

Geochemistry and mineralogy of detritic rocks from Verrucano type-sequences of Northern Apennines (Monti Pisani and Punta Bianca), Italy

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ABSTRACT. — Major- and trace-element geochemistry is used to obtain information on the primary mineralogical composition, the depositional environment and the source rocks of early-alpine, fluvio-marine, clastic metasediments (Verrucano, Triassic) of Northern Apennines, Italy.

Two Verrucano type-sequences (Monti Pisani and Punta Bianca) have been considered. Within Monti Pisani sequence the chemical and mineralogical data differentiate the two formations established by previous sedimentological studies; for the Verruca Formation the following primary mineralogy may be inferred: quartz + micas + kaolinite and/or montmorillonites + minor amounts of feldspars (mostly Na-feldspar), while Monte Serra Formation original mineralogical assemblage was: quartz + micas + feldspars (mostly K-feldspar) + lesser amounts of chlorites. At Punta Bianca a highly uniform composition of the clastic terrigenous fraction over the whole sequence is observed; its primary mineralogical assemblage was: quartz + micas + subordinate chlorites and/or montmorillonites + minor feldspars. On the whole the chemistry (and the primary mineralogy) of Punta Bianca sediments matches that of middle Monti Pisani sequence, i.e. upper Verruca F. and lower Monte Serra F. members.

FeO/Fe₂O₃ ratio trend suggests weathering and erosion under highly oxidizing conditions. In Monti Pisani sequence the same conditions were dominating in the deposition basin too, while Punta Bianca deposition basin appears to have evolved from reducing to oxidizing conditions.

Alumina and alkali patterns record intense breakdown of parent materials, more advanced in the lower Verruca Formation (Monti Pisani sequence), where reworking of previously developed lateritic crusts most probably occurred.

Comparison of Verrucano Triassic sediment compositions with those of known pre-Triassic rocks from Tuscany basement allows tracing of the main source rocks. For Mt. Pisani sequence such sources may be recognized in «Permian Red Porphyries», «S. Lorenzo

Schists» and «Buti Quartzites and Phyllites» units, while for Punta Bianca sequence the main source may be found in a unit equivalent to «Buti Quartzites and Phyllites».

Key words: Verrucano, detritic sediments, Northern Apennines, geochemistry, mineralogy, source rocks.

RIASSUNTO. — I dati geochimici relativi agli elementi maggiori e ad alcuni elementi in traccia (Rb, Ba e Sr) sono stati utilizzati per determinare la composizione mineralogica primaria, caratterizzare l'ambiente di deposizione ed individuare le rocce sorgenti dei metasedimenti clastici triassici del Verrucano dell'Appennino settentrionale.

Sono state prese in considerazione due sequenze-tipo del Verrucano, meglio conosciute dal punto di vista sedimentologico: la sequenza dei Mt. Pisani e la sequenza di Punta Bianca. Nell'ambito della prima i dati chimici e mineralogici hanno permesso di distinguere le due formazioni della «Verruca» e del «Monte Serra», già evidenziate su basi sedimentologiche. La composizione mineralogica originaria dei sedimenti della F. della Verruca risulta caratterizzata da: quarzo + mica + kaolinite e/o montmorillonite + quantità minori di feldspati (principalmente albite), quella dei sedimenti della F. del Monte Serra appare costituita da: quarzo + mica + feldspati (principalmente K-feldspato) + quantità minori di clorite. A Punta Bianca si osserva una composizione molto uniforme della frazione clastica terrigena lungo l'intera sequenza; la composizione mineralogica primaria risulta rappresentata dall'associazione: quarzo + miche + cloriti e/o montmorilloniti (in quantità subordinata) + feldspati (in piccole quantità). Nel complesso le composizioni chimica e mineralogica (primaria) dei sedimenti di Punta Bianca coincidono con quelle della parte mediana della sequenza dei Mt. Pisani (membri superiori della F. della Verruca ed inferiori della F. del Monte Serra).

Il rapporto FeO/Fe₂O₃ suggerisce processi di alterazione ed erosione in condizioni altamente ossidanti; nei Mt. Pisani tali condizioni dovevano essere presenti an-

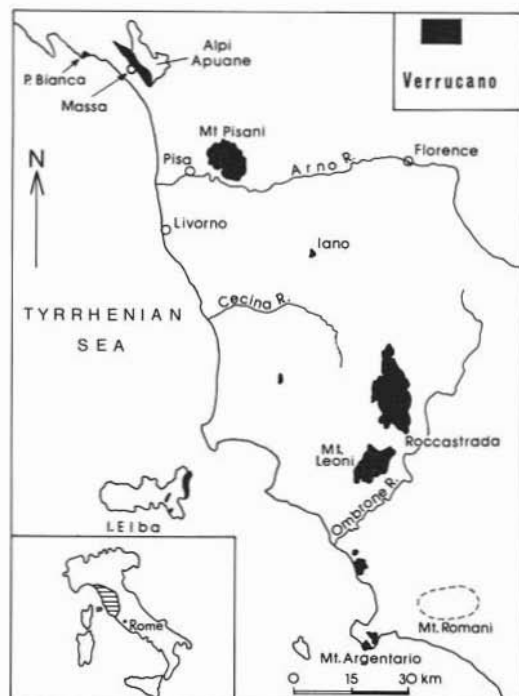


Fig. 1. — Location of the main Verrucano outcrops.

che nel bacino di sedimentazione, mentre a Punta Bianca quest'ultimo appare essersi evoluto da condizioni riducenti a condizioni ossidanti.

La distribuzione dell'allumina e degli alcali segnala un'intensa alterazione delle rocce primarie, più spinta nella parte inferiore della «Verruca», dove appare evidente il contributo di materiali derivanti da depositi lateritici.

Il confronto delle composizioni dei sedimenti studiati con quelle di formazioni note nel basamento paleozoico della Toscana ha consentito di individuare le principali rocce sorgenti dei materiali sedimentari costituenti le due sequenze. Tali rocce sorgenti sono individuabili, per la sequenza dei Mt. Pisani, nei «Porfidi Rossi Permiani», negli «Scisti di S. Lorenzo» e nelle «Quarziti e Filladi di Buti», per la sequenza di Punta Bianca in unità litologicamente equivalenti alle «Quarziti e Filladi di Buti».

Parole chiave: Verrucano, sedimenti detritici, Appennino settentrionale, geochimica, mineralogia, rocce sorgenti.

Introduction

The clastic sedimentary sequences known as Verrucano represent in the Tuscan Domain of Northern Apennines (Italy) the basal quartz-arenite sedimentary assemblage of the Alpine geosyncline (CASSINIS et al., 1979);

they are regarded as being Middle to lower Upper Triassic in age (ELTER and FEDERICI, 1964; FEDERICI, 1966; ELTER et al., 1966; RAU and TONGIORGI, 1974; COCOZZA et al., 1975). These sequences outcrop in discontinuous areas, covering widely variable surfaces in a belt about 200 km long from Punta Bianca (Southern Liguria) to Monte Argentario (Southern Tuscany) (Fig. 1).

Considerable work has been done on geology and stratigraphy of Verrucano; an extensive literature review up to 1963 is reported in BRANDI (1964). More recent works on the subject had the objectives to further enhance the knowledge of sedimentology and stratigraphy of Verrucano (TONGIORGI et al., 1977; MARTINI et al., 1986) and to establish correlations between the well studied northern sequences (Mt. Pisani and Punta Bianca) with the little known sequences of Southern Tuscany.

Even in the most studied sequences very little work has been done on the geochemistry of these sediments. During alpine orogenesis the Verrucano sediments have been affected by a low grade metamorphism. After metamorphism and in absence of fossils chemical data are often the only clues to their genesis and to possible stratigraphic correlations. Important papers on this subject are a comparative geochemical and mineralogical study of Valle Giove (Elba Island) and Mt. Pisani Verrucano outcrops (DESCHAMPS, 1980) and a geochemical investigation of carbonatic and ferruginous horizons in the Verrucano of Southern Tuscany (ANNOVI et al., 1980). Mineralogical parageneses and petrographical features of the Verrucano metasediments are reported by SCHIAFFINO and TONGIORGI (1962) and FRANCESCHELLI et al. (1986).

The objective of this investigation is to improve the knowledge of mineralogy and geochemistry of Verrucano clastic sediments and then to present data which may be useful in stratigraphic correlations, in geochemical assessment of source rocks and for characterization of depositional environments.

Stratigraphic setting

In the present stage the investigation has

been applied to the Mt. Pisani and Punta Bianca sequences, which are the best known Verrucano outcrops. Detailed information on stratigraphy, sedimentology and geology of these sequences is given in RAU and TONGIORGI (1974), TONGIORGI et al. (1977) and

MARTINI et al. (1986); here we merely report the stratigraphic columns (Figs. 2 and 3) derived from these previous works.

In the Mt. Pisani area the thick terrigenous sequence (700 m) of Triassic age has been subdivided into two formations, namely the «Ver-

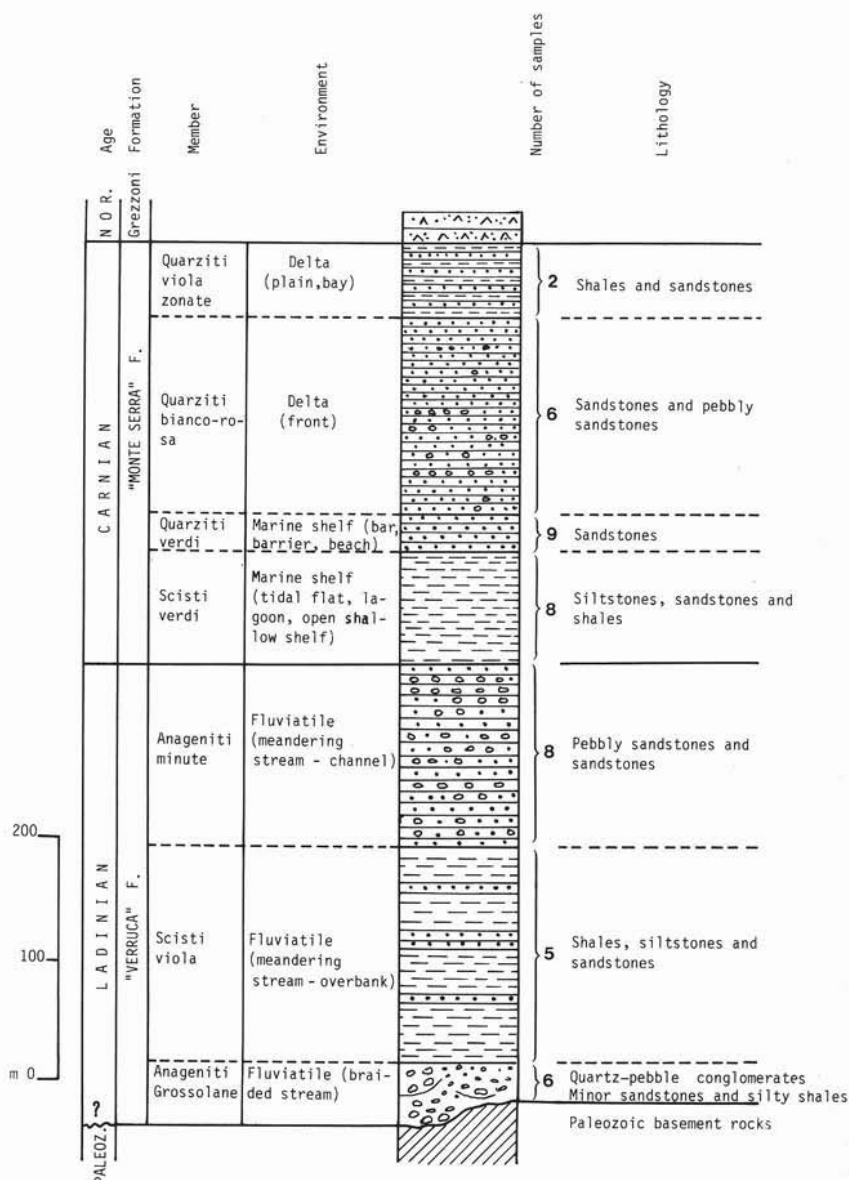


Fig. 2. — Stratigraphic column of Monti Pisani Verrucano sequence (after Rau and Tongiorgi, 1974, modified according to Tongiorgi et al., 1977). («Anageniti grossolane»: «Coarse orthoquartzitic conglomerates»; «Scisti viola»: «Purple shales»; «Anageniti minute»: «Fine orthoquartzitic conglomerates»; «Scisti verdi»: «Greenish shales»; «Quarziti verdi»: «Greenish quartzites»; «Quarziti bianco-rosa»: «Light-pinkish quartzites»; «Quarziti viola zonate»: «Purple-banded quartzites»).

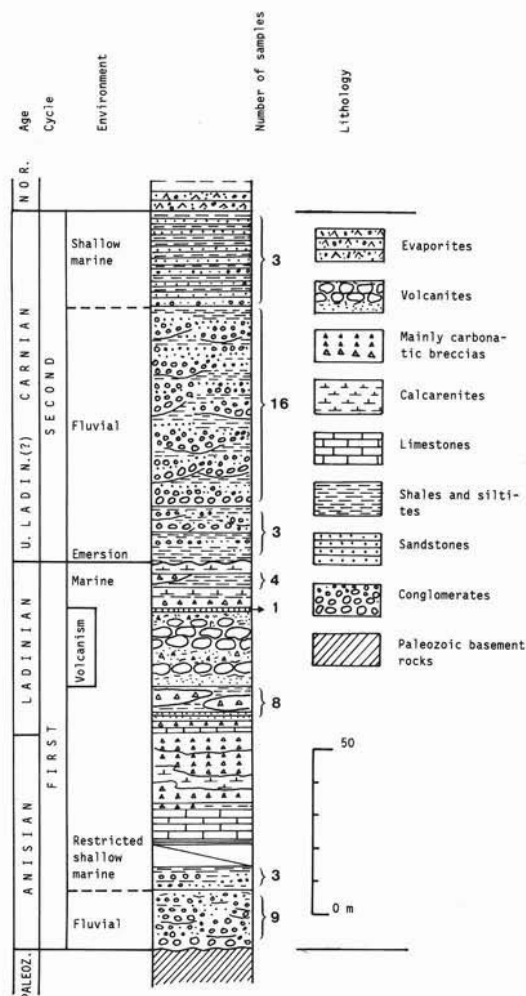


Fig. 3. — Stratigraphic column of Punta Bianca sequence (after Martini et al., 1986).

ruca F.» (Middle Triassic) and the «Monte Serra F.» (lower Upper Triassic) by RAU and TONGIORGI (1974); the first formation is regarded as an alluvial sequence while the second one is considered a marine shelf to deltaic sequence (TONGIORGI et al., 1977). Within such formations RAU and TONGIORGI (1974) distinguished seven members («Anageniti grossolane», «Scisti viola», etc.), whose names were later retained only as facies names (TONGIORGI et al., 1977). At Punta Bianca a 250 m thick Middle Triassic sedimentary sequence contains two cycles of sedimentation: a lower cycle (I cycle) and an

upper cycle (II cycle) (MARTINI et al., 1986; RAU et al., in press). At first the whole sequence of Punta Bianca was regarded as a distal equivalent of Mt. Pisani and Southern Tuscany Verrucano sequences (ELTER et al., 1966; RAU and TONGIORGI, 1974; TONGIORGI et al., 1977). Recently MARTINI et al. (1986) interpreted the lower cycle as the sedimentary and volcanic fill of an «abortive» continental rift; according to these authors only the upper cycle would correspond to the Verrucano Triassic sequence of Mt. Pisani, that is the base of the most important «Alpidic» sedimentary cycle. Within the Punta Bianca sequence the same authors distinguished sixteen sedimentological units (not reported in Fig. 3), which formed in several environments.

For the present work 44 and 47 samples were collected respectively from Mt. Pisani and Punta Bianca sequences. Only the terrigenous lithotypes were considered, hence all the carbonate and volcanic products in Punta Bianca I cycle were carefully avoided.

Methods

Qualitative mineralogical composition of bulk samples and clay fractions has been studied mainly by X-ray diffraction analysis; complementary data have been obtained through thin section study. Quartz and calcite were quantitatively determined by X-ray diffractometry through an external-standard technique; hematite (+ iron hydroxides and magnetite) and feldspar contents have been estimated through modal analysis of thin sections. Deficiency of total non-sheet silicate components per cent from 100 was entirely assigned to the sheet-silicate assemblage. Semi-quantitative estimations of these last components were again made by X-ray diffractometry through an external standard technique.

The determination of major chemical components and some trace elements (Mn, Rb, Sr and Ba) on bulk samples was performed by X-ray fluorescence analysis according to the procedure given by FRANZINI et al. (1975). FeO was determined by colorimetric titration; loss on ignition was obtained by heating at 850° C. Mineralogical data are reported in

Table 1; chemical compositions are listed in Table 2. Tables 3 and 4 give the correlation coefficients (r) between the major and trace-element components. For each pair of components two (r) values are reported, since both in Mt. Pisani and in Punta Bianca sediments two sub-groups of samples have been distinguished; in the first sequence the two sub-groups correspond to the two different formations and in the second one they refer to the two different cycles established by previous sedimentological studies (RAU and TONGIORGI, 1974; TONGIORGI et al., 1977; MARTINI et al., 1986).

Mineralogy

Present mineralogical features of Mt. Pisani and Punta Bianca sequences (Table 1) are, at least in part, a consequence of metamorphic reactions and provide little information on the sediment original mineralogical composition. More clues are given by chemical compositions, which are regarded to have undergone only slight changes during metamorphism; this approach to the subject will be mainly treated later, within the geochemical data discussion.

Monti Pisani sequence

Monti Pisani sequence clastic sediments are mostly made up of quartz and mica, sometimes associated with minor chlorite and, in the lower Verruca formation, also with paragonite and pyrophyllite. Low amounts of hematite (+ iron hydroxides and magnetite), ranging from < 1% to 4%, and scarce feldspars are present all over the sequence; zircon, apatite and tourmaline are relatively common trace components.

A comparative analysis of hematite (+ iron hydroxides and magnetite), total iron and $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio distributions shows that most of the element occurs as ferric iron, which in the Verruca formation rocks resides primarily in hematite, iron hydroxides and magnetite, while in Monte Serra formation is mainly contained in a light green-coloured phengitic muscovite; the highly phengitic composition of such mica is confirmed by diagrams of Figs. 5, 6 and 7.

Further mineralogical difference between Verruca and Monte Serra formations lies in the presence of pyrophyllite and paragonite in the lower members of the former. Pyrophyllite crystallization is clearly related to a high alumina/alkalis ratio (Fig. 6, upper part), which explains also the normal composition of the associated muscovite (that is an Al-rich mica); in such conditions the relatively high Na/K ratio entails the appearance also of paragonite. In the upper formation (Monte Serra formation) the distinctly lower alumina/alkalis ratio resulted in the crystallization of a Fe-rich dioctahedral mica and the reduced presence of free iron oxides (hematite).

Punta Bianca sequence

In both cycles the clastic terrigenous metasediments are presently chiefly composed of quartz and muscovite, associated with chlorite and minor amounts of hematite; relatively common trace components are apatite, tourmaline and zircon. The main mineralogical differences between the rocks of the two cycles consist in the chlorite and hematite distributions (and in the presence of more or less abundant non-terrigenous carbonates in the lower cycle). In the II cycle chlorite contents range from < 3 to 10%, hence they are very similar to those observed in Mt. Pisani sequence central part, that is upper Verruca formation («Anageniti minute» and part of «Scisti viola» members) and lower Mt. Serra formation («Scisti verdi» member). In the I cycle chlorite is much more abundant (9-20%) in all the layers, except those close to the volcanic products. The high chlorite contents appear strictly related to high $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio values, which, in turn, presumably reflect reducing conditions in the deposition basin. This trend is particularly evident within the basal conglomerates.

Hematite is homogeneously distributed within the upper cycle sediments, where it ranges from 1 to 5%. In the lower cycle the content is very low in the basal conglomerates, but shows significant increases in the siltstones associated with carbonate breccias;

TABLE 1

Range of mineralogical compositions of Triassic detritic rocks from Mt. Pisani and Punta Bianca (for member names reader is referred to caption of Fig. 2)

		Mt. Pisani sequence								
Member	N	Qz	Hem.	Feldsp.	Calc.	Mi	Ch	Parag.	Py	
"Mt. Serra" Formation	Quarziti viola zonate	2	28 - 44	<0.5 - 2	<0.5 - 1	n.d.	54 - 65	<3 - 3	n.d.	n.d.
	Quarziti bianco rosa	6	12 - 69	<0.5 - 2	<0.5	n.d.	32 - 86	<3	n.d.	n.d.
	Quarziti verdi	9	22 - 53	<0.5 - 3	<0.5	n.d.	40 - 95	<3 - 9	n.d.	n.d.
	Scisti verdi	8	26 - 59	<0.5 - 2	<0.5	n.d.	50 - 68	<3 - 8	n.d.	n.d.
"Mt. Verruca" Formation	Anageniti minute	8	32 - 72	<0.5 - 4	<0.5 - 1	n.d.	18 - 52	<3 - 12	n.d.	n.d.
	Scisti viola	5	48 - 58	1.5 - 4	<0.5 - 1	n.d.	18 - 38	<3 - 7	<4 - 14	<3 - 15
	Anageniti grossolane	6	54 - 87	<0.5 - 3	<0.5 - 1	n.d.	3 - 23	<3 - 3	<4 - 6	3 - 16
Punta Bianca sequence										
Environment and dominant lithotype		N	Qz	Hem.	Feldsp.	Calc.	Mi	Ch	Parag.	Py
Second Cycle	Shallow marine (sandst.)	3	32 - 80	1.5 - 3	<0.5	<2	15 - 55	3 - 10	n.d.	n.d.
	Fluvial (congl.)	19	34 - 93	2 - 5	<0.5	<2 - 5	7 - 52	<3 - 9	n.d.	n.d.
First Cycle	Marine (clastic matrix of carbonatic breccias)	10	28 - 45	<0.5 - 8	<0.5	<2 - 7	31 - 53	5 - 16	n.d.	n.d.
		1*	28	50	<0.5	<2	16	6	n.d.	n.d.
		3*	27 - 41	2 - 3	<0.5	15 - 39	23 - 40	<3 - 10	n.d.	n.d.
	Fluvial to restricted shallow marine (congl.)	11	27 - 52	0.5 - 5	<0.5	<2 - 3	28 - 50	11 - 20	n.d.	n.d.

N = Number of samples; • Thin iron-rich sedimentary layer overlying volcanic products; * Siltites containing carbonate clasts. Hematite (+ iron hydroxides and magnetite) and Feldspars estimated through modal analysis of thin sections; Qz = Quartz; Hem. = Hematite (+ iron hydroxides and magnetite); Feldsp. = Feldspars (K-feldspar + Na-feldspar); Calc. = Calcite; Mi = Muscovite; Parag. = Paragonite; Py = Pyrophyllite; Ch = Chlorite; n.d. = Not detected.

the hematite becomes still more conspicuous close to the volcanic products, where 50% hematite contents can locally be found (thin sedimentary layers directly overlying lavas and volcanoclastic products).

Chemistry and chemical-mineralogical relationships

In order to establish connections between chemistry and primary mineralogical composi-

TABLE 2

Range of chemical compositions of Triassic detritic rocks from Mt. Pisani and Punta Bianca (for member names reader is referred to caption of Fig. 2)

Member	N	Mt. Pisani sequence											Sr (ppm)	Ba (ppm)		
		SiO ₂ (wt.%)	TiO ₂ (wt.%)	Al ₂ O ₃ (wt.%)	Fe ₂ O ₃ (wt.%)	FeO (wt.%)	MgO (wt.%)	CaO (wt.%)	Na ₂ O (wt.%)	K ₂ O (wt.%)	P ₂ O ₅ (wt.%)	L.I. (wt.%)			Mn (ppm)	Rb (ppm)
Quartziti viola	2	58.02-67.79	0.72-0.82	16.15-21.21	3.86-5.44	0.38-0.53	2.03-2.75	0.02-0.05	0.17-0.41	5.95-7.44	0.05-0.06	2.56-3.49	23-25	173-228	19-20	447-634
zone																
Quartziti bianco	6	57.80-81.77	0.49-1.03	8.99-21.37	2.15-6.68	0.19-0.23	1.26-2.54	0.01-0.04	0.04-0.06	3.59-9.45	0.01-0.02	1.67-3.54	<4-27	98-253	6-9	92-134
rosa																
Quartziti verdi	9	51.63-68.19	0.73-1.13	17.61-23.02	0.88-7.17	0.13-1.03	0.93-2.89	0.01-0.03	0.07-0.41	4.40-10.47	0.01-0.10	2.74-4.32	10-75	160-267	6-26	72-689
Scisti verdi	8	57.45-70.22	0.74-0.95	15.13-20.71	3.58-6.09	0.45-1.91	1.79-3.04	0.02-0.15	0.08-0.81	4.63-7.57	0.02-0.18	2.50-4.14	15-378	146-206	16-27	288-584
verdi																
Anageniti minute	8	56.59-80.34	0.54-0.94	9.16-23.36	0.99-6.28	0.36-2.46	1.10-2.31	0.02-0.18	0.29-1.26	2.03-5.73	0.02-0.18	1.69-3.80	11-52	65-283	20-50	270-773
Scisti viola	5	66.51-72.34	0.51-0.78	16.29-18.51	3.23-4.75	0.13-0.79	0.21-2.36	0.02-0.06	0.64-0.91	1.97-3.85	0.02-0.06	2.42-2.92	10-360	103-153	28-79	551-855
Anageniti grossolane	6	74.43-93.12	0.08-0.45	4.58-15.84	0.42-3.67	0.01-0.35	0.03-0.69	0.01-0.02	0.25-0.62	0.25-2.38	0.01-0.04	0.69-2.27	10-72	12-105	17-82	117-367
Punta Bianca sequence																
Environment dominant lithotype	N	SiO ₂ (wt.%)	TiO ₂ (wt.%)	Al ₂ O ₃ (wt.%)	Fe ₂ O ₃ (wt.%)	FeO (wt.%)	MgO (wt.%)	CaO (wt.%)	Na ₂ O (wt.%)	K ₂ O (wt.%)	P ₂ O ₅ (wt.%)	L.I. (wt.%)	Mn (ppm)	Rb (ppm)	Sr (ppm)	Ba (ppm)
Shallow marine (sandst.)	3	58.06-87.87	0.27-0.99	6.03-21.33	2.04-3.91	0.18-2.36	0.65-3.82	0.02-0.04	0.10-0.24	1.58-6.06	0.02-0.03	0.72-4.17	<4-42	44-184	8-18	243-836
Second Cycle																
Fluvial (cong.)	19	54.86-95.34	0.09-0.98	2.43-21.33	0.71-6.42	0.01-0.34	0.15-3.66	0.02-3.88	0.12-0.71	0.52-5.40	0.01-0.09	0.34-7.47	<4-895	18-226	6-46	50-771
Marine (clastic matrix)	10	53.65-64.86	0.70-1.24	15.61-22.59	1.84-8.04	0.01-2.53	1.36-2.86	0.10-3.64	0.34-1.01	3.40-5.88	0.03-0.32	2.66-5.19	80-255	52-193	25-233	552-883
Matrix	1	35-58	0.39	8.56	50.00	<0.01	1.42	0.71	0.32	1.56	0.11	1.34	47	39	17	178
Matrix	3*	40.40-55.57	0.56-1.02	11.50-14.90	3.28-5.56	1.17-1.52	1.60-2.00	8.31-20.49	0.35-0.46	2.71-3.83	0.04-0.07	8.56-16.26	475-1460	114-130	59-107	315-576
Matrix																
First Cycle																
Fluvial (cong.)	11	55.53-69.11	0.54-1.10	13.58-24.49	1.05-7.39	1.65-4.96	1.60-2.66	0.05-1.44	0.30-0.62	2.93-5.88	0.02-0.13	2.58-5.18	128-740	119-249	43-59	316-794
to restricted shallow marine (cong.)																

N = Number of samples; * Thin iron-rich sedimentary layer overlying volcanic products; * Siltites containing carbonate clasts; L.I. = Loss on ignition.

tion of Verrucano detrital rocks and to derive information on their environment of deposition, some of the diagrams proposed by de LA ROCHE (1978) have been used.

Monti Pisani sequence

Major element distribution

The diagrams of de LA ROCHE (1978), chosen to plot the data in this paper, emphasize some chemical and mineralogical differences between Verruca and Monte Serra formation rocks. Diagram of Fig. 4, designed to estimate the relative proportion of quartz, feldspars and sheet-silicates shows an overall scattering of sediment compositions; in fact they appear to range from quartzites to sandstones s.s. to shales, with a tendency of Monte Serra rocks to group mainly in the shale field. Diagram of Fig. 5, which emphasizes the behavior of some chemical components, namely alumina and alkalis, shows a general trend of Monti Pisani clastic sediments to evolve from greywackes to arkoses, the Verruca formation rocks being closer to the former and the Monte Serra

sediments approaching the latter field. Diagram of Fig. 6 ignores the role of quartz and carbonates and reveals the nature and abundance of feldspars, compared to sheet-silicates; it indicates a very scarce contribution of feldspars to the composition of all the sediments, especially to those of Verruca formation, with K-feldspar entirely dominant over plagioclase in Monte Serra formation and Na-feldspar more important in Verruca rocks. In the diagram of Fig. 7 albite (but not K-feldspar), quartz and carbonates are eliminated. The representative points of major sheet-silicate groups (kaolinite, montmorillonites, illites and chlorites) are clearly separated. The Monti Pisani sediment compositions appear to scatter over the full range from montmorillonites through illite field to the phengitic mica composition. Verruca and Monte Serra formation rocks are here again clearly differentiated. The former had a primary clay mineralogy where the dominant illitic component was mixed with an Al-rich, alkali-poor material (kaolinite and/or montmorillonites), particularly important in the basal conglomerates («Anageniti grossolane»). The Monte Serra clastic sediments had a

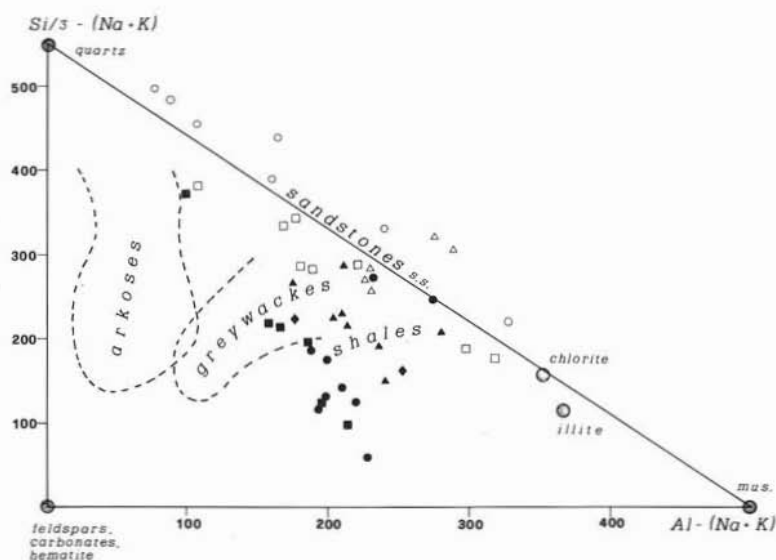


Fig. 4. — $[Si/3 - (Na + K)]$ vs. $[Al - (Na + K)]$ diagram (DE LA ROCHE, 1978) for Monti Pisani sequence (Verruca Formation members: \circ = Anageniti grossolane; Δ = Scisti viola; \square = Anageniti minute; Mt. Serra Formation members: \blacktriangle = Scisti verdi; \bullet = Quarziti verdi; \blacksquare = Quarziti bianco-rosa; \blacklozenge = Quarziti viola zonate (RAU & TONGIORGI, 1974).

primary clay mineralogy dominated by micaceous minerals, presumably associated with lesser amounts of chlorites (possibly more frequent in «Scisti verdi» and «Quarziti verdi» members). The micas have compositions within illite field in the formation lowest

member («Scisti verdi»), appear to approach phengitic mica composition in the upper members. We consider this latter composition a metamorphic effecty on sedimentary compositions characterized by higher K/Al ratios due to higher K-feldspar contents.

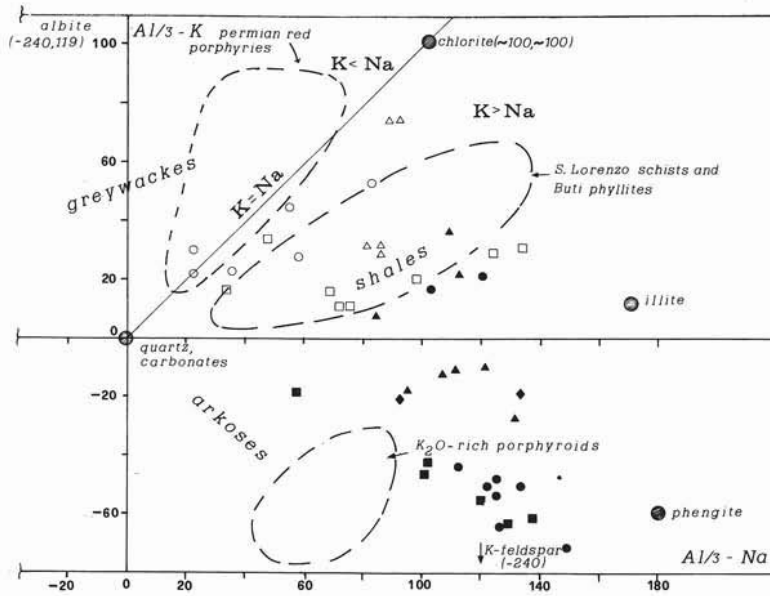


Fig. 5. — (Al/3 - K) vs. (Al/3 - Na) diagram for Monti Pisani sequence (legend as in Fig. 4).

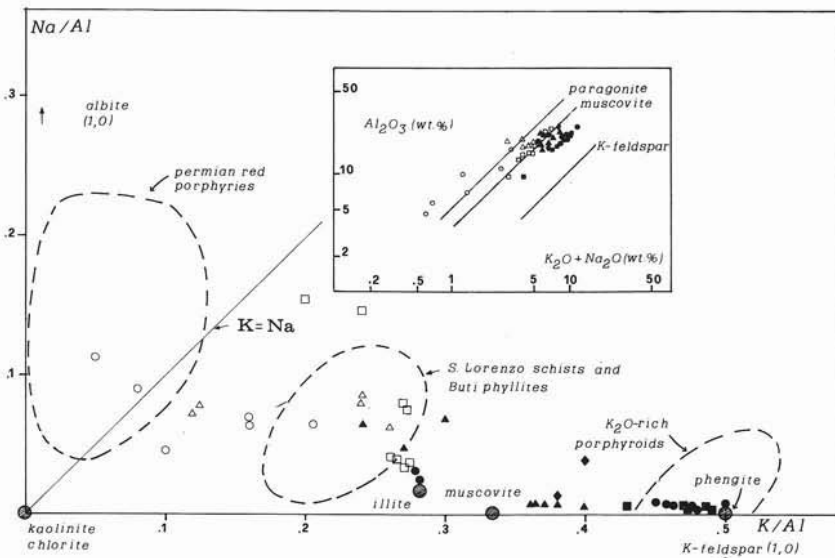


Fig. 6. — (Na/Al) vs. (K/Al) and (Al₂O₃) vs. (Na₂O + K₂O) diagrams for Monti Pisani sequence (legend as in Fig. 4).

The chemical component correlation coefficients (Table 3) confirm a dominant two component quartz-clay-mineral mixing model

for Verruca rocks. The elements Mg, Al, K, Ti, Fe, Rb are all positively correlated in abundance. These elements occur in the clay matrix

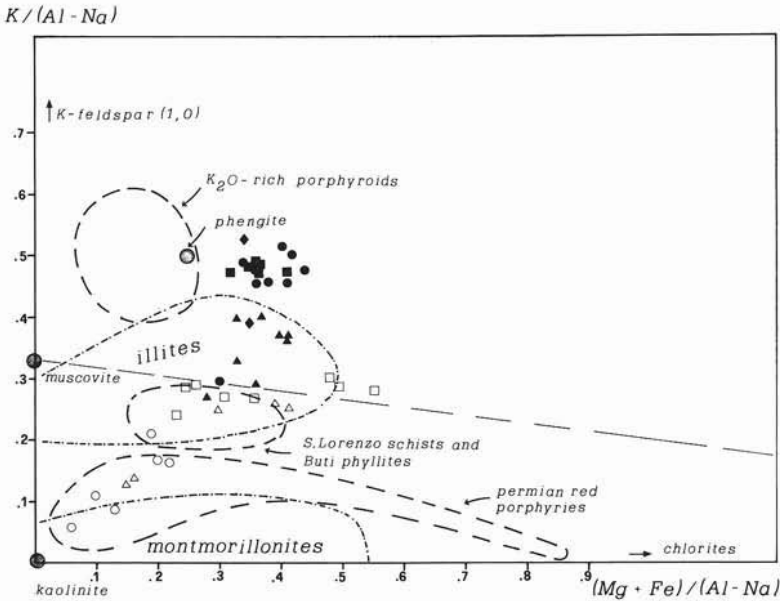


Fig. 7. — $[K/(Al - Na)]$ vs. $[(Fe + Mg)/(Al - Na)]$ diagram for Monti Pisani sequence (legend as in Fig. 4).

TABLE 3

Correlation matrix for detritic rocks of Mt. Pisani sequence. Only values of «r» > 0.50 (for which significance level $\alpha < 0.02$) are listed

	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe	Rb	Sr
Mg	— ^a — ^b											
Al	— ^a — ^b	0.57 0.50										
Si	— ^a — ^b	-0.76 -0.71	-0.96 -0.90									
P	— ^a — ^b	0.61 —	— —	— —								
K	— ^a -0.58	0.83 0.55	0.86 0.62	-0.95 -0.82	— -0.50							
Ca	— ^a 0.70 ^b	0.64 —	— —	— —	0.98 0.94	— -0.53						
Ti	— ^a — ^b	0.59 0.59	0.71 0.81	-0.76 -0.81	— —	0.69 0.59	— —					
Mn	— ^a — ^b	0.61 —	— —	— —	0.55 0.83	— —	0.52 0.68	— —				
Fe	— ^a — ^b	0.83 0.64	0.84 0.58	-0.95 -0.82	— —	0.92 0.67	— —	0.76 0.55	— —			
Rb	— ^a — ^b	0.68 —	0.90 0.64	-0.94 -0.72	— —	0.96 0.71	— —	0.69 —	— —	0.88 0.55		
Sr	— ^a 0.54 ^b	— —	— —	— —	— 0.52	— —	— 0.55	— —	— —	— —	— —	— —
Ba	— ^a 0.50 ^b	— —	0.90 —	-0.84 —	— 0.51	0.68 —	— —	0.73 —	— —	0.73 —	0.75 —	— 0.82

(a) «Verruca» Formation samples (N = 19); (b) «Mt. Serra» Formation samples (N = 25).

and all have a strong negative correlation with Si, and by inference, with quartz. Clay minerals containing all of these elements and quartz, together constitute the bulk of Verruca analyzed rocks (Table 1) and it is clear that the primary mineralogy of the rocks was dominated by the two components, quartz and clay minerals. Moreover the mineral mix was probably of sufficiently uniform composition to produce the relatively high degree of inter-element correlation.

The abundance of Na is not significantly correlated with that of any other element, suggesting the contribution of very small and variable amounts of albitic plagioclase to the sediment composition (Verruca F.). For Monte Serra rocks the correlation coefficients between the clay-mineral group of elements listed above are much lower; this may indicate a non-uniform mixing of quartz and clay matrix and/or a non-uniform composition of the latter. Moreover the poor correlation coefficients of K with the clay-mineral-elements suggest that K significantly occurs both in the clay matrix and in feldspars.

CaO is very low all over the sequence (0.01 - 0.05%). This may suggest erosion of carbonate-lacking source rocks and/or strong leaching processes. The highly positive correlation coefficient of Ca with P indicates that calcium is mostly present in apatite. Also manganese is chiefly resident in phosphates, which may contain in addition subordinate amounts of Mg (Verruca f.) or Na (Monte Serra f.).

Rb, Sr and Ba distribution

In Verruca formation Rb is highly correlated with all the clay-matrix-elements (Mg, Al, K, Ti, Fe, Ba) and hence its distribution is dominantly controlled by micaceous minerals. In Monte Serra sediments the correlation coefficients suggest an important control of Rb distribution also by the relatively more frequent K-feldspar component. This is reflected also by K/Rb ratio trend; Verruca f.: K/Rb range = 160 - 250, K/Rb average = 200; Monte Serra f.: K/Rb range = 250 - 350, K/Rb average 300. It is well known that K/Rb ratio in K-feldspars is definitely higher than in micas (HEIER and ADAMS, 1964;

LANGE et al., 1966). However the difference in K/Rb ratio between the two formations may have been further enhanced by differences in weathering processes; the more advanced the weathering processes, the more Rb-enriched the sediment (BILLINGS, 1970).

Most Sr contents appear lower (Verruca f.: 17 - 82 ppm, \bar{X} = 44 ppm; Monte Serra f.: 6 - 27 ppm, \bar{X} = 16 ppm) than those reported in literature for undifferentiated sandstones (sandstones s.l.: 40 - 150 ppm; VEIZER, 1978). The nearly complete absence of carbonate may account for such low Sr values. However the element distribution is controlled not only by carbonates, but most probably also by detrital and authigenic plagioclases and K-feldspars (VEIZER, 1978). Due to this multiple mineralogical control the correlations with major elements may be of low significance as in Verruca formation (Table 3). In Monte Serra formation a highly significant positive correlation of Sr with Ba is explained by their present residence mostly in a common phase, barite, after diagenetic (and/or metamorphic) processes mobilized them from the original phases.

In Verruca formation Ba is highly correlated with most the clay-matrix-elements, while in Monte Serra sediments Sr is the only element highly correlated with Ba. High Ba/Sr ratios (10 - 30) confirm that in these latter rocks Ba may be mostly resident in diagenetically formed barite.

FeO/Fe₂O₃ ratio

The FeO/Fe₂O₃ ratio is very low all over the sequence (range: < 0.01 - 0.7); this suggests highly oxidizing conditions in both the source rock area and the deposition basin. Such conditions are typically realized in continental areas, under a hot, semi-arid climate with a seasonal rainfall or even under a hot, humid climate with a high rate of organic matter destruction.

The first climatic situation closely matches that proposed by RAU and TONGIORGI (1974) for Tuscany Triassic clastic sequences. Small FeO/Fe₂O₃ ratio variations can be observed; they are regarded as due to variations in the sedimentation rate.

TiO₂/Al₂O₃-quartz relationships

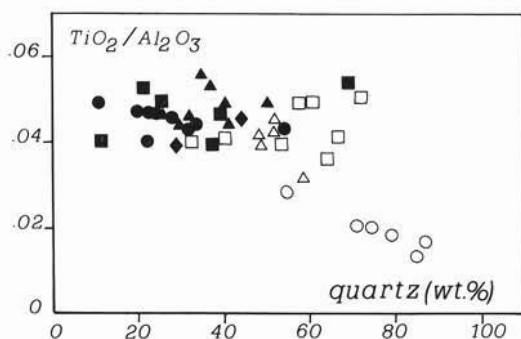


Fig. 8. — $(\text{TiO}_2/\text{Al}_2\text{O}_3)$ ratio vs. quartz content in Monti Pisani sequence (legend as in Fig. 4).

Ti is positively correlated in abundance with Al, Fe, Mg, K, Ba and Rb and hence is mostly contained in the clay matrix.

For clastic sediments the ratio $\text{TiO}_2/\text{Al}_2\text{O}_3$ may be important in assessing significant sedimentological parameters. According to SPEAR and KANARIS-SOTIRIOU (1976) the ratio is controlled by grain size, degree of sorting and maturity; moreover it is influenced by chemistry and mineralogy of source rocks as well as by climatic conditions during weathering processes. For well-sorted sandstones they

found a positive relationship between $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio and the quartz content. In Monte Serra formation no relationship between quartz and $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio has been observed (Fig. 8); this would point to a low maturity and/or a poor sorting of these sediments. On the contrary in a large part of Verruca formation («Anageniti grossolane» and a part of «Scisti viola» and «Anageniti minute» members) the $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio is negatively correlated with quartz content.

This is interpreted as caused by the mixing of materials from different source rocks: a) sediments developed from weathering of metasedimentary rocks of Paleozoic basement, which contributed most of Ti; b) sediments, mainly quartz bearing, resulting from alteration of acid volcanic rocks. This model, which is confirmed by other geochemical and petrographical data, explains the anomalously low $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratios (< 0.03) exhibited by the lower Verruca formation. In fact acid magmatites are known to have much lower $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratios (~ 0.014) than normal shales and sandstones (~ 0.04 and ~ 0.10 , respectively) (SPEARS and KANARIS-SOTIRIOU, 1976).

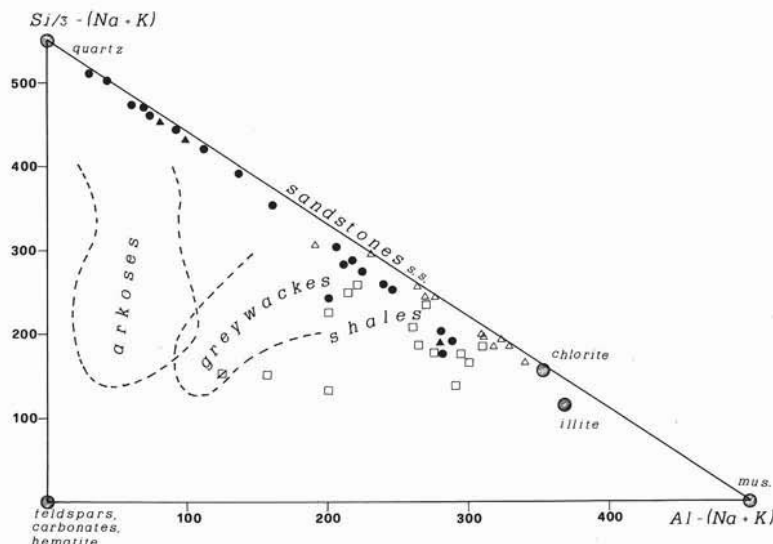


Fig. 9. — $[\text{Si}/3 - (\text{Na} + \text{K})]$ vs. $[\text{Al} - (\text{Na} + \text{K})]$ diagram (DE LA ROCHE, 1978) for Punta Bianca sequence (I Cycle environments and dominant lithotypes: Δ = Fluvial to restricted shallow marine (conglomerates); \square = Marine (clastic matrix of carbonatic breccias); \boxtimes = Marine (thin iron-rich sedimentary layer overlying volcanic products). II Cycle environments and dominant lithotypes: \bullet = Fluvial (conglomerates); \blacktriangle = Shallow marine (sandstones) (MARTINI et al., 1986).

Punta Bianca sequence

Major element distribution

Diagram of Fig. 9 shows that, like Monti Pisani rocks, Punta Bianca sediments range from quartzites to sandstones to shales, most of their representative points being very close

to the quartz-muscovite line; few of them appear rather off set due to high hematite and/or calcite contents. As to the relative distribution of alkalis and alumina, diagrams of Figs. 10 and 11 show a high uniformity of composition over the whole sedimentary sequence. Rocks of both cycles plot into the shale field

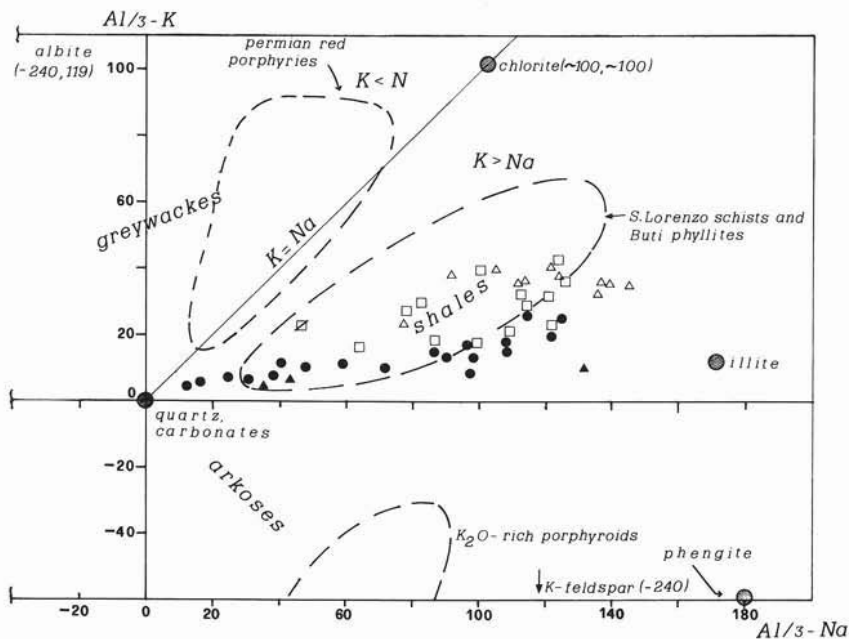


Fig. 10. — $(Al/3 - K)$ vs. $(Al/3 - Na)$ diagram for Punta Bianca sequence (legend as in Fig. 9).

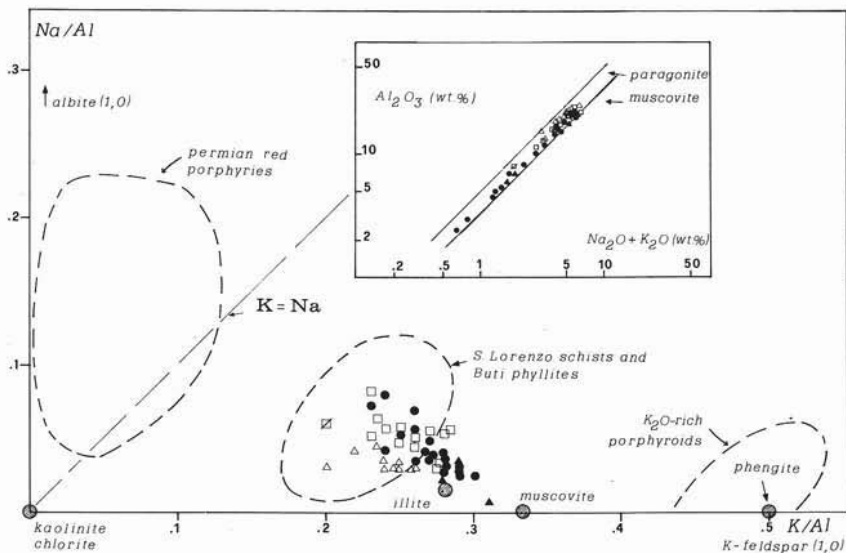


Fig. 11. — (Na/Al) vs. (K/Al) and (Al_2O_3) vs. $(Na_2O + K_2O)$ diagrams for Punta Bianca sequence (legend as in Fig. 9).

(Fig. 10); in both cases the feldspar contribution appears to have been scarce (Fig. 11). Yet the tendency of I cycle rock representative points to plot more close to the $K = Na$ line must be stressed; this suggests a slightly more important Na-feldspar contribution to the composition of cycle I sediments.

nearly purely detritic terrigenous deposits, carbonate breccias mixed with detritic terrigenous matrix, and even volcanoclastics (Fig. 3). Though sampling has been performed with care in order to avoid non-terrigenous materials, the influence of these latter is rather evident. This is reflected in a very low degree

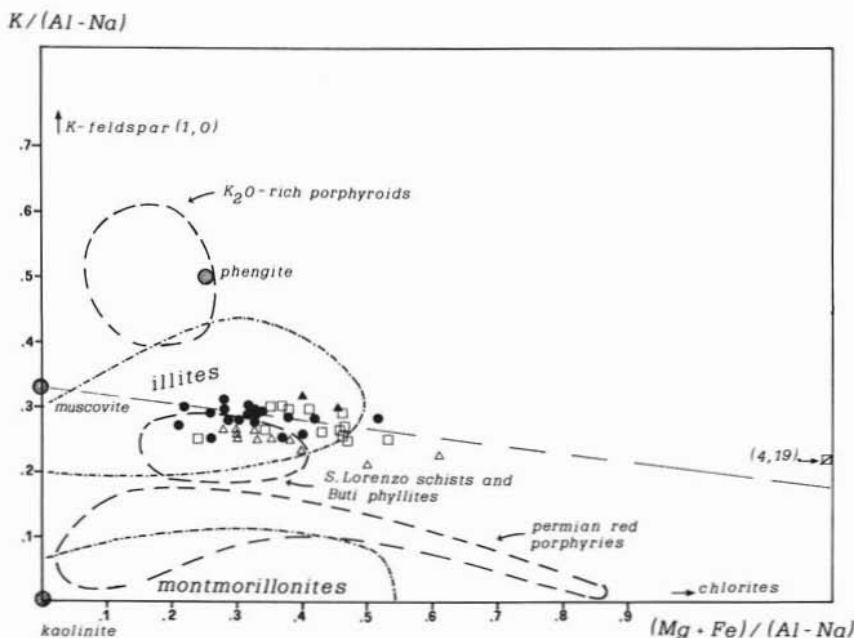


Fig. 12. — $[K/(Al - Na)]$ vs. $[(Fe + Mg) / (Al - Na)]$ diagram for Punta Bianca sequence (legend as in Fig. 9).

Further difference between the two cycles may be found in alumina/alkalis ratio, which results somewhat higher in the I cycle sediments (range 3.10 - 4.60) than in the II cycle rocks (range 3.10 - 3.75) (Fig. 11, upper part); this feature is reflected in a present higher chlorite content. Diagram of Fig. 12 indicates a substantially uniform primary clay mineralogy, dominated by illites associated with subordinate amounts of ferro-magnesian, Al-rich components; these latter, more important in I cycle sediments (chiefly in basal conglomerates), were presumably composed of chlorites and/or montmorillonites.

The chemical component correlation coefficients (Table 4) stresses the differences between the two cycle sediments in terms of overall homogeneity. The lower cycle sediments are very heterogeneous, including

of inter-element correlation. Among the components commonly occurring in the clay fraction only Mg, Al, K and Ti still appear positively, though not highly, correlated in abundance. K is positively correlated also with Na and Al; this may imply a partial control of potassium distribution by the minor feldspar component too. Fe shows no inter-element correlation when the whole I cycle is considered, results highly correlated with other clay-matrix-elements when only the basal conglomerate compositions are taken into account. These data support the suggestion that a portion of the element in I cycle upper horizons is not terrigenous in origin, but rather genetically linked to the volcanic activity which produced lavas and volcanoclastic materials. The II cycle rock compositions show very high positive correlation coeffi-

coefficients between most of the elements held in the clay matrix (Na, Mg, Al, K, Ti, Fe, Rb) and a strong negative correlation of the former with Si, thus suggesting a uniform mixing of quartz with a clay matrix of very uniform composition.

Mn contents of carbonate levels associated with the clastic Triassic sequences of Tuscany have already been reported and discussed by ANNOVI et al. (1980).

Rb, Sr and Ba distribution

TABLE 4

Correlation matrix for detritic rocks of Punta Bianca sequence. Only values of $|r| > 0.50$ (for which significance level $\alpha < 0.02$) are listed

	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe	Rb	Sr
Mg	— ^a 0.58 ^b											
Al	0.52 ^a 0.80 ^b	0.55 0.80										
Si	— ^a -0.83 ^b	— -0.86	— -0.98									
P	— ^a 0.62 ^b	— —	— 0.58	— -0.62								
K	0.50 ^a 0.75 ^b	0.50 0.80	0.96 0.99	— -0.97	— 0.56							
Ca	— ^a 0.53 ^b	— —	-0.52 —	-0.60 -0.50	— 0.51	— —						
Ti	0.50 ^a 0.73 ^b	0.51 0.73	0.66 0.96	— -0.93	— 0.70	0.70 0.96	— —					
Mn	— ^a — ^b	— 0.51	— —	— —	— 0.50	— —	0.73 0.88	— —				
Fe	— ^a 0.77 ^b	— 0.85	— 0.97	— -0.97	— 0.58	— 0.97	— —	— 0.93	— —			
Rb	— ^a 0.84 ^b	— 0.81	0.63 0.99	0.50 -0.98	— 0.65	0.52 0.97	— —	— 0.95	— —	— 0.98		
Sr	— ^a 0.93 ^b	— 0.69	— 0.87	— -0.91	— 0.67	— 0.83	— 0.60	— 0.80	— 0.50	— 0.86	— 0.91	
Ba	— ^a 0.51 ^b	0.50 0.72	0.79 0.83	— -0.81	— 0.50	0.75 0.85	— —	0.67 0.81	— —	— 0.84	0.51 0.81	— 0.57

(a) First cycle samples (N = 22); (b) Second cycle samples (N = 25).

Therefore, on the basis of de LA ROCHE's diagrams and chemical component correlation coefficients, it is reasonable to conclude that Punta Bianca sediments are characterized by a clastic terrigenous fraction having a substantially uniform composition over the whole sequence; in the lower cycle the mixing of such fraction with highly variable non-terrigenous materials causes very heterogeneous bulk chemistry and mineralogy.

In II cycle the overall Ca contents are again very low; the element distribution is interpreted as controlled both by apatite and by carbonates. Mn replaces Ca in both phases.

In I cycle the Ca distribution appears controlled only by carbonates; minor Ca-bearing components are obscured by the abundance of calcite. Also in this cycle manganese is positively correlated with Ca. The Mn contents appear to be here the highest of Punta Bianca and Monti Pisani sequences. The high

Owing to the remarkably uniform composition of Punta Bianca clastic terrigenous sediments, in II cycle the correlation of Rb, Sr and Ba with major chemical components, when present, is highly significant. Sr is positively correlated with nearly all major components, being simultaneously resident in clay matrix, feldspars, carbonates and perhaps also in apatite. Nearly the same is true also for Rb and Ba, which however are absent in carbonates.

Due to the large, but highly variable amounts of carbonates, in I cycle no significant correlation of Sr with any other component has been observed; on the contrary Rb distribution still appears to be mostly controlled by K-feldspar and micas, while Ba exhibit positive correlations with Mg, Al, K, Ti, Rb, that is with most of clay-matrix-elements.

FeO/Fe₂O₃ ratio

In Punta Bianca sequence the $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio appears highly variable. The upper cycle rocks show $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios usually very low (range: $< 0.02 - 0.17$), similar to those of Monti Pisani Verrucano. In the lower cycle two main groups of sediments may be differentiated: a) the basal conglomerates, which exhibit high and nearly invariant $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios (range: 2.00 - 4.8); b) the silty-clay matrix of carbonatic breccias, which exhibit variable, but commonly low, $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios (range: $< 0.01 - 2.00$): the lowest values are shown by sedimentary levels very close to the volcanics. The striking difference between the two groups is considered to be mostly due to marked differences in Eh conditions occurring in the deposition basin; such conditions must have been predominantly reducing during basal conglomerate deposition.

The high variability in $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios shown by silty-clay sediments of I cycle upper horizons is regarded as caused by mixing of iron from different (terrigenous and volcanogenic) sources.

$\text{TiO}_2/\text{Al}_2\text{O}_3$ -quartz relationships

Also in this sequence titanium appears mostly confined into the clay matrix.

The $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio shows different trends in the two cycles (Fig. 13). In II cycle the ratio doesn't exhibit any correlation with quartz, thus qualifying these sediments as poorly sorted and/or scarcely mature. In the I cycle the trend is somewhat more intricate. Most of shales and siltites of the cycle middle-upper horizons shows a tendency toward a positive correlation between $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio and quartz content; they are thus interpreted as better sorted and/or more mature clastic terrigenous sediments. The basal conglomerates and the lower shales and siltites have a tendency toward negatively correlated $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio-quartz content. They may have formed through mixing of two different grain-sized populations from different sources; in this case, however, there is no ground suggestive of a volcanic rock source.

Paleoenvironmental implications

Some important paleoenvironmental im-

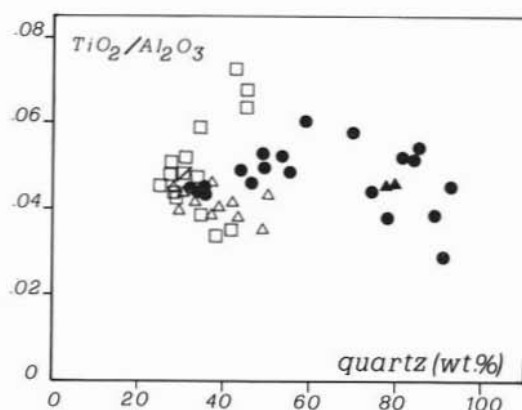


Fig. 13. — $(\text{TiO}_2/\text{Al}_2\text{O}_3)$ ratio vs. quartz content in Punta Bianca sequence (legend as in Fig. 9).

plications arise from geochemical data. Alkali and alumina distribution and their reciprocal relationships indicate, chiefly for the lower Verruca formation, intense weathering processes, resulting in leaching of most alkalis and formation of Al-enriched clays, that is lateritization processes. On the other hand the very low $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios shown by Monti Pisani sequence and Punta Bianca upper cycle sediments suggest climatic conditions similar to the «climat rubéfiant d'accumulation» (CHOUBERT, 1950; MILLOT, 1964), with characteristics intermediate between those of desertic and humid tropical climates. These seemingly discrepant indications are accounted for by IRVING'S (1964) paleogeographic reconstructions. According this author during the Permian the Equator was crossing Tuscany area; this explains the climatic conditions favourable to an intense breakdown of parent materials. In the Upper Permian-Early Triassic period more arid conditions (area latitude: $10 - 15^\circ$ North; IRVING, 1964) certainly favoured a more reduced weathering and a widespread reddening of clastic materials. These suggestions are in full agreement with the environmental model proposed by RAU and TONGIORGI (1974) and TONGIORGI et al. (1977) for Tuscany clastic Triassic sequences.

As for Mt. Pisani, Punta Bianca geochemical data provide useful paleoenvironmental informations, though somewhat more complicated due to the complex

stratigraphical, sedimentological and lithological features of this sequence.

The very low $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio values of II cycle sediments suggest strongly oxidizing conditions both in the source area and in the deposition basin, that is conditions favourable to reddening processes. We may infer climatic conditions not dissimilar from those prevailing during Mt. Pisani sequence deposition.

In the I cycle the $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio values are interpreted as recording a transition from reducing to oxidizing conditions in the deposition basin. It doesn't seem reasonable to associate such changes with changes in climatic conditions not otherwise documented during the brief time between the Anisian and the Ladinian (IRVING, 1964). Moreover the presence of some oxidized thin horizons even within the basal conglomerates documents short episodes of high Eh conditions prevailing also in the deposition basin of the latter and proves that the I cycle overall change in $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios is only a matter of sedimentary conditions. The basal conglomerate deposition environment is reported as mostly fluvial by sedimentologists (MARTINI et al., 1986). Since such environment usually is not a reducing one, we must suppose: 1) that the sampled section represents a more distal, or flatter portion of an alluvial fan, transitional to a lacustrine or swampy environment; or 2) that an early diagenetic reddening of the deposits was prevented by the rapid submersion by an encroaching shallow sea (MARTINI et al., 1986).

Source rocks

In diagrams of Figs. 5, 6, 7 and 10, 11, 12, which emphasize the distribution of some chemical components in Verrucano of Monti Pisani and Punta Bianca, the compositional fields of the most important rocks from the Paleozoic basement of Northern Tuscany are also plotted (data from DESCHAMPS, 1980, and PUXEDDU et al., 1984). In Monti Pisani area the main Paleozoic formations, ranging in age from Silurian to Permian, are the following: «Buti Phyllites and Quartzites», «S. Lorenzo Schists» and «Asciano Breccias and Conglomerates» (these last most probably of low

significance as Verrucano clast source). The «Permian Red Porphyries», actually known only as clasts in Triassic basal conglomerates, are believed to close the Permian period in the area. In the same diagrams it has been plotted also the «Porphyroids», a unit older than «Buti Quartzites and Phyllites», which doesn't outcrop in Mt. Pisani area, but it is known from Apuan Alps and Elba Island Paleozoic basements. The «Porphyroids» are metavolcanics (or meta-psammities derived from erosion of the former), of Middle-Upper Silurian age (TONGIORGI and BAGNOLI, 1981). Two subsets of «Porphyroids» have been distinguished: 1) sodic potassic rhyolites, mainly from Apuan Alps; and 2) potassic rhyolites, mainly from Elba Island («K₂O-rich-Porphyroids») (PUXEDDU et al., 1984). Figs. 5, 6 and 7 clearly show an evolution of Mt. Pisani clastic sequence from compositions relatively close to the Permian Red Porphyry field to a chemistry approaching the K₂O-rich-Porphyroid field. The Verruca lowest member («Anageniti grossolane») sediments plot close to Permian Red Porphyry field; they may be interpreted as resulting from the mixing of materials mainly eroded from this unit with subordinate amounts of detritus from deeper, older units like S. Lorenzo Schists and Buti Quartzites and Phyllites. Moving upward in the Verruca formation from «Anageniti grossolane» through «Scisti viola» to «Anageniti minute» members a gradual transition of sediment compositions is observed; ultimately they appear fully matching the chemistry of metapelites and metapsammities of the Paleozoic basement (S. Lorenzo Schists and Buti Quartzites and Phyllites). Within the Monte Serra formation the transition is continued from this field toward compositions approaching those of K₂O-rich-Porphyroids. Such a vertical trend conforms to a general picture of a basement undergoing a progressively deeper erosion. The composition of clastic sequence basal materials («Anageniti grossolane» member) records also advanced weathering processes in a pre-erosion stage.

As for Punta Bianca sediments, whose clastic terrigenous fraction appears highly uniform over the whole sequence, rocks of both cycles result to plot nearly completely

within the compositional field of S. Lorenzo Schists and Buti Quartzites and Phyllites (Figs. 10, 11 and 12). No contribution from Permian Red Porphyries is apparent; no significant evolution (or only a slight tendency to evolve) toward the field of K_2O -rich-Porphyrroids can be observed.

Such geochemical implications confirm the geological data on the Paleozoic basement outcropping in Punta Bianca area. According to RAU et al. (1986), in fact, it appears chiefly composed of a unit equivalent to Buti Quartzites and Phyllites; in this area the Permian Red Porphyries seem completely lacking. This is probably related to the discontinuous character of such ignimbritic cover (BAGNOLI et al., 1978). The lack (or the very small contribution) of materials from units older than Buti Quartzites and Phyllites, such as Porphyroids, may be explained by an erosion of the Paleozoic basement relatively mild compared to that active in Mt. Pisani area; the whole Punta Bianca sequence is in fact much thinner than Monti Pisani sequence (about 250 m and 700 m respectively; MARTINI et al., 1986; TONGIORGI et al., 1977). This implies significant differences in the morphology of erosion zone and deposition basin between the two sequences.

Furthermore, comparison of Figs. 5, 6 and 7 with Figs. 10, 11 and 12 clearly shows that the chemistry (and the primary mineralogy) of Punta Bianca terrigenous sediments essentially matches that of middle Monti Pisani sequence, that is the composition of «Scisti viola», «Anageniti minute» and «Scisti verdi» members.

Final remarks

The observed substantial chemical variations can not be explained by the diagenetic or the slight metamorphic changes which affected the two sequence. Therefore the geochemical data and the derived primary mineralogy of Mt. Pisani and Punta Bianca sediments can be regarded as providing significant informations for paleoenvironmental reconstructions; these in fact result to be in full agreement with data drawn from sedimentological studies. Such information may thus

represent an important tool, through comparison with correspondent data, for extending such reconstructions to sequences where little or no sedimentological data are available (Verrucano sequences of Southern Tuscany).

These data allow the main source rocks of the Verrucano clastic materials to be traced. The composition range of these latter seems mostly related to the sequence thickness, and by inference to the degree of basement erosion involving more or less numerous lithological units.

Furthermore, geochemical and mineralogical data on Verrucano sequences afford lithological correlations; for instance this study reveals that the clastic terrigenous materials of the whole Punta Bianca sequence lithologically correspond to the middle members of Monti Pisani sequence. This obviously doesn't imply an equivalence in time, at least not a close one. However when no evidence from fossils is available, even such lithological correlations may be useful in assessing the approximate stratigraphical situation of early-alpine clastic sequences of uncertain or disputed position such as those of Southern Tuscany.

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REFERENCES

- ANNOVI A., FONTANA D., GELMINI R., GORGONI C., SIGHINOLFI G.P. (1980) - *Geochemistry of carbonate rocks and ferruginous horizons in the Verrucano in Southern Tuscany - paleoenvironmental and paleogeographic implications*. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 30, 1-16.
- BAGNOLI G., GIANELLI G., PUXEDDU M., RAU A., SQUARCI P., TONGIORGI M. (1978) - *The Tuscan Paleozoic basement: a critical review*. In: M. Tongiorgi (Editor), *Report on the Tuscan Paleozoic basement*; Rapp. Inter., Sottoprogetto Energia Geotermica, Progetto Finalizzato Energetica, Pisa, pp. 9-26.
- BILLINGS J.K. (1970) - *Rubidium: Behavior during weathering and abundance in soils*. In: *Handbook of Geochemistry*, vol. II/4, Springer-Verlag, Berlin, Heidelberg.

- BRANDI P. (1964) - *La bibliografia scientifica riguardante le formazioni del Verrucano s.l. in Toscana (dal 1818 al 1963)*. Atti Soc. Tosc. Sc. Nat., Mem., ser. A, 71, 288-316.
- CASSINIS G., ELTER P., RAU A., TONGIORGI M. (1979) - *Verrucano: a tectofacies of the Alpine-Mediterranean South Europe*. Mem. Soc. Geol. It., 20, 135-149.
- CHOUBERT G. (1950) - *Refléxions au sujet du Pliocène continental*. C.R. Acad. Sci. Fr., 243-504.
- COCOZZA T., LAZZAROTTO A., PASINI M. (1975) - *Segnalazione di una fauna triassica nel conglomerato di M. Quoio (Verrucano del Torrente Farma - Toscana Meridionale)*. Riv. Ital. Paleont. Stratigr., 81, 425-436.
- DESCHAMPS Y. (1980) - *Contribution à l'étude des gisements à pyrite-bématite de Rio Marina (Ile d'Elbe - Italie). Approche pétrographique, géochimique et structurale*. Thèse Dr. spécialité, Université Claude Bernard, Lyon 1, pp. 448.
- ELTER P., FEDERICI P.R. (1964) - *Sulla presenza di terreni attribuibili al Trias medio nel promontorio orientale del Golfo di La Spezia*. Boll. Soc. Geol. It., 83, 395-402.
- ELTER P., GIGLIA G., RAU A., TONGIORGI M. (1966) - *Il Verrucano della Verruca (Monti Pisani) nel quadro delle serie del Carbonifero, del Permiano e del Trias della Toscana Settentrionale*. Atti del Symposium sul Verrucano. Soc. Tosc. Sc. Nat., Pisa, 3-33.
- FEDERICI P.R. (1966) - *Gasteropodi ladinici nei calcari di Punta Bianca (Golfo di La Spezia)*. Riv. Ital. Paleont., 72, 999-1022.
- FRANCESCHELLI M., LEONI L., MEMMI I., PUXEDDU M. (1986) - *Regional distribution of Al-silicates and metamorphic zonation in the low grade «Verrucano» metasediments from Northern Apennines (Italy)*. J. metamorphic Geol. (In press).
- FRANZINI M., LEONI L., SAITTA M. (1975) - *Revisione di una metodologia analitica per fluorescenza X, basata sulla correzione completa degli effetti di matrice*. Rend. Soc. It. Miner. Petrol., 31, 365-378.
- HEJER K.S., ADAMS J.A.S. (1964) - *The geochemistry of alkali metals*. Phys. Chem. Earth, 5, 253-381.
- IRVING E. (1964) - *Paleomagnetism and its applications to geological and geophysical problems*. Wiley and Sons, New York.
- LANGE I.M., REYNOLDS R.C., LYONS J.B. (1966) - *K/Rb ratios in coexisting K-feldspars and biotites from some New England granites and metasediments*. Chem. Geol., 1, 317-328.
- LA ROCHE H. DE (1978) - *La chimie des roches présentée et interprétée d'après la structure de leur faciès minéral dans l'espace des variables chimiques: fonctions spécifiques et diagrammes qui s'en déduisent. Application aux roches ignées*. Chem. Geol., 21, 63-87.
- MARTINI I.P., RAU A., TONGIORGI M. (1986) - *Syntectonic sedimentation in a Middle-Triassic rift, Northern Apennines, Italy*. Sediment. Geol., 47, 191-219.
- MILLOT G. (1964) - *Géologie des argiles*. Masson, Paris.
- PUXEDDU M., SAUPÉ F., DÉCHOMETS R., GIANELLI G., 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.
- RAU A., TONGIORGI M. (1974) - *Geologia dei Monti Pisani a sud-est della Valle del Guappero*. Mem. Soc. Geol. It., 13, 227-408.
- RAU A., TONGIORGI M., MARTINI I.P. (In press) - *La successione di Punta Bianca: un esempio di rift «abortivo» nel Trias Medio del Dominio Toscano*. Mem. Soc. Geol. It. (In press).
- SCHIAFFINO L., TONGIORGI M. (1962) - *Stratigrafia del Verrucano dei Monti Pisani*. Atti Soc. Tosc. Sc. Nat., Mem., ser. A, 69, 382-446.
- SPEARS D.A., KANARIS-SOTIRIOU R. (1976) - *Titanium in some Carboniferous sediments from Great Britain*. Geochim. Cosmochim. Acta, 40, 345-351.
- TONGIORGI M., RAU A., MARTINI I.P. (1977) - *Sedimentology of early-alpine, fluvio-marine, clastic deposits (Verrucano Triassic) in the Monti Pisani (Italy)*. Sediment. Geol., 17, 311-332.
- TONGIORGI M., BAGNOLI G. (1981) - *Stratigraphie du socle paléozoïque de la bordure continentale de l'Apennin septentrional (Italie centrale)*. Bull. Soc. Géol. France, 23, 319-323.
- VEIZER J. (1978) - *Strontium: Abundance in common sediments and sedimentary rock types*. In: Handbook of Geochemistry, Vol. II/4, Springer-Verlag, Berlin-Heidelberg.