

INVESTIGATION OF THE MINERALOGICAL PETROGRAPHIC, GEOCHEMICAL AND PHYSICAL PROPERTIES OF CARBONATE ROCKS FROM ILEIA PREFECTURE AND ASSESMENT FOR INDUSTRIAL APPLICATIONS

Tseni X.¹, Koutsopoulou, E.¹, Tsikouras B.¹, Hatzipanagiotou K.¹

¹University of Patras, Department of Geology, Section of Earth Materials, 265 00 Patras, Greece
tseni@upatras.gr, ekoutsop@upatras.gr, v.tsikouras@upatras.gr, k.hatzipanagiotou@upatras.gr

ABSTRACT

Research on carbonate rocks has been increasingly important during the last few decades, due to their numerous applications. In this paper, we examined the properties of Cretaceous carbonate rocks from the Olonos-Pindos Zone from Ileia Prefecture. The relationships between various physical properties and between petrographic features and physical properties were defined. This may lead to preliminary evaluation of carbonate rocks using microscopic investigation, which unlike the elaboration of a series of physical and mechanical properties, is a fast and inexpensive method. In addition, these properties, along with their geochemical characteristics, were used to assess the suitability of these carbonate rocks as fillers in various applications. Detailed petrographic study of the collected samples revealed the occurrence of biomicrite, intramicrite (mudstone και wackestone), biosparite (packstones and grainstones), intrasparite and rudstone. From the lower to the upper members, a decrease of the grain size of calcite is observed. X-ray diffraction study of the insoluble residue revealed the presence of quartz, chlorite, illite, smectite, and mixed layer illite-chlorite. The colour index of the investigated powdered samples is negatively influenced by the increase of organic and insoluble residue contents. The water absorption is inversely correlated with CaO content while moisture is positively correlated with insoluble residue. The grainstone and rudstone are characterized as ultra-high pure calcium limestones, except for Mg-rich crystalline dolomitic limestones. The packstones are calcium limestones of high to medium purity. Mudstones and wackestones are characterized as low calcium limestones. The results suggest that all the examined lithotypes can be used as soil conditioners and animal feed supplements; however only grainstones and rudstones are suitable for desulfurization of exhaust gasses and cement production.

Key Words: *limestone, physical properties, Pindos Zone, Peloponnesus*

ΔΙΕΡΕΥΝΗΣΗ ΤΩΝ ΟΡΥΚΤΟΠΕΤΡΟΓΡΑΦΙΚΩΝ, ΓΕΩΧΗΜΙΚΩΝ ΚΑΙ ΦΥΣΙΚΩΝ ΙΔΙΟΤΗΤΩΝ ΑΝΘΡΑΚΙΩΝ ΠΕΤΡΩΜΑΤΩΝ ΤΟΥ ΝΟΜΟΥ ΗΛΕΙΑΣ ΚΑΙ ΕΚΤΙΜΗΣΗ ΤΗΣ ΚΑΤΑΛΛΗΛΟΤΗΤΑΣ ΤΟΥΣ ΣΕ ΒΙΟΜΗΧΑΝΙΚΕΣ ΕΦΑΡΜΟΓΕΣ

Τσένη Ξ., Κουτσοπούλου Ε., Τσικούρας Β., Χατζηπαναγιώτου Κ.

Περίληψη

Η έρευνα των ανθρακικών πετρωμάτων σε παγκόσμια κλίμακα παρουσιάζει τις τελευταίες δεκαετίες αυξανόμενους ρυθμούς, γιατί παρέχουν πληροφορίες για την εξέλιξη της τοπογραφίας και τις συνθήκες που επικρατούσαν στην επιφάνεια της Γης κατά τη γένεση τους και επειδή μπορούν να αποτελέσουν εξαίρετη πρώτη ύλη σε πολυάριθμες βιομηχανικές εφαρμογές. Επιπλέον παίζουν σημαντικό ρόλο στη γεωλογία πετρελαίου ως μητρικά πετρώματα και ταμειυτήρες (Tissot and Velte, 1984). Στη εργασία αυτή εξετάζεται η δυνατότητα αξιοποίησης των ανθρακικών πετρωμάτων του Ν. Ηλείας ως πληρωτικών υλικών. Τα δείγματα των ανθρακικών πετρωμάτων ελήφθησαν από τη γεωτεκτονική Ζώνη Ωλονού-Πίνδου, είναι Κρητιδικής ηλικίας και αντιπροσωπεύονται, με βάση την ορυκτολογική τους σύσταση, από ασβεστόλιθους και δολομιτικούς ασβεστόλιθους. Ιδιαίτερη προσοχή δόθηκε στη συσχέτιση των ορυκτοπετρογραφικών με τις φυσικές ιδιότητες, με σκοπό να εκτιμηθεί η ποιότητα των ασβεστόλιθων με βάση την μικροκοπική τους εξέταση, η οποία είναι απλή και μη δαπανηρή μέθοδος σε σύγκριση με την εκπόνηση δοκιμών φυσικών ιδιοτήτων. Τα δείγματα εξετάστηκαν σε πολωτικό μικροσκόπιο και έγινε παρατήρηση των ιστολογικών χαρακτηριστικών τους, του μεγέθους των κόκκων τους και της ορυκτολογικής τους σύστασης. Η ταξινόμηση τους έγινε σύμφωνα με τα συστήματα ταξινόμησης των Folk (1959, 1962) και Dunham (1962) και βρέθηκε ότι τα δείγματα που συλλέχθηκαν είναι βιομικρίτες, ενδομικρίτες (mudstone και wackestone), βιοσπαρίτες (packstones και grainstones), ενδοσπαρίτες και rudstone. Επίσης υπολογίστηκε το αδιάλυτο υπόλειμμα, το οποίο στη συνέχεια εξετάστηκε με τη μέθοδο της περιθλασιμετρίας ακτίνων Χ. Από την ανάλυση των περιθλασιογραμμάτων προέκυψε ότι σε αυτό το μη ανθρακικό υλικό συμμετέχουν χαλαζίας, αλκαλικοί άστριοι, χλωρίτης, ιλλίτης, βερμικουλίτης, σμεκτίτης και άργιλοι με μικτή δομή ιλλίτη-χλωρίτη. Επιπρόσθετα, σε σκόνες των δειγμάτων προσδιορίστηκαν οι δείκτες χρώματος, με το δείκτη λευκότητας να κυμαίνεται από 78 έως 95. Επιπλέον στα δείγματα προσδιορίστηκε και η συμμετοχή του οργανικού υλικού και φάνηκε ότι πρόκειται για ασβεστόλιθους χαμηλής περιεκτικότητας σε οργανικό υλικό. Η λευκότητα των υλικών επηρεάζεται αρνητικά από την παρουσία του οργανικού υλικού και των οξειδίων του Fe, καθώς η παρουσία τους συμβάλλει στην υποβάθμιση της ποιότητας τους. Με αύξηση του περιεχόμενου ανθρακικού ασβεστίου μειώνεται η υδαταπορροφητικότητα, ενώ η περιεχόμενη υγρασία συσχετίζεται θετικά με το αδιάλυτο υπόλειμμα. Επίσης, υπολογίστηκε η χημική σύσταση των ασβεστόλιθων που συλλέχθηκαν. Με βάση τη περιεκτικότητα τους σε CaCO_3 , οι rudstone και οι grainstones χαρακτηρίζονται ως υλικά υψηλής καθαρότητας, με εξαίρεση το δολομιτικό ασβεστόλιθο, οι packstones ταξινομούνται ως υλικά υψηλής και μέσης καθαρότητας ενώ οι mudstone και wackestone αποτελούν πετρώματα χαμηλής καθαρότητας. Γενικά τα δείγματα στα οποία κυριαρχούν σπαριτικοί κρύσταλλοι εμφανίζουν υψηλότερη καθαρότητα και λευκότητα σε σύγκριση με αυτά στα οποία κυριαρχεί μικριτικό υλικό. Τέλος, πραγματοποιήθηκε συγκριτική μελέτη των εργαστηριακών αποτελεσμάτων με σκοπό αφενός να διαπιστωθούν οι μεταξύ τους σχέσεις μέσω στατιστικών παραμέτρων και αφετέρου να διερευνηθεί αν πληρούν προδιαγραφές για την αξιοποίησή τους σε βιομηχανικές εφαρμογές. Η στατιστική ανάλυση των φυσικών ιδιοτήτων των ασβεστόλιθων με απλή γραμμική παλινδρόμηση έδειξε πολύ καλούς έως εξαιρετικούς συσχετισμούς. Τέλος

προέκυψε ότι όλοι οι λιθότυποι που εξετάστηκαν μπορούν να χρησιμοποιηθούν ως εδαφοβελτιωτικά (διότι περιέχουν $Mg < 5\%$), και είναι κατάλληλοι για χρήση ως συμπληρώματα ζωικών τροφών, ενώ μόνο οι grainstone και οι rudstone είναι κατάλληλοι για παραγωγή τσιμέντου και για περιβαλλοντικές εφαρμογές όπως η αποθείωση των καυσαερίων.

Λέξεις Κλειδιά: Ασβεστόλιθοι, Ζώνη Πίνδου, Φυσικές Ιδιότητες, Πελοπόννησος

1. Introduction

Limestones are industrial rocks which are mainly used as crushed rocks for construction purposes, as dimension stones and fillers in concrete, and as road aggregates. Generally, limestone can be used in cement when the Mg content is below 5%, because high Mg contents causes expansion after setting, hence reducing its strength. Ground limestone is widely used to raise the pH of acid soils, as well as an additive in fertilizers and animal foodstuffs. Large amounts of limestone are used in blast furnaces as slag conditioners and in the steel production to form slag; however the large amounts of energy that required to decompose limestone to lime generally limits its use. Limestone is widely used as a fluxing agent in smelting of metals, as well as in bauxite processing and production of alumina. The most widespread use of limestone is the production of quicklime.

Petrophysical properties of sedimentary rocks are influenced by size, shape, and packing of grains, porosity, cement and matrix content, all controlled strongly by depositional fabric and postdepositional processes. This paper aims at investigating the physical properties of Cretaceous limestones from the Pindos Zone of Ileia Prefecture, in order to establish their inter-relationships, to study the relationships of physical properties with their petrographic characteristics and to evaluate their suitability as indus-

trial rocks in various applications. These limestones are the most abundant in the investigated area occupying approximately 72 km², including a large variety of different lithotypes. They are also of potential industrial interest; hence study of their physical properties is important.

Geological setting

The geological setting of the Ileia Prefecture, west Peloponnesus, is characterized by the presence of the Ionian, the Gavrovo-Tripolitza and the Olonos-Pindos geotectonic Zones. During the Mesozoic, the Ionian zone corresponded to a vast, intra-platform rift basin bounded on both sides by shallow platforms (Katsikatsos 1992). The early shallow character, of the Ionian basin, during the pre-rift period, is reflected on its older rocks, which include the Permian-Triassic evaporites and dolomites and the neritic Pantokrator limestones of Upper Triassic age, extending mainly to the west part of the study area. During the Lower Jurassic – Upper Jurassic rift period, the Lower siliceous shales with Posidonomya, the red-blue limestones with ammonites (Ammonitico Rosso), the filamentous limestones and the Upper siliceous shales with Posidonomya were deposited (Renz, 1955). The syn-rift formations are overlain by the Upper Jurassic – Lower Cretaceous pelagic Vigla Limestone Formation (Aubouin, 1959; Karakitsios and Koletti, 1992; Karakitsios et al., 2004). The Gavrovo-Tripolitza

Zone includes shallow platform carbonate rocks of Cretaceous-Eocene age, which are covered by vast quantities of detrital sediments (De Wever, 1975; Fleury, 1980). The sedimentary rocks of the Pindos Zone (Fig. 1) originate from an elongate remnant ocean basin that formed during mid-Triassic, consisting typically of deep-water carbonate, siliciclastic and siliceous rocks, ranging in age from Late Triassic to Eocene, covered by thick detrital, late Paleocene to Oligocene flysch sediments (Fleury, 1980; Robertson et al., 1991; Robertson, 1994; Degnan and Robertson, 1998; Degnan and Robertson, 2006).

The lower stratigraphic unit in the Pindos Zone is the Priolithos formation of Kar-

nian age comprising medium-grained sandstone with mudstone intercalations (Fig. 2). Overlying to the Priolithos formation is the Drimos formation composed of turbiditic and hemipelagic limestone. The Lestenna formation overlies the Drimos formation comprising, from bottom to top, the Kastelli mudstone member, mainly composed of multicolored mudstone, the Aroania member, consisting of Jurassic radiolarites and the first flysch, which includes pelites, limestone and sandstone, red mudstone. Subsequently, Lower Cretaceous to Maastrichtian, redeposited limestone and pelagic limestone were formed. The Kataraktis Passage member overlies this formation, comprising the transition from car-

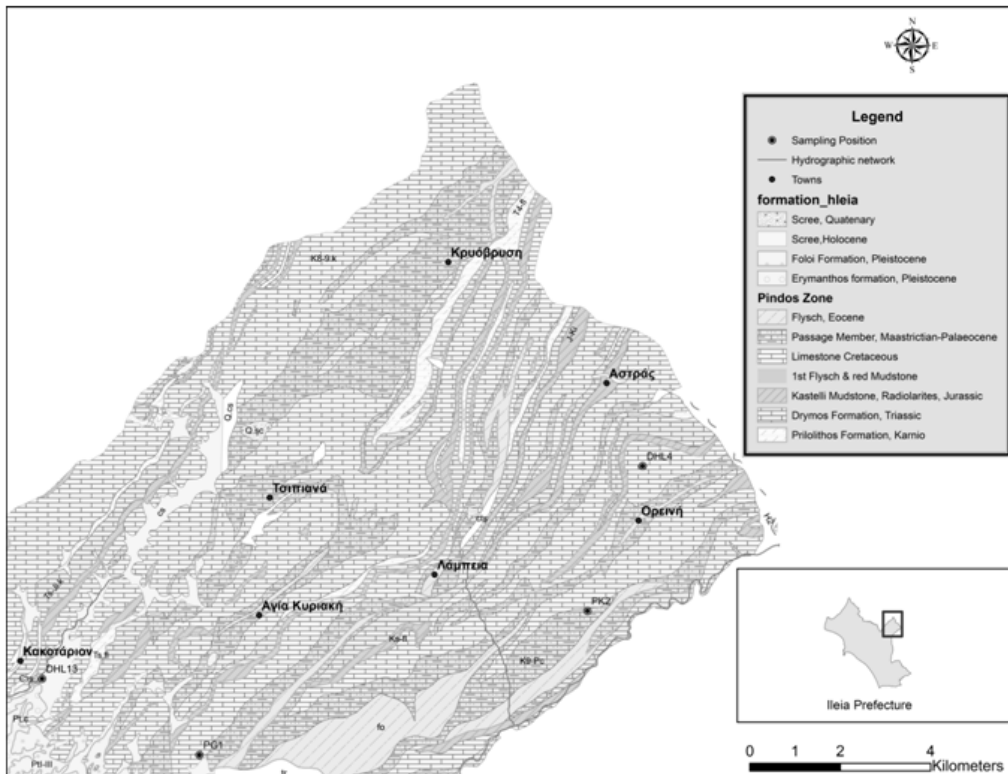


Fig. 1. Geological map of eastern Iliia Prefecture.

Εικ. 1. Γεωλογικός χάρτης της περιοχής της ανατολικής Ηλείας.

bonate to detrital sedimentation. It includes pure limestone deposition at its base with increasing clastic input towards the top. 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 Peloponnese (Piper, 2006). The investigated Cretaceous carbonate rocks record a transitional time period between major orogenic cycles in the Hellenides (Kaf-

ousia et al., 2010). These cycles culminated in the latest Jurassic – Early Cretaceous (Eohellenic phase) and the latest Cretaceous to Tertiary (Mesohellenic and Neohellenic phases) and led to the westerly directed progressive suturing of the Hellenides (Neumann and Zacher, 2004).

Analytical methods

Determination of physical properties of

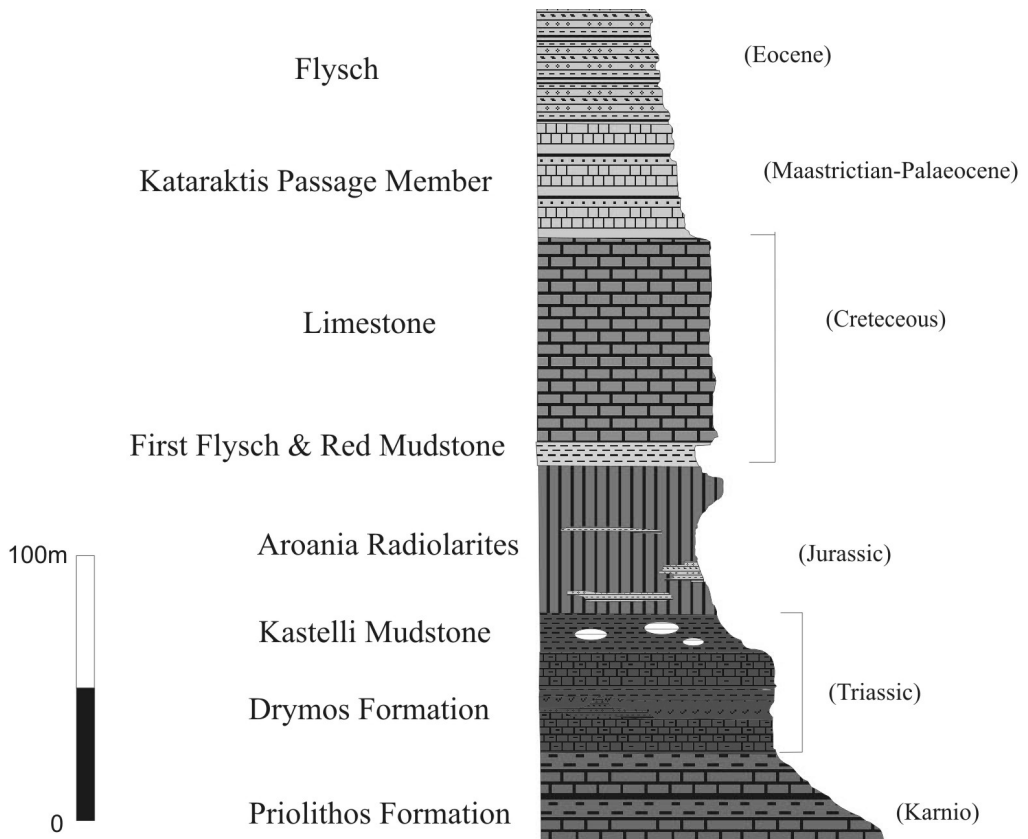


Fig. 2. Simplified stratigraphic section of the Pindos zone at Ileia Prefecture.

Εικ. 2. Απλοποιημένη στρωματογραφική διάρθρωση της Ζώνης Πίνδου στο Ν. Ηλείας.

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 mineralogical composition of the insoluble residue was determined by X-Ray Diffraction (XRD), using a Bruker D8 Advance diffractometer equipped with a LynxEye® detector, at a 3-70° 2θ range with, a scanning step of 0.015° and 0.2 seconds time per step. The diffractograms were evaluated using the EVA v.12 software. The clay mineralogy was determined from three XRD patterns in oriented samples (after air-drying at 25°C, with ethylene glycol treatment, and after heating at 490°C for 2 hours). 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 thrice 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 colour 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.

Results

Petrography

Thirty five samples were collected from the Cretaceous limestones and petrographically examined, representing the whole stratigraphic sequence and geographic distribution. The investigated samples were classified after the classification schemes of Dunham (1962) and Folk (1959, 1962). The observed lithotypes include medium-sorted rudstones or oolite-trabecular microsparite, which are clast-supported monomict rocks but matrix supported fabric are also detected. Clasts are sub-rounded, mostly composed of micrite and dark oolites (Fig. 3a). Other clasts include reworked limestone containing benthic foraminifera (textularia, miliolidae) (Fig. 3b). These samples occur at the slope of the pelagic formations attached to the Gavrovo-Tripolitza Zone. Coarse crystalline, sub-hedral dolostones contain rhombohedral dolomite grains (Fig. 3c), which frequently display cloudy cores and clear rims (a common feature in replacement dolomite) that have completely obliterated primary fabric and micritic matrix.

These samples are classified as crystalline dolomitic limestones according to Dunham (1962) and as dolocalcitic sparstones according to Wright (1992). Primary and secondary types of porosity were also observed and classified according to the Choquette and Pray (1970) scheme (Fig. 3d). Mudstones or dismicrites contain micritic calcite while mudstones with bioclasts or-fossiliferous micrites contain micritic calcite with bioclasts mainly foraminifera (Figs 4a, b). Wackestones or mudstones with bioclasts are composed predominately of

micrite matrix that supports sparse bioclast. Radiolarian fauna (Fig. 4d), typically found in Early and mid-Cretaceous, in these wackestones show poor to medium preservation due to reworking and corrosion (Neumann and Zacher 2004). The presence of stylolites is associated with uplift and load release, which commonly leads to separation of the rock fabric along weak surfaces (Figs 3c, 4a, 4c). Sometimes clay rich stylolites (Fig. 4b, 4c) generate elongated and often unconnected secondary porosity zones (Scholle and Ulmer-Scholle, 2003).

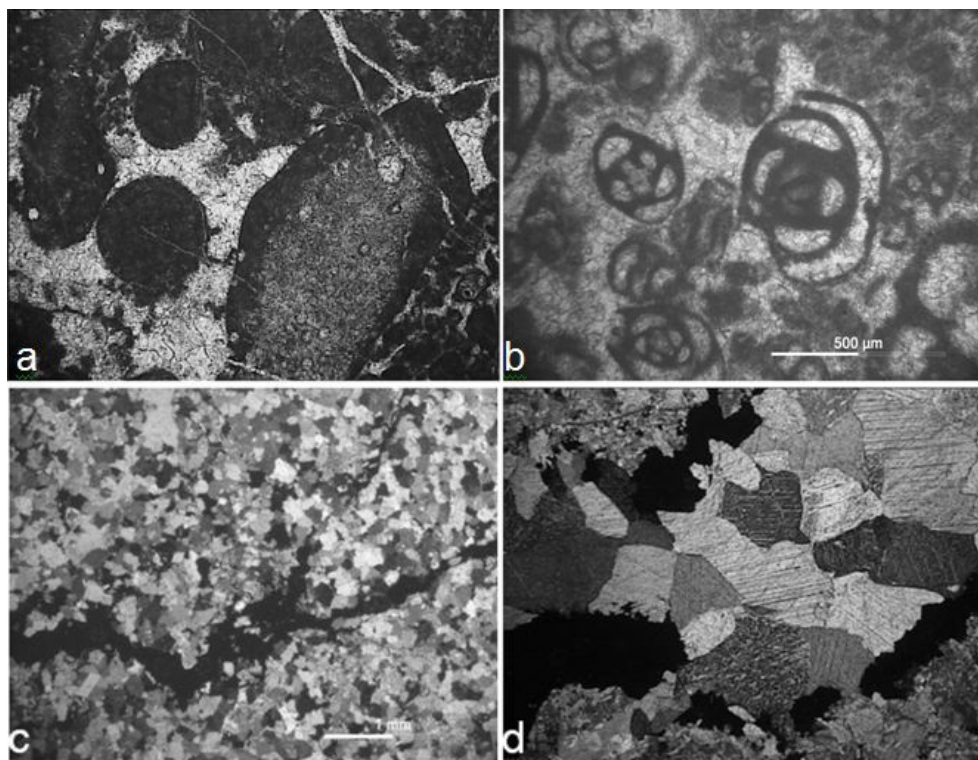


Fig. 3. Photomicrographs of the studied limestones: (a) Intraclast with oolite in a rudstone (sample DHL 13, plane polarized light); (b) Abundant foraminifera cemented with fine-crystalline calcite (rudstone sample DHL 13, plane polarized light); (c) Coarse crystalline, rhombohedral dolomite in crystalline dolomitic limestone (sample DHL 12B, crossed polarized light); (d) Channel porosity within crystalline calcite (sample DHL 12B, crossed polarized light).

Εικ. 3. Φωτομικρογραφίες των ασβεστολίθων που μελετήθηκαν: (α) Ενδοκλάστες και ωολίθοι σε rudstone (δείγμα DHL 13, παράλληλα nicols), (β) Πλήθος απολιθωμάτων μέσα σε rudstone συγκολλημένων με σπαρτικό ασβεστίτη (δείγμα DHL 13, παράλληλα nicols), (γ) Ρομβοεδρικοί κρύσταλλοι δολομίτη (δείγμα DHL 12B, διασταυρωμένα nicols), (δ) Πορώδες τύπου καναλιού μέσα σε κρυστάλλους ασβεστίτη (δείγμα DHL 12B, διασταυρωμένα nicols).

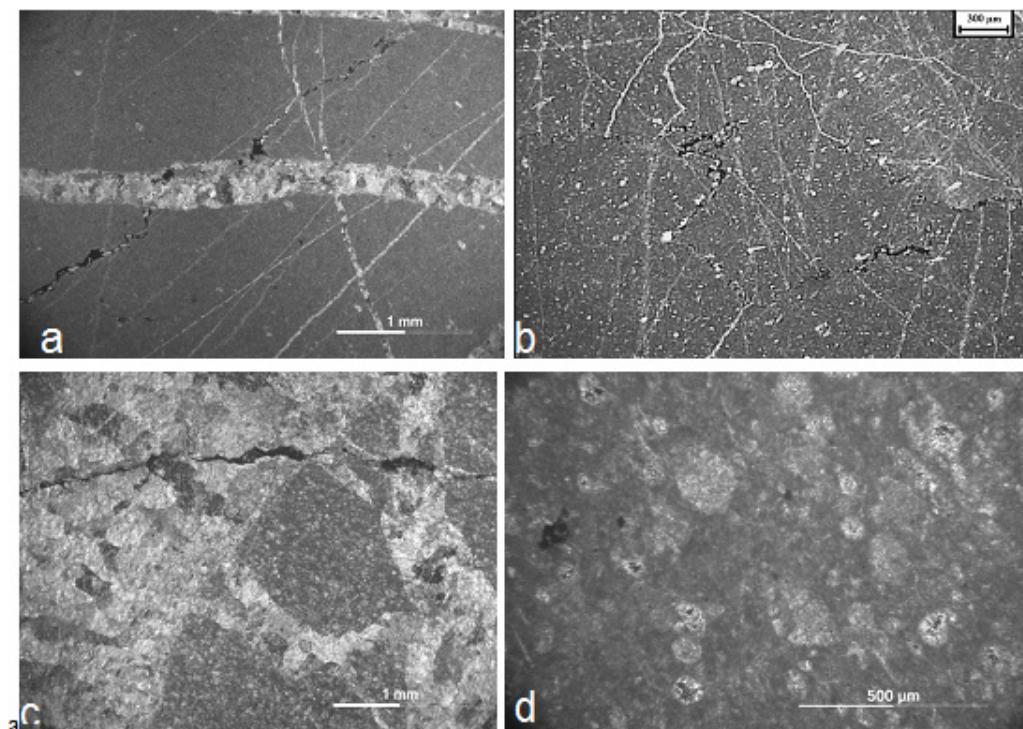


Fig. 4. (a) Dismicrite with veins and stylolite filled with calcite (sample DHL 4B, crossed polarized light); (b) fossiliferous micrite with stylolite filled with clay minerals (sample DHL 23B, crossed polarized light); (c) calcite vein and stylolite in a wackestone (sample PF1B, crossed polarized light); (d) radiolarian bioclasts in a wackestone (sample DHL 19, crossed polarized light).

Εικ. 4. (α) Δισμικρίτης που διατέμνεται από σπαρτικές φλέβες και στυλόλιθο, ο οποίος πληρώνεται με κρυστάλλους ασβεστίτη (δείγμα DHL 4B, διασταυρωμένα nicols), (β) απολιθωματοφόρος μικρίτης με στυλόλιθο, ο οποίος πληρώνεται με αργιλικό υλικό (Δείγμα DHL 23B, διασταυρωμένα nicols), (γ) ευρεία σπαρτική φλέβα που διατέμνεται από στυλόλιθο σε wackestone (Δείγμα PF1B, διασταυρωμένα nicols), (δ) παρουσία ακτινόζωνων σε wackestone (δείγμα DHL 19, διασταυρωμένα nicols).

X-Ray Diffraction

X-Ray diffraction patterns of random powder mounts revealed the presence of calcite in all samples except for dolomitic limestones where dolomite is also present. The insoluble residue is dominated by smectite, chlorite, illite and vermiculite. In some samples traces of mixed-layer illite-chlorite were also present. The presence of smectite was detected by a diffraction maximum at 15Å in the air dried sample, which is shifted at 16.9Å after treatment with ethylene glycol and at 10 Å after heating at 490o. Il-

lite is identified by the reflections at 10Å, 5Å and 3.3Å, which remain unaffected after ethylene glycol treatment and heating (Moore and Reynolds, 1989). Chlorite was identified by the reflections at 14.2Å, 7.1Å, 4.77Å and 3.55Å and vermiculite by the peak at 14.5Å, which remains unaffected after ethylene glycol treatment. The mixed layer illite-chlorite was identified by the diffraction maximum at 12Å and at about 7 to 7.98Å, which was not affected by ethylene glycol treatment (Thorez, 1976, Reynolds, 1980, Ruiz-Cruz, 2001).

Physical properties

Knowledge of the physicochemical properties of carbonate rocks is essential in order to determine their quality. Physical properties were determined in ten representative samples and the results are given in Table 1.

Moisture content of the studied limestone ranges between 0.07-0.42% whereas their water absorption (Wa) values range between 0.07-2.67% (Tab. 1). Total porosity (nt) is an important factor in rock strength, since a small change in pore volume can produce an appreciable mechanical effect (ISRM, 1981). The nt values obtained for the limestones range between 0.37 - 0.85%. Total Organic Carbon (TOC) ranges between 0.09-0.29% and insol-

ble residue range between 1.08-5.69%. Rudstone and grainstone have the lowest content in TOC and insoluble residue. The positive values of colour parameter b^* (yellowness) in the packstones, which have low TOC contents and insoluble residue, show that these samples are in the range of light yellow colour (Tab. 1). Mudstone and wackestone have higher parameter b^* values than other lithotypes. With increasing total organic carbon and insoluble residue redness-greenness and yellowness of the samples increase. The TOC and insoluble residue are inversely correlated to the colour index L with the following empirical equations: $TOC = -0.0142 L + 1.421$ and $IR = -0.2691 L + 27.266$ (Fig. 5).

Sample	DHL 4B	DHL 12B	DHL 13	DHL 19	DHL 20B	DHL 21	DHL 23B	G1B	PF1B	PK2A
Dunham(1962)	mudstone	Crystalline dolomitic limestone	Rudstone	wackestone with radiolarian	mudstone	packstone	mudstone with bioclast	grainstone	wackestone	packstone
moisture content (%), n=3	0.10	0.14	0.08	0.42	0.14	0.31	0.53	0.07	0.40	0.13
water absorption (%), n=3	0.46	2.67	0.09	0.83	0.32	0.80	1.57	1.32	0.07	0.05
void ratio	1.51	2.55	1.34	0.58	1.36	7.53	2.05	5.75	3.53	3.43
ap.spec.grav (gr/cm ³), n=3	2.69	2.62	2.69	2.62	2.64	2.64	2.64	2.61	2.65	2.65
bulk spec.gravity (gr/cm ³), n=3	2.73	2.69	2.72	2.64	2.68	2.84	2.69	2.76	2.74	2.74
total porosity (%)	0.60	0.72	0.57	0.37	0.58	0.88	0.67	0.85	0.78	0.77
L	93.03	95.12	93.72	83.08	78.97	84.20	89.46	93.97	90.25	90.79
a	0.42	0.19	0.37	-0.90	7.81	2.07	0.35	0.43	0.73	0.84
b	4.08	2.80	3.16	2.65	11.32	5.03	5.69	4.31	7.05	4.49
WD	62.39	76.03	70.40	21.03	11.65	41.21	48.07	66.47	43.59	56.98
insol. Residue (%)	2.94	1.08	1.23	5.40	5.69	3.26	5.43	1.25	3.49	2.69
TOC (%), n=3	0.09	0.03	0.10	0.26	0.29	0.24	0.15	0.14	0.14	0.14
CaO (%)	54.71	49.93	55.03	48.84	48.64	53.73	51.48	55.37	52.16	55.67

Tab. 1. Mean values of physical properties of the investigated carbonate samples from the Ileia Prefecture.
Πίν. 1. Μέσες τιμές των φυσικών ιδιοτήτων των δειγμάτων ανθρακικών πετρωμάτων που μελετήθηκαν στην περιοχή της Ηλείας.

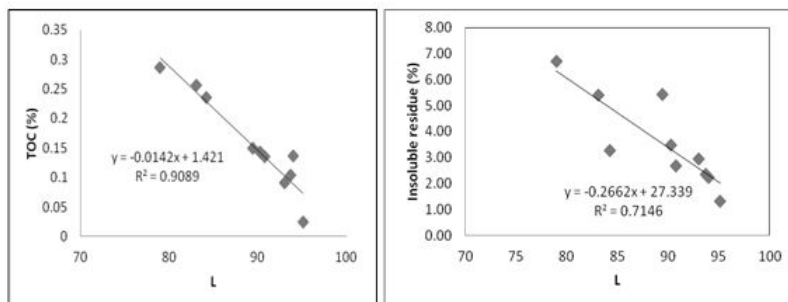


Fig. 5. Correlation diagrams of the total organic carbon and insoluble residue with the colour L^* parameter.
Εικ. 5. Διαγράμματα συσχέτισης ολικού οργανικού άνθρακα κα αδιάλυτου υπολείμματος με τη χρωματική παράμετρο L.

Water absorption shows well defined inverse correlation with the CaO content, except for the mudstone samples (Fig. 6a). Moisture content is positively correlated with insoluble residue, suggesting that clay minerals are the prevalent water adsorbents (Fig. 6b). However, in samples containing abundant quartz in the insoluble residue (DHL 19, DHL 20B) the relationship is not well determined. They are related each other with the empirical equations: $Wa = -0.4371 CaO + 1.421$ and $IR = 8.6576 m.c + 0.8631$

Geochemistry

Whole-rock geochemical analyses from representative carbonate rocks are listed in Tab. 2. The analyzed limestone samples have CaO content between

48.64 and 55.67 wt.% with minor to moderate SiO_2 and Al_2O_3 abundances (Fig. 7). According to the chemical classification based on $CaCO_3$ content (Oates 1998), grainstone and rudstone are characterized as ultra-high pure calcium limestones ($CaCO_3 > 98.5\%$), except for the crystalline dolomitic limestone, which due to the presence of MgO shows much lower $CaCO_3$ contents. Packstones are characterized as calcium limestones of high purity ($CaCO_3 = 97-98.5\%$) and median purity limestones ($CaCO_3 = 93.5-97.0\%$). Mudstones and wackestones are characterized as low calcium limestones ($CaCO_3 = 85.0-93.5\%$) except for DHL 4B which is classified as highly pure limestone.

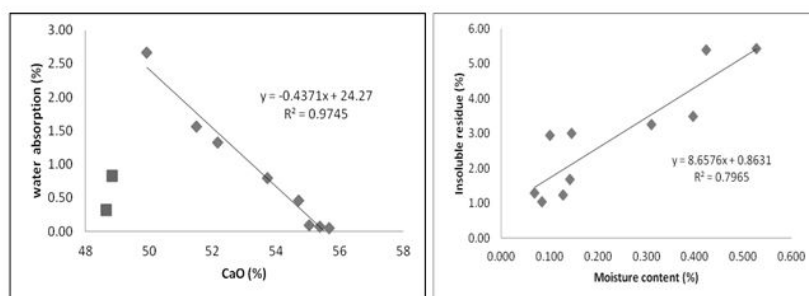


Fig. 6. Plot of water absorption vs. CaO content and moisture content vs. insoluble residue for the Cretaceous carbonate samples from Ilea Prefecture.

Εικ. 6. Διάγραμμα υδατοαπορροφητικότητας ως προς CaO και περιεχόμενης υγρασίας ως προς αδιάλυτο υπόλειμμα για τα ανθρακικά πετρώματα ηλίκας Κρητιδικού του Ν. Ηλείας.

Major elements (wt.%)	DHL 4B	DHL 12B	DHL 13	DHL 19	DHL 20B	DHL 21	DHL 23B	PF1 B	G1 B	PK2 A
SiO_2	1.86	1.63	0.64	10.32	11.15	2.40	5.70	4.72	0.34	0.92
Al_2O_3	0.35	0.35	0.11	0.72	1.00	0.28	1.09	0.72	0.08	0.18
Fe_2O_3	0.26	0.14	0.13	0.44	0.43	0.33	0.51	1.34	0.11	0.15
MnO	0.06	0.02	0.04	0.13	0.11	0.04	0.06	0.09	0.03	0.04
MgO	0.34	3.84	0.36	0.54	0.52	0.34	0.48	0.34	0.31	0.31
CaO	54.71	49.93	55.03	48.84	48.64	53.73	51.48	52.16	55.37	55.67
Na_2O	0.05	0.04	0.06	0.03	0.07	0.02	0.05	0.02	0.03	0.03
K_2O	0.07	0.07	-	0.15	0.18	0.06	0.18	0.12	0.04	0.06
TiO_2	-	-	-	0.025	0.021	-	0.039	0.022	-	-
P_2O_5	0.03	0.03	0.02	0.01	0.04	0.02	0.03	0.02	0.01	0.02
LOI	42.70	43.27	43.43	39.00	38.36	42.56	40.64	41.37	43.51	43.14
Total	100.40	99.34	99.81	100.20	100.50	99.78	100.30	100.90	99.83	100.5
$CaCO_3$	97.02	93.82	98.65	87.66	86.57	96.50	91.84	92.70	99.05	98.32

Trace elements (ppm)										
Ba	45	12	5	78	27	7	25	16	6	6
Co	5	4	6	5	9	3	4	3	4	4
Cr	3	4	5	27	8	3	13	9	2	3
Cu	8	3	4	4	55	3	11	8	5	4
Ni	5	2	2	5	30	4	19	9	3	3
S (%)	0.011	0.005	0.014	0.008	0.017	0.009	0.009	0.008	0.01	0.009
Sc	0.7	1.3	0.3	1.4	1.6	0.5	1.5	1	0.2	0.4
Sr	660	74	343	431	590	628	811	945	392	671
Y	5	61	5	15	14	3	5	5	2	2
Zn	5	7	4	9	16	5	13	7	3	4
Zr	3	360	30	9	10	4	19	9	3	15

Tab. 2. Whole-rock geochemical analyses of representative samples of Cretaceous limestones from Ileia Prefecture (-): below detection limit).

Πίλ. 2. Γεωχημικές αναλύσεις ασβεστόλιθων ηλικίας Κρητιδικού του Νομού Ηλείας (-): κάτω από το όριο ανιχνευσιμότητας).

The total amount of impurities (sum of all oxides excluding CaO and CO₂) for grainstone and rudstones ranges between 0.01 and 3.34 wt.%. The SiO₂ content is 0.34-1.65% and the Al₂O₃ content ranges between 0.08 and 0.35%. The SiO₂ content is higher in the packstones than in the grainstones. Mudstones and wackestones show the highest amount of SiO₂ and Al₂O₃. High SiO₂ and Al₂O₃ contents are related with the presence of quartz and clay minerals in the insoluble residue in these samples. All samples are poor in MgO (<1%), except for the dolomitic limestone with MgO content of 3.84 wt.%, due to the presence of dolomite. The mudstones have higher amounts of Fe₂O₃ than the rest samples. The concentrations of MnO, Na₂O, are very low in all the analyzed samples. The low concentration of phosphorus reflects the absence of apatite in the samples, a mineral that is easily altered during diagenesis (Parekh et al., 1977; Cullers, 2002). Sr was detected in all samples, however the amount of Sr in the dolomitic limestone (DHL 12B) is lower than the rest samples. Sr is easily mobilized during weathering, especially in oxidizing, acid environments, thus it is incorporated in clay minerals.

Sr plays an important role to the cycling (Zhao et al., 2009, Kabata-Pendias 2011). The mudstone samples display high Ba contents. The enrichment of Ba in limestones indicates high productivity in the upper part of the sea column similar to the high concentrations of barite reported at the bottom of the Mediterranean (Passier et al., 1999; Tenger et al., 2005). Ba is also strongly adsorbed by clay minerals and it commonly substitutes for K in feldspars (Kabata-Pendias, 2011). Sample DHL 20B demonstrates the highest Cu values compared to the remaining samples.

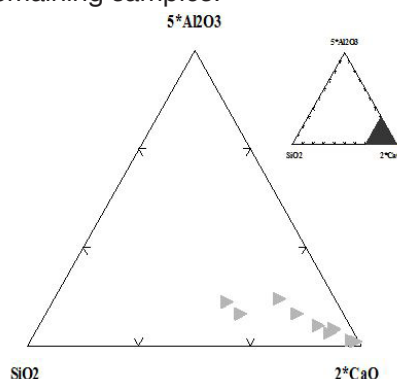


Fig. 7. Plot of the analysed samples on the Al₂O₃-SiO₂-CaO diagram for sedimentary rocks.

Εικ. 7. Προβολή των αναλυμένων δειγμάτων στο τριγωνικό διάγραμμα Al₂O₃-SiO₂-CaO για ιζηματογενή πετρώματα.

Discussion-Conclusions

The Cretaceous succession of the Olonos –Pindos Zone has recorded the sedimentary history of a complex marginal basin aligned to the north eastern Apulian passive margin, in which tectonism, sediment supply and palaeoceanographic effects have influenced the slope and basin plain sedimentation. The autochthonous rocks compose pelagic limestone while the allochthonous ones comprise thin intercalation siliceous, pelitic and organic rich facies of Early and Mid Cretaceous age (Neumann and Zacher, 2004). The carbonate samples include a variety of lithotypes such as mudstones, wackestones, packstones, grainstone and rudstones. In thin sections veinlets of calcite are observed and stylolites are often associated with insoluble material (mainly clay minerals) accumulated as a result of pressure-induced dissolution.

Physical properties of the studied samples were determined on both the whole-rock and powdered material. There is an excellent negative relationship between water absorption and CaO content, except for the mudstones, which are rich in SiO₂ indicating that impurities play a significant role in the absorption of water. Furthermore, moisture content is positively correlated with insoluble residue probably due to the presence of absorbent clay minerals. The colour index is negatively correlated with the insoluble residue and TOC, suggesting that they both have a negative affection on the aesthetic appearance of limestones. Impurities in carbonate rocks may show variable compositions and amounts and may affect their properties. A considerable amount of some impurities may be tolerated 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).

Generally, high contents of magnesium carbonate are undesirable in cement industries. The level of MgO in the clinker should not exceed 5% and indeed, many cement producers favour an upper limit of 3%, so dolomitic and magnesium limestones are unsuitable for cement production. The CaCO₃ content in all analyzed samples lies above 87% (Tab. 2, Fig. 8a) and the samples have low MgO contents, thus comprising suitable materials for cement production, except the dolomite horizons occurring in the Cretaceous carbonate rocks (Fig. 8b). According to Rigas et al. (1990) pure limestones have insoluble residues less than 0.03%, while impure limestones show insoluble residues higher than 5.5%. The Cretaceous limestone from Ileia show a broad range of insoluble residues (Fig. 8c) and they are characterized as pure, medium pure (with insoluble residue between 0.03 and 5.50%) and impure.

The CaCO₃ content in the Ileia Cretaceous carbonates exceeds the limit of 65% for suitability in cement production. However, the Mg abundance, the insoluble residue, the total organic carbon and the colour index suggest that only grainstones (G1B) and rudstone (DHL 13) are suitable for cement production (Fig. 8). All the studied limestones are suitable as pH regulators in acid soils, as well as additives of fertilizers because the CaCO₃ content exceeds 60% and the MgO content is below 5% (Fig. 8). The grainstones (G1B), rudstones (DHL 13) and packstones (DHL 21, PK2A) are suitable for desulphurization of exhaust gases because the CaCO₃ content ex-

ceeds 95%, and very low Al_2O_3 (< 1%), SiO_2 and MgO contents (< 2%; Figs 8 and 9).

.From this study, it appears that petrographic investigation coupled by miner-

alogical and geochemical analysis are useful in assessing the quality of limestones, despite the fact that several physical properties cannot be directly evaluated.

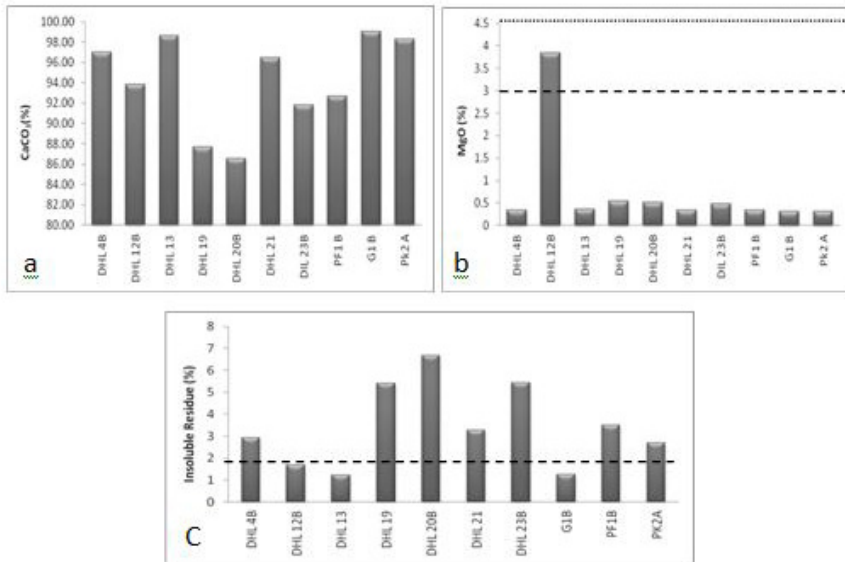


Fig. 8. Variation of CaCO_3 content (a), MgO (b) and insoluble residue (c) of the analyzed Cretaceous limestone samples. Dashed lines indicate the suitability limits for use of carbonate rocks in cement industry. Dotted lines indicate the suitability limits for use of carbonate rocks as fertilizers (Boynton, 1980; Harben, 1992; Oates, 1998).

Εικ. 8. Διακύμανση της περιεκτικότητας σε CaCO_3 (a), MgO (b) και αδιάλυτου υπολείμματος (c) των αναλυμένων ασβεστόλιθων Κρητιδικής ηλικίας. Οι διαγραμμισμένες ευθείες δείχνουν τα όρια που απαιτούν οι προδιαγραφές για χρήση ανθρακικών πετρωμάτων στην τσιμεντοβιομηχανία. Οι διάστικτες ευθείες δείχνουν τα όρια που απαιτούν οι προδιαγραφές για χρήση ανθρακικών πετρωμάτων ως εδαφοβελτιωτικών (Boynton, 1980; Harben, 1992; Oates, 1998).

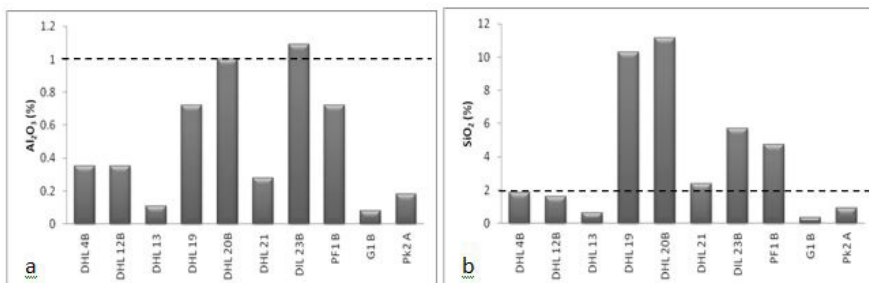


Fig. 9. Variation of Al_2O_3 (a) and SiO_2 (b) contents of the analyzed Cretaceous limestone samples. Dashed lines indicate the suitability limits for use of carbonate rocks in desulphurization of exhaust gases (Boynton, 1980; Harben, 1992; Carr et al., 1994; Oates, 1998).

Εικ. 9. Διακύμανση του Al_2O_3 (a) και SiO_2 (b) των αναλυμένων ασβεστόλιθων Κρητιδικής ηλικίας. Οι διαγραμμισμένες ευθείες δείχνουν τα όρια που απαιτούν οι προδιαγραφές για χρήση ανθρακικών πετρωμάτων στην αποθείωση των καυσαερίων (Boynton, 1980; Harben, 1992; Carr et al., 1994; Oates, 1998).

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References

- Aashato T147. The Field Determination Of Density Of Soil In-Place (1954-70).
 Aashato T T85. Specific gravity and absorption of coarse aggregates
 American Society for Testing and Materials C97-47. Standard Test methods for Laboratory determination of water absorption
 American Society for Testing and Materials D2216-10. Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass
 Aubouin, J., 1959. Contribution a l'etude geologique de la Grèce septentrionale: les confins de l' Epire et de la Thessalie. *Annales Géologiques des Pays Helléniques*, 10, 1-483
 Billmeyer, F.W., Saltzman, M., 1981. *Principles of color technology*, 2nd edition. Wiley Interscience, New York.
 Boynton, S.R., 1980. *Chemistry and Technology of Limestone*. 2nd edition, New York, Wiley & Sons.
 Carr, D. D., Rooney, L. F., Freas, R.C., 1994. Limestone and dolostone. In: Carr, D.D. (Ed.), *Industrial minerals and rocks, 6th Edition, Society for Mining, Metallurgy and Exploration, Littleton*. Colorado, pp. 605-629.
 Choquette, P.W., Pray, L.C., 1970. Geological nomenclature and classification of porosity in sedimentary carbonates. *American Association of Petroleum Geologists Bulletin*, 54, 207-250.
 Christidis, G.E., Sakellariou, N., Repouskou, E., Markopoulos, Th., 2004. Influence of organic matter and iron oxides of the color properties of a micritic limestone from Kefalonia. Kefalonia. *Bulletin Geological Society of Greece. Proceedings of the 10th International Congress*, Thessaloniki 2004, 72-79
 Cullers, R.L., 2002. Implications of elemental concentrations for provenance, redox conditions and metamorphic studies of shales and limestones near. *Chemical Geology*, 191, 305-327.
 De Wever, P., 1975. *Etude géologique des séries apparaissant en fenêtre sous l' alloctone pindique (série de Tripolitza et série épimetamorphique de Zarouchla). Peloponnèse septentrional, Grèce*. These 3eme cycle, France, Université de Lille.
 Degnan, P.J., Robertson, A.H.F., 1998. Mesozoic-early Tertiary passive margin evolution of the Pindos ocean (NW Peloponnese, Greece). *Sedimentary Geology*, 117, 33-70
 Degnan, P. J., Robertson, A.H.F., 2006. Synthesis of the tectonic-sedimentary evolution of the Mesozoic-Early Cenozoic Pindos ocean: Evidence from the NW Peloponnese, Greece. In: Robertson, A.H.F., Mountrakis, D. (Eds.). *Tectonic development of the Eastern Mediterranean region*. Geological Society London, Special Publications 260, 467-491.
 Dunham, R. J., 1962. Classification of carbonate rocks according to their depositional texture. In: Ham, W. E. (Ed.), *Classification of carbonate rocks*. American Association of Petroleum Geologists Memoir 1, 108-121.
 Fleury, J.J., 1980. Les zones de Gavrovo-Tripolitza et du Pinde-Olonos

- (Grèce Continental), et Péloponnesse du Nord. Evolution d'une plate-forme et d'un bassin dans leur cadre Alpin. *Société de la Géologie de Nord, Lille Publication*, 4, 1-651.
- Folk, R. L., 1959. Practical petrographic classification of limestones. *American Association of Petroleum Geologists Bulletin*, 43, 1-38.
- Folk, R. L., 1962, Spectral subdivision of limestone types. In: Ham, W. E. (Ed.), *Classification of carbonate rocks*. American Association of Petroleum Geologists Memoir 1, 62-84.
- Harben, P.W., 1992. The industrial minerals handybook - A Guide to Markets, Specifications, and Prices. *Industrial Minerals Division, Metal Bulletin PLC*, United Kingdom.
- Hirst, D.M., Nicholls, G.D., 1958. Techniques in sediment geochemistry-I. Separation of the detrital and non-detrital fractions of limestones. *Journal of Sedimentary Petrology*, 28, 461-481.
- ISRM, 1981. In: Brown, E.T. (Ed.), ISRM Suggested Methods: Rock 654 Characterization, Testing and Monitoring. Pergamon Press, London. 211 pp
- Kabata-Pendias, A., 2011. *Trace elements in soils and plants*, 4th edition. CRS Press, New York.
- Kafousia, N., Karakitsios, V., Jenkyns, H.C., 2010. Preliminary data from the first record of the early Toarcian oceanic anoxic event in the sediments of the Pindos zone (Greece). *Bulletin of the Geological Society Greece, Proceedings of the 12th International Congress of the Geological Society of Greece, Patras 2010*, 627-633.
- Karakitsios, V., Kolletti, L., 1992. Critical revision of the age of the basal Vigla limestones (Ionian Zone, western Greece), based on nannoplankton and calpionellids with paleogeographical consequences. In: Hamrsmid, B., Young, J. (Eds.), *Proceedings of the Forth International Nannoplankton Association Conference*, Prague 1991, Knihovnicka ZPN, 14a, 1, 165-177.
- Karakitsios, V., Tsikos, H., Van Breugel, Y., Bakopoulos, I., Koletti, L., 2004. Cretaceous oceanic anoxic events in western continental Greece. *Bulletin of the Geological Society of Greece*, 38, 846-855.
- Katsikatsos, G., 1992. *Geology of Greece*. Lecture notes, University of Patras
- Moore, D.M., Reynolds, R.C.Jr., 1989. *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*. Oxford University Press, New York.
- Neumann, P., Zacher, W., 2004. The Cretaceous sedimentary history of the Pindos Basin (Greece). *International Journal of Earth Sciences* 93, 119-131.
- Oates, J.A.H., 1998. *Lime and limestone. Chemistry and technology, production and uses*, Wiley-VCH Verlag.
- Parekh P.P., Moler, P., Dulski, P., Basch W.M., 1977. Distribution of trace elements between carbonate and non carbonate phases of limestone. *Earth and Planetary Science Letters* 34, 39-50.
- Passier, H.F., Bosch, H., Lourens, L.J., Böttcher, M.E., Leenders, A., Damste, J.S.S., de Lange, G.J., de Leeuw, J.W., 1999. Sulfidic Mediterranean surface waters during Pliocene sapropel formation. *Nature*, 397, 146-149.
- Piper, D.J.W., 2006. Sedimentology and tectonic setting of the Pindos Flysch of the Peloponnese, Greece, In: Robertson, A.H.F., Mountrakis, D. (Eds.), *Tectonic Development of the Eastern Mediterranean Region*. Geologi-

- cal Society, London, Special Publications 260, 493-505.
- Renz, C., 1955. *Die Vorneogene stratigraphie der Normalm sedimentaeren Formationen Griechenlands*. Institute for Geology and Subsurface Research, Greece 637 pp.
- Reynolds, R.C., 1980. Interstratified clay minerals, In: Brindley, G.W., Brown, G. (Eds.), *Crystal Structures of Clay Minerals and their X-Ray Identification*. Monograph 4, Mineralogical Society London, 249-304.
- Rigas, K., Soundoulounakis, N., Georgousis, G., 1990. Mineralogical - chemical composition, structure and physicommechanical properties of the Greek marbles. *Proceedings of the 1st Panhellenic Congress "The Hellenic Marble"*, Thessaloniki 25-26/5/1989, Geotechnical Chamber of Greece, 179-187.
- Robertson, A.H.F., 1994. Role of the tectonic facies concept in orogenic analysis and its application to Tethys in the Eastern Mediterranean region. *Earth-Science Reviews*, 37, 139-213.
- Robertson A. H. F., Clift, P.D., Degnan, P.J., Jones, G., 1991. Palaeographic and palaeotectonic evolution of the eastern Mediterranean Neotethys. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 87, 289-343.
- Ruiz-Cruz, M.D., 2001. Mixed-layer mica-chlorite in very low-grade metaclastites from the malaguide Complex (Betic Cordilleras, Spain). *Clay Mineralogy*, 36, 307-324.
- Scholle, P.A., Ulmer-Scholle, Dana S., 2003. A color Guide to the Petrography of Carbonate Rocks: Grains, textures, porosity, diagenesis. *AAPG Memoir No. 77*, AAPG Publications, Tulsa, OK,
- Tenger, K., Khoroshyy, P., Leitgeb, B., Rákhely, G., Borovok, N., Kotlyar, A., Dolgikh, DA., Zimányi, L., 2005. Complex kinetics of the electron transfer between the photoactive redox label TUPS and the heme of Cytochrome. *Journal of Chemical Information and Modeling*, 45, 1520-1526.
- Thorez, J., 1976. *Practical identification of clay minerals*. A handbook for teachers and students in clay mineralogy. Dison Lelotte Belgium.
- Tissot, B.P., Velte., 1984. *Petroleum Formation and Occurrence*. Springer Verlag, Berlin, New York.
- Walkley, A., Black, I.A., 1934. An examination of the Degtjareff method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science*, 63, 251-263.
- Wright, V.P., 1992. A revised classification of limestone. *Sedimentary Geology*, 76, 177-185.
- Zhao, Y.-Y., Zheng, Y.-F., Chen, F., 2009. Trace element and strontium isotope constraints on sedimentary environment of Ediacaran carbonates in southern Anhui, South China. *Chemical Geology*, 265, 345-362.