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**Investigations on the importance of early diagenetic processes for the
mineralogical stabilisation and lithification of heterozoan carbonate
assemblages
(Oligo-Miocene, Maltese Islands and Sicily)**

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ABSTRACT

Diagenetic studies of carbonate rocks focused for a long time on photozoan carbonate assemblages deposited in tropical climates. The results of these investigations were taken as models for the diagenetic evolution of many fossil carbonates. Only in recent years the importance of heterozoan carbonates, generally formed out of the tropics or in deeper waters, was realized. Diagenetic studies focusing on this kind of rocks are still scarce, but indicate that the diagenetic evolution of these rocks might be a better model for many fossil carbonate settings ("calcite-sea" carbonates) than the photozoan model used before.

This study deals with the determination of the diagenetic pathways and environments in such shallow-water heterozoan carbonate assemblages. Special emphasis is put on the identification of early, near-seafloor diagenetic processes and on the evaluation of the amount of constructive diagenesis in form of cementation in this diagenetic environment.

As study area the Central Mediterranean, the Maltese Islands and Sicily, was chosen. Here two sections were logged in Oligo-Miocene shallow-water carbonates consisting of different kinds of heterozoan assemblages. The study area is very suitable for the investigation of constructive early diagenetic processes, as the rocks were never deeply buried and burial diagenetic pressure solution and cementation as cause of lithification could be ruled out. Nevertheless, the carbonate rocks are well lithified and form steep cliffs, implying cementation/lithification in another, shallower diagenetic environment.

To determine the diagenetic pathways and environments, detailed transmitted light and cathodoluminescence petrography was carried out on thin sections. Furthermore the stable isotope ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) composition of the bulk rock, single biota and single cement phases was determined, as well as the major and trace element composition of the single cement phases.

Petrographically three (Sicily) to four (Maltese Islands) cementation phases, two phases of fabric selective and one of non-fabric selective dissolution, one phase of neomorphism and one of chemical compaction could be distinguished. The stable isotope measurements of the single cement phases pointed to cement precipitation from marine, marine-derived and meteoric waters. The trace element analysis indicated precipitation under reducing conditions, (A) in an open system with low rock-water interaction on the Maltese Islands and (B) in a closed system with high rock-water interaction on Sicily. For the closed systems case, aragonite as cement source could be concluded because its chemical composition was preserved in the newly formed cements.

By integrating these results, diagenetic pathways and environments for the investigated locations were established, and the cement source(s) in the different environments were determined. The diagenetic evolution started in the marine environment with the precipitation of fibrous/fibrous-bladed and epitaxial cement I. These cements formed as **H**igh **M**g **C**alcite (HMC) directly out of marine waters. The paleoenvironmentally shallowest part of the section on the Maltese Islands was also exposed to meteoric diagenetic fluids. This meteoric influence led to the dissolution of aragonitic and HMC skeletons, which sourced the cementation by **L**ow **M**g **C**alcitic (LMC) epitaxial cement II in this part of the Maltese section. Entering the burial-marine environment the main part of dissolution, cementation and neomorphism started to take place. The elevated CO_2 content in this environment, caused by the decay of organic matter, led to the dissolution of aragonitic skeletons, which sourced the cementation by LMC epitaxial cement II, bladed and blocky cements. The earlier precipitated HMC cement phases were either partly dissolved (epitaxial cement I) or neomorphosed to LMC (fibrous/fibrous-bladed and epitaxial cement I). In the burial environment weak chemical compaction took place without sourcing significant amounts of cementation. In a last phase the rocks entered the meteoric realm by uplift, which caused non-fabric selective dissolution.

This study shows that early diagenetic processes, taking place at or just below the sediment-water-interface, are very important for the mineralogical stabilization of heterozoan carbonate strata. The main amount of constructive diagenesis in form of cementation takes place in this environment, sourced by dissolution of aragonitic and, to a lesser degree, of HMC skeletons.

The results of this study imply that the primary amount of aragonitic skeletons in heterozoan carbonate sediments must be carefully assessed, as they are the main early diagenetic cement source. In fossil heterozoan carbonate rocks, aragonitic skeletons might be the cement source even when no relict structures like micritic envelopes or biomolds are preserved. In general, the diagenetic evolution of heterozoan carbonate rocks is a good model for the diagenesis of “calcite-sea” time carbonate rocks.

ZUSAMMENFASSUNG

Diagenetische Untersuchungen an Karbonatgesteinen beschränkten sich lange Zeit auf photozoische Karbonatvergesellschaftungen der tropischen Breiten. Die Ergebnisse dieser Untersuchungen wurden als modellhaft für den Diageneseverlauf vieler Karbonatgesteine angesehen. Erst in den letzten Jahren wurde die Bedeutung heterozoischer Karbonatvergesellschaftungen, die sich im Allgemeinen außerhalb der Tropen oder in tieferem Wasser bilden, erkannt. Diagenetische Untersuchungen an dieser Art von Karbonatgesteinen sind immer noch selten, deuten aber an, dass der Diageneseverlauf in diesen Karbonaten ein besseres Model für viele fossile Karbonatgesteine ("Calcit-See"-Karbonate) darstellt als das bisher benutzte photozoische Diagenesemodell.

Ziel dieser Studie war die Bestimmung des Diageneseverlaufs in solch flachmarinen Karbonaten mit heterozoischer Biogenvergesellschaftung. Die Milieus, in denen die diagenetischen Veränderungen stattfanden, sollten bestimmt werden. Besonderes Augenmerk lag auf der Art und Menge von Veränderungen, die frühdiagenetisch, nahe dem Meeresboden, stattfanden. Dabei war vor allem der Anteil an konstruktiver Diagenese in Form von Zementation von Interesse.

Das Arbeitsgebiet wurde im zentralen Mittelmeerraum gewählt und befindet sich auf den Maltesischen Inseln und Sizilien. Hier wurden zwei Profile in Flachwasserkarbonaten oligomiozänen Alters aufgenommen, die sich aus unterschiedlichen heterozoischen Biogenvergesellschaftungen zusammensetzen. Dieses Arbeitsgebiet ist für die Untersuchung konstruktiver frühdiagenetischer Prozesse besonders geeignet, da die Gesteinsabfolgen niemals tief versenkt wurden und versenkungsdiagenetisch bedingte Drucklösung und Zementation als Ursache für die Lithifizierung ausgeschlossen werden können. Trotzdem sind die untersuchten Karbonatgesteine gut verfestigt und bilden steile Kliffs, was auf Zementation/Verfestigung in einem anderen, flacheren Diagenesemilieu hinweist.

Zur Bestimmung der Diageneseabfolge und der diagenetischen Milieus wurden detaillierte petrographische Untersuchungen im Durchlicht und mit Kathodolumineszenz an Dünnschliffen durchgeführt. Außerdem wurden die Verhältnisse der stabilen Isotope $\delta^{18}\text{O}$ und $\delta^{13}\text{C}$ am Gesamtgestein, an einzelnen Biogenen und an einzelnen Zementphasen bestimmt. Die Haupt- und Spurenelement Zusammensetzung (Ca, Mg, Fe, Mn und Sr) wurde an den einzelnen Zementphasen ermittelt.

Petrographisch lassen sich drei (Sizilien), beziehungsweise vier (Maltesische Inseln) Zementationsphasen, zwei Phasen von materialabhängiger und eine Phase von materialunabhängiger Lösung, sowie eine Phase von Neomorphismus und eine chemische Kompaktionsphase unterscheiden. Die Messungen der stabilen Isotopenverhältnisse an den einzelnen Zementphasen deuten auf Zementausfällung aus marinen und meteorischen Wässern sowie aus Fluiden marinen Ursprungs hin. Die Spurenelementanalyse lässt außerdem auf Zementausfällung unter reduzierenden Bedingungen schließen. Diese fand einerseits, im Falle der Maltesischen Inseln, in einem offenen System mit geringer Gesteins-Wasser-Interaktion, andererseits, im Falle von Sizilien, in einem geschlossenen System mit großer Gesteins-Wasser-Interaktion statt. Bei der Zementation in einem geschlossenen System konnte Aragonit als Zementquelle bestimmt werden, da seine charakteristische chemische Zusammensetzung im neu gebildeten Zement erhalten blieb.

Durch die Integration aller Ergebnisse konnten für die beiden Lokalitäten die Diageneseabfolgen und die diagenetischen Milieus sowie die Zementquelle(n) in diesen Milieus bestimmt werden. Die diagenetische Entwicklung begann im marinen Milieu mit der Ausfällung von fibrösem bis fibrös-blättrigem und epitaxialem Zement I. Diese Zemente wurden als **H**och **M**agnesium **C**alcit (HMC) direkt aus marinem Wasser ausgefällt. Die paläogeographisch flachsten Abschnitte des Profils auf den Maltesischen Inseln gelangten dann unter den Einfluss meteorischer Wässer. Dieser meteorische Einfluss führte zur Lösung

von aragonitischen und HMC Schalen, was die Zementation mit Niedrig (Low) Magnesium Calcitischem (LMC) epitaxialem Zement II in diesem Profilabschnitt speiste. Im marinen Versenkungsmilieu fand anschließend der Hauptteil an Lösung, Zementation und Neomorphismus statt. Der erhöhte CO₂-Gehalt in diesem Milieu, verursacht durch den Zerfall von organischem Material, führte zur Lösung von aragonitischen Schalen, was die Zementation mit LMC epitaxialem Zement II, blättrigem und blockigem Zement speiste. Die vorher ausgefällten HMC Zementphasen wurden entweder teilweise gelöst (epitaxialer Zement I) oder in LMC umgewandelt (fibrös/fibrös-blättriger und epitaxialer Zement I). Im versenkungsdiagenetischen Milieu fand anschließend geringe chemische Kompaktion statt, ohne aber die Ausfällung von größeren Mengen an Zement zu speisen. In einer letzten Phase gelangten die Gesteine durch Hebung wieder ins meteorische Milieu, was materialunabhängige Lösungserscheinungen verursachte.

Diese Untersuchung zeigt, dass frühdiagenetische Prozesse, die an der Sediment-Wasser-Grenzfläche oder knapp darunter stattfinden, sehr wichtig für die mineralogische Stabilisierung von heterozoischen Karbonatabfolgen sind. Der Hauptteil der konstruktiven Diagenese in Form von Zementation findet in diesem Milieu statt, gespeist durch die Lösung von aragonitischen und, zu einem geringern Teil, HMC Schalen.

Die Ergebnisse dieser Studie implizieren, dass der ursprünglich vorhandene Anteil an aragonitischen Schalen in heterozoischen Karbonatsedimenten sehr sorgfältig bestimmt werden muss, da diese Schalen die wichtigste frühdiagenetische Zementquelle darstellen. In fossilen heterozoischen Karbonatgesteinen können aragonitische Schalen die wichtigste Zementquelle darstellen, auch wenn keine Reliktstrukturen wie mikritische Hüllen oder Biomolds erhalten geblieben sind. Im Allgemeinen stellt der Diageneseablauf in heterozoischen Karbonaten ein gutes Modell für die Diagenese von "Calcit-Meer"-Karbonatgesteinen dar.

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GENERAL INTRODUCTION

1.1 INTRODUCTION

The diagenetic evolution of photozoan carbonate associations (*sensu* James, 1997), most prominently represented by present-day tropical chloralgal reef complexes, has been the aim of study for many decades (e.g. Bathurst, 1975; Schneidermann and Harris, 1985; James and Choquette, 1990a; James and Choquette, 1990b). The diagenetic processes and pathways taking place in these rocks are well understood, and have been taken as models for the diagenetic evolution of many carbonate rocks in Earth history.

In contrast to this well investigated tropical carbonate environments, carbonate formation out of the tropical reef belt, in the subtropical, temperate and polar regions was considered unimportant for a long time. Only in the last decades an increasing number of investigations (e.g. Nelson, 1988; Bone and James, 1993; Betzler et al., 1997; James and Clarke, 1997; Brachert et al., 2001) started to deal with the biogenic associations, environmental conditions and facies distribution typical of these carbonates defined as heterozoan (*sensu* James, 1997). It was realised that not only the biogenic composition of photozoan and heterozoan carbonates varies significantly, but also their diagenetic behaviour and evolution are distinctively different. Until now only a limited number of studies (e.g. Nelson et al., 1988a; James and Bone, 1991; Nicolaides, 1995; Nelson and James, 2000) has dealt with the diagenetic processes and pathways in heterozoan carbonates and their diagenetic evolution is still poorly understood.

To tackle this problem Oligo-Miocene shallow-water heterozoan carbonates, outcropping in the Central Mediterranean, were selected and investigated with respect to their diagenetic pathways and environments. Special emphasis was put on the evaluation of early, near-seafloor diagenetic processes. The results of this study can not only be applied to other heterozoan carbonate settings, but could also help to better understand the diagenetic evolution of many other carbonate rocks predominantly consisting of low Mg calcite.

To clarify the particularities of the diagenetic evolution of heterozoan carbonates, a general overview of the factors controlling their development and their spatial distribution will be given, furthermore the expected alterations in the different diagenetic environments will be described. Finally, the aims and key issues of this study will be presented and the choice of the study area will be explained.

1.2 SHALLOW-WATER BIOGENIC CARBONATE ASSOCIATIONS

James (1997) proposed a subdivision of shallow-water carbonates, depending on the trophic requirements of the biota, into two general carbonate associations: into a heterotrophic biogenic association, the so called “heterozoan” assemblage, consisting of bryozoans, molluscs, echinoderms, smaller benthic foraminifera and coralline red algae and an autotrophic association, the “photozoan” assemblage, containing calcareous green algae, hermatypic corals, larger benthic foraminifera and rudists. The first is dependent on food supply as organic matter; the second has light-dependent growth.

1.2.1 Limiting factors and spatial distribution

The distribution of the heterotrophic and autotrophic shallow-water biogenic associations is mainly controlled by two factors: the temperature of the sea water and its nutrient content (Fig. 1). When sea-water temperatures are low (generally below 22°C) and/or the nutrient content is high, heterozoan biogenic associations develop. In warm, nutrient poor waters photozoan associations dominate the shallow water carbonate environments.

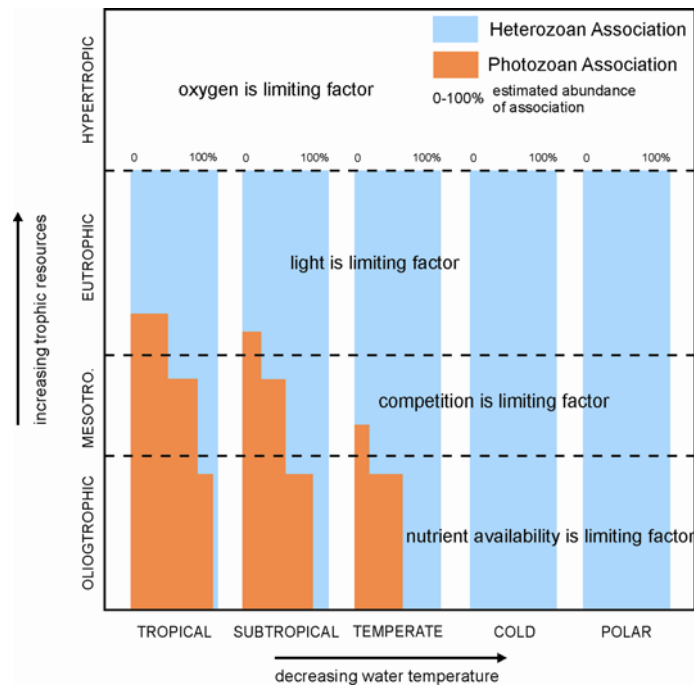


Figure 1 Schematic distribution of heterozoan and photozoan biogenic associations in dependence on the nutrient content and the sea water temperature (modified after Mutti and Hallock, 2003)

In general these limiting factors lead to a spatial distribution of the two associations paralleling the latitudinal arrangement of the climatic zones (Fig. 2). The boundary between the two associations mainly follows the 30° degree of latitude, corresponding to the boundary of the subtropics. Only in areas with high continental runoff and therefore elevated nutrient contents, e.g. at the present day mouth of the Ganges, the Niger and the Red River, or in upwelling regions where cold, nutrient-rich waters reach the surface, e.g. today on the west coast of America and Africa, heterozoan associations can also develop within the subtropics and even tropics.

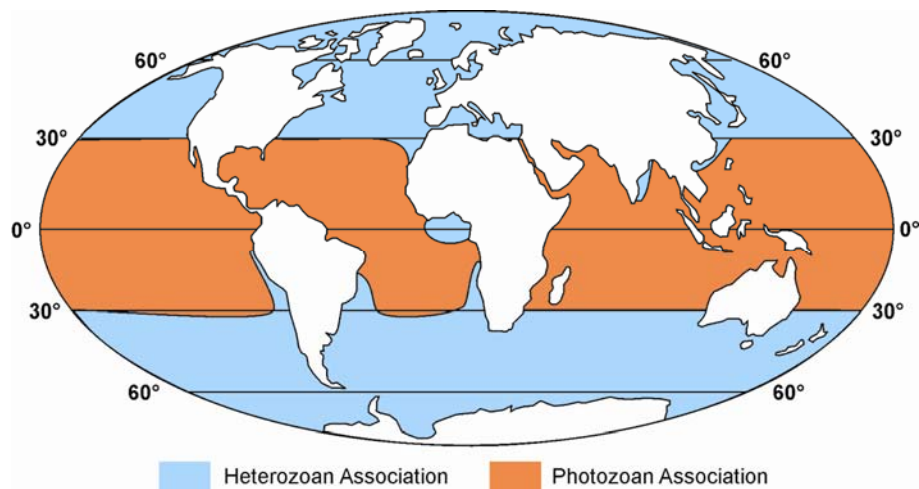


Figure 2 Present day global distribution of photozoan and heterozoan biogenic associations (modified after James, 1997)

1.2.2 Factors controlling the development of heterozoan associations in the study area

This study deals with Oligo-Miocene shallow-water carbonate successions outcropping in the Central Mediterranean (Maltese Islands and Sicily) termed “heterozoan” based on detailed petrography of the biogenic association. In the first place no statement on the boundary conditions (temperature and/or nutrients), leading to the development of this biogenic association, is implied. However, paleogeographic reconstructions locate the study area, the Central Mediterranean, during the Oligo-Miocene between 28° and 31°N at the boundary between the subtropical and temperate climatic realm (Dercourt et al., 2000, see CHAPTER 3). Reconstructions of paleotemperatures based on stable isotope measurements of bivalve and barnacle calcite (see CHAPTER 2), consistently resulted in temperature values between +17° and +23°C. Therefore, even if the influence of the nutrient content can not be ruled out, temperature seems to have been the controlling factor for the development of the studied heterozoan carbonate strata.

1.3 DIAGENESIS IN HETEROZOAN CARBONATE STRATA

The subdivision of shallow-water carbonates into photozoan and heterozoan associations is not only justified by their different biogenic composition, but it is also reflected by their contrasting diagenetic evolution. In the following, the generally accepted course of diagenesis in heterozoan carbonate sediments will be discussed in detail. For a detailed description of the general diagenetic evolution of photozoan carbonates, the reader is referred to literature (e.g. Bathurst, 1975; Choquette and James, 1990; James and Choquette, 1990a; James and Choquette, 1990b; Tucker, 1990).

1.3.1 Marine diagenetic environment

The marine diagenetic environment comprises the seafloor and tens of cm within the sediment (Tucker, 1990). In this environment the diagenetic potential of carbonate sediments depends on the saturation state of the seawater with respect to carbonate minerals. In general, the highest carbonate saturation states are found in equatorial regions, where CO₂ is released to the atmosphere, whereas the lowest carbonate saturation states occur in polar regions where CO₂ is absorbed by cooler waters (Opdyke and Wilkinson, 1990).

As heterozoan carbonate assemblages often develop in higher latitudes (north and south of the 30° degree of latitude), sea waters have a low saturation state or are even undersaturated with respect to CaCO₃. Therefore the marine diagenesis in heterozoan carbonates often is destructive, including bioerosion, maceration and dissolution of the metastable mineral phase aragonite. According to Smith and Nelson (2003) hardly any marine cement precipitation takes place out of these low saturated waters.

1.3.2 Meteoric diagenetic environment

The meteoric diagenetic environment acts where carbonate strata get in contact with meteorically derived waters. The diagenetic potential of carbonate strata in this environment is mainly determined by the amount of metastable aragonite and **H**igh **M**g **C**alcite (HMC, > 4 mole % MgCO₃) in the sediment. During diagenesis these minerals might either be dissolved or be transformed to stable **L**ow **M**g **C**alcite (LMC, 0-4 mole % MgCO₃).

(1) Aragonite and HMC might be dissolved in the meteoric environment because they are more soluble than LMC and meteoric waters are generally undersaturated with respect to them. Their dissolution leads to a supersaturation of the fluid with respect to LMC and to the precipitation of LMC cements (Dodd and Nelson, 1998).

(2) Aragonite and HMC can also be transformed to LMC by thin-film dissolution-reprecipitation processes. During this transformation relic fabrics might be retained, but the trace element and stable isotope composition of the minerals are modified (Tucker, 1990).

In contrast to photozoan carbonate assemblages, which are predominantly formed by aragonitic biota, heterozoan carbonate associations mainly include LMC and HMC biota. In this carbonate association only gastropods, some bivalves and some bryozoans have aragonitic shells (James, 1997, Fig. 3). Therefore, taking into account the general scarcity of aragonitic skeletons and the fact that some of them might already have been dissolved on the seafloor due to the low saturation state of the seawater, heterozoan carbonates have a very limited potential for dissolution and cement precipitation in the meteoric environment. Consequently, meteoric cements or biomolds after aragonitic biota are hardly observed (James and Bone, 1989).

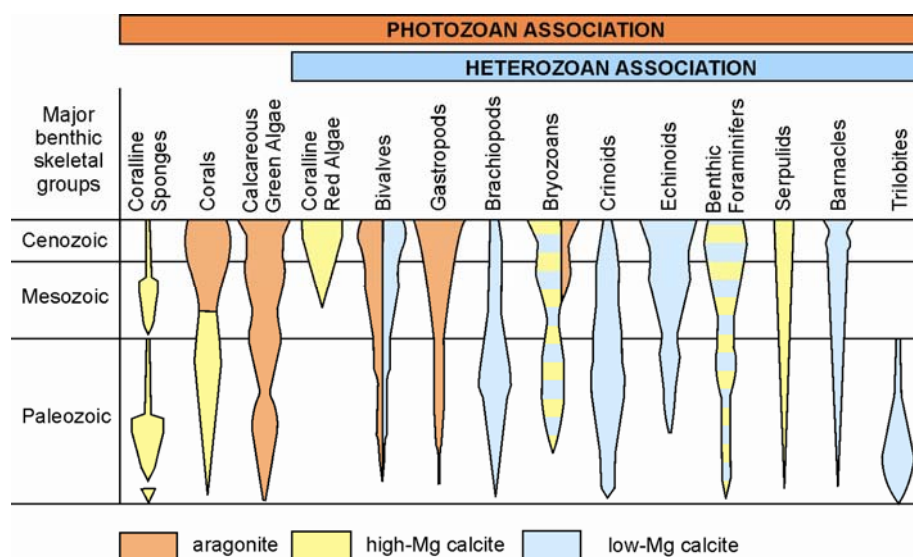


Figure 3 Generalized relative abundance and mineralogy of Phanerozoic carbonate-producing biota belonging to the photozoan and/or heterozoan association (after James, 1997)

1.3.3 Burial diagenetic environment

The burial diagenetic environment starts some tens of meters below the sediment-water interface and reaches down to the zone of metamorphic dehydration (Tucker, 1990). In this environment the main cement source is chemical compaction. Due to the increasing sediment overload, pressure solution between grains starts, leading to grain-to-grain, then to concavo-convex and then to sutured contacts. In a final stage, microstylolithes develop. Diagenetic fluids in the burial environment are generally supersaturated with respect to CaCO_3 . Only in organic rich strata the decay of organic matter can elevate the CO_2 content, leading to undersaturation of the pore fluid and to dissolution (Tucker, 1990).

It is suggested that in heterozoan carbonate assemblages the main part of dissolution and cementation takes place in the burial diagenetic environment (Nelson et al., 1988a; Nicolaidis and Wallace, 1997a). Here pressure solution of LMC grains acts as the main cement source, leading to extensive precipitation of LMC cements.

1.4 AIMS AND STUDY AREA

The aim of this study is to determine diagenetic pathways and environments in shallow-water heterozoan carbonate assemblages and to identify the amount and kind of early, near-seafloor diagenetic processes. Special emphasis is set on the evaluation of the character of constructive diagenesis in the form of cementation in this diagenetic environment.

The results of this study would not only hold implications for recent or fossil heterozoan carbonates, but could also be applied to other geologic time intervals with predominantly LMC mineralogy of the biota and cements. During the so called “calcite-sea” times Cambrian - Early Carboniferous and Late Jurassic - Eocene (Stanley and Hardie, 1998) the inorganically

precipitated cements and also the predominate fossil groups had a LMC mineralogy. Therefore, these sediments had a very stable primary mineralogy not very susceptible to alterations in the meteoric environment, similar to heterozoan carbonate strata. A similarity in the diagenetic behaviour of these two carbonate rock types was already noticed by Dodd and Nelson (1998), who suggested that heterozoan carbonates might be better models for the diagenetic evolution of “calcite-sea” carbonates than the usually used aragonite-rich photozoan strata.

The Central Mediterranean was selected as study area. Two sections, one on the Maltese Islands and one on Sicily, were logged in Oligo-Miocene shallow-water carbonate rocks comprising different kinds of heterozoan assemblages. The study area is very suitable for the investigation of constructive early diagenetic processes, because the rocks were never deeply buried and because burial diagenetic pressure solution and cementation as cause of lithification can be ruled out. Nevertheless, the carbonate rocks are well lithified and form steep cliffs. This implies that cementation/lithification took place in another, most probably, shallower diagenetic environment.

In order to test the hypothesis that significant amounts of constructive early, near-seafloor diagenesis occurred, three key questions were investigated:

1. How did the depositional environment influence the amount and kind of cementation? Is there a link between the depositional environment and early cementation?
2. How do the diagenetic pathways look like? Which were the diagenetic environments of alteration and cementation and what happened in the early, near-seafloor realm?
3. If there is early cementation, what was the source for these cements?

In order to answer these questions detailed field studies were carried out to determine the depositional environments of the rocks. The rock composition was quantitatively analysed with petrography in terms of biogenic associations and diagenetic features to determine the diagenetic pathways. The stable isotope composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of the bulk rock and the single cement phases was measured to determine the diagenetic environments of cement precipitation/alteration. The major and trace element composition of the individual cement phases was studied to further assess the diagenetic environment and to gain better understanding of the early diagenetic cement source.

1.5 ORGANISATION OF THE THESIS

With exception of Chapter 1 (General introduction) and Chapter 5 (Conclusions), each chapter of this thesis has been submitted to a peer-reviewed journal or to a peer-reviewed special publication. Chapter 2 (“Controls of facies and sediment composition on the diagenetic pathway of shallow-water heterozoan carbonates: the Oligocene of the Maltese Islands” by Andrea Knoerich and Maria Mutti) is published in the *International Journal of Earth Science*, 2003, v. 92, p. 494-510. Chapter 3 (“Missing aragonitic biota and the diagenetic evolution of heterozoan carbonates: a case study from the Oligo-Miocene of the central Mediterranean” by Andrea Knoerich and Maria Mutti) has been submitted to the *Journal of Sedimentary Research* and is in review. Chapter 4 (“Epitaxial calcite cements in heterozoan carbonates” by Andrea Knoerich and Maria Mutti) has been reviewed and accepted with minor revisions for publication in the *Geological Society of London Special Publication: Cool-water carbonates – depositional systems and paleoenvironmental controls*.

CONTROLS OF FACIES AND SEDIMENT COMPOSITION ON THE DIAGENETIC PATHWAY OF SHALLOW-WATER HETEROZOAN CARBONATES: THE OLIGOCENE OF THE MALTESE ISLANDS

2.0 ABSTRACT

Relatively few studies have so far addressed diagenetic processes in heterozoan carbonates and the role that sediment composition and depositional facies exert over diagenetic pathways. This paper presents a study of Oligocene shallow-water, heterozoan carbonates from the Maltese Islands. We investigate stratigraphic distribution, abundance and timing of diagenetic features and their relationship to sediment composition and depositional facies.

The studied carbonate rocks comprise rud- to packstones of the heterozoan association predominantly containing coralline red algae, bryozoans, echinoids and benthic foraminifers. XRD analyses show that all high-Mg calcite has been transformed to low-Mg calcite and that no aragonite is preserved. Diagenetic processes include dissolution of aragonitic biota, neomorphism of high Mg calcitic biota to low Mg calcite and cementation by fibrous, bladed, epitaxial and blocky cements. Stable isotopes on bulk rock integrated with petrographic data suggest that the study interval was not exposed to significant meteoric diagenesis. We interpret early cementation to have taken place in the marine and marine burial environment.

The distribution and abundance of early diagenetic features, determining the diagenetic pathway, can be related to the primary sediment composition and depositional texture. Sorting and micrite content are important controls over the abundance of diagenetic features.

2.1 INTRODUCTION

Shallow-water carbonates of the heterozoan association are very common in the rock record (James and Clarke, 1997). In the modern world they tend to occur in cooler waters, at intermediate and high latitudes. However, ocean circulation also plays a role in the distribution of heterozoan carbonate systems, which tend to develop on the cooler eastern sides of the oceans, impacted in part by upwelled nutrient-rich waters. In the past decades several studies have focused on the biogenic associations, environmental conditions and facies distribution typical of this type of carbonate strata as well as on the differences existing between non-tropical and tropical carbonate environments (Nelson et al., 1988b; Bone and James, 1993; Hayton et al., 1995; Betzler et al., 1996; Clarke et al., 1996; James, 1997; Betzler et al., 2000; James et al., 2000). However, surprisingly in this context, only a few studies have addressed diagenetic processes in non-tropical carbonates (Nelson et al., 1988a; Nicolaides and Wallace, 1997a; 1997b; Nelson and James, 2000).

Sea-floor marine cements are absent or rare in most temperate and cool water carbonate environments (Nelson et al., 1988b), in great contrast to tropical carbonate settings (James and Choquette, 1990b). The potential for abiotic precipitation of cements depends on the saturation state of the seawater, which is, as alkalinity values stay rather constant in the oceans, mainly controlled by temperature (Morse and Mackenzie, 1990). The highest carbonate saturations are found in equatorial regions, where CO₂ is released to the atmosphere, whereas the lowest saturation states occur in the polar regions where CO₂ is absorbed by cooler waters (Opdyke and Wilkinson, 1990). As a consequence, extensive precipitation of marine cements ("constructive diagenesis"-cementation) is mainly occurring in supersaturated tropical environments. In contrast, non-tropical environments are characterized by early diagenetic destructive processes such as bioerosion, maceration and

dissolution of metastable grains, which take place in less saturated or even undersaturated waters with high CO₂ contents (Smith and Nelson, 1994).

The scarcity of metastable aragonite and high Mg calcite (HMC) in non-tropical carbonates compared to tropical settings can account for the lack of meteoric cements since the main source for these cements in tropical carbonates is the dissolution of metastable aragonite and the reprecipitation as calcite in the meteoric diagenetic environment (Dodd and Nelson, 1998). Because aragonite is rare in non-tropical carbonates, alterations in the meteoric realm are expected to be more or less unimportant and early marine and meteoric cementation to be very limited (James and Bone, 1989).

In general, the majority of diagenetic processes in non-tropical carbonates is delayed to later stages in the shallow to deep burial environment (Nelson et al., 1988b; Dodd and Nelson, 1998). Lithification of the rocks is caused by chemical compaction and cementation with, often ferroan LMC. The source for these cements is pressure-solution of calcitic skeletal grains (Nelson et al., 1988a; Nicolaidis and Wallace, 1997a; Dodd and Nelson, 1998).

This paper presents a study of Oligocene shallow-water, non-tropical heterozoan carbonates from the Maltese Islands which are well lithified and form the backbone of the islands. This raises the question of when and how cementation occurred in the heterozoan limestones. We investigate the timing of diagenetic features, their stratigraphic distribution and abundance and how these relate to the sediment composition and the depositional facies. To better understand this relationship we integrate field observations with petrographic, mineralogical and isotopic data to establish a diagenetic pathway and to determine the factors controlling its development.

2.2 GEOLOGIC SETTING

During the Late Oligocene to Miocene the Maltese Islands were part of a geographically extensive carbonate ramp located on the more distal segment of the African continental margin. Paleogeographic reconstructions (Fig. 1) locate the Maltese Islands at about 28°N in Early Chattian times moving northward to about 30°N in the Burdigalian (Dercourt et al., 2000). Sedimentation took place on the inner ramp to deeper slope of this temperate to subtropical setting. The sedimentary succession outcropping on the Maltese Islands comprises four major lithostratigraphic units (Fig. 2a and b) and records a step-wise evolution as described by several stratigraphic and sedimentological studies (Pedley, 1978; DiGeronimo et al., 1981; Carbone et al., 1987; Pedley, 1998).

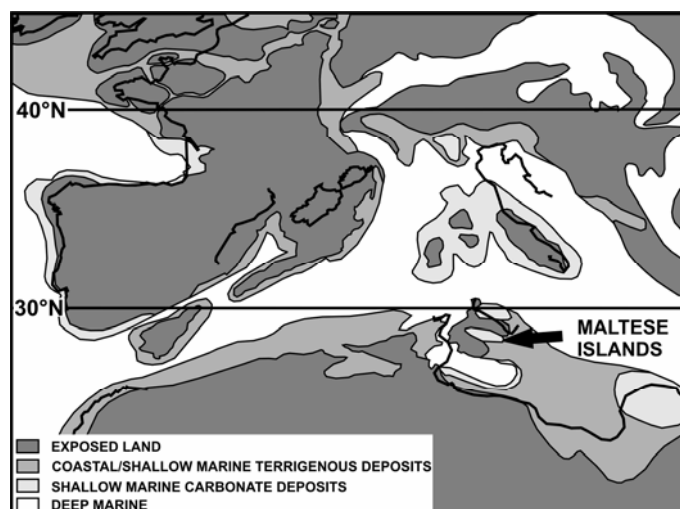


Figure 1 Paleogeographic reconstruction of the Mediterranean region during Early Chattian times (~ 28 Ma) (Dercourt et al., 2000)

The basal unit (Lower Coralline Limestone Formation/Chattian) was deposited on an inner- to outer-ramp and consists of rud- and packstones comprising skeletal fragments typical of heterozoan carbonates. This unit progressively drowned, as recorded by the development of several phosphatic hardgrounds, and is overlain by hemipelagic wackestones rich in planktonic foraminifers (Globigerina Limestone Formation/Aquitanian-Langhian). The deepening trend continued throughout the Serravallian and lower Tortonian when hemipelagic clay- to marlstones were deposited (Blue Clay Formation). This unit is unconformably overlain by shallow water carbonates of the photozoan association (including green algae and Porites patch reefs) (Upper Coralline Limestone Formation/Tortonian to Messinian).

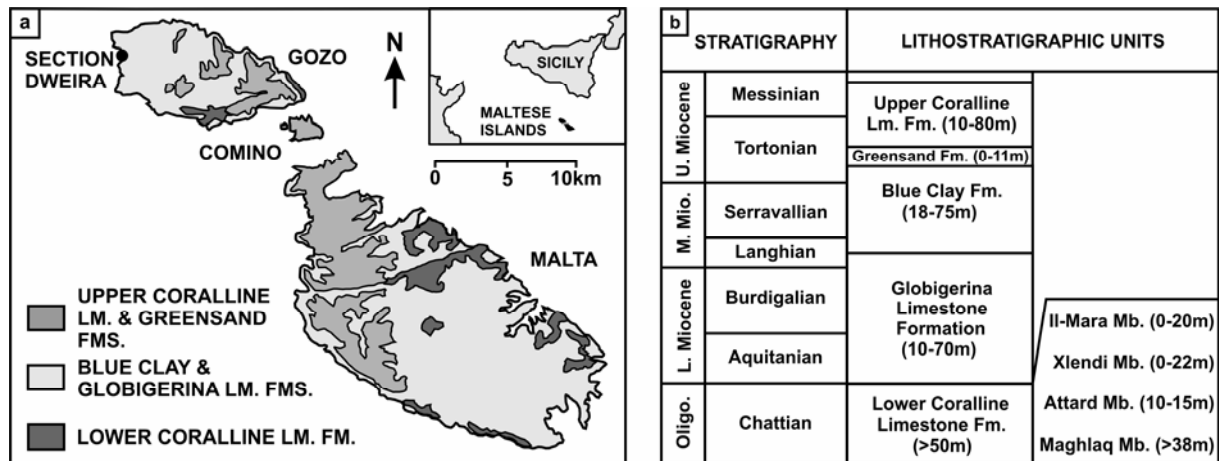


Figure 2 a. Geological map of the Maltese Islands showing the lithostratigraphic units after Felix (1973) and Carbone et al. (1987) and the location of the measured section Dweira; LM: Limestone; FM(S): Formation(s). b. Overview of the lithostratigraphy and age of the units outcropping on the Maltese Islands (Debono and Xerri, 1993); LM: Limestone; FM: Formation; Mb: Member

Our study focuses on the lowermost unit, the Lower Coralline Limestone Formation, which has a minimum thickness of 50 m (base not exposed) and is exposed along the coasts of the Maltese Islands where it forms steep cliffs (Fig. 3a). The restriction of outcrops to these cliffs allows a subdivision of the units at the facies level, but has always precluded a more detailed lithological subdivision of these strata.

Sedimentation of the Lower Coralline Limestone Formation took place on a gently inclined carbonate ramp (Pedley, 1998). The deposits were subdivided (see Fig. 2b) into four lithological members by Pedley (1978). Sedimentation started in a sheltered lagoon (biomicrites of the Maghlaq Member), which with progressive submergence was colonized by rhodolitic algae (Rhodolite biosparites of the Attard Member) (Pedley, 1978). In the western areas, sea-floor stability allowed biohermal structure development by encrusting red algae. Shallowing continued and gave rise to intertidal cross-bedded units of the Xlendi Member (Scutella beds and cross-bedded biosparites, Pedley, 1978, p.4). In the sheltered inter-shoal areas large numbers of Scutella developed, and renewed subsidence led to the accumulation of the Il Mara Member (Bryozoan and Lepidocyclina beds).

Overall the constituents of the Lower Coralline Limestone include varying amounts of coralline red algae, bryozoans, echinoids, barnacles, benthic and larger foraminifers, with bivalves and gastropods in subordinate amounts. These are typical of a heterozoan association (James, 1997) deposited in a warm-temperate setting (Betzler et al., 1997). Using the nomenclature of Hayton et al. (1995) these sedimentary rocks belong to the rhodalgal, rhodechfor and echinofofor associations.

2.3 METHODS

Due to the confinement of the Lower Coralline Limestone outcrops mainly to cliff exposure, our sampling strategy was two-fold. Isolated samples were collected for reference where possible along the cliffs and the stratigraphically most complete section was investigated in detail in the field for sedimentological and biogenic facies and sampled at a resolution of approximately 1 sample/2 m.

Compositional and diagenetic characteristics of the investigated lithologies are based on transmitted light microscopy on >40 thin sections. Point counting was performed on 40 thin-sections for biotic components and diagenetic features (cement types, secondary porosity). In addition, 11 thin sections were polished and examined under cathodoluminescence (CL) microscopy. Operating conditions for the Citl Cold Cathode Luminescence (model 8200 mk 3) at the Institute of Geology and Palaeontology of the University of Stuttgart were maintained at approximately 22 kV beam energy and 0.8 mA beam current.

The point counting results were analysed statistically by a hierarchical cluster analysis after the Ward-Method with squared Euclidean distance using the program SPSS 11.0 for Windows. Before the cluster analysis was performed a factor analysis of the main components was carried out. Employing the varimax rotation the factor loading for each main component was adjusted to -1 to +1. Components with factor loadings below +/- 0.7 were excluded due to their low correlation to the respective factor. Main components with factor loadings above +/- 0.7 were standardized to 100% and used for the hierarchical cluster analysis. For the analysis of the cements no standardisation to 100% was performed, because of the low share of cements on the sediment total which makes a standardisation useless.

X-ray diffraction analysis and quantification of the inorganic carbon content were performed on bulk rock. XRD measurements were carried out with a Bruker D8 Advance with 2 Theta = 25°-35°. The increment used was 0,005 degree; the scan speed was 1 degree/minute. For each measurement four scans were stacked to minimise the error. The inorganic carbon content was determined with a UIC 5014 Carbon Dioxide Coulometer with a CM 5240 TIC-Autosampler.

A total of 63 powdered microsamples ranging in size from 0.5 to 4 mg were analysed for carbon and oxygen stable isotopes at the Laboratory for Stable Isotope Geochemistry at the University of Southern California. Stable isotope measurements were performed on bulk rock (42 samples) and on bivalves and barnacles composed of low magnesium calcite (21 samples). Analyses were performed according to on-line common acid bath method using a PRISM mass spectrometer. The analytical precision of the mass spectrometer is ± 0.1 or better for $\delta^{13}\text{C}$, and ± 0.2 or better for $\delta^{18}\text{O}$. The $\delta^{18}\text{O}$ values have been corrected for calcite phosphoric acid fractionation. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are given in the PDB notation.

2.4 SEDIMENT COMPOSITION AND DEPOSITIONAL FACIES

The data presented in this paper are based on a section measured on the island of Gozo, near the so called Inland Sea, where the most continuous succession of the Lower Coralline Limestone crops out (Fig. 3a). The basal part of the formation is not exposed, while at the top the unit grades into the overlying Globigerina Limestone Formation.

The outcropping 63 m can be subdivided into six units (U1 to U6) on the basis of changes in depositional facies, bedding and sedimentary structures (see Fig. 4; Table I). The compositional data, based on point-counting, are presented in Table II.

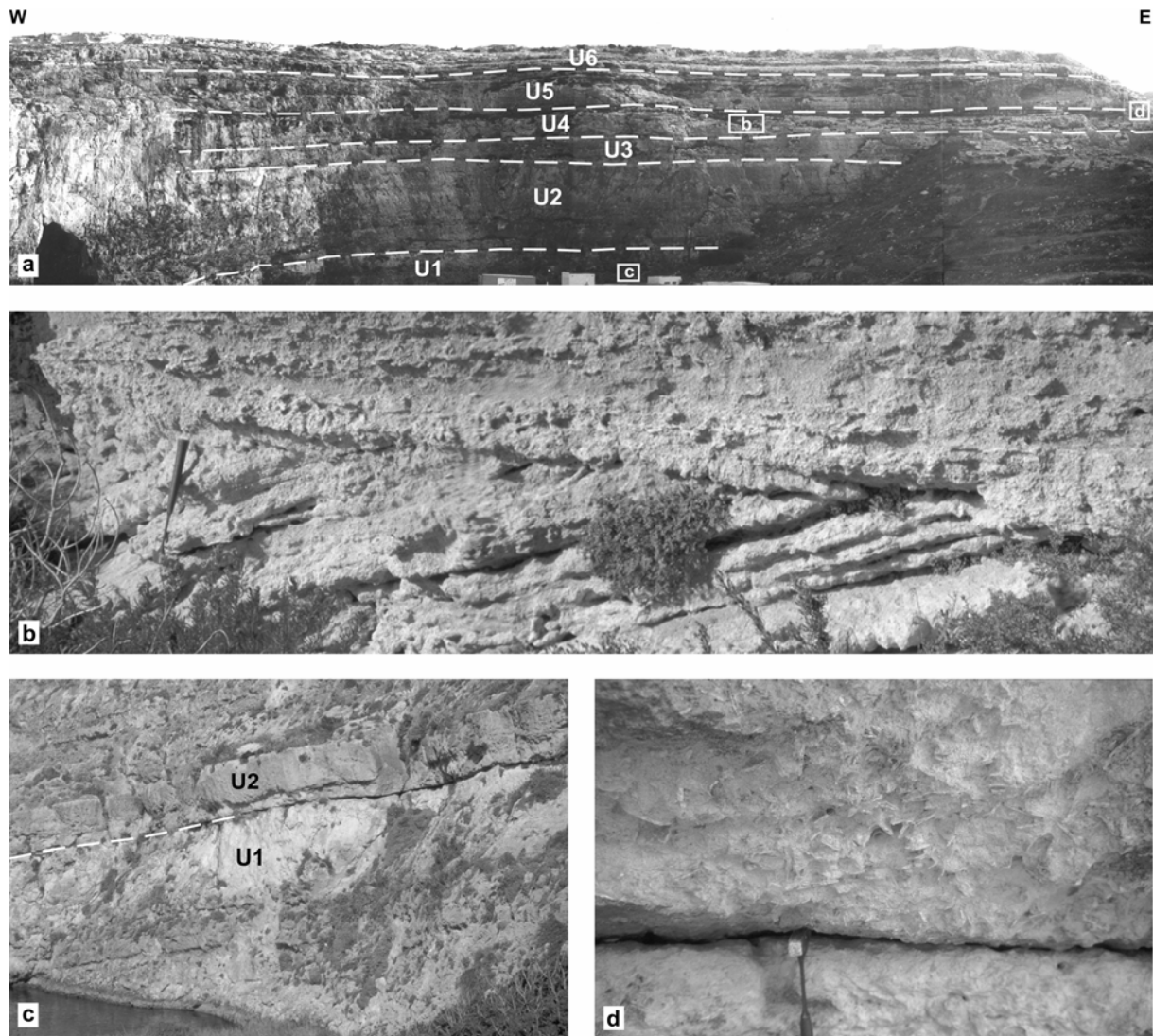


Figure 3a-d Outcrop photographs; **a.** panoramic view of section Dweira, indicated are the facies (U1-U6) and the location of the close ups (b-d); **b.** close up of the planar and trough-cross bedded facies U4; **c.** close up of the boundary between unit U1 and unit U2, clearly visible is the erosive contact between the two units; height app. 7m, **d.** close up of the rudstone shell beds above the boundary between unit U4 and unit U5; note the enrichment in *Scutella* in the upper bed

2.4.1 Hierarchical cluster analysis of the rock composition

The compositional data have been treated with a hierarchical cluster analysis. The main components chosen for the analysis have factor loadings above ± 0.7 , and include bryozoans of different growth forms, coralline red algae (of rhodolitic and articulated growth form), bivalves, small and larger benthic foraminifers, echinoids, unidentified biota (this includes all fragments too small to be identified) and detrital micrite. Gastropods and barnacles were excluded according to the factor analysis. The cluster analysis resulted in four distinguishable clusters (see Table III). Cluster 1 is characterised by a high content of echinoids (18%), calcareous red algae (21%), foraminifers (17%) and the least micrite (23%). Cluster 2 is dominated by calcareous red algae (47%), both of the articulated growth form as well as rhodolites, with micrite (27%). Cluster 3 is characterised by the highest amounts of unidentified, broken biota (28%), bryozoans (11%), echinoids (15%) and micrite (36%). Cluster 4 is the richest in micrite (54%) and comprises a relative high amount of foraminifers (14%).

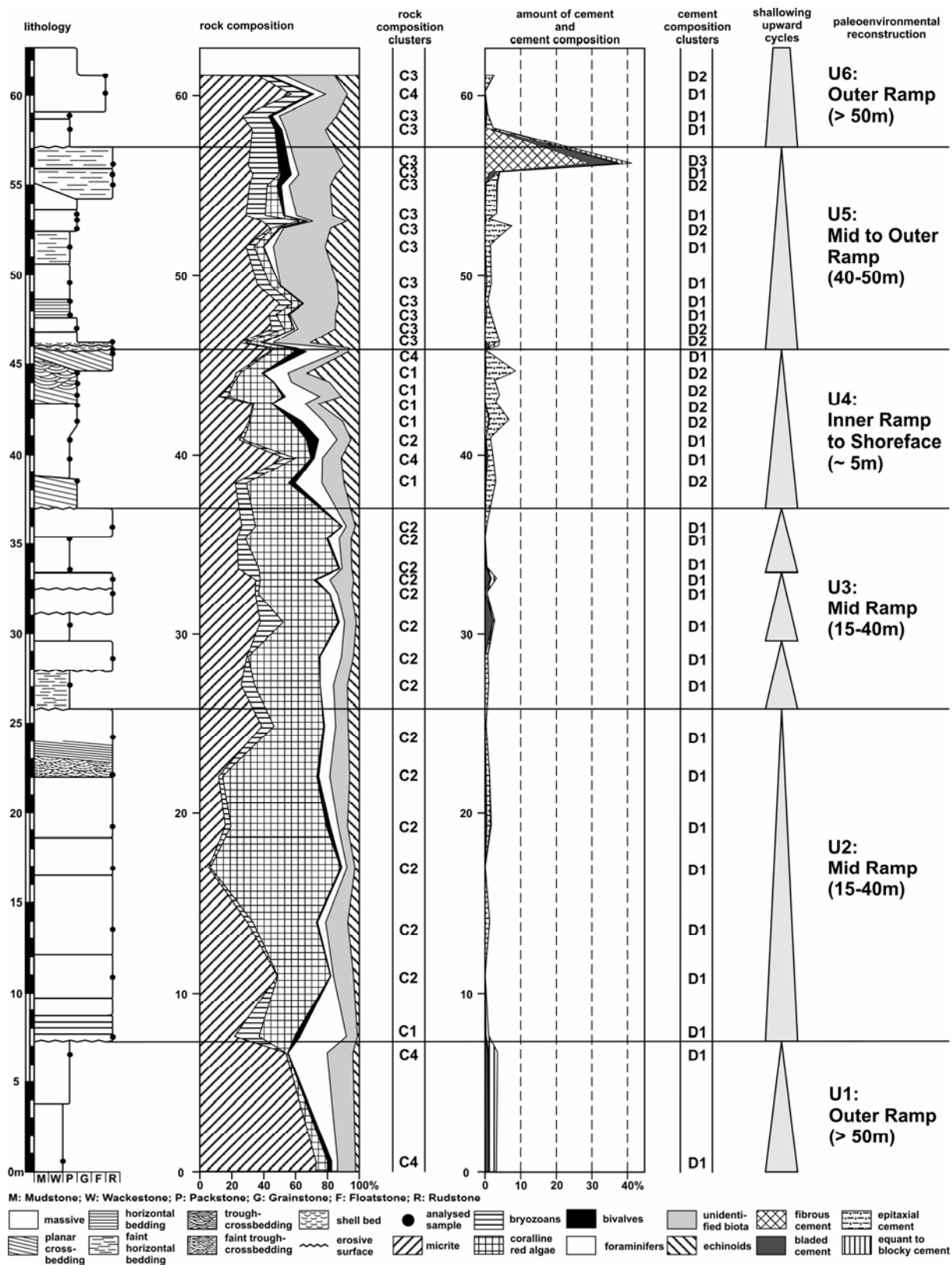


Figure 4 Measured section of the Lower Coralline Limestone Formation on Gozo. To the right of the stratigraphic profile are depicted lithology, including sedimentary textures (see Table I), and the rock and cement composition based on point-counting (see Table II). Moreover the results of the hierarchical cluster analysis of the rock (C1-C4) and of the cement composition (D1-D3) are shown. Also included are the interpreted depositional environments (U1-U6)

Table I - Depositional lithofacies; LB: Lower Boundary; UB: Upper Boundary

Facies	Boundaries	Lithology	Bedding, Sedimentary Structures	Sediment Composition (see Table II for details)	Depositional Environment
U1 (0-7 m)	LB: not accessible UB: erosive	wackestones and packstones	massive beds, mean thickness 3 m	micrite is dominant, subordinate biota: benthic foraminifers (up to 15%), coralline red algae (5%), bivalves and echinoids (4%)	outer ramp (>50 m water depth)
U2 (7-26 m)	LB: erosive UB: erosive	rudstones	lower 15 m massive, followed by 2 m of trough and planar cross bedding (dm scale); topmost 2 m again massive	dominated by coralline red algae (up to 77%, mean 40% mostly rhodolitic growth form), minor constituents include encrusting bryozoans (up to 10%), small and larger benthic foraminifers, echinoids, micrite	mid-ramp (15-40 m water depth)
U3 (26-37 m)	LB: erosive UB: erosive	alternation of rudstones and packstones	massive rudstone beds (mean thickness 1.5 m), sometimes with erosive bases; packstones (mean thickness 2 m) with faint horizontal lamination	dominated by coralline red algae (23% rhodolitic growth form, 17% articulated), minor constituents include different bryozoans (up to 12%), small and larger benthic foraminifers, echinoids, micrite	mid-ramp (15-40 m water depth)
U4 (37-46 m)	LB: erosive UB: erosive	grainstones with some packstones and rudstones	bed thickness varies between 2-4 m; Beds show trough and planar cross bedding, some beds pinch out laterally	articulated coralline red algae (20%), larger benthic foraminifers (up to 10%), small benthic foraminifers (10%), echinoids (12%), bivalves and bryozoans, micrite	inner ramp to shoreface (ca. 5 m water depth)
U5 (46-57 m)	LB: erosive UB: erosive	rudstone shell banks (pectinids, <i>Scutella</i>) grainstones and packstones	shell beds (0.3 m) have erosive bases; with faint horizontal lamination in the remaining strata; some beds pinch out laterally	broken, unidentified biota (23%), echinoids (14%), bryozoans (8%), micrite; coralline algae are subordinate (up to 8%)	mid to outer ramp (40-50 m water depth)
U6 (57-63 m)	LB: erosive UB: not accessible	packstones and rudstones	massive beds; mean thickness 2 m	broken, unidentified biota (24%), echinoids (12%), bryozoans (11%); occurrence of planktonic foraminifers	outer ramp (>50 m water depth)

Table II - Point-counting results; ID: Identification; 1: fibrous, epitaxial and bladed-prismatic cement; 2: blocky sparry calcite cement; 3: primary porosity; 4: secondary porosity

Sample ID	Facies	Micrite	Bryozoans	Coralline red algae		Benthic foraminifer		Plankt. foram.	Echinoids	Unident. biota	Cement				Porosity	Rock Cluster	Cement Cluster
				Rhodolites	Articulated	Small	Larger				Bivalves	1	2	3			
DW-1	U1	73.13	0.00	0.00	0.00	5.97	2.24	0.00	1.99	9.20	1.00	2.24	1.24	3.00	C4	D1	
DW-2	U1	64.86	0.00	0.00	0.00	0.74	0.25	0.00	2.73	11.17	0.99	2.48	0.00	1.50	C4	D1	
DW-3	U2	31.62	12.97	4.99	14.21	2.99	2.99	0.00	1.00	5.99	0.25	0.75	0.00	8.25	C1	D1	
DW-4	U2	46.25	0.25	12.66	12.66	0.25	0.25	0.00	2.73	9.68	0.00	0.00	0.00	7.25	C2	D1	
DW-5	U2	32.61	3.50	15.25	22.00	4.50	0.75	0.00	6.75	13.00	1.25	0.00	0.00	4.00	C2	D1	
DW-6	U2	9.48	1.00	77.75	0.00	0.00	0.75	0.00	2.50	4.75	0.00	0.00	0.75	3.25	C2	D1	
DW-7	U2	26.65	2.99	50.12	0.75	2.24	2.24	0.00	6.23	4.99	1.50	0.25	0.00	5.25	C2	D1	
DW-8	U2	25.91	2.00	43.64	3.49	4.99	1.00	0.00	4.74	9.98	1.25	0.00	2.49	3.75	C2	D1	
DW-9	U2	39.81	7.48	16.96	13.47	6.23	0.50	0.00	6.73	7.73	0.25	0.00	0.00	3.75	C2	D1	
DW-10	U3	26.37	7.75	29.00	11.25	7.25	1.00	0.00	7.25	8.50	1.00	0.00	0.00	2.50	C2	D1	
DW-11	U3	35.62	0.75	7.75	32.25	4.25	0.50	0.00	3.25	6.75	0.75	0.00	0.25	4.50	C2	D1	
DW-12	U3	42.10	9.25	23.36	7.30	2.68	0.24	0.00	1.70	6.57	2.19	0.49	0.00	5.25	C2	D1	
DW-13	U3	35.58	2.00	27.93	15.71	3.99	0.75	0.00	4.49	8.73	0.50	0.00	0.00	6.75	C2	D1	
DW-14	U3	42.90	0.99	8.37	19.70	5.17	1.97	0.00	2.96	12.32	1.72	1.48	0.00	4.25	C2	D1	
DW-15	U3	31.89	11.50	18.25	26.00	1.25	0.00	0.00	4.25	5.25	0.50	0.00	0.00	2.50	C2	D1	
DW-15A	U3	24.37	4.95	31.93	18.32	4.95	1.98	0.00	4.95	7.43	0.00	0.00	0.00	2.50	C2	D1	
DW-16	U3	30.86	7.98	37.41	12.22	1.00	1.25	0.00	2.24	5.24	0.50	0.00	1.00	1.50	C2	D1	
DW-17	U4	20.65	6.50	0.00	24.25	12.75	2.75	0.00	8.75	12.75	3.00	0.00	0.00	9.50	C1	D2	
DW-18A	U4	51.74	6.20	0.00	9.43	4.47	0.50	0.00	10.92	11.41	2.23	0.00	0.00	2.50	C4	D1	
DW-18B	U4	28.08	2.48	0.00	35.64	10.15	0.25	0.00	4.70	7.92	1.49	0.00	0.00	14.50	C2	D1	
DW-18C	U4	31.81	0.74	0.00	23.21	12.10	0.00	0.00	9.14	10.62	6.67	0.00	0.00	10.75	C1	D2	
DW-18D	U4	34.35	0.75	0.00	10.50	11.50	7.75	0.00	23.75	7.75	3.00	0.00	0.00	3.25	C1	D2	
DW-19A	U4	19.67	4.24	0.00	30.17	12.97	5.74	0.00	9.73	11.97	3.99	0.00	0.00	6.50	C1	D2	
DW-19B	U4	27.09	0.74	0.00	21.84	9.18	0.50	0.00	16.63	21.09	2.73	0.00	0.00	6.25	C1	D2	
DW-19C	U4	22.90	2.25	0.00	12.25	10.00	3.50	0.00	29.00	10.50	8.50	0.00	0.00	6.00	C1	D2	
DW-20A	U4	44.54	1.25	1.75	12.50	9.00	10.75	0.00	6.75	6.00	0.00	0.00	0.00	12.25	C4	D1	
DW-20B	U5	45.55	1.25	0.00	10.00	8.75	12.75	0.00	5.50	8.00	1.50	2.25	0.75	6.50	C4	D1	
DW-21	U5	29.12	3.24	0.00	8.48	4.74	0.75	0.00	27.43	20.70	3.99	0.00	0.00	13.75	C3	D2	
DW-22	U5	46.29	7.00	0.00	6.25	2.00	0.00	0.00	13.75	21.75	2.75	0.00	0.00	0.75	C3	D2	
DW-23A	U5	45.77	3.73	0.00	6.72	0.50	0.00	0.00	13.68	26.37	1.49	0.00	0.75	2.75	C3	D1	
DW-23B	U5	50.01	7.50	0.00	5.75	1.00	0.00	0.00	12.25	20.75	0.75	0.00	2.00	1.00	C3	D1	
DW-24	U5	37.32	6.98	0.00	5.49	0.25	0.00	0.25	12.47	33.17	1.75	0.00	0.00	4.75	C3	D1	
DW-25	U5	35.12	4.25	0.00	5.00	4.50	0.50	0.00	19.00	29.00	1.50	0.00	0.00	11.25	C3	D1	
DW-26A	U5	42.06	1.25	0.00	3.50	1.50	1.00	0.00	15.25	25.25	7.50	0.00	2.50	0.25	C3	D2	
DW-26B	U5	43.33	11.50	0.00	3.00	1.75	1.00	0.00	7.00	19.00	1.00	0.25	0.25	10.25	C3	D1	
DW-26C	U5	34.06	8.68	0.00	10.17	5.21	1.24	0.00	14.64	20.10	3.23	0.00	0.00	9.50	C3	D2	
DW-27	U5	40.96	2.72	0.00	4.95	1.98	1.98	0.00	14.60	20.79	3.22	0.25	0.00	12.25	C3	D2	
DW-28	U5	47.14	2.92	0.00	0.73	2.43	0.73	0.00	9.98	16.06	3.89	0.24	0.73	21.25	C3	D1	
DW-29	U5	18.75	1.00	0.00	0.25	1.50	0.75	0.00	5.00	16.00	37.75	3.50	1.25	9.50	C3	D3	
DW-30	U6	39.73	10.50	0.00	0.00	1.25	0.25	0.25	16.75	19.75	2.24	0.00	4.75	7.25	C3	D1	
DW-31	U6	34.13	13.00	0.25	0.25	1.50	1.75	0.75	12.50	32.00	0.74	0.00	0.00	2.00	C3	D1	
DW-32A	U6	56.23	8.25	0.00	0.00	1.75	4.50	0.25	7.00	13.00	0.00	0.00	0.00	20.75	C4	D1	
DW-32B	U6	40.32	5.24	0.25	0.25	4.24	1.25	2.99	13.22	28.18	2.49	0.00	0.00	8.50	C3	D2	

Table III - Cluster analysis of compositional data; n: number of samples; SD: standard deviation

Component	Cluster 1			Cluster 2			Cluster 3			Cluster 4		
	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
micrite	8	23.43	6.35	15	27.28	11.05	14	36.09	7.15	6	54.09	10.67
bryozoans	8	4.50	4.93	15	5.13	4.37	14	10.94	6.31	6	3.60	4.91
coralline red algae	8	21.14	8.75	15	46.59	13.51	14	4.26	3.41	6	7.33	5.78
bivalves	8	2.38	2.13	15	1.32	1.87	14	1.98	2.25	6	3.02	2.42
foraminifers	8	16.77	7.03	15	5.98	3.51	14	3.75	2.64	6	14.20	9.82
unidentified biota	8	14.25	6.24	15	8.88	3.13	14	27.80	5.05	6	11.38	3.54
echinoids	8	17.53	6.24	15	4.82	1.85	14	15.18	3.81	6	6.38	3.08

2.4.2 Paleoenvironmental reconstruction

In this section we integrate data presented in Fig. 4, as well as Tables I, II and III to discuss a paleoenvironmental interpretation for each of the six units distinguished in the Lower Coralline Limestone.

The first unit (U1) consists of massive wacke- to packstones (Fig. 3c). The rocks are rich in micrite and the only common biota are small and larger benthic foraminifers (compositional cluster 4, Table III, Fig. 5a). This unit corresponds to the Maghlaq Member. The absence of planktonic foraminifers as well as cross-stratification, and the micritic nature of the sediment led Felix (1973) and Pedley (1978) to interpret these sediments as deposited in a "shallow gulf-type area" in a water depth of about 50 m. Our data support deposition in an outer ramp setting below storm wave base, where no winnowing of the micrite occurred.

Unit 2 consists of massive rudstones at the base which pass over to the top to planar- or trough cross-bedded rudstones. Unit 2 is erosionally overlain by alternating pack- and rudstone beds of unit 3, which sometimes display horizontal bedding. Both units consist predominantly of calcareous red algae and correspond to composition cluster 2 (Table III). The lower, unbedded part (U2) is dominated by pavement forming rhodolites (Fig. 5b) whereas in the upper part (U3) rhodolites successively disappear but articulated calcareous red algae increase in content (Fig. 5c). Abrasion and reworking of the sediment particles, as well as cross-bedding (U2) and erosive surfaces (U3), indicate strong current action. Unit 2 and 3 correspond to the Attard Member. The presence of *Lithotamnion* requires high-energy in water depth between 12 to 25 m (Johnson, 1963). For this reason Pedley (1978) assigned a paleowater depth shallower than 25 m. This data suggest that Unit 2 formed in a mid to inner ramp setting between the storm and the fair weather wave base, where wave agitation occasionally turned the rhodolites around, but did not winnow all the micrite out of the sediment, whereas unit 3 was closer to the fair weather wave base and sediment was more often subject to wave action and reworking.

Unit 4, consisting of well sorted, planar- and trough-cross bedded grain- and rudstones (Fig. 3b), is rich in small and larger benthic foraminifers and echinoids (compositional cluster 1, Table III, Fig. 5d). The sediments show clear signs of current action (cross-bedding, reworking, sorting) and were deposited above the fair weather wave base on the inner ramp to shoreface. The abundance of light dependent larger foraminifers (up to 10%) is consistent with sedimentation in the photic zone. This unit corresponds to the Xlendi Member, which Pedley (1978) interpreted as deposited below 5 m of water depth.

Unit 5 consists of grain- to packstones and rudstones. This unit is dominated by echinoderms and unidentified broken biota with micrite (compositional cluster 3, Table III, Fig. 5e). The base of the unit is formed by two shell beds comprising (1) pectinids and (2) echinoderms (*Scutella*), which erosionally truncate the underlying beds (Fig. 3d). The remaining strata contain hints of horizontal lamination. The micrite implies deposition in quiet waters, while the strong fragmentation of the grains together with the relative enrichment of echinoderms resistant to mechanic abrasion, suggests reworking in agitated waters. These beds could be interpreted as storm deposits on a deepening ramp where material was washed

down from the shallower areas. Unit 5 most probably equals the so called II Mara Member of Pedley (1978) that was deposited in water depth less than 50 m.

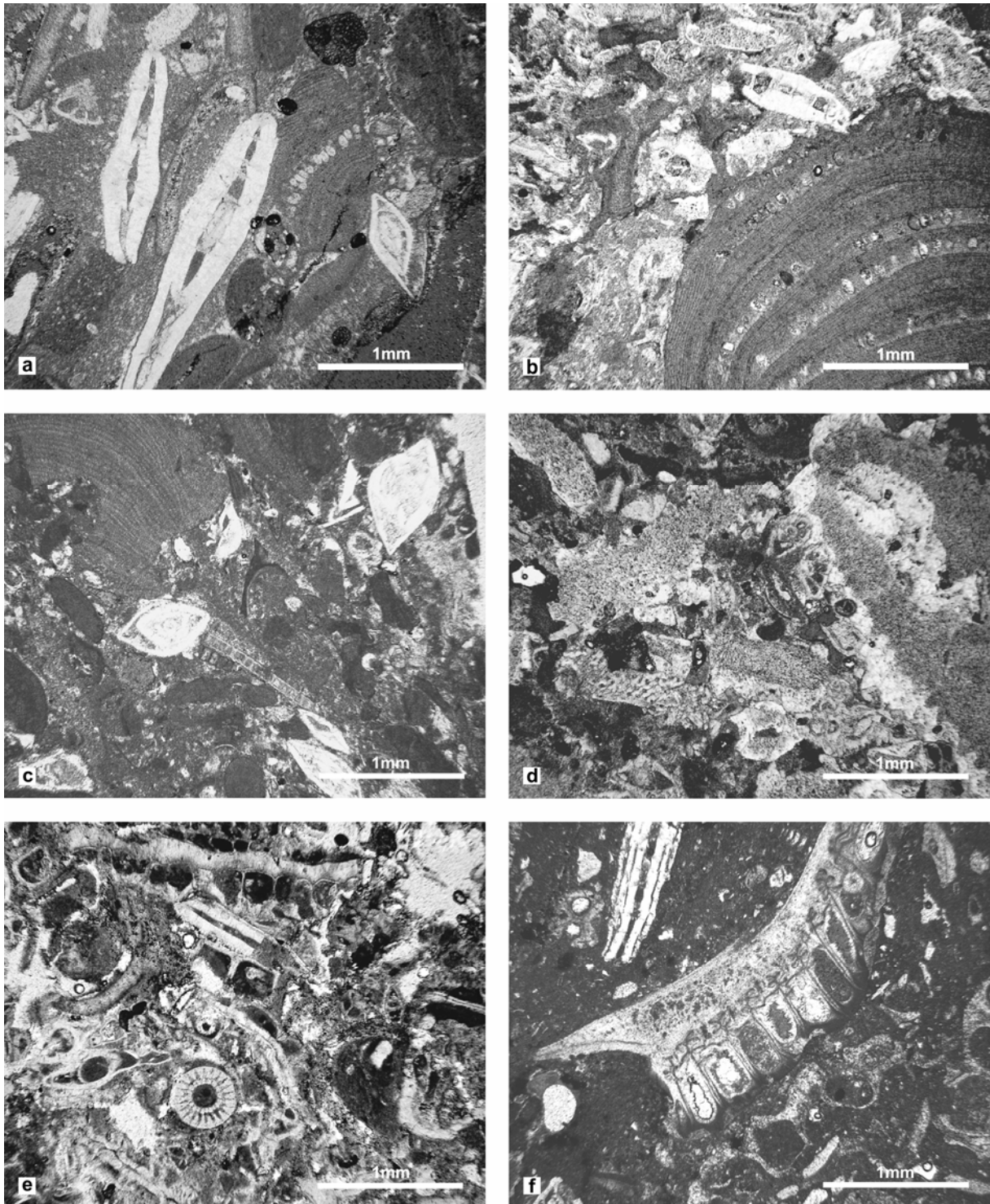


Figure 5a-f Microphotographs of biofacies. **a.** Unit 1, Note the high content in micrite and in small and larger benthic foraminifers; **b.** Characteristic thin section of unit 2 dominated by coralline red algae of the rhodolitic growth form; **c.** Unit 3, dominated by abraded rhodolites, articulated coralline red algae and benthic foraminifers; **d.** Unit 4, well sorted, micrite poor facies rich in echinoid fragments; **e.** Unit 5, dominated by strongly abraded and fragmented biota; **f.** Unit 6, note the high micrite content and the barnacle fragment

The topmost unit 6 (Fig. 5f) consists of massive grain- and rudstones and contains the same association of biota as the underlying unit 5. The only difference is the first appearance of planktonic foraminifers, indicating the transition to the overlying Globigerina Limestone Formation. The lack of storm deposits within this unit suggests a water depth below the storm wave-base, probably deeper than 50 m.

Overall, these carbonate facies can be attributed to a ramp setting where facies boundaries from outer ramp to near shoreface are mainly related to a hydrodynamic zonation (Fig. 6). The lack of a protective rim in this type of carbonate setting exposes the entire shelf to wave action ('wave sweeping', Osleger, 1991), so that wave base, storm frequency and intensity as well as water depth control sedimentation (e.g. James and Clarke, 1997). In the Mediterranean sea, which in contrast to open-ocean settings is characterized by relatively quiet shelves, sediment can also accumulate in the higher-energy shallow water areas.

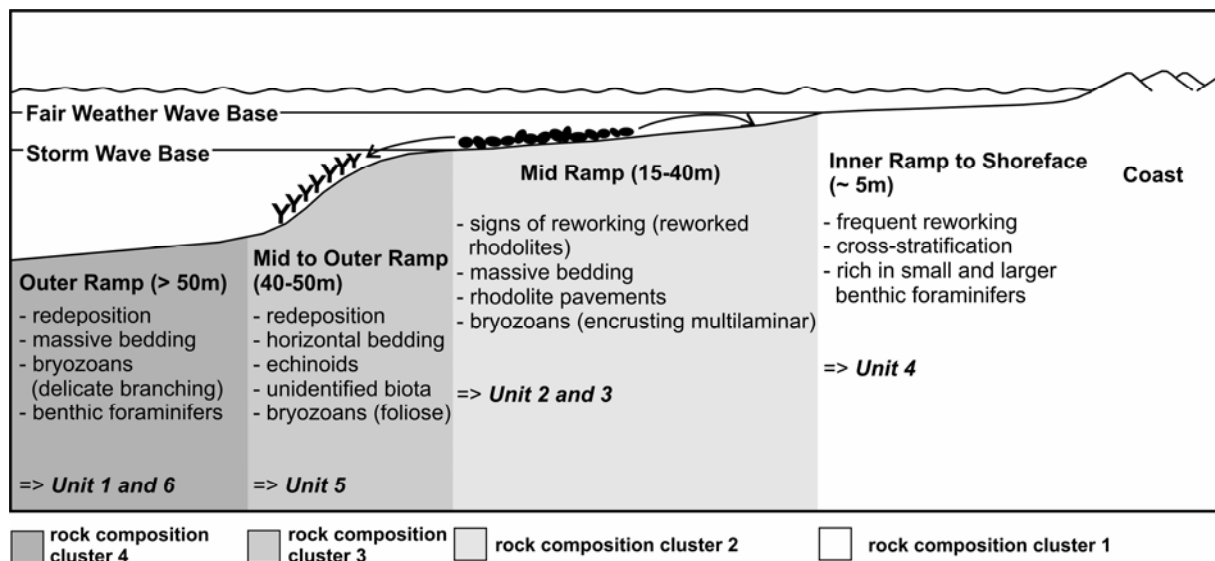


Figure 6 Reconstruction of the depositional environments and the paleobathymetry of the sedimentary units (Unit 1 – Unit 6) and their correlation with the rock composition clusters (1-4, indicated by shading)

2.4.3 Stable isotopes

2.4.3.1 Bulk rock measurements

Bulk $\delta^{18}\text{O}$ values range from -0.5‰ to -3.3‰ , and $\delta^{13}\text{C}$ values vary between 0.3‰ and -2.5‰ (Fig. 7). Plotted against the stratigraphic profile, carbon and oxygen isotopes display mainly a covarying trend (Fig. 8).

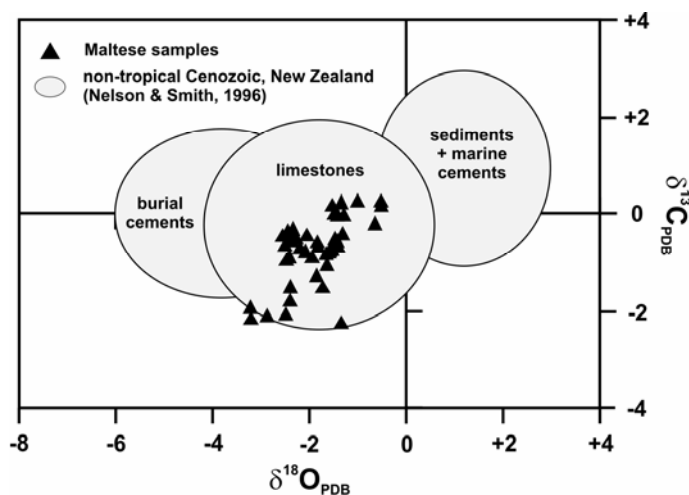


Figure 7 Cross-plot of carbon and oxygen isotopic values of the bulk-rock Maltese samples in comparison with non-tropical data from New Zealand (Nelson and Smith, 1996)

Unit 2 has fairly constant $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of about -1.5‰ and -0.7‰ respectively. Unit 3 displays varying values for $\delta^{18}\text{O}$ (between -0.5‰ and -2.5‰) and $\delta^{13}\text{C}$ (ranging from 0.5‰ to -2.0‰). The most depleted values in both oxygen and carbon occur in Unit 4, where the $\delta^{18}\text{O}$ values reach -3.2‰ and the $\delta^{13}\text{C}$ values -2.5‰ . Unit 5 and 6 display again rather constant values for $\delta^{13}\text{C}$ (around -0.5‰), but show a slight trend to more positive $\delta^{18}\text{O}$ values towards the top of the profile (from -2.2‰ to -0.5‰).

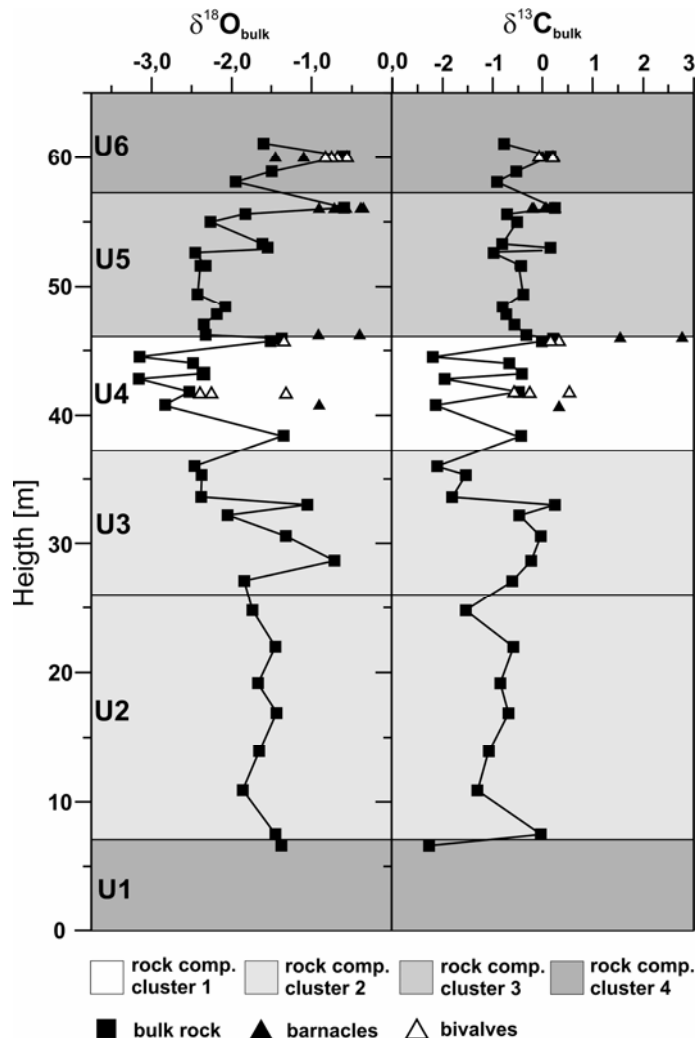


Figure 8 Carbon and oxygen isotopic composition of bulk rock and shell samples from the Lower Coralline Limestone, plotted versus section height (see section in Fig. 4). Indicated are the depositional units (U1 – U6) and, by shading, the sediment composition clusters (1-4)

2.4.3.2 Stable isotopic measurements of barnacle and bivalve calcite

In order to obtain geochemical constraints on paleotemperatures at the time of deposition, we have measured the isotopic composition of low-magnesium calcite shells of barnacles and bivalves. Sampled bivalve shells comprise pectinids, whereas barnacle shells occur in fragments too small to be further identified. Because low magnesium calcite is the primary mineralogy of these shells, their isotopic composition is likely to retain the original marine signature. The $\delta^{18}\text{O}$ values of 14 measured barnacle calcite samples range between -0.4‰ and -1.0‰ , the $\delta^{13}\text{C}$ values vary between 2.8‰ and -0.3‰ (Fig. 9A). The measurement of 7 bivalve calcite samples resulted in values between -1.3‰ and -2.5‰ , $\delta^{13}\text{C}$ values range from 0.5‰ to -0.5‰ .

The measured samples come from the upper part of the section from unit 4, 5 and 6. In Units 5 and 6 the measured $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the biota calcite are consistent with the results of the bulk rock analysis (Fig. 8). Only the samples taken in unit 4 show an offset

between bulk rock and single biota measurements, with shell samples systematically heavier than bulk rock samples.

Temperatures of precipitation were calculated for bivalve calcite using the general equation by Epstein et al. (1953), and for barnacle calcite the specific equation by Killingley and Newman (1982). Taking a $\delta^{18}\text{O}$ value for the Late Oligocene ocean water between -0.3 and -0.9 ‰ (Zachos et al., 2001; Billups and Schrag, 2002), which assumes permanent ice on Antarctica at that time, the calculated paleotemperatures range between 17° and 23°C (Fig. 9b), which is typical of temperate to subtropical carbonates (Betzler et al., 1997; James, 1997).

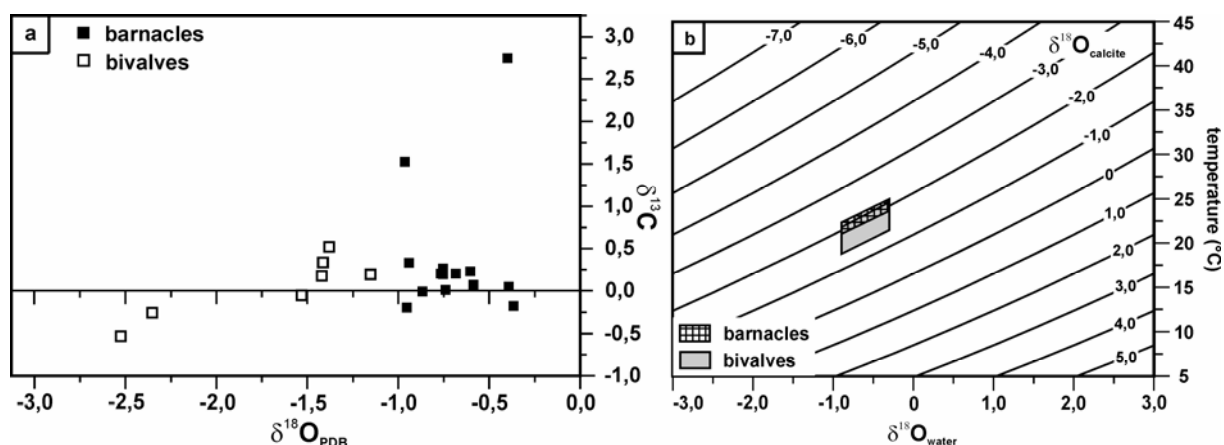


Figure 9 a. Plot of the $\delta^{18}\text{O} - \delta^{13}\text{C}$ isotopic composition of barnacle and bivalve calcite samples. **b.** This diagram displays the paleotemperature range (hatched and shaded areas) calculated for bivalve (Epstein et al., 1953) and barnacle (Killingley and Newman, 1982) calcite in relationship with the $\delta^{18}\text{O}$ composition of seawater. For the Oligocene ocean waters, a $\delta^{18}\text{O}$ range of -0.3 to -0.9 ‰ was assumed (Billups and Schrag, 2002)

2.5 DIAGENESIS

2.5.1 Paragenesis of diagenetic features

Several diagenetic features have been observed in the studied section including different episodes of cementation, dissolution, neomorphism and compaction. Cement types comprise fibrous, bladed - prismatic, epitaxial and blocky calcite cements. See Fig. 4 and Table II for the abundance of cement types in the studied section. Below they are described according to their paragenesis.

Fibrous cements line the grains in isopachous rinds. The elongated crystals nucleate picket-fence style on the substrate and have an average length of 10 to 20 μm . The crystals are inclusion-rich (Fig. 10a) and show a patchy pattern under CL (Fig. 10b) indicating that the cement is recrystallized (see neomorphism). In general fibrous cements fringe intra particle pore spaces such as bryozoans or foraminifer chambers (Fig. 10c). Rarely can they also be found in interparticle pore spaces. This cement type is normally scarce, forming only 1 to 2% of the total rock volume (Fig. 4). Only one sample contains 29% of fibrous cement which is formed by exceptionally large crystals of up to 150 μm length (Fig. 10a, b; Fig. 11a, b).

Epitaxial cement I, precipitated in optical continuity with the substrate and formed mostly around echinoderms. It consists of a thin rim (30 μm) of inclusion rich crystals with prismatic terminations that grew perpendicular to the substrate (Fig. 10d, e, f, Fig. 11c). The crystals display a patchy pattern under CL (Fig. 10f, h), indicating that the cement is recrystallized. In some places this epitaxial cement I is dissolved (see Fabric selective dissolution II) (Fig. 10d, e).

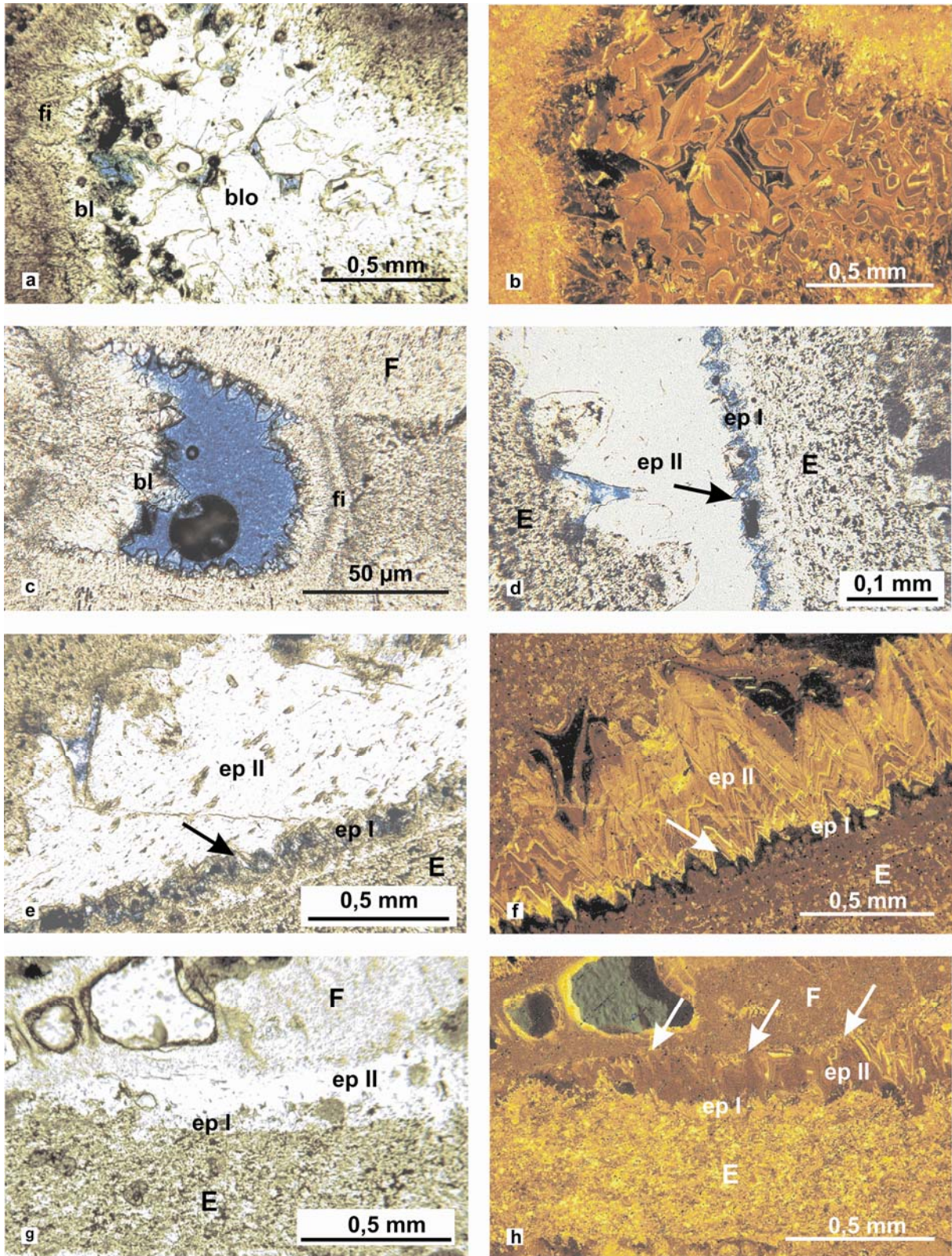


Figure 10a-h Photomicrographs of cements and other diagenetic features. **a.** Note fibrous, inclusion-rich cement (fi) and bladed – prismatic cement (bl) postdated by blocky calcite cement (blo). **b.** as a, in CL. Note the patchy luminescence in the fibrous cement and the clear zonation in the bladed – prismatic and blocky calcite cements. **c.** Fibrous (fi) and bladed - prismatic (bl) cements precipitated in an interparticle pore within a foraminifer (F). **d.** Two phases of epitaxial cements, growing on echinoids fragment (E), the first (ep I) is inclusion-rich and has been partially dissolved (arrow), the second (ep II) is inclusion-free. **e.** Two phases of epitaxial cements, growing on echinoids fragments (E). The first (ep I) is inclusion-rich and has been partially dissolved (arrow), the second (ep II) is inclusion-free. **f.** as e, in CL. Note the patchy luminescence in the ep I cement and the clear zonation in

the ep II cement. **g.** Note the sutured contact between a foraminifer (F) and an echinoid (E) overgrown by epitaxial calcite cements I and II (ep I and ep II). **h.** as **g.** in CL. Note how the epitaxial cement II (ep II) has been partially dissolved by pressure solution (arrows), indicating that precipitation of epitaxial cement II predated compaction

Neomorphism occurs as alteration of metastable high Mg calcitic (calcareous red algae, echinoderms) and aragonitic (bivalves, foliose bryozoans) biota to low Mg calcite. Fibrous and epitaxial cement I are also neomorphosed as suggested by the “patchy” pattern under CL (see Fig. 10b, f, h). This indicates that neomorphism and alteration took place after the precipitation of these cements.

Fabric selective dissolution I took place as dissolution of aragonitic biota like gastropods, bivalves and foliose bryozoans.

Bladed – prismatic cement consists of elongated scalenohedral crystals with prismatic terminations. Crystals are on average 20 to 90 μ m long and 5 to 10 μ m across and form rims of uneven thickness in intra and inter particle pore spaces (Fig. 10a, b, c, Fig. 11b). The original crystal fabric of this cement type is well preserved, with clearly recognizable zonations under CL (Fig. 10b). This cement type constitutes on average 1 to 2% of the sediment total, but can reach volumes up to 8% (Fig. 4).

Epitaxial cements II precipitated in optical continuity with the substrate, formed mostly around echinoderms, but is also occasionally found around foraminifers. This second phase of epitaxial cementation postdates epitaxial cements I (Fig. 10d, e, Fig. 11c). Larger volumes of inclusion free epitaxial calcite (average crystal size of 200 μ m) with zonations clearly visible under CL (Fig. 10f) precipitated atop the first phase, often forming a poikilotopic texture. This is the volumetrically most important cement type as it often contributes up to 6% to the sediment total and frequently dominates the cement fabric.

Fabric selective dissolution II especially affected the first phase of epitaxial cement (I) and, to minor amounts, high-Mg calcitic biota such as calcareous red algae and echinoderms. Echinoderms were partly dissolved along the cleavage planes of the calcite crystals whereas the red algae were more patchy dissolved. Dissolution of the first, inclusion rich epitaxial cement phase I leads to characteristic molds with prismatic terminations lining the host echinoderm (Fig. 10d, e, f).

Blocky sparry calcite cement comprises plane-sided, equant crystals with an average width of 40 to 60 μ m. The original crystal fabric is well preserved with clearly visible zonations under CL (Fig. 10b). This cement phase either grew poreward postdating fibrous and/or bladed cements or directly on the substrate, where the other cement phases are missing. Blocky cements on average form 1 to 2% of the sediment total (see Table II).

Compaction includes mechanical and chemical compaction (pressure solution). Mechanical compaction can be very intense on fragile components such as larger foraminifers. Chemical compaction includes grain to grain contacts, concave–convex contacts and even sutured contacts. No real microstylolithes were found. Chemical compaction postdates precipitation of epitaxial cements (Fig. 10h)

Dissolution III is non-fabric selective dissolution forms small vugs and channels, cross-cutting biota, matrix and cements. These vugs and channels either stay open or, more seldom, are filled with blocky calcite cements, and also postdate compaction features, suggesting that this phase of dissolution occurs quite late in the diagenetic sequence.

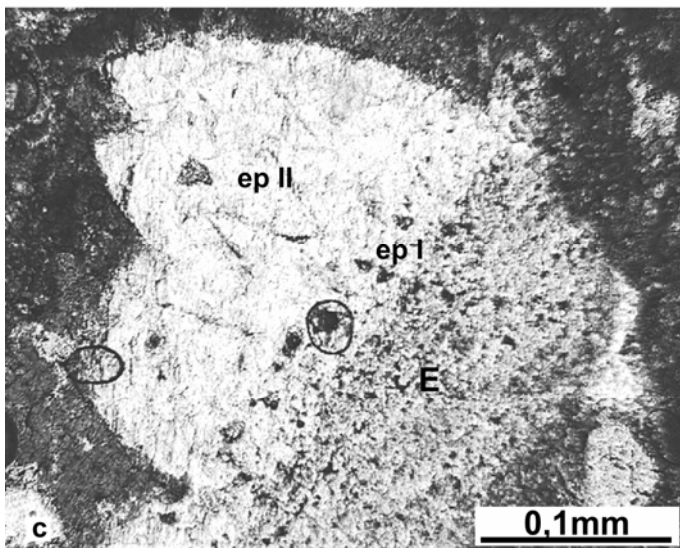
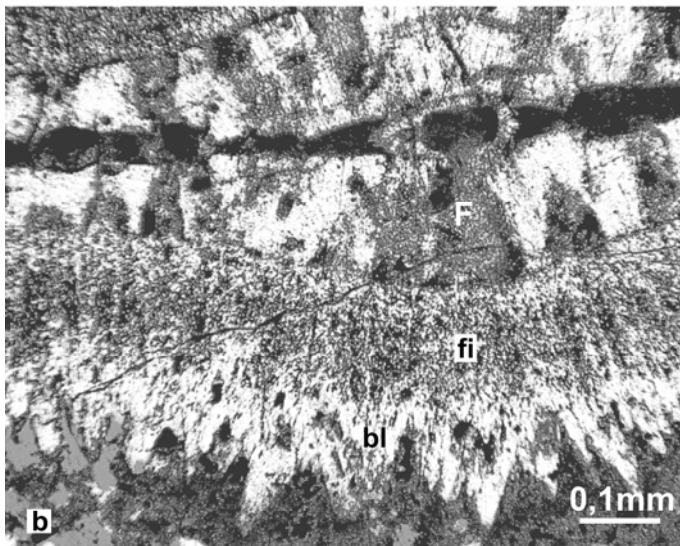
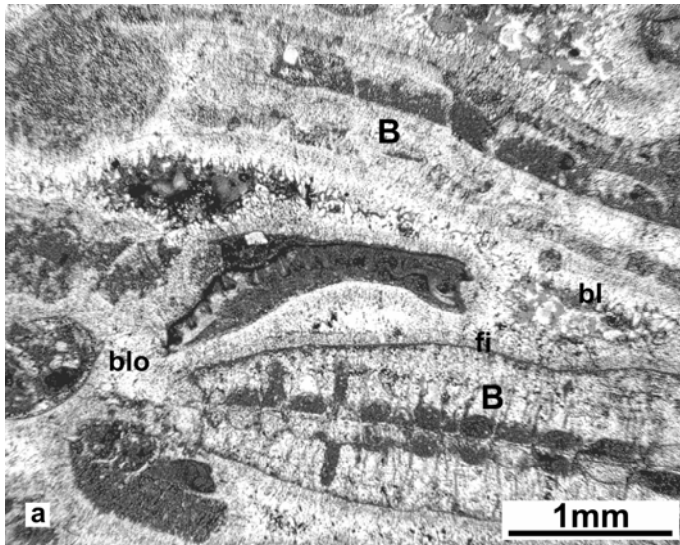


Figure 11a-c Microphotographs. **a.** Note the abundance of fibrous (fi) and bladed – prismatic (bl) cements lining and blocky cements (blo) filling the depositional pore space. Bryozoa (B) has been neomorphosed. **b.** Close-up showing the relationships between fibrous (fi) and bladed – prismatic (bl) cements growing on a foraminifer (F). **c.** Echinoid fragment (E) overgrown by epitaxial calcite cements I and II (ep I and II). Note the abundance of inclusions in ep I

2.5.2 Hierarchical cluster analysis of the cements

In analogy to the compositional data, the abundance of cement types has also been treated with a hierarchical cluster analysis. All cements observed (fibrous, bladed - prismatic, epitaxial and blocky cement) have factor loadings above +/- 0.7 and were included in the analysis. In contrast to the cluster analysis of the compositional data no standardisation to 100% was performed, because of the low share of cements on the sediment total which makes a standardisation useless. The cluster analysis resulted in three clusters (Table IV).

Cluster 1, which includes the most samples (n=30), contains only minor amounts of cement. Cluster 2, comprising 12 samples, has a mean of 4% cement. Cluster 3, including only one sample, is characterised by 42% cement (see Fig. 4, Fig. 11a, Table II). Epitaxial cement determines cluster 2, whereas cluster 3 contains 30% of fibrous, 8% of bladed - prismatic and 4% of blocky cement. In this cluster, epitaxial cement is rather unimportant.

Table IV- Cluster analysis of cement data; n: number of samples; SD: standard deviation

Cement type	Cluster 1			Cluster 2			Cluster 3		
	n	Mean	SD	n	Mean	SD	n	Mean	SD
fibrous	30	0.12	0.26	12	0.15	0.29	1	29.25	-
bladed-prismatic	30	0.35	0.63	12	0.02	0.07	1	7.75	-
epitaxial	30	0.61	0.55	12	4.09	1.95	1	0.75	-
blocky	30	0.35	0.74	12	0.02	0.07	1	3.50	-

2.5.3 Origin of diagenetic phases

Fibrous and epitaxial cement I. These two cements precipitated first, in direct contact to the particular host grain (Fig. 12). Most likely both cement types formed in the same diagenetic phase, but on different substrate (single crystal epitaxial cement on echinoderms, fibrous cement on other grains).

The petrographic characteristics of these cements have similarities to those of marine cements precipitated at or just below the sea-floor in tropical environments (James et al., 1976; Macintyre and Marshall, 1988). Such tropical marine cements typically consist of aragonite or Mg-enriched calcite which is nonluminescent due to precipitation from oxidizing fluids (James and Choquette, 1990b; Major and Wilber, 1991). The blotchy luminescence observed in the inclusion-rich calcite in the Maltese samples suggests that the cements are also the product of replacement of a former carbonate mineral phase. The well preserved crystallographic fabrics of the inclusion-rich calcite rules out an aragonitic origin and suggests an original calcitic mineralogy. Transformation from Mg-calcite to low Mg-calcite is known to occur as a dissolution precipitation process with preservation of the primary texture but modification of the chemical composition (Morse and Mackenzie, 1990; Major and Wilber, 1991; Melim et al., 1995). Similar cements have also been described in Oligocene cool-water carbonates from New Zealand (Nelson, 1978; Nelson et al., 1988a; Hood and Nelson, 1996) and from the Eucla platform in Australia (James and Bone, 1991; Nicolaidis and Wallace, 1997b), which were interpreted as the product of precipitation from marine water later modified under meteoric conditions. The lack of features related to meteoric diagenesis would point to a replacement process at or near the sea-floor or a marine-modified environment.

Bladed - prismatic cement. The precipitation of this cement phase postdates fibrous cement formation and predates blocky sparite growth (Fig. 10a, b, c; Fig. 12). As indicated by the original crystal fabrics and the clearly visible zonations under CL, no recrystallization/neomorphism occurred. This cement phase most likely precipitated as low Mg calcite from marine derived waters in the burial marine environment.

Epitaxial cement II and blocky sparry calcite. Both cement phases postdate earlier cement phases (epitaxial cement I, fibrous and bladed - prismatic cements respectively, see Fig. 12).

As both cements have well preserved crystal fabrics with similar zonation patterns under CL (Fig. 10b, f), it is likely that they formed at the same time on different host substrates. Epitaxial cement as well as blocky or equant spar has been described as forming in the meteoric, burial marine or deep burial environment (James and Choquette, 1988; James and Choquette, 1990a; Melim et al., 1995). Since there is no isotopic evidence, based on bulk samples, of meteoric diagenesis, the most likely environment of precipitation of these cements is burial marine, as described by Nelson et al. (1988a) and Melim (1995). The timing of precipitation of this cement, postdating sea-floor features and predating chemical compaction, is consistent with precipitation in the marine burial diagenetic environment.

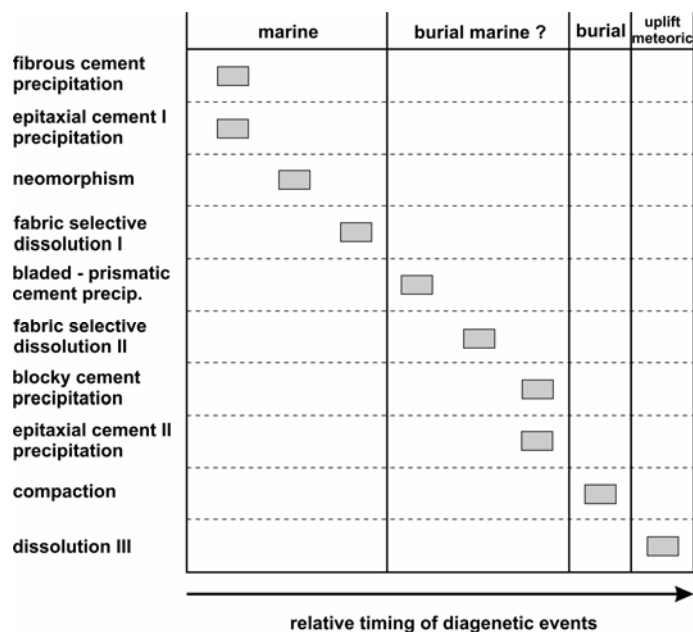


Fig. 12 Paragenetic pathway of the diagenetic events recorded in the heterozoan carbonates of the Upper Coralline Limestone Formation

2.6 CONTROL OF SEDIMENT COMPOSITION AND DEPOSITIONAL FACIES ON THE DIAGENETIC PATHWAY

Although all features discussed occur in most samples analysed in the heterozoan limestones of the Maltese Islands, there is a clear, facies-dependent variability in the intensity of cementation. Generally the intensity of cementation seems to be controlled by micrite content, sorting, primary porosity and, to a lesser degree, the biotic sediment composition. Fundamentally, there are two main diagenetic "facies": micrite-rich lithologies tend to be lithified by minor amounts of fibrous, bladed, epitaxial and blocky cement, in total only 1-2% of the total rock (mainly cement cluster 1), whereas well-sorted, micrite-poor lithologies are dominated by precipitation of large amounts of epitaxial cements on echinoids (mainly cement cluster 2). A third "facies", which can be seen more as an exception as it comprises only one sample, is characterized by the precipitation of large volumes of fibrous and bladed cements (cluster 3). This occurrence is probably controlled by the stratigraphic position of the sample as discussed below.

2.6.1 Micrite-rich lithologies (Facies U1, U2, U3, U6)

Micrite-rich, massive sediments can be found throughout the section, but are more common in the lowermost 37 m. Here matrix supported wacke- to pack- or rudstones were deposited in an outer- to mid-ramp environment with little wave agitation (below storm wave base/fair weather wave base respectively). Due to the high micrite content (up to 40 %) the primary permeability of these sediments was rather low.

The diagenesis of these rocks is characterised by limited cementation (1-2% of the sediment total), and sometimes by strong mechanical compaction. Chemical compaction features like grain to grain contacts or concave–convex contacts are scarce.

Low primary permeability and the presence of micrite in the interparticle pore spaces likely reduced the rate of fluid flow in the sediment which resulted in limited cementation. Moreover echinoderms, which are the nuclei for the crystallisation of the volumetrically most important epitaxial cements, are rather scarce in these sediments (mean 5%, maximum 7% of the sediment total).

Mechanical and chemical compaction occurred where components were in direct contact to each other. Larger foraminifers preferential suffered strong in-situ fragmentation because they are fragile and large enough to have several grain to grain contacts with neighbouring components. Where large amounts of micrite were present they prevented grain to grain contacts and acted like buffers during compaction.

2.6.2 Micrite-poor lithologies (Facies U4, U5)

Micrite poor, bedded sediments preferentially occur in the upper part of the section and were deposited in an inner-ramp to shoreface/mid- to outer-ramp setting (Figs. 4 and 6). High energy and wave agitation characterize both environments, resulting in good sorting, abrasion and breaking of grains, enrichment of components resistant to abrasion (echinoderms) and low micrite contents. These conditions promote high primary permeability values.

The diagenesis of these sediments is characterised by relative high cement contents (6 to 8% of the sediment total), and strong mechanical and chemical compaction. Cementation of these carbonates was supported by high primary porosity and permeability, allowing high rates of fluid flow through the sediment, and by the relatively high content of echinoderms (average of 16%), acting as nuclei for the epitaxial cements.

The abundance of echinoids in these settings is important for the diagenetic pathway: echinoderm-rich intervals (e.g., see Unit 5) undergo enhanced cementation which promotes later resistance to mechanical compaction. However, the amount of epitaxial cements is also relatively high in intervals which do not contain more echinoids than the rest of section, but are characterized by textures with high permabilities (see Unit 4). This indicates that the combination of the right substrate and adequate permabilities results in a higher abundance of epitaxial cements than in the micrite-rich facies. Low micrite contents have the effect of promoting mechanical compaction, and grain to grain as well as sutured contacts are common.

2.6.3 Exceptions - influence of the stratigraphic position

It has been shown (e.g. Nelson and James, 2000) that intervals in non-tropical carbonates that are particularly rich in early cements can be related to a specific stratigraphic position within the sedimentary column. Such a scenario could account for one sample (section meter 57) which was lithified by 40% of different cement types, mainly fibrous and bladed cements, followed by blocky calcite. These diagenetic features occur in a lithology consisting of well sorted, horizontal bedded, micrite poor rudstone at the top of Unit 5 (Fig. 4).

The explanation for this unusually high cement content is difficult. Bulk rock isotope data of this sample show a marine signal ($\delta^{18}\text{O}$ -0.5‰ ; $\delta^{13}\text{C}$ 0.0‰), which – given the significant volume of the cement within the bulk rock – is consistent with precipitation of the cements from marine or marine-derived fluids. As described by Nelson and James (2000) large amounts of marine cements can precipitate in non-tropical carbonates in specific strata or under special conditions (e.g. stacked, cross-bedded sand bodies, meter-scale, subtidal carbonate cycles or associated with certain unconformities). These cements precipitate as intermediate Mg-calcite from marine waters undersaturated with respect to aragonite and typically form isopachous rinds of fibrous to bladed spar. Poreward of the isopachous cement rinds equant spar is often found.

So the precipitation of the large amounts of fibrous, bladed and blocky cements could perhaps be associated with an unconformity, most probably with a condensed section. This could as well account for the high cement amount that strongly lithified the rock as for the strong dissolution of aragonitic biota, because the water at the same time promoted dissolution of aragonite and precipitation of intermediate Mg calcite.

2.7 CONCLUSIONS

We have recognized the occurrence of several diagenetic features in the late Oligocene heterozoan carbonate ramp of the Maltese Islands, which were formed in early marine to burial marine and burial environments. No evidence for early meteoric exposure was found.

An integrated analysis of sediment composition, depositional environments and diagenetic features has shown that the diagenetic pathway in heterozoan carbonates outcropping in the Maltese Islands depends on the primary sediment composition as well as the hydrodynamics of the sedimentary environment, which controls the depositional texture. These determine the overall porosity and permeability of the rocks, the occurrence of metastable grains, that provide a cement sources when dissolving, as well as the presence/absence of substrates for epitaxial cements.

Although all observed diagenetic features occur in most samples, there is a clear, facies-dependent variability in the intensity of cementation. Two main diagenetic facies occur. The first is characterized by minimal cementation (1-2%) and relatively strong mechanical compaction and it typically occurs in micrite-rich lithologies of Units 1, 2 and 3 (mid to outer ramp). The second is characterized by dominant cementation by epitaxial cements and subordinate fibrous and bladed cements and typically occurs in micrite-poor, well-sorted strata of Units 4 and 5 (inner to mid ramp). One sample lithified by over 40% of different cement types (mainly fibrous and bladed cements), constitutes an exception to this pattern and can be related to a specific stratigraphic position.

MISSING ARAGONITIC BIOTA AND THE DIAGENETIC EVOLUTION OF HETEROZOAN CARBONATES: A CASE STUDY FROM THE OLIGO-MIOCENE OF THE CENTRAL MEDITERRANEAN

3.0 ABSTRACT

Relatively few studies have so far addressed the diagenetic evolution in heterozoan carbonate assemblages. Generally it is assumed that early diagenetic processes in these settings are mainly destructive, including abrasion and dissolution at the sea floor. Constructive diagenesis (cementation) is delayed to later stages in the burial environment, with pressure solution of calcitic grains acting as cement source. This paper presents a study of Oligo-Miocene shallow-water heterozoan carbonates from the Central Mediterranean (Maltese Islands and Sicily) that indicates that early diagenetic processes in these settings are more complex than previously assumed. The spatial relationships and abundances of diagenetic features, together with the stable isotope and trace element composition of the single cement phases, enable us to determine the diagenetic environments, pathways and cement source(s).

The studied carbonate rocks are deposited in inner- to outer-ramp settings and consist of different heterozoan carbonate assemblages. Four to five different cement types, including fibrous, two types of epitaxial, bladed and blocky cements, can be distinguished. Based on cathodoluminescence microscopy a differentiation between primary high Mg calcitic (fibrous and epitaxial cement I) and primary low Mg calcitic (epitaxial cement II, bladed and blocky) cements can be made. Stable isotope data indicate cement precipitation out of marine, marine-derived and meteoric waters. Trace element analyses point to cementation under reducing conditions once in an open system (Maltese Islands) once in a closed system (Sicily). The synopsis of these data enables us to determine the diagenetic pathways, the main environment of diagenetic stabilization/cementation (burial marine) and to conclude on the main cement source (aragonite).

Our investigations show that in contrast to the general acceptance the majority of constructive diagenetic processes occurs rather early in the burial marine environment with aragonite being the main cement source. We suggest re-evaluating the importance of aragonitic components in heterozoan carbonate settings, which seem to be more abundant than previously assumed and act as a major early cement source. Our findings also hold implications when considering the reservoir qualities of these rocks, as primary porosity is occluded early and the secondary porosity formed is not preserved.

3.1 INTRODUCTION

Numerous studies have so far dealt with the diagenetic evolution of photozoan carbonates (*sensu* James, 1997) deposited in shallow water environments. In these settings, the importance of early seafloor and meteoric processes in modifying and stabilizing the sediment is undoubted (James and Choquette, 1990b; James and Choquette, 1990a; Dodd and Nelson, 1998). Inorganic cement precipitation as aragonite or high Mg calcite (HMC) on the seafloor occurs commonly as the result of the high carbonate saturation state in equatorial regions (Opdyke and Wilkinson, 1990). Moreover, typical photozoan carbonate sediments mainly consist of metastable aragonitic and high Mg calcitic skeletons, giving the sediment a high early diagenetic potential. When entering the meteoric environment these components are dissolved or neomorphosed in solutions undersaturated with respects to aragonite and HMC, but supersaturated with respect to low Mg-calcite (LMC). This leads on the one hand to the development of secondary moldic porosity and on the other hand to extensive cementation by

LMC. When entering the burial environment these rocks are mineralogically stable, well lithified, have lost much of their primary porosity, but also gained a high amount of secondary porosity.

In heterozoan carbonate settings (*sensu* James, 1997) it has been generally assumed that the potential for early diagenetic processes is low because seafloor cements are volumetrically unimportant. This does also account for the meteoric environment where hardly any dissolution of metastable biota and precipitation of stable cement take place. Hence when entering the burial environment much of the primary porosity of heterozoan carbonates has been preserved and hardly any secondary porosity has been formed. Only at the stage of burial diagenesis the main cementation of heterozoan carbonates takes place – with pressure solution of LMC grains being the cement source (Nelson et al., 1988a; Nicolaides and Wallace, 1997a; Dodd and Nelson, 1998).

Generally the scarcity of early seafloor cements in heterozoan carbonates has been attributed to: (1) the low saturation state of the seawater with respect to CaCO₃, unfavourable for inorganic cement precipitation (Morse and Mackenzie, 1990); (2) the biotic assemblage of heterozoan carbonates mainly consists of mineralogically stable LMC skeletons (Nelson et al., 1988b; Smith and Nelson, 1994). Only in recent years many authors (Brachert and Dullo, 2000; Cherns and Wright, 2000; Smith and Nelson, 2003; Wright et al., 2003) stated that metastable aragonitic biota are not so scarce in heterozoan settings as assumed before, but because they are removed early from the sediment record by dissolution their amount is largely underestimated. This leads to a misinterpretation of the primary biotic assemblage and to the underestimate of an important source for early diagenetic cementation.

This paper deals with the diagenetic evolution recorded in Oligo-Miocene shallow-water, heterozoan limestones outcropping in the Central Mediterranean (Maltese Islands and Sicily). In these two locations inner to outer ramp deposits composed of different types of heterozoan biotic assemblages are well exposed and form an ideal study area. Although these rocks were never deeply buried, they are very well lithified and form in the case of the Maltese Islands steep coastal cliffs. This raises the question of the source and the timing of cementation and lithification. The sections on the Maltese Islands and Sicily were chosen for comparison because both islands belonged during the Oligo-Miocene to the same, extended carbonate ramp system, but represent different facies associations. Therefore the influence of facies types on the diagenetic evolution of heterozoan carbonates can be ideally studied by comparing these two settings.

3.2 GEOLOGICAL SETTING AND STRATIGRAPHY

The studied sedimentary succession comprises shallow-water carbonate deposits of Upper Oligocene to Lower Miocene age, outcropping on the Maltese Islands and in SW Sicily (Fig.1A+B). During this time interval, these two locations were part of a geographically extensive carbonate ramp system located on the more distal part of the passive African continental margin (Pedley, 1998). The sedimentary rocks deposited on the Sicilian Ragusa Platform form the northern margin of a submarine rise which extends 80 km south to the Maltese Islands (Pedley, 1981). Paleogeographic reconstructions (Fig. 2A+B) locate both areas between 28° and 30°N in Early Chattian times moving northward to about 29° and 31°N in the Early Burdigalian (Dercourt et al., 2000). This is an appropriate location, on the boundary between the subtropical and the temperate climatic zone, for the development of heterozoan biotic assemblages. Sedimentation of the studied rocks took place in open, oceanic waters since the separation of the Proto-Mediterranean-Atlantic Region from the Prot-Indo-West Pacific Region was completed only in the Late Burdigalian times (Harzhauser et al., 2002).

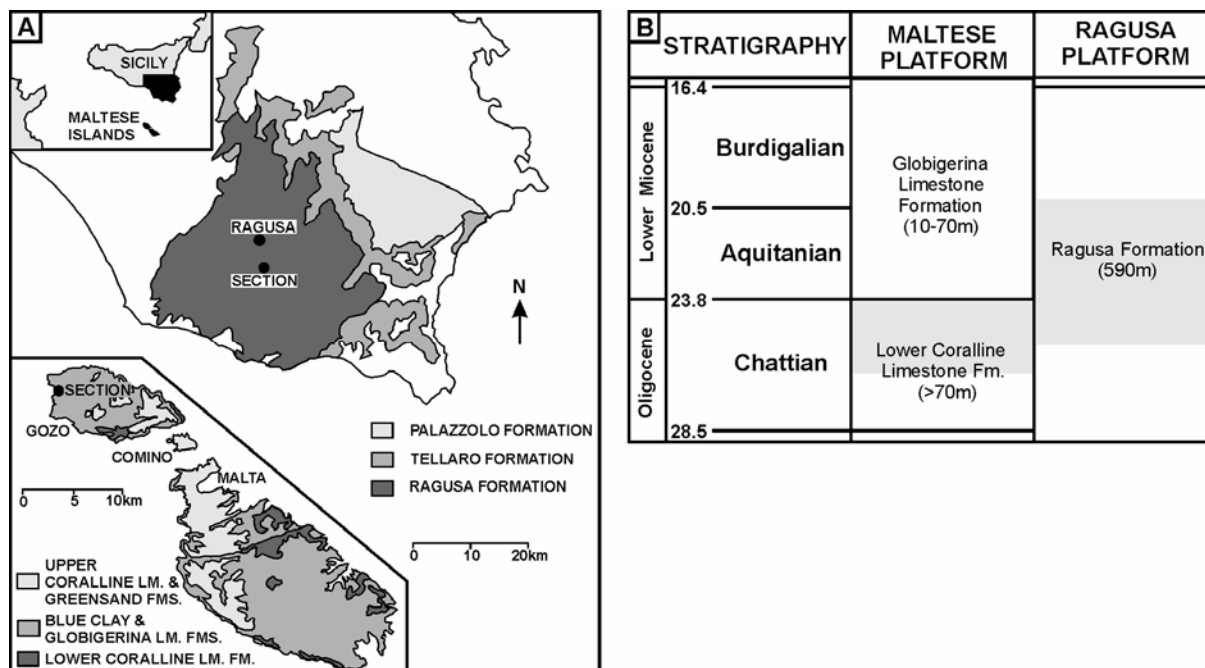


Figure 1 A. Geological map of the Maltese Islands and SE Sicily. For the Maltese Islands the lithostratigraphic units are displayed according to Felix (1973) and Carbone et al. (1987), for Sicily according to Pedley (1981) and Grasso and Lentini (1982). The location of the measured sections Dweira on Gozo and Ragusa on Sicily is indicated. LM Limestone; FM(S) Formation(s). **B.** Comparison of the studied lithostratigraphy and the age of the units. FM Formation

3.2.1 Stratigraphic setting

Maltese Islands.— The Oligo-Miocene sedimentary succession outcropping on the Maltese Islands comprises four major lithostratigraphic units (Fig. 1A) and records a step-wise evolution as described by several stratigraphic and sedimentological studies (Pedley, 1978; DiGeronimo et al., 1981; Carbone et al., 1987; Jacobs et al., 1996; Pedley, 1998; John et al., 2003).

The unit of interest in this study is the Lower Coralline Limestone Formation (Chattian, Fig. 1B). It was deposited in an inner- to outer-ramp setting and consists of rud- and packstones comprising skeletal fragments typical of heterozoan carbonates. This unit progressively drowned, as recorded by the development of several phosphatic hardgrounds (Jacobs et al., 1996; John et al., 2003), and was overlain by hemipelagic wackestones rich in planktonic foraminifers (Globigerina Limestone Formation/Aquitanian-Langhian). The deepening trend continued throughout the Serravallian and lower Tortonian when hemipelagic clay- to marlstones were deposited (Blue Clay Formation). The trend is reversed when the Blue Clay Formation is unconformably overlain by shallow water carbonates of the Upper Coralline Limestone Formation. This unit was deposited during the Tortonian to Messinian and is composed of photozoan associations (*sensu* James, 1997).

Sicily.— The Oligo-Miocene sedimentary succession of the Ragusa Platform (Fig. 1A+B) starts with the Ragusa Formation (Chattian to Upper Burdigalian); (Grasso and Lentini, 1982). This formation can be subdivided into a lower, more marly (Leonardo Member) and an upper more micritic part (Irminio Member). The Leonardo Mb. is about 400m thick, consists predominantly of planktonic foraminiferal debris and micrite and was deposited in an outer shelf environment (Pedley, 1981). The Irminio Mb., the object of this study, is about 190m thick and consists of shallow-water deposits comprising small and larger benthic foraminifers, echinoids, coralline algae fragments and subordinate planktonic foraminifers (Grasso and Lentini, 1982). In this part small to medium-scale submarine channels occur (Pedley, 1981).

Hemipelagic marls and marly limestones (Tellaro Formation/Langhian to Upper Tortonian) and marls and biomicrites (Palazzolo Formation/Serravallian to Tortonian) overly the Ragusa Fm. and are indicative of a deepening trend (Pedley, 1981). In analogy with the Maltese setting, the Palazzolo Fm. shallows upwards and is topped by Messinian evaporites (Grasso and Lentini, 1982).

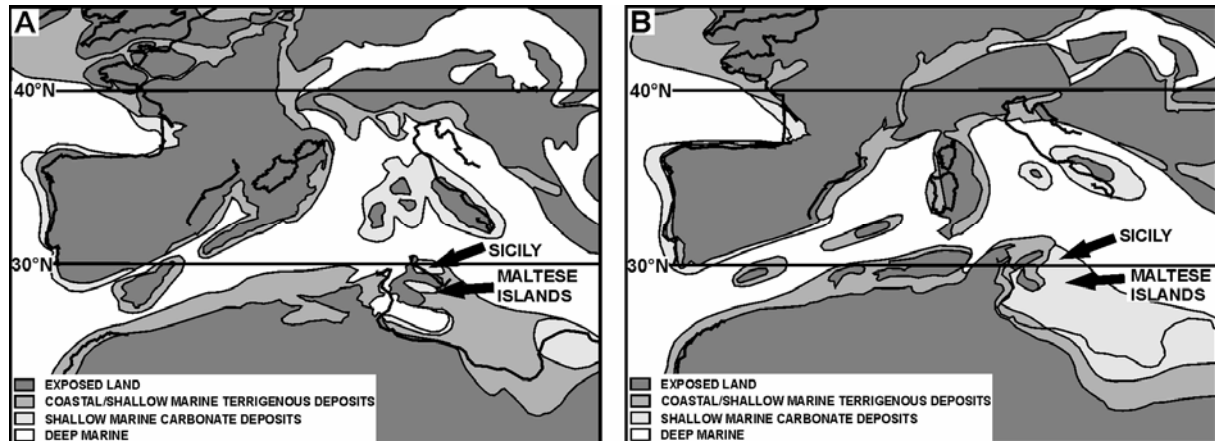


Figure 2 Paleogeographic reconstruction of the Mediterranean region. The studied locations are indicated by black arrows. **A.** Early Chattian times (~ 28 Ma). **B.** Early Burdigalian times (20.5-19 Ma) (after Dercourt et al., 2000)

3.2.2 This study

This study focuses on the lowermost formation in both areas, the Lower Coralline Limestone Formation of the Maltese Islands and the Irmino Member of the Ragusa Formation in Sicily, respectively. Both formations are approximately time equivalent (Chattian to Aquitanian) and consist of heterozoan biogenic assemblages deposited in shallow-water carbonate environments. Two sections were logged in both locations (Dweira on Gozo, Maltese Islands and Ragusa on Sicily), sampled and described in detail with respect to the sediment structures and the biotic assemblages (Figs. 3, 4). Sr isotope dating was carried out to determine the depositional ages of both sections (Tab. 1). Thin sections of the samples were quantitatively analyzed for rock composition and diagenetic features by point counting (400 points per thin section). Field study and petrographic analysis enabled the grouping of the strata into different depositional environments, usually bounded by erosional unconformities. The section below summarizes the main depositional and textural characteristics of the units investigated, with the purpose of providing the background for the diagenetic observations.

Table 1 Strontium isotope results. Column one contains the sample location and name, column two its section height. $^{87}\text{Sr}/^{86}\text{Sr}$ results are indicated in column three and the analytical error in column four. The fifth column contains the age obtained after conversion of the $^{87}\text{Sr}/^{86}\text{Sr}$ with the help of the scale of McArthur et al. (2001)

Sample ID	Section height [m]	$^{87}\text{Sr}/^{86}\text{Sr}$	Analytical error	Age [Ma]
Dweira 12	30.6	0.708173	0.000003	25.5 ± 0.7
Dweira 30	58.1	0.708224	0.000003	24.4 ± 0.7
Ragusa 9593	15.2	0.708200	0.000003	24.9 ± 0.7
Ragusa 9598	35.0	0.708328	0.000003	22.5 ± 0.7
Ragusa 95101	46.4	0.708370	0.000003	21.4 ± 0.7

Section Dweira (Gozo, Maltese Islands). — The section Dweira (Fig. 3) includes a range of environments from outer- to inner-ramp settings. The different depositional environments are separated from one another by erosional contacts and are characterized by strong differences in rock texture and fabric and bioclastic content.

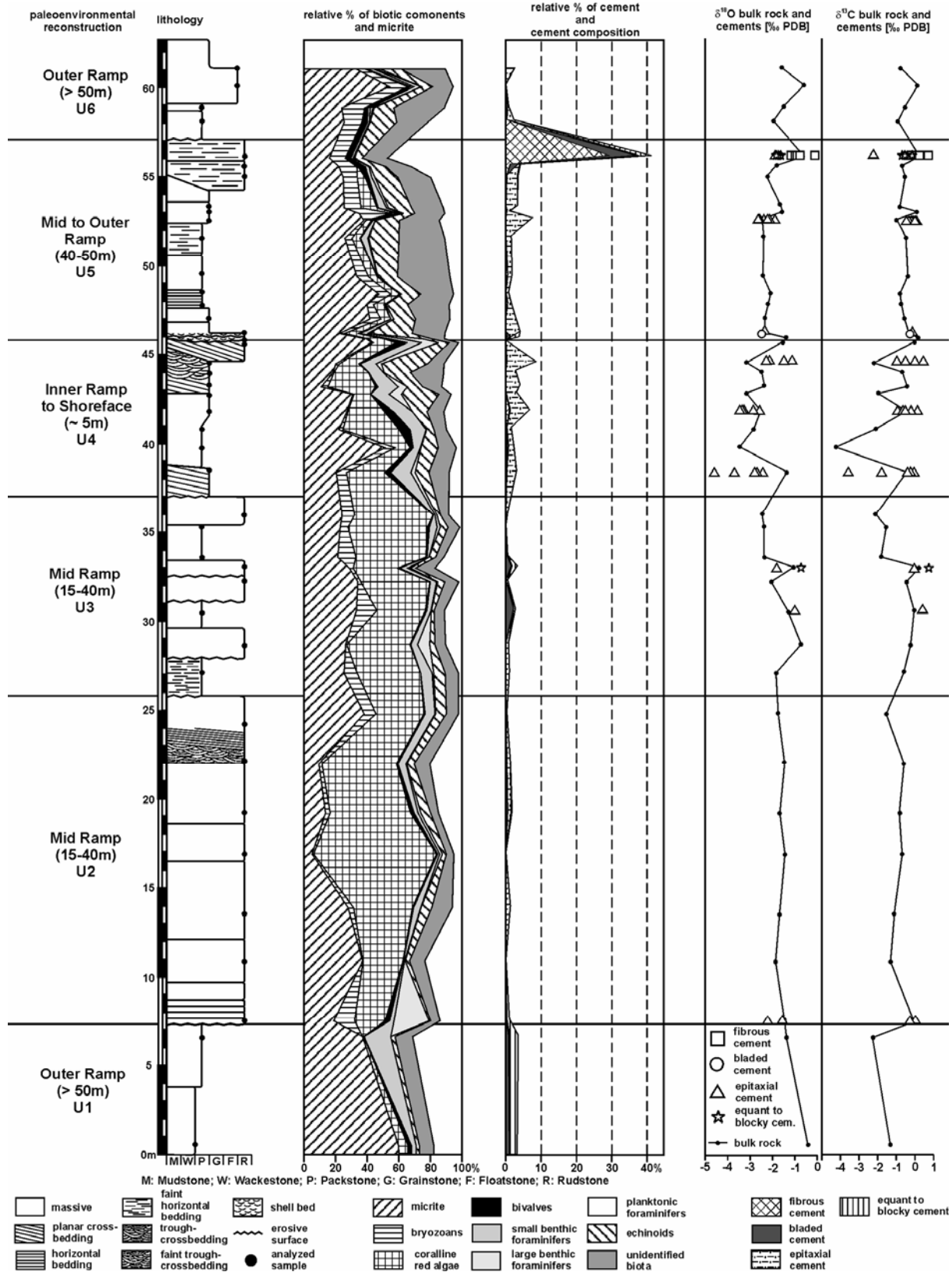


Figure 3 Measured section (“Dweira”) of the Lower Coralline Limestone Formation on Gozo. The lithology, including sedimentary textures, the amount of biotic components and micrite and the cement amount and composition based on point counting are displayed to the right of the stratigraphic profile. The stable isotope composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of the bulk rock and the different cement types is presented. The reconstructed depositional environments are shown to the left of the stratigraphic profile

The outer-ramp unit (U1) consists of massive wackestones to packstones. The mid-ramp units U2 and U3 are pack- to rudstones predominantly consisting of coralline red algae, displaying an increasing degree of fragmentation towards the top. Evidence for strong reworking of the grains and the common occurrence of erosional contacts in unit 3 indicate an increase in water energy towards the top. Both units (U2+U3) are in general massively bedded. The inner-ramp unit (U4) includes pack- to grainstones and rudstones with planar and trough cross-bedding. Grains show signs of strong reworking, echinoids get increasingly abundant towards the top of the unit. This indicates deposition in a high energetic environment. At least one subaerial exposure surface could be identified in the field. The topward mid- to outer-ramp unit (U5) follows above a pronounced erosional unconformity with two shell layers. Unit 5 comprises pack- to grainstones and sometimes rudstones and shows abundant horizontal bedding. The rocks mainly consist of micrite and echinoid fragments. Strongly abraded, unidentifiable biota also form a major part of the rocks, pointing to sediment transport down slope towards the environment of deposition. The topmost outer-ramp unit (U6) consists of massive wacke- to floatstones. Micrite and unidentifiable biota are the main rock components. Planktonic foraminifers start to appear, pointing to a progressive drowning of the succession.

Overall the section Dweira displays a shallowing upward trend from an outer- to an inner-ramp setting (U1-U4), which is reversed after a pronounced erosional unconformity and followed by the drowning of the succession. For a detailed description of the biotic assemblages and depositional environments, the reader is referred to Knoerich and Mutti (2003).

In general the cement content of the Dweira section does not exceed 10%. The dominant cement phase (up to 8%) is represented by epitaxial calcite cement precipitated around echinoid fragments. This cement type becomes especially abundant in the inner-ramp and upper mid-ramp unit (U4 and U5) and occurs predominantly in well-sorted, well-bedded, grain-supported strata. One especially well cemented horizon, containing over 40% of cement, occurs in a specific position in the stratigraphic column corresponding to the drowning surface.

Section Ragusa (SE Sicily). — The section Ragusa (Fig. 4) also comprises depositional systems ranging from inner to outer-ramp environments. The depositional units are often separated by erosional unconformities and display marked differences in rock composition.

The lowermost unit (U1) was deposited in a mid-ramp environment and consists of pack- to grainstones. Intercalated channel structures with internal planar cross-bedding and erosional bases are common features. Echinoid fragments and unidentifiable biogenic components are the main rock constituents. Except of the channel structures the bedding is massive, the fabric is generally grain supported. The erosive channel structures together with abundance of echinoid fragments indicate sorting and deposition of the sediments by agitated waters.

The topward following inner-ramp unit (U2) nearly completely consists of planar cross-bedded channel bodies with erosional bases. The micrite content of the rocks diminishes towards the top of this unit, whereas smaller and larger benthic foraminifera become important rock contributors. This indicates sedimentation in agitated waters close to the photic zone.

Above this inner-ramp unit a second mid- to outer-ramp unit (U3) was deposited. It is composed of an intercalation of massive packstones and grainstones, frequently exhibiting hummocky-cross stratification. Towards the top of the unit the micrite and planktonic foraminifer content increases while the amount of larger benthic foraminifers and echinoid fragments decreases, indicating a drowning of the succession.

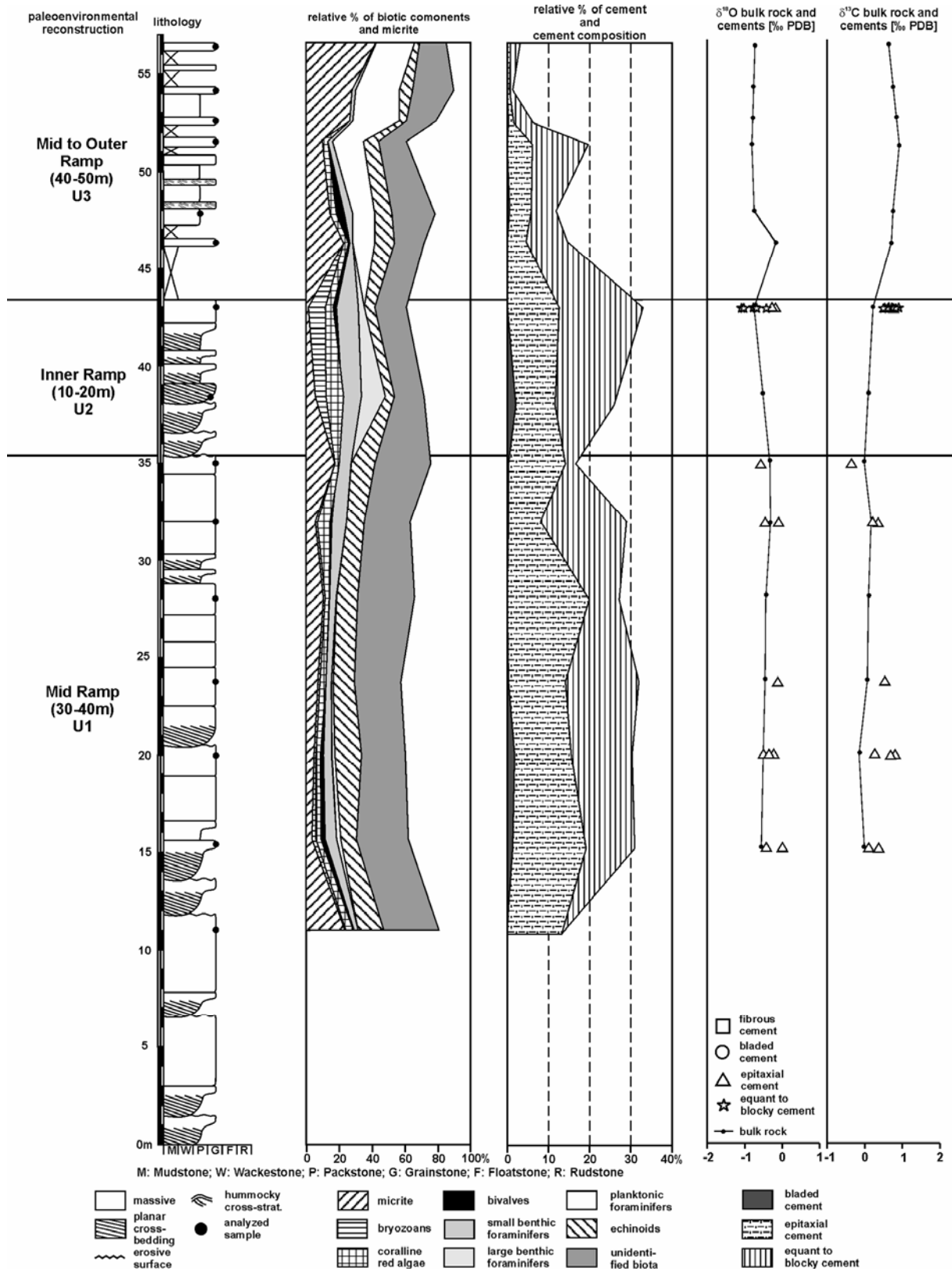


Figure 4 Measured section (“Ragusa”) of the Ragusa Formation on Sicily. The lithology, including sedimentary textures, the amount of biotic components and micrite and the cement amount and composition based on point counting are displayed to the right of the stratigraphic profile. The stable isotope composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of the bulk rock and the different cement types is presented. The reconstructed depositional environments are shown to the left of the stratigraphic profile

Overall the section Ragusa displays a parallel trend to the section Dweira, with first a shallowing upward from a mid- to an inner-ramp setting (U1+U2), followed by a rapid deepening (drowning) trend towards the top of the section (U3).

Section Ragusa in average contains about 30% of cements, consisting to equal parts of epitaxial and equant to blocky calcite cement. Only in the uppermost unit, which experienced drowning (U3), the cement content starts to decrease. Overall the cement content in this section is inversely correlated with the micrite content, being the highest where micrite is least abundant.

3.3 ANALYTICAL METHODS

Diagenetic and compositional characteristics of the investigated samples are based on transmitted light microscopy on forty-three thin sections from the Maltese Islands and fifteen thin sections from Sicily. Point counting was performed on fifty-eight thin-sections for biotic components and diagenetic features (cement types, secondary porosity).

Eleven thin sections from Malta and six from Sicily were polished and examined under cathodoluminescence (CL) microscopy. Operating conditions for the Citl Cold Cathode Luminescence (model 8200 mk 3) at the University of Stuttgart (Germany) were maintained at approximately 22 kV beam energy and 0.8 mA beam current.

Eight thin sections from Malta and six from Sicily were polished for electron microprobe analysis. Measurements were performed using a Cameca SX 100 at the University of Stuttgart. Conditions were 15 kV accelerating potential, 8 nA beam current on Faraday cup, 60 seconds counting time on peaks. Measurements were carried out with defocused beam (diameter 20 μ m) in order to avoid evaporation of the carbonate minerals. Standards were acquired under the same beam conditions (periclase for Mg; wollastonite for Ca; hematite for Fe; rhodonite for Mn; coelestite for Sr).

Mineralogical and geochemical analyses were performed on powdered bulk rock samples. X-ray diffraction analyses and quantification of the inorganic carbon content were performed on forty-three samples from Malta and twelve samples from Sicily. XRD measurements were carried out with a Bruker D8 Advance with 2 Theta = 25°-35° at the University of Stuttgart. The increment used was 0.005 degree; the scan speed was 1 degree/minute. For each measurement four scans were stacked to minimize the error. The inorganic carbon content was determined on 40 to 60 mg of sample material with a Coulometer 5020 from UIC Inc. attached to a CM TIC Auto sampler from Orbis bv at the University of Stuttgart. Results were converted to calcite values by multiplying the TIC (Total Inorganic Carbon) result by the appropriate factor (8.33).

Forty-two powdered bulk rock microsamples from Malta ranging in size from 0.5 to 4 mg were analyzed for carbon and oxygen stable isotopes at the Laboratory for Stable Isotope Geochemistry at the University of Southern California. Analyses were performed according to on-line common acid bath method using a PRISM mass spectrometer. The analytical precision of the mass spectrometer is ± 0.1 or better for $\delta^{13}\text{C}$, and ± 0.2 or better for $\delta^{18}\text{O}$. The $\delta^{18}\text{O}$ values have been corrected for calcite phosphoric acid fractionation. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are given in the PDB notation.

Eleven powdered bulk rock samples from Sicily and fifty-six micro drilled cement samples from Malta and Sicily were analyzed for their stable carbon and oxygen isotopic composition at the University of Bremen (Germany). The powder was dissolved in phosphoric acid and the resulting CO₂ gas was measured with a FINNIGAN MAT 251 mass-spectrometer. An internal standard calibrated against the international NBS 19 standard was used. Standard deviation was 0.07‰. Oxygen and carbon isotopes results are expressed in the PDB notation.

Sr-isotope composition was measured for five bulk rock samples, two from the section Dweira and three from the section Ragusa, with the Re-double filament technique on a

Finnigan MAT 262 RPQ+ in static mode at the Geomar Kiel (Germany). Usually 100 to 200 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were collected for each measurement, which resulted in an internal precision better than 10 ppm (2SE) of the $^{87}\text{Sr}/^{86}\text{Sr}$ value for most of the samples. The whole procedure Sr blank is less than 500 pg. However, sample sizes are sufficiently large (approx. 1 μg of Sr) that blank corrections are negligible. A mean $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.710236 ± 34 (2 standard deviation) for the NIST 987 standard solution was calculated from 12 analyzes, covering the whole measurement period of the data set. It represents the minimum uncertainty assigned to any individual sample measurement.

3.4 PETROGRAPHY OF THE DIAGENETIC PARAGENESIS

Based on detailed petrographic observations and quantification of cement content by point counting several diagenetic features can be distinguished (Figs. 5-7), including different episodes of cementation, dissolution, neomorphism and compaction. In both localities the paragenesis of the diagenetic features is similar. Therefore, they are combined in the following description according to their paragenetic occurrence from oldest to youngest.

Fibrous to fibrous-bladed cements (Fi) occur in significant quantities only in one sample from Dweira (Fig. 3), where this cement type forms about 30% of the total sediment volume (Fig. 5A-C). In all the other samples from Dweira and Ragusa fibrous to fibrous-bladed cement is volumetrically unimportant (1-2%).

Fibrous to fibrous-bladed cements nucleate on grain surfaces and line them in isopachous rinds. The single crystals are elongated along the c-axis and nucleate in a picket-fence style on the substrate. Their average length is 10 to 20 μm . In the Ragusa samples this cement type is not so elongated and has a more bladed appearance (Fig. 7A). The crystals are inclusion-rich and show a patchy pattern under CL (Fig. 5B), indicating that they have been recrystallized. In general fibrous to fibrous-bladed cements fringe intraparticle pore spaces such as bryozoan or foraminifera chambers. Rarely can they also be found in interparticle pore spaces.

Epitaxial cement I (Ep I) precipitated in optical continuity with single crystal grains. It commonly grows as the first precipitate around echinoid fragments, where it forms thin rims (10-20 μm) (Figs. 5D+E, 6A, 7A+C). This cement type only constitutes 1-2% of the rock volume in Dweira and Ragusa. The crystals are inclusion-rich, grew perpendicular to the substrate and have prismatic terminations. Under CL they display a patchy pattern, indicating that this cement type is recrystallized (Figs. 5F, 6B, 7D). In some places the outermost rim of the epitaxial cement I is dissolved and forms moldic porosity (Figs. 5E-F, 7A).

Fabric selective dissolution I took place as dissolution of aragonitic biota (gastropods, bivalves and foliose bryozoans) creating moldic porosity in the samples from Dweira (up to 9%) (Figs. 5C, 6C). In the Ragusa samples no biomoldic porosity was observed, but "oversized" interparticle pore spaces in some areas (Fig. 7B), later filled with cement, indicate selective dissolution of grains.

Epitaxial cement II (Ep II) precipitated in optical continuity with the substrate usually around echinoid fragments, but occasionally also around benthic foraminifers. This second phase of epitaxial cementation postdates epitaxial cement I (Figs. 5D+E, 6C, 7A-C, E). Epitaxial cement II consists of inclusion-free calcite (average crystal size of 200 μm) with zonations clearly visible under CL (Figs. 5F, 7D), often forming a poikilotopic texture. This is the volumetrically most important cement phase contributing up to 8% of the rock volume in Dweira and between 10 and 20% in Ragusa.

Fabric selective dissolution II preferentially affected high Mg calcitic cement phases and, to a minor amount, biota. Epitaxial cement I was dissolved in some places leading to the formation of moldic porosity (Figs. 5E+F, 7A), both in the samples from Dweira and from Ragusa. Echinoids were partly dissolved along the cleavage planes of the crystals whereas coralline red algae display a more patchy dissolution.

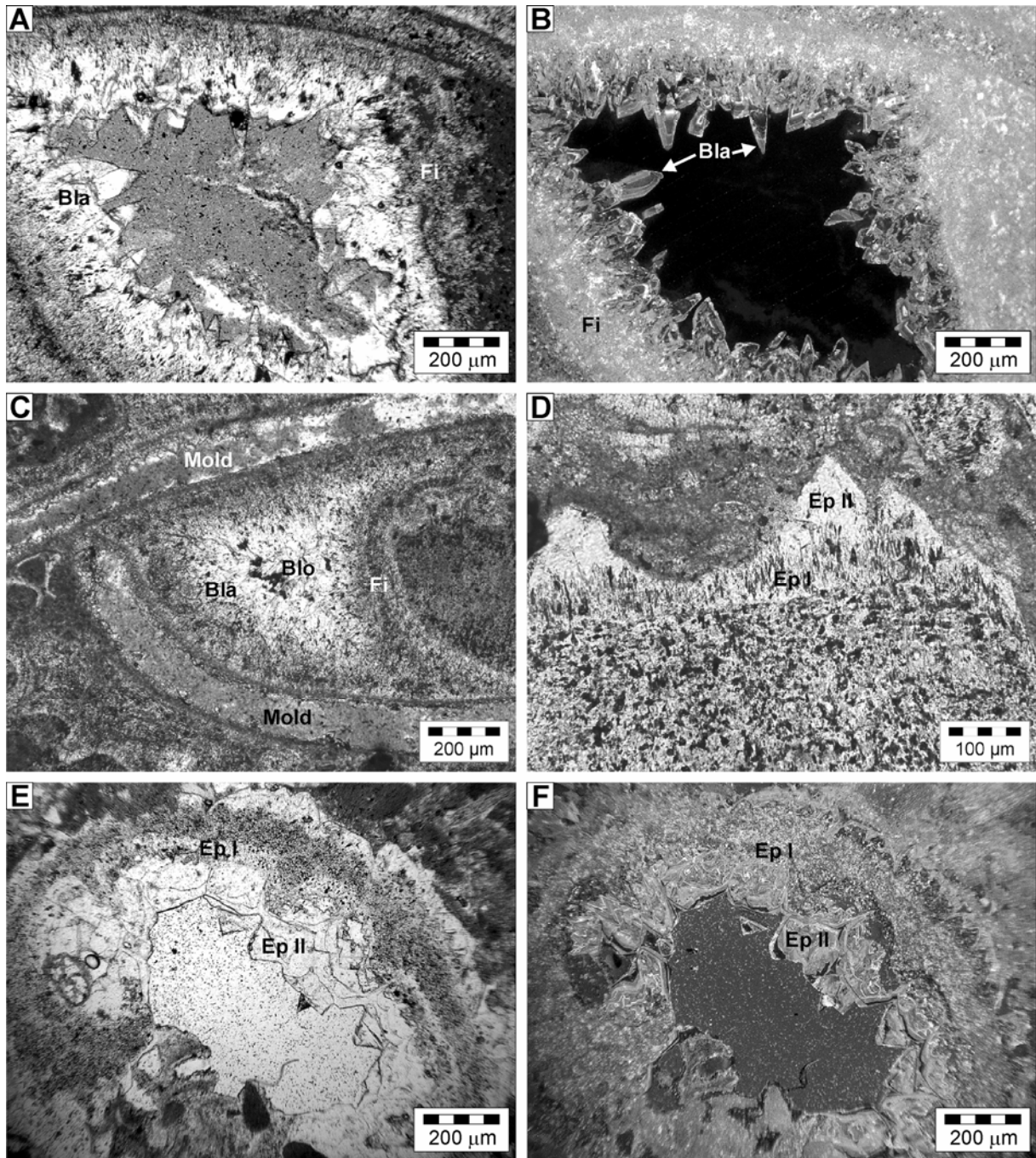


Figure 5A-F Photomicrographs of cements and dissolution features observed in the samples from Dweira (Maltese Islands). **A.** Note fibrous, inclusion-rich cement (Fi) followed by inclusion-free bladed-prismatic cement (Bla). **B.** as in a. in CL. Note the patchy luminescence in the fibrous cement and the clear zonations visible in the bladed-prismatic cement. **C.** Fibrous, inclusion-rich cement (Fi) postdated by inclusion-free bladed-prismatic (Bla) and blocky cements (Blo). Note that the molds after aragonitic biota are totally cement-free and not compacted. **D.** Two phases of epitaxial cements growing on an echinoid fragment. The first (Ep I) is inclusion-rich, the second (Ep II) is inclusion-free. **E.** Part of an echinoid shell overgrown by two phases of epitaxial cement. The first (Ep I) is inclusion-rich and its outermost rim is partly dissolved. The second (Ep II) is inclusion-free. **F.** as in e. in CL. Note the patchy luminescence in the epitaxial cement I and the clearly visible zonations in epitaxial cement II

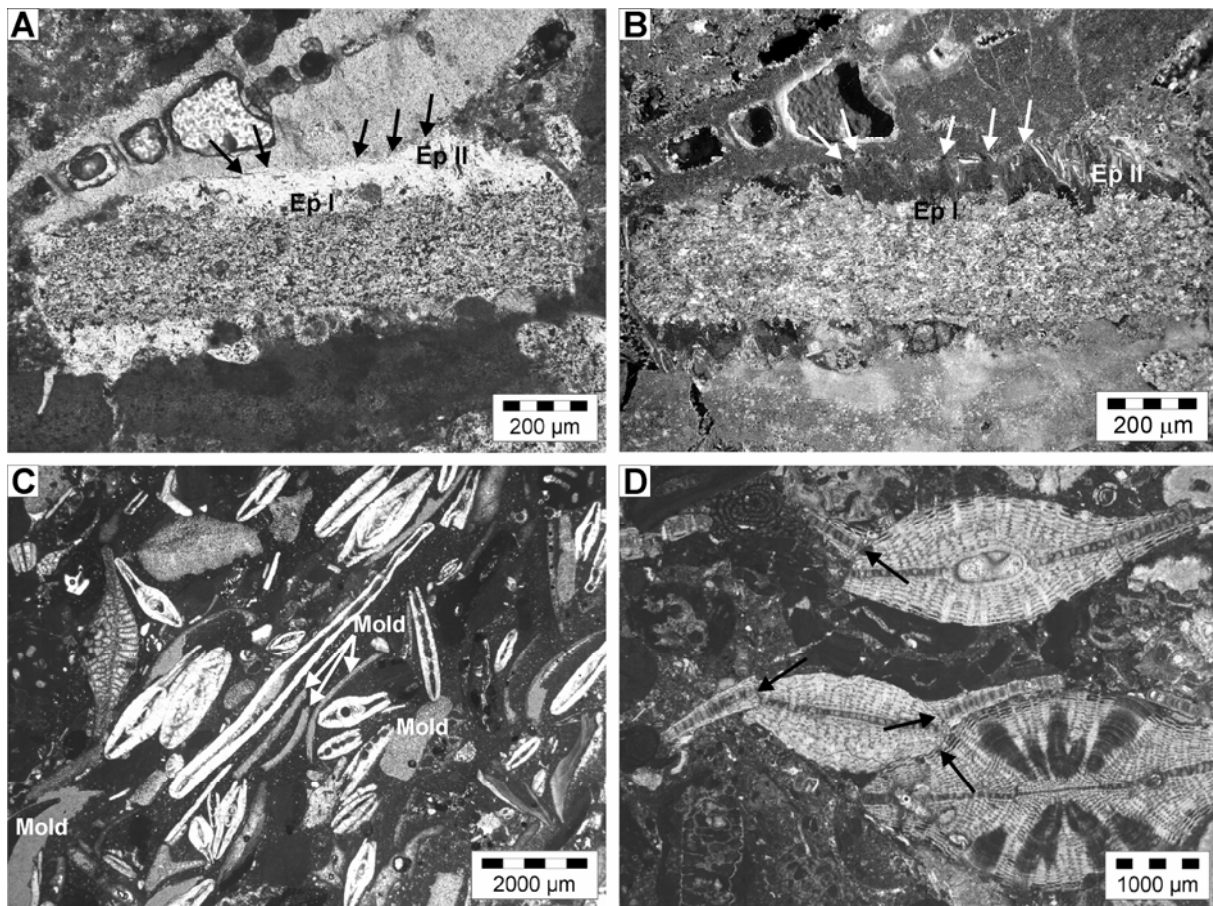


Figure 6A-D Photomicrographs of dissolution and compaction features observed in the samples from Dweira (Maltese Islands). **A.** Note the sutured contact between the foraminifer and the echinoid overgrown by epitaxial calcite cement I and II (Ep I and Ep II). **B.** as a. in CL. Note how the epitaxial cement II (Ep II) has been partially dissolved by pressure solution (arrows), indicating that precipitation of epitaxial cement II predated compaction. **C.** Note the abundance of molds after aragonitic biota and that all molds are cement-free and not compacted. **D.** Note the occurrence of mechanical (breaking) and chemical (concavo-convex and sutured contacts) compaction in the foraminiferal packstone

Neomorphism occurs as alteration of metastable high Mg calcitic biota (calcareous red algae and echinoids) and cement phases (fibrous and epitaxial cement I) to low Mg calcite as indicated by their patchy appearance under CL (Fig. 5B).

Bladed-prismatic cement (Bla) consists of elongated scalenohedral crystals with prismatic terminations. Crystals are on average 20 to 90 μ m long and 5 to 10 μ m across and form rims of uneven thickness in intra- and inter-particle pore spaces (Fig. 5A+C). The original crystal fabric of this cement type is well preserved, with clearly recognizable zonations under CL (Fig. 5B). In the Dweira samples this cement type constitutes on average 1 to 2% of the rock total volume, but can reach volumes up to 8%. In Ragusa this cement phase was not recorded.

Blocky sparry calcite cement (Blo) comprises plane-sided, equant crystals with an average width of 40 to 60 μ m. The original crystal fabric is well preserved with clearly visible zonations under CL. This cement phase either grew poreward postdating fibrous and/or bladed cements or directly on the substrate, where the other cement phases are missing (Fig. 5C). In the Dweira samples blocky cement on average contributes 1 to 2% to the rock total. In Ragusa this cement phase is equally important as the epitaxial cement II and forms between 10 and 20% of the rock volume (Fig. 7B-E).

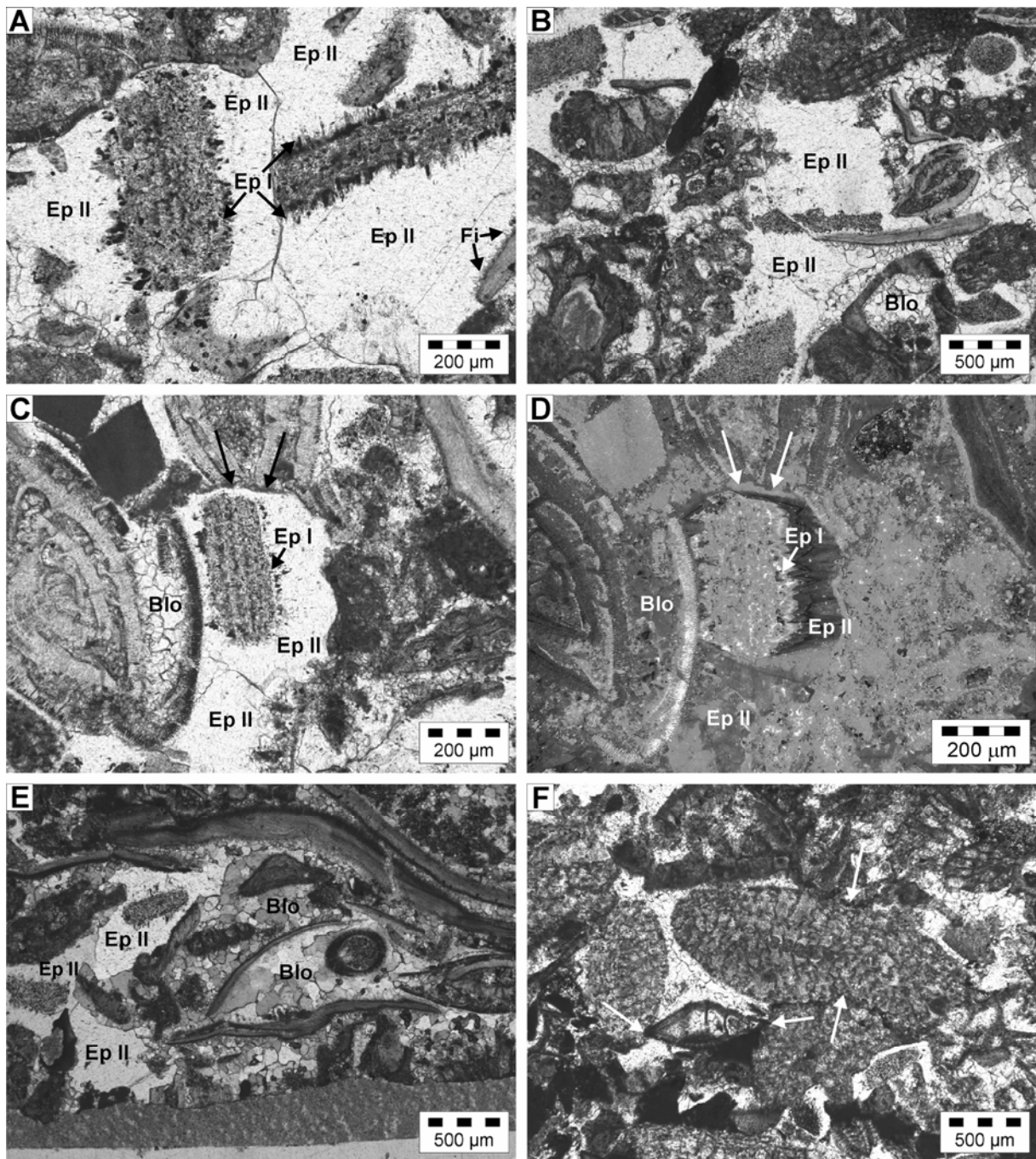


Figure 7A-F Photomicrographs of cements and other diagenetic features observed in the samples from Ragusa (Sicily). **A.** Note the paragenesis of the diagenetic features. Depending on the substrate either fibrous-bladed (Fi) or epitaxial cement I (Ep I) precipitated first, both phases are inclusion-rich. Epitaxial cement I is partly dissolved. Both cement phases are then overgrown by a second epitaxial cement phase (Ep II), inclusion-free and in parts poikilitic. **C.** Note the large, oversized pore spaces filled by inclusion-free epitaxial cement II (Ep II). **C.** Visible is an echinoid fragment overgrown by two phases of epitaxial cement (Ep I and Ep II). Inside a foraminifer chamber inclusion-free blocky cement (Blo) precipitated. Note the sutured contact of the foraminifer and the epitaxial cement II (arrows). **D.** as **C.** in CL. Note how the foraminifer has been partly dissolved by pressure solution against the epitaxial cement II (arrows), indicating that pressure solution postdated precipitation of this cement phase. **E.** Overview of the distribution and abundance of the volumetrically important epitaxial cement II (Ep II) and blocky cement (Blo). Picture taken with crossed nicols. **F** Note the concavo-convex and the sutured contacts between the foraminifers (arrows) indicating chemical compaction by pressure solution

Compaction includes mechanical and chemical compaction (pressure solution). Mechanical compaction can be very intense on fragile components such as larger foraminifers (Fig. 6D). Chemical compaction includes grain to grain contacts, concavo-convex contacts and even sutured contacts (Fig. 7F). No real microstylolithes were found. Chemical compaction postdates in both study areas precipitation of the volumetrically important epitaxial cement II (Figs. 6A-B, 7C-D).

Non fabric selective dissolution forms small vugs and channels, cross-cutting biota, matrix and cements. These vugs and channels either stay open or, more seldom, are filled with blocky calcite cements. Vugs also postdate compaction features, suggesting that this phase of dissolution occurred quite late in the diagenetic sequence. In Dweira, up to 13% of vuggy porosity was observed, whereas in the samples from Ragusa the vuggy porosity represents only 1%.

3.5 MINERALOGICAL AND GEOCHEMICAL ANALYSES

3.5.1 XRD and coulometer analyses of the bulk rock

XRD analysis showed that in both locations only LMC is preserved. No traces of aragonite or HMC were found. Both sections consist of nearly pure carbonate, with above 90% LMC content.

In both areas the non-carbonate content (most probably clay minerals) is facies dependent. The mid- and inner-ramp settings contain less clay minerals (Dweira: 0.4 to 2.5%, mean: 1.2%; Ragusa: 1.0 to 2.7%, mean: 2%) than the outer-ramp environments (Dweira: 0.9 to 5.8%, mean: 2.3%; Ragusa: 2.8 to 8.4%, mean: 4.5%).

3.5.2 Stable isotope composition

The stable isotope composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of the bulk rock and the different cement types was analyzed on the samples from Dweira and Ragusa.

Dweira. — Stable isotope values of the bulk rock and the different cement types have been plotted against stratigraphic depth (Fig. 3) and in a cross-plot (Fig. 8A). The values range from -0.5 to -3.3‰ for $\delta^{18}\text{O}$ and from +0.3 to -2.5‰ for $\delta^{13}\text{C}$. Generally, bulk and single cement values are similar; the only main exception is the inner ramp unit (U4) where the bulk rock is up to 4‰ higher than the single cement values.

The stable isotope values for the different cement types in Dweira generally vary between -0.1‰ and -4.6‰ for $\delta^{18}\text{O}$ and between +0.8‰ and -3.6‰ for $\delta^{13}\text{C}$ (Figs. 3, 8A). Fibrous cements display the highest values, both for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, ranging between +0.1 and -1.2‰ for $\delta^{18}\text{O}$ and between +0.7 and -0.2‰ for $\delta^{13}\text{C}$.

Since epitaxial cement I and II could not be sampled separately due to the small size of the cement rims, the isotopic values for this cement type represent a mixture of both epitaxial cement phases, but are more likely to represent the volumetrically more important epitaxial cement II. This cement type shows a wide range of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, varying between -1.0 and -4.6‰ for $\delta^{18}\text{O}$ and between +0.5 and -3.6‰ for $\delta^{13}\text{C}$. The lowest values, found in the inner ramp unit (U4) ($\delta^{18}\text{O}$: -3.3 to -4.6‰; $\delta^{13}\text{C}$: -0.7 to -3.6‰) correspond to the presence of a subaerial exposure surface observed in the field.

Bladed-prismatic and blocky cements display intermediate isotopic compositions, ranging from -1.0 to -1.9‰ for $\delta^{18}\text{O}$ and from -0.2 to -2.2‰ for $\delta^{13}\text{C}$.

Ragusa. — The stable isotope values of the bulk rock and different cement types in Ragusa are quite similar and do not show significant variation throughout the section (Figs. 4, 8B). The bulk rock samples range from -0.2 to -0.8‰ for $\delta^{18}\text{O}$ and from +0.9 to -0.2‰ for $\delta^{13}\text{C}$. The different cement types in Ragusa vary from 0.0‰ to -1.1‰ for $\delta^{18}\text{O}$ and from +0.9 to -0.4‰ for $\delta^{13}\text{C}$ (Figs. 4, 8B). The values for the combined epitaxial cement phases I-II, with predominance of epitaxial cement II, show slightly higher $\delta^{18}\text{O}$ (0.0‰ to -0.6‰) and

slightly lower $\delta^{13}\text{C}$ (+0.8‰ to -0.4‰) values than the blocky cements ($\delta^{18}\text{O}$: -0.2‰ to -1.1‰; $\delta^{13}\text{C}$: +0.9‰ to +0.5‰).

In comparison the cements from Dweira display lower ^{18}O and ^{13}C values than the cements from Ragusa and scatter over a much wider range.

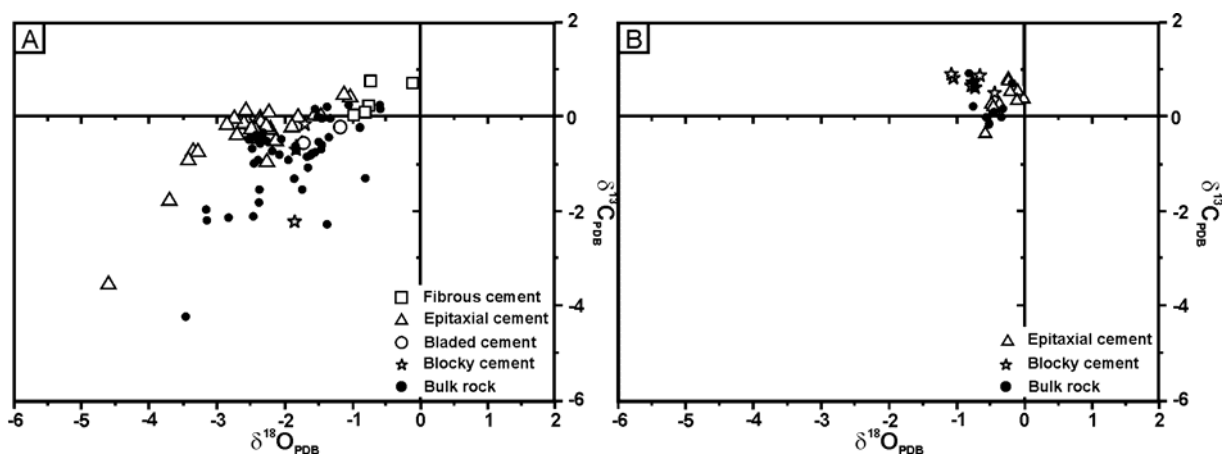


Figure 8 Cross-plot of the carbon and oxygen isotopic composition of the bulk rock and the different cement types. **A.** Data for the Dweira section on Gozo. **B.** Results for the Ragusa section on Sicily

3.5.3 Major and trace element composition of the cement types

The major and trace element composition (Ca, Mg, Sr, Fe and Mn) of the different cement types from Dweira and Ragusa was determined by measuring transects (Figs. 9 and 10) through the cement rims to document variations within single cement zones. The mean and maximum values as well as the standard deviation of the major and trace elements are displayed in Table 1 for Dweira and Table 2 for Ragusa.

Dweira. — The Mg content of the different cement types from Dweira ranges from 2500 to 3500 ppm, which corresponds to 1 to 1.4 mol % MgCO_3 , indicating that all cement types are LMC. The Sr, Fe and Mn values of the single cement types differ significantly from one another, with fibrous-bladed cements having the lowest Sr and the highest Fe and Mn (Sr: 87ppm; Fe: 429ppm; Mn: 102ppm) contents and epitaxial cement II having the highest Sr and lowest Fe and Mn (Sr: 317ppm; Fe: 101ppm; Mn: 37ppm) values.

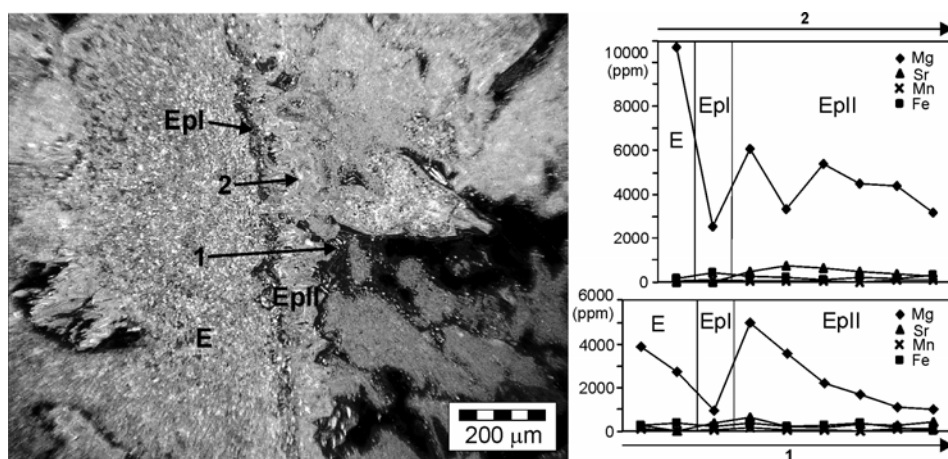


Figure 9 Cathodoluminescence photo of an inner-ramp sample from section Dweira (Maltese Islands) showing the two phases of epitaxial cement growing on top of an echinoid fragment. Lines (1 and 2) show the path of microprobe transects. Profiles of Mg, Sr, Mn and Fe are plotted beside, with zones labelled as on photo: E: echinoid fragment; Ep I: epitaxial cement I, Ep II: epitaxial cement II

Table 2 Trace element composition of the different cement types measured in the samples from Dweira (Maltese Islands). n: number of measurements; SD: standard deviation; Max: maximum value

Element	Fibrous cement				Epitaxial cement I				Epitaxial cement II				Bladed cement				Blocky cement			
	n	Mean	SD	Max	n	Mean	SD	Max	n	Mean	SD	Max	n	Mean	SD	Max	n	Mean	SD	Max
Ca	21	384991	3337	387990	56	393571	7166	402113	110	395452	6041	403266	44	389830	3806	399849	29	391516	4354	398530
Mg	21	3291	550	4002	56	2558	1333	6120	110	2858	1267	6466	44	3509	1493	6557	29	3216	1568	6476
Sr	21	87	159	542	56	251	204	871	110	317	193	1087	44	259	209	729	29	323	240	842
Fe	21	429	664	2093	56	176	203	1035	110	101	156	1135	44	313	374	1803	29	312	415	1789
Mn	21	102	72	226	56	74	155	625	110	37	87	685	44	82	143	662	29	78	104	475

Ragusa. — The Mg content in the cement samples from Ragusa ranges from 1600 to 3100 ppm (0.7 to 1.3 mol % $MgCO_3$), indicating a LMC composition. Of the two analyzed cement types epitaxial cement II has lower Sr and higher Fe and Mn (Sr: 1190ppm; Fe: 205ppm; Mn: 119ppm) values than the blocky cement type (Sr: 2658ppm; Fe: 139ppm; Mn: 63ppm).

In comparison the different cement types from Dweira contain less Sr and more Fe and Mn than the cements from Ragusa. In particular the quite high Sr value of the cements from Ragusa (up to 5900ppm) is rather remarkable. Moreover, the measured transects show that the trace element composition not only varies between the different cement types (Fig. 9), but also within single cement zones (Fig. 10).

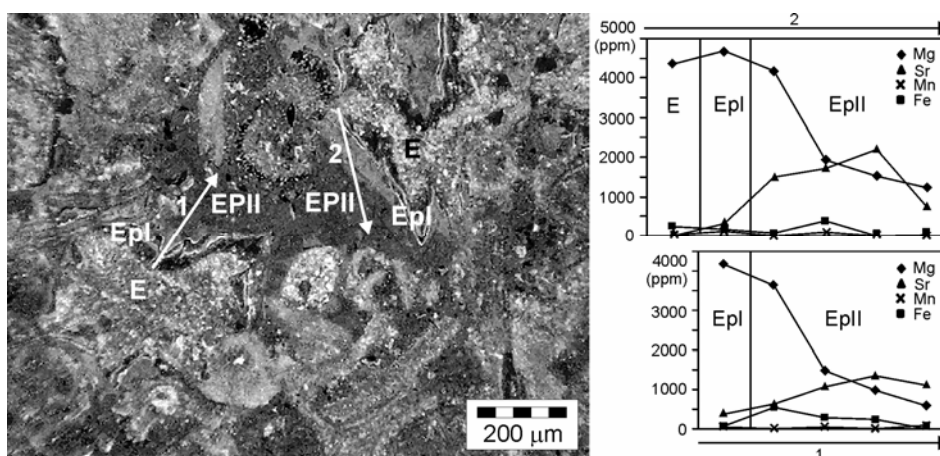


Figure 10 Cathodoluminescence photo of a mid-ramp sample from section Ragusa (Sicily) showing the two phases of epitaxial cement growing on top of echinoid fragments. Lines (1 and 2) show the path of microprobe transects. Profiles of Mg, Sr, Mn and Fe are plotted beside, with zones labelled as on photo: E: echinoid fragment; Epl: epitaxial cement I, EpII: epitaxial cement II

Table 3 Trace element composition of the different cement types measured in the samples of the Ragusa section (Sicily). n: number of measurements; SD: standard deviation; Max: maximum value

Element	Epitaxial cement II				Blocky cement			
	n	Mean	SD	Max	n	Mean	SD	Max
Ca	105	386782	6264	394420	28	389823	1897	392447
Mg	105	3167	1514	6161	28	1615	538	3652
Sr	105	1190	781	4898	28	2658	1477	5971
Fe	105	205	174	618	28	139	129	511
Mn	105	119	106	567	28	63	62	204

3.6 DISCUSSION

3.6.1 Diagenetic environments of cement precipitation and alteration

The following discussion aims to constrain the diagenetic environments of cement precipitation/alteration. To achieve this detailed petrographic data of the diagenetic features (spatial relationships and abundances) are combined with stable isotope and trace element measurements on the single cement phases.

Fibrous, fibrous-bladed and epitaxial cement I. — Fibrous, fibrous-bladed and epitaxial cement I are grouped together because they all grew in direct contact with their respective substrate. Therefore, they represent the first phase of cement precipitation. Under CL all three cement types display a patchy appearance indicating recrystallization. This, together with the elongated crystal shape of the fibrous and fibrous-bladed cements, supports an original HMC mineralogy for these cement phases (Given and Wilkinson, 1985). Cement precipitation most probably occurred early, in the marine environment. During later stages of diagenesis the metastable HMC was recrystallized to LMC, as observed.

Due to the recrystallization the isotopic and trace element composition of these cements can provide constrains on the diagenetic environment where neomorphism took place. Unfortunately, geochemical data of primary HMC cements are only available for Dweira. The stable isotope composition (Fig. 8A) suggests that neomorphism to LMC occurred in marine or marine-derived waters. The low Sr content of both, fibrous and epitaxial cement I (Tab. 2), indicates that alteration took place in an open system with little rock-water interaction (Fig. 11A). Therefore, the stable isotope data mirror the values of the diagenetic fluid and are not influenced by the surrounding rock. The elevated Mn and Fe contents (Tab. 2) indicate alteration under reducing conditions. This indicates that the diagenetic environment in which the neomorphism of HMC to LMC took place was most probably the burial marine as described by Melim et al. (2001).

Another remarkable phenomenon in both locations is the partial dissolution of the outermost rim of epitaxial cement I and the formation of moldic porosity. The inner part of the cement, in direct contact with the nucleus, is only altered to LMC. The formation of moldic porosity by dissolution of HMC is rather unusual since it generally dissolves incongruently, releasing its Mg without significant CaCO_3 transport (Morse and Mackenzie, 1990; Moore, 2001). Only Budd (1992) similarly described the partial to total dissolution of HMC grains (foraminifers) and attributed this atypical reaction pathway to the sudden influx of CO_2 . This led on the one hand to an exponential increase in the dissolution rate of HMC and on the other hand precluded LMC precipitation. Once equilibrium with respect to LMC was reached, stabilization continued as incongruent dissolution. Budd (1992) suggested meteoric interfaces, such as subaerial exposure surfaces and water tables, as places of such high CO_2 influx.

An increase in CO_2 could also explain the formation of HMC molds in our case. In contrast to the example described by Budd (1992) this CO_2 increase is not caused by meteoric influx, for which no evidence can be found in the stable isotope data, but was induced by the decay of organic matter in the burial marine environment. Because of the elevated CO_2 content the congruent dissolution of HMC was favoured and the reducing conditions led to the incorporation of Fe and Mn into the incongruently forming LMC (Melim et al., 2002).

Epitaxial cement II, bladed and blocky cement. — Epitaxial cement II, bladed and blocky cements are grouped together because they all show well-preserved internal zonations under CL and were therefore most probably precipitated as mineralogical stable LMC. This conclusion is also supported by the more equant shape of the epitaxial and the blocky calcite crystals indicating only little incorporation of Mg in the calcite lattice (Given and Wilkinson, 1985). The isotopic and trace element composition measured reflects the composition of the diagenetic fluid from which these cements precipitated and was not considerably altered during later stages of diagenesis.

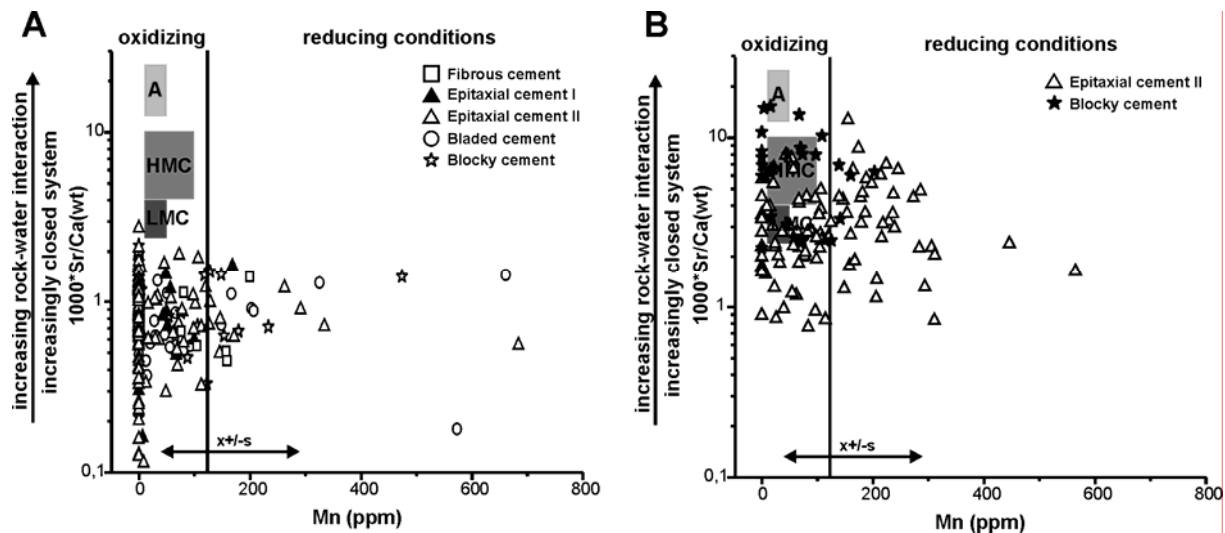


Figure 11 Cross-plot of the Mn and Sr content (normalized to Ca) of the different cement types and the possible precursor mineralogy. A: aragonite; HMC: high Mg calcite; LMC: low Mg calcite (plot by Brand and Veizer, 1980, modified by Lohmann, 1988). The Sr value shown on the y-axis indicates the amount of rock-water interaction and is a measure for the openness of the system. The Mn content displayed on the x-axis points to the redox conditions of the system during cement precipitation (availability of Mn assumed). **A.** Data for the Dweira section (Maltese Islands); **B.** Results for the Ragusa section (Sicily)

For primary LMC cements a differentiation between the samples from Dweira and Ragusa is necessary because their geochemical signals differ significantly. The LMC cements from Dweira (epitaxial cement II, bladed and blocky cement) all show quite low Sr contents (Tab. 2), indicating precipitation in an open system with low rock-water interaction (Fig. 11A). Therefore, the stable isotope composition of the cements (Fig. 8A) represents the composition of the diagenetic fluid, indicating precipitation from marine derived waters at elevated temperatures. Moreover the high Fe and Mn contents moreover point to precipitation under reducing conditions, most probably in the burial marine or burial environment.

Some samples of epitaxial cement II also exhibit rather negative isotopic values with $\delta^{13}\text{C}$ down to -3.6‰ PDB and $\delta^{18}\text{O}$ down to -4.6‰ PDB (Fig. 8A), indicating precipitation from meteorically derived fluids. Stratigraphically, these samples are only found in the shallowest, inner-ramp parts of the section (Fig. 3). Here, some subaerial exposure surfaces were also observed in the field, suggesting that this meteoric influence occurred early in the diagenetic history of the rocks.

The LMC cements from Ragusa (epitaxial cement II and blocky cement) show a different geochemical signal. Their elevated Sr contents (Tab. 3) point to precipitation in a nearly closed to closed system with high rock-water interaction (Fig. 11B). This caused an increasing enrichment of Sr in the fluid and consequently also in the precipitating LMC. The isotopic composition emphasizes this closed-system behaviour and displays only marine values (Fig. 8B), partly resulting from interaction of the fluid with the surrounding rock. The elevated Fe and Mn contents indicate precipitation under reducing conditions, most probably in the burial marine environment.

So the main cement precipitation with LMC took place in both locations in the same diagenetic environment (burial marine). The main difference, causing the contrasting geochemical signals, was the open character of the system.

3.6.2 Source(s) of the cements

Generally, it is assumed that the main cementation in heterozoan carbonates occurs late in the burial environment, with pressure solution being the cement source (Nicolaidis and

Wallace, 1997a; Dodd and Nelson, 1998). However, this source does not account for the study areas, where cementation took place in minor amounts in the early marine and meteoric, and to the main part in the burial-marine environment. Therefore pressure solution of calcitic grains as a major cement source can be excluded, especially because in both areas the cementation of the volumetrically important epitaxial cement II (8% in Dweira, 10-20% in Ragusa) clearly predates compaction (Figs. 6A-B, 7C-D). In addition, oxygen isotope data do not indicate cementation at elevated temperatures as it would be expected in the burial environment. This raises the question of the source(s) of the cements in the different diagenetic environments.

Early marine environment. — In the early marine environment primary HMC cements (fibrous, fibrous-bladed and epitaxial cement I) in both settings precipitated directly out of the water. Even in waters with a low saturation state with respect to CaCO_3 biochemical activities can induce precipitation, especially in intraparticle pore spaces of biota such as foraminifers or bryozoans, or along the outer rim of echinoid fragments (Smith and Nelson, 2003). Due to the high Mg/Ca ratio in seawater, this leads, depending on the substrate, to the precipitation of fibrous or epitaxial HMC cement (Given and Wilkinson, 1985). The generally low share of these cements in the studied samples (about 3% of the rock volume) can be satisfactorily explained by this process.

The high content of fibrous cement observed in one sample from Dweira (30%) also precipitated directly out of marine waters. However, to explain such a high amount of early marine cement in a heterozoan setting another process has to be claimed. As shown by Nelson and James (2000), large amounts of early marine HMC cements can precipitate in heterozoan carbonate settings under special conditions (e.g. stacked, cross-bedded sand bodies, meter-scale, subtidal carbonate cycles or associated with certain unconformities). Here the cement precipitation is promoted for example by the high permeability of the rocks or the prolonged exposure time at the sediment-water interface. This process could also account for the sample from Dweira because it is associated with an unconformity, most probably with a condensed section (Knoerich and Mutti, 2003).

Meteoric environment. — Some epitaxial cements of the inner-ramp setting in Dweira precipitated in the meteoric environment. The source for these cements most probably was the dissolution of aragonitic biota, as suggested by the occurrence of biomoldic porosity after aragonite shells in this part of the section (Fig. 6C). Since cement precipitation in Dweira occurred in an open system, no further hints to an aragonitic cement source, such as elevated Sr contents, could be observed.

Burial marine environment. — In both study areas the main part of cementation (with primary LMC epitaxial cement II, bladed and blocky cement) occurred in the burial marine environment. For the samples from Dweira the source of these cements is unknown because cement precipitation occurred in an open system and the geochemical signature of the cement source was lost.

In contrast, in the Ragusa section cement precipitation took place in a nearly closed to closed system. Therefore, the geochemical signature of the cement source was retained, possibly allowing its determination. Lasemi and Sandberg (1993) already pointed out that the trace element composition of the starting mineralogy can be preserved under closed-system conditions. Therefore the exceptional high Sr content (mean between 1200ppm and 2600ppm, maximum up to 6000ppm, Tab. 3) in the LMC cements points to an aragonitic cement source.

Moreover, the constantly increasing Sr and decreasing Mg contents within single cement zones from the grain towards pore centre (Fig. 10) mirrors the evolution of the diagenetic fluid. With increasing aragonite dissolution the Sr content in the fluid rises, but the Mg content proportionally decreases because aragonite incorporates more Sr but less Mg than calcite in its lattice.

The decreasing Mg content in the fluid is also responsible for the blocky morphology of the cements in Ragusa. Generally, this morphology is interpreted as indicative for the meteoric environment and is caused by the low Mg/Ca ratio in fresh water (James and Choquette, 1990a). However, the shift towards low Mg/Ca ratio can also be caused by an aragonitic cement source as noted by Melim et al. (2002). As stable isotope measurements display only marine values, a meteorically influenced cement source can be excluded in this case.

The open question is the source of the aragonite because no molds after aragonitic biota were observed in the samples from Ragusa, and because it is stated that cement precipitation took place in a closed system. The biotic assemblage of the rocks lacks primary aragonitic biota. No micritic envelopes, chalky preservation or open molds can be found. However, so called “oversized” pore spaces and molds, both now filled with blocky cement, were observed (Fig. 12). This indicates that the biotic assemblage is strongly biased towards calcitic biota and that the aragonitic constituents were totally removed by dissolution.

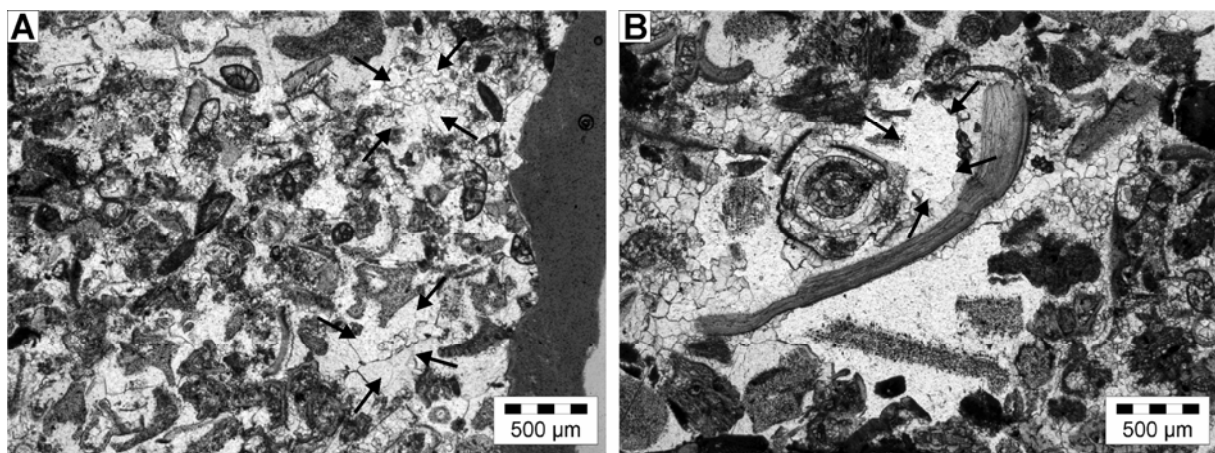


Figure 12A-B — Photomicrographs of “oversized” pore spaces and filled “bio” molds in the samples from Ragusa (Sicily). **A.** “Oversized” pore spaces (arrows) with respect to the mean grain size of the sediment. **B.** Hardly visible “bio” mold (arrows) now filled with LMC epitaxial cement II

As no molds after aragonitic biota were observed the dissolution must have occurred early, as described by Brachert and Dullo (2000) and Smith and Nelson (2003) for other heterozoan carbonate settings. This process was also reported from other predominantly calcitic settings in the Silurian and Jurassic (Cherns and Wright, 2000; Wright et al., 2003). Here the depletion of aragonitic biota took place at an early stage of burial, before any calcitic replacement of shells. The lack of molds is explained by rapid dissolution while the sediment was unconsolidated and lacked sufficient matrix strength to preserve the mold space against collapse (Cherns and Wright, 2000). If such a process was also acting in our case and the fluid generated was prevented from leaving the system, for example by the overlaying more micritic and more clayey lithologies, this fluid could be the source of the observed cements in Ragusa.

Another possible source for aragonite derived cements in non-tropical settings could be the occurrence of tunicates. These have been found to be important sediment contributors in Pleistocene heterozoan carbonates from Australia (Saxena and Betzler, 2003). As tunicate spicules are very small (below 0.1 mm) they are very prone to dissolution and leave no visible molds. The problem is that it is hardly possible to explain 30% of cement by this source.

Another process that could have caused extensive cementation with aragonite derived cements is a kind of differential diagenesis as described by Westphal et al. (2000). Here some carbonate beds act as cement exporters, others as cement importers. The aragonite that was preferentially dissolved in more marly beds would have been transported and reprecipitated in

more carbonatic beds in a “nearly” closed system (Munnecke and Westphal, 2004). Since the section gets more clayey towards the top, as indicated by the XRD/Coulometer measurements, this process could also have played a part in our case.

Despite the uncertainty about the source of the aragonite, geochemical data clearly indicate aragonite as the main cement source in the burial marine environment.

3.6.3 Diagenetic pathways

By combing the detailed petrographic descriptions of the cements with the interpretation of the diagenetic environments, based on geochemical data, it is possible to establish diagenetic pathways for the two study areas (Figs. 13, 14). Despite the different amounts of cement (Dweira: below 10%; Ragusa: between 20 and 30%) the pathways appear quite similar.

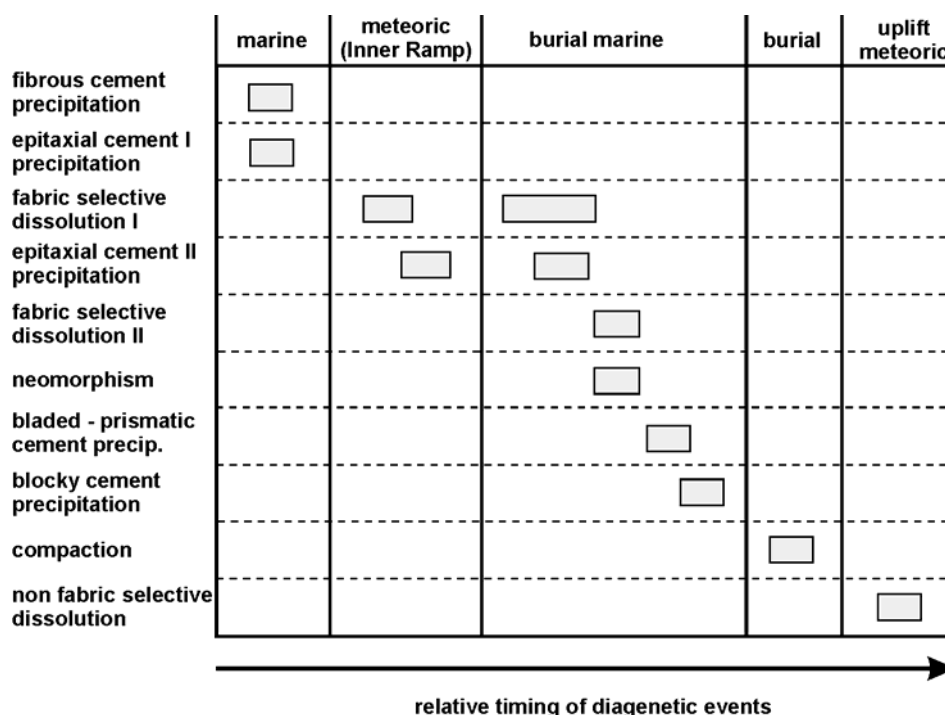


Figure 13 Paragenetic pathway of the diagenetic events recorded in the heterozoan limestones of the Dweira section (Maltese Islands). Note that the meteoric environment only refers to the paleobathymetrically shallowest part of the section

In both areas the diagenetic evolution starts with the early marine precipitation of HMC fibrous and epitaxial cement I. The paleoenvironmentally shallowest parts of the Dweira section were exposed to meteoric influence, which caused fabric-selective dissolution of aragonitic biota and precipitation of LMC epitaxial cement II in this part.

When entering the burial marine environment the main part of dissolution, neomorphism and cement precipitation took place. The process started with the fabric selective dissolution of aragonitic biota in all parts of the section. In Dweira biomolds of these biota are preserved, for Ragusa this process is inferred, as discussed above. This dissolution is the main source for the precipitation of LMC epitaxial cement II. After the precipitation of this cement, another phase of fabric-selective dissolution and neomorphism occurred, preferentially affecting the HMC epitaxial cement I and HMC biota. After that precipitation of LMC bladed-prismatic and blocky cement took place.

When entering the burial environment mild chemical compaction, causing concavo-convex and some sutured contacts, occurred. Successively both areas were tectonically

uplifted and re-entered the meteoric environment, which caused some late, non-fabric selective dissolution.

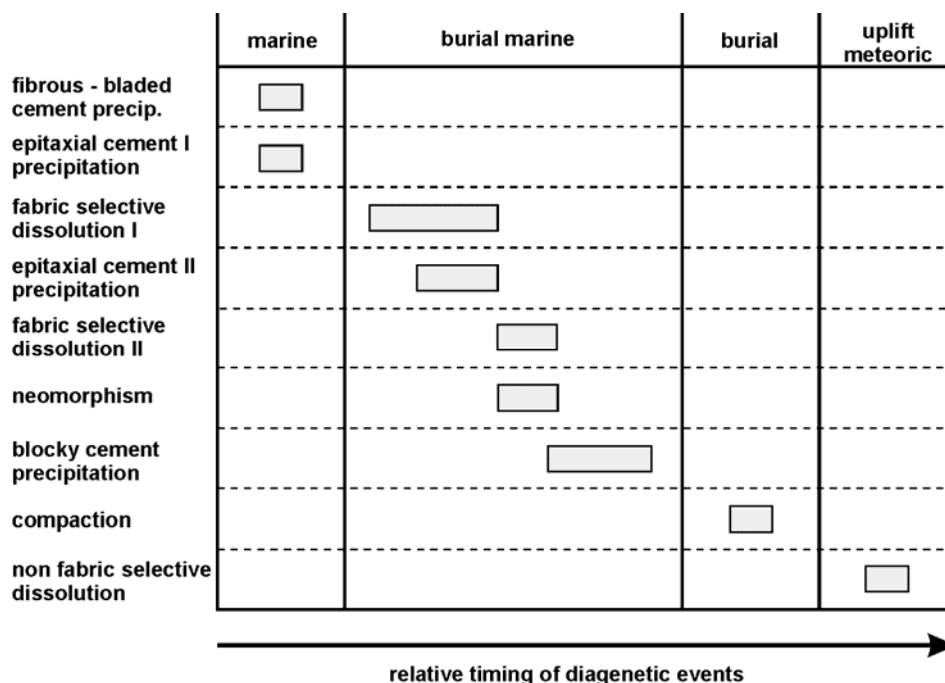


Figure 14 Paragenetic pathway of the diagenetic events recorded in the heterozoan limestones of the Ragusa section (Sicily)

3.7 CONCLUSION

Our investigations show that even in heterozoan carbonates early cementation takes place in the marine environment and leads to the precipitation of HMC fibrous and epitaxial cement. At specific stratigraphic positions (condensed sections?) this early marine cements can reach up exceptional high volumes of up to 30% and can cause an early lithification of the rocks. Meteorically influenced cementation with LMC (epitaxial cement II) can be observed depending on the paleoenvironmental position. This is rather unusual for heterozoan carbonates since it is generally assumed that they are unaffected by meteoric alteration because of their stable mineralogy.

The main part of mineralogical stabilization, dissolution and cementation by LMC takes place near the seafloor in the burial marine environment. In this setting, the CO₂ produced by the aerobic bacterial oxidation of organic matter leads to a net decrease in pore water pH and favors aragonite or even HMC dissolution (Hendry, 1993). The source for the LMC cements most probably is the dissolution and neomorphism of early marine precipitated HMC cements (epitaxial cement I) and of aragonitic and HMC biota. This is especially distinct in Ragusa where cement precipitation occurred in a nearly closed system, which allowed the preservation of the high Sr content of the precursor aragonite. In contrast to the general acceptance, hardly any cement precipitation takes place in the burial environment and pressure solution is unimportant as a cement source.

These results hold three implications. (1) The importance of the early, pre-burial diagenesis for the chemical stabilization and cementation of heterozoan carbonate rocks must be carefully considered. Especially the burial marine environment seems to play an important role in this process. (2) It seems that the amount of aragonitic biota in heterozoan carbonate settings has been largely underestimated. This does not only lead to a biased taphonomic record as stated by some authors (Brachert and Dullo, 2000; Smith and Nelson, 2003), but also to a misjudgement of the early diagenetic potential of many heterozoan carbonates. Even in rocks with no visible molds after aragonite and with cement precipitation taking place in a

closed system, aragonite can be the major cement source. (3) This also holds implications when considering the reservoir qualities of these rocks. Our findings show that the primary porosity of the rocks was occluded early by cementation and the secondary porosity formed by dissolution of aragonitic skeletons was not preserved. In contrast to photozoan carbonates, in heterozoan limestones the framework of the grains is not stabilized by early cements and the open mold spaces often collapse, leaving no secondary porosity. Only in areas where the grains support each other, oversized pore spaces or filled molds can be observed.

Epitaxial calcite cements in heterozoan carbonates

4.0 ABSTRACT

Epitaxial calcite overgrowths on echinoderm fragments are important contributors to the rock record during several time intervals in the Earth history (so called “calcite seas” times). In heterozoan carbonate associations these cements often form the volumetrically most important cement type. The origin as well as the environment in which this cement forms is controversially debated, reaching from early marine, meteoric, formation burial to meteoric uplift.

In heterozoan carbonate sediments it is generally assumed that epitaxial cement precipitation occurs primarily in the burial diagenetic environment and it is sourced by the dissolution of calcitic components. Formation in the meteoric environment is not reported for such sediments. New data from the central Mediterranean area show that the main phase of epitaxial cement precipitation occurred early, either in the meteoric (examples from the Maltese Islands) or in the burial marine (examples from the Maltese Islands and Sicily) environment. In both cases cement precipitation was not sourced by pressure solution, which clearly postdates cement growth, but by the dissolution of aragonitic biota.

These findings underline the importance of aragonitic components in heterozoan carbonate sediments for their diagenetic evolution. In contrast to the general belief, the main mineralogical stabilisation and cement precipitation occurs early, in the meteoric and burial marine rather than in the deep burial environment.

4.1 INTRODUCTION

Epitaxial calcite overgrowths precipitate in crystallographic continuity with their substrate, which in general consists of a single calcite crystal. The most important monocrystalline seeds in limestones, and therefore the preferred nucleation sites of epitaxial cements, are echinoderm skeletal elements. Echinoderms were important sediment producers during extended time intervals in earth history, with a shift from crinoids in the Palaeozoic and Mesozoic to echinoids in Cenozoic times.

Especially in Tertiary and present-day heterozoan carbonate sediments echinoids are major sediment constituents, as indicated by the nomenclature of these rocks (e.g. **molech** for and **bryonoderm** facies, James 1997). In these sediments echinoids and their fragments tend to get enriched because they are very robust and resistant against mechanical abrasion, quite in contrast to mechanically instable biota such as bryozoans. Because of this abundance of suitable seeds the fast-growing epitaxial cements, precipitated around echinoid fragments, are often the main cementing phase in heterozoan carbonate settings (Knoerich and Mutti, 2003).

4.2 NOMENCLATURE AND ORIGIN

The nomenclature for overgrowth on echinoderm fragments varies between syntaxy or syntaxial used by Bathurst (1958) and epitaxy or epitaxial used by Braithwaite (1966) and later by James and Choquette (1990a). In the following, the term epitaxial will be used.

The origin of echinoderm overgrowth has been debated by many authors. Early workers (e.g. Bathurst, 1958; Bathurst, 1975) thought that epitaxial overgrowths could either form by filling of open pore spaces (“rim cements”/**active cement growth**) or by neomorphic replacement of the surrounding lime mud (“syntaxial rims”/**replacive growth**). But soon it was realised that interparticle lime mud inhibits the formation of epitaxial overgrowth and that therefore a replacement origin of these overgrowths is rather unlikely (Lucia, 1962).

Some authors (Walkden and Berry, 1984) also found epitaxial cements passively growing into so called “solution coronas” around crinoid fragments. They stated that these coronas developed early during near-surface meteoric diagenesis and were then passively filled by epitaxial cements, first in the meteoric and then in the burial diagenetic environment (“**passive**” cement growth).

Maliva (1989) reported also a **displacive** mode of epitaxial overgrowth which worked quite early under phreatic conditions in a still unlithified sediment. This process results in a fabric in which the echinoderm fragments “float” in authigenic calcite.

In general the “active cement growth”, where the cement precipitates in a previously existing open pore space, is the most abundant origin of epitaxial overgrowth on echinoderm fragments.

4.3 DIAGENETIC ENVIRONMENTS OF FORMATION

Like the origin, the diagenetic environment of the formation of epitaxial overgrowth on echinoderm fragments is controversial. Precipitation may occur from marine (Stow and Miller, 1984; Kim and Lee, 1996), meteoric (Meyers, 1974), formation-burial (Scholle and Halley, 1985) or formation-emergence (Lee and Harwood, 1989) fluids, but in general it is interpreted that the majority of epitaxial overgrowth formed in the meteoric environment (e.g. Meyers, 1974; Meyers and Lohmann, 1978; Walkden and Berry, 1984; James and Choquette, 1990a).

Meyers and Lohmann (1978) argued also for a mixing zone origin of epitaxial overgrowth in the meteoric and marine phreatic environments. They stated that about 1% of the epitaxial cement they studied in Mississippian limestones was formed in the marine environment, up to 16% was of meteoric-marine phreatic mixing zone origin, but the majority of 83% of the epitaxial overgrowths were of phreatic fresh-water origin.

Walker et al. (1990) were one of the first who stated that syntaxial overgrowths can form in multiple diagenetic environments and over extended length of time, the final stages often consisting of ferroan calcite, precipitated in the burial environment. For early, marine epitaxial cement they suggested that it is only abundant in times of “calcite seas”, especially during the Ordovician and maybe the Cretaceous.

4.4 COMPARISON OF “CALCITE SEA TIMES” WITH HETEROZOAN CARBONATE ENVIRONMENTS

A literature compilation of epitaxial cements (see Tab. 1) has revealed a striking correlation between the description of early epitaxial cements (e.g. Braithwaite and Heath, 1989; Maliva, 1989; Wilson and Palmer, 1992; Kim and Lee, 1996) and the distribution of “aragonite” and “calcite” seas as stated by Stanley and Hardie (1998) (Fig. 1). The occurrence of early epitaxial cements is recorded from the Early Ordovician to the Early Carboniferous and from the Middle Jurassic (Evamy and Shearman, 1965) to the Early Miocene. No descriptions could be found for the Late Carboniferous to the Early Jurassic, a fact also reported by Walker et al. (1990). The (notable) occurrence of early epitaxial cements seems to be limited to time intervals of so called “calcite seas”.

These former times “calcite seas” are in many aspects quite similar to present-day heterozoan carbonate environments. In both settings the saturation state of the sea water with respect to CaCO_3 is/was low, promoting the inorganic precipitation of low Mg-calcite (LMC) (Sandberg, 1983; Smith and Nelson, 1994), rather than aragonite or high Mg-calcite (HMC).

Also aragonitic biotic components were generally considered to be only minor sediment contributors in both environments, a statement just recently revised. New findings by Cherns & Wright (2000) and Wright et al. (2003) for Silurian and Mesozoic strata and by Brachert & Dullo (2000) and James (pers. comm.) for Miocene to recent heterozoan carbonate environments suggest that the amount of aragonitic biota in both settings is/was much higher

than previously assumed. But due to the low saturation state of the sea water with respect to CaCO_3 these components are generally dissolved early, without leaving a trace, often not even moldic porosity. This has been seen as a problem leading to a taphonomically biased record of the biogenic association.

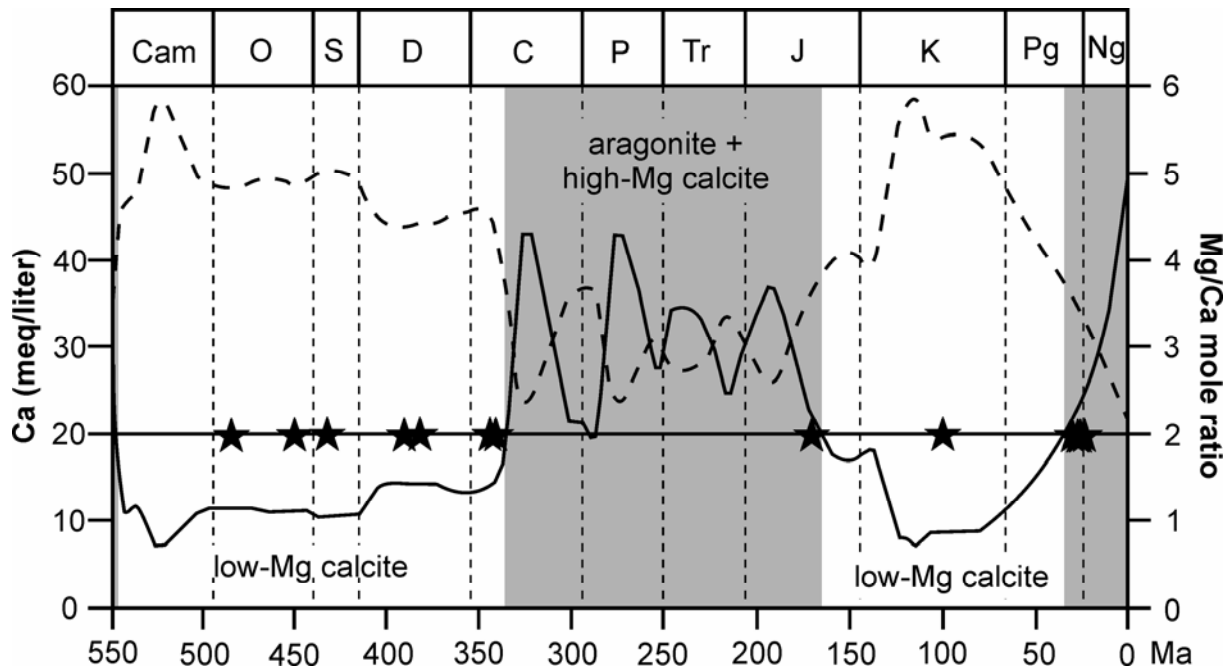


Figure 1 Comparison of the times of so called “calcite and aragonite seas” as described by Stanley & Hardie (1998) with the reported occurrence of epitaxial overgrowth on echinoderm fragments (see Table 1). Note that epitaxial cements are only abundant in times of “calcite seas”. solid line: Mg/Ca ratio; dashed line: Ca; shaded area: aragonite sea; white area: calcite sea; asterisk: reported occurrence of epitaxial overgrowth

On the other hand, the dissolved aragonite is expected to leave a trace in the early diagenetic record. We suggest that this dissolved aragonite is an important source of early cements, such as the epitaxial cements discussed in this study.

But why are early epitaxial cements so abundant in “calcite seas”/heterozoan environments? Meyers & Lohmann (1978) recognised that a high substrate selectivity of cement growth (nearly exclusively around echinoderm fragments) together with the development of large crystals points to a low saturation state of the pore waters with respect to CaCO_3 . In this environment the rapid growth of echinoderm overgrowths, in comparison with other contemporary cements, is favoured by their larger particle size in combination with a high density of dislocation sites in the single crystals. These dislocations favour the seeding of cement on top of the echinoderm fragment (Dickson, 1993) even in waters with a low saturation state.

Walker et al. (1990) moreover suggested that marine epitaxial overgrowth was favoured during “calcite sea” intervals as the competition for nucleation sites was reduced due to the absence of aragonite cements. Both, the low saturation state and the absence of aragonite cements, apply for “calcite seas” as well as for heterozoan carbonate environments and maybe an explanation for the abundance of this cement type in these settings.

Table 1 Compilation of the recorded occurrence of epitaxial overgrowth

Author	Location	Time slice	Palaeogeographic location	Substrate	Origin
Kim & Lee (1996)	Korea, Dumugol Fm.	Lower Ordovician	~ 20° N	echinoderms	marine
Braithwaite & Heath (1989)	Norway, Skoyen sandstone	Upper Ordovician-Lower Silurian	~ 20° S to 0°	pelmatozoan	?
Lucia (1962)	Texas, Andrews south Devonian field	Devonian	~ 30° S	crinoids	?, maybe early marine to shallow burial
Walkden & Berry (1984)	England, Derbyshire	Lower Carboniferous	~ 0°	crinoids and echinoids	meteoric to deep burial
Meyers & Lohmann (1978)	New Mexico, Lake Valley Fm.	Mississippian	~ 20° S	echinoderms	meteoric, meteoric-marine mixing
Evamy & Shearman (1965)	France, Ambleon, Ain	Jurassic (Bajocian)	~ 30° N	echinoderms	?
Maliva (1989)	England (Upper greensand)	Cretaceous (Albian)	~ 40° N	echinoderms	phreatic, marine to burial
	New York State (Onondaga Limestone)	Devonian (Eifelian)	~ 15° S		phreatic, marine to burial
Nelson et al. (1988)	New Zealand, Te Kuiti Group	Oligocene	~ 70° S	echinoids	burial, 400-1100m
Nicolaides (1995)	SE Australia, Heytesbury Group	Oligo-Miocene	~ 60° S	echinoids	marine to moderate burial (up to 700m)
Hood & Nelson (1996)	New Zealand, Te Kuiti and Te Aute Megafacies	Oligo-Miocene	~ 70° S	echinoids	shallow burial (10s of meters)
Kyser et al. (1998)	Australia, Gambier Limestone	Oligo-Miocene	~ 60° S	echinoids	marine, shallow burial
Knoerich & Mutti (this study)	Maltese Islands, Lower Coralline Limestone Fm.	Oligo-Miocene	~ 30° N	echinoids	marine, meteoric, burial marine
	Sicily, Ragusa Fm.	Oligo-Miocene	~ 30° N	echinoids	marine, burial marine

4.5 EPITAXIAL CEMENTS FROM THE MALTESE ISLANDS AND SICILY

To test if the main cementation in heterozoan carbonates is really limited to the burial diagenetic environment we studied an Oligo-Miocene carbonate succession cropping out on the Maltese Islands and on Sicily. In both locations an inner to outer ramp sequence consisting of heterozoan biogenic assemblages as defined by James (1997) is exposed. The limestones are well lithified and predominantly cemented by epitaxial overgrowths on echinoid fragments. The carbonate strata record first a shallowing upward trend from an outer to inner ramp environment which is followed towards the top by a pronounced deepening (drowning). Detailed petrography (transmitted light and cathodoluminescence) of the biogenic facies and diagenetic features, combined with stable isotope and major and trace element analysis allowed the determination of the environment and source of the epitaxial cement overgrowth.

4.5.1 First epitaxial overgrowth (EPI): petrography and geochemistry

In both locations a first, inclusion-rich epitaxial cement could be distinguished from a second, inclusion-free phase (Fig. 2a, c). The first cement phase (EPI) precipitated in direct contact with the host grain, constitutes only 1-2% of the sediment volume and displays a patchy appearance under CL (Fig. 2d). In the studied sections this cement is partially dissolved, leaving open moldic porosity between the host grain and the epitaxial cement II that grew on top of it (Fig. 2a, b). Due to the small crystal size of this first epitaxial cement rim no stable isotope analysis was possible, but the major and trace element analysis showed the lowest Mg and Sr contents, indicating strong recrystallization and a present-day LMC mineralogy. Therefore it can be stated that the EPI most probably precipitated early in the marine environment as primary HMC. Later in the course of burial or under the influence of meteoric waters this HMC was either neomorphosed to LMC or selectively dissolved.

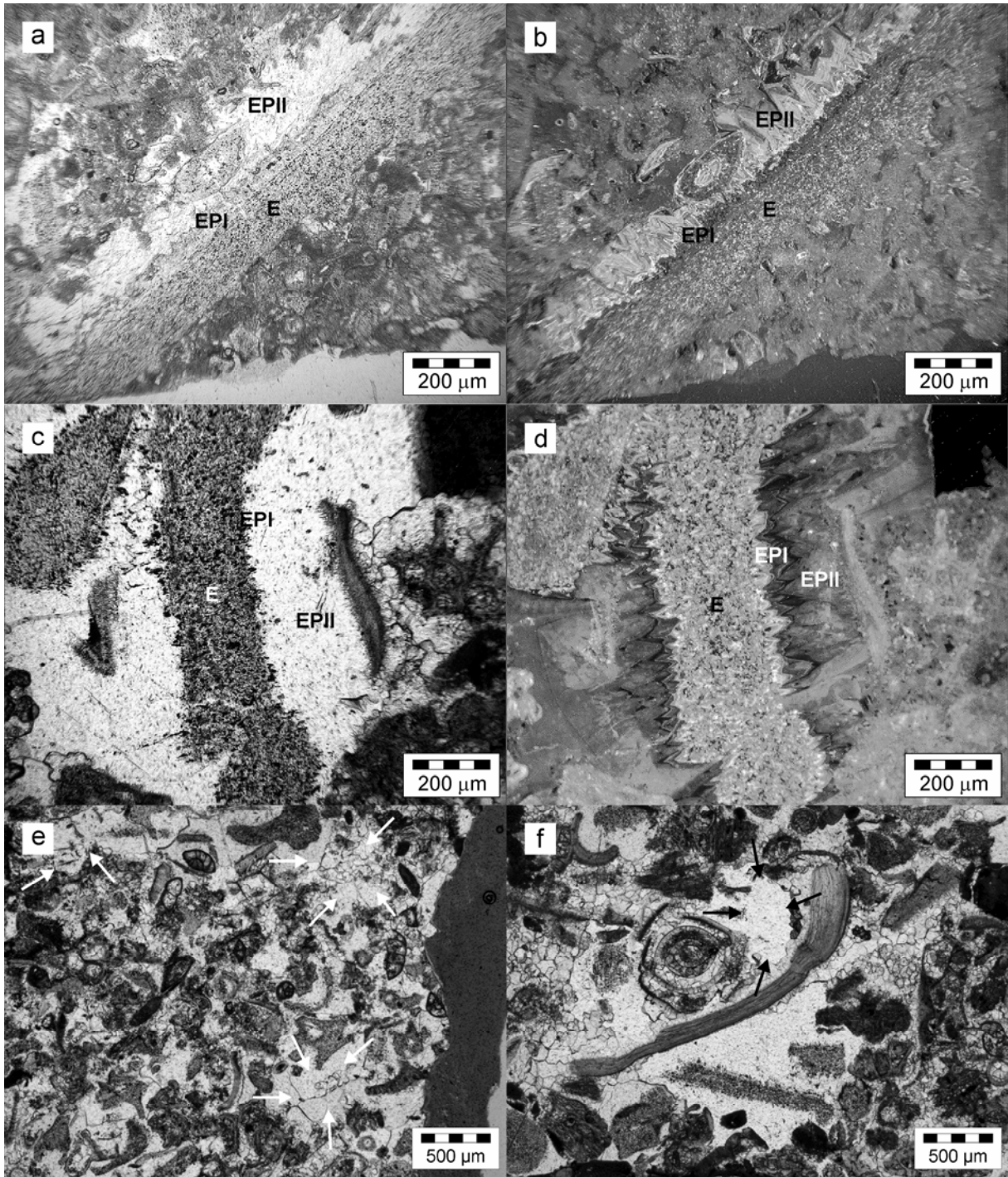


Figure 2a-f Photomicrographs of epitaxial overgrowths and oversized pore spaces/cemented molds in the samples from the Maltese Islands and Sicily. **a.** Sample from Malta: Echinoid fragment (E) overgrown by two epitaxial cement rims (EPI and EPII). Note that the EPI in this case has been totally dissolved and leaves an open mold between the echinoid fragment and the epitaxial cement II. **b.** as **a.** in CL: Note the well-preserved internal zonation visible in the second epitaxial cement rim (EPII). **c.** Sample from Sicily: Echinoid fragment (E) overgrown by two types of epitaxial cement (EPI and EPII). Note that the EPI is inclusion rich. **d.** as **c.** in CL: Note that the epitaxial cement I (EPI) displays a patchy appearance, quite in contrast to the well zoned epitaxial cement II (EPII). **e.** Sample from Sicily: Note the large, oversized pore spaces (indicated by arrows) filled by inclusion-free epitaxial cement II (EPII). **f.** Sample from Sicily: Visible is a dissolution mold (arrows) filled by inclusion free epitaxial cement II (EPII)

4.5.2 Second epitaxial overgrowth (EPII): petrography

The second epitaxial cement phase (EPII) observed precipitated on top of the first and is volumetrically much more important. On the Maltese Islands it contributes up to 6-8% to the sediment volume, in Sicily generally around 20%, which is rather exceptional for a heterozoan carbonate setting. Petrographically this cement is quite similar in both locations (Fig. 2 a, c). It is clear, inclusion free and displays well preserved internal zonations under CL (Fig. 2 b, d). Its precipitation clearly predates compaction as biota are dissolved against it or it even indents into biota. The well preserved internal zonations and the low Mg content of this cement type point to a primary LMC mineralogy.

4.5.3 Second epitaxial overgrowth (EPII): geochemistry of the samples from the Maltese Islands

From a geochemical point of view the epitaxial cement II found in the two locations shows pronounced differences (Fig. 3 + 4). The samples from the Maltese Islands display more negative $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values than the samples from Sicily, ranging from -1.0 to -4.7 for $\delta^{18}\text{O}$ and from 0.5 to -4.0 for $\delta^{13}\text{C}$. The Sr content is strongly depleted, the Mn content moderately enriched in comparison with carbonate minerals (aragonite, HMC, LMC) precipitated in equilibrium with marine waters.

The isotope data indicate cement precipitation in the shallow burial (negative $\delta^{18}\text{O}$ values) and in the meteoric phreatic (negative $\delta^{13}\text{C}$ values) environment. Especially the meteoric-cement samples correlate well with the depositional environment as they are only found in the inner ramp part of the section. Here subaerial exposure surfaces have been recorded in the field, pointing to an early meteoric diagenetic event.

The trace element data indicate precipitation in a quite open system with little rock water interaction (depleted Sr contents) under slightly reducing conditions (elevated Mn values). These conditions can be found in the lower, dysoxic meteoric or the burial marine environment (*sensu* Melim et al., 1995). In both environments the source of the EPII cement could be the dissolution of aragonitic biota and reprecipitation as LMC cement. As little EPII cement was found in the samples from the Maltese Islands (6-8%, corresponding to the same amount of biomoldic porosity) and only a low saturation state of the fluid is needed to induce epitaxial overgrowth this explains the cementation in this case well.

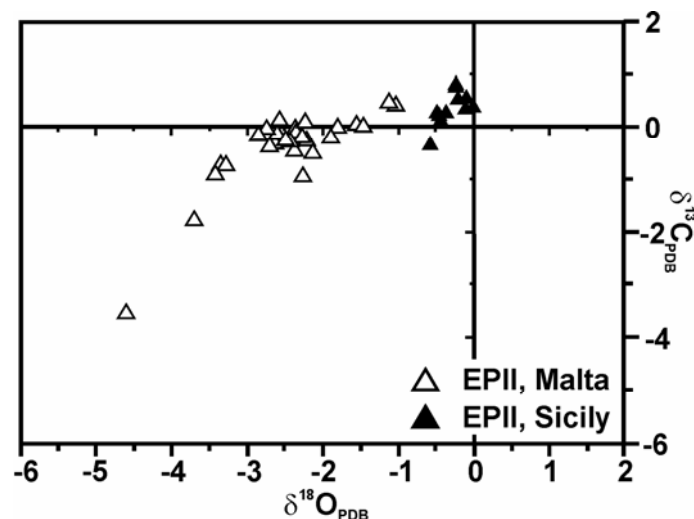


Figure 3 Cross plot of the $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ isotopic composition of the epitaxial calcite II sampled on the Maltese Islands and on Sicily

4.5.4 Second epitaxial overgrowth (EPII): geochemistry of the samples from Sicily

The samples from Sicily display more positive isotope values compared with the samples from the Maltese islands, ranging from 0.0 to -0.6 for $\delta^{18}\text{O}$ and from 0.7 to -0.5 for $\delta^{13}\text{C}$ (Fig. 3). The Sr content shows minimal depletion (some values were as high as 5000ppm), the Mn values moderate enrichment in comparison to carbonate minerals precipitated in equilibrium with marine waters.

The isotope data indicate precipitation of the EPII cement from marine or marine derived waters. No indications of mixing with meteoric fluids or elevated temperatures during cement precipitation were found.

The nearly undepleted Sr contents point to cement precipitation in a closed system with high rock-water interaction (Fig. 4). The elevated Mn values indicate cement growth under reducing conditions. Such a setting can be found in a marine burial environment, where cement precipitation occurs from marine derived waters under reducing conditions. The source of the cement would be, like in the samples from the Maltese Islands, the dissolution of aragonite and re-precipitation as LMC. This aragonitic cement source can be postulated due to the high Sr content preserved in the newly formed cements because cementation took place in a closed system.

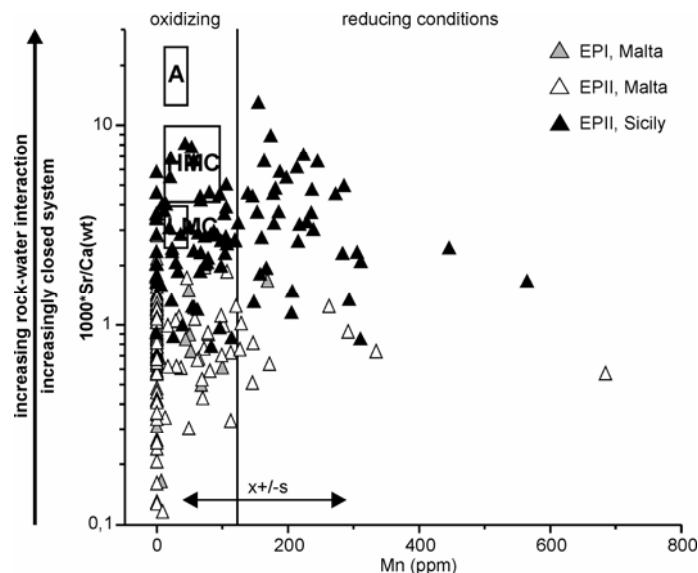


Figure 4 Cross-plot of the Mn and Sr content (normalized to Ca) of the epitaxial cements from the Maltese Islands and Sicily. Indicated are also the typical values for carbonate minerals precipitated in equilibrium with marine water. A: aragonite; HMC: high Mg calcite; LMC: low Mg calcite (plot by Brand and Veizer (1980), modified by Lohmann (1988)). The Sr value shown on the y-axis indicates the amount of rock-water interaction and is therefore a measure for the openness of the system. The Mn content displayed on the x-axis points to the redox conditions of the system during cement precipitation (availability of Mn assumed)

4.6 DISCUSSION

4.6.1 Implications of the data from the Maltese Islands and Sicily

The exceptional high amount of early epitaxial cement sourced by aragonite dissolution seems to be difficult to explain in a heterozoan carbonate setting. This is especially true for the samples from Sicily where around 20% of epitaxial cement precipitated in a closed system, i.e. no external source for CaCO_3 was available, and where no moldic porosity was found acting as evidence for former aragonitic components. The only indications of once existing aragonitic components are sometimes visible filled molds and oversized pore spaces (Fig. 2 e, f).

But, as stated above, it seems that the amount of aragonitic biota in heterozoan carbonate environments has been largely underestimated because they are normally dissolved early on

the sea floor. In Sicily, it seems that sedimentation was fast enough to bury the aragonite (and the organic matter) before it could dissolve/decay on the seafloor and therefore it could drive the burial marine diagenesis. As cementation occurred in a closed system no moldic porosity was preserved but immediately occluded by newly formed cement. As the former aragonitic biota (most probably molluscs and bryozoans as these biota are strongly underrepresented) had no micritic rims around, the only visible remains are the oversized pore spaces.

Epitaxial cement growth on the Maltese Islands worked quite similar with the exception that cement precipitation occurred in an open system where CaCO_3 could be exported and imported. Therefore the geochemical signal of the former aragonite was not preserved in the newly formed LMC but in exchange open biomoldic porosity could be found. Moreover stable isotope data revealed that epitaxial cement precipitation occurred not only in the burial marine but also in the meteoric phreatic diagenetic environment.

4.6.2 Importance of epitaxial cements in heterozoan carbonate settings

In general it can be said that epitaxial overgrowths are an important cement phase in heterozoan carbonates since the substrate they need for nucleation, echinoderms, is very abundant and epitaxial cements have a fast growth rate. This fast growth rate often even restricts the development of other cement types as reported by Nelson et al. (1988a).

Epitaxial cement precipitation often begins early, close to the seabed in the marine phreatic realm and is probably sourced by the dissolution of aragonitic biota (Nicolaidis, 1995; Hood and Nelson, 1996; Anastas et al., 1998). This first phase of epitaxial cement growth is generally volumetrically unimportant and constitutes only a few percents to the cement total (Kyser et al., 1998).

The main phase of epitaxial cement precipitation is said to take place in the burial environment from marine derived water. In the shallow burial (around 200m), during mechanical compaction, cementation is sourced by mild chemical compaction (Anastas et al., 1998), in the deep burial the source of the cements is chemical compaction and dissolution of marine skeletal material below a threshold limit of 500 m (Nelson et al., 1988a). Precipitation of epitaxial cements in the meteoric environment, although reported from calcite seas settings, was assumed to be of no importance in heterozoan carbonate sediments, but evidently occurs.

4.7 CONCLUSIONS

1. We provide data showing that epitaxial cement precipitation took place as a multi-phase event in different diagenetic environments, recording a complex story. Precipitation occurred in both cases studied (1) in the marine diagenetic environment as primary HMC. This cement phase is volumetrically unimportant (1-2% of the sediment volume). Only in the Maltese Islands additional precipitation occurred (2) in the meteoric diagenetic environment as primary LMC. Both cases finally record (3) precipitation in the burial marine diagenetic environment also as primary LMC. In this environment the main cement precipitation (6-8% in Malta, up to 20% in Sicily) took place.
2. We can clearly distinguish between epitaxial cement precipitations taking place in (1) a closed system versus precipitation taking place in (2) an open system.
 - (1) In a closed system (examples from Sicily) the geochemical signal (isotopes as well as trace elements) of the precursor mineralogy (aragonite) is preserved. No open moldic porosity is formed since the calcium carbonate is mainly “redistributed” in the system.
 - (2) In an open system (examples from the Maltese Islands) the geochemical signal of the precursor mineralogy is not preserved since the fluids were highly diluted. In contrast to the closed system open biomoldic porosity is formed and isotope data clearly indicate the influence of meteoric waters, leading to aragonite dissolution and

epitaxial cement precipitation. This epitaxial cement precipitation in the meteoric environment has not been described before for heterozoan settings.

3. Cementation in the meteoric and burial marine diagenetic environment is sourced by the dissolution of meta-stable aragonitic components, not by pressure solution of mineralogical stable calcite grains. Therefore we have a key to show that aragonite in heterozoan carbonate settings was always a major sediment contributor and we can prove that also in this environment it was a major driving force for early diagenesis, especially favouring the precipitation of epitaxial cements.

CONCLUSIONS

The main objective of this study was to determine the diagenetic pathways and environments in shallow-water heterozoan carbonate assemblages and to identify the amount and kind of early, near-seafloor diagenetic processes. Special emphasis was put on the evaluation of the amount of constructive diagenesis in form of cementation in this diagenetic environment. In order to test the hypothesis that significant amounts of constructive early, near-seafloor diagenesis occurred, three key questions were investigated:

1. How did the depositional environment influence the amount and kind of cementation? Is there a link between the depositional environment and early cementation?
2. How do the diagenetic pathways look like? Which were the diagenetic environments of alteration and cementation and what happened in the early, near-seafloor realm?
3. If there is early cementation, what was the source for these cements?

(1) The depositional environment had a clear influence on the amount and kind of cementation. In general, the amount of cement is inversely correlated with the micrite content, which is highest in the lower-energy mid- to outer-ramp parts of the sections. The amount of the volumetrically most important epitaxial cement II is bound on the occurrence of echinoderm fragments. These fragments are most common in the high energy inner- and mid-ramp parts of the logged sections. Epitaxial cement II predominantly occurs in well-sorted, well-bedded, grain-supported fabrics. Meteoric cementation was exclusively found in the paleoenvironmentally shallowest inner-ramp part of the Malta section. The close spatial relationship of this cementation with subaerial exposure surfaces indicates that the meteoric influence was syndepositional. At specific stratigraphic positions of prolonged exposure at the sediment-water interface, up to 30% of early marine, fibrous HMC cement could be observed.

These results indicate that the amount of cement strongly varies with depositional environment and sediment fabric, being the highest in grain-supported fabrics of inner-ramp and the lowest in mud-supported fabrics of outer-ramp facies. Indications for a link between the depositional environment and early cementation could be found at specific stratigraphic intervals, in the marine and meteoric environment. This is an important result because it is generally stated, that early cementation in heterozoan carbonates is only limited. This study shows that there might be a higher early diagenetic cementation potential than previously assumed.

(2) Detail petrography and geochemistry (stable isotope and major and trace elements) of the different cement types allowed the development of diagenetic pathways and the determination of different diagenetic environments. The diagenetic evolution started in the marine environment with the precipitation of HMC fibrous/fibrous-bladed and epitaxial cement I. The paleoenvironmentally shallowest part of the section on the Maltese Islands was then exposed to meteoric diagenetic fluids. This led to the dissolution of aragonitic and HMC skeletons and to cementation with LMC epitaxial cement II. The strata then entered the burial-marine environment (*sensu* Melim et al., 2002). Here the aragonitic skeletons and the earlier precipitated HMC epitaxial cement I were partially or totally dissolved. Large amounts (up to 30%) of LMC epitaxial cement II, bladed and blocky cement precipitated. The earlier precipitated fibrous/fibrous-bladed and epitaxial cement I were neomorphosed to LMC. In the burial environment mild chemical compaction took place without causing significant amounts

of cementation. In a final phase the rocks entered the meteoric realm by uplift, which caused non-fabric selective dissolution.

It can be concluded that the main part of dissolution, cementation and neomorphism took place early, near the seafloor in the burial marine diagenetic environment. This environment is the most important for the mineralogical stabilisation and lithification of the investigated heterozoan carbonate rocks. The burial diagenetic environment was unimportant for this process.

(3) Early cements formed in three diagenetic environments, the marine, the meteoric and the burial marine environment (*sensu* Melim et al., 2002). For each environment a cement source could be assigned. In the marine diagenetic environment HMC cements precipitated directly out of marine waters. At specific stratigraphic positions up to 30% of early marine cement could be formed in this way. In the meteoric and burial diagenetic environment LMC cements originated from the dissolution of aragonitic and HMC skeletons and cements. As the main cementation phase with epitaxial cement II clearly predates compaction, pressure solution could be ruled out as a main cement source in the investigated heterozoan strata.

The results of this study clearly show that significant amounts of constructive diagenesis in heterozoan strata can occur early, near the sea-floor. The early diagenetic potential of the rocks is very much dependent on the amount of aragonite present in the original sediment.

This study shows that aragonite is not that scarce in heterozoan carbonate settings as previously assumed. Studies in recent heterozoan sediments already indicated this (Brachert and Dullo, 2000, James pers. com., 2004), but in fossil heterozoan rocks the primary amount of aragonite is difficult to assess and therefore not very well investigated. Especially important is the fact that, in contrast to photozoan carbonates, no relict structures of former aragonitic biota need to be preserved in heterozoan rocks. Geochemistry is then the only way to prove the aragonitic cement source.

The results of this study hold also implications for carbonates formed during so called "calcite-sea" times (Stanley and Hardie, 1998). Like in heterozoan carbonate settings, also here the amount of aragonitic biota seems to have been largely underestimated. Only in the last years authors like Cherns and Wright (Cherns and Wright, 2000; Wright et al., 2003) revised this opinion. Like in heterozoan strata, also in "calcite sea" carbonates only indirect proves of the former existence of aragonitic skeletons can be found. These rocks might also have had a higher share of aragonite and a larger early diagenetic potential for cementation than previously assumed. In contrast to photozoan carbonates, where marine cementation is able to stabilize the framework of the grains, heterozoan/"calcite-sea"-carbonates lack this ability. Therefore, molds after aragonitic biota do not stay open, but collapse or, where the grains support each other, are filled by calcite cement. This results in an early occlusion of the primary porosity, but in contrast to photozoan carbonate rocks, the secondary porosity developed is not preserved.

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