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Geotechnics, mineralogy and geochemistry of the Cutro Clay Formation, Calabria, Southern Italy

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ABSTRACT - This paper deals with the geotechnical and the minero-chemical characterization of Plio-Pleistocene fine-grained deposits from the coastal area of the Crotone Basin (Calabria Region, Southern Italy). Eleven representative surface samples from the Cutro Clay Formation were investigated by means of geotechnical laboratory tests and geochemical and mineralogical analyses. The obtained results provided interesting physical and mineralogical information. The comparison between geotechnical analyses and geochemical and mineralogical investigations suggests a direct correlation allowing for a wider characterization of the sediment properties. From the activity index, determined by geotechnical laboratory tests, it was possible to predict the dominant clay minerals in the studied samples. Considering the typical values of Liquid and Plastic Limits and Activity index the studied samples fall in the range of limited and low activity. Thus, these results indicate that the Plio-Pleistocene mudrock samples mainly consist of illite and kaolinite as confirmed by the minero-chemical analyses.

Keywords: Activity index; Atterberg limits; Cutro Clay Formation; geotechnical analysis; XRD and XRF analysis; Calabria (Southern Italy).

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1. INTRODUCTION

In this paper we present a geotechnical characterization and analyze mineralogical assemblages and chemical compositions of a set of Plio-Pleistocene samples collected from various sectors of the coastal areas in the Crotone Basin (Calabria, Southern Italy).

Geotechnical laboratory tests were carried out to detail the physical properties of fine-grained sediments. The grain size distribution curves and other tests, such as Atterberg limits, were used to classify the mudrock samples (e.g., Skempton, 1953; Al-Rawas et al., 2000; Kaliakin, 2017). In fact, considering the stratigraphy of the study area, consisting of the superimposition of the calcarenite strata over the Cutro Clay Formation (Barone et al., 2008; Zecchin et al., 2011; 2012; 2020; Muto et al., 2015) that have different geomechanical features, the physical state (degree of plasticity and liquidity) and the geotechnical characteristics of the mudrocks play an important role in the slope stability context and are a major aspect of the prediction and estimation for susceptibility for landslides (e.g., Yalcin, 2007; Hassan et al., 2010; Carrière et al., 2018). For example, one of the main factors that generate the evident degree of fracturing of the calcarenite, and the precarious stability conditions of the slopes is represented by the physical-mechanical characteristics of the Clay Formation studied and reported in the following paragraphs. Therefore, the Atterberg limits and the various indexes assume great importance in order to understand the current geological-geomorphological scenario of the study area (e.g. Yalcin, 2011; Deng et al., 2017; Carrière et al., 2018; Ahmad et al., 2019).

In this paper, non-destructive analytical techniques were used for material characterization. By combining the information deduced from the X-ray diffraction (XRD) patterns of whole-rocks and the clay mineral fractions after thermo-chemical treatments (heating and ethylene glycol treatments) with the elemental analyses of major and trace elements concentrations obtained by X-ray fluorescence spectrometry (XRF), it was possible to explain and predict the sedimentary evolution and geological processes affecting fine-grained sediments and, thus, the relationships between the source area and the sedimentary basin (e.g. Martin-Martin et al., 2018; Hurst et al., 2021).

Moreover, thanks to these analyses, it was also possible to evaluate chemical weathering intensity in the source area and recognize provenance signatures (e.g., Bahlburg and Dobrzinski, 2011; Perri, 2018, 2020; Perri et al., 2021; Price and Velbel, 2003).

Finally, the relationships among compositional, physical and mechanical features of the fine sediments can be used to investigate their role in the triggering of landslides (e.g. Ohlmacher, 2000; Gullà et al., 2008; Neupane and Adhikari, 2011; Borrelli et al., 2012; Zecchin et al., 2011, 2018; Martinčević et al., 2013). In particular, the saturation-desaturation cycles produce changes in fabric and bonding and affect the density of soil slips in fine-grained soils and their degradation reducing their shear strength (e.g., Gullà et al. 2006, 2008). The mineralogical characteristics related to the presence of high swelling clay mineral and/or low swelling clay minerals, which can be affected by saturation-desaturation cycles, play an important role in controlling the recurrence of landslides in the coastal area of the Crotone Basin.

2. GEOLOGICAL SETTING OF THE STUDY AREA

The investigated area is located in a portion of the Crotone Basin, Calabria (Southern Italy). This sector represents the exposed part of a Neogene to present sedimentary basin developed along the Ionian Sea (e.g., Critelli et al., 2017; Critelli, 2018; Zecchin et al., 2020), located in the eastern part of the Calabrian Arc, Southern Italy (Mellere et al., 2005). The Plio-Pleistocene tectonic episodes, affecting the Calabrian Arc (interpreted by Malinverno and Ryan, 1986 as a "subduction-rollback system") during its migration towards SE which led to the subduction of the Ionian plate and the spreading of the Tyrrhenian back-arc Basin in the central Mediterranean (Sartori, 2003; Reitz and Seeber, 2012; Loreto et al., 2021), were recorded in the depositional history of the Crotone Basin succession (Zecchin et al., 2012). The stratigraphic setting of this basin is well documented by several authors (e.g., Ogniben, 1955; Roda, 1964; Moretti, 1994; Mellere et al., 2005; Zecchin et al., 2006; Barone et al., 2008). The succession, considering the complex geological evolutive context, is composed by several units delimited by unconformities (Roda, 1964; VanDijk, 1990; Zecchin et al., 2004).

The Plio-Pleistocene fine-grained succession is well exposed, with thicknesses ranging from several tens of meters up to hundreds of meters, along the entire coastal area of the Crotone Basin, especially from Crotone to Capo Colonna. The considerable exposure of these sediments encouraged several scientists, in the past, to carry out various paleontological, biostratigraphic, and magnetostratigraphic studies (e.g., Cita et al., 2006 and reference therein). Then, in the studied area (Vrica locality), the Calabrian strato-type was established (Gignoux, 1910), consisting of the GSSP (Global Stratotype Section and Point) of the Gelasian-Calabrian boundary (Aguirre and Pasini, 1985; Cita et al., 2012) at the base of the marine mudrock overlying sapropelic bed (Cita et al., 2012). Therefore, that the stratigraphic succession intervals studied for this work concerned the marine mudrock portion.

3. SAMPLING AND METHODS

Eleven samples belonging to the Plio-Pleistocene Cutro Clay Formation in correspondence of well exposed outcrops were studied. The sampling took place, manually, in a semi-disturbed way in order to obtain not only the particle size composition and the water content but also the physical and mechanical characteristics. The samples were taken along sub-vertical slopes at varying heights of the mudrock stratigraphic sequences. Furthermore, the intervals of the most preserved, freshest and less altered stratigraphic sequences were chosen for the sampling.

A set of 11 mudrock samples were taken from different areas of the Crotone basin (Fig. 1), at the well exposed outcrops: Campolongo location close to Le Castella (PGC_1, PGC_2 and PGC_3 samples), Isola di Capo Rizzuto (PGC_4, PGC_5 and PGC_6 samples), Capo Colonna (PGC_7, PGC_8 and PGC_9 samples) and via Capo Colonna between Semaforo and Vrica (PGC_10 and PGC_11 samples). These samples were studied using laboratory geotechnical analysis (physical characterization), XRD analysis (qualitative mineralogical analysis), XRF analysis (quantitative mineralogical analysis) and LOI.

The physical characterization of the studied samples was performed by carrying out the following laboratory analyses. The first analyses involved the determination of the water content (w; according UNI CEN ISO/TS 17892 - 1: Feb. 2005), the weight of the natural volume unit (γ_n; considering UNI CEN ISO/TS 17892 - 2: Feb. 2005) and particle size distribution (through sieve and hydrometer analysis; as per UNI CEN ISO/TS 17892 - 4: Feb 2005).

As the granulometric composition alone becomes insufficient if the soil consists of a high percentage of fine (silt and clay over 30%), in order to classify the fine material, the plasticity characteristics were identified through the Atterberg limits (Atterberg, 1910), as per CNR - UNI 10014: 1964.

Successively, qualitative and quantitative analyses were performed on all mudrock samples. The qualitative analysis of the mudrock samples took place by analyzing whole-rock powder and the fine fractions (clay fraction <2 μm) through the Bruker's X-ray Diffractometer D8 Advance at the University of Calabria (Italy).

Using the WINFIT program (Krumm, 1999), semi-quantitative measurements of the mineralogical components of the sample powders were carried out by calculating the areas of each mineral peak on the diffractograms. The amount of phyllosilicates was

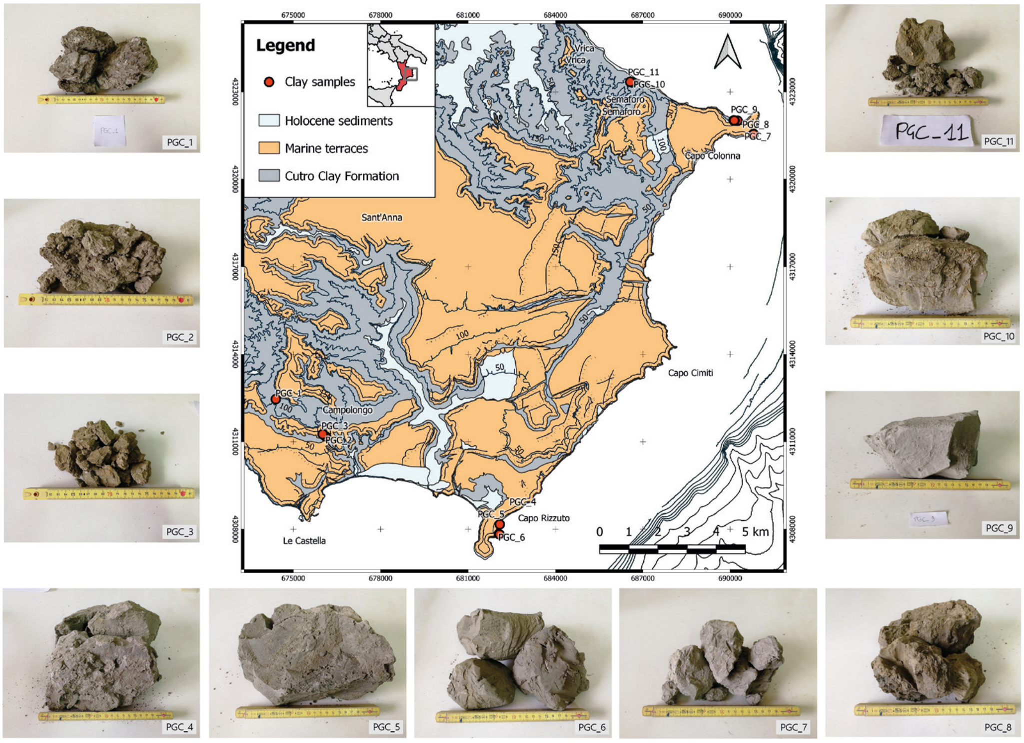

Fig. 1 - Geological sketch map (modified from Zecchin et al., 2004) showing samples location. Gray (late Pliocene-early Pleistocene): Cutro Clay Formation consisting of clays, marly clays and siltstones; Orange (middle and late Pleistocene): marine terraces consisting of calcarenites, sandstones, conglomerates and biocalcarenites; Light blue (Holocene): alluvial deposits made up of gravels and sands.

estimated measuring the 4.5 Å peak area, whereas for quartz was considered the peak at 4.26 Å instead of that at 3.34 Å because their overlap on the values of the 10 Å-minerals and mixed layer series of clays. To identify the percentage of phyllosilicates in the bulk rock, the XRD pattern of the random powder was observed, and three areal divisions (peak areas) were considered as follows: 10-15 Å (I/S=Illite/Smectite mixed layers+Chl/S=chlorite/smectite mixed layers), 10 Å (illite+micas), and 7 Å (kaolinite+chlorite) minerals (e.g. Cavalcante et al., 2007; Perri et al., 2011).

To better distinguish the clay minerals present in the inter-layered packets the gravity settlement method was used. The whole rock powders (<2 µm grain-size fraction) were separated by settling in distilled water and then a concentration of 4-10 mg/cm^2 was obtained by evaporation of clay-water suspension (Lezzerini et al., 1995). Then, the air-dried specimens were subjected to treatments: ethylene glycol treatments (specimens glycolated at 60 °C for 8 hours) and heat treatments at 370 °C (for 1 hour) and 550 °C (for 1 hour). The percentage of illite (% I) and the stacking order (Reichweite R; Jadgozinski, 1949) of the illite/smectite mixed-layers were determined on the samples treated with ethylene glycol using the Δ2θ method according to Moore and Reynolds (1989).

The mudrocks were previously cleaned from weather coats and veined surfaces and subsequently crushed and milled with an agate mortar to obtain a very fine powder. Through the Bruker S8 Tiger equipment of the University of Calabria the chemical composition (major and trace elements) of the studied samples was determined by X-ray fluorescence spectrometry (XRF). The mineralogical composition of the whole rock was recalculated by combining the major element chemical composition (XRF) of all samples and semiquantitative results (XRD) using the vbAffina software (e.g., Laviano, 1987; Leoni et al., 1989; Leoni et al., 2008; Cesarano et al., 2018;). Finally, the Loss of Ignition (LOI) was calculated considering 400 mg of whole rock samples previously pulverized and placed in a platinum crucible in an oven at 900 °C for about an hour.

4. RESULTS

4.1. GEOTECHNICAL DATA - DETERMINATION OF THE PHYSICAL FEATURES

The physical characterization was performed for eleven samples. The obtained values of the water content (w) and weight of the natural volume unit (γ_n) for six samples are reported in table 1.

Through the sieve and hydrometer analysis eight samples were classified based on particle size distributions. The Cutro Clay Formation consists mainly of silt (particles <0.06 mm and >0.002 mm) and clay (particles <0.002 mm). Therefore, the particle size analysis was performed by hydrometer analysis. Only for PGC_2 and PGC_3 samples mechanical sieving was performed. The results

Tab. 1 - Average of the water content and the weight of the volume unit. The volume weight values of the water content were obtained from the preliminary phase of undisturbed sampling.

Sample	w (%)	γn (kN/m³)
PGC_4	27,45	18,28
PGC_5	21,75	19,77
PGC_6	28,89	17,9
PGC_8	19,97	19,53
PGC_9	18,49	18,72
PGC_10	19,22	19,39

obtained from the particle size analysis are represented in figure 2. The table 2 shows the granulometric percentages of the fine fraction and the relative nomenclature.

For seven samples the liquid limit (W_L) and the plastic limit (W_P) were determined through laboratory tests (Tab. 3), while the plasticity index, the consistency index and the activity of the samples were obtained through empirical formulas (e.g., Kaliakin, 2017). Once W_L and W_P were determined, it was possible to obtain a representative value of each mudrock sample in the "Casagrande plasticity chart" (Fig. 3). Four samples (PGC_2; PGC_3; PGC_10 and PGC_11) fall into the ML or OL fields (low plasticity silt), while three samples (PGC_1; PGC_6; PGC_8) in the MH or OH areas (high plasticity silt). It must be considered that the sampling took place in June 2019, in the full dry period characterized by the absence of important rainfall events; therefore, it is plausible that in conditions of heavy rainfall, with the increase of the water content, the material could reach the conditions of plasticity or even liquidity, compromising the stability of the limestone blocks above and consequently of the entire slope (Fig. 4). For example, for saturated samples, rainfall would have no impact on the water content of the clay. This is different if the clay is unsaturated just below the terrain surface. The same applies with the swelling minerals. Swelling will not occur if the soil is saturated and not subjected to changes in stress conditions.

Based on the I_P value (obtained from the difference between W_L and W_P), which represents the humidity range within which the soil is in a plastic state, the samples are placed in a classification range of "low plastic" and "plastic". Subsequently, the consistency index $[Ic=(W_L-W)/I_P]$ indicative of the physical state of few samples has been calculated and resulted "semi-solid" or "solid" (Tab. 4).

A further subdivision for the studied samples can be carried out by defining the activity index A ($A=I_P/C_F$, where C_F is the clay fraction). The ability to adsorb water is directly proportional to the amount of clay contained and even more depends on the constituent minerals, which may have a greater or lesser specific surface: those minerals with a greater specific surface are more active. In particular, considering the typical values of Liquid Limit, Plastic Limit and Activity reported in literature (e.g., Skempton, 1953), the studied samples fall in the "limited activity" and "low activity" fields (Tab. 5 and Fig. 5).

Skempton (1953) shows that for a specific soil, the plasticity index increases linearly in proportion to the percentage of clay particles in the samples. This correlation can be found in the Lambe and Whitman (1991) diagram within which there are three straight lines (passing through the origin) representative of three soil groups with Plasticity Index values directly proportional to the percentage of clay fraction. This can be explained because different soils with the same clay fraction percentage can contain different minerals and consequently the slope of the curve may change accordingly. Therefore, each terrain will have its own straight line. Indeed, a new curve

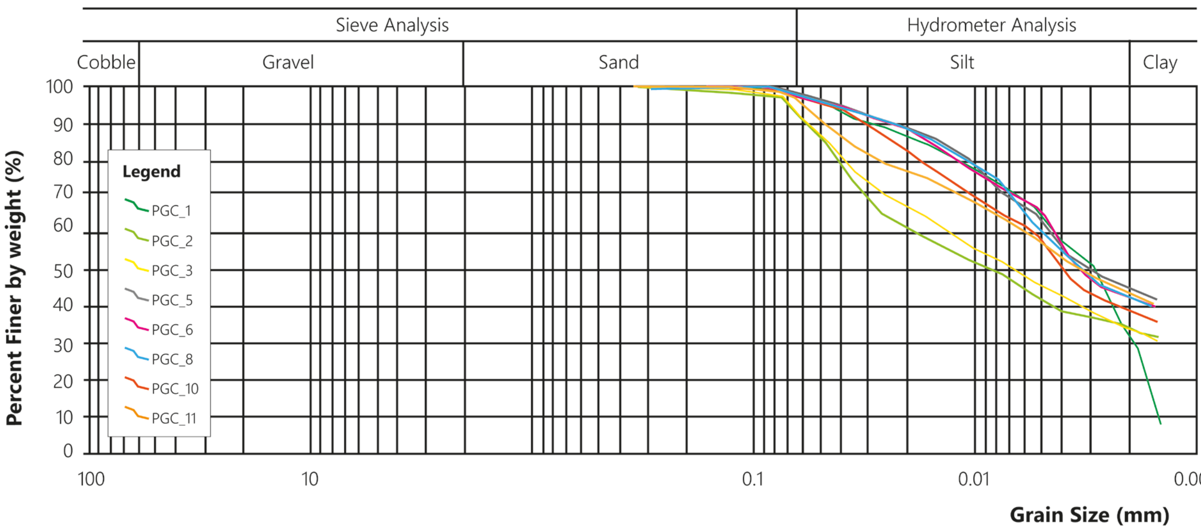

Fig. 2 - Particle size distribution curves for each sample.

Tab. 2 - Percentage of grain size classes and nomenclature.

Sample	Sand (%)	Silt (%)	Clay (%)	Nomenclature
PGC_1	1.93	62.84	35.21	Silt with clay
PGC_2	8.16	57.08	34.69	Silt with clay slightly sandy
PGC_3	7.91	58.26	33.83	Silt with clay slightly sandy
PGC_5	1	53.80	45.200	Silt with clay
PGC_6	1	56.40	42.60	Silt with clay
PGC_8	1	55.10	43.90	Silt with clay
PGC_10	1	59.60	39.40	Silt with clay
PGC_11	3.12	53.21	43.66	Silt with clay

Tab. 3 - Summary table of the W_L (Liquid Limit) and W_P (Plastic Limit) values for each studied sample.

Sample	Atterberg limits (%)
PGC_1	W_L=61.6; W_P=41.9
PGC_2	W_L=40; W_P=28
PGC_3	W_L=43.8; W_P=28.2
PGC_6	W_L=54.22; W_P=31.70
PGC_8	W_L=56.23; W_P=30.43
PGC_10	W_L=48.85; W_P=32.19
PGC_11	W_L=47.3; W_P=31.6

was obtained (Fig. 5) testifing that the seven samples fall into the field of limited and low activity. By comparing the values obtained with the typical activity values of clay minerals as illite, kaolinite, montmorillonite (e.g., Skempton, 1953), the clay fractions mainly consist of illite and kaolinite. To verify whether the content of fine material consists of these mineralogical phases, a comparison was made with the XRD patterns reported in the next section.

4.2. MINERALOGY

The XRD patterns (Fig. 6) and the semiquantitative results (Tab. 7) of the studied mudrocks show that the samples are mainly composed of phyllosilicates that prevail over quartz and feldspar. In detail, the phyllosilicates consist of illite, mixed-layer clay minerals, chlorite and kaolinite. The non-phyllosilicate phases include quartz, calcite, feldspars and dolomite, in order of abundance. The studied samples show similar XRD data about mineralogical composition and were divided into four groups according to the sampling areas (Tab. 6).

The first group is composed by PGC_1, PGC_2 and PGC_3 and is located close to Le Castella (Campolongo location). The samples are characterized by abundant phyllosilicates, ranging from 48% to 52% and lesser quartz (from 21% to 23%), carbonate minerals (18-21% calcite and poor-absent dolomite) and feldspars (plagioclase and minor K-feldspar) with a P/F ratio of 0.69.

Samples from the second group (PGC_4, PGC_5 and PGC_6) are from the Capo Rizzuto coast and contain

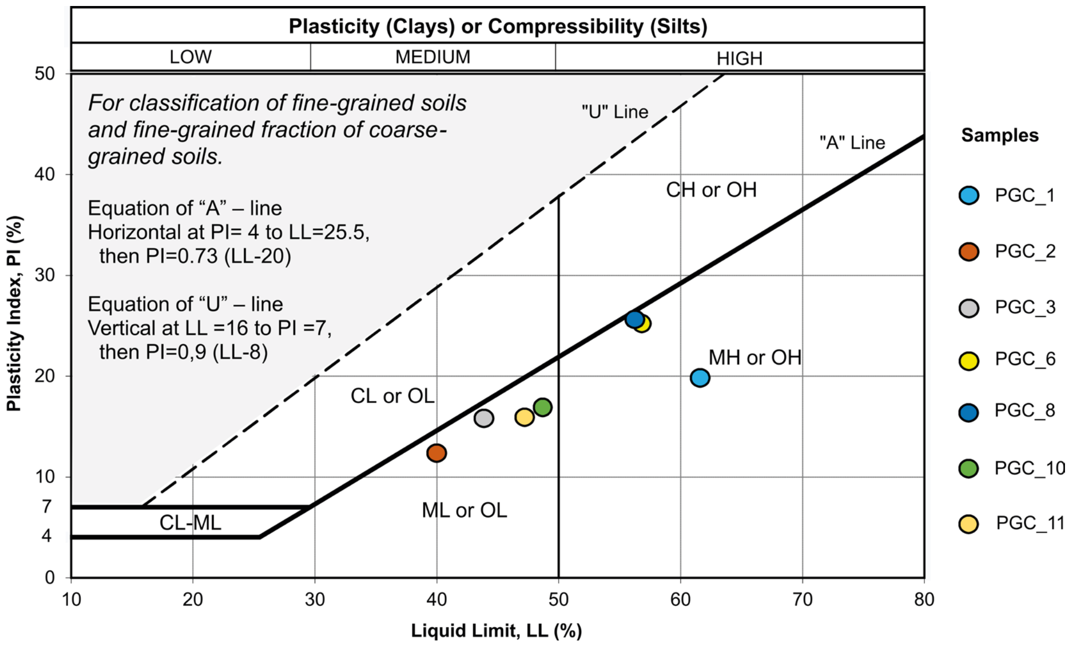

Fig. 3 - Projection of studied samples in the Casagrande Plasticity chart. Within this diagram it is possible to identify areas that define the different types of soil: clays with low plasticity (CL), clays with high plasticity (CH), inorganic silts with low plasticity (ML-OL) and organic silts with high plasticity (MH-OH). "A" Line identifies two areas: the silty soils with appreciable organic content have a lower humidity interval to pass from the semi-solid to the semi-liquid state and are positioned below the line, while the clays remain above the straight line. In our case, the samples are plotted below the "A" Line: this mean that the samples are considered as silts ranging from low to high plasticity.

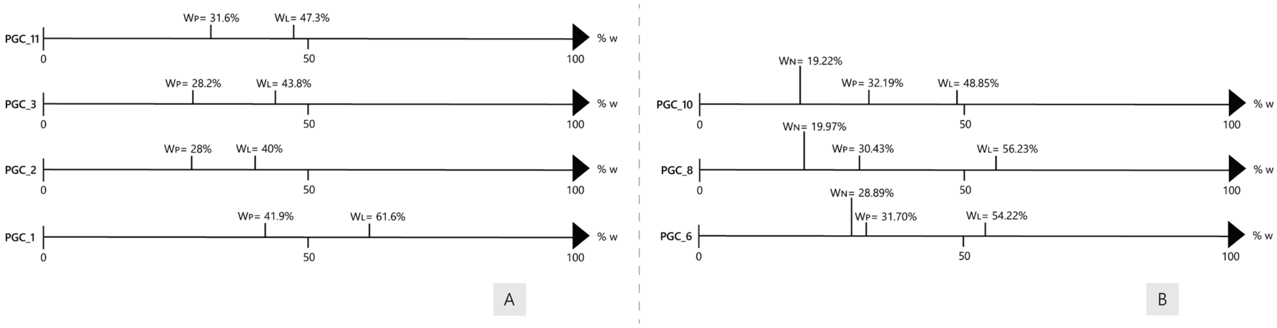

Fig. 4 - Consistency values of seven samples. On the bar are reported the moisture content (w), the Plastic limit (W_P), and Liquid limit (W_L) of each mudrock sample analyzed. For four samples it was not possible to obtain the natural water content, therefore: in (A) there are only W_P and W_L, while in (B) there is also the natural water content (W_N).

Tab. 4 - Plasticity index and soil consistency.

Sample	I_P and I_C	Classification considering I_P	Classification considering I_C
PGC_1	I_P=19.7 I_C=nd	low plastic	nd
PGC_2	I_P=12 I_C=nd	low plastic	nd
PGC_3	I_P=15.6 I_C=nd	plastic	nd
PGC_6	I_P=22.52 I_C=1.08	plastic	Semi-solid or solid
PGC_8	I_P=25.80 I_C=1.41	plastic	Semi-solid or solid
PGC_9	nd	nd	nd
PGC_10	I_P=16.66 I_C=1.78	plastic	Semi-solid or solid
PGC_11	I_P=15.6 I_C=nd	plastic	nd

nd= not detected

Tab. 5 - Determination of Activity index for each studied sample.

Sample	I_P (%)	C_F (%)	A
PGC_1	19,70	35,21	A=0.6
PGC_2	12,00	34,69	A=0.3
PGC_3	15,60	33,83	A=0.5
PGC_6	22,52	42,60	A=0.53
PGC_8	25,80	43,90	A=0.59
PGC_10	16,66	39,40	A=0.42
PGC_11	15,60	43,66	A=0.4

Note: I_P= plasticity index; C_F= clay fraction (weight in% of the particles <0.002mm); A=Activity factor.

abundant phyllosilicates (from 46% to 50%) and quartz (23-24%). They contain medium calcite content (from 18% to 26%) and lesser dolomite percentage (2-3%), and feldspars (plagioclase and minor K-feldspar) with a P/F ratio of 0.71.

The third group (PGC_7, PGC_8 and PGC_9) collected in the southern and northern Capo Colonna coast is composed of abundant phyllosilicates, ranging from 49% to 55% and lesser quartz (quartz is present in low concentrations, varying from 18% to 20%) as well as feldspars (plagioclase and minor K-feldspar) with a P/F ratio of 0.57.

The fourth group is composed by PGC_10 and PGC_11 samples located between Semaforo and Vrica area close to Capo Colonna. This group is characterized by abundant phyllosilicates (56-59%) with minor amounts of quartz (19-21%) and carbonate minerals (calcite 19% and minor-absent dolomite 1-2%), with a P/F ratio of 0.73.

The XRD data obtained on the treated <2 μm samples show that the fine fraction is mainly characterized by disordered I/S mixed layers and illite, with minor amounts of chlorite and kaolinite. The XRD patterns of the treated <2 μm samples are also used to evaluate the percentage of illite in the interstratified mineral and, thus, the stacking order of the I/S mixed layers. The low illite content (40-50%) and the random I/S mixed-layers (R0) are typical of low-medium temperatures (Pollastro, 1985); therefore, the diagenetic degree for these rocks corresponds to the low degree.

4.3. GEOCHEMISTRY

The Herron's geochemical classification diagram (1988) for the studied fine-grained sediments was considered. The SiO_2/Al_2O_3 allows to distinguish between quartz-rich, high-ratio sandstones and clay-rich, low-ratio shales; the

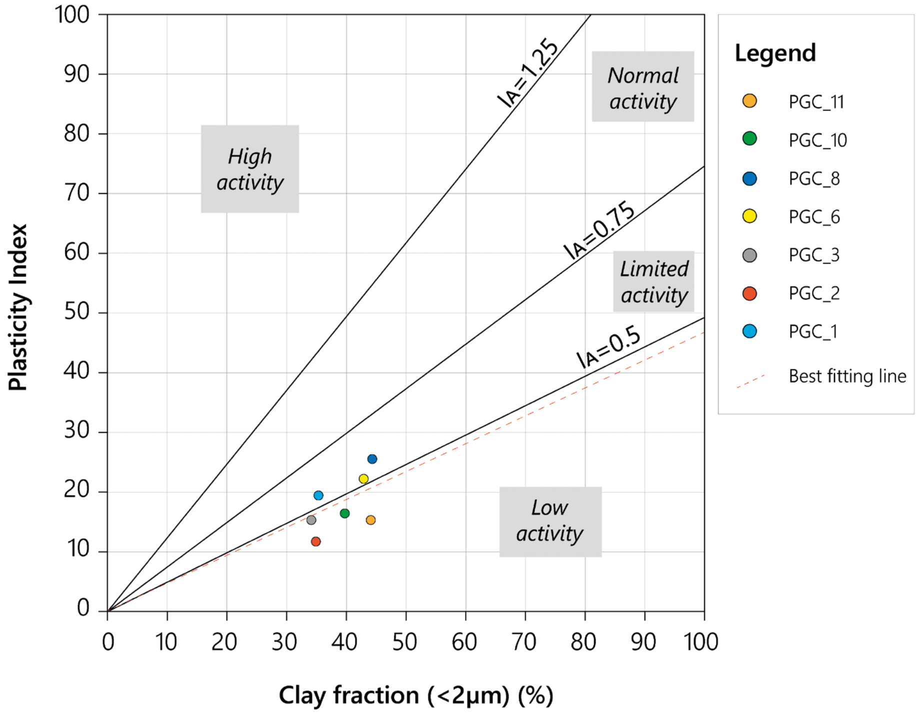

Fig. 5 - Relationship between the Plasticity Index and clay percentage. The red dotted line represents the best fitting line for our studied samples. Modified from Lambe and Whitman (1969).

Tab. 6 - Quantitative data of the mineralogical composition of the bulk rock.

Sample	ΣPhyll	Qtz	K-feld	Pl	Calc	Dol
PGC_1	52	21	2	4	18	3
PGC_2	48	23	4	9	22	0
PGC_3	48	23	2	4	21	1
PGC_4	50	24	1	3	18	3
PGC_5	46	23	1	3	24	3
PGC_6	47	23	1	2	26	2
PGC_7	49	20	2	4	22	2
PGC_8	55	18	10	9	16	2
PGC_9	53	20	1	3	20	2
PGC_10	56	21	2	4	19	2
PGC_11	59	19	3	8	19	2

Qtz - quartz; ΣPhyll - phyllosilicates; Feld= feldspars; Calc= calcite; Dol= dolomite.

Fe_2O_3/K_2O ratio on y axis is an indicator of mineralogical stability (Herron, 1988). All the studied samples fall in the shale field as expected (Fig. 7). The studied samples were normalized to standard shales (UCC - Upper Continental Crust; McLennan et al., 2006); the variation of the PAAS (Post-Archean Australian Shales, Taylor and McLennan, 1985) is also plotted for comparison.

Chemical composition of the studied mudstones in terms of major and trace element concentrations are listed in table 8. The studied samples show a narrow compositional change similar to the PAAS (Fig. 8) and are characterized by a depletion of Si, Al, Na, K, Mn and P and an enrichment of Ca, Ti, Mg and Fe relative to the UCC (Upper Continental Crust; McLennan et al., 2006).

The Mg and Ca oxide concentrations for all samples are strongly enriched relative to the PAAS. The distribution

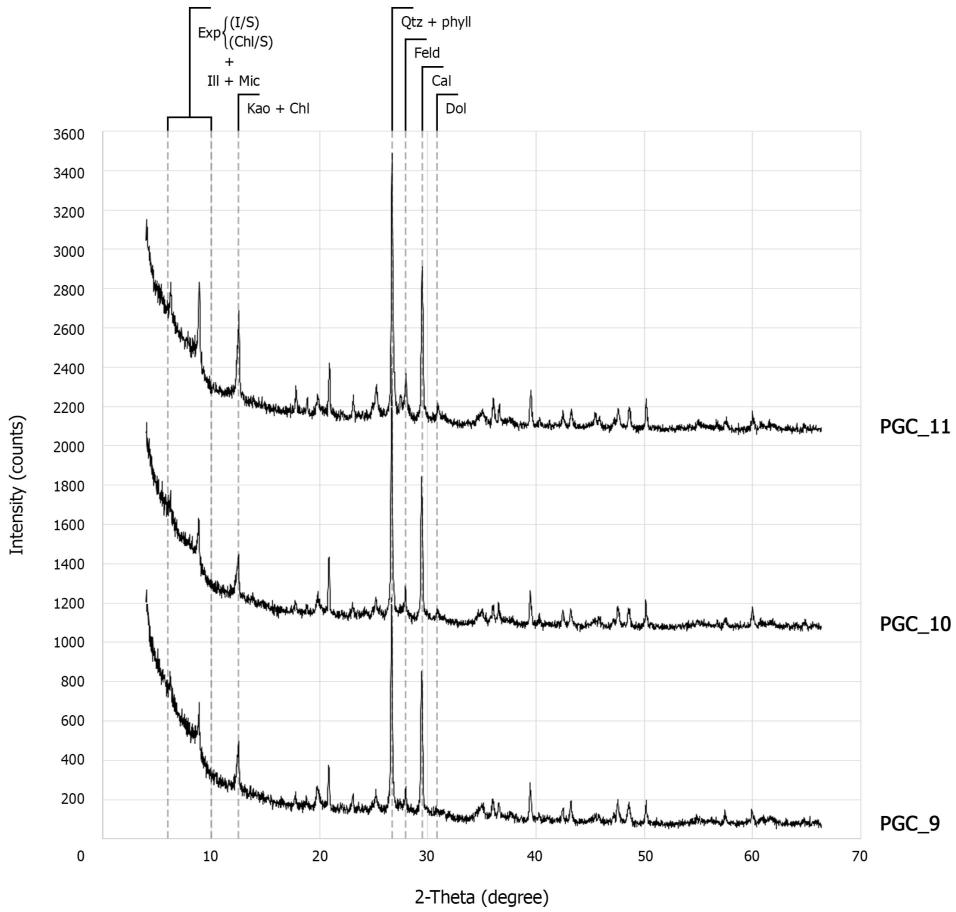

Fig. 6 - XRD patterns. The mineralogical components are indicated in correspondence with the most significant peaks.

Tab. 7 - Semiquantitative data of the mineralogical composition of the mudrock samples (<2μm fraction).

Sample	Kao	Chl	Ill	Mixed layer phases (I/S)
PGC_1	++	++	++	+++
PGC_2	+	+	+++	+++
PGC_3	+	+	++	+++
PGC_4	++	++	++	+++
PGC_5	++	++	++	+++
PGC_6	++	++	+++	+++
PGC_7	+	+	+++	+++
PGC_8	++	+	++	+++
PGC_9	++	++	+++	++
PGC_10	+	++	+++	+++
PGC_11	++	++	+++	++

Kao-kaolinite; Chl - chlorite; Ill - illite; I/S - illite/smectite mixed layers; layers; +, increasing intensity where: += x≤10, ++= 10<x≤20, +++= x>20.

of the trace elements is similar to the PAAS with a marked depletion for Ba, Co, Cu, Zr, La and Ce relative to the UCC (Upper Continental Crust; McLennan et al., 2006). In particular, the Ca and Sr abundance is related to enrichment in the calcite and dolomite, as also shown by XRD analysis revealing high contents of calcium-carbonate phases (e.g., calcite and dolomite), especially for PGC_2, PGC_3, PGC_5 and PGC_6 samples.

5. DISCUSSION

The ratio between the plasticity index and the clay fraction defined the 'activity' of a fine-grained material (Skempton, 1953) that could be related to its chemical-mineralogical composition and geotechnical properties. The soil plasticity and activity of a fine-grained soil are strongly influenced by the type and amount of minerals (e.g., Dobrescu et al., 2017). In particular, samples characterized by high plasticity index and activity are mainly composed of montmorillonite, illite and minor kaolinite, whereas samples characterized by medium-low plasticity index and limited and low activity are mainly composed of illite, kaolinite and minor montmorillonite. The geotechnical analyses of the studied mudrocks indicate a limited-low activity for the samples based on

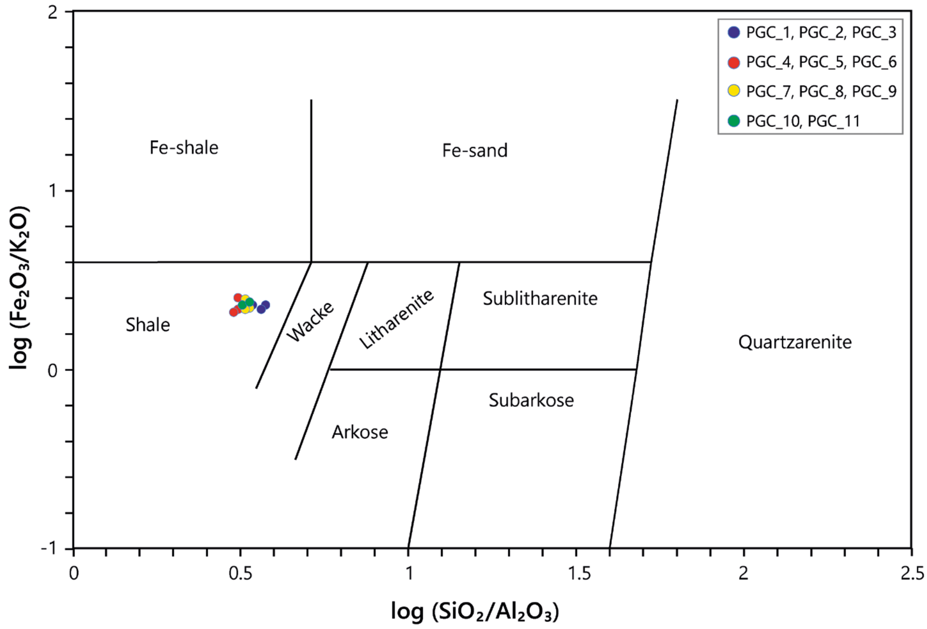

Fig. 7 - Geochemical classification diagram for the fine-grained samples (e.g., Herron, 1988).

their plasticity index and clay content. The mineralogical analyses of the studied mudrocks indicate that the samples are mainly composed of phyllosilicates that prevail over quartz and feldspar. In detail, the phyllosilicates mainly consist of illite, mixed-layer clay minerals, chlorite and kaolinite, in accordance with the activity values obtained by geotechnical analyses.

The mineralogical, chemical, physical and mechanical properties of soils have been influenced by weathering processes (e.g., Trotter, 1993; Gullà et al., 2008; Perri et al., 2012; Borrelli et al., 2012, 2014). Weathering processes can be produced clay mineral alteration and removal of other mineralogical phases promoting gradually increasing slope instability (e.g., Trotter, 1993). Chemical variations of the studied samples were used to define the weathering conditions of the sources and the recycling effects during the sedimentary evolution of the studied mudrocks and their source-area provenance.

The chemical composition of terrigeneous sediments and the distribution of some elements can be affected by mechanical sorting during transport and deposition. These processes, in fact, fractionate Al_2O_3 (clay minerals) fromSiO_2 (quartz and feldspars) and TiO_2 (mostly present in clay minerals and Ti-oxides) from Zr (present in zircon, and sorted with quartz). Therefore, a ternary plot based on Al-Ti-Zr may be used to show the presence of sorting-related fractionations, which are recognized by mixing trends on this diagram (Garcia et al., 1991; Fig. 9). Generally, mature sediments consisting of both sandstones and shales show a wide range of TiO_2/Zr variations whereas immature sediments show a more limited range of TiO_2/Zr variations (Garcia et al., 1994). The studied samples are confined to the center of this diagram, with a limited range of TiO_2/Zr variations, suggesting poorly sorting and rapid deposition of sediments.

Commonly, recycling processes are also related to the amounts of feldspars in the sediments; the paucity or absence of feldspars in the rocks may record a recycling effect (Mongelli et al., 2006; Zaghloul et al., 2010). The XRD results of the studied samples show moderate amounts of feldspars and thus negligible recycling effects for the studied mudrocks in accordance with the distribution on the Al-Ti-Zr plot.

Various indices have been used as measures of weathering, including the chemical index of alteration (CIA: Nesbitt and Markovics, 1980; Nesbitt and Young, 1982), the chemical index of weathering (CIW; Harnois, 1988) and the plagioclase index of alteration (PIA; Fedo et al., 1995). The CIA is the most accepted of available weathering indices. In this study both the CIA, with CaO values of the silicate fraction only, and the CIA', expressed as molar volumes of $[Al/(Al+Na+K)]\times100$ and, thus, calculated without the CaO content, were considered (see also Cullers, 2000; Perri et al., 2014). The studied samples have an average CIA value of 70 typical of low-moderate paleoweathering conditions and fall between smectite and illite-muscovite points in the A-CN-K plot (Fig. 10A). Furthermore, the studied mudrocks show an average CIA' value of 75 with a trend that also testifies moderate paleoweathering conditions (Fig. 10B).

Elemental ratios such as Al/K ratios (Schneider et al., 1997) and Rb/K ratios (Peltola et al., 2008), due their contrasting mobility in the supracrustal environment, are generally used to measure the source weathering conditions. In particular, high Al/K ratios reflect the dominance of kaolinite, a product of intensive weathering conditions, over feldspar (or other K-bearing minerals). The Al/K ratios for the studied samples are low and

Tab. 8 - Major, trace element and ratios distribution in studied samples.

	PGC_1	PGC_2	PGC_3	PGC_4	PGC_5	PGC_6	PGC_7	PGC_8	PGC_9	PGC_10	PGC_11
						Oxides (wt.%)					
SiO2	46.46	47.09	45.4	40.96	39.85	37.81	43.61	46.08	45.14	45.56	46.32
TiO2	0.65	0.61	0.6	0.63	0.61	0.6	0.65	0.65	0.65	0.67	0.67
Al2O3	13.74	12.52	12.51	13.12	12.77	12.34	13.3	13.83	13.77	13.88	14.01
Fe2O3	5.49	5.05	4.77	5.77	4.92	4.66	5.32	5.5	5.47	5.68	5.75
MnO	0.06	0.07	0.07	0.06	0.08	0.08	0.08	0.08	0.06	0.09	0.08
MgO	3.51	2.73	2.72	3.27	3.15	2.84	2.92	3.26	3.33	3.24	3.15
CaO	12.14	13.66	12.95	11.7	14.77	15.86	13.77	11.66	12.22	12.29	12.06
Na2O	0.62	0.65	0.83	0.92	1.04	0.69	0.59	1.12	0.86	1.27	1.04
K2O	2.33	2.17	2.15	2.27	2.22	2.17	2.16	2.32	2.45	2.38	2.35
P2O5	0.12	0.13	0.11	0.12	0.11	0.13	0.14	0.13	0.12	0.13	0.14
LOI	14.35	14.78	14.6	14.76	17.57	18.14	16.21	14.88	15.74	14.93	15.38
						Trace elements (ppm)					
Sr	414	391	415	393	651	657	467	376	405	395	384
Rb	139	118	124	140	138	137	129	135	141	137	138
Ba	297	349	345	294	324	442	297	322	300	307	325
Ni	53.75	43.8	47.58	82.8	75.24	69.16	59	55.8	54.09	60.02	50.2
Co	14.93	10.94	18.91	20.23	16.64	13.22	13.59	13.68	10.69	10.86	15.25
Zn	109.75	93.14	95.71	120.52	111.12	116.67	113.63	102.86	113.31	115.35	105.63
Cu	28.76	17.81	25.24	40.81	40.54	35.1	22.71	22.72	30.48	29.77	27.69
Cr	122	101	97	136	128	126	124	112	125	122	122
V	159	117	123	173	152	158	161	150	166	156	153
Nb	16	15	16	17	16	17	17	17	15	18	18
Zr	142	177	179	137	131	135	152	150	132	155	158
Y	31	35	31	34	31	33	28	32	30	33	32
La	22	17	13	29	22	21	21	21	28	29	21
Ce	61	49	54	62	56	57	63	60	60	60	63
						Ratios					
CIA	71.91	69.56	69.31	71.33	70.21	70.23	72.59	61.49	72.12	68.89	72.1
CIA'	79.48	78.52	77.23	76.79	75.67	77.99	80.08	76.04	77.19	74.82	76.71
CIW	81.46	78.47	78.24	80.89	79.58	79.4	81.45	68.2	82.29	77.59	81.39
PIA	78.2	74.75	74.53	77.48	75.99	75.74	78.36	63.7	78.96	73.82	78.16

constant with an average value of 5.84 suggesting moderate weathering without important fluctuations in weathering intensity. With regard to the Rb/K ratios (generally used as signals of paleoweathering) because both elements are incorporated in clay minerals and also because K is preferentially leached over Rb with increased intensity of weathering (Peltola et al., 2008; Wronkiewicz and Condie, 1990). Very low and homogeneous values of Rb/K ratios (0.059) are found in the sediments, indicating weak to moderate weathering in a warm-humid climate (typical of the Mediterranean area; Scarciglia et al., 2007) with minimal or negligible variations over time (e.g., Mongelli et al., 2012 and references therein).

The V-Ni-La*4 ternary diagram, showing fields

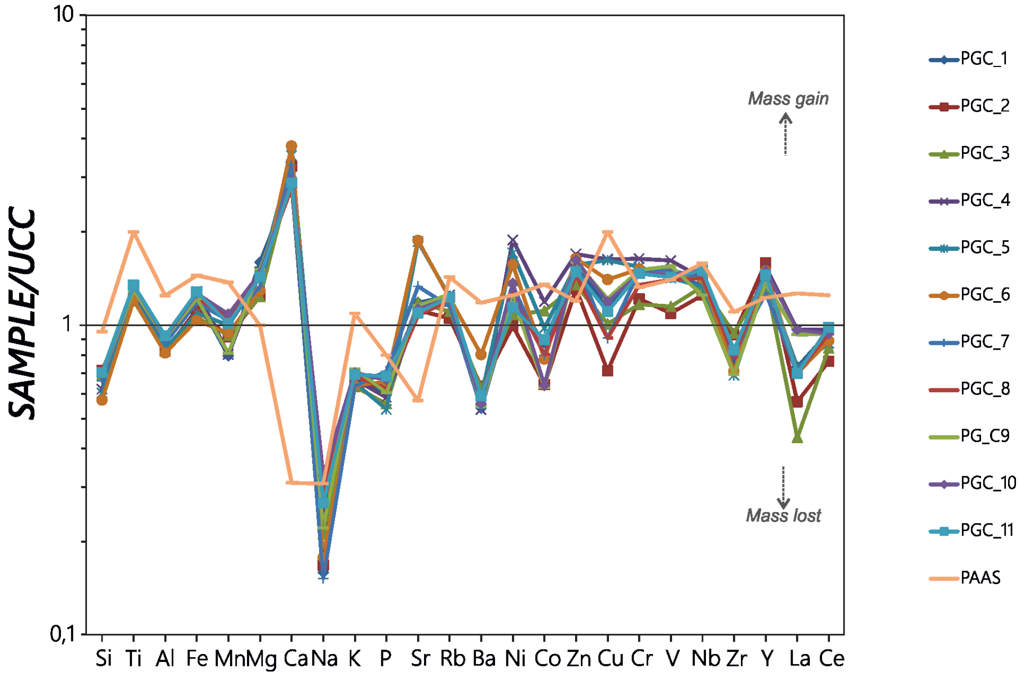

Fig. 8 - Major and trace element average values normalized to the UCC (Upper Continental Crust; McLennan et al., 2006).

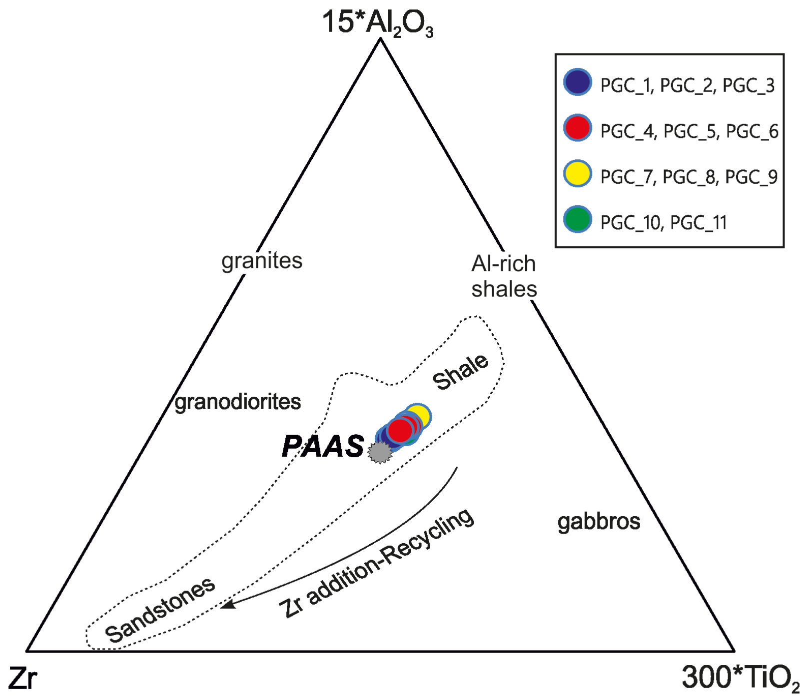

Fig. 9 - Ternary diagram showing the possible sorting effects for the studied samples (after García et al., 1991).

representative of felsic, mafic and ultramafic sources separately (e.g., Perri et al., 2011), indicates that the Crotone Basin samples mainly derived from felsic rocks with a minor mafic supply (Fig. 11A). This behavior is further confirmed by the Cr/V vs Y/Ni and Cr vs Ni diagrams (Fig. 11B) suggesting a provenance from mainly felsic rocks with minor mafic sources that commonly show low ferromagnesian abundances evidenced by an increasing Y/Ni ratio and decreasing Cr/V ratio (see also, Amendola et al., 2016; Hiscott, 1984; Perri et al., 2016, 2017). This is also in accordance with the spider plot diagram (Fig. 8) in which was observed the variations of those elements (Cr, Ni, Fe and Mg) that are well-matched with those of PAAS and UCC.

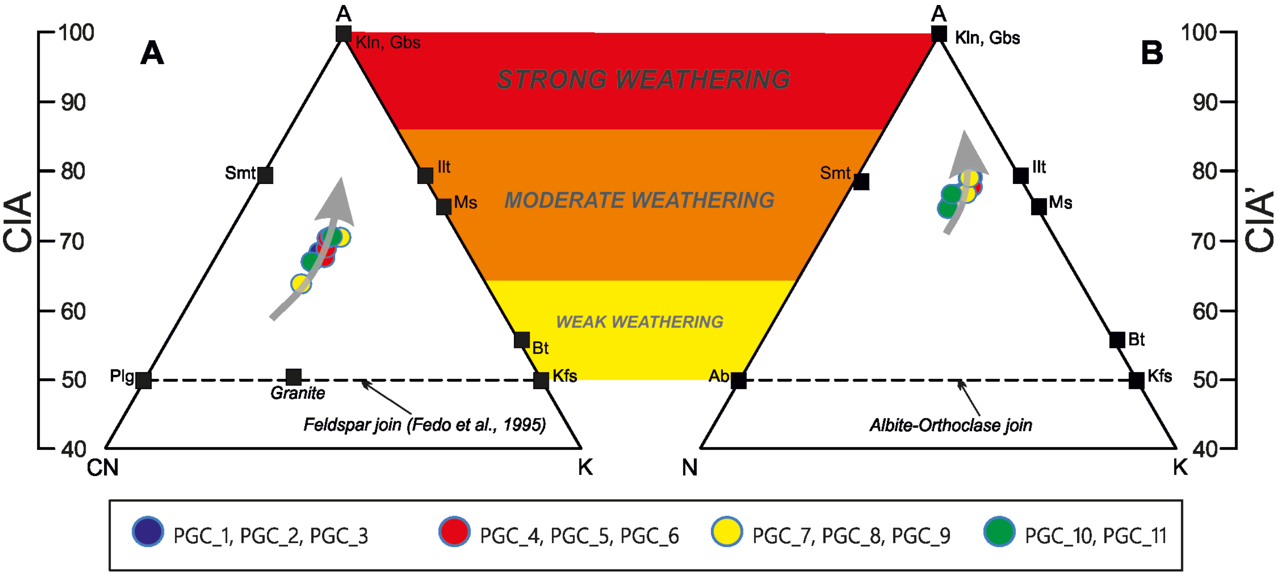

Fig. 10 - Ternary diagram for CIA and CIA'. Ms, muscovite; Ilt, illite; Kln, kaolinite; Gbs, gibbsite; Smt, smectite; Bt, biotite; Kfs, K-feldspar; Pl, plagioclase; A, Al_2O_3; CN, $CaO+Na_2O$; K, K_2O; CIA, Chemical Index of Alteration.

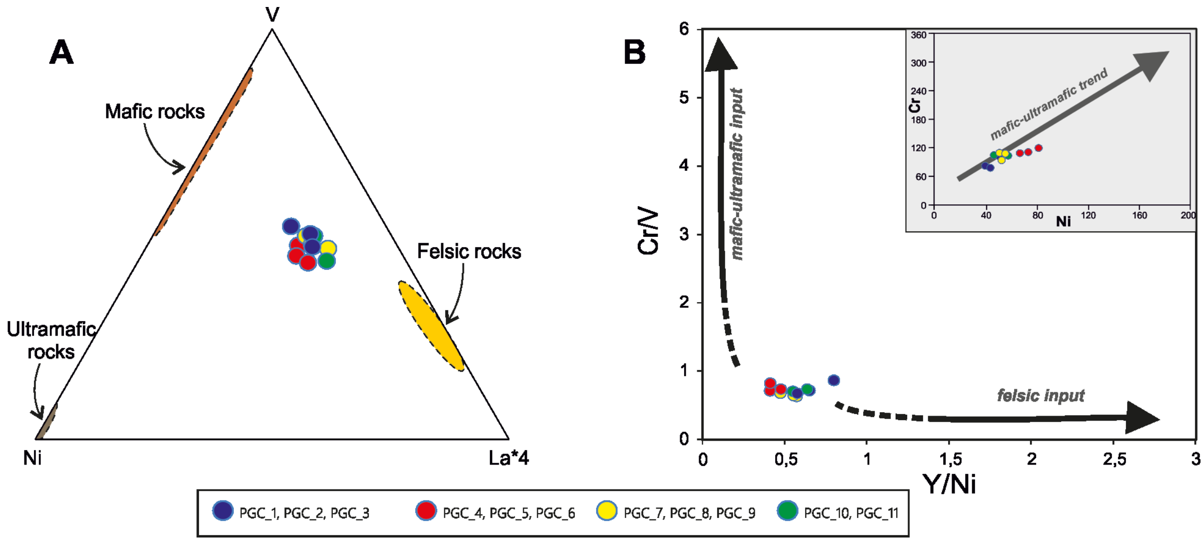

Fig. 11 - A) Ternary diagram of provenance. The colored fields are representative of felsic, mafic and ultramafic rocks. B) Provenance diagram based on the Cr/V vs. Y/Ni and Cr vs Ni relationships (after Hiscott, 1984).

6. CONCLUSIONS

This study highlights the importance of geotechnical and minero-chemical analyses to characterize the physical features and composition of the samples of Cutro Clay Formation. The main results show an abundance of phyllosilicate phases in all samples and medium-low activity for the clayey minerals.

Important considerations on the plasticization of clayey slopes can be made considering the water content. Considering that the sampling took place in June (period that coincided with dry weather conditions) the natural water content measured for some samples shows relatively high values (between a minimum of 20% and maximum values of 30%). Therefore, when comparing the plasticity and liquidity indexes, a plastic behavior can be easily reached. In the rainy season, the water content would certainly be higher and therefore ranging between the liquid and plastic limits or close to the liquid boundary. Therefore, if the water content is already relatively medium-high at the time of sampling (summer season) it means that the samples are made up of moderately swelling minerals like illite/smectite mixed layers. This is well documented by XRD analysis which shows moderate proportions of mixed-layer clay minerals in all samples.

Moreover, interesting observation regarding water retention is the comparison between the ratio between the plasticity index and clay fraction, i.e. the activity index. The activity factor it is important as the presence of a certain content of clay minerals in a soil can have a significant effect on the properties of the soil itself. Furthermore, the identification of the type of clay minerals and their quantity may be necessary in order to predict the behavior of the soil. In fact, the activity is often used as an identification index of the swelling of clay soils. As seen from the obtained results, the presence of the illite and kaolinite is confirmed by the mineralogical analyses which showed an abundance of phyllosilicates.

The comparability of the results obtained from the geotechnical laboratory tests with the diffractometric ones demonstrates the good reliability of the calculation of various limits (liquidity and plasticity) and indices (activity) performed by hand starting from the Atterberg Limits.

The relationships among compositional and mechanical properties of the fine sediments improve the characterization of fine grained soils involved in soil slip phenomena. In particular, the mineralogical characteristics related to the presence of swelling clay mineral affecting by water adsorption and retention, play an important role in controlling the slopes instability in the coastal area of the Crotone Basin (Zecchin et al., 2018). This approach could be crucial to better understand the magnitude and distribution of shallow landsliding events in the soil portions of the weathering profiles.

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