

SUITABILITY ASSESSMENT OF CARBONATE ROCKS FROM THE KATARAKTIS PASSAGE MEMBER OF THE OLOS – PINDOS ZONE (ILEIA PREFECTURE, WESTERN GREECE) FOR INDUSTRIAL APPLICATIONS

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Abstract

The potential industrial uses of Maastrichtian-Paleocene carbonate rocks from the Kataraktis Passage Member of Olos-Pindos Zone from Ileia Prefecture are evaluated based on their petrographic and geochemical characteristics, as well as their physical properties. Moreover, inter-relationships of the physical properties and geochemical composition were determined using simple linear regression analysis, in order to establish their mutual interactions. Investigation of the petrographic and geochemical characteristics of carbonate rocks may contribute to their quality assessment for their use in industrial applications.

Key Words: Limestone, Physical properties, Peloponnesus.

Περίληψη

Στην εργασία αυτή εκτιμώνται οι πιθανές βιομηχανικές χρήσεις των ανθρακικών πετρωμάτων των Στρωμάτων Μετάβασης του Καταρράκτη, ηλικίας Μαιστρίχτιου-Παλαιόκαινου, της ζώνης Πίνδου του Ν. Ηλείας, με βάση τα πετρογραφικά και γεωχημικά τους χαρακτηριστικά καθώς και τις φυσικές τους ιδιότητες. Επιπλέον καθορίστηκαν οι αμοιβαίες σχέσεις των φυσικών ιδιοτήτων και της γεωχημικής σύστασης με τη χρήση γραμμικής ανάλυσης παλινδρόμησης με σκοπό να καθοριστούν και οι αλληλεπιδράσεις των ιδιοτήτων αυτών. Η διερεύνηση των πετρογραφικών και γεωχημικών χαρακτηριστικών των ανθρακικών πετρωμάτων μπορεί να συμβάλει σημαντικά στην εκτίμηση της ποιότητας τους για χρήση τους σε βιομηχανικές εφαρμογές.

Λέξεις Κλειδιά : Ασβεστόλιθοι, Φυσικές ιδιότητες, Πελοπόννησος.

1. Introduction

Limestones are industrial rocks mainly used as construction, concrete and road aggregates, as well as dimension stones and fillers. Ground limestone is widely used to raise the pH of acid soils and as additive in fertilizers. Large amounts of limestone are used in blast furnaces as slag conditioners and in the steel production to form slag. Physical and geotechnical properties of Cretaceous and Maastrichtian-Paleocene limestones from different localities have been studied by several authors (Spyropoulos, 2007; Sabatakakis *et al.*, 2008; Mpalatsas *et al.*, 2010; Koulouris, 2011; Tseni *et al.*,

preserved as thrust imbricated slices (Degnan and Robertson, 1998) and includes pure limestone deposition at its base, comprising the investigated rocks, with increasing clastic input towards the top. The increased input of terrigenous clastic sediments to the basin during Late Cretaceous-Paleocene suggests that relative sea-level fell because of the erosion to the continental basement to the west and north. The member is dated as Maastrichtian-Paleocene and is marked by the disappearance of *Globotruncana sp.* and *Globorotalia sp.* (Degnan, 1998). Finally, the Late Palaeocene-Early Eocene Pindos flysch lies at the top of the pile, likely extending also to Mid-Eocene age in the SE Peloponnesus (Piper, 2006).

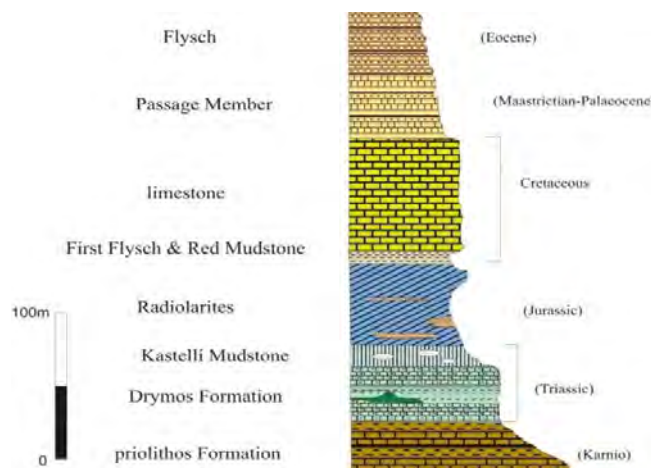


Figure 2 – Simplified stratigraphic section of the Pindos zone at Ileia Prefecture.

3. Analytical Methods

Determination of physical properties of the limestones was conducted in the Research Laboratory of Minerals and Rocks, Department of Geology, University of Patras. The insoluble residue was determined after digestion in 25 vol.% acetic acid (Hirst and Nicholls, 1958). The organic carbon content was determined with titration according to Walkley and Black (1934).

A Hunter color measuring system (Hunter Color Diff. Meter, Miniscan XE plus, Hunter Associates Laboratory Inc., Reston, VA) was used to measure the color. Individual corms were cut transversely and each sample was measured twice for color values. The information given by L*, a*, and b* is generally expressed as the total color, with L* representing the brightness or dullness, a* for redness to greenness, and b* for yellowness to blueness. The color properties of the carbonate powder were measured according to the CIELAB system using a Diffusion Systems. The source UV content is nominal match to D65 with port diameters 45/0.

The physical properties investigated included moisture content (ASTM D2216), water absorption (ASTM C97-47), bulk specific gravity (AASHTO T100-T85) and apparent specific gravity (AASHTO T147). Three tests were performed for each property and the mean values were recorded. Porosity values (n %) were calculated on rock powders using a pycnometer, according to the ISRM (1981) specification. The total volume of pores is calculated as the difference between the volume of the specimen and that of the powdered particles. Whole rock chemical analyses were performed at Activation Laboratories LTD, Ancaster, Ontario, by fusion ICP-OES for major elements and combined ICP-MS and INAA for trace elements. Detection limit for major elements is 0.01%, except for TiO₂ which is 0.005%. Replicate analyses suggest precision better than 5% for major elements and most trace elements. The determination of CO₂ was carried out by coulometry.

4. Results

4.1. Petrographic Characteristics

Petrographic study was performed on twenty thin sections, which were classified according to the schemes of Dunham (1962) and Folk (1959, 1962). Allochems are represented by fossil remains, intraclasts and lithoclasts.

Mudstones with bioclasts or *fossiliferous micrites* contain micritic calcite with few skeletal grains (5-15%) represented principally by pelagic foraminifera. *Wackestones* with pelagic foraminifera or *packed biomicrites* are also composed predominately of micritic matrix that supports packed distributed bioclasts (Figure 3a). The petrographic investigation reveals different types of porosity (after Choquette and Pray, 1970; Scholle and Ulmer-Scholle, 2003), which are represented by vug and intraparticle porosity (Figure 3b) along with irregular microchannels of stylolites, which are often associated with insoluble residue (mainly clay minerals), accumulated as a consequence of pressure-induced dissolution. Laminated *wackestone-packstone* include pelagic foraminifera, ranging in size from 50-250µm. The lamination comprises skeletal grains such as pelagic foraminifera (Figure 3c) and bioclast in size of fine sand and some lithoclast such as detrital grains of quartz, chlorite and muscovite (Figure 3c, d). Calcite veins and stylolites occur, too.

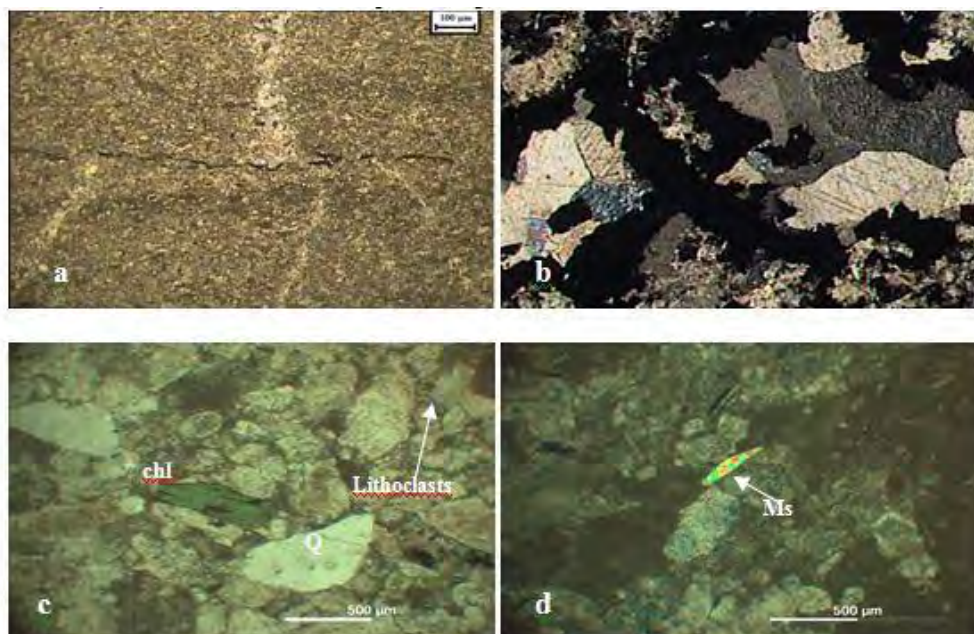


Figure 3 – Photomicrographs of representative carbonate samples from the Kataraktis Passage Member: (a) wackestone with packed bioclasts; calcite veins and a stylolite filled with clay minerals are also present (sample DHL7G, plane polarized light); (b) vug porosity filled with sparry calcite (sample DHL7A, crossed polarized light); (c, d) laminated wackestone-packstone with pelagic foraminifera and detrital grains of quartz (Q) and chlorite (chl) and muscovite (Ms) (sample DHL16B, crossed polarized light).

4.2. Physical Properties

The results of physical and physicochemical properties of the studied samples were determined from the mean values of three measurements and are listed in Table 1. Moisture contents of the Maastrichtian-Paleocene carbonates are rather low (0.06-0.07%), whereas their water absorption values range between 0.05-0.57. These values are lower than the underlying Cretaceous limestone from the Pindos Zone in the Ileia Prefecture (Tseni *et al.*, 2012). Density is one of the most

Table 1 – Mean values, range and standard deviation (sd) of physical and physicochemical properties of the Maastrichtian-Paleocene carbonate samples from the Ileia Prefecture.

Sample	DHL7A			DHL7G			DHL16A			DHL16B			PK1A		
	Wackestone			wackestone			laminated wackestone-packstone			laminated wackestone-packstone			wackestone		
	mean	range	sd	mean	range	sd	mean	range	sd	mean	range	sd	mean	range	sd
Rock-type (after Dunham, 1962)															
moisture content (%), n=3	0.07	0.06-0.09	0.015	0.06	0.05-0.07	0.010	0.070	0.06-0.09	0.016	0.060	0.489-0.493	0.002	0.070	0.065-0.074	0.005
water absorption (%), n=3	0.25	0.23-0.27	0.021	0.050	0.03-0.09	0.031	0.570	0.47-0.65	0.096	0.490	0.45-0.53	0.040	0.160	0.14-0.185	0.023
void ratio (%)	1.11	1.08-1.15	0.035	1.100	1.09-1.13	0.021	2.330	2.24-2.42	0.091	2.350	2.34-2.41	0.038	1.870	1.78-1.94	0.080
Apparent specific gravity (g/cm ³), n=3	2.70	2.69-2.72	0.015	2.730	2.69-2.77	0.042	2.580	2.54-2.65	0.059	2.550	2.51-2.63	0.064	2.680	2.65-2.72	0.035
bulk specific gravity (g/cm ³), n=3	2.73	2.73-2.76	0.015	2.760	2.73-2.78	0.025	2.640	2.61-2.66	0.026	2.610	2.59-2.65	0.035	2.730	2.69-2.77	0.040
total porosity (%)	0.53	0.5-0.58	0.040	0.520	0.49-0.55	0.031	0.700	0.703-0.706	0.002	0.700	0.61-0.79	0.090	0.650	0.68-2.76	0.042
L	92.42	92.33-92.55	0.111	90.100	89.65-90.25	0.317	89.460	89.458-89.463	0.003	78.160	77.23-79.52	1.165	94.980	94.33-95.35	0.572
a*	0.35	0.31-0.38	0.035	0.300	0.24-0.35	0.056	0.350	0.347-0.351	0.002	1.410	1.33-1.47	0.071	0.400	0.38-0.44	0.032
b*	3.54	3.51-3.56	0.025	6.260	6.15-6.34	0.097	5.690	5.688-5.692	0.002	5.080	4.85-5.39	0.279	3.970	3.97-3.985	0.010
insoluble residue (%)	0.05	0.03-0.09	0.031	0.010	0.08-0.12	0.025	2.010	2.007-2.012	0.003	3.260	3.16-3.97	0.407	0.010	0.07-0.11	0.020
TOC (%), n=3	0.08	0.04-0.11	0.035	0.080	0.06-0.11	0.026	0.200	0.199-0.202	0.002	0.250	0.21-0.29	0.040	0.040	0.038-0.046	0.004

important properties of rocks, mainly controlled by their texture and mineral composition. The bulk density depends on petrographic and structural features of the diagenetic processes and geotectonic conditions (Trafimov and Karalov, 1993; Rashed and Sediek, 1997). Bulk specific gravity ranges from 2.61 to 2.76 g/cm³, in the investigated lithologies. Total porosity, which is an important factor in rock strength since a small change in pore volume can produce appreciable mechanical effect (ISRM, 1981), ranges between 0.52 and 0.70%. Laminated wackestone packstone samples of the formation have higher porosities. The total organic carbon is low ranging from 0.04 to 0.25%, while the insoluble residue shows a wider range of 0.05-3.26%. Samples DHL16A and DHL16B (laminated wackestone-packestone) with the highest total organic carbon and insoluble residue values are found towards upper members, unlike the rest samples that lie at the base of the Kataraktis Passage Member. Moisture content and bulk density are inversely correlated to the insoluble residue (Figure 4a, b), suggesting that clay minerals are not the prevalent water absorbents. The TOC is inversely correlated to the color index L with the following the empirical equation $TOC = -0.0122L + 1.2179$ with a correlation coefficient $R^2=0.75$ (Figure 4c). From Figure 4d it is clear that the bulk density of the Kataraktis member limestones decreases with increasing porosity.

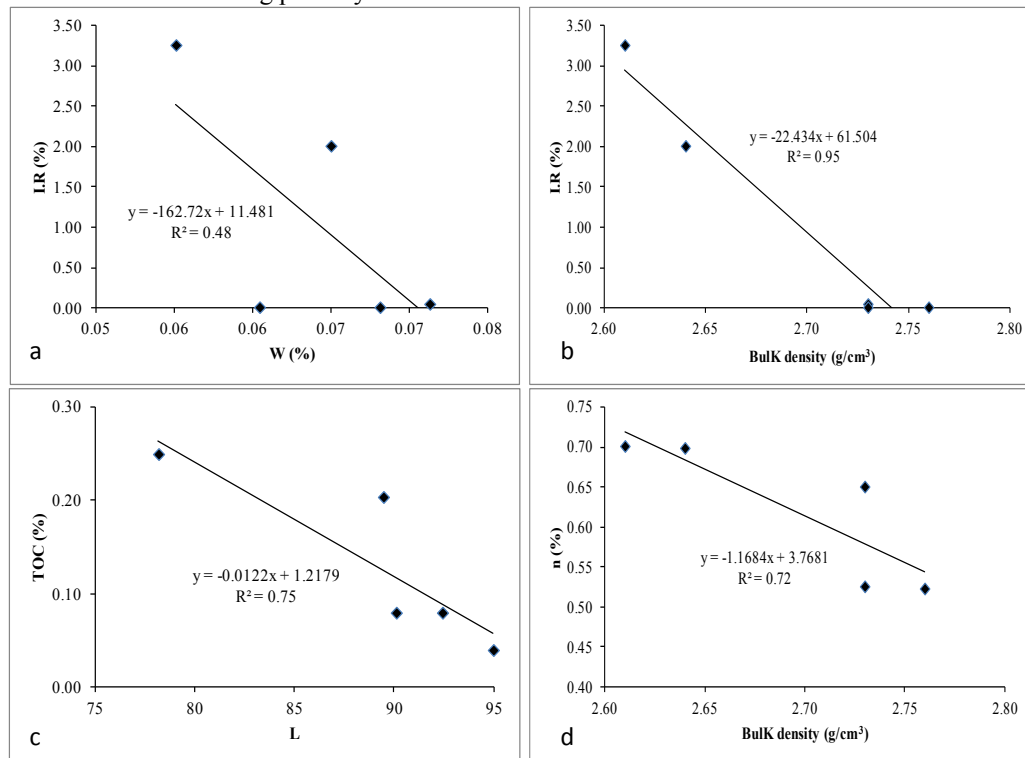


Figure 4 – Correlation diagrams of: a) moisture content (W) with insoluble residue (I.R.); b) bulk density with insoluble residue (I.R.); c) color index L with total organic carbon; d) bulk density with total porosity (n).

4.3. Geochemical Affinities

Whole-rock geochemical analyses from representative carbonate rocks are listed in Table 2. The CaO contents of the analyzed samples vary between 38.40 and 55.67 wt. %. According to the chemical classification based on CaCO₃ content (Oates, 1998), samples DHL7G and PK1A (wackestone with bioclasts) are calcium limestone of high purity (CaCO₃ = 97-98.5%) whereas samples DHL7A (mudstone with bioclasts) and DHL16A (laminated wackestone with bioclasts) are median purity limestones (CaCO₃=93.5-97.0%); sample DHL16B is a poor purity limestone

containing abundant siliciclastic material. The total amount of impurities (sum of all oxides excluding CaO and CO₂) for the four samples except DHL16B, is rather low to moderate (Table 2). The concentrations of MgO, Fe₂O₃, MnO and Na₂O are low in the analyzed samples. The low concentration of phosphorus reflects the absence of apatite in the samples (Parekh *et al.*, 1977;

Table 2 – Whole-rock geochemical analyses of representative samples of Cretaceous and Maastrichtian-Paleocene limestones from Ileia Perfeture (Fe₂O₃^t: total Fe as Fe₂O₃; -: below detection limit).

Sample	DHL7A	DHL7C	DHL16A	DHL16B	PK1A
<i>Major elements (wt. %)</i>					
SiO ₂	1.93	1.73	1.43	20.32	0.92
Al ₂ O ₃	0.32	0.21	0.33	2.95	0.18
Fe ₂ O ₃ ^t	0.23	0.19	0.25	1.10	0.15
MnO	0.05	0.05	0.13	0.10	0.04
MgO	0.37	0.42	0.64	1.02	0.31
CaO	54.64	55.09	54.17	38.40	55.67
Na ₂ O	0.08	0.06	0.22	0.73	0.03
K ₂ O	0.13	0.07	0.08	0.47	0.06
TiO ₂	0.01	0.01	0.01	0.19	0.00
P ₂ O ₅	0.01	0.01	0.09	0.06	0.02
LOI	43.20	43.13	42.74	34.72	43.14
Total	101.00	101.00	100.10	100.10	100.50
CaCO ₃	96.87	97.25	96.81	73.05	98.32
<i>Trace elements (ppm)</i>					
Ag	0.7	-	-	-	0.6
As	-	-	-	2	-
Ba	12	7	-	495	6
Co	6	4	9	19	4
Cr	5	5	12	124	3
Cs	-	-	-	0.7	-
Cu	13	6	6	7	4
Hf	-	-	-	1.5	-
Ni	7	2	9	40	3
Pb	-	-	9	10	-
S	110	150	590	1010	90
Sb	-	-	-	0.2	-
Sc	0.4	0.4	0.6	2.9	0.4
Sr	600	508	513	372	671
Th	-	-	-	1.3	-
U	-	-	1.2	1.2	-
V	-	-	12	23	-
W	10	21	88	186	25
Y	5	4	11	10	2
Zn	4	5	5	20	4
Zr	21	12	4	62	15

Cullers, 2002). Chemical analyses for the amount of trace elements show that only one sample (DHL16B) present higher concentrations of Cr and Ni compared to the other samples. Sulfur content is fairly coherent displaying inconsiderable variations between 90 and 150 ppm (apart from sample DHL16A with S = 1010 ppm). Sr was detected in all samples, however the amount of Sr in the wackestone with bioclast (PK1A) is higher than the rest samples. Sr is easily mobilized during weathering, especially in oxidizing, acid environments, thus it is incorporated in clay minerals (Kabata-Pendias 2011). Sample DHL16B displays high Ba contents. Ba is also strongly adsorbed by clay minerals and it commonly substitutes for K in feldspars (Kabata-Pendias 2011). Sample DHL7A demonstrates the highest Cu values compared to the remaining samples

5. Discussion-Conclusions

The Maastrichtian-Paleocene carbonate rocks of the Kataraktis Passage Member are divided into 3 microfacies: (i) mudstones with bioclast, (ii) wackestones with bioclast, and (iii) laminated wackestone-packstone. The color index L is negatively correlated with TOC, suggesting that increasing organic components in carbonate rocks have a negative affection on their whiteness, high values of which are commonly desirable in most applications. Organic matter, in carbonate rocks, may shows variable compositions and amounts and may affect their properties. A considerable amount of some impurities may be acceptable in carbonate rocks for some uses, if they are finely disseminated throughout the rocks. On the other hand, if the impurities are concentrated in distinct laminae, they may form planes of weakness that seriously affect the performance of the rocks (Boynton, 1980; Harben, 1992; Carr *et al.*, 1994; Oates, 1998; Christidis *et al.*, 2004).

The CaCO₃ content in all analyzed samples exceeds 96.5%, except sample DHL16B with CaCO₃ = 76% (Table 2). The high SiO₂ and Al₂O₃ contents in sample DHL16B are consistent with the presence of quartz and clay minerals in its insoluble residue. Ba content is low in all samples, except DHL16B with rather high Ba contents (Table 2), likely related to its significant amounts of clay minerals (Kabata-Pendias 2011).

The CaCO₃ content in the Maastrichtian-Paleocene carbonates from the Kataraktis Passage Member exceeds the limit of 65%. Furthermore their MgO content is small indicating that these carbonate rocks could be suitable as calciferous raw material for cement production. Also, the insoluble residue, the total organic carbon and the color index, which affect the rock properties, suggest that all samples are suitable for cement production, apart from and the laminated wackestone-packstone of the Maastrichtian-Paleocene limestone (sample DHL16B).

All the studied limestones are suitable as pH regulators in acid soils as well as additives in fertilizers since CaCO₃ content exceeds 60% and their MgO contents are below 5%. Finally all examined samples (except the laminated wackestone-packstone sample DHL16B) are suitable for desulphurization of exhaust gases since their CaCO₃ contents exceed 95% while their concentrations in Al₂O₃ (< 1%), SiO₂ (<2%) and MgO (<2%) are low.

From this study, it is evident that petrographic investigation coupled with mineralogical and geochemical analysis is useful for preliminary assessment of limestones' quality.

6. Acknowledgments

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