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CORRELATION OF INORGANIC AND ORGANIC THERMAL INDICATORS IN THE EASTERN SICILY FOLD-AND-THRUST BELT

CORRELAZIONE DI INDICATORI TERMICI INORGANICI ED ORGANICI NELLA CATENA A PIEGHE E SOVRASCORRIMENTI DELLA SICILIA ORIENTALE

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PAROLE CHIAVE: *strati misti illite-smectite, riflettanza della vitrinite, Sicilia orientale.*

1. INTRODUCTION

One of the main problems of correlating clay minerals and organic matter in thermal reconstructions is that they may react differently to the physical conditions of sedimentary burial. In fact, the kinetic response of clay mineral reactions in sedimentary sequences can be significantly different from that of vitrinite. Several studies in sedimentary basins with abnormally high or low geothermal gradients have suggested that clay mineral reaction may be more sensitive to geological heating rates than organic materials (Frey & Robinson, 1999 for a review). In contrast, vitrinite may mature in response to intrusive events, whereas clay minerals may not because of the short duration of the heating event (e.g., Mancos shale studied by Nadeau & Reynolds, 1981).

Hence correlation between organic and clay mineral reaction progress is dependent on thermal history, particularly on basinal heat flow features and geological rates of heating.

Lithology is a further issue when correlating reaction progress mineral indicators with organic matter. Generally, limestones and sandstones, including greywackes are not suitable for metapelite grade studies, largely because they do not contain sufficient clay. Moreover, these lithologies can either inhibit clay mineral reactions, through early cementation or promote reactions through porosity and pore fluid movement, which are not comparable with reaction conditions in pelitic rocks. Strong inhibiting effects of the release of Na^+, Ca^{2+} and Mg^{2+} on the illitization of smectite have been demonstrated experimentally by Roberson & Lahann (1981) and Howard & Roy (1985).

In this paper, we present the first results of a correlation between vitrinite reflectance and illite content in illite-smectite (I-S) mixed-layers from clay- and silt-rich sediments cropping out in eastern Sicily from the inner to the outer units of the Apennine-Maghrebian south-verging orogen.

Despite of the limitations described above and the high variability of the analysed lithologies, an acceptable correlation between inorganic and organic thermal indicators was found. Furthermore the integration of two independent methodologies allowed us to obtain maximum paleotemperatures for various stratigraphic units typical of different geodynamic settings.

2. GEOLOGICAL SETTING

The Apennine-Maghrebian orogen or Southern Apennine Arc in the central Mediterranean region developed as a result of convergence between the Europe and Africa-Adria plates, mainly during Tertiary times. The Southern Apennine Arc, formed by the Southern Apennines and the Maghrebian chain in Sicily, is a collisional belt consisting of distinct units of the Africa paleomargin and Tethys (Fig. 1).

The most elevated structural unit in the eastern Sicily fold-and-thrust belt is represented by units derived from the deformation of the Sicilide Domain (Mt. Soro and Troina Units). Analogous units, traditionally ascribed to this inner paleogeographic domain and nowadays mapped in the frontal zone of the belt, escaped the involvement into the subduction trench in the early stages of its development. Consequently they did not experience any huge loading and travelled far to form the present-day frontal belt of the chain.

Tectonically beneath the Sicilide Units, various imbricated thrust sheets developed. They formed at the expense of the Afro-Adriatic continental palaeomargin and consist of allochthonous units derived from the deformation of pelagic basin successions (Mt. Judica) of Triassic to Eocene age. Deformation related to plate collision started in the early Miocene and is documented by syn-tectonic deposits. Compressive deformation was accompanied by the development of foreland basins and coeval thrust-top basins within the chain (Catalano & D'Argenio, 1982; Oldow *et al.*, 1990; Butler & Grasso, 1993).

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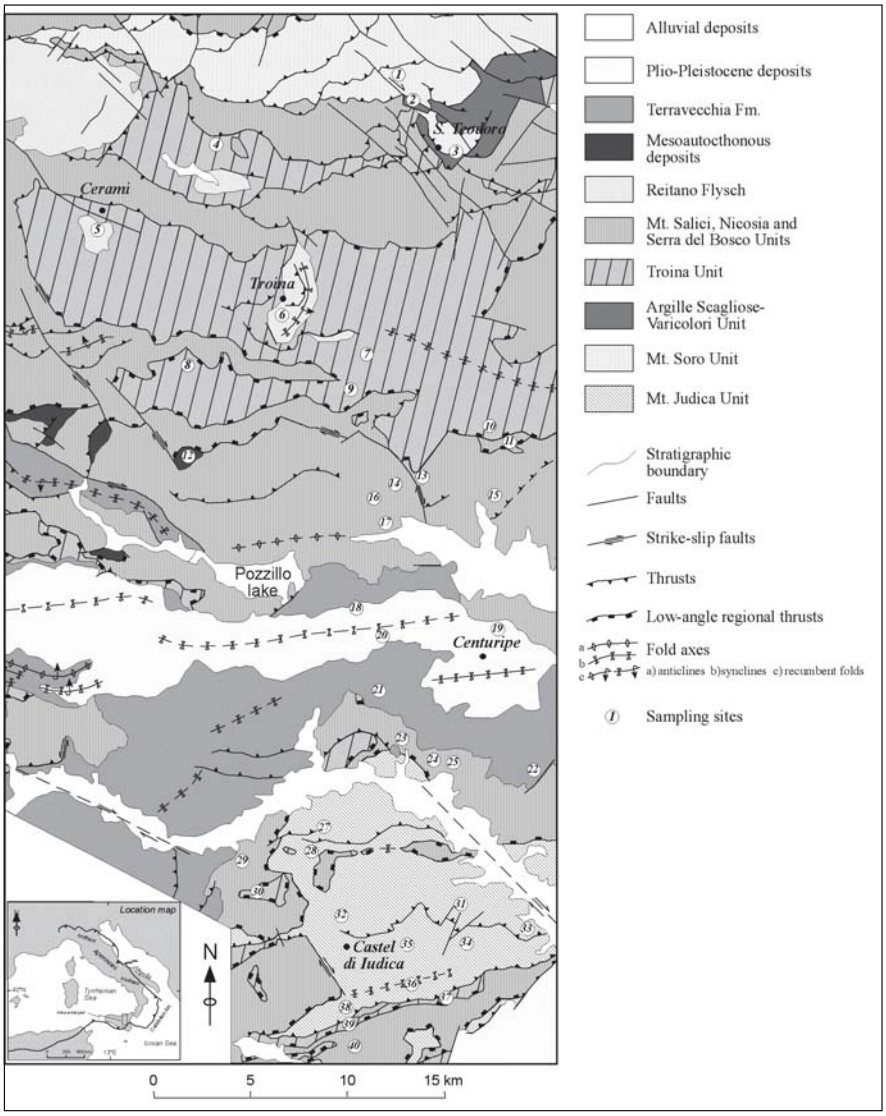

Fig. 1 - Structural sketch map of the studied area and samples location.
Schema strutturale dell'area indagata con siti di campionamento.

A widespread turbiditic succession, the Numidian Flysch (upper Oligocene-lower Miocene) is considered to be the first foreland sedimentary deposit predating orogenic activity. Catalano *et al*. (1996) suggested that compressive deformation started during Langhian-early Tortonian times and was followed by the deposition of the upper Tortonian clastic deposits of the Terravecchia Fm., unconformably sealing the older deposits. Terrigenous sedimentation continued until mid-Pliocene times in central Sicily and until early–mid-Pleistocene times along the southern Sicilian margin (Bigi *et al*., 1990).

Two main compressive phases generated the present day structural setting. The first one caused the juxtaposition of the allochthonous units onto the Mesozoic-Paleogene Hyblean foreland carbonates through low-angle thrusts in lower Miocene times (Bianchi *et al*., 1989). The second phase is considered to have occurred in late Miocene-early Pliocene times. It completely modified the geometric relationships of the allochtonous units, producing internal stacking of the Mt. Judica succession, backthrusting and syntectonic depressions (Bello *et al*., 2000).

3. METHODS

A suite of 81 samples for XRD analysis and 23 samples for organic matter optical analysis were collected from the various structural units cropping out in eastern Sicily (Fig. 1).

Qualitative identification and quantification of illite-smectite mixed layers was performed with a Scintag X_1 XRD system (CuKα radiation, solid state detector, spinner) on the <2μm grain-size fraction. Oriented air-dried samples were scanned from 1 to 48 °2θ with a step size of 0.05 °2θ and a count time of 4 s per step at 40 kV and 45 mA. The presence of expandable clays was determined for samples treated with ethylene glycol at 25°C for 15h. Ethylene-glycol solvated samples were scanned at the same conditions as air-dried aggregates with a scanning interval of 1-30 °2θ.

Expandability measurements were determined according to Moore & Reynolds (1997) using the delta two-theta method after decomposing the composite peaks between 9-10 °2θ and 16-17 °2θ using the Scintag X_1 software program with a split Pearson VII function.

Whole-rock samples, prepared for vitrinite reflectance analysis, were mounted on epoxy resin and polished according to standard procedures. Random reflectance (Ro%) was measured under oil immersion, with a Zeiss Axioplan microscope, in reflected monochromatic non-polarised light. An average 15 measurements were performed on vitrinite fragments for each sample (never smaller than 5 μm and only slightly fractured and/or altered). Mean reflectance and standard deviation values were calculated for all measurements.

Inorganic and organic data have been preliminary converted into paleotemperatures according to Hoffman & Hower (1979) and Barker (1988) respectively.

4. RESULTS

Main results are described for the different tectonic units in their specific geodynamic setting moving from the north toward the south.

Subduction trench (Troina and Mt. Soro Tectonic Units): these units are charactherized by I-S mixed layers with high illitic contents in the range of 70 to 80% and mean Ro% values comprised between 0.65 and 0.76%. Calculated maximum temperatures are in a maturity level coinciding with catagenesis and the first stages of the late diagenetic

Geodynamic setting		Tectonic Unit	Stratigraphic Unit (Age)	T (°C) Based on vitrinite reflectance† (mean T)	T (°C) Based on clay mineralogy‡	T (°C) Based on thermal modelling§
Subduction trench	Internal Sicilide Units	Troina Unit	Troina-Tusa Flysch (Lower Miocene)	98 – 111 (105)	100-170	-
			Argille Scagliose-Varicolori (Oligocene)	-	100-170	
		Mt. Soro Unit	Argille Scagliose-Varicolori (upper Cretaceous-Oligocene)	83 - 144 (118)	100-170	-
			Mt. Soro Flysch (Cretaceous)	103 - 118 (111)	100-170	-
Early thrust-top basin			Reitano Flysch (middle Miocene)	42 - 67 (55)	<60	-
Early foredeep		Mt. Salici Unit	Gagliano marls (middle Miocene)	29 - 67 (50)	60-100	-
			Numidian Flysch (Upper Oligocene-lower Miocene)	-	60-100	-
		Nicosia Unit	Numidian Flysch (Upper Oligocene-lower Miocene)	-	60-100	-
Late thrust-top basin			Clays and marls (middle Pliocene)	<20	<60	-
			Terravecchia Fm. (upper Miocene)	36 - 88 (65)	60 or little more	-
Early foredeep			Clays and glauconitic sandstones (Oligocene-middle Miocene)	-	100-110	100-112
Africa passive margin-derived units		Mt. Judica Unit	'Scaglia facies' limestones (upper Cretaceous-Eocene)	-	100-110	112-115
			Radiolarian cherts (Jurassic)	-	110-125	115-117
			Calcari con Selce (upper Triassic)	-	110-125	117-126
External to the subduction trench	Far-travelled Sicilide Units of the Mt. Judica area		Polizzi Fm. equivalent (Eocene)	-	60 or little more	-
			Argille Scagliose-Varicolori (upper Cretaceous-Eocene)	-	60 or little more	-

† temperatures obtained by using BARKER's equation (1988); [$T\ (°C) = 104\ (\ln Ro\%) + 148$]
‡ temperatures obtained by using Hoffman and Hower time-temperature model (HOFFMAN & HOWER, 1979; POLLASTRO, 1990; 1993)
§ temperatures obtained by using BASIN MOD 1D (1996)

Tab. 1 - Summary of calculated and estimated maximum temperatures for the different structural units.

Quadro sinottico delle temperature massime calcolate e stimate per le differenti unità strutturali.

zone (according to MERRIMAN & FREY, 1999; Tab. 1).

Early thrust-top basin (Reitano Flysch Fm.): this deposit records a thermal evolution correlated to the early diagenetic zone and the immature stage of hydrocarbon generation. Mean Ro% value is about 0.40%. Clay mineralogy revealed two distinct illite crystal populations for pelites and coarse-grained sandstones. Only data coming from pelites have been used for paleotemperatures conversion avoiding'detrital' phases of mica-rich sandstones. Calculated maximum temperature are lower than 60°C.

Early foredeep (Gagliano Marls and Numidian Flysch Fms.): the illite content in the I-S mixed layers ranges between 50 and 60%, whereas vitrinite is almost absent. The only organic matter data derive from the *Gagliano Marls* with values of about 0.40%. Thus, smectite-to-illite reaction may record a maturity level more pronounced than that estimated by organic thermal indicators. A detrital supply should be considered as a possible source of error for determining the illitic content in the I-S mixed layers and therefore calculated paleotemperatures could be overestimated. Based on clay mineralogy early foredeep deposits experienced paleotemperatures in the range of 60 to 100°C characteristic for the last stages of the early diagenetic zone. A lower temperature range can be established if compared to Ro%-converted temperatures for the *Gagliano Marls* (about 50°C).

Late thrust-top basin (Pliocene clays and marls and Terravecchia Fms.): deposits filling late thrust-top basin record the lowest thermal evolution among the analysed samples. They show mean Ro% value ranging from 0.2 to 0.29% and from 0.36 to 0.42% for the *Pliocenic clays and marls* and the *Terravecchia Fm.* respectively. The illitic content in I-S mixed layers ranges from 30 to 45% (Fig. 2). Estimated temperatures (Tab. 1) are characteristic for the early diagenetic zone and the immature stage of hydrocarbon generation. Sedimentary burial is the main factor responsible for the acquired thermal maturity.

Africa passive margin-derived units (Mt. Judica Unit): only clay mineralogy provided results for the various thrust sheets forming the Mt. Judica Unit. A general trend of increasing thermal maturity moving from the younger to the older lithostratigraphic unit has been recognized. The percentage of illite in I-S mixed layers ranges from 55 to 75% in the inner and upper thrust sheet, from 55 to 70% in the intermediate thrust sheet and is about of 65% in the outer one. Calculated maximum temperatures are characteristic for the first stages of the late diagenetic zone and are in the range of 100 and 125°C (Tab. 1). Furthermorme, the same maturity profile is recorded for the different thrust sheets forming this unit (Fig. 2). Thus the Mt. Judica Unit thermal evolution has been acquired before the late Miocene-early Pliocene deformation phase that caused its internal thrust stacking. Nevertheless, a tectonic loading of ca. 3,000 m is considered to be the main factor affecting the thermal maturity of the Mt. Judica succession. It might be represented by more internal units (e.g., far-travelled Sicilide and early foredeep Units) emplaced in middle Miocene times.

Far-travelled Sicilide Units external to the subduction trench: only clay mineralogy provided reliable results (Fig. 2). The percentage of illite in I-S mixed layers ranges from 30 to 45% recording a thermal evolution in the early diagenetic zone. Estimated temperatures are close or little bit higher than 60°C suggesting that these units did not experience huge loading even if they derive from the innermost paleo-geographic domain represented along the examined transect (cfr. subduction trench).

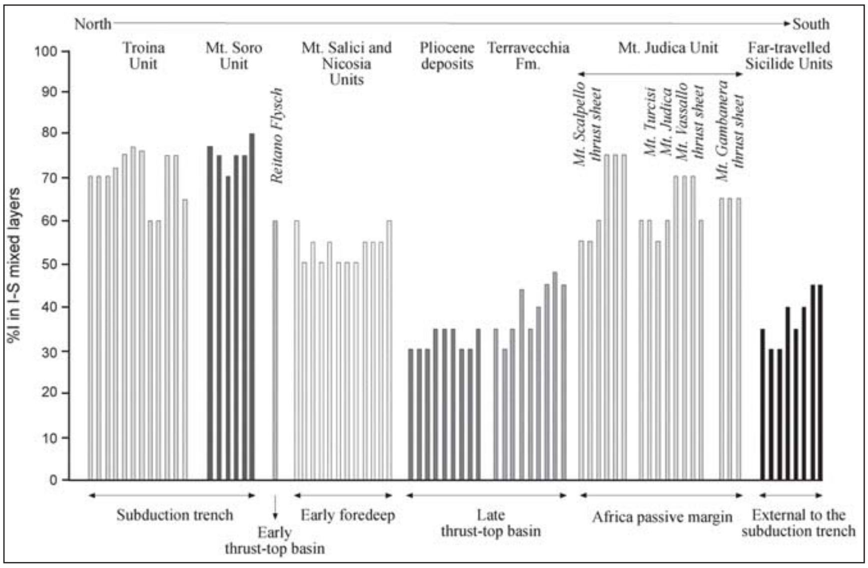

Fig. 2 - Distribution of the illite content in I/S mixed layers for the different structural units. Note how structural units belonging to various geodynamic settings can be differentiated on the basis of the illitic content in the I-S mixed layers of the <2 μm grain-size fraction.

Distribuzione del contenuto di illite nell'interstratificato I/S nelle diverse unità strutturali campionate. Le distinte unità strutturali appartenenti a diverse ambientazioni geodinamiche possono essere differenziate sulla base del contenuto in illite negli interstratificati I-S della frazione <2 μm.

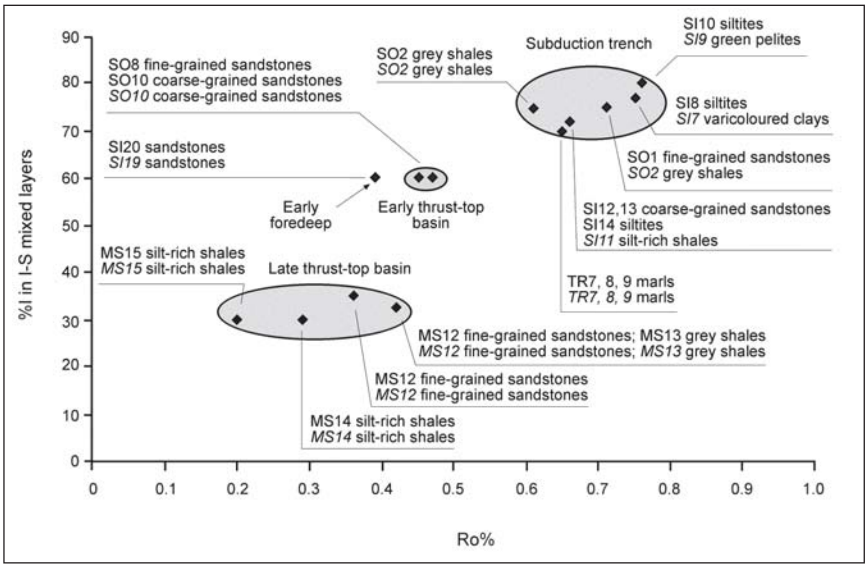

Fig. 3 - Correlation of organic and inorganic thermal indicators: illitic content in I-S mixed layers measured in the <2 μm grain-size fraction (*italic*) vs. vitrinite reflectance (*regular*).

Correlazione di indicatori termici organici ed inorganici: contenuto in illite negli strati misti I-S misurati nella frazione granulometrica <2 μm (*in corsivo*) vs. riflettanza della vitrinite (*normale*).

5. CONCLUSIONS

The integration of two independent methodologies allowed us to constrain the thermal evolution of various units cropping out in the eastern Sicily fold-and-thrust belt. The distribution of both organic and inorganic parameters of Fig. 3 shows that data group into clusters corresponding to the various geodynamic settings, mostly independently from lithology.

The more thermally evolved domain is represented by the subduction trench, while both foredeep and thrust-top environments show lower values of vitrinite reflectance and illite content in the I-S mixed-layers.

For specimen from early thrust-top and early foredeep basins a possible detrital contamination must be considered as only coarse and medium-grained sandstones have been sampled. Thus these lithologies are generally unsuitable to provide paleo-temperatures estimates from expandability measurements.

On the other hand, clay mineralogy data provided reliable results in terms of paleo-temperatures for clay-rich units where organic matter was hardly preserved and sedimentation rate was low (e.g., Mt. Judica Unit and far travelled Sicilide units, see Fig. 2 and Tab. 1). These data are in reasonable agreement with the tectonic evolution of the area in Neogene times.

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