Provenance of shales and sedimentary history of the Monte Soro Unit, Sicily

GIOVANNI BARBERA[1], PAOLO MAZZOLENI[1*], SALVATORE CRITELLI[2], ANNA PAPPALARDO[1],
ANTONIO LO GIUDICE[1], ROSOLINO CIRRINCIONE[2]

[1] Dipartimento di Scienze Geologiche – Università degli Studi di Catania, Corso Italia 57 – 95129 Catania, Italy
[2] Dipartimento di Scienze della Terra – Università degli Studi della Calabria, via P. Bucci –
87036 Arcavacata di Rende (Cosenza), Italy

ABSTRACT. — Source area weathering, provenance and tectonic setting from the Lower Cretaceous Monte Soro Unit shales (North-eastern Sicily) have been analysed for mineralogical and chemical compositions. Samples are characterized by high values of MMI index. Among clay minerals I/S mixed-layered and illite are prevailing on chlorite and kaolinite. The amount of illite layers among mixed-layered smectite/illite reflects late diagenetic post depositional conditions reasonably reached during the post-Cretaceous subduction and related collision involving the European and African plate margins.

Major and trace elements abuncances indicate the dominant detrital nature of the shales with minimal or absent hydrothermal and biogenic contributions. TiO_2/Al_2O_3 ratios are distinctive of shales produced by weathering of felsic to intermediate continental crustal rocks. High CIA and CIW values suggest that the source area was subjected to a prolonged and/or intense chemical weathering.

The chemical composition and trace element ratios Zr/Y, Zr/Nb, Zr/Ti, Nb/Y, Th/Cr, Th/Co, La/Co, K/Rb are close to those of the metamorphic basement of the Monti Peloritani segment of the European block. However, in our case, it is difficult to distinguish between a first-cycle sediment production and a recycling of the Upper Triassic – Lower Jurassic Verrucano continental sediments, being the metamorphic basement mainly formed by metagraywakes and metapelites.

RIASSUNTO. — L'analisi mineralogica e geochimica delle argille Tardo-Cretaciche dell'Unità di Monte Soro (Sicilia nord-orientale) ha permesso di individuare i complessi processi di alterazione meteorica alla sorgente, la provenienza e l'assetto tettonico di questa Unità. I campioni sono caratterizzati da un elevato valore dell'indice MMI. Tra i minerali argillosi, gli interstratificati I/S e l'illite sono prevalenti su clorite e caolinite. Il contenuto in illite all'interno degli interstratificati illite/smectite riflette condizioni post-deposizionali tardo-diagenetiche ragionevolmente raggiunte durante il processo subduttivo post-Cretacico e la relativa collisione continentale che hanno coinvolto i margini delle placche Africana ed Europea.

Le concentrazioni degli elementi maggiori e in tracce hanno evidenziato la natura detritica delle argille con un contributo idrotermale e biogenico minimo o assente. I valori del rapporto TiO_2/Al_2O_3 sono caratteristici di argille originatesi dall'alterazione di rocce crostali di composizione da felsica ad intermedia. Gli alti valori di CIA e CIW suggeriscono che l'area di alimentazione è stata sottoposta ad alterazione chimica intensa e/o prolungata.

La composizione chimica e i rapporti Zr/Y, Zr/Nb, Zr/Ti, Nb/Y, Th/Cr, Th/Co, La/Co, K/Rb sono molto simili a quelli delle rocce del basamento metamorfico costituente il segmento Peloritano del blocco continentale europeo. Tuttavia, dal momento

* Corresponding author, E-mail: pmazzol@unict.it

che questi terreni sono costituiti principalmente da metasedimenti, è difficile distinguere tra una derivazione diretta dal basamento cristallino e il riciclo delle relative coperture sedimentarie costituite dai sedimenti continentali tardo-Triassico/Giurassici indicati con il termine 'Verrucano'.

INTRODUCTION

Mineralogical and chemical compositions of shales are used for detailed informations about source areas (Wronkiewicz and Condie, 1987; Roser and Korsh, 1988; Girty *et al.*, 1996; Hassan *et al.*, 1999; Asiedu *et al.*, 2000; Cullers, 2000; Cullers and Podkovyrov, 2000; Di Leo *et al.*, 2002; Cavalcante *et al.*, 2003). Interpretation of chemical and mineralogical data from shales, however, is difficult because it requires a correct evaluation of the effects of weathering, transport and diagenesis (Van Moort, 1971; Nesbitt *et al.*, 1980; Kish, 1983; Harnois, 1988; Nesbitt and Young, 1989; Wintsch and Kvale, 1994; Cox *et al.*, 1995; Zhang *et al.*, 1998; Cullers and Podkovyrov, 2000) since the compositional characters of fine grained sediments are strongly controlled by all these processes. In particular, alkaline and alkaline-earthy elements are thought as the most susceptible to weathering, recycling and diagenesis while Al_2O_3, TiO_2 and HFSE trace elements concentrations are usually used for provenance studies thanks to their geochemical features. On the other side, the study of the shales is useful because it permits to have a representative view of the average crust in the region being compositionally more homogeneous than coarser siliciclastic sediments (Taylor and McLennan, 1985; Cox and Lowe, 1995). In this paper, we characterize the shales of the Monte Soro Unit outcropping in the Sicilian segment of the Appenninic-Maghrebian chain. This Unit is comparable, for paleogeographic and structural position, to the Betic-Maghrebian chain-belonging Maurétaniens-like flysches (Los Nogales - Andalusia, Jebel Tisirene - Morocco, Guerrouch - Algeria) characterized by settlement in internal basins that received sediments coming from more internal terranes formed by crystalline rocks and Mesozoic sedimentary covers (Gelard, 1969).

The aim of this work is to assess how source area weathering and recycling influenced sediment composition and the diagenetic and provenance history. In this context the Monte Soro Formation provides a good opportunity to associate the data coming from fine grained sediments with the abundant petrographic analysis of quartz-feldspatic sandstones strata reported in previous works (Puglisi, 1981; Carmisciano and Puglisi, 1983; Puglisi, 1987).

GEOLOGY AND STRATIGRAPHY

The present-day geological setting of Sicily is the result of the Neogene Europe-Africa collision. It is characterized by two main structural domains composing a chain-foreland system made up of the Kabilo-Calabride and Appenninic-Maghrebian chains advancing towards the Hyblean undeformed foreland.

In the nappe edifice three different overlapping sectors formed by several thrust sheets, derived from different paleogeographic domains, are distinguished (Lentini *et al.*, 1999): i) the Kabilo-Calabride chain, at the top of the nappe edifice, made up of units deriving from the deformation of the European continental margin; ii) the Apenninic-Maghrebian chain, in intermediate position, that consists of Neo-Tethyan deriving terranes; iii) the Sicanian and Hyblean units derived from deformation of the African continental margin (Lentini *et al.*, 1999 and references therein).

Convergence of African and European plate margins caused the final closure of the Neo-Tethyan oceanic realm (Roure *et al.*, 1990). Remnants of the Neo-Tethyan terranes consist in several tectono-stratigraphic units overlying the African foreland domain and underlying the nappe-edifice deriving from the deformed European continental margin.

In Sicily, some of these units are well exposed along a NW-SE ridge that comprises the Nebrodi mountain belt at the Tyrrhenian side, and the Piedimonte area at the Ionian edge. These units, reported as "Sicilide Complex" by Ogniben (1960), consist of Upper Cretaceous to Palaeocene-Eocene pelagic sequences. In the Monte Soro area, inside this complex, on the basis of structural and stratigraphic data, Lentini and Vezzani (1978) distinguished two units: the Monte Soro, and the

Troina units. Authors consider these two units belonging respectively to the internal and external position of the same sedimentary basin (Lentini *et al.*, 1990; 1999).

In spite of the absence of oceanic basement or blocks with MORB-affinity, the Sicilide Complex has been considered a sedimentary sequence of the Neo-Tethyan domain for the close analogies with the Liguride Units of southern Appennines (Amodio Morelli *et al.*, 1976; Boccaletti *et al.*, 1984).

In this paper, we report data on a pelagic succession of the Sicilide Complex located in the Monte Soro area (Nebrodi Mountains, NE Sicily, Fig. 1). It belongs to the Monte Soro Unit consisting of several slices, tettonically stacked, of turbiditic successions. This Unit can be subdivided in three members: i) pelitic-calcareous basal member; ii) pelitic-quartzarenitic intermediate member evolving to quartzarenitic strata in the upper part of this section; iii) argillitic member upwards. On the basis of tectonic position the succession
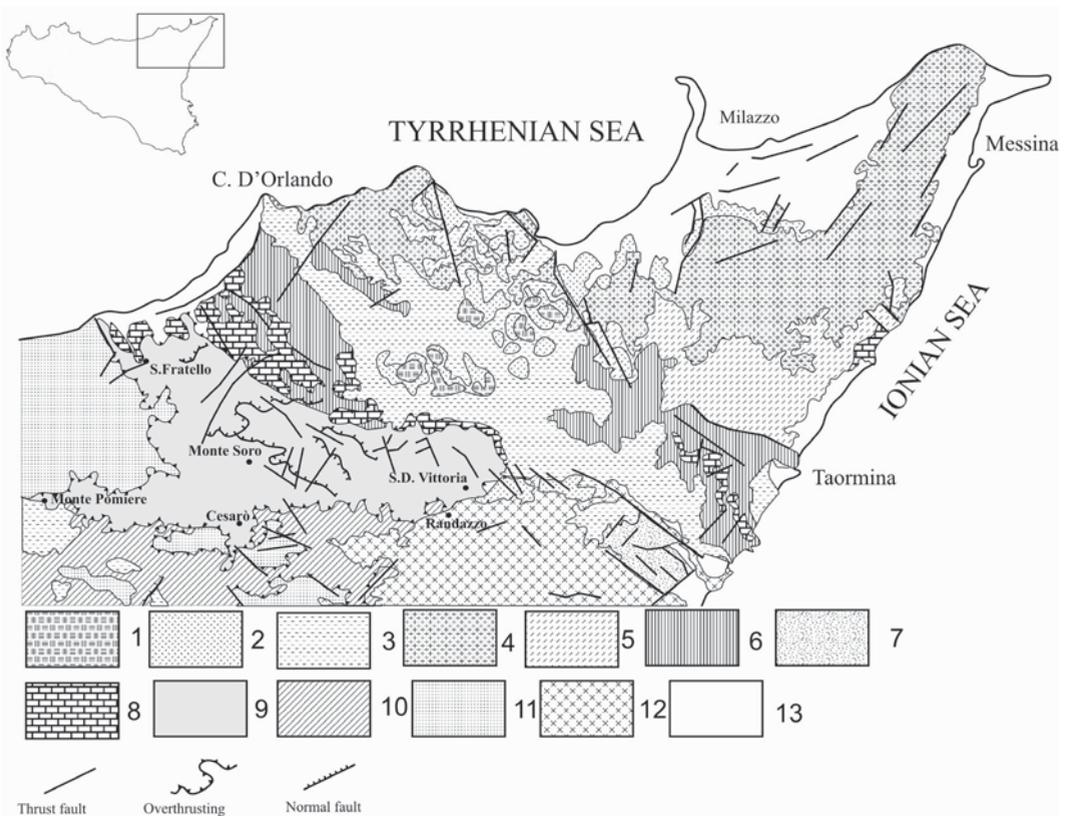
Fig. 1 – Schematic geological map of north-eastern Sicily including the Monte Soro Unit area; 1) Floresta calcarenites (Late Burdigalian-Langhian); 2) 'Antisicilide' complex (Cretaceous-Early Miocene); 3) Capo d'Orlando Flysch (Late Oligocene-Early Miocene); 4) Medium-high grade metamorphic basement (Aspromonte Unit); 5) Low-medium grade metamorphic basement (Mandanici Unit); 6) Epimetamorphic basement; 7) Piedimonte fm (Middle Eocene-Lower Oligocene); 8) Meso-Cenozoic sedimentary covers consisting of 'Verrucano' continental clastic deposits (Liassic) + basinal limestones and marls (Liassic-Eocene); 9) Monte Soro Unit (Cretaceous); 10) 'Troina' Unit (Cretaceous-Oligocene); 11) Numidian flysch (Oligocene-Upper Langhian); 12) Monte Etna alkaline volcanics; 13) Pliocene-Quaternary.

was further subdivided in different structural-stratigraphic units (from the bottom upwards: S. Maria del Bosco, Monte di Trearie, Serra del Re, Monte Peturizzo; Puglisi, 1981; Carmisciano and Puglisi, 1983).

We sampled the succession in the typical outcrop from the village of San Fratello to the main area of Monte Soro; in the southeastern zone it reaches the villages of S.Teodoro and Cesarò and from east to west it crops out along S.D.Vittoria village to Monte Pomiere.

Sampling & methods

Twenty shales of the pelitic-quartzarenitic and argillitic members, that represent the main part of Monte Soro Formation, were sampled for this investigation. The macroscopic main feature of these green to grey coloured clay rich sediments is the wide fissility; in many cases a scaly fabric with quite undulating and smooth anastomosing surfaces was observed. From the grain size point of view all the samples are classified as silty clay (Shepard 1954).

The mineralogical compositions of bulk samples, <2μm and <0.5μm grain-sized fractions were obtained by X-ray powder diffraction (Siemens D 5000; measuring conditions: CuKα radiation Ni filtered, window 1 mm, 1 mm, 0.2 mm, 40 kV, 30 mA). Whole rock analysis was carried out on powders crushed in agate hand mortar and laterally loaded into the sample holder. The clay-sized fraction was prepared by gentle crushing in a ceramic mortar, suspending by a mixer, dispersing in an ultrasonic bath and then by centrifugation in distilled water; <2μm and <0.5μm fractions were settled and then piped and dried at room temperature on glass slides to produce a thin oriented layer; ethylene-glycol solvated slides were prepared too.

Amounts of minerals in bulk samples and in the < 2 μm fraction were obtained by correcting the area of the characteristic peak of minerals for the mineral intensity factor (MIF; Moore and Reynolds, 1989; Lynch, 1997). The percentage of illite in I/S and the 'Reichweite' ordering index were determined according to Moore and Reynolds (1989).

Major and trace elements concentrations were obtained by X-Ray fluorescence (XRF; Philips PW 2510) on powder-pressed pellets of whole rock; total loss on ignition (LOI) was estimated after 12 hours heating at 900°C. Quantitative analysis was carried out using a calibration line based on 45 international rocks standards. The accuracy, evaluated using an international standard, is good (< 5%) for all elements, except for the following: Th = 7.8%, Co = 8.4%, Nb = 9.1%, La = 8.2% and Ce = 8.4%.

Results

Mineralogy

The mineralogical compositions of the analysed shales are given in Table 1. On the whole, the shales from the Monte Soro Unit reveal a high mineralogical maturity in agreement with data obtained from the arenitic levels which have subarkosic composition with high quartz content. All the samples exhibit high proportions of clay minerals and high values of the Mudrock Maturity Index (from 83 to 95) [Table 1; MMI = phyllosilicates / (phyllosilicates + quartz + feldspars); Bathia, 1985]. In the diagram quartz – feldspars –phylllosilicates the samples plot in the phyllic mudrock field (Fig. 2). Considering the detrital component, quartz prevails on feldspars [average quartz /(quartz + feldspars) = 0.74] as observed in pelitic sediments originated by weathering of crystalline rocks and / or by recycling of sedimentary deposits (Cullers, 2000).

The composition of the < 2 μm fraction is dominated by smectite/illite mixed clay minerals (I/S) and illite while, with the exception of few samples, chlorite and kaolinite abundances are below 10% (Table 1). However the kaolinite and chlorite abundances are strictly related to the grain size and probably, on the whole, in the bulk rocks they are higher relative to those of < 2 μm grain size fraction as showed, for similar shales, by Mongelli *et al.* (1996). The I/S mixed clay minerals are probably linked to the diagenetic transformation of predominantly smectitic clay minerals. These later are interpreted in other South Apennine Cretaceous shale as originated by the degradation of illite (Fiore and Mongelli, 1991; Mongelli *et al.*, 1996). The I/S ratio suggests

TABLE 1 – *Mineralogical composition of whole rocks and of the < 2 µm fraction detected by XRD with the Moore and Reynolds (1989) method. CM = clay minerals; Qz = quartz; Feld = K-feldspar + plagioclase; S+I/S = smectite + illite/smectite mixed layers; I = illite; Ch = chlorite; K = kaolinite; MMI = Mudrock Maturity Index.*

Sample	Whole rock			< 2 µm				
	C M	**Qz**	**Feld**	**S + I/S**	**I**	**Ch**	**K**	**MMI**
C1	92	6	2	47	38	8	7	92
C2	83	16	1	62	36	2	–	83
C3	93	5	2	57	27	4	12	93
C4	93	5	2	45	45	4	6	93
C5	95	3	2	63	23	7	7	95
C6	88	9	3	73	17	6	4	88
C7	92	6	2	64	24	4	8	92
C8	89	7	4	77	15	4	4	89
C9	90	8	2	47	45	4	4	90
C10	91	7	2	38	43	13	6	91
C11	88	9	3	63	27	5	5	88
C12	93	5	2	66	26	3	5	93
C13	93	5	2	43	49	5	3	93
C16	92	6	2	62	35	2	1	92
C20	92	6	2	53	28	6	13	92
MS 3	89	8	3	80	20	–	–	89
MS 4	87	9	4	65	25	4	6	87
MS 5	88	9	3	84	12	4	–	88
MS 6	89	8	3	79	19	2	–	89
MS 7	92	5	3	69	26	3	2	92

reconstruction of the temperature pattern and burial history of the Monte Soro Formation during diagenesis (Hoffman and Hower, 1979; Pollastro, 1993 and references therein). In Fig. 3 the diffraction patterns of the < 0.5 µm fraction of two representative samples are reported and used for the evaluation of the percentage of illite layers in the I/S mixed clay minerals and for the 'Reichtewite' order according to the method proposed by Moore and Reynolds (1989). The identification of the phases was obtained comparing the observed diffractometer traces with those calculated by means of Newmod software (Reynolds, 1985). The modelled diffractogram was carried out with the method proposed by Jaboyedoff and Thelin (1996) and assuming that the peaks were the results of the sum of the diffraction effects due to different phases (Lanson and Velde, 1992).

The presence in all of samples of a R3 I/S indicates, in accord with Hoffman and Hower (1979), that during the diagenetic history, late diagenesis conditions were reached. As total thickness of the Monte Soro Unit reaches up to 1000 m. (Lentini *et al.*, 1999), sediment weight would not be consistent with previous inferences; nevertheless, the post-Cretaceous subduction
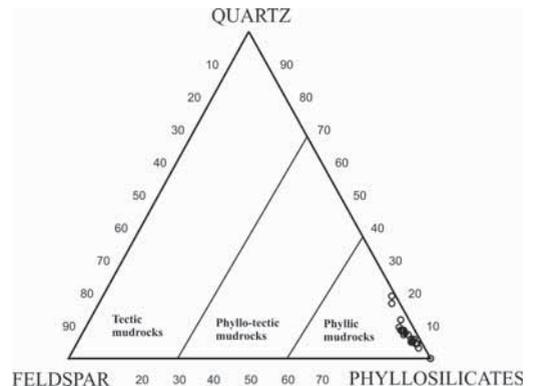
Fig. 2 – Mineralogical classification of shales from the Monte Soro Unit (open circles), (after Bathia, 1985).

Sample	Mineral	Interlayer	%layer	R	Layer number		wt%
C6	I/S	2 gly	80 Il	1	1	8	40
	I/S	2 gly	90 Il	3	3	14	35
	Il	2 gly	95 Il	0	5	30	20
	Chl	2 gly	95 Chl	0	1	10	5
C3	I/S	2 gly	70 Il	1	1	8	10
	I/S	2 gly	80 Il	1.5	1	8	35
	Il	2 gly	90 Il	3	3	14	20
	Il	2 gly	95 Il	0	5	30	20
	Chl	2 gly	95 Chl	0	1	10	10
	K	2 gly	95 K	0	90	100	5
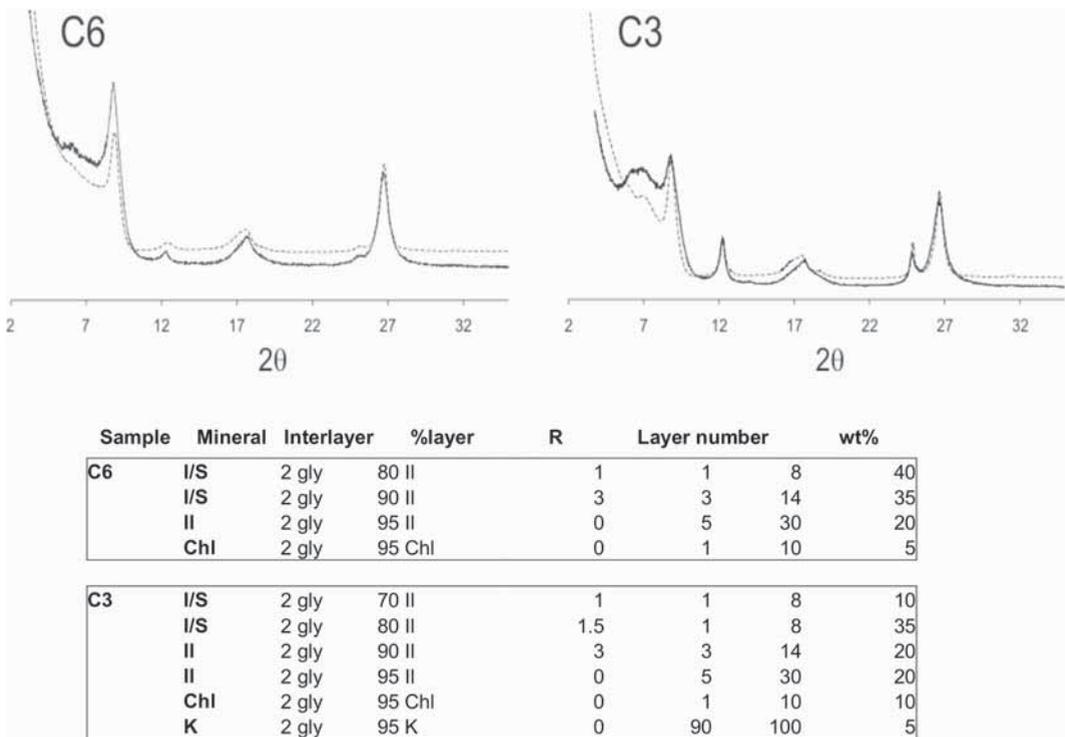
Fig. 3 – XRD patterns of glycolated < 0.5 μm fraction; solid lines from samples C3 and C6, dashed lines are simulations by Newmod; phases identified and utilized for the Newmod simulations are reported in the attached tables.

associated with the collision involving the European plate and the African margin with the consequent formation of a Neo-Tethyan accretionary wedge, should be responsible for the overlapping of the nappes with consequently increasing of total thickness and temperature (Roure *et al.*, 1990).

Geochemistry

The major and trace element composition of whole rock are shown in Table 2. Chemical data of selected samples are compared with Post Archean Australian Shale (PAAS; data from Taylor and McLennan, 1985) by means of enrichment factors (F_e) (Fig. 4; Hassan *et al.*, 1999 and references therein) calculated as follows: $F_e = (C_e$ sample/ C_{Al} sample)/ (C_e PAAS/ C_{Al}PAAS); where $C_e =$ elemental concentration; $C_{Al} = $ Al concentration). The Al normalization is used in order to avoid the variability linked to the clay fraction abundance.

Enrichment factors are close to unity for the great part of elements except for MnO (excluding sample MS6), P_2O_5, Nb, Zr, alkaline-earthy and alkaline elements showing a substantial depletion if compared to the standard shale. K_2O and Rb enrichments are due to clay minerals as suggested by strong correlations $K_2O – Al_2O_3 = 0.85$ and Rb $– Al_2O_3 = 0.83$.

The absence of positive spikes relative to MnO, Cr and V, rules out a hydrothermal contribution to the shale formation. This is testified also by the diagram Fe_2O_3/TiO_2 *vs* $Al_2O_3/(Al_2O_3+Fe_2O_3+MnO)$ (Fig. 5) in which all samples are plotted near the terrigeneous end-member close to the PAAS. Also the good correlation observed in the diagrams TiO_2,

TABLE 2 – *Major (wt%) and trace (ppm) element compositions.*

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C16	C20	MS 3	MS 4	MS 5	MS 6	MS 7
SiO_2	54.14	64.20	53.60	56.60	52.60	55.90	55.00	53.50	56.00	53.00	52.40	55.00	54.50	51.01	53.00	54.80	54.10	55.20	53.80	51.00
TiO_2	1.17	0.64	0.97	1.04	1.00	0.83	0.90	1.04	0.90	0.96	0.95	0.99	0.96	1.08	0.90	0.86	1.03	0.97	1.01	1.20
Al_2O_3	23.09	14.40	22.30	22.50	23.30	19.20	22.00	21.40	19.00	21.60	21.60	22.10	21.20	24.18	21.00	18.60	21.60	20.60	17.90	23.00
Fe_2O_3	5.02	7.43	6.18	3.77	5.99	7.75	5.60	6.40	8.70	8.61	8.49	6.06	6.62	5.79	8.40	6.62	6.19	6.54	9.95	5.80
MnO	0.02	0.02	0.01	0.01	0.02	0.02	b.d.	0.03	b.d.	0.02	0.02	0.01	0.03	0.03	b.d.	0.08	0.02	0.03	0.60	b.d.
MgO	2.50	3.40	2.53	2.11	2.59	3.04	2.60	3.10	2.50	2.56	2.73	2.45	3.17	3.09	2.20	2.79	2.08	1.98	3.06	2.40
CaO	0.10	0.32	0.17	0.40	0.09	0.35	0.10	0.47	0.40	0.27	0.23	0.22	0.62	0.59	0.30	0.95	0.37	0.49	0.55	0.40
Na_2O	0.49	0.33	0.37	0.30	0.30	0.33	0.30	0.64	0.40	0.28	0.30	0.29	0.51	0.37	0.20	0.71	0.71	0.73	0.66	0.70
K_2O	4.63	2.80	4.90	5.16	5.23	4.83	5.40	4.62	4.60	4.49	4.77	5.28	4.87	6.11	3.80	4.13	4.54	4.11	4.03	5.30
P_2O_5	0.05	0.06	0.05	0.04	0.05	0.06	0.10	0.06	0.10	0.06	0.07	0.05	0.06	0.07	0.10	0.16	0.14	0.13	0.12	0.10
LOI	8.81	6.42	8.92	8.01	8.77	7.66	8.00	8.68	6.90	8.11	8.44	7.57	7.40	7.67	10.00	9.45	8.13	8.16	7.57	8.50
Pb	12	9	20	9	16	12	14	24	14	17	16	29	14	15	18	10	12	15	14	17
Zn	100	90	100	54	99	116	143	109	83	97	98	92	102	91	108	123	100	92	96	103
Th	13	10	12	12	12	12	11	14	13	13	14	15	13	14	12	8	11	16	11	17
Ni	172	115	70	125	145	112	146	134	150	165	126	127	163	167	45	184	146	383	156	178
Co	34	13	25	5	26	15	23	21	18	22	24	17	17	17	18	13	17	14	52	21
Cr	175	113	157	158	165	140	167	131	130	162	166	153	148	154	159	135	125	130	123	141
La	70	40	61	51	66	40	65	55	52	56	55	51	47	64	48	45	75	60	45	70
Rb	187	129	203	223	218	201	231	191	187	202	205	232	198	237	184	185	209	192	195	223
Nb	14	7	12	12	10	12	11	12	11	13	13	13	11	14	10	12	14	12	9	16
Zr	240	120	147	169	151	133	139	162	191	157	152	165	135	158	132	126	150	130	138	185
Y	39	25	31	25	28	26	34	30	25	35	36	27	23	29	29	25	33	26	28	30
Sr	132	84	112	105	108	83	103	186	91	101	121	99	111	214	90	98	249	169	135	217
Ce	146	91	137	124	124	96	126	126	104	116	110	107	100	119	107	81	113	121	105	123
V	158	108	147	170	155	130	154	144	112	133	140	147	141	167	147	148	154	145	126	163
Ba	336	274	321	325	337	317	321	1131	302	374	385	411	330	473	345	246	423	389	463	432
Al_2O_3/TiO_2	19.7	22.5	23.0	21.7	23.3	23.2	24.2	20.6	20.5	22.5	22.8	22.3	22.1	22.4	23.6	21.6	20.9	21.3	17.8	20.0
K_2O/Al_2O_3	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2
D*	0.8	0.7	0.8	0.9	0.8	0.7	0.8	0.8	0.7	0.7	0.7	0.8	0.8	0.8	0.7	0.7	0.8	0.8	0.6	0.8
ICV	0.6	1.0	0.7	0.6	0.7	0.9	0.7	0.8	0.9	0.8	0.8	0.7	0.8	0.7	0.8	0.9	0.7	0.7	1.1	0.7
CIA	80	79	79	78	79	76	78	77	76	80	79	78	76	76	81	74	77	77	75	76
CIW	96	95	97	96	98	96	98	94	95	97	97	97	94	95	97	90	94	93	92	94

LOI: loss on ignition
D*: $Al_2O_3/(Al_2O_3+MnO+FeO_{tot})$; (Machour et al., 1994)
ICV: $FeO_{tot}+K_2O+CaO+MgO+Na_2O+TiO_2/Al_2O_3$; (Cox et al., 1995)
CIA: $Al_2O_3/(Al_2O_3 + Na_2O + CaO* + K_2O) * 100$; (Nesbitt and Young, 1982)
CIW: $Al_2O_3/(Al_2O_3 + Na_2O + CaO*) * 100$; (Harnois, 1988)
b.d.: below detection limit
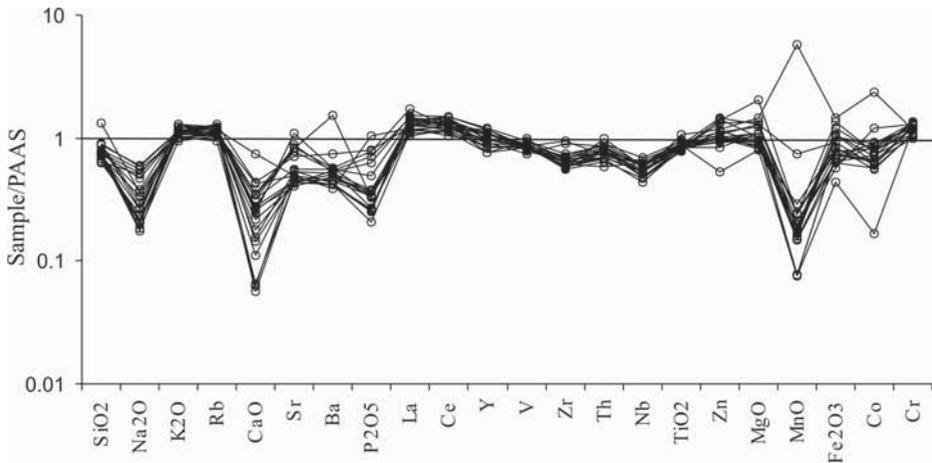
Fig. 4 – Enrichment factors of major and trace elements relative to PAAS (data from Taylor and McLennan, 1985).
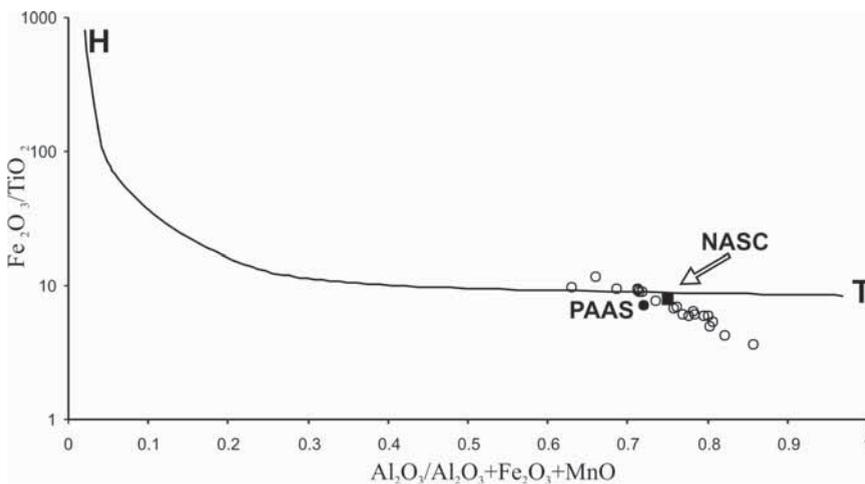
Fig. 5 – Bostrom (1973) diagram; analysed sediments are compared to argillite (T) and hydrothermal (H) end members whose mixing is modeled by the H-T curve. PAAS (filled circle) and NASC (filled square; data from Gromet *et al.*, 1984) data are reported for comparison.

Cr, and V *vs* Al_2O_3, and the ratio close to PAAS and NASC (North American Shale Composite, Gromet *et al.*, 1984) values support the detrital features of the shales (Fig. 6). The absence of an important biogenic SiO_2 contribution is showed by the SiO_2 – Al_2O_3 relationship (Fig. 7).

On the whole, the detrital features and continental crust provenance of the analysed shales are suggested by the high values (min = 0.65, max = 0.87, average = 0.77) of the parameter $D^*=Al_2O_3/(Al_2O_3+MnO+FeO_{tot})$ (Machhour *et al.*, 1994) which connects Al_2O_3, strongly assembled in the
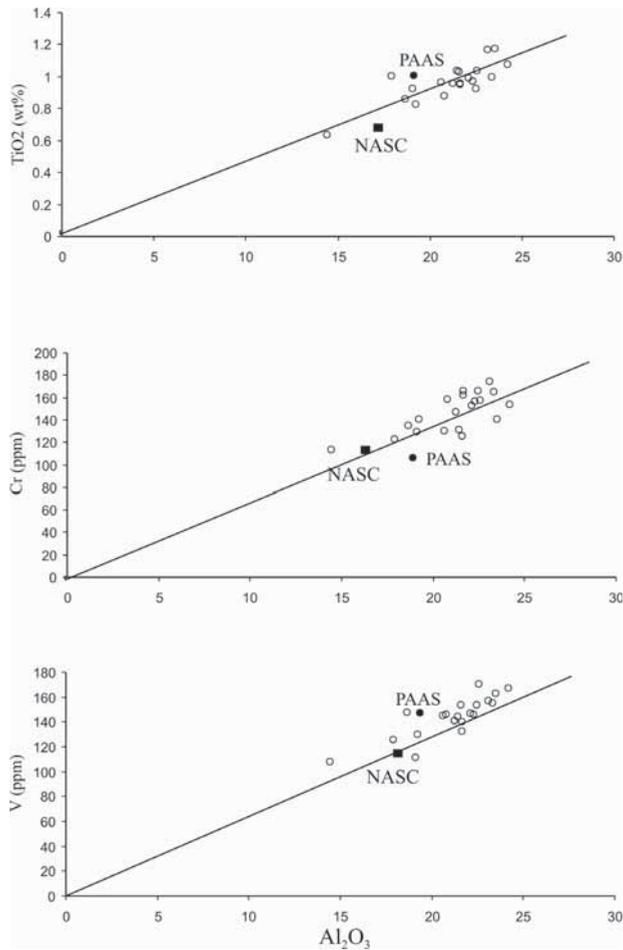
Fig. 6 – Binary diagrams of Al_2O_3 vs TiO_2, Cr, V; samples plot close to the standard shales NASC and PAAS.

continental crust (D*=0.79; Taylor and McLennan, 1985), with FeO and MnO characterized by oceanic crust affinity (D*=0.68; Taylor and McLennan, 1985).

DISCUSSION

Weathering, recycling and diagenesis

Several factors contribute to explain the chemical composition of the shales from the Monte Soro Unit. Combined effects of weathering, recycling and diagenesis will be evaluated in order to interpret the actual elemental distribution of these shales and to reveal the source area composition.

In order to asses the degree and intensity of chemical alteration, two weathering indexes, using molecular proportions, are applied: CIA (Chemical index of alteration) and CIW (Chemical index of weathering) proposed by Nesbitt and Young (1982) and Harnois (1988) respectively:

$$CIA = Al_2O_3/(Al_2O_3 + Na_2O + CaO^* + K_2O) * 100$$
$$CIW = Al_2O_3/(Al_2O_3 + Na_2O + CaO^*) * 100$$

where CaO* is the silicate fraction of the rocks.
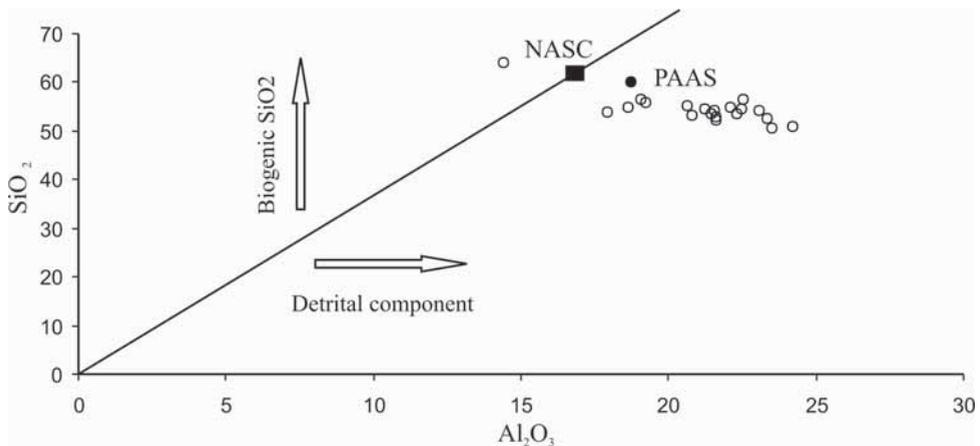
Fig. 7 – Al_2O_3 vs SiO_2 diagram showing the absence of biogenic contribution in the examined shales.

According to Nesbitt and Young (1982) who ascribe CIA values of about 70 - 75 for standard shales, and to Condie (1993) who reports CIW values of about 90 up to 98 for many intensely weathered Archean shales, the Monte Soro samples exhibit very high CIA and CIW values (CIA average = 77; CIW average = 95; see Table 2) as a result of the general CaO and Na_2O depletion providing evidence of an intense or prolonged source area weathering.

A further attesting comes from the index of compositional variability (ICV; Cox *et al.*, 1995; Cullers and Podkovyrov, 2000):

$$ICV = FeO_{tot} + K_2O + CaO + MgO + Na_2O + TiO_2/Al_2O_3$$

ICV values (average = 0.77; see Table 2) for shales of Monte Soro are typical of clay-rich mature sediments related either to intracratonic environments, where the recycling of old sediments is an active process, or to provenance from intensely weathered crystalline basements.

In Fig. 8 data are plotted on an A-CN-K diagram (Nesbitt and Young, 1982), where A is the mole fraction of Al_2O_3, CN is the sum of the mole fractions of CaO* and Na_2O, and K is the mole fraction of K_2O; samples plot fairly close to the A-K tie-line suggesting an intense chemical weathering. In particular, the data are coherent with a derivation from the Monti Peloritani crystalline basement rocks submitted to an alteration process which

produced a considerable loss of Na, Ca while the K/Al ratio slightly increases (see weathering trend in Fig. 8). Based on this hypothesis the shales, when compared to the bulk chemical composition of the Monti Peloritani crystalline basements (Fig. 9) exhibit enrichments of the elements adsorbed on clay minerals (K_2O and Rb) while the relative strong CaO and Na_2O depletion appears to reflect an intense source area weathering.

Wyborn and Chapell (1983) stressed that the described trend may be linked to recycling of older sediments. Cassola *et al.* (1990) suggested, by means of mineralogical compositions of quartzarenites from the Monte Soro Unit, the recycling of infraLiassic Verrucano sediments cropping out in the Monti Peloritani area. However, according to this hypothesis, the Verrucano pelites should plot, in the A-CN-K diagram, most likely along the alteration trend while in contrast they are closely related with the Monte Soro shales.

The above described data are closely related with the compositional features of the sandstones strata from the Monte Soro Unit which have a quite homogeneous subarkosic composition with high monocrystalline quartz content (~70%) and low plagioclases and lithic fragments abundances (Carmisciano and Puglisi, 1983).

The chemical and mineralogical compositions are however complicated by effects of the burial history that, as results from mineralogical
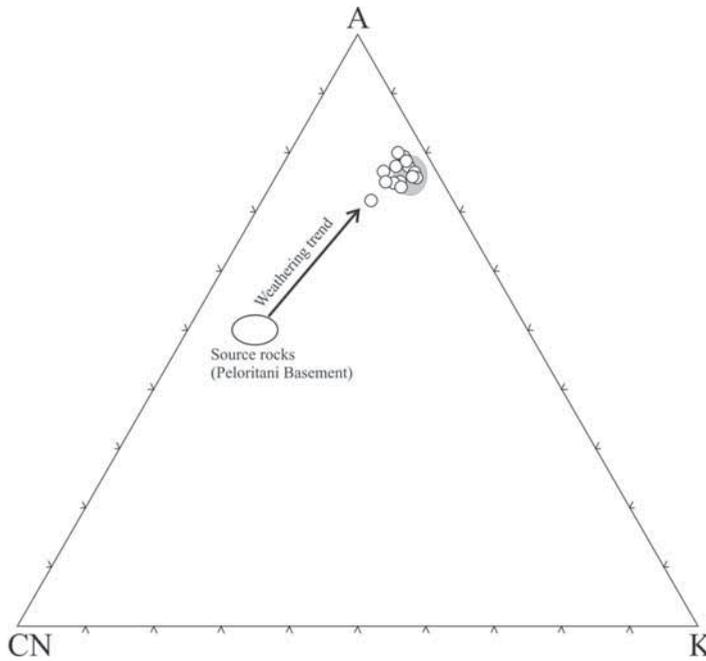
Fig. 8 – Ternary plot of molecular proportions of Al_2O_3-(Na_2O+CaO*)-K_2O for Monte Soro shales (open squares); grey area: 'Verrucano' pelites (data from Di Leo *et al*., 2000); for source rocks (Monti Peloritani crystalline basement) data from Atzori *et al.*, 2003).
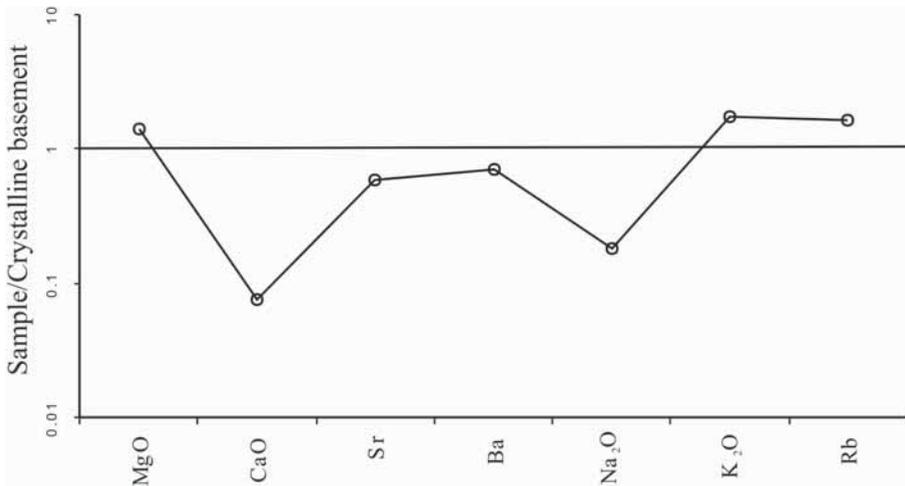
Fig. 9 – Alkaline and alkaline-earthy elements normalized to the bulk Peloritani metamorphic basement; data from Atzori *et al.* (2003). Elements are arranged in order of increasing ionic radius within each valence group.

investigation of the of < 0.5 μm fraction, lead to the achievement of late diagenetic conditions. In this P-T conditions, phases are differently resistant: mixed-layered smectite/illite show some changes both in the number of illitic layers and in the degree of stacking ordering; kaolinite may be converted to illite (Moon J. Lee and Chaunduri, 1976); smectite, if present, alters to mixed-layered smectite/illite and chlorite/smectite and diagenetic chlorite can be formed; illite increases its crystallinity index and the (001)/(002) intensity ratio (Van Moort, 1971; Foscolos and Kodama, 1973).

The key geochemical modifications during the diagenesis concern K_2O and CaO (Wintsch and Kvale, 1994), in fact the low CaO content might be due to mineralogical modifications such as plagioclase albitization (Land, 1984; Wintsch and Kvale, 1994) and smectite illitization (Velde 1995). Ca^{2+} released during such processes could represent a source for calcite cements precipitation in sandstones of the Monte Soro formation. K_2O in arenaceous-clayey sediments, is generally added to mudstones by means of smectite illitization (Hower et al., 1976). This added K_2O is supplied likely by K-feldspar dissolution from mudrocks associated to sandstones; if so, it could partially adduce reasons for the k-feldspar lack in sandstones of the examined sedimentary Unit

referred up to now (Puglisi, 1987) to volcanic contribution.

PROVENANCE

Geochemistry of mudrocks generally reflects the provenance of their detrital source rocks (Roser and Korsch, 1986).

To characterize the provenance of terrigenous sediments, it is necessary to rely on elements that are the least mobile during weathering, transport, diagenesis and metamorphism (Wronkiewicz and Condie, 1987). The Al_2O_3/TiO_2 ratio ranging from 17 to 24 (Table 2) suggests the absence of a mafic contribution characterized by ratio values lesser than 14 (Taylor and McLennan, 1985; Girty et al, 1996). In the Fe_2O_3/TiO_2 vs $Al_2O_3/Al_2O_3+Fe_2O_3$ diagram (Girty et al. 1996) the Monte Soro shales are plotted into the area representing an old continental crust provenance (Fig. 10).

Trace elements are mainly assembled in clay minerals and mechanically carried from the source area to sedimentary basin (McLennan, 1989); their abundances reflect the source rock composition. In the spider diagram of Fig. 11 some elemental ratios normalized with respect to the upper crust composition (data from Taylor and McLennan
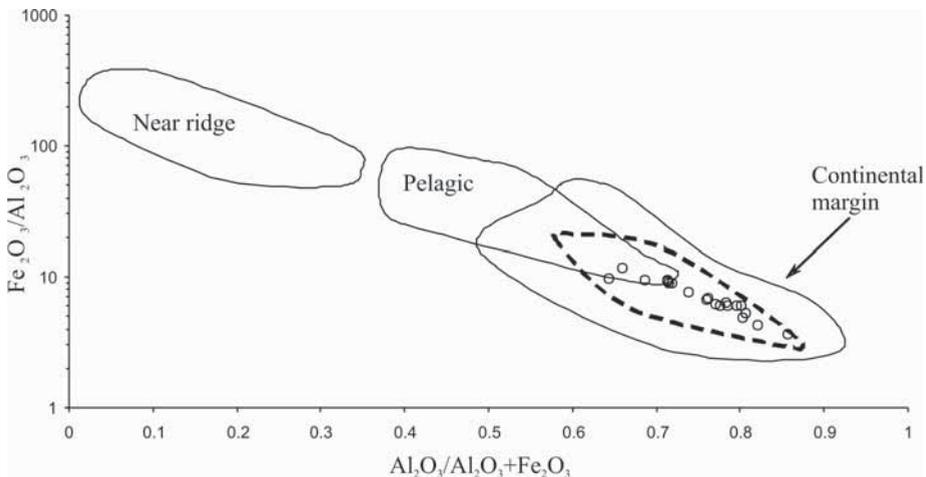
Fig. 10 – Murray (1994) diagram realized to discriminate depositional environments of sediments; near ridge, pelagic and continental margin settings are distinguished. Girty et al. (1996) added the old upper continental crust provenance subfield (dashed line-delimited area).
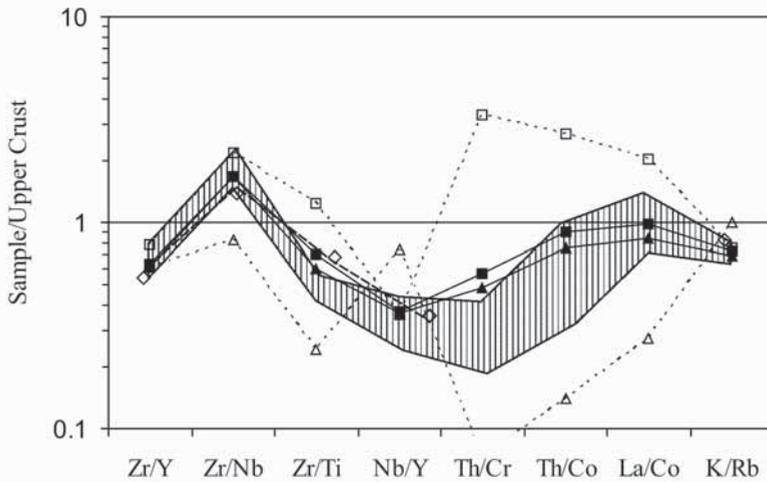
Fig. 11 – Spider diagram of some elemental ratios critical of provenance. Together with the Monte Soro shales (vertical striped area), average ratios of Verrucano pelites and metapelites (open diamonds; data from Di Leo *et al.*, 2000) and of Monti Peloritani basement rocks are represented: bulk crystalline basement (closed squares); metapelites and metagraywackes (closed triangles); orthogneiss (open squares); amphibolites (open triangles); data from Atzori *et al.* (2003).

1985) have been considered since such elements are the less susceptible to secondary processes (Wronkiewicz and Condie, 1987; Cullers, 1994; Cullers and Podkovyrov, 2000; Di Leo *et al.*, 2002). With the exception of Zr/Ti and Th/Cr, the analysed shale ratios are similar to the value of the bulk Peloritani metamorphic basement and of metagraywakes and metapelites that constitutes the dominant lithologies of their basements (Atzori *et al.*, 2003). On the contrary, there are differences with the elemental ratios of the Monti Peloritani Hercynian amphibolite and orthogneiss representative of basic and acid source rocks respectively. Finally, the data are also comparable with the Verrucano pelites and metapelites (data from Di Leo *et al.*, 2000).

The source area composition was also investigated by multivariate discriminant statistical approach applied to major elements used by Roser and Korsch (1988; Fig. 12). Shales of the Monte Soro Unit mainly plot in the quartzose sedimentary provenance field, near the felsic igneous provenance field. Geochemical data suggest a provenance from strongly weathered Peloritani crystalline rocks or from recycling of early Mesozoic 'Verrucano' strata. In this case, however, discriminate between

these two provenance is difficult since the Monti Peloritani basement is composed mainly of metagraywake and metapelites (Atzori *et al.*, 2003).

CONCLUSIONS

Integrated mineralogical and chemical analyses of shales from the Monte Soro Unit suggest contribution of weathering, transport and diagenesis on final rock composition and provide insights for determination of the source rock composition.

The studied shales have dominantly detrital features characterized by a high mineralogical maturity and high chemical indexes of weathering (CIA and CIW) testifying intense and prolonged chemical weathering and/or a recycling from older sediments as suggested also by the mineralogical composition of associated subarkosic levels.

The abundance of major and trace elements, considered mainly related to the source rock composition, is in accord with a provenance from the continental crust (felsic to intermediate igneous rocks and quartz rich sediments).
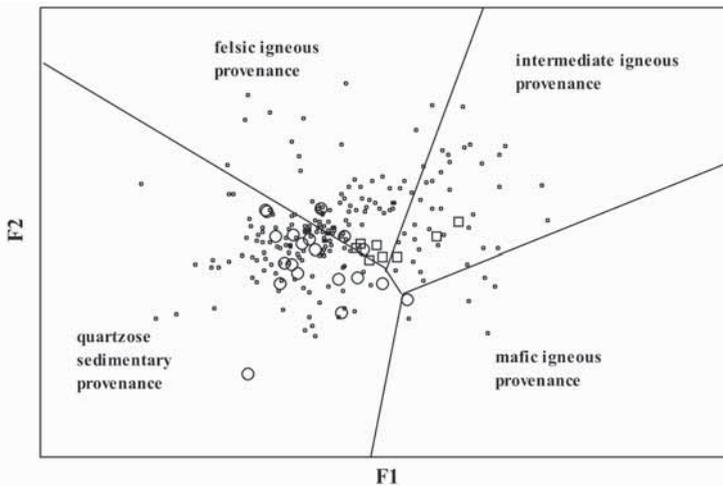
Fig. 12 – Discriminant function diagram (Roser and Korsch, 1988) comparing shales from the Monte Soro Unit (open circles) to metapelites and metagraywackes from the Monti Peloritani area (small open circles; data from Atzori *et al.* (2003).) and to Verrucano pelites (open squares, data from Di Leo *et al.* 2000). $F1: -1.773TiO_2 + 0.607Al_2O_3 + 0.76Fe_2O_3 - 1.5MgO + 0.616CaO + 0.509Na_2O - 1.224K_2O - 9.09$; $F2: 0.445TiO_2 + 0.07Al_2O_3 - 0.25Fe_2O_3 - 1.142MgO + 0.438CaO + 1.475Na_2O + 1.426K_2O - 6.86$.

The obtained data can contribute to the paleogeographic reconstruction of the source/basin system. The Monte Soro sequence was deposited within a part of the Neo-Tethyan domain being probably isolated from the African terranes (Roure *et al.*, 1990). In particular, it is correlated with other Maurétaniens-like flysches (Los Nogales - Andalusia, Jebel Tisirene - Morocco, Guerrouch - Algeria) occurring in proximity with the European margin (Bouillin, 1978; Durand Delga and Fontbote, 1980; Abbate *et al.*, 1986; Bouillin *et al.*, 1986; Cassola *et al.*, 1990). Furthermore, the Sicilide Units are characterized by the lack of ophiolites but the oceanic setting for the Monte Soro basin is suggested for the close affinity with the ophiolite-bearing Liguride units of the southern Apennines (Boccaletti *et al.*, 1984).

In this context, the source area for the studied shales is identifiable with the metamorphic basements of the Mesomediterranean terranes (Guerrera *et al.*, 1993; Critelli, 1999). Major and trace elements abundance and their ratios are in agreement with a provenance from the basement rocks of the Peloritani mountain belt. Alternatively, the source rocks could be recognized in the Liassic 'Verrucano' units which are the first sedimentary unit coming from the erosion of the Peloritani basement. However, in this case, the dominant metapelites and metarenites in the upper crust crystalline basement (Atzori *et al.*, 2003) and the lower abundance of granitic and basic magmatic rocks (or orthogneiss and metabasites) make difficult the distinction between the two provenance hypotheses.

The post depositional history of the studied shales is characterized by the reaching of late diagenetic conditions as testified by the presence of ordered I/S mixed layered clay minerals. This is probably related to the tectonic overload due to the nappe piling during the post-Cretaceous subduction.

REFERENCES

Abbate E., Bortolotti V., Conti M., Marcucci M., Principi G., Passerini P., Treves B. (1986) – *Appennines and Alps ophiolites and the evolution*

of western Tethys. Mem. Soc. Geol. It., **31**, 23-44.

AMODIO-MORELLI L., BONARDI G., COLONNA V., DIETRICH D., GIUNTA G., IPPOLITO F., LIGUORI V., LORENZONI V., PAGLIONICO A., PERRONE V., PICARETTA G., RUSSO M., SCANDONE P., ZANETTIN-LORENZINI E., ZUPETTA A. (1976) – *L'arco Calabro-Peloritano nell'orogene Appenninico-Magrebide.* Mem. Soc. Geol. It. **17**, 1-60.

ASIEDU D.K., SUZUKI S., NOGAMI K., SHIBATA T. (2000) – *Geochemistry of Lower Cretaceous sediments, inner zone of south Japan: constraints on provenance and tectonic environment.* Geochem. J., **34**, 115-173.

ATZORI P., CIRRINCIONE R., KERN H., MAZZOLENI P., PEZZINO A., PUGLISI G., PUNTURO R., TROMBETTA A. (2003) – *The abundance of 53 elements and petrovolumetric models of the crust in north-eastern Peloritani Mountains (Site 8).* Accademia nazionale delle Scienze detta dei XL, Scritti e documenti, **32**, 319-327.

BATHIA M.R. (1985) – *Composition and classification of Paleozoic Flysch Mudrocks of eastern Australia: implications in provenance and tectonic setting interpretation.* Sedim. Geol., **41**, 249-268.

BOCCALETTI M., NICOLICH R., TORTORICI L. (1984) – *The Calabrian Arc and the Ionian sea in the dynamic evolution of the central Mediterranean.* Marine Geol., **55**, 219-245.

BOUILLIN J.P. (1978) – *La transversale del Collo et d'El Milia (Petite Kabylie): una region-clef pour l'interpretazion de la tectonique alpine de la chaine littoral d'Algerie.* Mem. Soc. Geol. Fr., **135**, 1-84.

BOUILLIN J.P., DURAND DELGA M., OLIVIER PH. (1986) – *Betic-Rifian and Tyrrhenian Arcs: distinctive features, genesis and development stages.* In: Wezel F.C. Ed. The origin of Arcs. Developments in Tectonics, **21**, Elsevier, Amsterdam, 281-304.

BOSTROM K. (1973) – *The origin and fate of ferromanganoan active ridge sediments.* Stockholm Contrib. Geol. 27, 149-243.

CARMISCIANO R., PUGLISI D. (1983) – *Studio composizionale delle arenarie del Flysch di Monte Soro (Monti Nebrodi, Sicilia centro-settentrionale).* Miner. Petr. Acta, **27,** 73-90.

CASSOLA P., GIAMMARINO S., PUGLISI D. (1990) – *Il Flysch di Monte Soro: caratteri e significato geodinamico di un flysch cretacico ad affinità "Maurétaniens" nel segmento siculo della Catena Maghrebide.* Boll.Acc. Gioenia Sc. Nat., **23**, 93-117.

CAVALCANTE F., FIORE S., PICARRETA G., TATEO F. (2003) – *Geochemical and mineralogical approaches to assessing provenance and deposition of shales: a case study.* Clay Miner., **38**, 383-397.

CONDIE C.K. (1993) – *Chemical composition and evolution of the upper continental Crust: contrasting results from surface samples and shales.* Chem. Geol, **104**, 1-37.

COX R., LOWE D.R. (1995) – *A conceptual review of regional-scale controls on the composition of clastic sediment and the co-evolution of continental blocks and their sediment cover.* J. Sedim. Res., **A65 No 1**, 1-12.

COX R., LOWE D.R., CULLERS R.L. (1995) – *The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States.* Geochim. Cosmochim. Acta, **59**, 14, 2919-2940.

CRITELLI S. (1999) – *The interplay of lithospheric flexure and thrust accomodation in forming stratigraphic sequences in the southern Apennines foreland basin system, Italy.* Rend. Fis. Acc. Lincei (1999) **10**, 257-326.

CULLERS R.L. (1994) – *The controls on the major and trace element variation of shales, siltstones and sandstones of Pennsylvanian-Permian age from uplifted continental blocks in Colorado to platform sediment in Kansas, U.S.A.* Geochim. Cosmochim. Acta **58**, 4955-4972.

CULLERS R.L. (2000) – *The geochemistry of shales, siltstones and sandstones of Pennsylvanian-Permian age, Colorado, USA: implications for provenance and metamorphic studies.* Lithos **51**, 181-203.

CULLERS R.L., PODKOVYROV V.N. (2000) – *Geochemistry of the MesoProterozoic Lakhanda shales in south-eastern Yakutia, Russia: implication for mineralogical and provenance control, and recycling.* Precamb. Res., **104**, 77-93.

DI LEO P., DINELLI E., MONGELLI G., SCHIATTARELLA M. (2002) – *Geology and geochemistry of Jurassic pelagic sediments, 'Scisti Silicei' Formation, southern Appennines, Italy.* Sedim. Geol., **150**, 229-246.

DI LEO P., MONGELLI G., CRITELLI S., LAVIANO R., LE PERA E., PERRONE V. (2000) – *Chemistry and mineralogy of early Mesozoic pelite layers from continental redbeds 'Verrucano', Peloritani Mountains, Sicily, Italy.* Per. Mineral., **69 No 1**, 19-34.

DURAND DELGA M., FONTBOTE J.M. (1980) – *Le cadre structural de la Mediterranee occidentale.* In: '*Geologie des chaines alpines issues la Tethys*'.

26° Congr. Inter. Paris, Mem. B.R.G.M., **15**, 67-85.

FIORE S., MONGELLI G. (1991) – *Hypothesis on the genesis of clay minerals in the fine fraction of 'Argille varicolori' from Andretta (southern Apennines).* Miner. Petrogr. Acta, **34**, 183-190.

FOSCOLOS A.E., KODAMA H. (1974) – *Diagenesis of Clay minerals from lower Cretaceous shales of north-eastern British Columbia.* Clays Clay Miner., **22**, 319-335.

GELARD J.P. (1969) – *Le flysch a base schisto-greseuse de la bordure meridionale et orientale du massif de Chellata (Grande Kabylie, Algerie).* Bull. Soc. Geol. Fr., **11**, 677-686.

GIRTY G.H., RIDGE D.L., KNAACK C., JOHNSON D., AL-RIYAMI R.K. (1996) – *Provenance and depositional setting of Paleozoic Chert and Argillite, Sierra Nevada, California.* J. Sedim. Res., **66**, 107-118.

GROMET L.P., DYMEK R.F., HASKIN L.A., KOROTEV R.L. (1984) – *The 'North American shale composite': Its compilation, major and trace elements characteristics.* Geochim. Cosmochim. Acta, **48**, 2469-2482.

GUERRERA F., MARTIN-ALGARRA A., PERRONE V. (1993) – *Late Oligocene-Miocene syn/late-orogenic successions in western and central Mediterranean Chains from the Betic Cordillera to the southern Apennines.* Terra Nova **5**, 525-544.

HARNOIS L. (1988) – *The CIW index: a new chemical index of weathering.* Sedim. Geol., **55**, 319-322.

HASSAN S., ISHIGA H., ROSER B.P., DOZEN K., NAKA T. (1999) – *Geochemistry of Permian-Triassic shales in the Salt Range, Pakistan: implication for provenance and tectonism at the Gondwana margin.* Chem. Geol., **158**, 293-314.

HOFFMAN J., HOWER J. (1979) – *Clay mineral assemblages as low grade metamorphic geothermometers: application to the thrust faulted disturbed belt of Montana (U.S.A.).* SEPM, Spec. Publ., **26**, 55-79.

HOWER J., ELSINGER E.V., HOWER M.E., PERRY E.A. (1976) – *Mechanism of burial metamorphism of argillaceous sediment:1. Mineralogical and chemical evidence.* Geol. Soc. Am. Bull. **87**, 725-737.

KISH H.J. (1983) – *Mineralogy and petrology of burial diagenesis (burial metamorphism) and incipient metamorphism in clastic rocks.* In 'Diagenesis in sediment and sedimentary rocks', eds Larsen, G. and Chilingar, G.V., Elsiever, Amsterdam. **Vol 2**, 289-493 and 513-541.

JABOYEDOFF M., THELIN P. (1996) – *New data on low-grade metamorphism in the Brianconnais domain of the Prèalpes, Western Switzerland.* Eur. J. Mineral., **8**, 577-592.

LAND L.S. (1984) – *Frio sandstone diagenesis, Texas Gulf Coast; a regional isotopic study.* American Association of Petroleum Geologists Manual, **37**, 47-62.

LANSON B., VELDE B. (1992) – *Decomposition of X-Ray diffraction patterns: a convenient way to describe complex I/S diagenetic evolution.* Clays Clay Miner., **40,** 629-643.

LENTINI F., CARBONE S., CATALANO S., GGRASSO M., MONACO C. (1990) – *Tettonica a thrust neogenica nella catena Appenninico-Maghrebide: esempi dalla Lucania e dalla Sicilia.* Studi geologici Camerti, Vol. Spec. (1990), 19-26.

LENTINI F., CATALANO S., CARBONE S. (1999) – *Carta geologica della provincia di Messina.* Scala 1:50000. S.El.Ca., Firenze.

LENTINI F., VEZZANI L. (1978) – *Tentativo di elaborazione di uno schema strutturale della Sicilia orientale.* Mem. Soc. Geol. It., **19**, 495-500.

LYNCH F.L. (1997) – *Mineralogy of Frio Formation shale and the stoichiometry of the smectite to illite reaction – the most important reaction in clastic sedimentary diagenesis.* Clays Clay Miner., **45**, 618-631.

MACHHOUR L., PHILIP J., OUDIN J.L. (1994) – *Formation of Laminite deposits in anaerobic-dysaerobic marine environments.* Mar. Geol., **117**, 287-302.

McLENNAN S.M. (1989) – *Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes.* In 'Lipin, B.R. and McKay G.a., Eds., Geochemistry and Mineralogy of Rare Earth Elements: Washington, Min. Soc. Am., 169-200.

MONGELLI G., CULLERS R.L., MUELHEISEN S. (1996) – *Geochemistry of Late Cretaceous-Oligocene shales from the Varicolori Formation, southern Apennines, Italy: implications for mineralogical, grain size control and provenance.* Eur. J. Mineral., **8**, 733-754.

MOON J.L., CHAUNDHURI S. (1976) – *Clay mineral studies of the Lower Permian Havensville shale in Kansas and Oklahoma.* Clays Clay Miner., **24**, 239-245.

MOORE D.M., REYNOLDS R.C. (1989) – *X-Ray diffraction and the identification and analysis of clay minerals. Oxford University Press.* 332 pp.

MURRAY R.W. (1994) – *Chemical criteria to identify depositional environments of chert: general*

principles and applications. Sedim. Geol., **90**, 213-232.

NESBITT H.W., MARKOVICS G., PRICE R.C. (1980) – *Chemical processes affecting alkalies and alkaline earths during continental weathering.* Geochim. Cosmochim. Acta, **44**, 1659-1666.

NESBITT H.W., YOUNG G.M. (1982) – *Early Proterozoic climate and plate motions inferred from major element chemistry of lutites.* Nature, **299**, 715-717.

NESBITT H.W., YOUNG G.M. (1989) – *Formation and diagenesis of weathering profiles.* J. Geol., **97**, 129-147.

OGNIBEN L. (1960) – *Nota illustrativa dello Schema geologico della Sicilia nord-orientale.* Riv. Min. Sic. **64-65**, 183-212.

POLLASTRO R.M. (1993) – *Considerations and Applications of the illite/smectite Geothermometer in Hydrocarbon-Bearing Rocks of Miocene to Mississippian Age.* Clays Clay Miner., **41**, 119-133.

PUGLISI D. (1981) – *Studio geologico petrografico del Flysch di Monte Soro nei Peloritani occidentali (Sicilia).* Miner. Petr. Acta, **25**, 103-115.

PUGLISI D. (1987) – *Le successioni torbiditiche cretacico-terziarie della Sicilia nord-orientale nel quadro dell'evoluzione del settore meridionale dell'arco calabro-peloritano e della catena maghrebide siciliana.* G. Geol., 167-185.

REYNOLDS R.C. JR. (1985) – *NEWMOD, a computer program for the calculation of one dimensional diffraction patterns of mixed-layered clays.* R.C. Reynolds, Jr., 8 Brook Dr., Hanover, NH 03755, U.S.A.

ROSER B.P., KORSH R.J. (1986) – *Determination of tectonic setting of sandstone-mudstone suites using SiO_2 content and K_2O/Na_2O ratio.* J. Geol., **94**, 635-650.

ROSER B.P., KORSH R.J. (1988) – *Provenance signatures of sandstone-mudstone suites determined using discriminant function analysis of major-element data.* Chem. Geol., **67**, 119-139.

ROURE F., HOWELL D.G., MULLER C., MORETTI I. (1990) – *Late Cenozoic subduction complex of Sicily.* J. Struct. Geol., **12 No 2**, 259-266.

SHEPARD F. (1954) – *Nomenclature based on sand-silt-clay ratios.* J. Sedim. Petrol., **24**, 151-158.

TAYLOR S.R., MCLENNAN S.M. (1985) – *The continental Crust: Its composition and evolution.* Blackwell Scientific Pubblications, Oxford, 312 pp.

VAN MOORT J.C. (1971) – *A comparative study of the diagenetic alteration of clay minerals in Mesozoic shales from Papua, New Guinea, and in Tertiary shales from Louisiana, U.S.A.* Clays Clay Mineral., **19**, 1-20.

VELDE B. (1995) – *Origin and mineralogy of clays.* Eds Velde, B. Springer, Berlin, 334 pp.

WINTSCH R.P., KVALE C.M. (1994) – *Differential mobility of elements in burial diagenesis of siliciclastic rocks.* J. Sedim. Res., **A64**, 349-361.

WRONKIEWICZ D.J., CONDIE K.C. (1987) – *Geochemistry of Archean shales from the Witwatersrand Supergroup, South Africa: Source-area weathering and provenance.* Geochim. Cosmochim. Acta, **51**, 2401-2416.

WYBORN L.A.I., CHAPPELL B.W. (1983) – *Chemistry of the Ordovician and Silurian greywackes of the Snowy Moutains, south-eastern Australia: an example of chemical evolution of sediments with time.* Chem. Geol., **39**, 81-92.

ZHANG L., SUN M., WANG S., YU X. (1998) – *The composition of shales from the Ordos basin, China: effects of source weathering and diagenesis.* Sedim. Geol., **116**, 129-141.