiano; *22* = Boccheggiano Formation l.s., upper part of the drillings; *23* = Boccheggiano Formation l.s., lower part of the drillings and mine of Niccioleta; *24* = Lower Phyllite, outcrop of San Pantaleone; *25* = Micaschist, Gneiss and Amphibolite. *Asterisks* indicate presence of fossils.

Recognition of the *mineralogical composition* corresponding to the chemical composition requires several diagrams. It is thus possible to ascertain the nature and abundance of the principal mineral groups present in the sample: quartz, feldspars, sheet-silicates and carbonates (Moine, 1971; Moine et al., 1974).

The diagram [Si/3—(Na + K)] vs. [Al—(Na + K)] (Figs. 4, 7 and 11) is designed to estimate the relative proportions of quartz, feldspars and sheet-silicates. The major petrographic subdivisions of sedimentary rocks (Pettijohn et al., 1973) occupy distinct fields in the diagram: quartzites, sandstones s.s., arkoses, graywackes and shales.

The diagram (Na/Al) vs. (K/Al) (Figs. 5, 8 and 12) ignores the role of quartz and carbonates and reveals the nature and abundance of the feldspars, compared to the sheet-silicates.

In the diagram [K/(Al—Na)] vs. [(Fe + Mg)/(Al—Na)] (Figs. 9 and 13) albite (but not K-feldspar), quartz and carbonates are eliminated. The representative points of the major sheet-silicate groups (kaolinites, montmorillonites, illites and chlorites) are clearly separate.

The trace elements of the rocks under consideration are mainly concentrated in the fine-grained fractions and occasionally in the feldspars. To avoid a "dilution" effect by quartz, introducing meaningless variations of the trace-element contents, the latter were recalculated to a constant quantity of Al_2O_3, arbitrarily fixed at 18 g. Using these data, a discrimination was attempted within the following pairs of units:

(1) Carboniferous units vs. the Buti Group s.s. and the Upper Phyllites.

(2) Gneisses and Micaschists vs. Calamita Schists.

Snedecor's *F*-test was applied, successively checking the hypotheses of equality of variances and of means. No important indications were derived from this work.

Metamorphites, derived from basic igneous rocks, are also reported in the various diagrams, but can only reasonably be interpreted with the diagrams of Figs. 3 and 10. The Ti vs. Y/Nb and the Ti/100—Zr—Y·3 diagrams were also used (Floyd and Winchester, 1975) (Figs. 14 and 15).

1.5. Geographic origin of the analyzed samples

The 364 analyses were divided into two sets. The first set includes the units of known stratigraphic and/or tectonic position:

(1) Permian Red Porphyries;

(2) Carboniferous rocks of the San Lorenzo and Farma Groups, also including samples from Rio Marina (Elba), the Roman Hills and Jano;

(3) Buti Quartzites and Phyllites ("Quarziti e Filladi di Buti" — Pisan

TABLE II

Selected representative analyses from the reference groups (major elements in %, traces in ppm)

	PTNA *305*	PTPI *031*	PTNA *260*	PTPI *117*	PTPI *002*	PTPI *124*	PTPI *006*	PTPI *119*	PTPI *921*	PTPI *112*	PTNA *208*	PTPI *108*
SiO_2	65.32	86.15	49.46	68.72	56.70	75.39	71.96	64.67	59.49	69.23	71.67	69.53
Al_2O_3	17.98	08.64	27.41	14.29	17.58	10.34	11.52	15.78	19.23	13.90	14.62	14.71
$Fe_2O_3{}^t$	7.10	0.18	7.47	8.08	7.23	2.22	4.12	6.61	6.87	3.58	2.82	3.89
MnO	0.02	0.03	0.09	0.02	0.12	0.10	0.05	0.02	0.04	0.05	0.08	0.06
MgO	0.84	0.05	1.45	1.11	2.48	0.78	1.80	2.36	3.23	0.81	0.58	1.20
CaO	—	—	—	—	—	1.96	1.01	—	0.53	1.19	—	0.08
Na_2O	1.57	0.50	0.68	0.54	0.58	0.71	3.09	2.32	2.06	3.10	1.15	0.43
K_2O	2.99	1.82	5.59	3.38	4.67	2.15	1.87	2.64	3.71	3.42	7.58	4.41
TiO_2	1.14	0.52	1.04	0.73	0.93	0.54	0.60	0.79	0.71	0.48	0.25	0.51
P_2O_5	—	—	—	0.15	0.08	0.08	0.14	0.14	0.17	0.24	—	0.22
L.O.I.	3.50	1.61	7.29	3.06	8.21	4.83	2.80	3.81	3.95	2.96	1.37	4.14
Total	100.46	99.50	100.48	100.08	98.58	99.10	98.96	99.14	100.00	98.96	100.12	99.23
Ba	748	278	1,070	892	807	303	314	565	—	545	1,209	505
Cr	106	37	176	71	95	43	58	79	—	<10	20	35
Cu	11	<10	34	<10	35	30	<10	<10	—	<10	<10	<10
Ni	52	37	39	52	52	45	40	69	—	31	<10	31
Sr	130	46	229	77	78	79	106	51	—	23	99	65
V	162	51	210	151	134	78	72	106	—	13	52	77
Rb	112	60	—	135	194	86	56	85	—	95	298	181
Zn	—	<10	—	54	105	24	89	134	—	37	—	51

The last two letters indicate the origin of the analysis: DE = École des Mines, Saint-Étienne; NA = C.R.P.G., Nancy (analysis by K. Govindaraju); analytical method: Govindaraju et al. (1976); PI = Istituto di Mineralogia, Pisa.
L.O.I. = loss on ignition. For further explanation see the Appendix.

Mounts), Upper Phyllites ("Quarziti e Filladi Superiori" — Apuan Alps) and the Risanguigno Formation;

(4) Porphyritic schists ("Scisti porfirici" — Apuan Alps) and Ortano Schists ("Scisti di Ortano" — Elba);

(5) Porphyroids ("Porfiroidi" — Apuan Alps);

(6) Lower Phyllites ("Quarziti e Filladi Inferiori" — Apuan Alps) and rocks from the San Pantaleone outcrop (Pisan Mounts);

(7) metabasites from Boccheggiano, Elba and the Giardino Valley.

In the diagrams, the fields corresponding to these different units are used as references where the fields of the units of uncertain position are matched.

The second set includes the following units of unknown stratigraphic or structural position:

(8) metapelites and metapsammites of the outcrops near Boccheggiano and Serrabottini;

(9) similar rocks found in mines or boreholes of the Boccheggiano—Niccioleta area;

(10) metabasites associated with units (9) and (14);

(11) micaschists;

(12) gneisses;

(13) amphibolites associated with units (11) and (12);

(14) Calamita Schists ("Scisti di Calamita" — Elba) and rocks from the small outcrops near Barabarca and Praticciolo (both on Elba).

Some selected analyses are reported in Tables II and III and amplified in the Appendix.

All the analyses dealt with here are computer-stored and can be obtained on request from one of the authors (F. Saupé).

2. ANALYTICAL RESULTS AND DISCUSSION

2.1. Reference groups

An almost total absence of arkoses (if considered as binary quartz—feldspar mixtures) is conspicuous in the reference groups reported in Figs. 3 and 4. Except in a few quartzites, the sheet-silicates are always abundant and the rocks are shales, sandstones s.s. (quartz and clay minerals only) and graywackes (rocks with ⩾ 15% clay minerals; Pettijohn et al., 1973).

The major distinctive feature, for sediments and metasediments, is the feldspar/(quartz + clay minerals) ratio. Its importance is apparent in Fig. 4 where three parallel bands can be distinguished, corresponding to (1) the Carboniferous; (2) the Buti Group (without the Porphyroids); and (3) the Lower Phyllites.

2.1.1. Permian Red Porphyries. The *Permian Red Porphyries* are pumiceous rhyolites made up of a strongly oxidized microcrystalline groundmass with quartz phenocrysts and lithic fragments. The silica content is very high

TABLE III

Selected representative analyses from the groups of uncertain or disputed position (major elements in %, traces in ppm)

	PTDE 052	PTDE 074	PTDE 079	PTDE 082	PTDE 060	PTPI 085	PTDE 044	PTDE 054	PTPI 127	PTPI 105	PTPI 098
SiO_2	76.30	50.23	66.60	67.21	66.70	68.83	68.12	67.92	66.36	60.62	67.94
Al_2O_3	10.32	26.92	14.39	14.26	12.93	13.22	14.07	15.71	16.40	17.58	15.07
$Fe_2O_3^t$	4.53	7.48	5.43	5.10	3.87	4.54	3.04	5.00	5.58	7.98	5.03
MnO	0.04	0.04	0.07	0.06	0.05	0.04	0.04	0.03	0.08	0.07	0.05
MgO	1.48	2.50	1.48	2.68	2.20	2.90	1.78	1.44	1.76	2.55	1.71
CaO	0.39	—	1.17	0.69	2.52	0.76	2.25	0.42	1.17	0.39	2.04
Na_2O	0.80	1.02	3.62	0.90	1.48	3.99	1.75	0.20	2.54	1.32	2.39
K_2O	2.50	5.78	3.19	3.71	5.14	1.57	4.42	3.30	2.64	3.29	2.80
TiO_2	0.52	0.96	0.83	0.80	0.75	0.72	0.65	0.85	0.92	1.48	0.76
P_2O_5	—	0.11	—	—	0.19	0.12	0.21	—	0.23	0.16	0.05
L.O.I.	3.21	4.49	2.93	3.75	2.81	2.54	3.61	4.69	2.00	3.84	1.11
Total	100.09	99.53	99.71	99.16	98.64	99.23	99.94	99.56	99.68	99.28	98.95
Ba	212	847	—	—	2,210	241	857	3,230	507	778	420
Cr	2,000	134	210	155	88	72	71	1,900	75	156	83
Cu	—	<10	—	—	<10	15	9	—	131	22	<10
Ni	10	22	75	75	43	57	28	39	51	48	45
Sr	46	120	66	92	480	112	212	80	221	290	175
V	—	161	—	—	119	105	95	—	108	332	105
Rb	5	275	108	145	223	52	208	132	16	153	110
Zn	—	—	83	58	—	37	47	—	<10	108	53

The last two letters indicate the origin of the analysis: DE = École des Mines, Saint-Étienne; NA = C.R.P.G., Nancy (K. Govindaraju); PI = Istituto di Mineralogia, Pisa.

L.O.I. = loss on ignition. For further explanation see the Appendix.

and the alkali content very low (Figs. 3—5). Their field never overlaps that of the Porphyroids (for a long time considered Permian) or that of the Porphyritic Schists.

2.1.2. Lower Permian—Carboniferous Groups. The different units assigned to the *Lower Permian—Carboniferous* (San Lorenzo Group, Farma Group, Rio Marina Formation) have similar mineralogical and petrographic compositions. The metasandstones of the San Lorenzo Group have a blastopsammitic texture and contain quartz clasts, lithic fragments, muscovite, subordinate chlorite and some plagioclase recrystallized into a quartz—sericite association; accessory minerals are tourmaline, zircon, apatite, as well as graphite, leucoxene and sulfides. The Farma metasandstones, compared to the San Lorenzo sandstone, contain more calcite, chlorite and K-feldspar, with chloritoid sometimes present. The phyllites of both groups cannot be distinguished. The Lower Permian—Carboniferous rocks of Tuscany underwent a low-grade metamorphism (Azzaro et al., 1975; Deschamps, 1980).

The chemical composition of the San Lorenzo and Farma Groups is fairly homogeneous. The rocks are shales and sandstones s.s., almost devoid of feldspars (Figs. 3 and 4). Illite was the dominating original clay mineral. Kaolinite and/or smectites were far from negligible (Fig. 5), and permitted

PTPI 099	PTNA 251	PTNA 245	PTNA 239	PTNA 234	PTNA 229	PTPI 905	PTPI 906	PTPI 916	PTNA 218	PTPI 917
67.47	83.51	62.77	59.42	72.32	81.63	43.57	44.43	46.81	45.93	47.15
15.14	7.67	17.51	23.77	14.01	9.63	16.07	16.36	14.56	14.18	15.38
5.61	4.04	6.21	3.13	3.40	1.61	10.37	10.80	12.83	12.31	14.19
0.08	0.02	0.05	0.03	0.01	—	0.17	0.16	0.15	0.21	0.22
2.11	0.32	2.40	0.90	0.75	0.62	7.77	6.65	5.74	5.58	6.35
3.19	—	0.07	0.92	0.47	0.20	7.39	7.06	5.88	9.18	9.23
1.73	0.14	0.48	4.19	4.45	2.33	1.78	3.41	2.10	1.06	2.42
1.69	1.30	4.57	2.84	2.30	2.08	1.11	0.44	0.95	2.73	0.94
0.85	0.31	0.85	1.58	0.48	0.67	1.17	1.37	2.28	2.25	1.40
0.18	—	0.15	0.29	—	—	0.21	0.23	0.28	0.54	0.11
1.64	1.75	3.36	2.35	1.02	1.20	10.37	9.09	8.42	5.07	2.60
99.69	99.06	98.42	99.42	99.21	99.97	99.98	100.00	100.00	99.04	99.99
243	303	574	817	1,073	396	—	—	—	578	—
93	43	94	67	32	49	—	—	—	240	—
13	26	133	148	<10	<10	—	—	—	156	—
67	46	53	34	14	45	—	—	—	99	—
190	65	76	192	105	98	—	—	—	191	—
122	104	124	125	90	81	—	—	—	213	—
74	48	219	81	109	104	—	—	—	152	—
90	—	—	—	—	—	—	—	—	—	—

the formation of the pyrophyllite described on Elba (Deschamps, 1980). Some rocks have higher chlorite content, as can be seen in the diagram of Fig. 9. All these rocks are very mature, with the exception of a few rocks of the Farma Group. These exceptions have a noteworthy detrital albite content, with a Na/Al ratio approaching that of graywackes (Fig. 5). This reflects a difference in the depositional environment: it is frankly marine and flysch-like for the Farma Group, and continental to marine-deltaic for the San Lorenzo Group (Bagnoli et al., 1979).

The degree of the Si/Al substitution in the phengites and the existence of pyrophyllite in the Carboniferous Rio Marina Formation indicate the following P—T conditions for the Alpine metamorphism: T = 345—450°C and P = 2 kbar (Deschamps, 1980; Deschamps et al., 1983).

2.1.3. Buti Group l.s. The *Buti Phyllites* (= Buti Group s.s.) and the *Upper Phyllites* consist of finely alternating quartzites and phyllites, with interbedded Fe-rich carbonates or hematite levels and minor metagraywackes. The *Risanguigno Formation* (Puxeddu et al., 1979), included in the Buti Group l.s., is made up of alternating quartzites, phyllites, dolostones and jaspers. All the rocks of the Buti Group l.s. underwent a low-grade metamorphism, generally in the chlorite zone. The rare occurrence of biotite

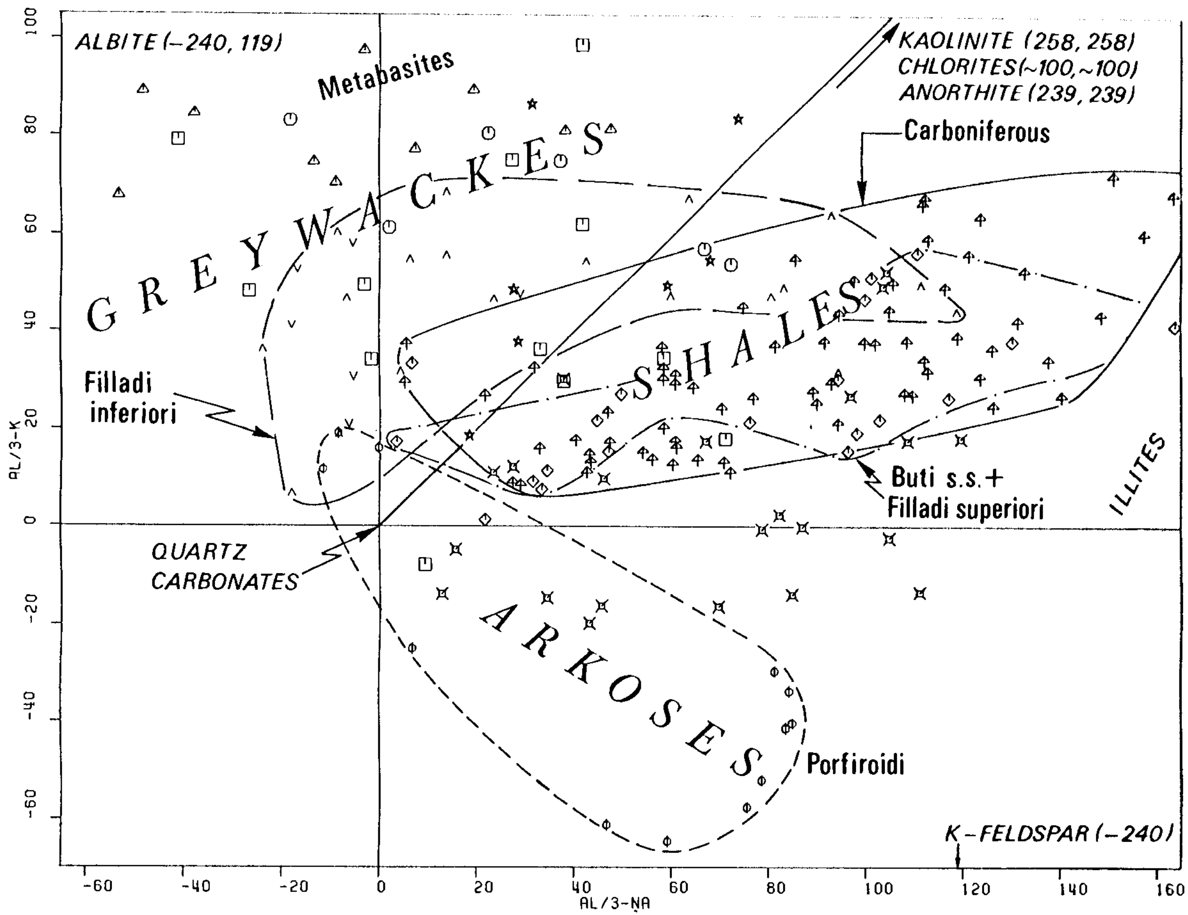


Fig. 3. (Al/3—K) vs. (Al/3—Na) diagram for the reference groups (same legend as Fig. 4).

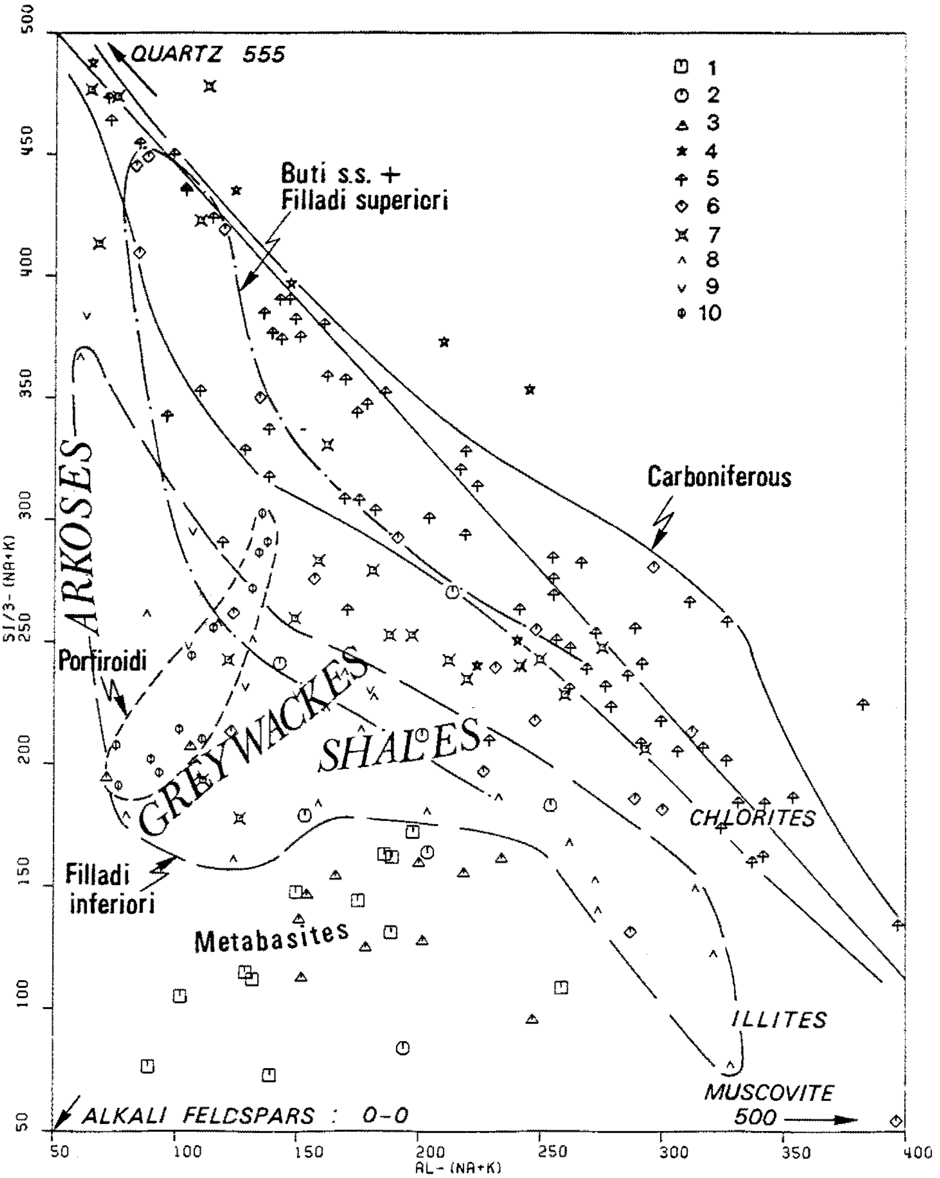


Fig. 4. [Si/3—(Na + K)] vs. [Al—(Na + K)] diagram for the reference groups (*1* = Metabasites (Elba and Niccioleta); *2* = Metabasites (amphibolites associated with Gneisses and Micaschists); *3* = Metabasites (Apuan Alps/Valle del Giardino); *4* = Red Porphyries; *5* = Carboniferous; *6* = Buti Phyllites, Upper Phyllites and Risanguigno Formation; *7* = Porphyritic Schists and Ortano Schists; *8* = Lower Phyllites; *9* = Lower Phyllites, var. S. Pantaleone; *10* = Porphyroids).

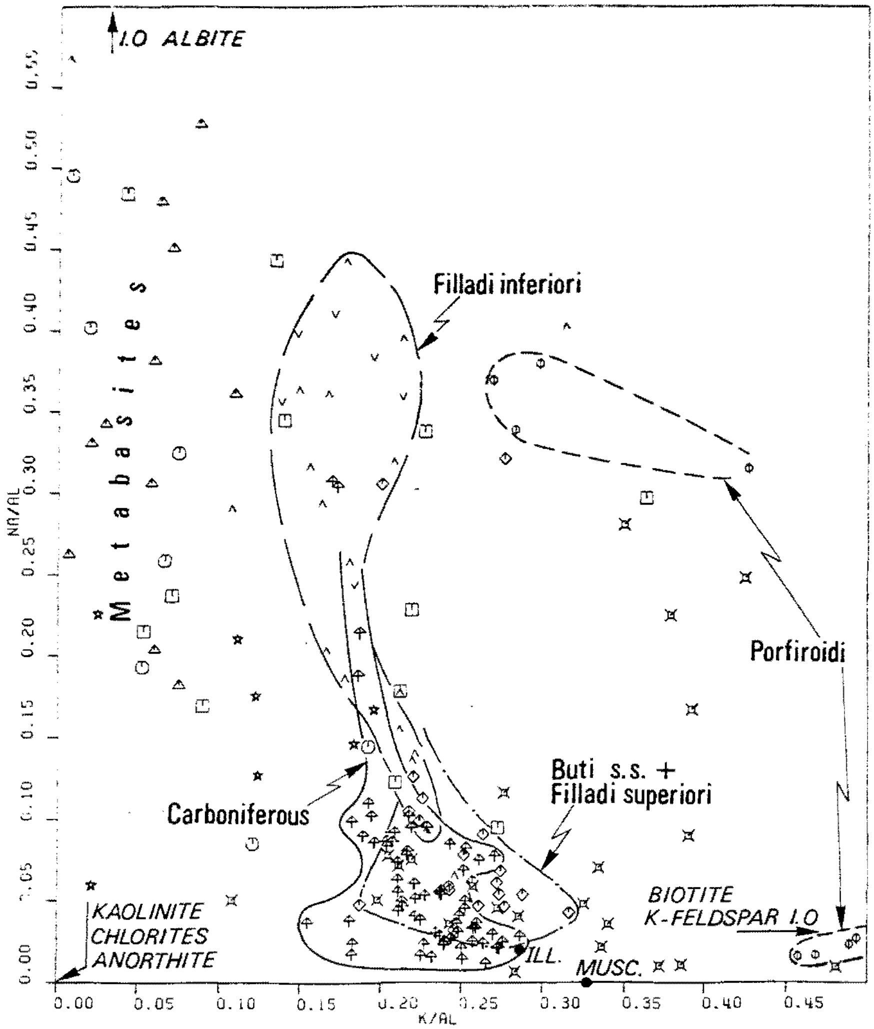


Fig. 5. (Na/Al) vs. (K/Al) diagrams for the reference groups (same legend as Fig. 4).

indicates that the biotite isograde was locally attained. All these rocks have chemical compositions of shales and sandstones (Fig. 4). Despite a markedly higher alkali content than the Permo-Carboniferous rocks, the rocks of the Buti Group l.s. are the metamorphic equivalents of extremely mature sediments, with a minor albite content. Illite was the dominating clay mineral (Fig. 5), with subordinate chlorite.

The *Porphyroids* are metavolcanites of acidic to intermediate composition, with abundant microcline and/or albite porphyroclasts, dispersed in a matrix of quartz and muscovite, with subordinate chlorite. Two subsets of Porphyroids can be distinguished in Figs. 3 and 5: (1) sodic–potassic rhyolites, mainly from the Apuan Alps; and (2) potassic rhyolites, mainly from Ortano (Elba Island).

The *Porphyritic Schists*, and the similar *Ortano Schists* are granolepidoblastic—blastoporphyritic rocks principally made up of quartz and muscovite. Subordinate minerals include albite, microcline, chlorite, chloritoid, biotite or stilpnomelane; Fe-rich carbonates or Fe-oxides are sometimes abundant; hematite layers or oolites may also be present; accessories are tourmaline, leucoxene, apatite and zircon. Levels of black phyllites often contain graphite and sulfides. Microcline porphyroclasts can be abundant in some samples. Chemically, the Porphyritic Schists and the Ortano Schists appear to be mixtures of quartzo—illitic shaly materials and Porphyroids. The quartz—illite shales, similar to the Buti Phyllites and sometimes trending towards quartzites, are easily distinguished in Fig. 4. The trend towards the two subsets of Porphyroids, mentioned above, is noticeable in Figs. 3 and 5.

2.1.4. Lower Phyllites Group. The *Lower Phyllites* are metagraywackes and albite-bearing quartzitic phyllites. The former consist of quartz, albite, rare microcline, muscovite, chlorite and accessories (ilmenite, leucoxene, sulfides, graphite, tourmaline, apatite and zircon) and have a granolepidoblastic texture. The quartzitic phyllites contain quartz, muscovite and chlorite and the same accessories as the metagraywackes. The rare occurrence of biotite, coexisting with muscovite, has been observed in samples from drillings in southern Tuscany (Gianelli et al., 1978). The Lower Phyllites have the lowest maturity of all the sediments discussed here. According to Fig. 4, they also have the highest feldspar content, are predominantly graywackes and shales, and include a few arkoses. The original clay minerals are illite and chlorite. Chlorites control the composition (Figs. 5 and 13) and derive from a partial contribution of basic volcanic materials. Compared to typical graywackes, the graywackes of the Lower Phyllites Group are Na-deficient.

2.2. Groups of uncertain or disputed position

2.2.1. Boccheggiano Formation l.s. The rocks of the outcrops are coarse-grained schist with quartz-clasts in a quartz—sericite matrix; some metaconglomerates contain quartz pebbles of up to 2 cm. In all diagrams, these rocks plot exactly in the field of the Tuscan Carboniferous rocks.

The rocks coming from boreholes can be divided into two associations:

(I) Carbonatic quartzites, phyllites, dolostones, minor anhydrite, graphitic schists, with sulfide orebodies and basic metatuffites. The quartzites and phyllites are fine- to medium-grained lepidoblastic rocks containing variable amounts of quartz, muscovite, chlorite and Fe-rich carbonates.

(II) Albite—chlorite schists, dolomitic marbles, anhydrite (containing interlayered dolostone levels and bordered by quartz—muscovite schists) and sulfide orebodies. Skarns are intercalated between schists and anhydrite.

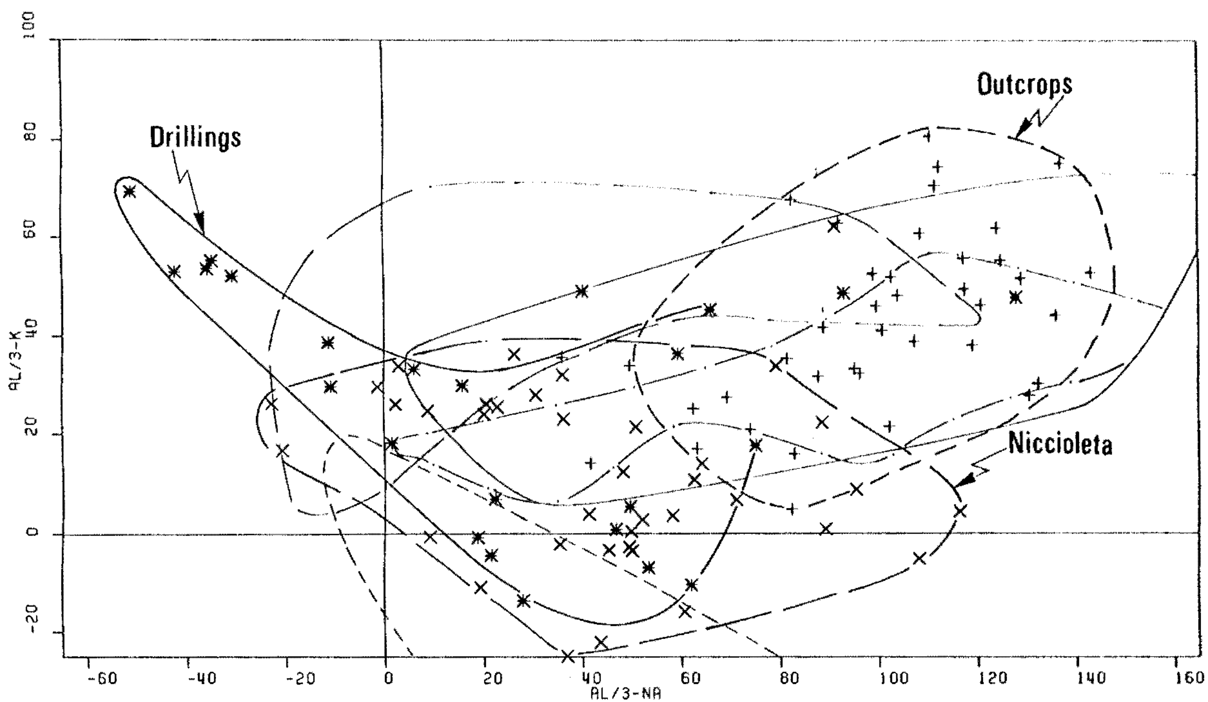


Fig. 6. (Al/3—K) vs. (Al/3—Na) diagram for the Boccheggiano Formation (same legend as Fig. 7; *coloured contours* same reference contours as in Fig. 3).

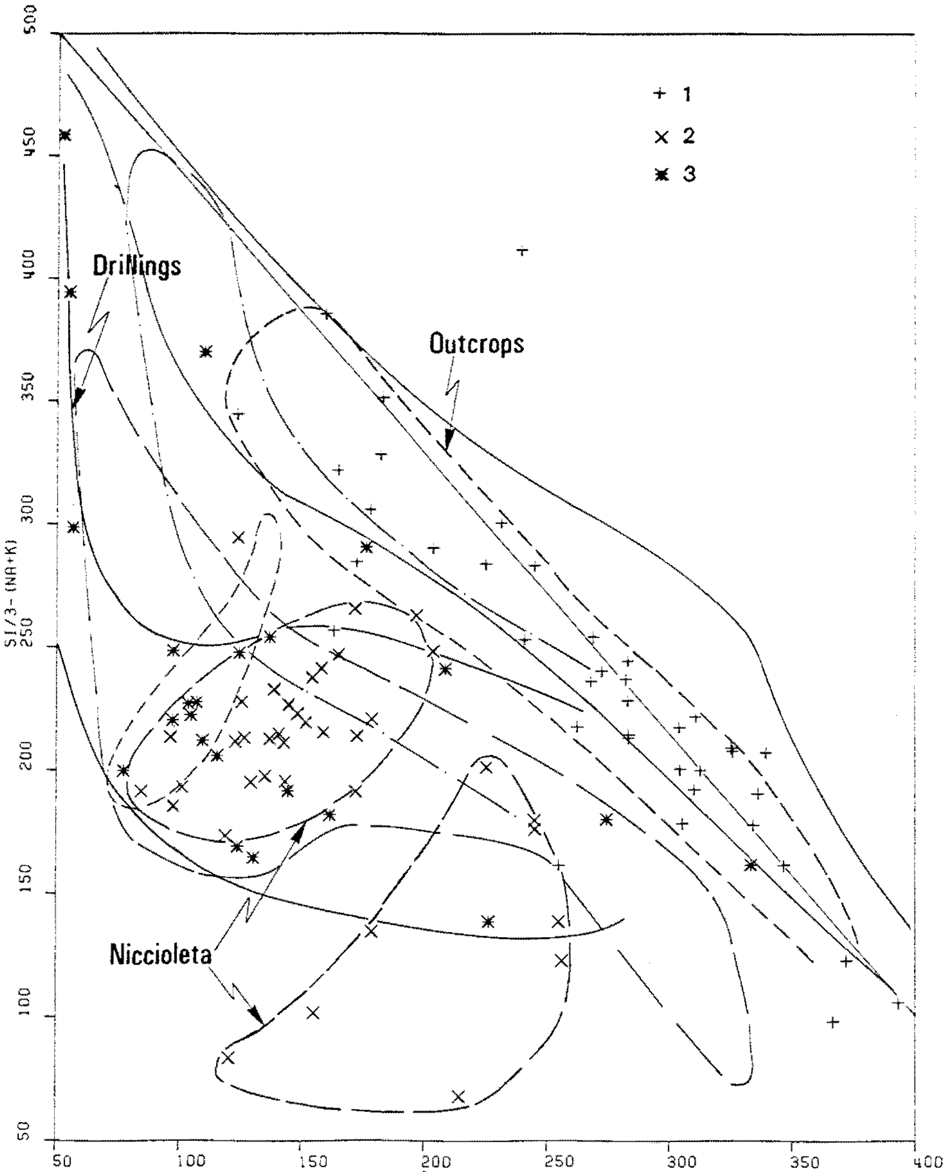


Fig. 7. [Si/3—(Na + K)] vs. [Al—(Na + K)] diagram for the Boccheggiano Formation (*1* = outcrops; *2* = drillings; *3* = Niccioleta mine). (*Coloured contours* same reference contours as in Fig. 4).

The skarns contain andradite, clinopyroxene or epidote, and derive from anhydrite, dolostone or schist respectively (Déchomets, 1983). A potassium-metasomatism, testified by late adularia, developed in the phyllites.

Underneath the worked orebodies, albite—chlorite schists are the prevailing rock, as shown by drilling. These schists are fine-grained granolepido-

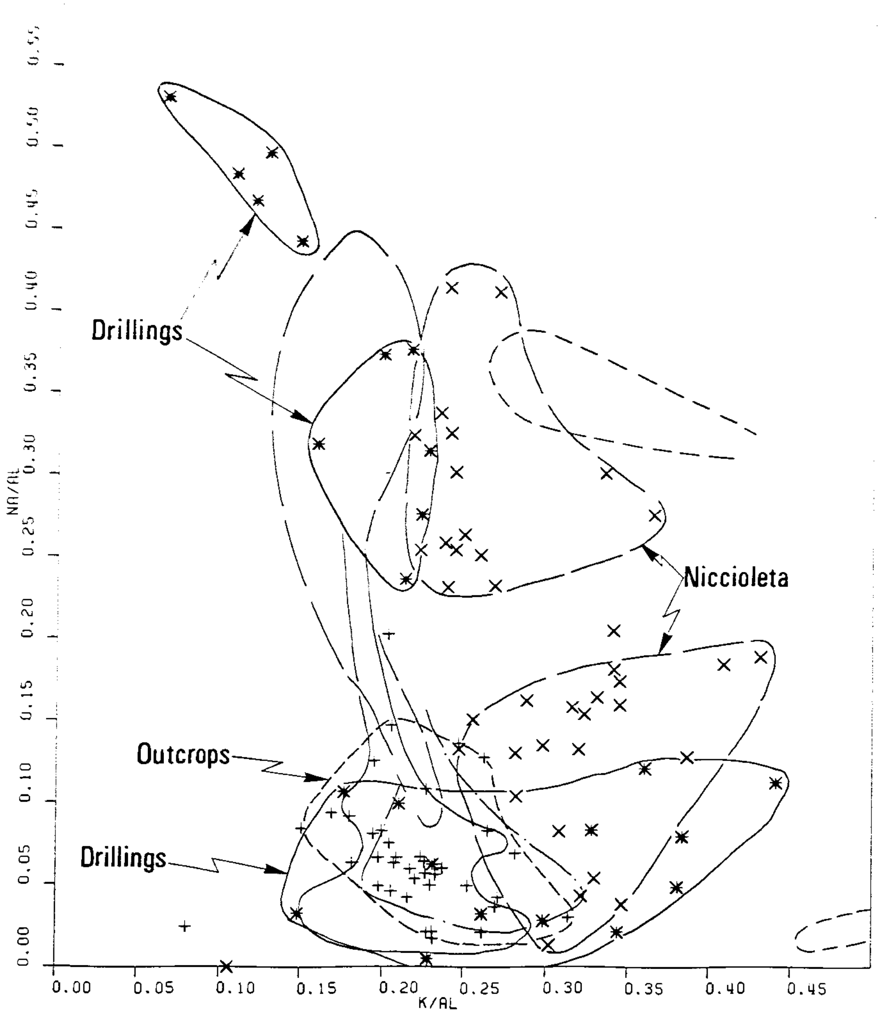


Fig. 8. (Na/Al) vs. (K/Al) diagram for the Boccheggiano Formation (same legend as Fig. 7; *coloured contours* same reference contours as in Fig. 5).

blastic rocks, made up of quartz and chlorite with minor muscovite, and of carbonates, ilmenite, apatite, graphite and sulfides. Rocks of somewhat similar mineralogical composition, containing albite, sphene and larger amounts of chlorite and ilmenite, are considered basic metatuffites.

In the four diagrams of Figs. 6—9, the rocks of the Boccheggiano Formation l.s. have been divided into three classes: (1) those from the surface, identical with Carboniferous formations and therefore considered as a Carboniferous unit; (2) those from boreholes; and (3) those from the Niccioleta mine. The phyllites from class (2) have a wide range of composition reflect-

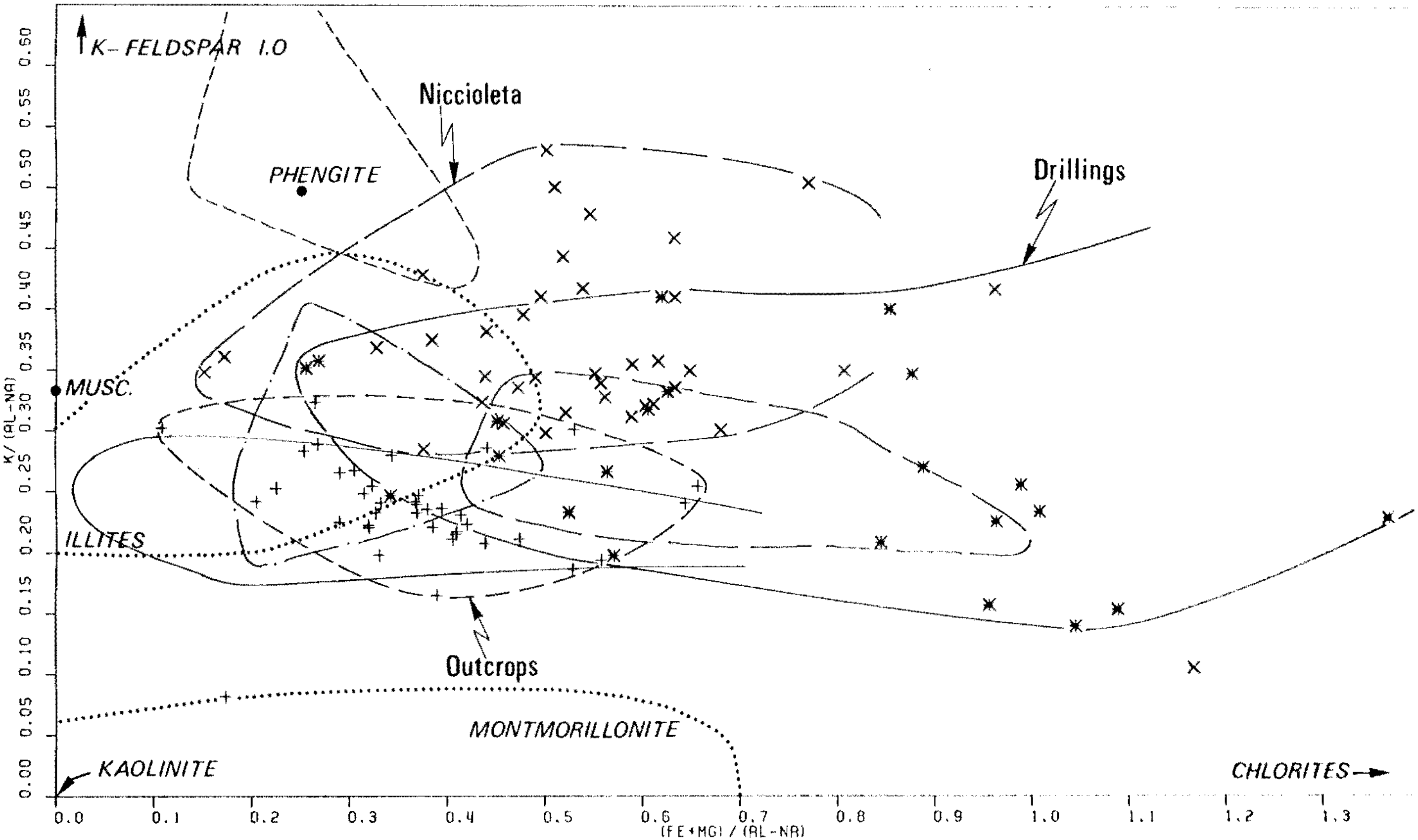


Fig. 9. [K/(Al—Na)] vs. [(Fe + Mg)/(Al—Na)] diagram for the Boccheggiano Formation (same legend as Fig. 7; *coloured reference contours: full* = Carboniferous; *points* and *dashes* = Buti s.s. and Upper Phyllites; *long dashes* = Lower Phyllites; *short dashes* = Porphyroids).

ing their petrographic variability, quite normal with respect to the depth of the drillholes. The phyllites of the upper parts of the wells correspond to the petrographical association (I). In the diagram of Fig. 7, these rocks are situated in a quartzite—shale range, similar to that of the rocks from the Buti Group l.s. In the diagrams of Figs. 6 and 8 they show higher K contents, like part of the Porphyritic Schists. Other features, however, such as higher Ti and lower Ba contents, clearly distinguish between the rocks of the upper parts of the boreholes and the Porphyritic Schists. Thus, the rocks under discussion should rather be compared with the Upper Phyllites, and their higher alkali content explained by a sedimentation or by diagenetic reactions in a restricted environment, as suggested by the presence of dolomite. The rocks from the deeper parts of the boreholes [part of class (2)] and from same depths in the Niccioleta mine [class (3)] are albite—chlorite schists: petrographical association (II). In all diagrams (Figs. 6—8) their representative points fall in the graywacke fields, as did the Lower Phyllites. The deepest samples have particularly high Na and (Fe + Mg) values, compared to the Lower Phyllites. Numerous samples from the Niccioleta mine have high K/Al ratios (Fig. 8). In the diagram of Fig. 7, some of these samples fall in a low-SiO_2 zone and contain little free SiO_2 (low values of (Si/3—(Na + K)). These samples are Ba-rich (1000—2200 ppm) and underwent a strong adularization. Most non-adularized samples coincide with the albite—chlorite schists from the boreholes and are similar to the graywackes of the Lower Phyllites. The quartz—muscovite schists, found near the anhydrite, have low Na/Al and high K/Al ratios, features that could also be related to a sedimentation in an evaporitic environment with an immature detrital contribution. As opposed to evaporitic conditions prevailing over a carbonate platform, there is no Mg excess induced by the Mg sheet-silicates (Moine et al., 1981). Traces of Mg clays are locally found at Niccioleta within the anhydrite only (Déchomets, 1983). In conclusion, the phyllites in the upper part of the Boccheggiano Formation are associated mainly with dolostones, and are similar to the Upper Phyllites. In the intermediate (mine) and lower part, the phyllites are associated with anhydrite and little dolomite, and closely resemble the Lower Phyllites.

2.2.2. Micaschist group. These rocks are polymetamorphic garnet-bearing plagioclase micaschists (Gianelli and Puxeddu, 1979). The almandine-rich garnet and the plagioclases (26% An) are pre-tectonic, as shown by a relict helicitic texture. The rare occurrence of kinked, pre-tectonic biotite, coexisting with garnet, indicates a crystallization in a low-grade garnet zone. The following reaction can be assumed (Thompson and Norton, 1968):

$$\text{chlorite + muscovite + quartz} \rightleftharpoons \text{almandine + biotite} + H_2O$$

In places, post-tectonic andalusite, cordierite and biotite develop in equilibrium with quartz, according to the reaction:

$$\text{chlorite + muscovite + quartz} \rightleftharpoons \text{cordierite + biotite + andalusite} + H_2O$$

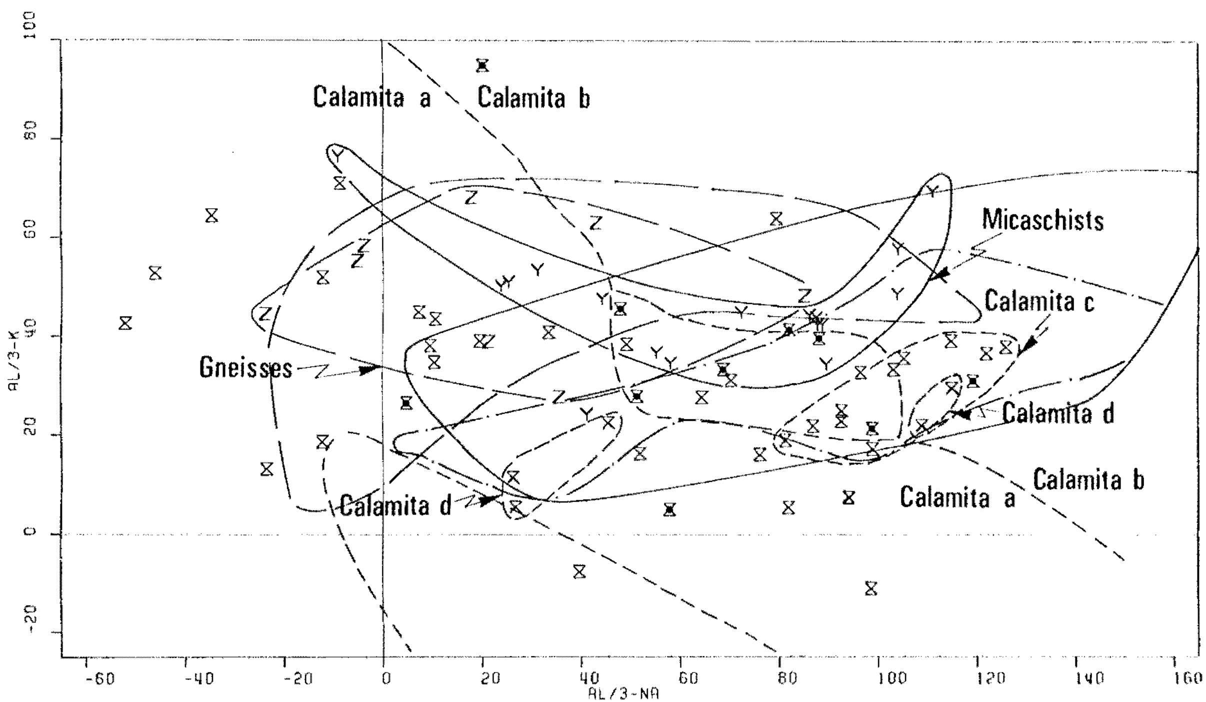


Fig. 10. (Al/3—K) vs. (Al/3—Na) diagram for the Micaschist Group, the Gneisses and the Scisti di Calamita (same legend as Fig. 11; *coloured contours* same reference contours as in Fig. 3).

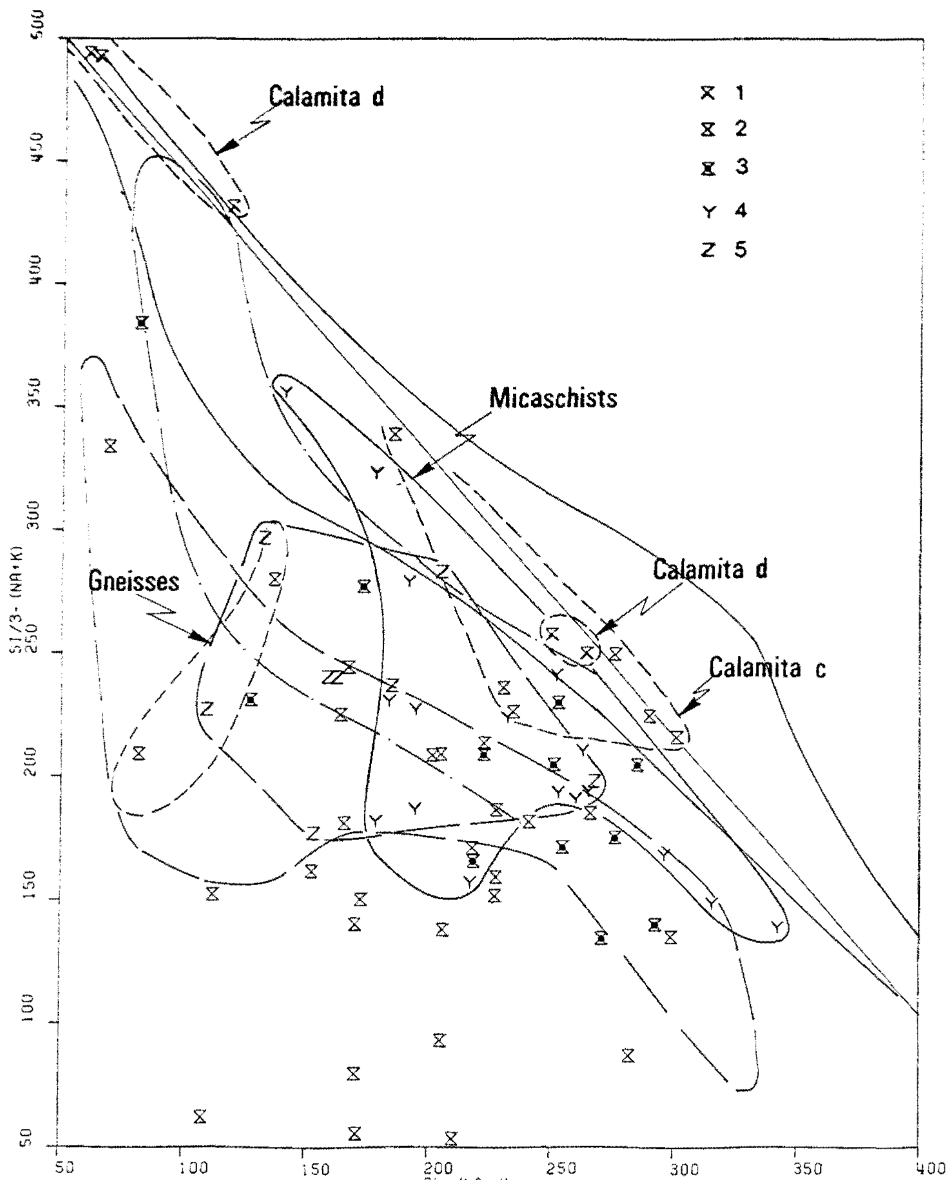


Fig. 11. [Si/3—(Na + K)] vs. [Al—(Na + K)] diagram for the Micaschist Group, the Gneisses and the Scisti di Calamita (*1* = Calamita Schists, subgroup d; *2* = Calamita Schists, groups a and c; *3* = Calamita Schists, group b; *4* = Micaschists; *5* = Gneisses (*coloured contours* same reference contours as in Fig. 4)).

This reaction corresponds to temperatures of 500—550°C for pressures between 0.5 and 4 kbar (Hirschberg and Winkler, 1968). The Rb/Sr dating of the muscovite gives a Hercynian age for this mineral (Del Moro et al., 1982). A post-tectonic metamorphism developed albite rims around the

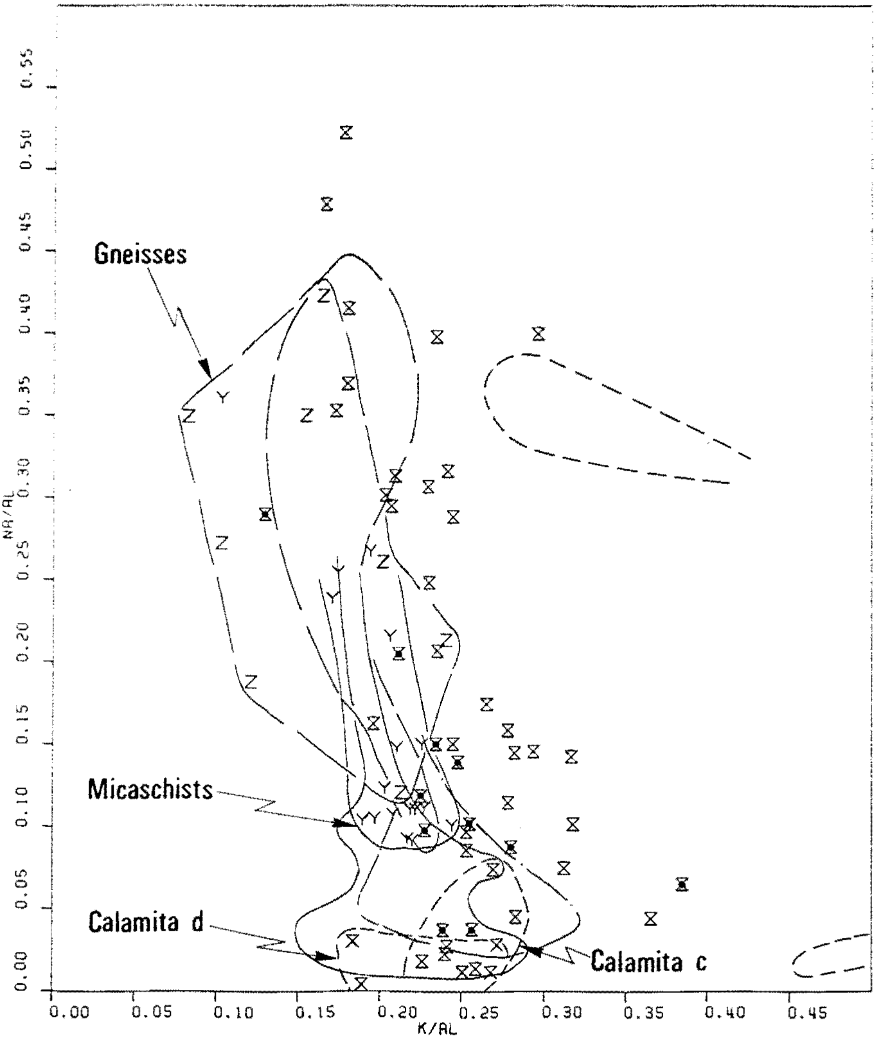


Fig. 12. (Na/Al) vs. (K/Al) diagram for the Micaschist Group, the Gneisses and the Scisti di Calamita (same legend as Fig. 11; *coloured contours* same reference as in Fig. 5).

older plagioclase and a younger poikiloblastic garnet. A polyphase metamorphism, with *P*—*T* conditions extending from intermediate-*P*—*T* to high-*T*—low-*P* conditions, is well documented for many Hercynian regions (see, e.g., Bard and Rambeloson, 1973; Boriani et al., 1974; Amodio-Morelli et al., 1976; Seyler, 1977; Ricci and Sabatini, 1978).

The Micaschists have chemical compositions of shales and quartz-rich shales and have quartz:clay:feldspar ratios similar to those of the Buti Group, sometimes trending towards the fields of the graywackes and of the shales of the Lower Phyllites (Fig. 11). Taking in account the sedimentary maturity (Figs. 10 and 12), the Micaschists show even a stronger similarity to some

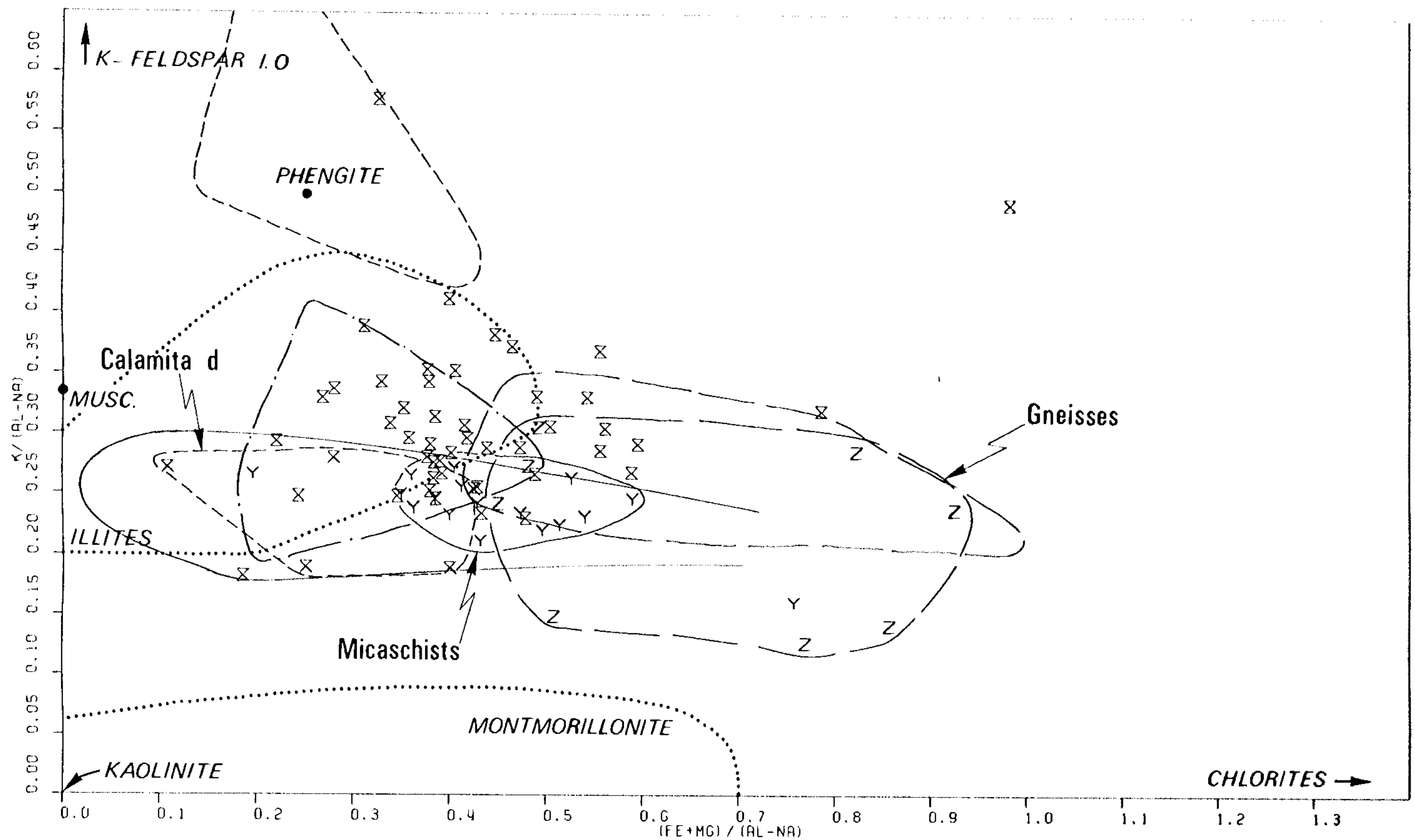


Fig. 13. [K/(Al—Na)] vs. [(Fe + Mg)/(Al—Na)] diagram for the Micaschist Group, the Gneisses and the Scisti di Calamita (same legend as Fig. 11; *coloured contours* same reference contours as in Fig. 9).

shales and graywackes of the Lower Phyllites: the Micaschists derive from sediments comparatively richer in quartz and poorer in Na and chlorites.

2.2.3. Gneisses. The *gneisses* of the *Sasso 22* well are fine-grained, granoblastic rocks showing alternating quartz and muscovite—biotite layers. A polyphase history is demonstrated by the coexistence of different metamorphic mineral assemblages. The oldest assemblage is that of quartz, plagioclase (35—40% An), biotite ± muscovite. The plagioclase and biotite often show kink bands and recrystallize into a later fine-grained aggregate of biotite and plagioclase, in equilibrium with quartz, cordierite and andalusite. In the deepest samples, muscovite reacts with quartz to give K-feldspar and Al_2SiO_5 (andalusite and/or sillimanite). In places, these rocks underwent a retrograde metamorphism with the following transformations: (1) biotite → chlorite; (2) plagioclase → albite; and (3) cordierite → muscovite. The gneisses probably represent a pre-Alpine unit that underwent a polyphase Hercynian metamorphism, similar to that undergone by the micaschists. The high-T—low-P phase reached the high grade, as shown by the breakdown of muscovite and formation of K-feldspar and sillimanite. This assemblage indicates a temperature > 600°C in a pressure range of 2—2.5 kbar (Evans, 1965; Chatterjee and Johannes, 1974). The chemical composition of these rocks classifies them as metagraywackes and the representative points fall in the fields of the Lower Phyllites (Figs. 10—12). However, the composition of the gneisses is more variable than that of the graywackes of the Lower Phyllites and the former have a higher chlorite content than the latter. The gneisses are similar to the micaschists but have higher Na and Mg contents (see Bertini et al., 1980).

2.2.4. Calamita Schist. The Calamita Schists are a rather monotonous unit, which is difficult to subdivide on field evidence only. Four groups of samples can be established on the basis of petrographic and geochemical data, and a tendency towards some geographical grouping can be observed if the sampling stations for the different groups are plotted on a map. Barberi et al. (1967) proposed several lithostratigraphic units and an outline distribution map of these units. The respective stratigraphic position of the four groups is still unknown, except for group d which overlies the other three.

Group d includes the muscovite—biotite quartzites of the type locality Barabarca (Calamita Promontory, Elba) and the micaschists and muscovite—biotite quartzites of the locality Praticciolo (Calamita Promontory, Elba). These formations were thought to rest on the Calamita Schists of the basement with a slight unconformity (Barberi et al., 1967). In fact, they seem rather to be interlayered with the Calamita Schists (C. Marignac, unpublished data, 1980). The chemical composition of these rocks is surprisingly similar to that of the Carboniferous sandstones and shales (Figs. 10—12).

Group c: on top of Mount Calamita (in the centre of the Calamita Promontory), and near the shore of Lido (NW of the promontory) occur sheet-silicate-rich micaschists, made up of muscovite, biotite and andalusite. Their chemical composition is that of shales and resembles that of the Carboniferous rocks. Some features indicate a possible analogy with the Upper Phyllites (of the Buti Group l.s.). (See Figs. 11 and 12, compared to Figs. 4 and 5, respectively.)

Group b. The muscovite- and biotite-rich gneisses of the Pareti area (between Capoliveri and the Calamita open pit) and of the Buzzancone area (NE of the Calamita Promontory) frequently contain andalusite porphyroblasts and thin layers of metabasites and metasedimentary carbonate rocks. Their chemical composition is similar to that of the Buti and Lower Phyllites Groups (Fig. 11). A clear K enrichment (Figs. 10—12), compared to the reference groups, shows that group b is more closely related to the Buti Group than to the Lower Phyllites.

Group a. Muscovite—biotite gneisses, that are graphitic and frequently contain albite porphyroblasts, occur in the eastern part of the promontory (Poggio Turco, Ginevro). Andalusite and cordierite are described in the "silico-aluminous hornfelses" from the Fe deposits of Ginevro and Sassi Neri (Dimanche, 1971). In the diagram of Fig. 11, the representative points of these rocks plot in the field of the shales of the Lower Phyllites Group, with only a few points approaching the graywacke field. Several points correspond to very low [Si/3—(Na + K)] values, i.e. to rocks poor in quartz. This trend effectively exists, but is enhanced by: (1) a few samples, collected just underneath the thrust plane separating the Triassic carbonatic host-rock of the Calamita Fe deposit, from the underlying Calamita Schists; and (2) by older, possibly less reliable analyses. The diagrams of Figs. 10 and 12 reveal higher Na contents, related to albite, and a chemical composition approaching those of the Lower Phyllites. These rocks are not graywackes, but albite-bearing shales recalling the micaschists. The highest Na contents correspond to quartz-poor rocks. A metasomatic origin of these features seems plausible: the albitization of muscovite, by reaction with solutions related to the granitic intrusion, could well lead to rocks of this type, according to the reaction:

$$3Na^{+} + KAl_2(AlSi_3)O_{10}(OH)_2 + 6SiO_{2(aq)} \rightleftharpoons 3NaAlSi_3O_8 + 2H^{+} + K^{+}$$

2.3. *Metabasites*

Four groups of metabasites can be distinguished according to their geographic location, a grouping that also corresponds to different host-rocks and, in part, to different chemical compositions.

2.3.1. Metabasites from the Apuan Alps. The metabasites of the Giardino Valley have a blastophitic to granolepidoblastic texture and are made up of quartz, plagioclase, chlorite, carbonates, ilmenite, leucoxene, sphene, apatite and rare epidote. A metamorphic recrystallization under a high CO_2 partial pressure is suggested by the rarity of epidote and of other Ca-silicates.

2.3.2. *Metabasites from Niccioleta.* These rocks do not differ substantially from the Giardino Valley metabasites, except for the existence of biotite and amphibole in places.

2.3.3. *Metabasites from Elba.* These rocks have granoblastic to nematoblastic texture and are made up of andesinic plagioclase (30—31% An in general, and up to 70% An in the amphibolite of Cala del Remaiolo, according to Barberi et al., 1967), tremolite—actinolite, sphene, ilmenite and apatite. They are associated with muscovite—biotite schists (Calamita Schists, group b), and with clinopyroxene—grossularite—felses (Barberi et al., 1967; Deschamps, 1980). This mesoscopic feature (thin amphibolite interbedded within phyllites and hornfelses) is analogous to the succession of metavolcanites, shales and carbonatic—sulfatic rocks present in the mines of Niccioleta and in the deepest part of the Solmine drillholes.

2.3.4. *Amphibolites interlayered in the gneisses.* The amphibolites in the gneisses contain green hornblende, plagioclase (40—50% An), some biotite, ilmenite and sulfides. Accessory minerals are apatite, sphene and tourmaline.

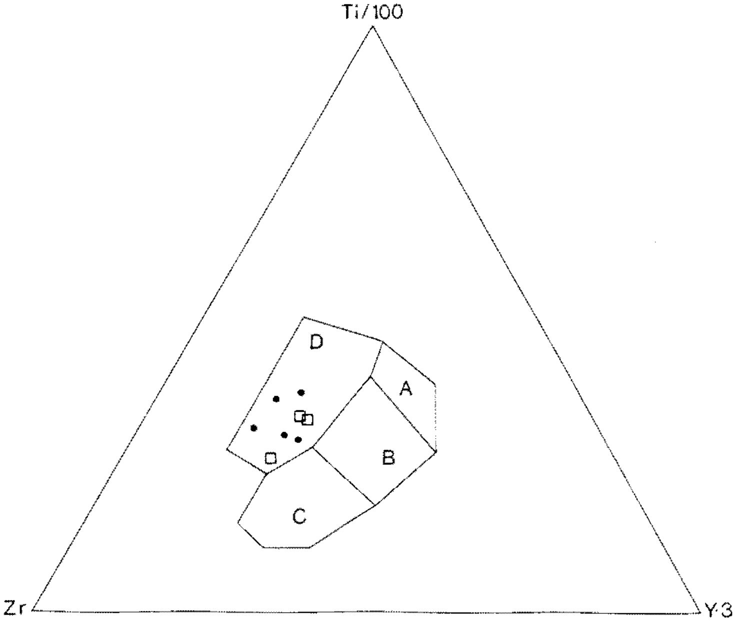


Fig. 14. Ti/100—Zr—Y • 3 diagram for the Tuscan Paleozoic metabasites (*dots* = metabasites from Niccioleta; *squares* = metabasites from Elba). (*A* + *B*) = low-K tholeiites; *B* = ocean-floor basalts; (*B* + *C*) = calcalkalibasalts; *D* = within-plate basalts.

This mineral association sometimes recrystallizes in a low-temperature assemblage of actinolite, albite and chlorite.

2.3.5. Geotectonic position of the metabasites. In a previous paper (Gianelli and Puxeddu, 1979) it was shown that the metabasites of the Giardino Valley are "within-plate basalts" (WPB), with a weak tholeiitic or a transitional affinity; those of the Boccheggiano Formation are also WPB, trending, however, towards the alkali basalts (Gianelli and Puxeddu, 1979). The three analyzed amphibolites from the Calamita Complex show a striking analogy with the samples from Boccheggiano and also fall in the WPB field in a Ti/100—Zr—Y · 3 diagram (Pearce and Cann, 1973) (Fig. 14). It has been shown that this diagram often fails to discriminate between WPB and OFB ("ocean-floor basalts"), as some continental tholeiites plot in the OFB field (Zeck and Morthorst, 1982, and related bibliography). However, both the alkaline affinity of the three samples and their chemical similarity with the metabasites from the Boccheggiano Formation s.s., permit the use of the Ti/100—Y · 3—Nb diagram. As opposed to the above-mentioned rocks, the amphibolites have a marked tholeiitic affinity: three samples out of five have Y/Nb > 5. Furthermore, their Ti, Zr, Y and Nb values closely fit with the average values for the OFB (Pearce and Cann, 1973; Table I). The distinction into two groups is confirmed by a plot in a TiO_2 vs. Y/Nb diagram (Pearce and Cann, 1973; Fig. 15).

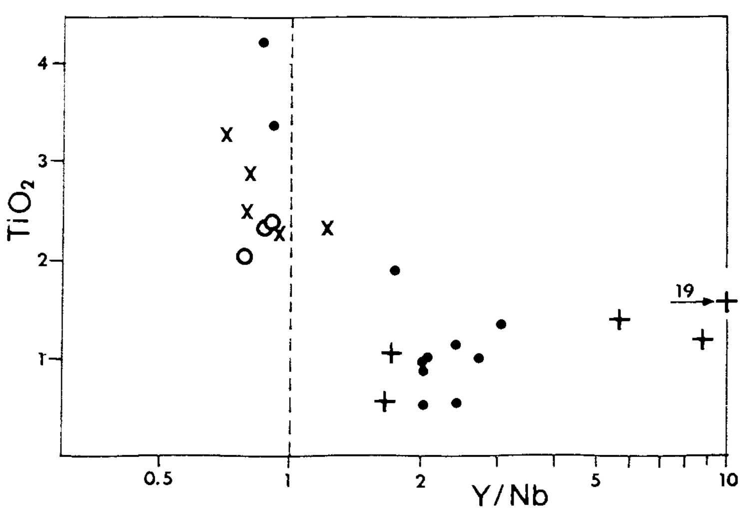


Fig. 15. Ti vs. (Y/Nb) diagram for the Tuscan Paleozoic metabasites (*dots* = metabasites from the Apuan Alps; *diagonal crosses* = metabasites from Niccioleta; *open circles* = metabasites from Elba; *crosses* = amphibolites associated with Gneisses and Micaschists).

3. CONCLUSIONS

The following results, listed in stratigraphical sequence, were obtained from comparison of the geochemical compositions of Paleozoic Tuscan Formations. The correlation diagram (Fig. 2) summarizes these results graphically.

(1) The *Permian Red Porphyries* differ chemically from the Porphyroids and from the Porphyritic Schists of the Buti Group and thus cannot belong to the same lithostratigraphic unit. The Red Porphyries have been compared with similar, better developed volcanic sequences of Permian age, well known in the Southern Alps, Provence, Corsica and Sardinia (Bagnoli et al., 1979; Gianelli and Puxeddu, 1979).

(2) The Carboniferous rocks are generally very mature and homogeneous shelf sediments, well singled out in the diagrams used. The *Farma Group* also includes less mature sediments, in agreement with the flyschoid character of this unit. It is noteworthy that, in all the chemical diagrams, the fields of the Carboniferous rocks show only minor overlapping with the fields of the other Tuscan Paleozoic rocks. This result, and the petrographic analogies already emphasized by Bagnoli et al. (1980), permit us to attribute to the Carboniferous the metamorphic outcrops of the Roman Hills, of the Boccheggiano—Serrabottini area and the core samples of the Mount Amiata boreholes.

(3) The rocks of the *Buti Phyllites* and the *Upper Phyllites* are also shelf sediments, similar to, but less mature than the Carboniferous. They show chemical features transitional towards those of the Porphyritic Schists.

(4) The *Porphyroids* from the two zones of occurrence also differ in their alkali content: those of the Apuan Alps are rich in both Na and K, whereas only K-rich metavolcanites are present on Elba. This could suggest the existence of two different volcanic sequences within the Porphyroids, but too few data have been gathered so far to confirm this hypothesis.

(5) The *Porphyritic Schists* and the analogous *Ortano Schists* are reworked Porphyroids. Vai (1972) referred the Porphyritic Schists to a flysch-like sequence of Lower—Middle Carboniferous age and considered the Upper Silurian Orthoceras Dolostone as olistoliths within the sequence; but the presence, among the Porphyritic Schists, of phyllites derived from quartz—illite shales similar to the Buti Phyllites indicates that the Porphyritic Schists are shelf sediments deposited together with the Orthoceras Dolostones in a near-shore marine environment.

(6) The geochemical features of the *Buti Group* indicate a mixture of shelf sediments and acidic (rhyolitic to rhyodacitic) volcanites. The deposition of the Buti Group in shallow-water intracratonic seas of varied physiography was suggested by Gianelli and Puxeddu (1978). Lithologic associations of Silurian—Devonian age, similar to that of the Buti Group, were described for the Cantabrian Belt by Truyols et al. (1974), for the Mouthoumet Massif by Ovtracht (1967a), for the Northern Pyrenean Belt by Ovtracht (1967b),

for Sardinia by Carmignani et al. (1978a, 1979) and for Corsica by Baudelot et al. (1976).

(7) The *Lower Phyllites* are sediments of low maturity associated with metabasites. A deposition in a marine environment deeper than that of the Buti Group can be suggested.

(8) The lithostratigraphic position of the *Boccheggiano Formation* s.s. is not definitively settled, but the geochemical and petrographic features allow two different interpretations of its composition and origin:

(a) The lithological association found in the upper part of the boreholes is comparable to the Upper Phyllites and the associated carbonatic levels described in the Apuan Alps, but differs from it in the absence of Porphyroids and Porphyritic Schists. The lower part of the wells is comparable to the Lower Phyllites with their Giardino Valley Metabasites. According to this interpretation a sequence of Paleozoic formations, unconformably overlain by the Verrucano, could be present in the Boccheggiano area. This sequence would comprise Carboniferous (outcrops of Boccheggiano and Serrabottini), Lower Devonian and Silurian formations (mines and wells).

(b) The chemical features of the rocks of the upper part of the boreholes are due to a lateral variation of the Lower Phyllites, chemically reflecting an evaporitic environment.

In both cases, the age of the Boccheggiano Formation must be similar to that of the Lower Phyllites, up to now considered as Silurian—Ordovician. The evidence of a glacial episode in the Gondwana during Upper Ashgill and Early Llandovery ages, and the analogies between the Lower Phyllites and the Boccheggiano Formation s.s. strongly suggest a post-Llandovery age for both formations. The presence of ferriferous sandstones and oolites or evaporitic levels in the Middle—Upper Silurian and Early Devonian sequences of northern Gondwana indicate a general subarid climate (see Ziegler et al., 1977) and hence a latitude of less than 40°S (for the definition of Gondwana, see Scotese et al., 1979) for this paleogeographic realm. Evaporitic levels are known from Silurian—Devonian series of Mauritania (Sougy, 1961), Algeria (Poueyto, 1952; Legrand, 1966), Normandia (Cayeux, 1930) and the Mouthoumet Massif (Ovtracht, 1967a). Fe-rich oolites have been found in Silurian—Devonian formations of the Cantabrian Belt (Truyols et al., 1974), the Montagne Noire (Feist, 1977), the North Pyrenean Belt (Ovtracht, 1967b) and Sardinia (Di Colbertaldo and Venerandi, 1962; Venerandi, 1965). Recently Del Rio et al. (1979) report, from sediments of Upper Llandovery—Lower Wenlock of Sardinia, Acritarchs belonging to the Iberian realm of Cramer (1971), thought to be placed in a paleolatitudinal belt lying between 20° and 40°S. Further evidence could suggest a Silurian age for the Boccheggiano Formation s.s. This formation contains strata-bound ore deposits interpreted as volcanogenic—hydrothermal—sedimentary deposits (Bodechtel, 1965; Gianelli and Puxeddu, 1978), more or less remobilized during the emplacement of post-tectonic Alpine granite (Dallegno et al., 1979). The association of strata-bound sulfide deposits with graphitic schists and volcano-sedimentary sequences are known in the Silurian of Sardinia (Garbarino et al., 1976; Padalino et al., 1978) and of the Eastern Alps (Brigo, 1971; Frizzo and Omenetto, 1974), for example.

(9) As for the Boccheggiano Formation l.s., the *Calamita Schists* include rocks similar to the Carboniferous, Upper Phyllites and Lower Phyllites. Some metabasites within the Calamita Schists are associated with Ca—Mg-hornfelses, considered to be metamorphosed dolostones, and have compositions (major and minor elements) similar to that of basic metavolcanites found in the Boccheggiano Formation s.s. at Niccioleta.

(10) The *metabasites* from the Apuan Alps and the *metavolcanites* from Niccioleta are WPB. The former are slightly tholeiitic, the latter slightly alkaline. They have been compared to the basic volcanites of Silurian—Devonian age of southern and central Europe (Gianelli and Puxeddu, 1979). The amphibolites interlayered within Micaschists and Gneisses seem OFB. A similar affinity is reported for many amphibolites of Cambrian or Brioverian age in Europe (Bebien and Gagny, 1980; Cogné and Wright, 1980).

(11) The *Micaschists* and the *Gneisses* derive from shales and graywackes respectively and, therefore, they recall the Lower Phyllites. However, there is no evidence for a lateral correlation with these rocks.

Some conclusions as to the method itself can also be derived from the work presented on Tuscany. The major elements are a powerful tool for the correlation of azoic (metamorphic) formations if some limiting conditions are respected. Chemical parameters are used in lieu of weight percentages or their ratios. These parameters are defined from two-dimensional networks of a few purposely selected minerals. The advantages of such a modus operandi are evident:

(1) Mineral compositions and rock compositions are dealt with in the same diagrams.

(2) The original mineral composition of metamorphic rocks is readily visualized.

(3) The necessary movement forth and back between the mineralogical composition (present and past) and the chemical composition is made easy. A correlation is valid, only if no diagram fails to corroborate it. Further, the method applies well to thick rock units, with an approximately isochemical metamorphism as regard major elements. In thin, alternating sequences of chemically very different rocks, possible metasomatic exchanges may need separate handling, an eventuality not illustrated in this paper.

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APPENDIX

Selected representative analyses

(1) REFERENCE GROUPS (Table II)

Red Permian Porphyries:
305: Asciano Formation

Lower Permian—Carboniferous Groups:
031: quartzitic type — M. Bellino *6* (Roman Mountains)
260: shale type — R. Marina (Elba)

Buti Group l.s.:
117: Buti Phyllites s.s.
002: Upper Phyllites (Apuan Alps)
124: Risanguigno Formation

Lower Phyllites:
006: Lower Phyllites (Apuan Alps)
119: Lower Phyllites (Pisan Mounts: S. Pantaleone)
*921**: drilling LP *1846*

Porphyroids and Porphyritic Schist:
112: Porphyroid (Apuan Alps)
208: Porphyritic Schist (Apuan Alps)
108: Porphyroid (Elba)

(2) GROUPS OF UNCERTAIN OR DISPUTED POSITION (TABLE III)

Niccioleta and Boccheggiano: surface:
052: quartzitic type
074: shale type

Niccioleta and Boccheggiano: mine:
079: albite-bearing type
082: normal type
060: adularized type

Niccioleta and Boccheggiano: drillings:
085: N *284* — 325 m
044: N *284* — 684 m
054: B *198* — 352 m

Micaschists:
127: drilling Serrezano Sperimentale — 2324 m
105: drilling Anqua — 2265 m

Gneisses:
098: drilling Sasso *22* — 3800 m
099: drilling Sasso *22* — 4028 m

Calamita Schists:
251 — group d: Praticciolo
245 — group c: Mount Calamita
239 — group b: Morcone
234 — group a: Poggio Turco (higher albite content)
229 — group a: Remaiolo (lesser albite content)

APPENDIX (*continued*)

Metabasites: Apuan Alps:
905
906

Metabasites: Niccioleta and Elba
916: Niccioleta, drilling N*82* —·340 m
218: Elba

Metabasites: amphibolites s.s.:
917: drilling Montecerboli 1 — 2315 m

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