PERIODICO di MINERALOGIA Volume 87, No. 5, 2018

Clay mineral assemblage of the Middle Triassic-Lower Jurassic mudrocks from western-central Mediterranean Alpine Chains

Francesco Perri*

Dipartimento di Scienze Geologiche, Università degli Studi della Basilicata, Campus di Macchia Romana, 85100 Potenza, Italy

Abstract — The Middle Triassic to Lowermost Jurassic mudrocks from continental redbeds of the western-central Mediterranean region (Sicily, Calabria, Betic Cordillera and Rif) have been analyzed in order to reveal the mineralogical composition of the sediments and their thermal/burial history within the geological evolution of the Mediterranean area; the redbeds studied in this work have a palaeogeographic and geodynamic importance at the regional scale.

The studied samples are characterized by the presence of abundant clay minerals; subordinately are present significant amounts of quartz and Fe-oxides (hematite or goethite), and minor concentrations of feldspars, calcite and dolomite. The <2 µm grain-size fraction of the samples is mostly composed by illite prevailing on illite-smectite mixed layers, kaolinite and chlorite. The proportions of illite in I-S mixed layers are in a range of 70-90 % of I/S (R>1), with an illite crystallinity value (IC) of 0.6-0.7° $\Delta 2\theta$ CuKα; these data suggest that the temperature experienced by the Mediterranean successions is in the range 100-150 °C. Thus the diagenetic/tectonic evolution should correspond to a lithostatic/tectonic loading of about 4-5 km.

Riassunto — Nel presente lavoro, sono stati analizzati da un punto di vista mineralogico, sedimenti pelitici continentali di tipo *redbed* di età Triassico-Giurassico inferiore campionati in alcune aree del Mediterraneo centro-occidentale (Sicilia, Calabria, Cordigliera Betica e Catena del Rif), al fine di studiare le loro caratteristiche mineralogiche e così contribuire alla ricostruzione della storia di seppellimento e/o termica di questi depositi, all'interno dell'evoluzione geologica del bacino del Mediterraneo. Queste successioni rivestono un ruolo importante nello studio dell'evoluzione paleogeografica e geodinamica del Mediterraneo occidentale.

I sedimenti campionati sono caratterizzati principalmente dalla presenza di abbondati minerali argillosi; quantità significative di quarzo e ossidi di Fe (ematite e goethite), e concentrazioni minori di feldspati; calcite e dolomite sono presenti in modo subordinato. La frazione <2 µm risulta composta principalmente da illite che prevale su strati misti illite-smectite, caolinite e clorite. La percentuale di strati illitici presenti nell'interstratificato I-S varia dal 70 al 90% (R>1), con un valore di cristallinità dell'illite (IC) pari a 0,6-0,7° $\Delta 2\theta$ CuK_{α}; questi dati suggeriscono che le temperature raggiunte dai sedimenti erano nell'intervallo 100-150 °C. Partendo da questi valori si può ipotizzare che queste successioni sedimentarie hanno subito, durante la loro evoluzione

diagenetica/tettonica, un carico litostatico/tettonico pari a circa 4-5 km.

Key Words: *Burial history, Diagenesis, Mediterranean area, Mesozoic, Redbeds*

Introduction

Clay minerals are the key constituents of the mud and soil that coat the Earth's surface, forming a thin buffer zone. Clay minerals are an essential group of minerals in a clay cycle that regenerates the crust and creates new crust from the underlying mantle (Merriman, 2002).

In sedimentary basins the predominantly juvenile clays formed by surface weathering are collected into large deposits and mature before they progress to the next stage of the cycle (Merriman, 2005). When clay minerals are buried in sedimentary basins they undergo wide transformations in response to the geothermal conditions within the basins and their geotectonic evolution.

Diagenetic clay mineral transformations of mudrocks were recognized by Hower *et al.* (1976) from their study of the Tertiary shales of the Gulf Coast, U.S.A.; during prograde diagenetic condition the amount of illite layers in mixed-layer illite-smectite increases (e.g., Burst, 1969; Shutov *et al.*, 1969a, 1969b; Weaver and Beck, 1971; Hower *et al.*, 1976). Prograde transformations are generally characterized by progressive increases in crystal thickness ("crystallinity") and decreases in crystal defect densities, lattice strain and compositional variability (Peacor, 1992).

The "illite crystallinity" (IC) method was developed during the early 1960s, first in Texas and later in France. Illite crystallinity (IC) is the measure of the full width at half maximum (FWHM) of the 10 Å illite diffraction peak. It was applied in petroleum exploration to detect diagenetic stages, and to characterize the ultimate evolution stages ("anchizone") before metamorphism.

According to Meunier and Velde (1989) and Środoñ *et al.* (1992), illite does not contain expandable layers. This absence of expandable layer was one of the features used to define the anchizone (Kübler, 1967). According to Moore and Reynolds (1997), illite can contain up to approximately 5 % of smectite layers, suggesting that anchizonal illites may contain a few percent of swelling layers.

In this paper, the thermal/burial history of a set of mudrock samples from selected sections of Upper Triassic to Lower Jurassic continental redbeds (Mediterranean area) has been studied using mineralogical tools. The history of these sediments, including source area weathering, provenance, recycling and burial, record an important phase of the geological evolution of the Mediterranean area (Mongelli *et al.*, 2006).

In the Alpine orogenic belts, from the Betic Cordillera to Apenninic Chain, clastic sediments preserve information on the Mesozoic Pangea supercontinent break-up, the Tethyan Ocean rifting and its closure during Tertiary orogenesis. The interpretation of the thermal/burial history of these sediments can be used to test palaeogeographic and palaeotectonic reconstructions during key orogenic phases (Critelli, 1999). The continental rift-valley phase and the proto-oceanic phase of the Tethyan rifting in the western-central Mediterranean region occurred during the Late Triassic to Early Jurassic, and in many tectonic units of the Alpine orogenic belts, continental redbeds, which mark the base of the Meso-Cenozoic covers, are interpreted as deposited during the rift-valley phase. The domain of these redbeds was located around small mountain areas, from which alluvial depositional systems provided siliciclastic supply to neighboring nascent continental sedimentary basins formed during Triassic rifting. They reveal the erosion of metamorphosed Paleozoic successions extensively intruded by felsic plutonic rocks. Chemical weathering of such rocks under tropical hot and episodically humid climate, with a prolonged dry season, allowed oxidation of iron and rubefaction of soils and sediments and caused concentration of quartz in thick soil profiles. These soils were later denudated by fluvial erosion, producing relatively mature, quartz-rich red deposits (Critelli *et al.*, 2004; Mongelli *et al.*, 2006).

Geological and stratigraphic setting

Orogenic belts, developed along the central and western Mediterranean region, preserve a record of the geodynamic events that occurred in the Mediterranean, from Pangea supercontinent break-up, to Tethyan Ocean opening and its closure during Alpine orogenesis. These paleotectonic phases occurred in the central-western Mediterranean and are marked by clastic sediments, that can be used to test alternate palaeogeographic and palaeotectonic reconstructions.

In the orogenic belts of the Mediterranean region, the proto-oceanic stage of the Tethyan rifting occurred in the Middle Triassic to Early Jurassic, and it is marked by continental redbeds. In the following rift stage, sedimentation evolves to transitional, shallow-marine and deep-marine carbonate/clastic sequences (Zuffa *et al*., 1980; Cecca *et al*., 2002).

These rifted-margin prisms are preserved in diverse tectonic units deriving from the Internal Domains of the Apenninic, Maghrebian and Betic Chains and are represented in the Calabrian-Peloritanian Arc, Kabylias, Rif and southern Spain (Fig. 1) (Guerrera *et al.*, 1993).

In the Calabrian-Peloritanian Arc, continental redbeds are well preserved in the Longi-Taormina (Sicily) and Sila (Calabria) Units, but they characterize all other units showing an Alpine cover (Bagni, Stilo, Mandanici, Piraino, Alì). These sediments are not dated but they reach the Hettangian, passing to Sinemurian shallow-marine sediments (Baudelot *et al.,* 1988; Santantonio and Teale, 1987).

In the Tellian Maghrebids, Triassic redbeds are known only in the Greater Kabylia, at the base of the "Chaine Calcaire" units. In the Rifian Maghrebids, redbeds occur in both Ghomaride and "Internal Dorsale" units, and, finally, in the Betic Cordillera, redbeds mark the base of the Malaguide Units (Saladilla Fm.) (Martín-Algarra *et al*., 1995). Redbeds, in the Tellian, Rifian and Betic chains, are Middle to Late Triassic in age and they pass to the Middle Liassic shallow-marine sediments (Wildi, 1983).

In all the circum-Mediterranean Orogenic Belts, redbeds nonconformably rest on Paleozoic metasedimentary basements. In the Calabrian-Peloritanian Arc redbeds rest also on Late Variscan plutonic rocks (Santantonio and Teale, 1987).

In the Rif and Betic Cordillera outcrops the contact between the metamorphic basements and the sedimentary successions is visible, whereas in the Sicily and Calabria outcrops the contact is not visible and many little faults are present, especially in transition to limestones.

Overall the stratigraphic successions are lithologically quite homogeneous. Conglomerates and coarse sandstones dominate in the lower portions, while mudrocks and fine sandstones are more abundant in the upper portions. Redbeds range from few metres to 200-300 metres in thickness, and they are reddish or purple, rarely greenish in color. The sedimentary facies associations suggest alluvial fan, braided and alluvial plain fluvial environments. In the Betic Malaguide Units, redbeds are interbedded with thin carbonate strata testifying local shallow-marine conditions. In all localities, redbeds abruptly pass to transitional and shallow-to-deep marine conditions.

Sampling and XRD measuring techniques

Fifty-nine Mediterranean mudrock samples, interbedded in the quartzarenite and conglomerate strata, were collected along the stratigraphic sections, and were analyzed by X-ray diffraction (XRD).

The whole-rock samples were first dried and then crushed by hand in an agate mortar. Randomly-oriented whole-rock powders were run in the 2-70 °2θ interval, at a scan speed of 1 °2θ/min, with a step size of 0.05 °2θ and a counting time of 3 sec per step, using a Scintag X_1 apparatus equipped with a solid-state Si (Li) detector. The tube current and the voltage were 30 mA and 40 kV, respectively. The intensities and diffraction angles of the identified minerals were compared to the database of the International Center for Diffraction Data (ICDD).

The mineralogical composition of the <2 μm grain-size was determined by a thin highly oriented aggregate; oriented air-dried samples were scanned from 1 to 48 °2θ at a scan speed of 0.75 °2θ/min with a step size of 0.05 °2θ and a counting time of 4 sec per step. The occurrence of expandable clays was determined after treatment with ethylene glycol at 25 °C for 15h. Glycolated samples were scanned at the same conditions used for the air-dried aggregates in the 1-30 °2θ interval. Expandability measurements (percent of illite in illite/EG-smectite) were determined according to Moore and Reynolds (1997) using

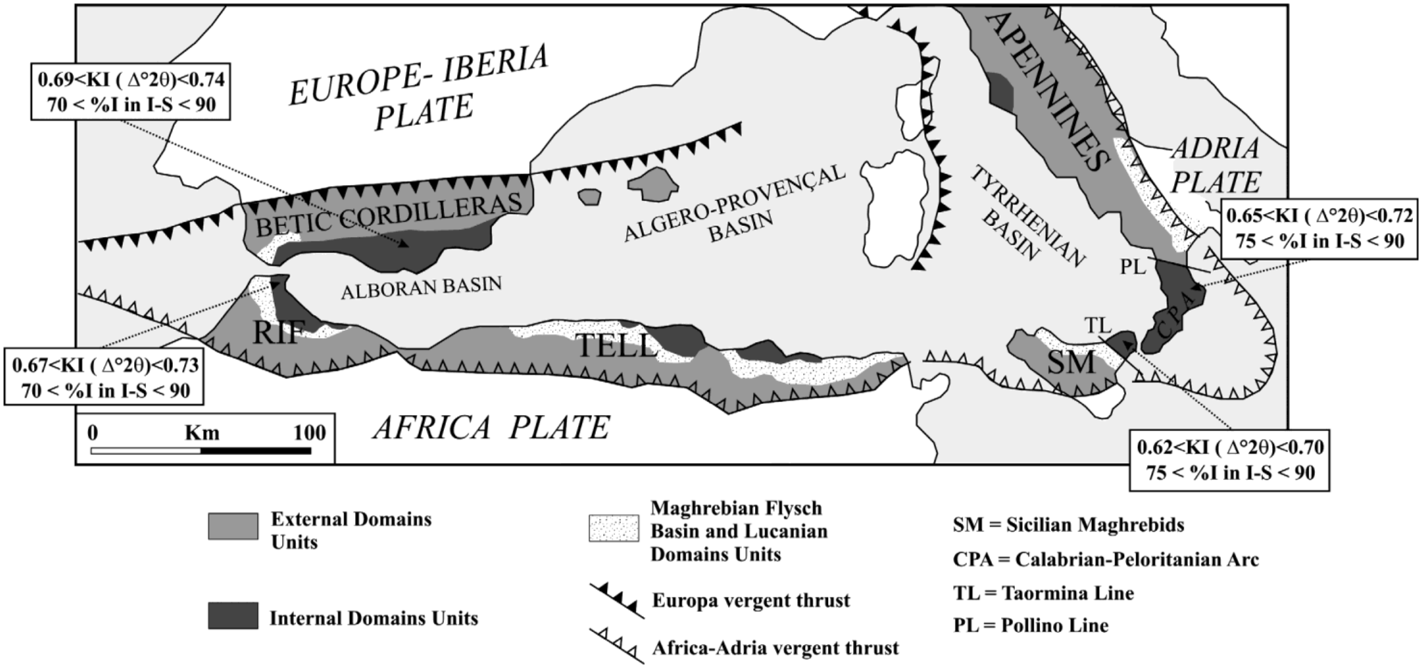

Fig. 1 – Geological sketch map of the Alpine Chains in the Central-Western Mediterranean Region (Guerrera *et al*., 1993; modified), showing sampling location and analytical data discussed in the text.

the delta two-theta method after decomposing the composite peak between 9-10 °2θ and 16-17 °2θ using the Scintag X1 software program with a split Pearson VII function and calculating the quantity Δ°2θ (Moore and Reynolds, 1997). The Pearson VII function (Goy *et al*., 1993) was used in the quantitative analysis for decomposition (Fig. 2) of overlapping reflections. The procedure adopted in this work for the "semiquantitative analysis", is based on the method proposed by Giampaolo *et al*. 2005, modified from Moore and Reynolds (1997).

Illite crystallinity (IC) value was measured on both air-dried and ethylene-glycol solvated oriented mounts; IC measurements are made here by interpolating the background under the peak by connecting the background on both sides of the peak and by using a profile fitting method (Lanson, 1997). This method involves matching an observed peak shape with a calculated shape based on various mathematical functions (in this case Pearson VII function) for the individual calculated peak components (Lanson, 1997).

The IC value is strongly dependent on the size of the studied fractions (Kübler, 1984) and on measurement conditions. The transition from one type of equipment to another required numerous calibrations. IC results were calibrated using four interlaboratory Crystallinity Index Standard (CIS) (Warr and Rice; 1994); IC value from this study (x) were transformed into IC_{CIS} data (y) according to the equation $y = 2.2366x + 0.0243$ ($R^2 = 0.98$), obtained in laboratory using the international standards. According to Kübler (1967) we adopted the metamorphic boundaries: 0.42° Δ2θ CuK_α for the diagenesis/anchizone boundary and 0.25° Δ2θ CuK_α anchizone/epizone boundary; a value of 0.30° Δ2θ CuK_α divides the anchizone in a lower and an upper part.

I-S mixed layers of a particular unit or a stratigraphic succession, coupled with the illite crystallinity method, are studied to detect vertical profiles and areal variations of basin thermal maturity and to reconstruct the tectonic loading the successions experienced during their history.

Mineralogical composition

The XRD patterns of whole-rocks show that the analyzed Mediterranean samples are rich in clay minerals associated to significant amounts of quartz and hematite or goethite (only in the Calabria samples), and negligible amounts of feldspar; minor amounts of calcite have been identified in three Calabria samples, whereas minor concentrations of calcite and dolomite have been identified in the Betic Cordillera XRD patterns (Figs. 3, 4 and 5).

The <2 μm grain-size fraction of the Calabrian-Peloritanian Arc (Sicily and Calabria) samples is composed of illite prevailing on illite-smectite mixed layers, kaolinite and negligible amounts of chlorite (Fig. 6); the <2 μm grain-size fraction of the Betic Cordillera and Rif samples is composed by illite prevailing on illite-smectite mixed layers and minor amounts of kaolinite and chlorite (Fig. 7).

The chemical composition of the "micaceous" phases can be obtained from the Rey & Kübler (1983) diagram. The X-ray diffraction intensity of the harmonic series (00*l*) measured on oriented preparations was corrected for both the intensity loss of the diffracted beam at the specific diffraction angles and for the sample thickness. Rey & Kübler triangle is based on the basal intensity ratios of micas with their chemical composition. Data from <2 μm grain-size fraction of the Mediterranean samples fall in the illite composition, with few samples falling slightly on the edge of the illite field and closed between illite and phengite fields (Fig. 8).

Table 1 gives the percentage abundance of the minerals detected in the analyzed samples; the table shows the mineral content of bulk samples (whole-rock mineralogy) and of <2 μm grain-size fraction.

The bulk mineralogical compositions of the four different successions (Sicily, Calabria, Betic Cordillera and Rif) determined from XRD data are quite similar. In general the clay mineral content are equal even if the Sicily samples are characterized by lower clay percentage, with a CM (clay minerals) average value of 62%. The Calabria samples are characterized by considerable amounts of quartz (average= 23%), whereas Fe-oxides (goethite) are present in minor amounts (average= 6%). The Betic Cordillera succession is the only one having considerable amounts of carbonate minerals (calcite and dolomite) likely due to the occurrence of the Ladinian platform metacarbonates (Delgado

Table 1
Mineralogical composition of bulk samples (whole-rock mineralogy) and of <2 µm grain-size fraction

	whole-rock mineralogy						*<2 µm*			
Betic Cordillera samples	**CM**	**Qz**	**Ca**	**Do**	**Fl**	**Hm**	**Ill**	**I/S**	**Ka**	**Ch**
FP76	70	10	2	2	2	14	64	32	2	2
FP75	48	26	1	16	1	8	60	35	2	3
FP74	79	5	8	2	2	5	75	21	1	2
FP73	74	11	-	2	1	12	67	28	2	3
FP71	57	6	23	2	2	10	72	23	2	3
FP70	69	6	5	-	2	18	75	25	-	-
FP69	83	5	2	-	1	9	79	21	-	-
FP68	66	9	5	-	2	18	73	27	-	-
FP56	62	9	-	3	5	21	78	17	2	3
FP53	62	13	1	1	5	18	60	27	10	3
FP49	63	9	-	-	4	24	85	15	-	-
FP47	61	20	-	4	3	12	80	17	1	3
Rif samples	**CM**	**Qz**	**Ca**	**Do**	**Fl**	**Hm**	**Ill**	**I/S**	**Ka**	**Ch**
FP25	72	7	-	-	3	19	58	27	7	8
FP28	80	5	-	-	1	13	59	21	18	2
FP30	70	8	-	-	2	21	57	31	4	7
FP32	71	8	-	-	2	20	57	23	6	14
FP34c	63	8	-	-	4	25	68	24	1	7
FP35b	62	11	-	-	2	25	70	27	1	2
FP36	65	10	-	-	2	24	69	25	2	4
FP38b	63	11	-	-	2	24	79	14	1	6
Calabria samples	**CM**	**Qz**	**Ca**	**Do**	**Fl**	**Go**	**Ill**	**I/S**	**Ka**	**Ch**
FP107	63	32	-	-	5	-	51	29	20	-
FP106	62	31	-	-	6	-	43	29	29	-
FP105	74	13	4	-	3	6	58	34	8	-
FP104	56	34	1	-	6	2	61	38	1	-
FP103	51	42	-	-	6	-	48	19	33	-
FP102	71	20	-	-	7	2	61	27	11	-
FP101	66	25	-	-	4	5	57	28	15	-
FP100	63	31	2	-	4	-	57	23	20	-
FP99	69	19	-	-	2	10	58	25	18	-
FP98	78	14	-	-	3	4	57	27	15	1
FP97	75	15	-	-	5	4	59	25	16	-
FP96	71	16	-	-	6	7	58	22	16	3
FP95	68	20	-	-	5	6	57	21	22	-

Table 1
continued....

	whole-rock mineralogy						***<2 μm***			
FP94	60	27	-	-	4	9	56	19	24	-
FP93	59	25	-	-	5	11	54	25	21	-
FP92	75	15	-	-	6	3	56	24	20	-
FP91	82	13	-	-	4	-	62	20	18	-
FP90	64	24	-	-	5	7	68	14	18	-
FP89	71	22	-	-	5	2	65	13	22	-
FP88	65	19	-	-	4	12	68	16	17	-
Sicily samples	**CM**	**Qz**	**Ca**	**Do**	**Fl**	**Hm**	**Ill**	**I/S**	**Ka**	**Ch**
VL19	63	19	-	-	2	17	68	24	7	1
VL18	64	16	-	-	2	18	67	24	8	1
VL17	62	17	-	-	1	20	66	25	9	1
VL16	58	21	-	-	1	20	60	24	14	3
VL15	60	17	-	-	2	21	62	22	14	3
VL14	63	14	-	-	2	21	73	18	9	-
VL13	59	14	-	-	2	25	71	14	12	3
VL12	60	19	-	-	2	19	67	18	16	-
VL11	53	24	-	-	1	21	61	19	20	-
VL10	61	14	-	-	4	21	71	17	11	1
VL9	62	18	-	-	3	17	66	18	13	3
VL8	63	17	-	-	2	18	76	18	6	1
VL7	64	16	-	-	3	18	79	17	3	1
VL6	65	16	-	-	3	17	84	12	3	1
VL5	64	19	-	-	2	15	79	18	2	1
VL4	58	27	-	-	3	13	81	12	7	-
VL3	67	15	-	-	-	17	73	21	4	1
VL2	64	20	-	-	2	15	79	17	4	-
VL1	60	22	-	-	3	14	83	13	3	1

CM = clay minerals; Qz = quartz; Fl = feldspars; Ca = calcite; Do = dolomite; Hm = hematite; Go = goethite; Ill = illite; Ka = kaolinite; I/S = illite-smectite mixed layers; Ch = chlorite.

et al., 1981; Sanz de Galdeano, 1997). Moreover most of the Betic Cordillera samples are collected along the upper part of the succession closed to the transition with carbonate sediments.

The <2 μm grain-size fraction of the four different successions (Sicily, Calabria, Betic Cordillera and Rif) shows similar clay mineral distribution. The main difference between the samples is mainly related to the kaolinite and chlorite amounts.

The Calabria-Peloritani successions (Calabria and Sicily samples) are characterized by higher amounts of kaolinite, whereas chlorite is rare or absent; this distribution is main marked in the Calabria samples. On the contrary, the Rif and the Betic Cordillera samples are characterized by few chlorite and kaolinite percentages.

The distribution of illite and I/S mixed layer is quite similar for the four succession, with a

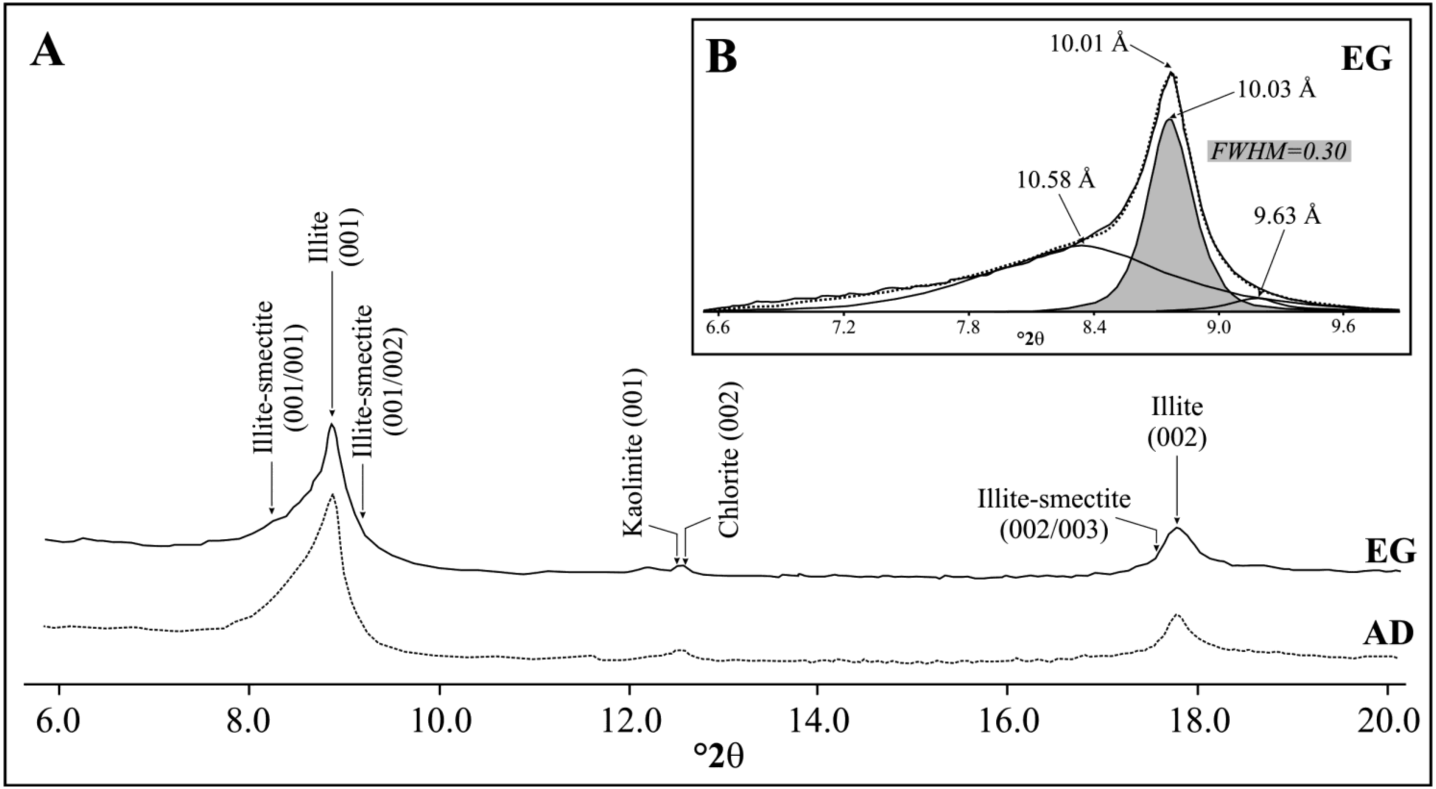

Fig. 2 – Example of decomposition of XRD pattern of the illitic phases in the mudrock samples of the Mediterranean area (sample FP35b - Rif succession) – A) air-dried and ethylene-glycol solvated oriented mounts; B) decomposition area of the ethylene-glycol solvated oriented mounts.

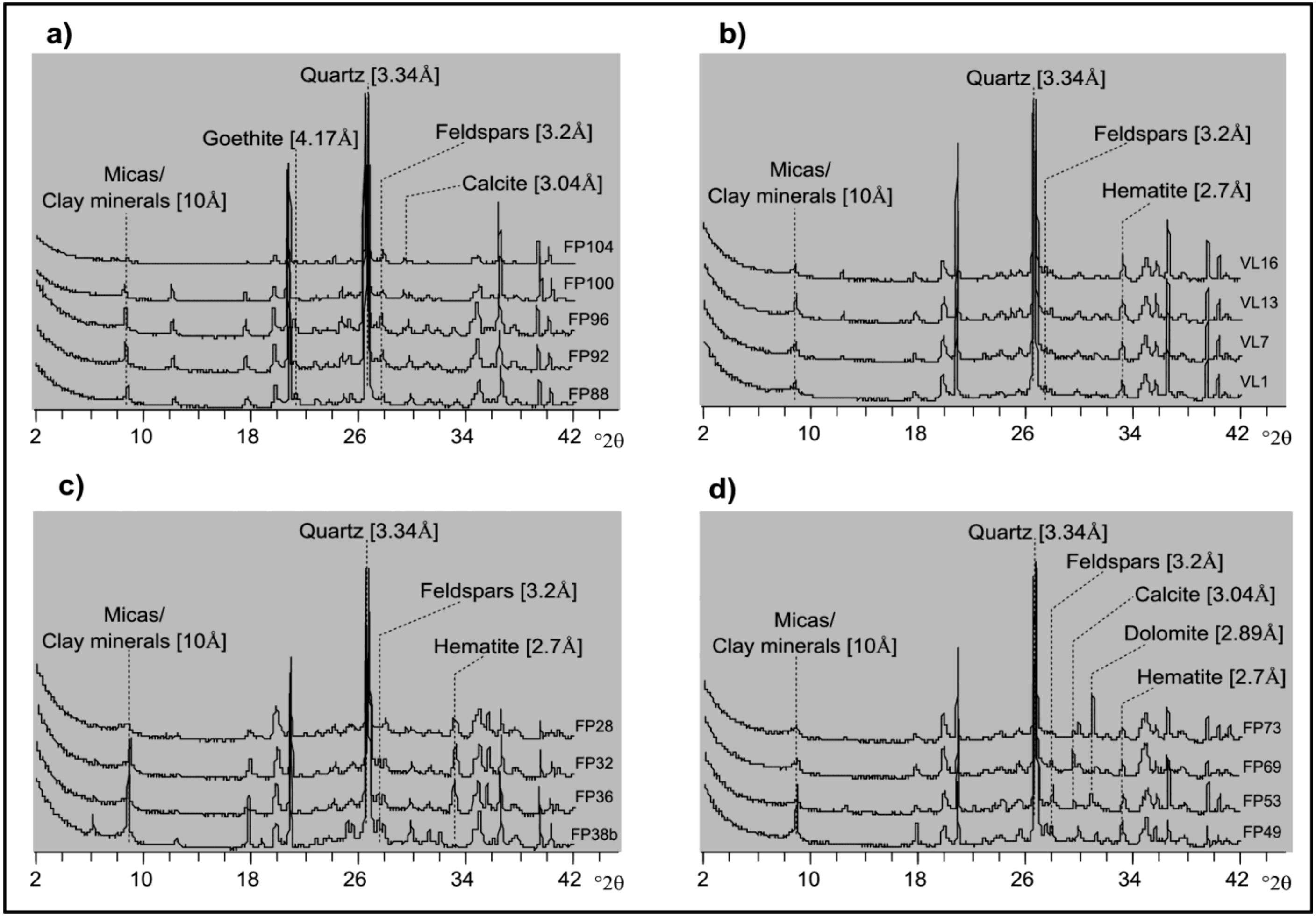

Fig. 3 – The XRD patterns of some whole-rock Mediterranean samples: a) Calabrian succession; b) Peloritanian succession; c) Rif succession; d) Betic Cordillera succession.

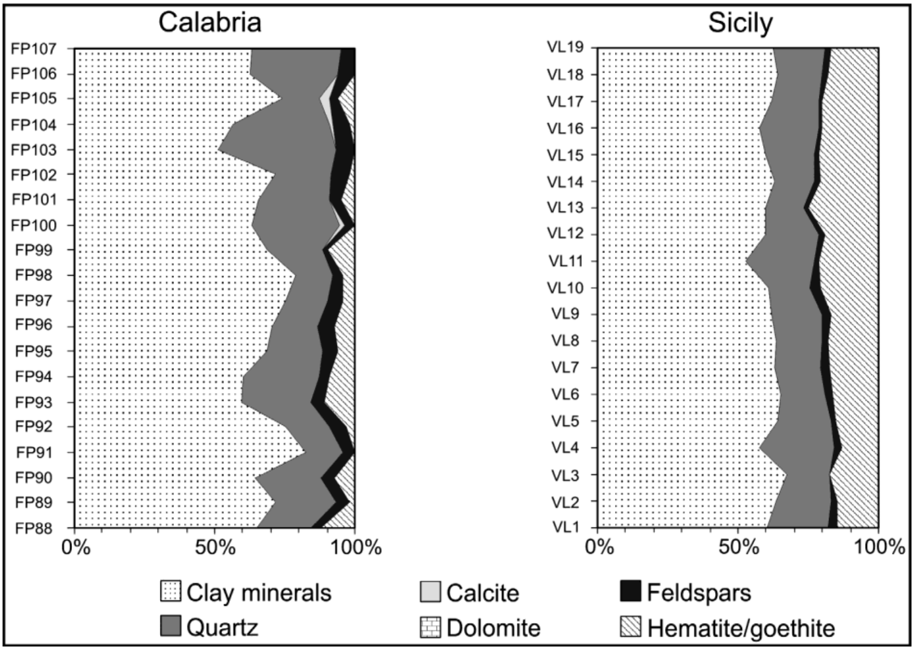

Fig. 4 – Distribution of the whole-rock mineralogy of the mudrock samples collected from Betic Cordillera and Rif successions; samples are in stratigraphic succession.

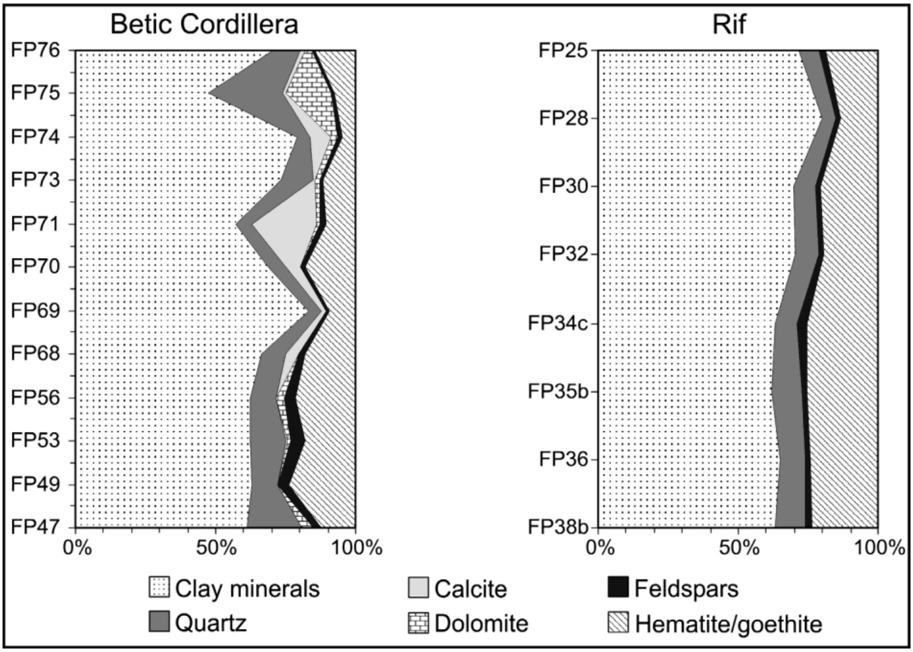

Fig. 5 – Distribution of the whole-rock mineralogy of the mudrock samples collected from Calabria and Sicily successions; samples are in stratigraphic succession.

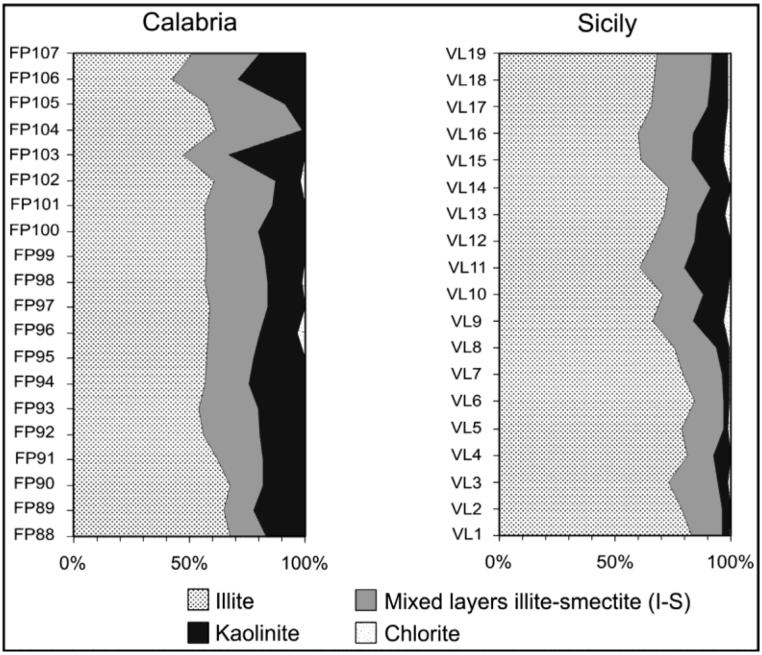

Fig. 6 – Distribution of the <2 μm grain-size fraction mineralogy of the Calabrian-Peloritanian Arc samples (Calabria and Sicily); samples are in stratigraphic succession.

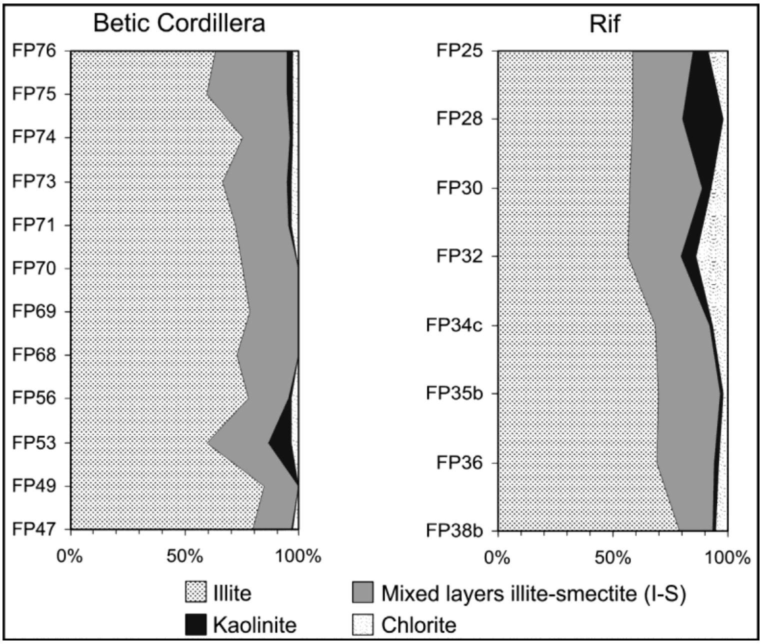

Fig. 7 – Distribution of the <2 μm grain-size fraction mineralogy of the Betic Cordillera and Rif samples; samples are in stratigraphic succession.

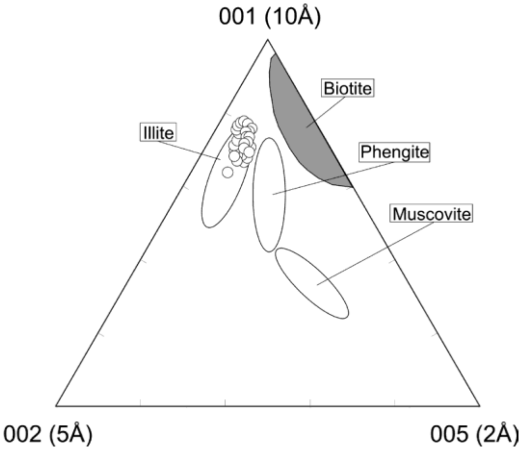

Fig. 8 – Rey & Kübler (1983) triangular plots, transformed for automatic divergence slit, of the <2 μm fraction of the studied samples. (001), (002) and (005) correspond to basal reflection intensities of "micaceous" minerals.

common noticeable increase of illite percentage in the lower portions, whereas the upper portions have higher amount of I/S mixed layer.

Quantitative analysis based on powder XRD data for bulk samples, shows minor variations in the mineral content over the interval studied (Fig. 9). In the Figure 9a (Shale/Mudstone Petrology) there is a little homogeneous dispersion mostly related to the carbonate phases observed in many Betic Cordillera samples; a major uniformity with a decrease of the kaolinite amounts from the shallower to the deeper samples is generally observed although it is more evident in both Sicily and Rif samples (Fig. 9b).

In our samples are clearly envisaged little variations in clay mineral compositions; these variations are mostly associated to the illite percentage, to the % of I-S mixed layers and to the content of illitic layers in I-S. The XRD patterns of the ethylene-glycol solvated oriented mounts show a decrease of expandable clays percentage in the lower samples (Figs. 6 and 7) with an increase of illitic layers content in the I-S mixed layered. Fig. 10 shows the variations of expandable clays from upper (FP106) to lower (FP88) samples, in which have been observed a different peak shape among 6-10 °2θ related to a different content of I/S mixed layers. This is probably associated to a significant diagenetic evolution recorded by the Mediterranean samples. Furthermore the detailed low-angle scans (Fig. 11) of the air dried and ethylene-glycol solvated <2 μm fraction specimens of the lower samples, show peaks of the 10 Å minerals relatively sharp and symmetrical with small peak shifts among the air-dried and the glycolated patterns, involving that the proportion of smectite-like layers in interstratified I-S is relatively low; in

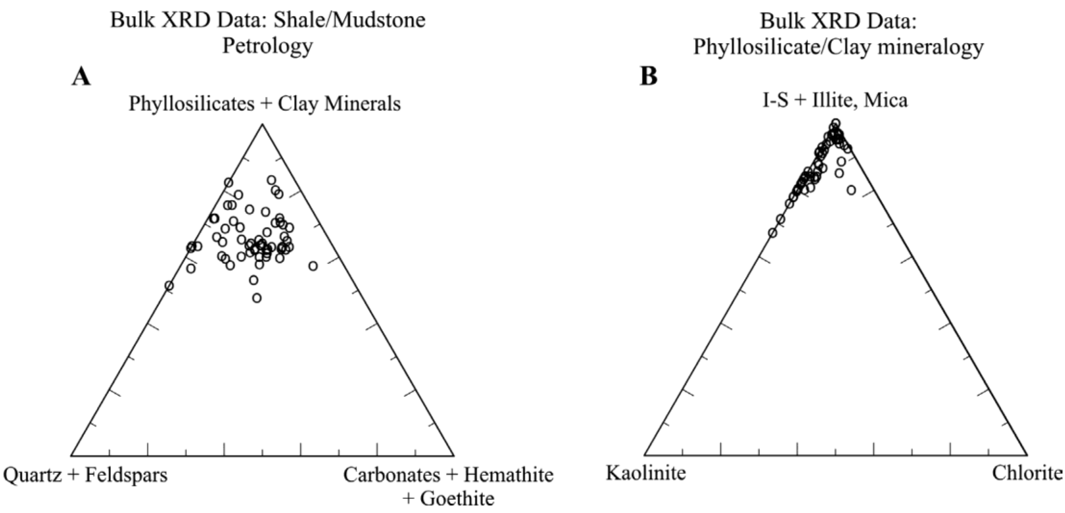

Fig. 9 – Bulk XRD shale/mudstone petrology and phyllosilicate/clay mineral assemblages presented on ternary plots showing little variations in the mineral content of the studied samples.

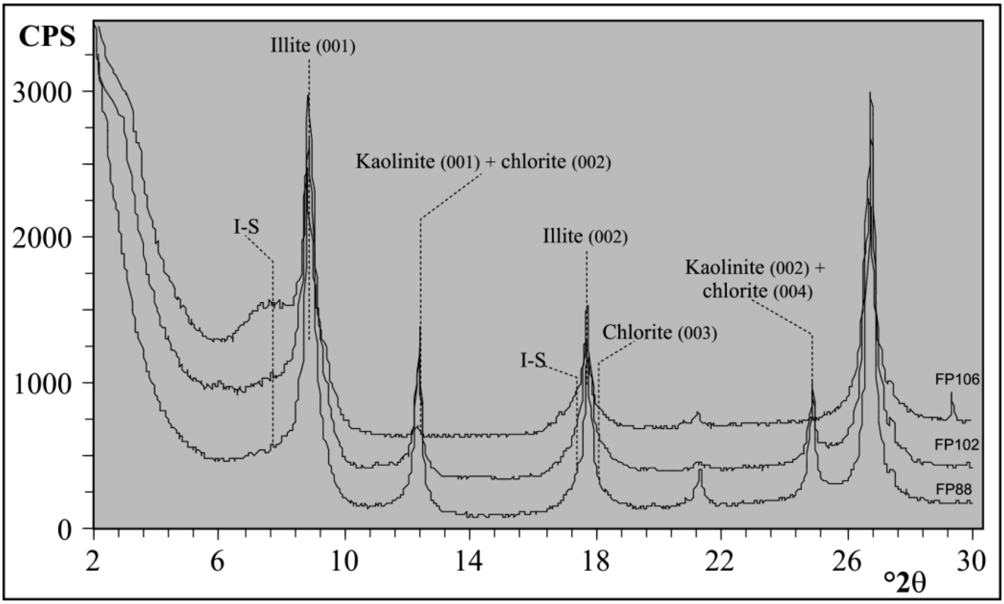

Fig. 10 – The XRD patterns of some ethylene-glycol solvated oriented mounts that show a decrease of expandable clays from lower (FP88) to upper (FP106) samples.

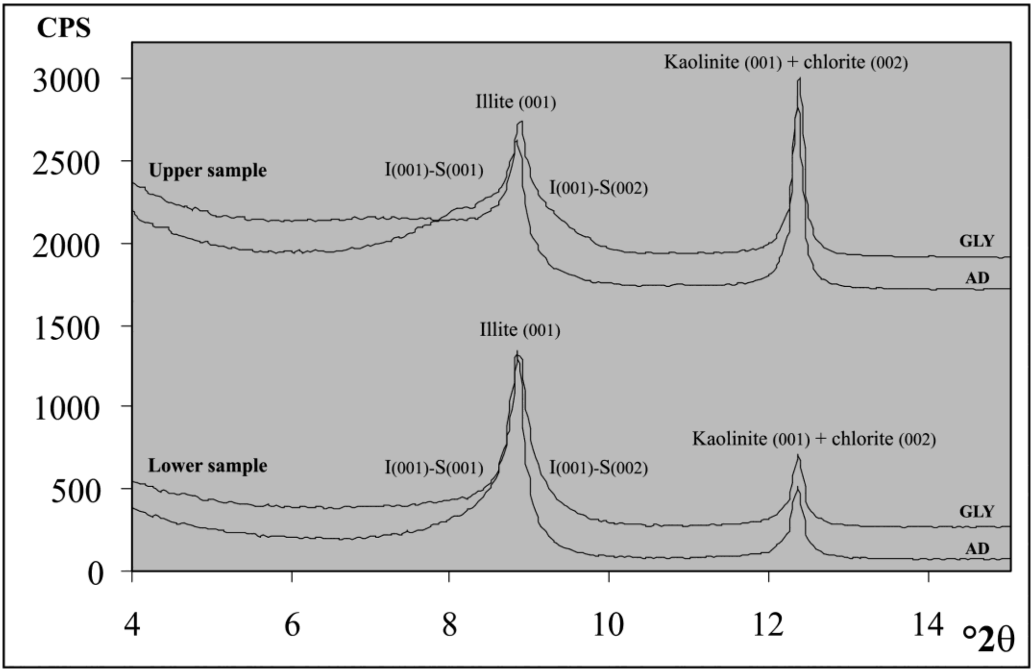

Fig. 11 – XRD detailed low-angle scans of the air dried (AD) and ethylene-glycol solvated (GLY) <2 µm fraction specimens of the upper and lower samples.

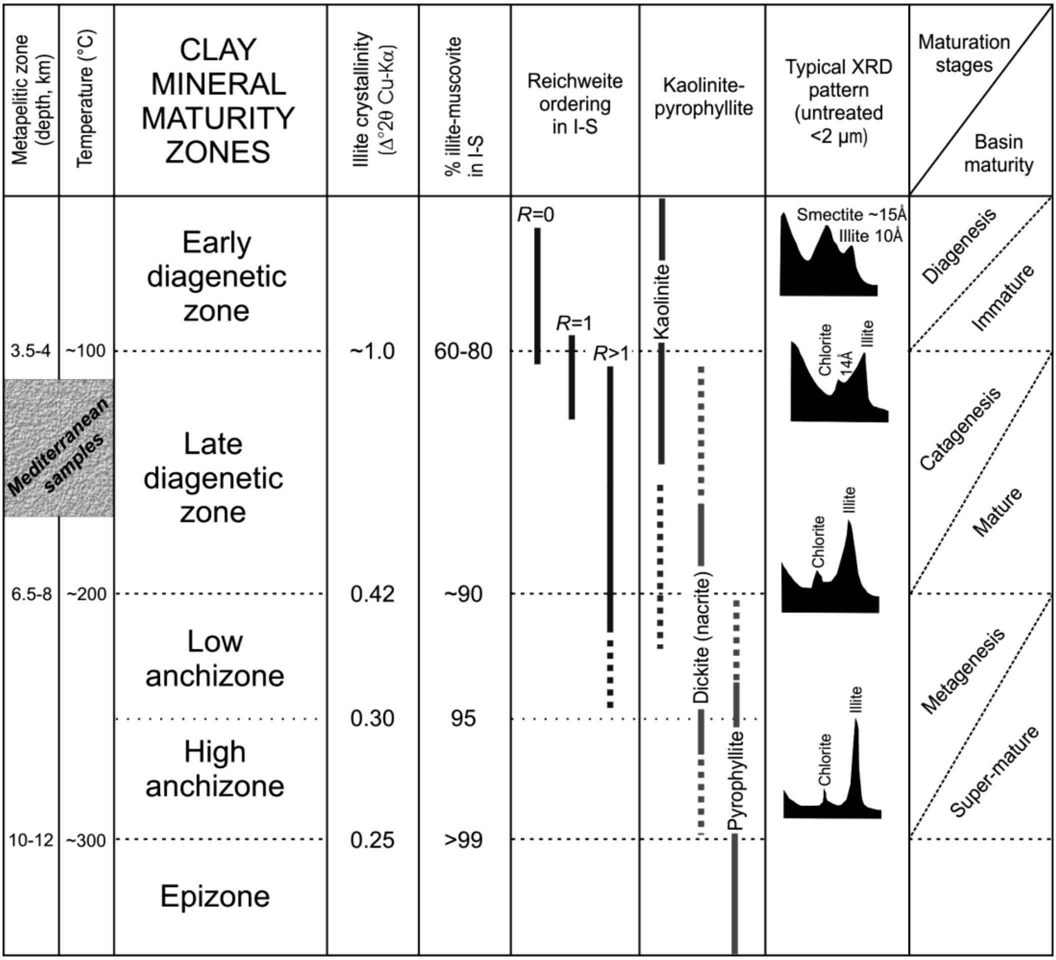

Fig. 12 – Clay mineral geothermometers used to study the transition from diagenesis to metamorphism (Basin Maturity Chart modified from Merriman and Frey, 1999); in the chart is reported the area in that falls the studied samples.

the upper samples are more evident the peak shifts of I-S, consequent to ethylene-glycol solvation. The XRD traces of the <2 μm fraction show a little decrease in the proportion of I-S mixed layered and of expandable layers in I-S with depth increasing.

The Mediterranean samples (Sicily, Calabria, Betic Cordillera and Rif) show a content of illitic layers in the I-S mixed layers in a range of 70-90 % (*R* ordering = 1-3; Reickeweite number); in particular, the samples collected in the lower part of the successions show a little higher percent of illitic layers in the I-S than the upper part samples.

The illite crystallinity value (IC) measured on both air-dried and ethylene-glycol solvated oriented mounts of the Mediterranean samples, are in a range of 0.6-0.7° Δ2θ CuK_α; the Sicily samples are characterized by a IC mean value of 0.68° Δ2θ; the Calabria samples are characterized by a IC mean value of 0.69° Δ2θ; the Betic Cordillera samples are characterized by a IC mean value of 0.72° Δ2θ and the Rif samples are characterized by a IC mean value of 0.70° Δ2θ (Table 2).

In the studied samples not were detected the C/V mixed layers (chlorite/vermiculite) as a peak at ~10Å that in general may interfere with illite

Table 2
Illite crystallinity value of some Mediterranean samples

Samples	Clay minerals	IC_{AD} (° Δ2θ)	IC_{CIS} (° Δ2θ)
Calabria			
FP103	Ill+Ka+I/S	0.31	0.72
FP98	Ill+I/S+Ka+Ch	0.31	0.72
FP95	Ill+Ka+I/S	0.30	0.70
FP90	Ill+Ka+I/S	0.28	0.65
FP88	Ill+Ka+I/S	0.28	0.65
Sicily			
VL16	Ill+I/S+Ka+Ch	0.30	0.70
VL10	Ill+I/S+Ka+Ch	0.30	0.70
VL8	Ill+I/S+Ka+Ch	0.30	0.69
VL7	Ill+I/S+Ka+Ch	0.29	0.67
VL4	Ill+I/S+Ka	0.27	0.62
Betic Cordillera			
FP74	Ill+I/S+Ch+Ka	0.32	0.74
FP70	Ill+I/S	0.32	0.74
FP49	Ill+I/S	0.31	0.72
FP47	Ill+I/S+Ch+Ka	0.30	0.69
Rif			
FP28	Ill+I/S+Ka+Ch	0.32	0.73
FP35b	Ill+I/S+Ch+Ka	0.30	0.70
FP36	Ill+I/S+Ch+Ka	0.29	0.67

Ill = illite; I/S = illite-smectite mixed layers; Ka = kaolinite; Ch = chlorite.

crystallinity determinations (Offler and Brime, 1994).

The IC value coupled with the high ordering of the mixed layers and the high content of illitic layer in I-S mixed layers, are compatible with high diagenetic conditions (upper limit of late diagenesis; Jaboyedoff and Théllin, 1996; Frey and Robinson, 1999).

Discussion

The mineralogical proxies generally used to assess basin evolution are: a) the clay mineral assemblage; b) quantification of mixed-layer minerals; c) clay mineral “crystallinity” (illite crystallinity value).

In a typical mudrocks, the products of the reaction series constitute the clay mineral assemblage and can be used to indicate the state of reaction progress in terms of maturity zones within the sedimentary basins. However is not possible to limit the stability of clay minerals to a single zone because of the metastable nature of clay assemblages since reactants and products of a series may coexist (Merriman, 2005).

The presence of neoformed clays such as smectite and kaolinite in assemblages records an immature stage of basin evolution (shallow diagenetic zone), whereas an assemblage of mature illite and chlorite indicates supermature basin (Merriman, 2005). Most mixed-layer minerals (*i.e.* illite-smectite mixed layers) are formed when immature clays are transformed to mature mudrocks (*i.e.* the transition from shallow to deep diagenetic zone), and become scarce or absent in supermature basins (Merriman, 2005).

The studied samples (Sicily, Calabria, Betic Cordillera and Rif) are characterized by the presence of abundant clay minerals; subordinately are present significant amounts of quartz and Fe-oxides (hematite or goethite), and minor concentrations of feldspars, calcite and dolomite. The <2 μm grain-size fraction of the samples is primarily composed by illite prevailing on illite-smectite mixed layers, kaolinite and chlorite (always presents in negligible amounts). The absence of smectite, the abundance of illite and significant amounts of illite-smectite mixed layers, testifying a mature mudrocks typical of deep/late diagenetic zone. Moreover, the little variations among the upper and lower part of the succession in the illite and I/S mixed layer contents are probably related to diagenetic effects.

The reaction progress in 2:1 layer silicates generates mixed-layer clays with varying proportions of reactant and product. Measurement of the proportions and degree of ordering in the smectite-I-S-illite reaction series is the most widely used indicator of reaction progress for the immature to mature stage of basin evolution (Środoń, 1999, and references therein).

The <2 μm grain-size fraction of the Mediterranean samples are characterized by high ordering mixed layers that, coupled with the high content of illitic layer in I-S mixed layers (70-90 %

of illite; *R* ordering = 1-3), indicates a mature stage of basin evolution containing mature mudrocks typical of deep/late diagenetic zone.

Furthermore, illite "crystallinity" has been widely used as indicator of reaction progress in mudrock lithologies found in mature and supermature basin. The illite crystallinity value can be used to indicate reaction progress when the smectite-to-illite reaction has progressed to >80 %illite. The illite crystallinity value, measured on both air-dried and ethylene-glycol solvated oriented mounts of the Mediterranean samples with a content of illitic layers in the I-S mixed layers of 75-90 %, are in the range of 0.6-0.7° $\Delta 2\theta$ CuK_{α}. The lack of random I/S mixed layering indicates that zone 3 of Eberl (1993) was reached; therefore the temperature was >100 °C.

The Basin Maturity Chart of Merriman and Frey (1999) starts from clay mineralogy investigation to estimates palaeotemperatures within sedimentary basins; in this model, the % of illitic layers in I-S mixed layers in a range of 60-80 % to 95 % (high ordering mixed layers, $R > 1$) coupled with an illite crystallinity value in a range of ~1° to 0.42° $\Delta 2\theta$ CuK_{α}, characterized the late (deep) diagenetic zone with a range of ~100-200 °C temperature.

Based on the Basin Maturity Chart (Merriman and Frey, 1999) the proportions of illitic layers in I-S mixed layers coupled with the illite crystallinity value suggesting a late/deep diagenetic stage with an estimated temperature experienced by the Mediterranean successions in the range of 100-150 °C (Fig. 12).-

Starting from this considerations, based on clay mineral features, the diagenetic/tectonic evolution should correspond to a lithostatic/tectonic loading of about 4-5 km.

Conclusions

The Triassic to Early Jurassic continental redbeds of the western and central Mediterranean, Spain, Morocco and Southern Italy provide a chance to study clay-mineral distribution and diagenesis in mudstone that have experienced an intense burial history and strong diagenesis.

These redbeds represent the onset of Mesozoic sedimentation along the Mesomediterranean margins, related to the progressive Neotethyan oceanic rifting. Following the Tertiary accretionary processes related to growth of the circum-Mediterranean orogeny, redbeds and related Mesozoic rifting sedimentary prism, were covered by extremely variable in thickness Cenozoic pelagic and clastic strata, and by tectonic nappes of the growing orogenic systems (Critelli *et al.*, 2004).

The total thickness of Mesozoic to early Miocene strata covering redbeds is about 2500 metres. Since early Miocene, the over described sequences of the Sila (Calabria), Longi-Taormina (Sicily), Malaguide (Betic Cordillera) and Ghomaride (Rif) units were involved in accretionary processes of the circum-Mediterranean orogeny, and then, locally, tectonically covered by tectonic nappes (Critelli *et al.*, 2004).

Clay-mineral distribution of studied mudstone shows that illite and mixed-layer illite-smectite dominate mudstone mineralogy, although subordinate amounts of kaolinite and chlorite are observed.

During burial history, clay minerals in redbed mudstones undergo considerable diagenetic reactions, such as increasing of illite in I/S mixed layers and slight variation of illite crystallinity values. The estimated temperature experienced by the Triassic to Early Jurassic continental redbed mudrocks, obtained coupling data relative to the percentage of illitic layers in I-S mixed layers with the value of the illite crystallinity, is in the range of 100-150 °C. Starting from the temperature estimates by clay-minerals-based geothermometres, the lithostatic/tectonic loading is of about 4-5 km that records an important diagenetic evolution typical of a mature sedimentary basin.

Acknowledgements

I wish to thank Profs. P. Mazzoleni and S. Critelli for their careful review and good suggestions for the manuscript. I am grateful to referees and Prof. M. Lustrino for their many helpful comments and revisions.

REFERENCES

Altaner S.P. and Ylagan R.F. (1997) - *Comparison of structural models of mixed-layer illlite/smectite and reaction mechanisms of smectite illitization.* Clays

Clay Min., **45**, 517–533.

Baudelot S., Bouillin J.P., Durand-Delga M., Giunta G. and Olivier P. (1988) - *Datazioni palinologiche dell'Hettangiano alla base della trasgressione mesozoica sul <<Verrucano>> della Sila (Calabria) e dei Monti Peloritani (Sicilia).* Boll. Soc. Geol. It., **95**, 49-74.

Bell T.E. (1986) - *Microstructure in mixed-layer illite-smectite and its relationship to the reaction of smectite to illite.* Clays Clay Min., **34**, 146–154.

Bethke C.M. and Altaner S.P. (1986) - *Layer-by-layer mechanism of smectite illitization and application of a new rate law.* Clays Clay Min., **34**, 136–145.

Burst J.F. (1969) - *Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration.* Am. Ass. Petrol. Geol. Bull., **53**, 73–93.

Cecca F., Critelli S., De Capoa P., Di Staso A., Giardino S., Messina A. and Perrone V. (2002) - *Nouvelle datation et interprètation de la succession sèdimentarie de Fiumara Sant'Angelo (Monts Pèloritains; Italie mèridionale): consèquences pour la palèogèographie mèsozoique de la Mèditerranèe centrale.* Bull. Soc. Geol. Fr., **2**, 77-90.

Critelli S. (1999) - *The interplay of lithospheric flexure and thrust accomodation in forming stratigraphic sequences in the Southern Apennines foreland basin system, Italy.* Atti Accad. Naz. Lincei Rend. Cl. Sci. Fis. Mat. Natur., **10**, 257-326.

Critelli S., Aiello M., Greco M.R., Mongelli G., Pappalardo A., Perri F., Sonnino M. and Spina A. (2004) - *Diagenesis and burial history of the Triassic to Early Jurassic continental redbeds of the western and central Mediterranenan, Spain, Morocco and Southern Italy.* 32nd IGC, Florence (August 2004), Abstr., Gen. Symp. G 21.15.

Delgado F., Estevez A., Martín J.M. and Martín-Algarra A. (1981) - *Observaciones sobre la estratigrafía de la formation carbonatada de los mantos alpujárrides (Cordillera Bética).* Estud. Geol., **37**, 45-57.

Drits V.A., Salyn A.L. and Sucha V. (1996) - *Dynamic and mechanism of structural transformations of illite-smectite from the hydrothermal deposits of Dolna Vis (Slovakiya).* Clays Clay Min., **44**, 181–190.

Drits V.A., Sakharov B.A., Lindgreen H. and Salyn A. (1997) - *Sequential structure transformation of illite-smectite-vermiculite during diagenesis of Upper Jurassic shales from the North Sea and Denmark.* Clay Min., **32**, 351–371.

Dunoyer De Segonzac G. (1969) - *Les minéraux argileux dans la diagenèse. Passage au métamorphisme.* Mém. Serv. Carte Géol., Als. Lorr., **29**, 321.

Eberl D.D. (1993) - *Three zones for illite formation during burial diagenesis and metamorphism.* Clays Clay Min., **41**, 26–37.

Frey M. and Robinson D. (1999) - *Low-Grade Metamorphism.* Blackwell Science, Oxford.

Goy-Eggenberger D., Rumley G. and Kübler B. (1993) - *'Illite Crystallinity' (IC), Scherrer Width (SW) or Full Width at Half Maximum (FWHM): critical appraisal of the measurement techniques and original analogical versus computerized measurements correlation.* Terra Abstr., **5**, 417.

Giampaolo C., Lo Mastro S. and Aldega L. (2005) - *Analisi quantitativa di minerali argillosi su polveri orientate per DRX.* In: "Argille e Minerali delle Argille", **5**, 75-90.

Guerrera F., Martín-Algarra A. and 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.

Hower J., Eslinger E.V., Hower M.E. and Perry E.A. (1976) - *Mechanism of burial metamorphism of argillaceous sediments: Mineralogical and chemical evidence.* Geol. Soc. Amer. Bull., **87**, 725-737.

Jaboyedoff M. and Thélin P. (1996) - *New data on low-grade metamorphism in the Briançonnais domain of the pre-Alps, Western Switzerland.* Eur. J. Mineral., **8**, 577-592.

Jagodzinski H. (1949) - *Eindimensionale Fehlordnung in Kristallen und ihr Einfluss auf die Röntgeninterferenzen. I Berechnung des ehlordnungsgrades aus den Röntgenintensitaten.* Acta Cryst., **2**, 201–207.

Kisch H.J. (1990) - *Calibration of the anchizone: a critical comparison of illite "cristallinity" scales used for definition.* J. Metam. Geol., **8**, 31-46.

Kübler B. (1967) - *La cristallinité de l'illite et les zones tout à fait supérieures de métamorphisme.* In: J.P. Schaer (Editor) - *Colloque sur les étages tectoniques.* À la Baconnière Neuchâtel, Switzerland, 105-122.

Kübler B. (1984) - *Les indicateurs des transformations physiques et chimiques dans la diagenèse, température et calorimétrie.* In : M. Lagache (Editor) - *Thermobarométrie et barométrie géologiques.* Soc. Franc. Miner. Cryst., Paris., 489-596.

Lanson B. (1997) - *Decomposition of experimental X-ray diffraction patterns (profile fitting); a convenient way to study clay minerals.* Clays Clay Min., **45**, 132–146.

Martín-Algarra A., Solé De Porta N. and Maate A. (1995) - *El Triásico del Maláguide-Gomáride (Formación Saladilla, Cordillera Bética Occidental y Rif Septentrional). Nuevos datos sobre su edad y* *significado palaeogeográfico*. Cuad. Geol. Iberica, **19**, 249-278.

Merriman R.J. (2002) - *The magma-to-mud cycle*. Geol. Today, **18**, 67-71.

Merriman R.J. (2005) - *Clay minerals and sedimentary basin history*. Eur. J. Mineral., **17**, 7-20.

Merriman R.J. and Peacor D.R. (1999) - *Very low grade metapelites: mineralogy, microfabric and measuring reaction progress*. In: M. Frey and D. Robinson (Editors) - *Low-grade Metamorphism*. Blackwell Science, Oxford, 10-60.

Merriman R.J. and Frey M. (1999) - *Patterns of very low-grade metamorphism in metapelitic rocks*. In: M. Frey and D. Robinson (Editors) - *Low-grade Metamorphism*. Blackwell Science, Oxford, 61-107.

Meunier A. and Velde B. (1989) - *Solid solutions in I/S mixed-layer minerals and illite*. Am. Mineral., **74**, 1106–1112.

Mongelli G., Critelli S., Perri F., Sonnino M. and Perrone V. (2006) - *Sedimentary recycling, provenance and paleoweathering from chemistry and mineralogy of Mesozoic continental redbed mudrocks, Peloritani Mountains, Southern Italy*. Geochem. J., **40**, 197-209.

Monnier F. (1982) - *Thermal diagenesis in the Swiss Molasse Basin: implications for oil generation*. Can. J. Earth Sci., **19**, 328–342.

Moore D.M. and Reynolds R.C. (1997) - *X-ray diffraction and the identification and analysis of clay minerals*. Second Edition; Oxford University Press, Oxford and New York.

Nadeau P.H. and Bain D.C. (1986) - *Composition of some smectites and diagenetic illitic clays and implications for their origin*. Clays Clay Min., **34**, 455– 464.

Nadeau P.H., Wilson M.J., McHardy W.J. and Tait J.M. (1985) - *The conversion of smectite to illite during diagenesis: evidence from some illitic clays from bentonites and sandstones*. Mineral. Mag., **49**, 393–400.

Offler R. and Brime C. (1994) - *Characterisation of the low-grade metamorphism in the Nambucca block (NSW, Australia)*. Rev. Geol. Chile, **21**, 285–293.

Peacor D.R. (1992) - *Diagenesis and low-grade metamorphism of shales and slates*. In: P.R. Buseck (Editor) - *Minerals and Reactions at the Atomic Scale: Transmission Electron Microscopy*. Rev. Mineral, **27**, 335-380.

Pollard C.O. (1971) - *Semi-displacive mechanism for diagenetic alteration of montmorillonite layers to illite layers*. Geol. Soc. Am. Spec. Pap., **134**, 79–96.

Pollastro R.M. (1993) - *Considerations of the illite-smectite geothermometer in hydrocarbon-bearing rocks of Miocene to Mississippian age*. Clays Clay Min., **41**, 119-133.

Santantonio M. and Teale T. (1987) - *An example of the use of detrital episodes in elucidating complex basin histories: the Caloveto and Longobucco Groups of N.E. Calabria, S. Italy*. In: J.K. Leggett and G.G. Zuffa (Editors). Marine Clastic Sedimentology, Graham and Trotman, London, 62-74.

Sanz De Galdeano C., Andreo B., García-Tortosa F. J. and López-Garrido A. C. (2001) - *The Triassic palaeogeographic transition between the Alpujarride and Malaguide complexes, Betic-Rif Internal Zone (S-Spain, N-Morocco)*. Palaeog. Palaeoclim. Palaeoecol., **167**, 157-173.

Shutov V.D., Drits V.A. and Sakharov B.A. (1969a) - *On the mechanism of post-sedimentary transformations of montmorillonite into hydromica*. In: L. Heller (Editor) - *Proceedings of the International Clay Conference, Tokyo, 1969*. Jerusalem, Israel, **1**, 523-532.

Shutov V.D., Drits V.A. and Sakharov B.A. (1969b) - *On the mechanism of a postsedimentary transformation of montmorillonite into hydromica: discussion*. In: L. Heller (Editor) - *Proceedings of the International Clay Conference, Tokyo, 1969*. Jerusalem, Israel, **2**, 126-129.

Środoń J., Elsass F., McHardy W.J. and Morgan D.J. (1992) - *Chemistry of illite–smectite inferred from TEM measurements of fundamental particles*. Clay Min., **27**, 137–158.

Środoń J. (1999) - *Nature of mixed-layer clays and mechanisms of their formation and alteration*. Ann. Rev. Earth Planet. Sci., **27**, 19–53.

Warr L.N. and Rice A.H.N. (1994) - *Interlaboratory standardization and calibration of clay mineral crystallinity and crystal size data*. J. Metam. Geol., **12**, 141-152.

Weaver C.E. (1960) - *Possible uses of clay minerals in search for oil*. Am. Ass. Petrol. Geol. Bull., **44**, 1505–1518.

Weaver C.E. and Beck K.C. (1971) - *Clay water diagenesis during burial: how mud becomes gneiss*. Geol. Soc. Amer. Spec. Pap., **134**, 1–78.

Wild W. (1983) - *La chaîne tello-rifaine (Algérie, Maroc, Tunisie): structure, stratigraphie et évolution du Trias au Miocène*. Rev. Géog. Phys. Géol. Dyn., **24**, 201-297.

Zuffa G.G., Gaudio W. and Rovito S. (1980) - *Detritial mode evolution of the rifted continental-margin Longobucco Sequence (Jurassic), Calabrian Arc, Italy*. J. Sedim. Petrol., **50**, 51-62.