Pre-Variscan volcanic activity in the Eastern Alps : the Southalpine porphyroids

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by *Sandro Meli[1]*

Abstract

Acidic metavolcanics ("porphyroids") are widespread in the eastern Southalpine basement, occurring as thick levels interlayered with Paleozoic phyllites; they often preserve remnants of the original magmatic features not completely annealed by the Variscan metamorphism. More than 200 rock samples coming from six different areas were investigated by XRF and ICP-MS techniques, to detect chemical parameters insensitive to the late- to post-magmatic element mobilization. All the porphyroids are silica-rich and have a peraluminous character. Alkalies and, to a lesser extent, alkali-earth elements, Pb, Zn and Cu, were found to be affected by mobilization, making their use as geochemical tracers somewhat difficult. The major element composition, together with the low contents of Zr, Nb, Hf, Ta, Ni, Co, Cr, V, the negative correlations of Nb, Ta, Zr, Hf vs SiO_2, and the high Ba concentrations, suggest a crustal origin for the volcanic protoliths of the porphyroids. The REE patterns are consistent with this interpretation, suggesting that melts have formed by vapour-absent reactions involving metapelites, leaving a granulite-like assemblage in the restite. Some major element trends indicate that the separation between magma and residuum was not always complete. The tectonic discriminant diagrams for acidic rocks do not give straightforward indications, even if a late- to post-orogenic scenario seems most likely, taking into account also the occurrence of cogenetic granitoids in the Austroalpine domain.

Keywords: porphyroids, Southalpine basement, element mobility, crustal anatexis, Eastern Alps, Ordovician.

1. Introduction

In the Southalpine metamorphic basement of the Eastern Alps, the so called "porphyroids" occur as thick layers interbedded within phyllites; they have been interpreted by several authors (SASSI and ZIRPOLI, 1989, and references therein) as metavolcanics and associated metavolcanoclastic rocks, whose protoliths were represented by prevailing acidic effusive bodies, like ignimbrites and lava flows. The magmatic age assigned to the volcanics on a stratigraphical basis is Upper Ordovician, at the Caradoc-Ashgill boundary (SASSI et al., 1979). It is based on a long distance correlation between the rock sequence in which the Comelico porphyroids occur and that described and dated by FLAJS and SCHÖNLAUB (1976) in the Northern Grauwackenzone. The age of metamorphism is Variscan; the two stage development of this event was recognized both from microstructural (SASSI and ZIRPOLI, 1989; SASSI and SPIESS, 1993) and geochronological data (DEL MORO et al., 1980, 1984; MELI, 1994). The metamorphic thermal conditions recorded in these rocks at the present erosion level range within the field of the greenschists facies. A slight increase of the metamorphic grade is recognizable moving northwards and westwards from the chlorite-zone (Comelico area) to the biotite-zone (Levico, Agordo-Cereda and Cima d'Arzon areas) and the almandine-zone (Val Sarentino area). Considering the $d_{33T,060}$ parameter of the white potassic mica in metapelites, a low pressure character (SASSI, 1972) and a thermal gradient of about 40 °C/km (MAZZOLI and SASSI, 1988) have been assigned to this metamorphic event.

Based upon lithostratigraphic criteria, the Southalpine metamorphic basement can be divid-

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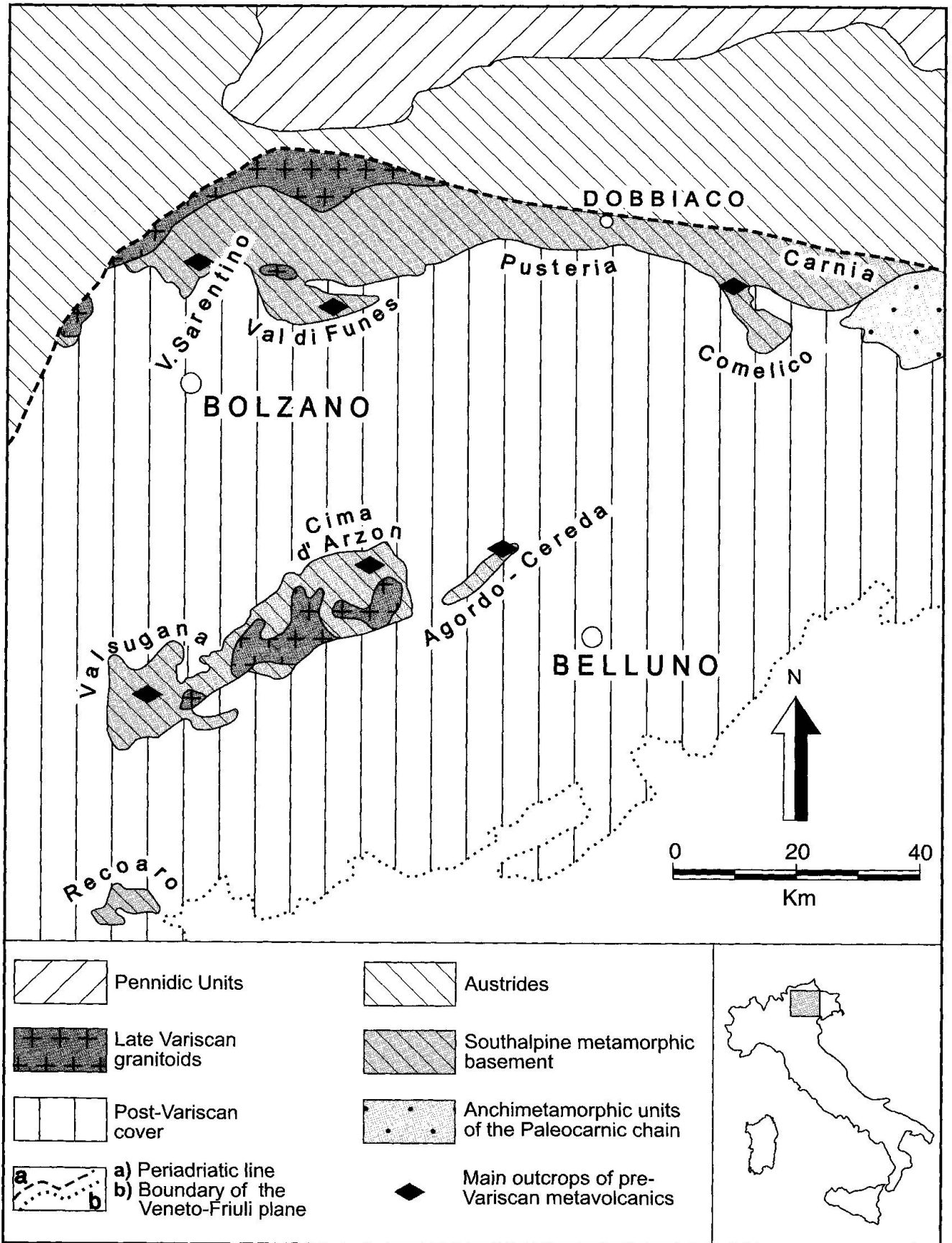
Fig. 1   Geological sketch map of the Eastern Alps (taken from SASSI and ZIRPOLI, 1989, modified after SASSI et al., 1995, for the Carnic sector).

ed into three units (SASSI and ZIRPOLI, 1989): 1) a Lower Pelitic-Psammitic Complex (LPC), which mainly consists of quartz-phyllites; 2) a Volcano-Sedimentary Complex (VSC), formed by a pelitic-psammitic sequence, in which metavolcanic and metavolcanoclastic intercalations occur; 3) an Upper Pelitic-Psammitic Complex (UPC), whose lithology is very similar to that of LPC. In the South-Eastern Alps the basement outcrops along three belts oriented SSW–NNE (Fig. 1), and por-
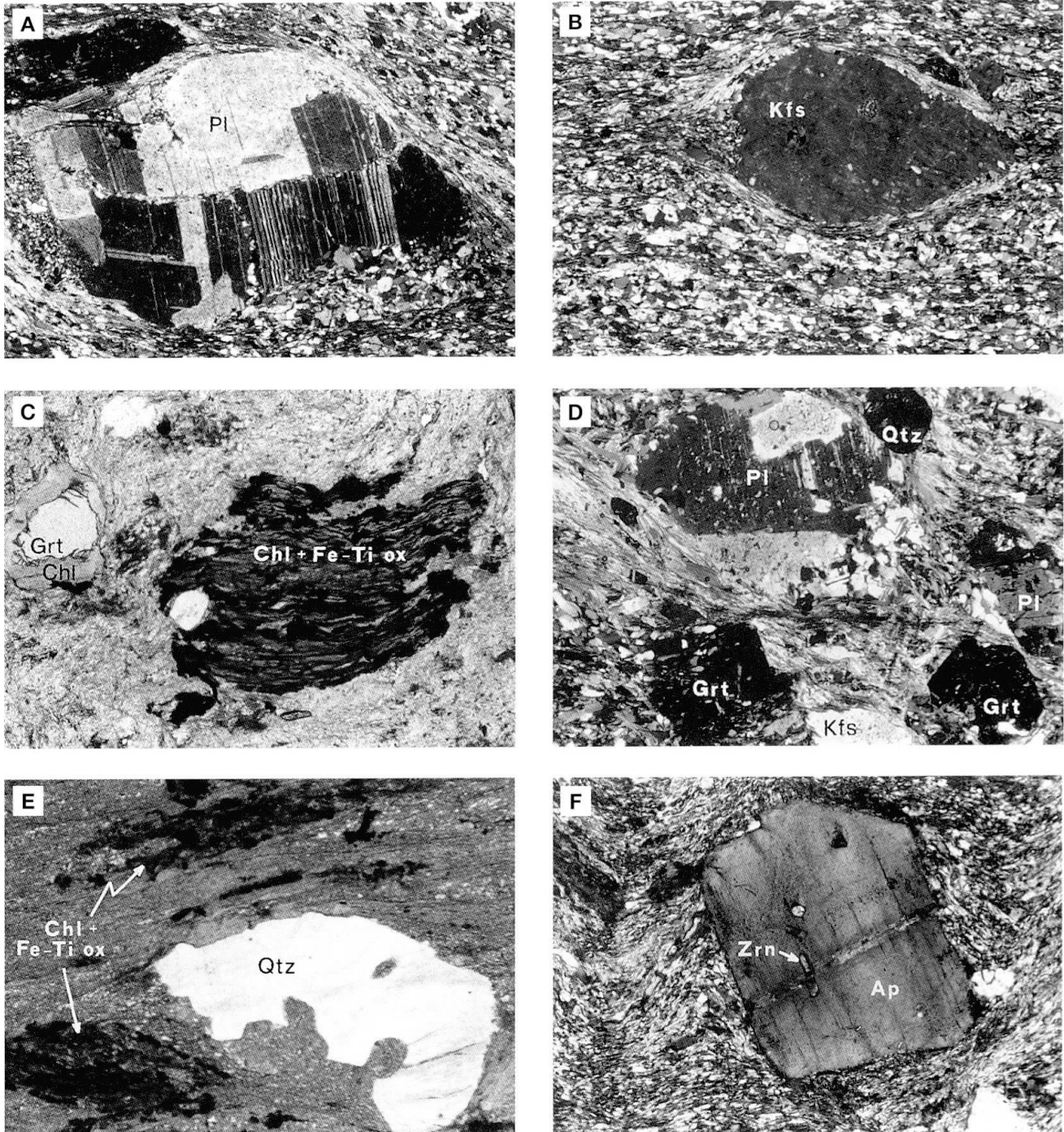
Fig. 2   Photomicrographs of the Southalpine porphyroids. Abbreviations following KRETZ (1983). Field of view = 4.8 × 3.2 mm (A–E), 1.2 × 0.8 mm (F). (A) Plagioclase porphyroclast surrounded by recrystallized matrix, from Levico; XPL. (B) Perthitic K-feldspar porphyroclast, from CA; XPL. (C) Garnet relic and Chl + Fe–Ti oxide intergrowths in a fine-grained weakly recrystallized groundmass, from CM; PPL. (D) Garnet porphyroblasts together with some feldspar porphyroclasts, surrounded by highly recrystallized matrix, from Sarentino; XPL. (E) Relics of magmatic phenocrysts in a very fine-grained matrix, from CM. Qtz shows corrosion embayments and Bt + Fe–Ti oxide intergrowths mimic old Bt phenocrysts; PPL. (F) Apatite microphenocryst with a zircon inclusion in a weakly recrystallized groundmass, from CM; PPL.

Tab. 1 Selected electron microprobe analyses of Sarentino and Comelico garnets; total iron as FeO. End member abbreviations following KRETZ (1983).

Sample Analysis	VS037 Grt1	VS037 Grt2	VS037 Grt3	VS037 Grt4	VS037 Grt5	CM063 Grt3	CM064 Grt5b	CM065 Grt5c	CM066 Grt1	CM066 Grt3
SiO_2	37.05	36.90	37.11	37.09	36.48	36.19	36.58	36.33	36.67	36.55
TiO_2	0.13	0.13	0.11	0.09	0.16	0.10	0.02	0.03	0.05	0.06
Al_2O_3	20.53	20.44	20.52	20.49	20.15	21.47	21.54	21.54	21.87	21.82
Cr_2O_3	0.01	0.02	0.01	0.02	0.00	0.00	0.00	0.02	0.04	0.00
FeO	17.52	16.71	18.07	18.45	18.07	33.50	33.38	33.57	33.13	33.09
MnO	16.71	17.13	15.75	15.86	16.68	1.84	1.77	1.74	1.53	1.41
MgO	1.21	1.09	1.24	1.19	1.33	5.22	5.25	5.03	5.12	5.47
CaO	6.88	6.96	6.88	6.82	6.79	1.39	1.41	1.53	1.43	1.54
Total	100.04	99.39	99.68	100.02	99.66	99.71	99.95	99.79	99.84	99.94
Xprp	4.78	4.35	4.94	4.70	5.24	20.32	20.47	19.65	20.07	21.30
Xalm	39.93	38.42	41.29	41.86	41.77	74.67	74.11	74.70	73.36	73.26
Xsps	37.53	38.84	35.61	35.82	37.31	4.07	3.92	3.86	3.41	3.12
Xgrs	17.72	18.32	18.13	17.57	15.68	0.94	1.51	1.72	3.04	2.32

phyroids are widespread throughout the whole basement, with the exception of the Recoaro area, where probably the VSC still lies under the present erosion surface.

BELLIENI and SASSI (1981) described these pre-Variscan eruptives as an "Upper Ordovician Rhyolitic Plateau", being a part of the "Upper Ordovician Granite-Rhyolite Association", which comprises coeval granitoids outcropping in the Austroalpine domain. MAZZOLI and SASSI (1992) pointed out the geochemical similarities between porphyroids and granitoids, and concluded that the Ordovician plutonism and volcanism can be referred to a unique cycle of magma generation.

During the present research, all porphyroid outcrops have been investigated in the field, and six representative areas have been chosen for sampling: Val Sarentino (Sarentino), Val Sugana, close to Levico (Levico), Cima d'Arzon (Arzon), Val di Funes (Funes), Agordo-Cereda (Agordo) and Comelico, near M. Elmo and M. Cavallino (Comelico).

2. Petrography and mineral chemistry

The main textural feature of the porphyroids is a marked grain size bimodality (Fig. 2): the larger crystals can be interpreted as relics of magmatic phenocrysts, while the surrounding grains, up to 50 times smaller, derive from a volcanic groundmass through various degrees of recrystallization. In order to distinguish between true igneous and volcanoclastic protoliths, which may contain variable amounts of non-magmatic material, the following petrographic constraints have been applied: 1) grain size homogeneity of the recrystallized matrix; 2) poorly defined schistosity (i.e.,

scarcity of alumina-rich minerals); 3) nearly isotropic orientation of the porphyroclasts.

The preserved pre-metamorphic mineralogical association of the porphyroids consists of quartz, K-feldspar, plagioclase, ilmenite, biotite, apatite and zircon; these latter can be defined as magmatic with a good level of confidence only in the Comelico area. The present composition of feldspar crystals does not reflect their original chemistry: plagioclase has been transformed into albite + epidote ± sericite, and alkali mobilization caused the growth of chess-board albite upon preexisting K-feldspar crystals (CALLEGARI and DE PIERI, 1966). The quartz porphyroclasts often preserve a typically magmatic embayment. Biotite relics are very seldom preserved, although the occurrence of this phase in the original magmatic paragenesis is deduced by the occurrence of chlorite + Fe–Ti oxide intergrowths. Garnet relics are occasionally present in the Levico samples and more frequently in the Comelico zone. They are rich in almandine and pyrope components (Tab. 1); these compositions are not consistent with crystallization under low greenschist facies conditions. In figure 3 their chemistry is compared to that of naturally occurring phenocrysts in rhyolites and rhyodacites, and to that of synthetic garnets grown during both crystallization and fluid absent melting experiments. Accordingly, also a near liquidus crystallization from a peraluminous melt can be excluded, while a cognate restitic origin is clearly suggested. Among the newly grown garnets in fluid absent melting experiments, those which better resemble the Comelico compositions derive from a pelitic source at 850 °C and 10 kbar (LE BRETON and THOMPSON, 1988).

The metamorphic assemblage of the porphyroids is consistent with the Variscan zoneography

described by MAZZOLI and SASSI R. (1988): as index minerals, only chlorite is found in the Comelico zone, while biotite is present also in the Agordo, Arzon, Levico and Funes areas. In Val Sarentino, garnet occurring in the interlayered metapelites marks the onset of the almandine zone (CARDIN et al., 1985). The chemistry of metamorphic garnets occasionally occurring in Sarentino metavolcanics differs from that typically found in the almandine zone metapelites (Tab. 1 and Fig. 3), due to bulk rock compositional constraints. Other metamorphic minerals, common to all porphyroid groups, are quartz, albite, K-feldspar, muscovite, epidote, and ilmenite. In Comelico volcanics syn-kinematic calcite also oc-

curs; it crystallized both in the microfold hinges and in the strain shadows of the porphyroclasts, testifying to a high CO_2 fugacity in this area during the Variscan event.

The hydrous minerals are always halogen-poor (Tab. 2); this suggests that the metamorphic fluids had low Cl and F contents, thereby excluding a halogen-rich fluid as an effective tool in mobilizing and fractionating the rare earths (MINEYEV, 1963). However, the lack of suitable fluid inclusions within minerals prevented more rigorous estimates of halogen fugacities. Muscovite has a significant phengitic substitution (Si^{IV} = 3.3–3.6 atoms p.f.u.), depending upon the bulk rock chemistry (occurrence type II, SASSI et al.,
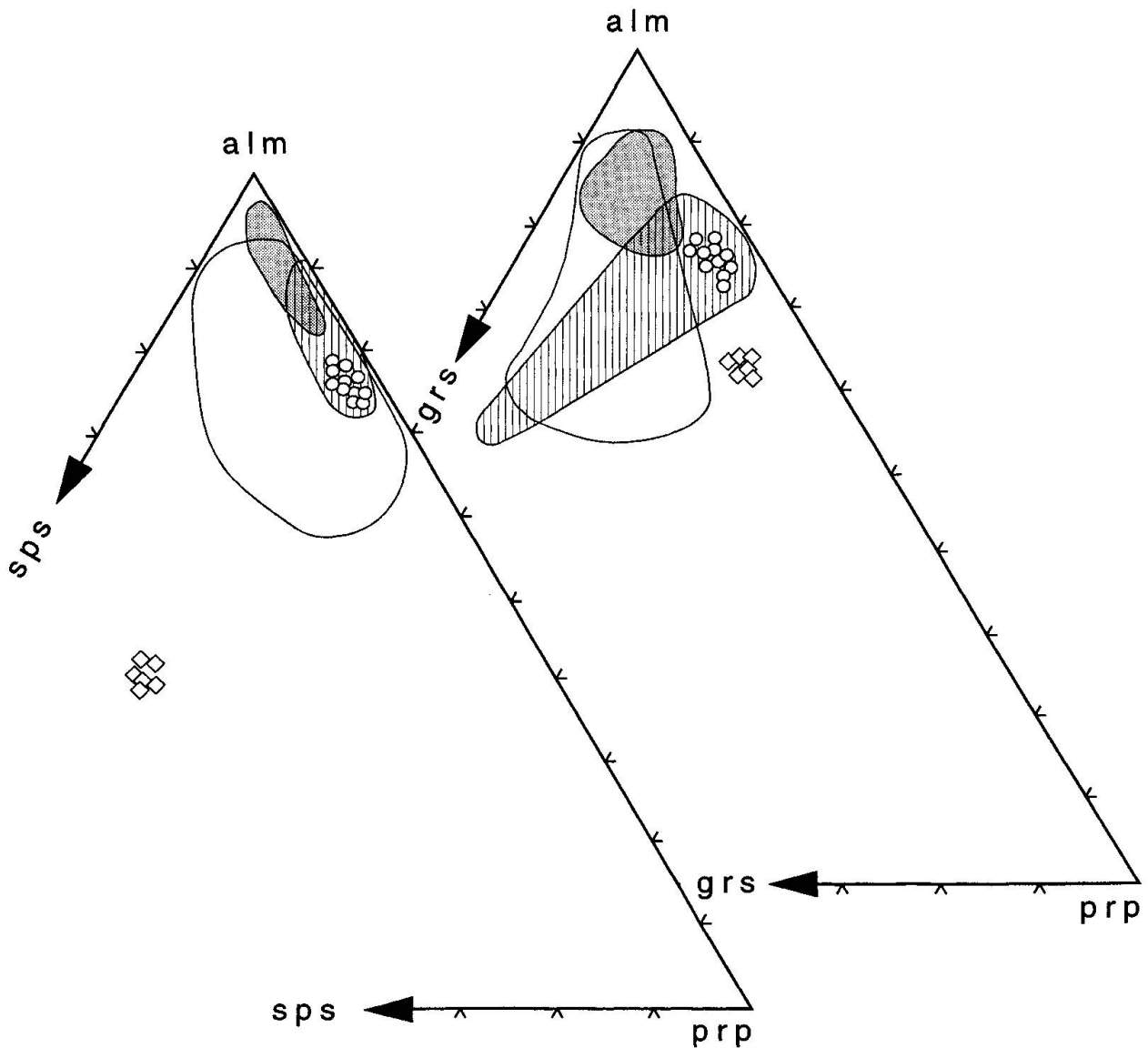
Fig. 3 Garnet chemistry in Comelico (circles) and Sarentino (diamonds) porphyroids, compared to: a) phenocrysts from rhyolites and rhyodacites (shaded fields. Data from: BARLEY, 1987; CLEMENS and WALL, 1984); b) synthetic garnets crystallized from peraluminous acidic melts (white fields. Data from: GREEN and RINGWOOD, 1968; CLEMENS and WALL, 1981; CONRAD et al., 1988); c) newly crystallized garnets during dehydration melting experiments (stippled fields. Data from: VIELZEUF and HOLLOWAY, 1988; LE BRETON and THOMPSON, 1988; SKJERLIE et al., 1993).

Tab. 2   Selected electron microprobe analyses of phyllosilicates. Abbreviations following KRETZ (1983).

Sample	LV054	VS054	CA011	CA011	LV054	CM066	VS054	CM066	LV054	CM066
Analysis	Bt	Bt	Bt	Ms	Ms	Ms	Ms	Chl	Chl	Chl
SiO_2	36.63	36.55	37.31	52.02	51.95	51.91	51.24	25.35	25.47	26.50
TiO_2	1.79	2.87	1.13	0.12	0.30	0.09	0.35	0.08	0.05	0.07
Al_2O_3	16.78	16.16	16.51	26.84	28.71	26.10	27.95	19.13	18.98	19.09
Cr_2O_3	0.05	0.02	0.01	0.04	0.06	0.08	0.01	0.02	0.02	0.01
FeO	24.28	22.89	21.25	3.85	3.56	5.40	4.84	31.49	33.80	27.44
MnO	0.25	0.33	0.15	0.05	0.08	0.08	0.06	0.08	0.37	0.50
MgO	6.73	7.67	10.19	2.97	2.22	2.74	2.21	10.17	8.68	13.07
CaO	0.03	0.03	0.02	0.03	0.00	0.03	0.01	0.01	0.02	0.08
Na_2O	0.03	0.05	0.03	0.37	0.10	0.06	0.13	0.00	0.01	0.03
K_2O	9.28	9.27	9.17	9.69	9.77	9.99	9.18	0.09	0.04	0.09
F	0.22	0.29	0.27	0.12	0.21	0.00	0.16	0.14	0.10	0.19
Cl	0.02	0.02	0.01	0.00	0.00	0.00	0.02	0.01	0.02	0.02
Total	96.09	96.14	96.05	96.10	96.96	96.49	96.16	86.57	87.54	87.10

1994). Chlorites have been classified as ripidolites (according to HEY, 1954), with minor dioctahedral and Tschermak substitutions. Their chemical variation is controlled by bulk rock composition rather than different metamorphic conditions. Biotites depart from the ideal phlogopite-annite join, the main deviations being Ti substitutions (up to 0.38 atoms p.f.u.), low Si^{IV} (5.58–5.84), and A-site vacancies (A < 1.88). Ti content is negatively correlated with the metamorphic grade.

3. Geochemical data

3.1. SAMPLING AND ANALYTICAL TECHNIQUES

After a severe sample selection based upon a careful petrographic study, 230 samples out of 450 collected have been chosen for chemical analyses. A further selection has been made on chemical grounds, using silica and alumina contents and the discriminant function of SHAW (1971). Some samples from each study area revealed to be volcano-sedimentary mixtures; therefore they have been excluded from further geochemical investigations. Finally, 196 samples have been taken into account (VF: 4 samples; CA: 41 samples; Levico: 50 samples; CM: 61 samples; Sarentino: 29 samples; AG: 11 samples). Representative analyses of samples from each area are reported in table 3. Major elements and the trace elements from Ni to Th have been determined by XRF for all the samples. The XRF raw data reduction for trace elements was made following LEONI and SAITTA (1976), except for Rb, Sr, Y, Nb, Zr (FAIRBAIRN and HURLEY, 1971). Other trace elements have been measured by ICP-MS on 57 specimens.

3.2. MAJOR ELEMENTS

Among the six study areas, some common chemical features can be pointed out. First of all, a prevailing silicic character of the metavolcanics is widespread throughout the whole Southalpine basement, as shown in the frequency hystogram of figure 4. Nearly 95% of the samples have SiO_2 >
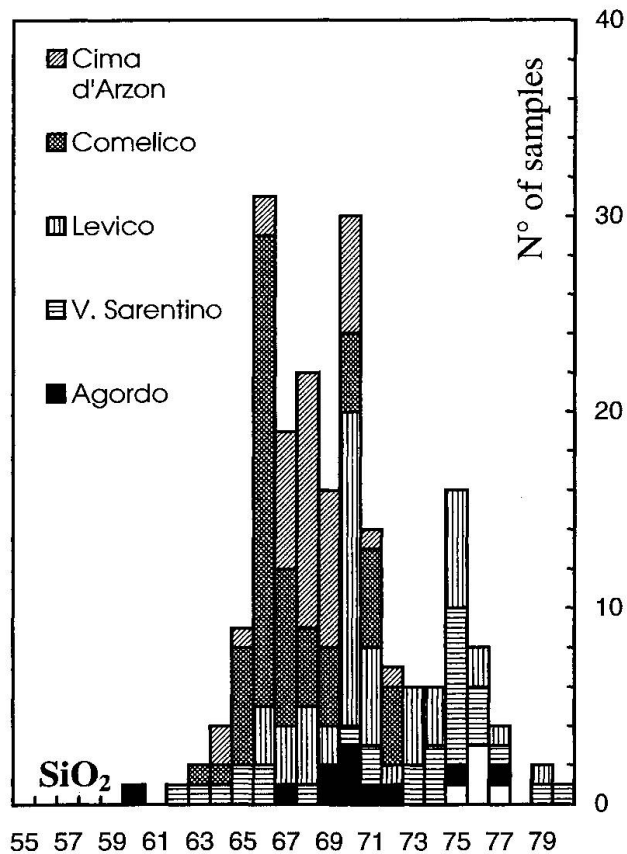

Fig. 4 SiO_2 wt% frequency distribution for the Southalpine metavolcanics.

Tab. 3 Representative analyses of the Southalpine porphyroids. Major oxides in wt%, total iron as Fe_2O_3, trace elements in ppm. L.O.I. = Loss On Ignition; – = not determined; < δ = below detection limit. The complete set of analyses will be sent, upon request, by the author.

	CM028	CM044	CM081	CM097	CM101	CA018	CA032	CA053	CA056	CA058	AG029	AG045	LV003	LV017	LV057	LV076	LV082	FU002	FU003	VD029	VD038	VD051	VD052	VD059
SiO_2	69.93	72.97	68.51	66.97	63.96	68.97	64.89	70.27	68.50	72.81	67.64	76.97	66.27	70.93	71.80	72.60	79.23	75.25	77.21	62.20	75.37	71.42	73.93	80.43
TiO_2	0.43	0.25	0.63	0.55	0.61	0.45	0.53	0.43	0.43	0.28	0.42	0.09	0.60	0.38	0.35	0.37	0.11	0.17	0.16	0.87	0.11	0.21	0.17	0.13
Al_2O_3	15.76	14.69	16.13	15.49	15.81	15.18	16.23	15.08	16.29	14.55	14.35	12.16	16.00	15.10	14.21	14.15	12.10	13.46	12.10	16.69	13.51	15.04	14.25	11.14
Fe_2O_3	2.71	2.02	3.35	3.48	3.90	3.43	4.94	2.22	3.29	2.24	3.03	0.77	4.73	2.55	2.40	2.46	0.94	1.64	2.37	6.26	1.46	2.26	1.30	1.08
MnO	0.03	0.02	0.05	0.03	0.05	0.03	0.06	0.04	0.07	0.02	0.10	0.07	0.04	0.01	0.01	0.04	0.02	0.02	0.04	0.11	0.01	0.07	0.02	0.01
MgO	0.98	0.66	1.09	1.30	1.38	1.75	2.37	1.67	0.97	0.75	2.50	0.50	2.05	0.97	1.46	0.72	0.50	0.55	2.14	2.67	0.49	0.88	0.42	0.32
CaO	0.28	0.18	0.45	1.28	2.64	1.84	2.15	1.16	0.18	0.22	0.97	0.27	0.43	0.29	0.17	0.50	0.18	0.07	0.62	1.08	0.05	1.24	1.37	0.79
Na_2O	4.61	3.36	3.32	4.88	4.89	2.87	4.10	4.67	3.69	3.16	5.86	1.25	3.75	1.85	0.89	0.55	0.69	3.42	2.08	6.66	2.45	4.22	7.00	5.13
K_2O	3.37	4.01	3.77	2.88	2.54	3.49	2.13	1.81	4.15	4.55	2.54	6.90	3.70	6.54	7.28	6.37	5.19	4.44	1.54	1.04	5.81	3.33	0.89	0.55
P_2O_5	0.19	0.16	0.23	0.21	0.20	0.13	0.10	0.10	0.12	0.15	0.11	0.11	0.17	0.16	0.16	0.17	0.16	0.05	0.04	0.22	0.04	0.05	0.05	0.04
L.O.I.	1.59	1.64	2.36	2.80	3.89	1.77	2.31	2.45	2.19	1.25	2.45	0.88	2.08	1.18	1.27	2.12	1.01	0.93	1.71	1.88	0.73	1.23	0.56	0.46
Ni	9	5	13	12	12	9	9	7	10	4	<5	8	14	8	10	5	<4	<4	<4	16	<3	<3	<3	<3
Co	<10	7	10	<10	<10	9	<8	8	10	10	7	<5	9	8	7	<10	7	9	<8	13	7	<9	8	<10
Cr	22	15	29	26	29	26	37	28	22	13	9	15	39	25	24	24	16	12	8	55	12	14	12	12
V	37	20	58	51	57	53	75	54	56	28	27	23	80	38	43	37	10	11	10	103	9	7	6	5
Cu	7	<10	10	11	8	9	10	<10	16	<5	<10	14	16	<8	<10	<10	<10	<5	<5	18	<8	<8	<8	<8
Zn	69	40	55	127	69	58	72	41	29	34	34	54	68	41	22	31	22	31	63	83	17	61	31	27
Ga	20	18	20	19	21	18	20	17	21	16	20	18	20	17	16	16	14	16	17	24	13	23	16	14
Sc	6	6	11	8	8	10	10	8	12	5	11	11	15	8	10	6	14	10	8	24	6	11	8	8
Ba	650	467	1033	846	912	800	802	764	713	555	1085	758	1024	745	638	834	761	981	637	495	773	1175	154	113
Th	13	8	17	18	17	18	21	17	19	14	20	15	19	15	13	15	6	15	14	18	17	23	19	15
Pb	30	18	11	21	19	26	20	16	14	20	29	21	20	23	15	19	12	12	16	19	16	21	28	17
Rb	157	154	149	129	112	95	82	72	124	165	72	189	136	255	151	228	177	135	76	61	170	156	55	28
Sr	48	55	38	112	183	157	214	96	38	34	68	33	63	32	40	46	33	33	73	138	25	262	153	255
Y	28	22	33	33	30	30	24	42	28	31	47	39	39	31	29	34	15	31	37	44	29	65	48	29
Zr	200	120	294	254	263	175	214	168	173	139	259	173	263	181	149	183	71	146	211	413	98	246	206	158
Nb	16	11	19	17	18	12	11	10	11	10	15	14	14	12	10	11	6	10	11	18	6	16	14	12
Li	21.99	18.69	27.35	52.39	56.64	25.89	29.02	35.64	15.81	17.04	–	–	30.89	18.50	23.26	47.91	31.91	25.50	14.3	56.57	18.27	54.06	23.60	23.67
Cs	4.14	6.38	7.31	6.60	6.06	3.13	4.11	4.56	4.88	1.86	–	–	3.58	6.10	2.02	3.46	8.17	2.60	1.6	3.26	1.46	2.98	1.15	1.74
Be	2.56	3.89	2.87	2.91	2.18	2.53	2.85	2.12	3.21	2.17	–	–	3.26	2.81	1.77	2.56	2.65	2.31	3.6	3.74	1.56	3.76	2.43	2.09
Ta	1.73	1.92	2.18	2.01	1.67	1.33	1.30	1.16	1.20	1.47	–	–	1.65	1.55	1.41	1.56	1.33	1.29	1.11	2.00	1.11	2.28	1.74	1.15
Hf	5.75	3.74	7.51	6.95	7.39	4.01	4.61	3.72	3.89	3.55	–	–	5.97	4.52	3.70	4.71	4.37	4.04	4.18	8.47	2.75	6.69	5.07	4.83
Mo	0.17	0.86	0.44	1.20	0.38	0.97	0.50	0.13	1.15	0.15	–	–	0.59	0.17	0.29	0.45	0.49	0.14	0.74	0.73	0.09	0.21	0.55	0.15
Sn	4.78	6.31	4.87	5.92	3.76	4.18	3.16	3.42	3.45	5.82	–	–	4.39	5.31	4.47	9.65	5.27	3.70	3.54	4.42	3.51	10.18	5.46	4.10
Tl	0.72	1.00	0.98	0.68	0.58	0.84	0.67	0.45	0.83	0.88	–	–	0.78	1.46	0.82	1.31	0.96	0.74	0.41	0.32	0.88	0.98	0.36	0.68
U	1.36	3.09	3.45	2.66	2.31	3.44	2.81	1.76	3.20	3.29	–	–	3.34	2.91	3.46	3.44	3.79	1.27	1.12	2.03	2.11	4.92	4.04	2.40
La	20.62	19.01	60.35	36.91	47.11	37.76	42.87	65.53	39.08	13.59	–	–	52.13	29.11	32.76	26.74	30.08	65.90	74.93	34.18	12.36	44.98	25.59	17.52
Ce	43.96	40.81	123.18	79.81	95.12	87.71	93.32	90.37	85.31	44.31	–	–	100.50	68.05	69.88	63.13	73.37	145.99	122.45	83.18	28.95	110.18	62.09	48.20
Pr	5.27	4.73	14.22	9.51	11.01	9.28	10.40	14.73	9.66	3.52	–	–	13.13	7.62	7.97	7.24	7.15	15.78	17.08	9.13	3.22	11.74	6.55	4.12
Nd	19.80	17.51	52.96	35.41	40.80	34.76	38.11	54.26	34.93	12.69	–	–	48.38	28.20	29.24	27.19	26.84	60.17	62.28	35.29	11.27	44.47	24.92	15.32
Sm	3.89	3.77	10.12	7.07	7.84	6.86	7.44	10.23	6.92	2.98	–	–	9.64	6.24	6.02	5.74	5.87	11.85	12.81	7.18	2.66	9.90	5.48	3.44
Eu	0.69	0.68	1.72	1.26	1.50	1.44	1.65	2.27	1.54	0.53	–	–	1.80	1.23	1.18	0.89	1.04	1.56	1.94	1.35	0.43	1.43	0.64	0.54
Gd	4.11	4.02	11.41	7.84	8.57	8.23	8.33	12.34	7.36	3.66	–	–	11.13	7.20	6.25	5.79	7.34	12.43	14.72	7.96	3.36	12.50	6.52	4.53
Tb	0.51	0.58	1.38	1.00	0.99	1.08	1.05	1.56	0.95	0.60	–	–	1.39	1.06	0.78	0.71	1.11	1.35	2.18	1.00	0.60	1.90	0.98	0.69
Dy	2.50	3.07	6.28	5.00	4.67	5.86	5.23	7.48	4.55	3.75	–	–	7.05	6.00	3.80	3.50	6.57	5.91	11.20	4.69	3.75	11.56	5.35	4.35
Ho	0.45	0.57	1.09	0.90	0.79	1.14	0.98	1.33	0.96	0.82	–	–	1.32	1.20	0.75	0.67	1.28	1.00	2.00	0.89	0.81	2.38	1.12	0.94
Er	1.30	1.81	3.06	2.54	2.25	3.18	2.81	3.50	2.44	2.54	–	–	3.77	3.56	2.21	1.94	3.61	2.91	5.39	2.53	2.44	7.12	3.38	2.93
Tm	0.18	0.26	0.37	0.33	0.27	0.42	0.35	0.41	0.32	0.37	–	–	0.49	0.49	0.29	0.27	0.49	0.37	0.72	0.36	0.36	1.05	0.48	0.43
Yb	0.99	1.44	2.28	1.98	1.63	2.57	2.11	2.45	1.92	2.34	–	–	2.85	3.05	1.83	1.64	2.80	2.20	4.54	2.21	2.30	6.67	3.00	2.85
Lu	0.14	0.23	0.33	0.29	0.24	0.36	0.31	0.36	0.27	0.35	–	–	0.40	0.43	0.30	0.25	0.39	0.34	0.61	0.34	0.35	0.97	0.42	0.42

65%, with the maxima of the distributions at 66%, 70% and 75%. All samples are peraluminous, with variable amounts of normative corundum. In Levico zone, the porphyroids show a compositional bimodality of SiO_2, with the main maximum at 70% and the other one at 75%. Likewise, Comelico porphyroids display a bimodal distribution, with the maxima shifted towards less silicic compositions (66% and 70% respectively). In the Arzon area, a well defined maximum at 68% SiO_2 is present, while in the Sarentino zone the distribution is not regular, although a smooth peak is evident at $SiO_2 = 75\%$. The occurrence of samples with $SiO_2 > 77\%$ in the Levico and Sarentino groups testifies to a slight silicization, which probably took place during the Variscan event. Many of the Funes and Agordo porphyroids are thought to be a mixture of magmatic and (meta)sedimentary components, as revealed by negative DF of SHAW (1971), and by anomalous Al_2O_3, Ba, Li, and Cs contents; moreover, the Agordo samples show evidence of extensive chemical mobilization, making them useless for geochemical investiga-

tions. As a consequence, only few samples from Funes are considered to satisfactorily approximate the pristine chemistry; the silica variability of these true volcanics is low, so that no trend is detectable.

Negative correlations of TiO_2, Al_2O_3, Fe_2O_3, MgO, P_2O_5, vs SiO_2 are present in Levico, Sarentino, Arzon and Comelico, while Na_2O, K_2O and CaO display a high scatter. TiO_2, Fe_2O_3, MgO and P_2O_5 linear arrays display a different x-axis intercept (Fig. 5, see also section 4.3). The Na, K and Ca scattering can be intepreted as due to alkali and, to a lesser extent, alkali-earth elements mobilization, which probably took place during deuteric alteration of the lavas. Despite of this, alkalies have a good negative correlation (Fig. 6), and the $Na_2O + K_2O$ parameter seems not to be drastically modified, probably reflecting local equilibria which caused alkali exchange and growth of either microcline or chess-board albite. The CaO content in Comelico is not related to the modal abundance of syn-kinematic calcite in the samples, indicating that the calcium content is proba-
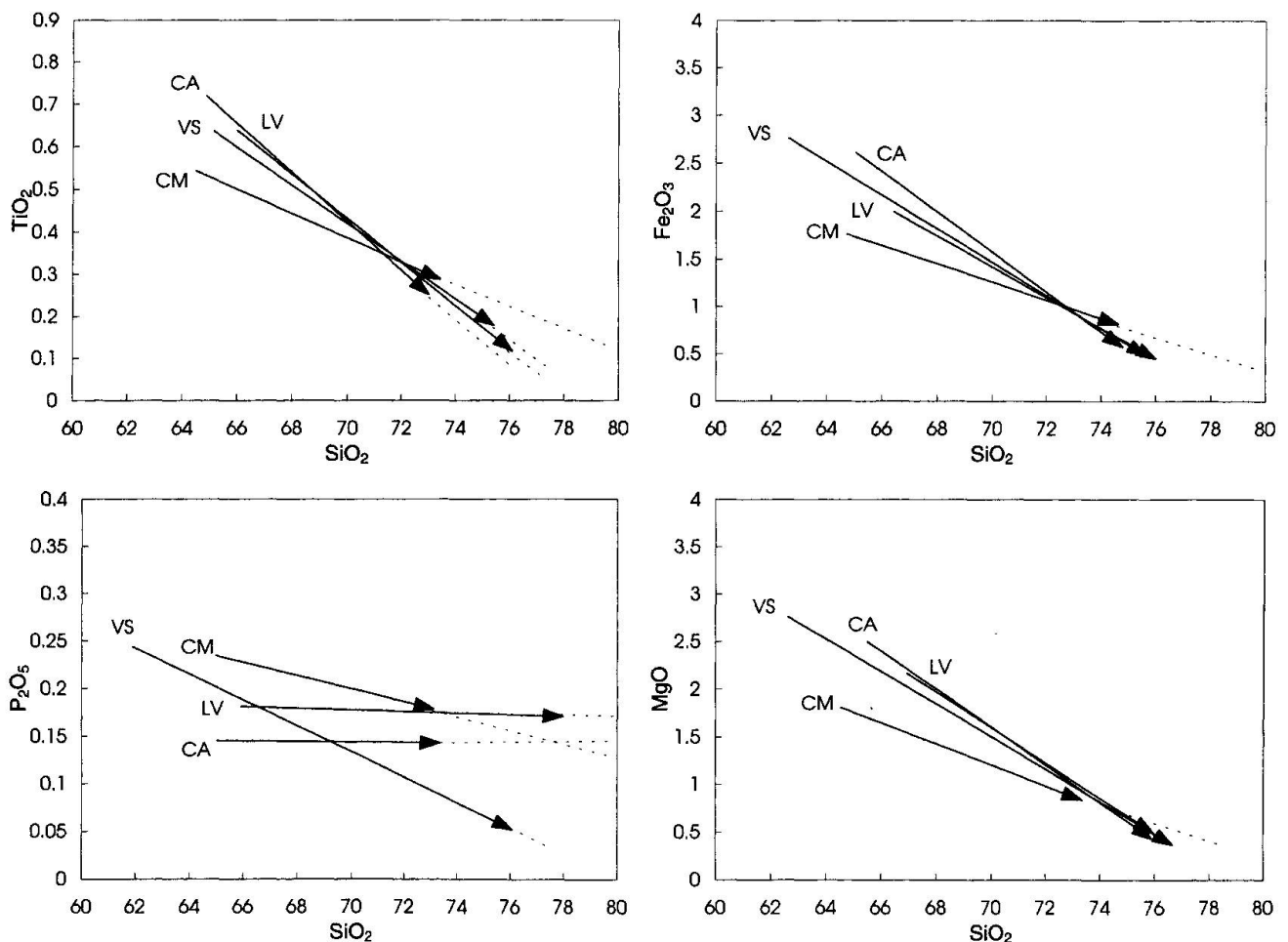

Fig. 5 TiO_2, MgO, Fe_2O_3 and P_2O_5 schematic variation diagrams vs SiO_2. Arrows indicate the average trend for each study area (silicized samples have not been considered).

bly a primary feature of the volcanics, and that only small amounts of CO_2 have been introduced from outside.

Owing to the observed chemical changes from the original igneous composition, the most reliable classification of the protoliths is provided by the diagram Nb/Y vs Zr/TiO_2 (WINCHESTER and FLOYD, 1977); accordingly, the volcanics are classified mainly as rhyodacites and rhyolites (Fig. 7).

3.3. TRACE ELEMENTS

The low content of HFSE, Ni, Co, Cr and V is a common feature of the study areas. Usually the HFSE behaved as immobile elements, as indicated by their negative correlations vs SiO_2, with the exception of Arzon, where good patterns can be detected only for geochemically coherent element pairs (e.g. K–Rb, Nb–Ta, Zr–Hf, Ca–Sr). Rb, Sr and, to a lesser extent, Ba, have been mobilized in Arzon, Sarentino and Funes, while in Levico and Comelico the pristine content has not been seriously modified; Ba content is always high. De-
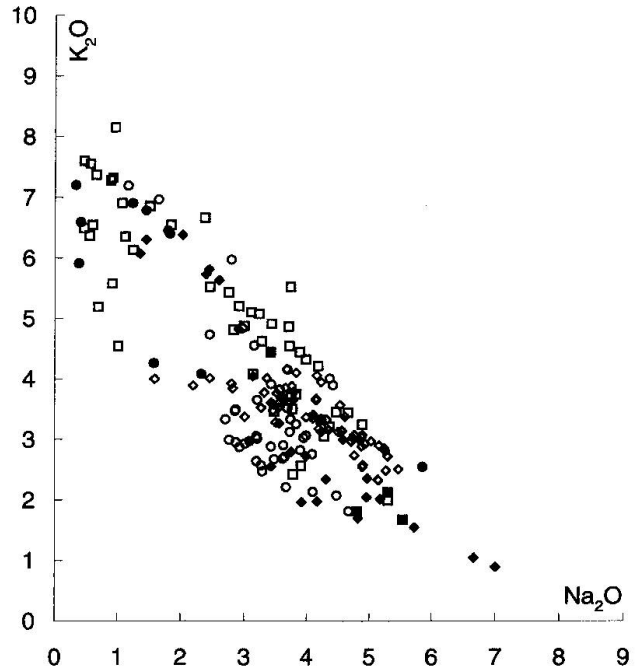
Fig. 6 Na_2O vs K_2O diagram. Open squares: Levico; filled squares: Funes; open circles: CA; filled circles: AG; open diamonds: CM; filled diamonds: Sarentino.
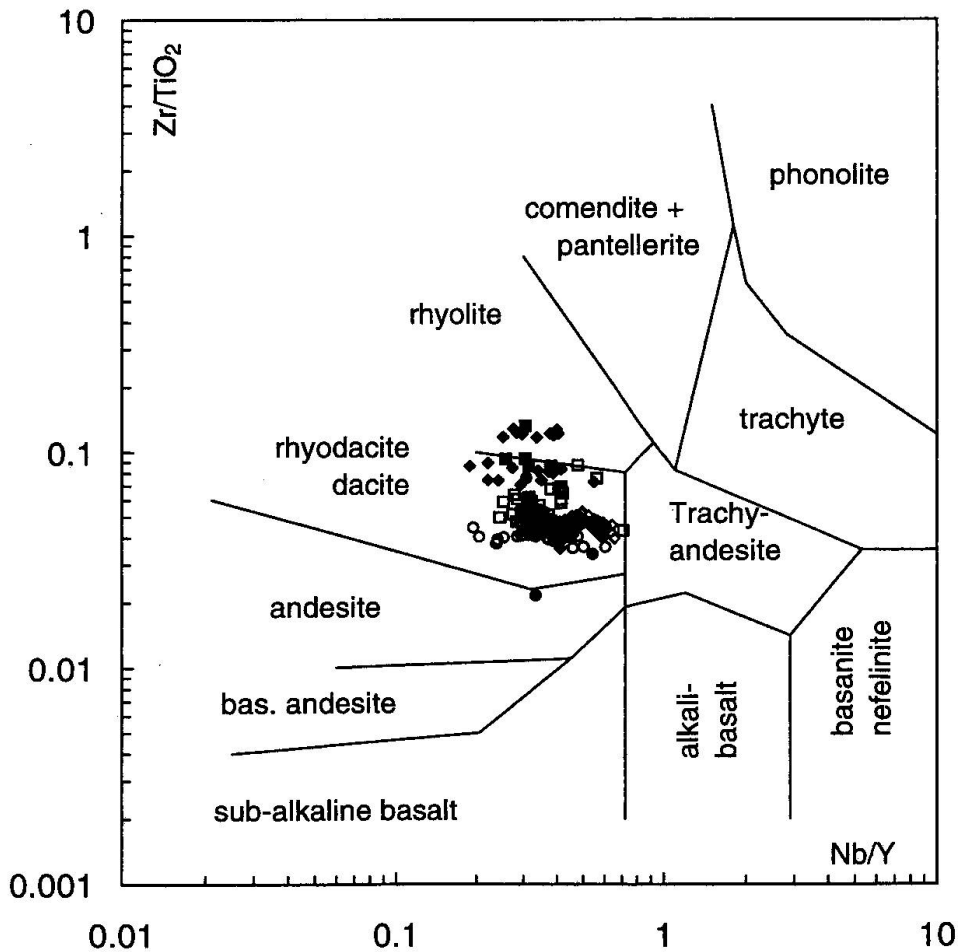
Fig. 7 Classification of the metavolcanics using immobile element ratios (from WINCHESTER and FLOYD, 1977). Symbols as in figure 6.

spite of a slight mobilization, Rb defines in Levico a rough negative correlation with SiO_2. Comelico porphyroids seem to have suffered negligible LILE mobilization; Rb and Ba are negatively correlated with silica, and the latter has a positive correlation with Eu. In few samples from Levico,

Zn, Pb, Sn and Cu anomalies indicate a weak contamination coming from the Calceranica-Vetriolo ores (FRIZZO, 1983), which has not affected the other components. Also a few Comelico samples have high Zn and Pb contents, maybe related to local concentration of sulphides.
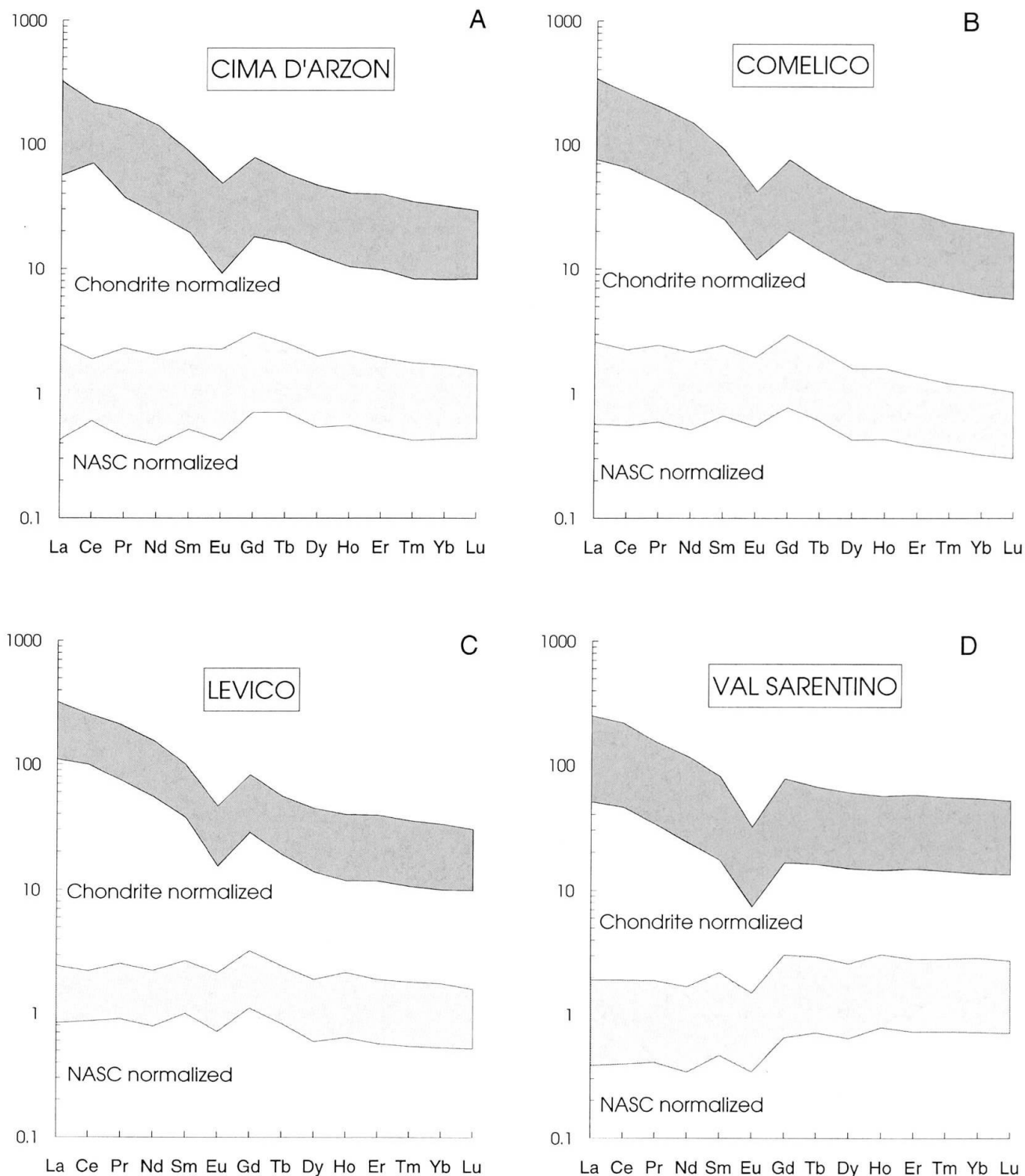
Fig. 8   Chondrite-normalized and NASC-normalized REE patterns (normalizing factors taken from EVENSEN et al., 1978, and GROMET et al., 1984, respectively). The shaded fields represent the pattern contours of selected porphyroid samples.

Tab. 4   Ranges of normalized REE parameters for the Southalpine porphyroids.

		CA	CM	LV	VS	VF
Chondrite	La/Yb	3.91–18.09	6.86–19.55	5.99–12.32	3.59–12.14	7.22–12.02
	La/Sm	2.87–4.03	3.02–4.08	2.14–3.43	2.94–3.97	3.39–3.50
	Tb/Yb	1.13–2.81	1.72–2.68	0.90–2.14	1.07–1.51	1.86–2.70
	Eu/Eu*	0.49–0.78	0.49–0.57	0.45–0.91	0.33–0.57	0.49–0.77
NASC	La/Yb	0.56–2.60	0.98–2.81	0.68–1.77	0.52–1.74	1.07–2.90
	La/Sm	0.88–1.14	0.86–1.16	0.77–0.97	0.86–1.12	0.96–0.99
	Tb/Yb	1.41–2.33	1.42–2.22	1.21–1.77	0.88–1.31	1.54–2.24
	Eu/Eu*	0.78–1.12	0.70–0.82	0.64–0.89	0.67–0.84	0.54–0.86

The REE normalized patterns are presented in figure 8 and some parameters are reported in table 4. Levico, Arzon and Comelico have similar arrays, even if Arzon shows more irregular patterns both in chondrite and NASC normalized plots. Sarentino have flatter HREE patterns and
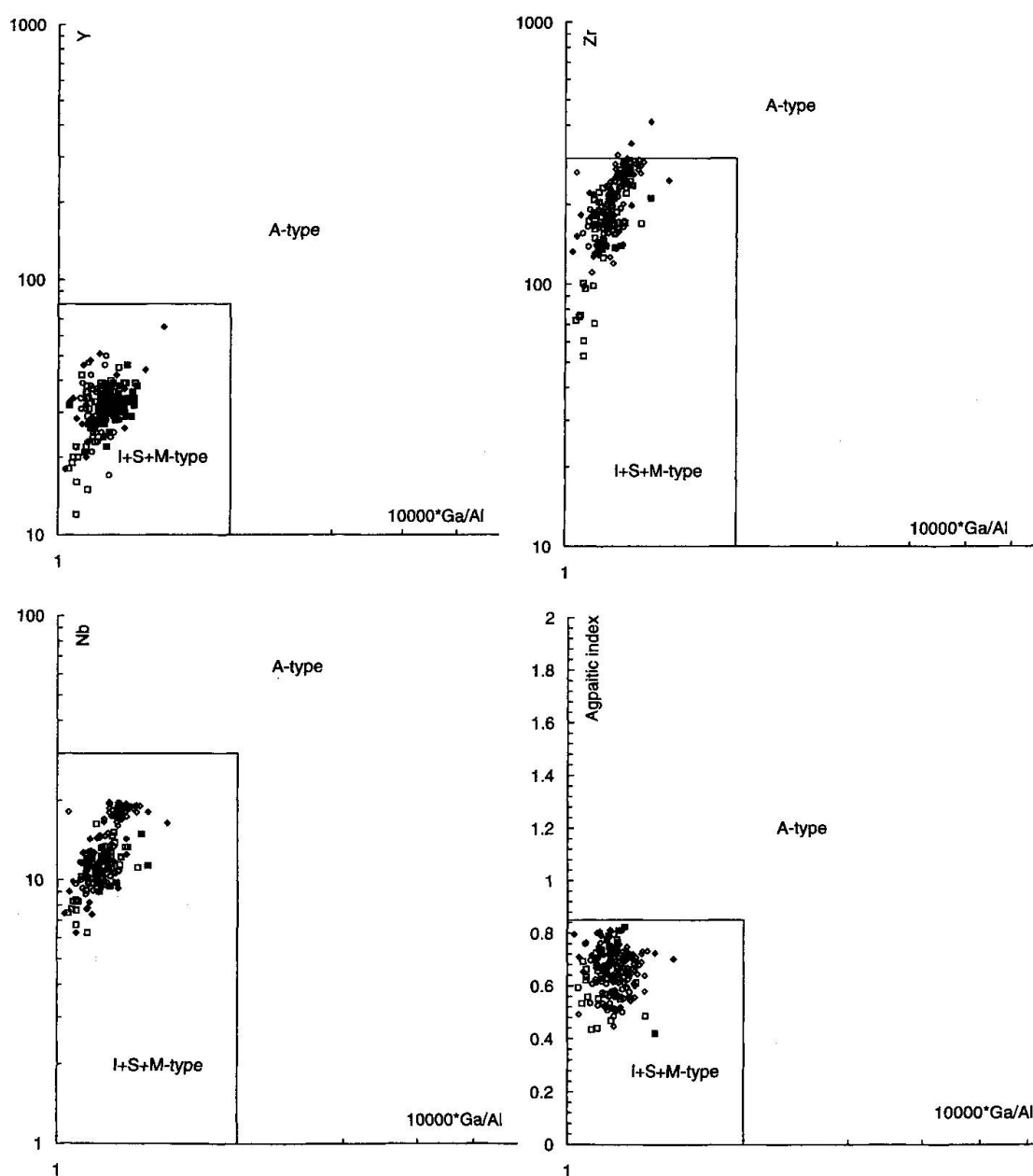
Fig. 9   Selected discriminant diagrams for A-type granitoid rocks (from WHALEN et al., 1987). Symbols as in figure 6.

more pronounced Eu anomaly. In the NASC (North America Shale Composite) normalized plots, LREE patterns tend to be horizontal; HREE are fractionated in Arzon, Comelico and Levico, while in Sarentino the patterns are horizontal. The Eu anomaly is smoother and not always present. Two REE patterns of the true magmatic samples from Funes (not reported in figure 8) reveal a fractionation of the LREE with respect to HREE, and a constant slope. When normalized to NASC, the LREE pattern is nearly horizontal and the HREE pattern is slightly fractionated. In Levico there is a good correlation between LREE and TiO_2, indicating that titanite, more likely than other accessory phases, played an important role in controlling LREE concentrations in this zone.

4. Discussion

4.1. LATE- TO POST-MAGMATIC ELEMENT MOBILIZATION IN THE PORPHYROIDS

First of all, attention should be focussed on whether and to what extent the chemistry of the present porphyroids reflects that of the protoliths.

As demonstrated by geochemical data, during late- to post-magmatic events the mobilization mainly affected alkalies and, to a lesser extent, alkali earth elements. Rb and Ba usually have a mobile behaviour, which produced scattered trends for all the areas, with the exception of CM. It has to be pointed out, however, that the order of magnitude of their concentrations is not likely to have changed: considering the most common transformations occurring after magma emplacement (sericitization of feldspars, recrystallization of glass, and, to a lesser extent, chloritization of biotites), no significant gain or loss of Rb and Ba can be postulated, and only local scale equilibria are responsible for the observed scatter. As a consequence, the high concentration of Ba must be considered as a magmatic feature.

In few cases a slight silicization of the samples took place, causing dilution of other elements. The effect of secondary sulphide mineralisations, such as those of Levico and Comelico, is easily detected by higher Pb, Zn, Sn and Cu in the bulk rock; these anomalies, however, did not affect the other components.

The above outlined chemical alterations affected the volcanic plateau at variable extents. This is obvious for the processes operating at a local scale (e.g. Pb, Zn mineralisations), but also those which acted on a larger scale (late-magmatic deuteresis and Variscan metamorphism) produced chemical mobilization of different intensi-

ty in different sites. Therefore, porphyroids may be recognized in which the pristine chemical composition of the volcanic protolith is well preserved. The most severe chemical changes took place in Agordo and Funes zone, while Comelico metavolcanics are nearly unaffected by late- to post-magmatic alteration. Sarentino and Levico porphyroids seem to have only slightly modified their original composition, while in Arzon area the late mobilization is more evident, and involved also the alkali-earth elements, with the exception of Mg. In each study area the occurrence of some volcanoclastics interlayered with "true" volcanics can be recognized on the basis of the porphyroclastic texture, the exceedingly high Al_2O_3 content and the Shaw's DF index < 0.

Although some chemical features of the volcanics have been modified by subsequent geological evolution, it is still possible to propose a geochemically framed interpretation of the genesis of the original magma and the possible tectonic environment in which the pre-Variscan volcanism developed.

4.2. PETROGENETIC CONSTRAINTS

The most relevant features for a first-level geochemical approach are some major element distributions: the prevailing acidic character (more than 95% of the porphyroids have $SiO_2 > 65\%$) and the high alumina content (0.5 to 6 wt% normative corundum). The peraluminous character and the silica frequency distribution, together with the low contents of Zr, Nb, Hf, Ta, Ni, Co, Cr, V, the negative correlations of Nb, Ta, Zr, Hf vs SiO_2, and the high Ba concentrations, are consistent with a crustal origin for the volcanics.

The LILE behaviour during anatexis is mainly conditioned by some major rock-forming minerals, such as biotite, plagioclase and K-feldspar. Plagioclase and biotite are reactants in the dehydration melting reactions; in a metapelitic assemblage the former tend to be consumed while the latter remains as a residual phase; the opposite happens for metagraywackes. K-feldspar has a variable behaviour, depending mainly on the water activity: in vapour-present reactions, Kfs does not form by incongruent melting (HARRIS and INGER, 1992), whereas in vapour-absent reactions its occurrence has been observed (PATIÑO DOUCE and JOHNSTON, 1991; SKJERLIE et al., 1993). The role of K-feldspar is critical to understand the behaviour of LILE and of Eu, because in an anatectic context it is the most effective phase in fractionating these elements. The high Ba content of the porphyroids indicates that only a small

amount released by the source material has been accommodated in the restite minerals. Although the bulk D^{Ba} for the dehydration melting of biotite (with Kfs in the restite) is supposed to be in the range 0.2–1 (HARRIS and INGER, 1992), the anatectic melt still contains much more Ba than a rhyolitic melt produced by fractional crystallization (see, for example, SPELL et al., 1993).

The Eu negative anomaly in the chondrite-normalized patterns can be an inherited signature from the crustal source, or alternatively it can derive from entrainment of Eu in the residuum.

A hint about the REE behaviour during anatectic processes is obtained considering the patterns normalized to the NASC (GROMET et al., 1984), indicating a hypothetical crustal source. In such diagrams, the LREE patterns tend to be flat, with a normalized value close to 1; a small Eu negative anomaly is detectable in some cases. The HREE are not fractionated only in the Sarentino samples. In the light of an anatectic origin of the magmas, the Eu anomaly is controlled both by source signature and K-feldspar behaviour. However, this latter cannot be clearly constrained: the small Eu anomalies in the NASC normalized patterns point to its occurrence in the residue, while the high Ba contents more likely suggest a K-feldspar free restite. In Comelico porphyroids, a positive correlation between Ba and Eu indicates that the behaviour of these two elements has been coupled during anatexis, and that K-feldspar is the most likely controlling phase in this zone. The HREE patterns also suggest the role played by the restitic Fe–Mg phases in the reaction: garnet, which strongly fractionates HREE, is a possible restitic mineral for Arzon, Levico and Comelico metavolcanics, while cordierite, which is not able to fractionate HREE (BEA et al., 1994), is a suitable restitic phase for Sarentino, suggesting shallower melting conditions.

Based upon these chemical characters and the previously described petrographic features, it is possible to put some constraints on the mechanism of magma production in the crust. It is now well accepted that anatectic processes lead to H_2O-undersaturated melts, through "dehydration melting" reactions (e.g., CLEMENS and VIELZEUF, 1987; JOHANNES and HOLTZ, 1990), and several experiments have been performed for anatectic-like environments, varying P, T, water activity and source materials. The control of accessory phases on anatectic melts has been also taken into account (e.g. WATT and HARLEY, 1993) and trace element models for pelite-derived granites have been developed (HARRIS and INGER, 1992).

In the peraluminous systems, two main stages of magma production are possible, taking place at

increasing temperatures: the muscovite breakdown (~ 665 °C at 5 kbar) and the biotite collapse (~ 850 °C at 5 kbar, CLEMENS and VIELZEUF, 1987, and references therein). The former has a low melt productivity, and therefore is not able to explain the large volumes of magmas requested to build up a plateau. The magma productivity of the dehydration melting involving biotite depends on the modal composition of the source rocks (PATIÑO DOUCE and JOHNSTON, 1991). Metapelites sometimes have an excess of components with limited solubilities in low-T melts (Al_2O_3, MgO, FeO*, TiO_2), and low amounts of plagioclase, which tend to lower the magma production at minimum temperatures. Metapelites whose modes are close to the stoichiometry of melting reactions can produce 70% melt. However, also metapelites which do not match exactly the mineral proportions defined by PATIÑO DOUCE and JOHNSTON (1991) have melt productivities in the range of 40–50% (CLEMENS and VIELZEUF, 1987; VIELZEUF and HOLLOWAY, 1988). The fertility of a metagraywacke depends markedly on temperature; the biotite breakdown is shifted towards higher T if an Al_2SiO_5 phase is lacking (CLEMENS and WALL, 1981). The reactions involving the biotite breakdown in metagraywackes leave Opx as a product of incongruent melting at P < 2000 MPa and Kfs is observed in the restite only at P ~ 1000 MPa (VIELZEUF and MONTEL, 1994); the magma productivity for metagraywackes is comparable to that of metapelites in the same T range only at P < 700 MPa, where Kfs has not been observed in the restite.

Magma productivity of metaigneous rocks is well described by PATIÑO DOUCE and JOHNSTON
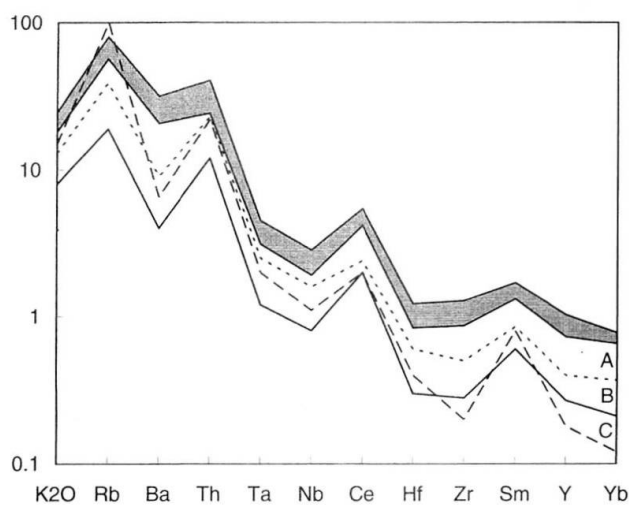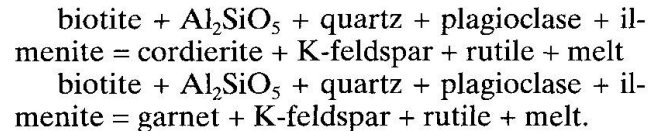

Fig. 10 ORG-normalized spiderdiagram for acidic rocks. The shaded field represents the pattern contour of the 57 selected samples. Reference lines: A) Chile VAG; B) Oman VAG; C) S.W. England COLG (taken from PEARCE et al., 1984).

(1991) and CLEMENS and VIELZEUF (1987). Only tonalites appear to be fertile enough to produce large amount of magmas; the temperatures are higher with respect to metapelites (> 950 °C) and the dehydration melting reactions leave pyroxenes in the residue (SKJERLIE and JOHNSTON, 1992). SKJERLIE et al. (1993) showed evidence of improved magma productivity in layered crustal sources.

Considering that high melt fractions are required to give rise to volcanic plateaus, and that the occurrence of Kfs (on geochemical grounds) and of garnet (on petrographic and geochemical grounds) can be assumed in the restitic assemblage, the most likely main source material is a metapelite, whose mode approaches that indicated by PATIÑO DOUCE and JOHNSTON (1991). However, a layered pelitic/psammitic source, quite common in the sedimentary successions, could enhance melt productivity, and therefore cannot be excluded. Accordingly, two anatectic reactions best explain the magma genesis:

biotite + Al_2SiO_5 + quartz + plagioclase + ilmenite = cordierite + K-feldspar + rutile + melt

biotite + Al_2SiO_5 + quartz + plagioclase + ilmenite = garnet + K-feldspar + rutile + melt.

The first reaction fits the geochemical arrays found in Sarentino, while the second one holds for the other investigated areas.

These reactions leave in the residuum garnet (cordierite), K-feldspar, rutile (plus quartz and biotite, considered in excess in metapelites); the resulting assemblage is similar to that of many typical felsic granulites.

4.3. CONTRIBUTION OF RESTITE COMPONENTS

The possible contribution of restitic material to the chemistry of the protoliths might not be negligible. Indeed, due to the high viscosity of acidic H_2O-undersaturated melts, it is unlikely that the present rocks are all representative of the original
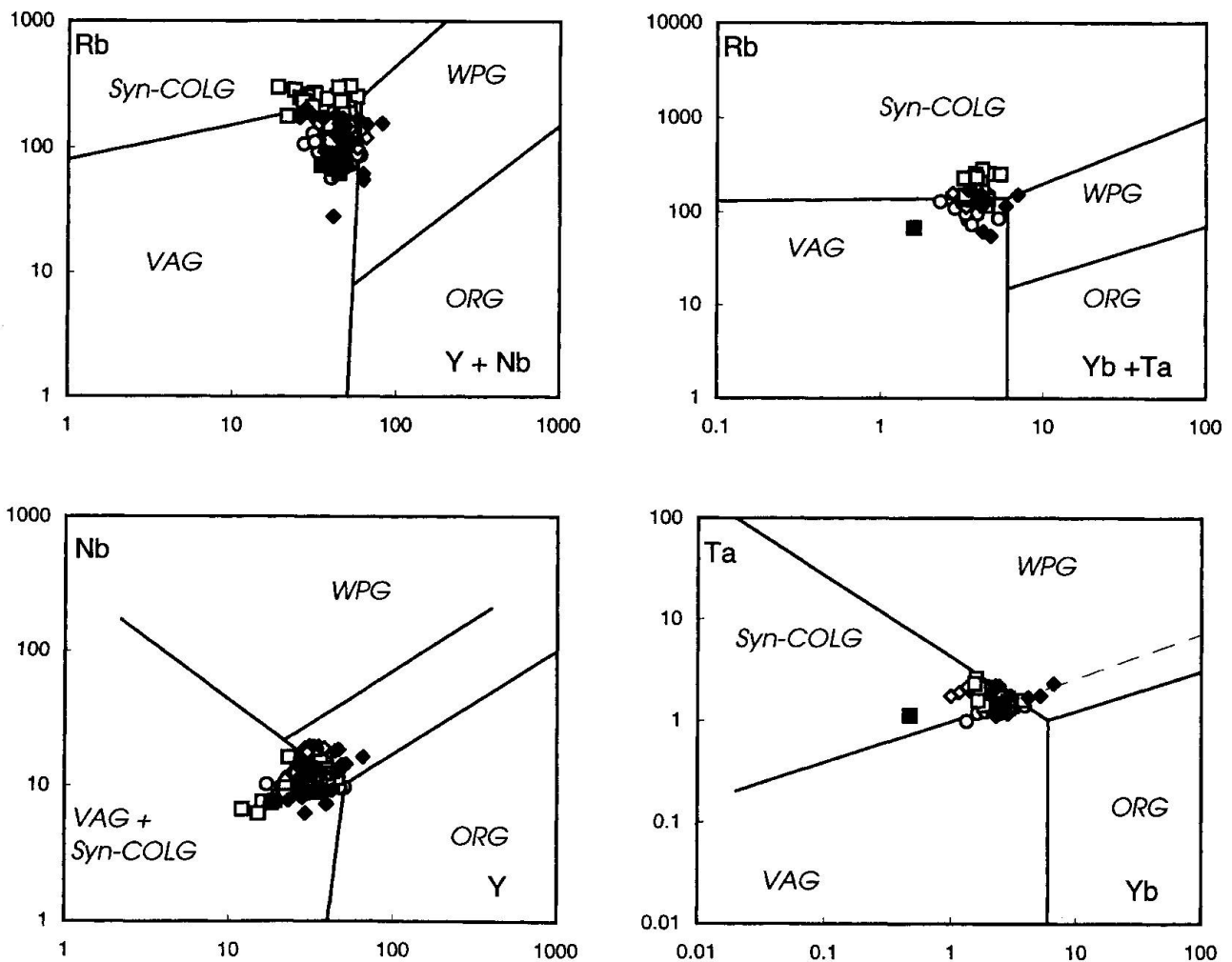

Fig. 11   Selected discriminant diagrams for granitoid tectonic setting (taken from PEARCE et al., 1984). Symbols as in figure 6.

liquids, completely segregated from the source material, but they can represent a mixture of variable amounts of melt plus residuum. According to WHITE and CHAPPELL (1977), the straight-line trends observed for most major elements vs SiO_2 can be interpreted as mixing lines between liquid and restite. As the solubility of mafic components in peraluminous minimum melts are considerably low (CLEMENS and WALL, 1981; PUZIEWICZ and JOHANNES, 1988, 1990), and tend to increase with the melt fraction produced, minimum melt mixing lines slope towards zero at $SiO_2 = 76\%$, while non minimum melt mixing lines have flatter trends, with a zero-intercept at $SiO_2 > 76\%$.

These straight-line arrays are clearly observed, with some differences, in Comelico, Sarentino, Levico and Arzon (Fig. 5). The Sarentino metavolcanics have chemical features which fit minimum melt mixing lines, while the others lie along non minimum melt trends. In Arzon and Levico, MgO, TiO_2 and Fe_2O_3 have a minimum melt trend, while P_2O_5 is nearly constant, indicating that its content in the magma and in the source rock was nearly equal. This fact can be well understood considering that the solubility of apatite is higher in peraluminous acidic melts (PICHAVANT et al., 1992) than in meta-aluminous to alkaline liquids (HARRISON and WATSON, 1984), so that a considerable amount of this phase can enter the melt only slightly above the minimum. Monazite, if present in the source, would not have melted, because of its very low solubility (MONTEL, 1986) and low dissolution rate (WATSON, 1988). In the Comelico zone a non minimum melt array is evident for all the immobile major oxides, indicating a probable higher melt fraction produced during anatexis.

The restite components have been directly recognized only in the Comelico and occasionally in Levico porphyroids; other possible restitic minerals (i.e., K-feldspar, biotite, quartz) are undistinguishable from the true magmatic crystals. No polymineralic xenoliths have been recognized, but their preservation through the Variscan metamorphic deformation appear to be less likely than that of single crystals.

4.4. TECTONIC SETTING

Taking into account the relationships between trace element geochemistry and tectonic setting, some constraints can be put on the possible geodynamic scenarios in which the Ordovician volcanism took place. Among the diagrams proposed by WHALEN et al. (1987), those involving immobile elements clearly exclude an A-type signature for the porphyroids (Fig. 9). Looking at the mean
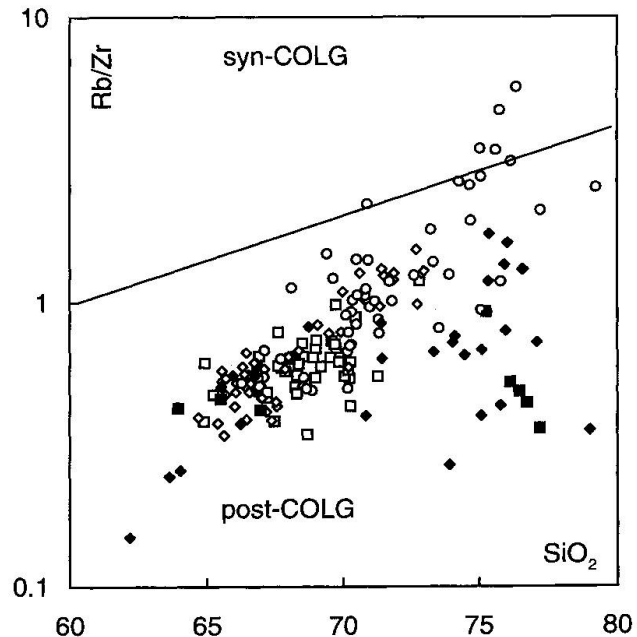

Fig. 12 Rb/Zr vs SiO_2 discriminant diagram (taken from HARRIS et al., 1986). Symbols as in figure 6.

value of the trace elements of different granitoid rocks, the chemistry of the Southalpine porphyroids is closer to S-type than any other one.

The Ocean Ridge Granite normalized pattern of the porphyroids (Fig. 10) has a shape which fits both the (syn- to post-) collisional and the volcanic arc (Chile-like active margins) patterns, even considering that the left-hand side of the plot could have been slightly distorted by the mobility of these elements.

Some discriminations can be also made in the Rb–Y–Nb and Rb–Yb–Ta space (PEARCE et al., 1984): figure 11 a) and b) show simple projections in the Y–Nb and in the Yb–Ta planes, which represent the most likely alteration-independent diagrams. The data points fall mainly in the VAG and syn-COLG fields, with a few of them in the WPG. The diagrams of figure 11 c) and d) also include Rb, which behaved as a mobile element; it can be stated however, that any Rb change would not shift the data points parallel to the Y+Nb axis; moreover, considering the uncertainty of the VAG/syn-COLG boundary, the only possible conclusion is that the proper field for metavolcanics is intermediate between VAG and syn-COLG. Finally, it is worth to note that in each diagram the post-COLG partially overlap VAG, syn-COLG and, to a lesser extent, WPG fields, thus preventing a definite answer. Although these diagrams are not straightforward to indicate a unique scenario, they rule out an anorogenic tectonic setting.

The Rb/Zr vs SiO_2 diagram (HARRIS et al., 1986) suggests a post-collisional environment

(Fig. 12). Assuming that the deuteresis only led to a small Rb gain or loss (see section 4.1), the position of the volcanics within the post-COLG field should be correct.

5. Conclusions

The Southalpine Ordovician porphyroids in the Eastern Alps represent acidic metavolcanics and metavolcanoclastics outcropping throughout the whole basement; they formed the so called "Upper Ordovician Rhyolitic Plateau". The observed bulk chemistry is not strictly representative of the original composition of the protoliths, as late- to post-magmatic events significantly mobilized alkalies and, to a lesser extent, alkali-earths, silica, Pb, Cu, Zn and Sn. However, such chemical changes did not act similarly in the study areas. The Comelico porphyroids appeared to be the most suitable samples to define the pre-Variscan magmatic events in the Southalpine basement, while the least reliable samples come from Agordo and Val di Funes zones. The main chemical features common to all the metavolcanics are the high SiO_2 content and the peraluminous character. Their protoliths are classified as rhyolites and rhyodacites/dacites, using immobile element ratios.

The geochemical features of the porphyroids, together with some petrographic observations, constrain the mechanisms of magma production, indicating a crustal origin for the magmas, through dehydration melting reactions. According to several trace elements and REE data, the most likely starting material for these reactions is a metapelite, even if a layered metasedimentary source cannot be excluded. The process involved quartz, plagioclase, biotite and a Al_2SiO_5 phase, and left garnet/cordierite, rutile and variable amounts of K-feldspar in the residuum. The major element trends suggest that many of the metavolcanics represent mixtures between variable amounts of restite and melt; similar magma evolution processes have been indicated by PECCERILLO et al. (1979) to explain some geochemical features of two Austroalpine granitoids (Casies and Anterselva), which are considered to be cogenetic (SASSI and ZIRPOLI, 1979).

Trace element signatures have also been employed to put some constraints on the possible tectonic setting in which the Ordovician volcanism developed. Some discriminant diagrams of the granitoid tectonic setting, although not straightforward, seem to exclude an anorogenic environment. Considering that compressional regimes are not favourable to allow large amounts

of magma to outpour at surface, and taking into account the projection of the metavolcanics in some discriminant diagrams from literature, the most likely tectonic setting for this old volcanism is a late orogenic environment. This confirms the scenario described by BELLIENI and SASSI (1981) and LOESCHKE and HEINISCH (1993). The hypothesis of a volcanic arc related to an outer mobile belt which comprises also the Austroalpine porphyroids (HEINISCH, 1981), although partially upheld by Pearce discriminant diagrams, is not supported by the frequency distribution of the rock types, which has a maximum for the rhyolite/rhyodacite compositions. The new data presented in this paper are consistent with a general picture which includes both Ordovician granitoids and porphyroids (MAZZOLI and SASSI, 1992; NEUBAUER et al., 1993; SASSI et al., 1994), as the similarity of the geochemical characters of these rocks, already remarked by previous workers, is further on confirmed.

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