

Quality Assessment of Eocene Limestones in Zakynthos Island, Western Greece, for Industrial Uses

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Introduction and Geological Background

Limestones are extremely valuable raw materials with a wide variety of chemical and industrial uses which are determined by their physical and chemical properties. The latter, in turn, directly depend on their depositional processes and environments but, also on the post-depositional (diagenetic) alterations that they have undergone. So, the geological, mineralogical and petrographic observations of the limestones are necessary to predict the chemical properties of the end products which can be produced from them (Freas *et al.*, 2006). Accordingly, Eocene Limestones from Zakynthos Island were examined in order to establish certain qualitative characteristics which could contribute to their assessment for various industrial uses. The studied limestones are part of the carbonate succession of the Paxos (or Pre-Apulian) tectonic unit that crops out on the Ionian Islands, in western Greece, and represents the foreland of the Hellenides. After the Early-Middle Jurassic rifting, the Paxos unit functioned as an isolated carbonate platform which received exclusively and almost uninterruptedly calcareous sediments until the Oligocene, when it was completely foundered. The older rocks of the Paxos unit exposed on Zakynthos are of Upper Cretaceous age, constituting the Vrachionas mountain range, a calcareous anticline with a NNW-SSE trending axis. The Eocene Limestones, as well as all the younger formations, occur mostly on the eastern sides of the Vrachionas, constituting an east-dipping monocline (Fig. 1A).

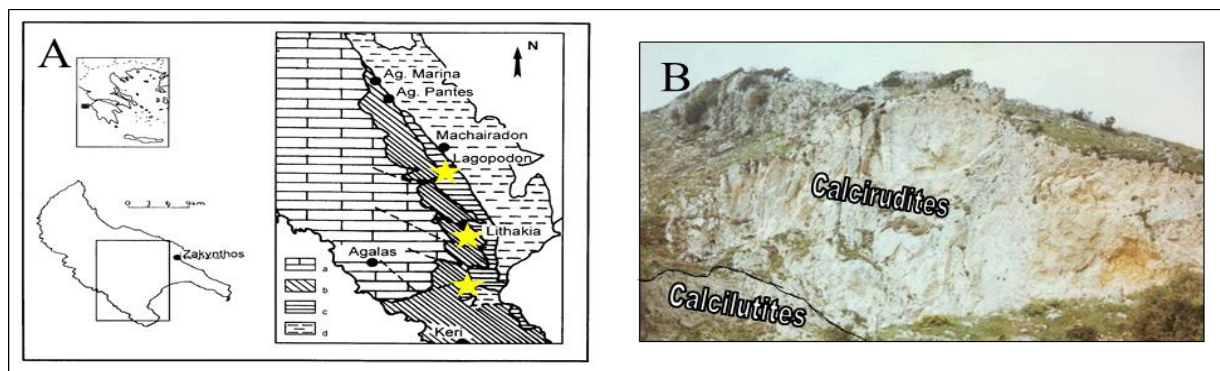


Figure 1. A. Simplified geological map (after IGME, 1980 and Accordi & Carbone, 1992) and the localities of the studied material, (a.Cretaceous, b.Eocene, c.Oligocene, d.Miocene). B. The two main lithofacies of Eocene Limestones (Lagopodon).

Material and Methods

Fieldwork included detailed facies analysis in three old quarries in central Zakynthos (Fig. 1A) and sampling of more than 50 selected samples. Polished slabs and thin sections were prepared of all the samples that were also stained with Alizarin red S and Potassium ferricyanide. The depositional and diagenetic characteristics were examined using transmitted light microscopy while the mineralogical composition of the non-carbonate material was determined through X-ray diffraction (XRD) analysis of the insoluble residue of the <30 μ m and <2 μ m fractions of selected samples, subsequent to their treatment with H₂O₂ to remove any organic matter. Chemical analysis of selected samples was performed using X-ray fluorescence spectrometry (XRF) technique.

Results

Two main lithofacies were identified: a) thinly to medium bedded calcilutites with alternating whitish and light-brown beds and some scattered chert nodules and b) massive to very thickly bedded white to very pale grey calcirudites (Fig 1B). The calcilutites comprise pelagic-hemipelagic carbonate deposits and are mainly represented by pelagic foraminiferal mudstones to wackestones (Fig. 2a), often with burrows, and fine-grained bioclastic packstones with abundant transported neritic skeletal fragments. Mineralogical study revealed that they consist mainly of non-ferroan low-magnesian calcite while their insoluble residue consists mostly of a-quartz (microquartz) and less clay minerals (smectite, illite, kaolinite and vermiculite) (Table 1). Chemical analysis showed CaO content of 54.75% (corresponding to limestone with 97.71% CaCO₃), MgO 0.63%, SiO₂ 0.14% while the percentages of all other oxides are in the range of <0.10% to negligible (Table 2). The calcirudites constitute very coarse-grained, polygenetic limestone breccias, with a grain-supported fabric, very poor sorting and without internal sedimentary structures. They consist of numerous reefal blocks (Fig. 2b) and bioclastic lithoclasts (Fig. 2c), originating from the platform-margin and shelf, and minor pelagic

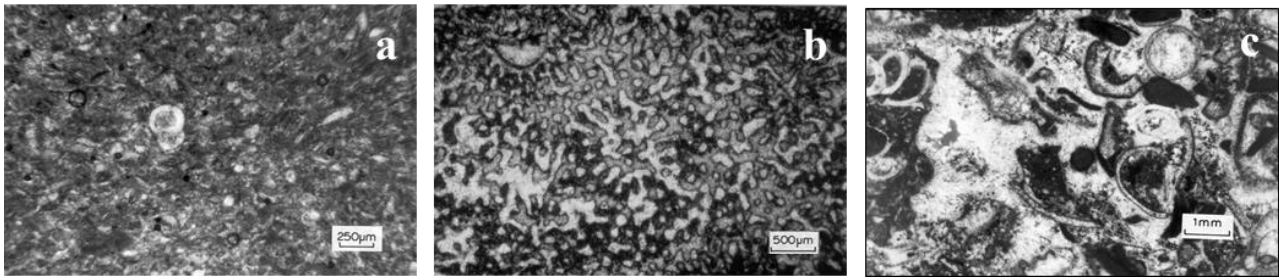


Figure 2. Characteristic lithotypes of the studied Eocene limestones: a. pelagic mudstone-wackestone b. coral boundstone c. bioclastic grainstone-rudstone.

intraclasts of similar composition to their minimal matrix (pelagic wackestone). Facies analysis and petrographic study clearly showed that they constitute resedimented limestones deposited mainly by debris flows at the base of a carbonate slope environment (Kati, 2006). Despite their clastic nature, they show great mineralogical homogeneity, the dominant mineral being the above low-Mg calcite. Their insoluble residue, although qualitatively and quantitatively is almost the same with that of the calcilutites, comprises mainly clay minerals and less a-quartz (Table 1). Their chemical composition showed CaO rates from 55.15-55.75% (corresponding to limestone with CaCO₃ from 98.5-99.1%), while of the other oxides only MgO is most abundant (0.51-0.68%) and the percentages of the remaining are < 0.05%. It should be noted that the organic content was essentially negligible in both lithofacies and dolomitization phenomena are entirely lacking.

Table 1. Semi-quantitative analysis of clastic insoluble residue (x = small amounts, xx = moderate, xxx = large, xxxx = almost pure, IR = insoluble residue).

| Sample/ Lithofacies | Kaolinite | Illite | Smectite | Vermiculite | Illite/Smectite | a-Quartz | IR (%) |
|---------------------|-----------|--------|----------|-------------|-----------------|----------|--------|
| ZK-1 / calcilutite | | | | | | xxxx | 1.80 |
| ZK-2 / calcilutite | x | x | xx | x | | x | 0.18 |
| ZK-3 / calcilutite | x | x | xxx | | | x | 0.18 |
| ZK-4 / calcilutite | x | x | x | x | | xx | 0.08 |
| ZK-5 / calcirudite | xx | | xxx | | | x | 1.44 |
| ZK-6 / calcirudite | x | | xxx | | | x | 0.18 |
| ZK-7 / calcirudite | x | x | xx | x | xx | x | 0.66 |

Conclusions

Based on their carbonate content, the two lithofacies constitute ultra-high-calcium limestones (more than 97% CaCO₃) (Oates, 1998) which are considered suitable for many high-value chemical and industrial uses. The two lithofacies, however, are diversified as to type, size and origin of their constituent grains, as well as their depositional mechanisms and diagenetic paths, resulting in differentiation of their chemical purity. Specifically, although calcilutites display the greatest homogeneity in their primary constituents, their qualitative characteristics appear to have been affected by the presence of detrital clays that arrived in their depositional setting, and also from extensive phenomena of silicification during diagenesis. Their carbonate content (<98.5% CaCO₃) classifies them as “high purity limestones” (Cox *et al.*, 1977) that can be used in cement manufacture, fertilizer industry, in metallurgy, for flue-gas desulphurization, in various environmental uses, etc. The calcirudites (limestone breccias), despite the considerable heterogeneity in their components show better quality characteristics in relation to calcilutites. The origin of most of their clasts and their early lithification are directly reflected in their mineralogical and chemical composition. Their impurities probably represent only clay minerals of detrital origin, since other main diagenetic alterations were not observed. Therefore, the studied breccias with CaCO₃ content >98.5% (“very high purity limestones”) can be used in applications even of higher value, as in production of lime, fillers and pigments in paper, paint and plastics industries and pharmaceutical uses.

References

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